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Etudes de Catalyseurs de Désulfuration

Arnaud Travert

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Mémoire

présenté devant l'Université de Caen/Basse-Normandie

pour l'obtention de

L'Habilitation à Diriger des Recherches

par

Arnaud TRAVERT

Etudes de Catalyseurs de Désulfuration

Soutenue le 7 décembre 2011

MEMBRES du JURY

- C. Geantet**, Directeur de Recherches CNRS, IRCELYON, Lyon. **Rapporteur**
- J.-F. Paul**, Professeur, UCCS, Université Lille Nord de France, Villeneuve d'Ascq. **Rapporteur**
- F. Maugé**, Directeur de Recherches CNRS, LCS, Caen. **Directrice, Rapporteur**
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- F. Dumeignil**, Professeur, UCCS, Université Lille Nord de France, Villeneuve d'Ascq.
- R.A. van Santen**, Professeur, Technische Universiteit Eindhoven, Pays Bas.
- R.F. Wormsbecher**, Manager of Exploratory Catalysis Research, W.R. Grace, Columbia, MD, USA.
- J.-P. Gilson**, Professeur, LCS, ENSICAEN, Caen.

HABILITATION [abilitasjō]. *n.f.* (1373, lat. mediev. *habilitatio*). *Dr.* Action de conférer la capacité à un incapable.

Remerciements

Tous mes remerciements vont à Hiroyuki Nakamura, Pieter Magusin, Rutger van Santen, (TU Eindhoven) ; Jean-François Paul, Sylvain Cristol, Edmond Payen, Edourd Veilly, Mickaël Badawi (UCCS, Lille) ; Ruizhong Hu, Yuying Shu, Rick Wormsbecher, Uday Singh, Mike Ziebarth, Wu-Cheng Cheng (W.R. Grace) ; Sylvette Brunet, Frédéric Richard, Yilda Romero (LACCO, Poitiers) ; Jean-Marie Krafft, Guylène Costentin (LRS, Paris) ; Mohan Rana, Jorge Ancheyta, Carolina Leyva (IMP, Mexico) ; Françoise Maugé, Laetitia Oliviero, Jean-Pierre Gilson, Jean-Claude Lavalley, Jacob van Gestel, Jean-Michel Goupil, Frédéric Thibault-Starzyk, Alexandre Vimont, Philippe Bazin, Valérie Ruaux, Sebastien Aiello, Yoann Levaque, Jacques Quillard, Philippe Groslier, Laurent Artu, Nathalie Perrier, Blandine Rabelle, Christophe Dujardin, Fabien Can, Marc-Antoine Lélias, Fatma Mahjoubi, Andrey Popov, Léna Kondratieva, Pawel Stelmachowski, Sergey Sirotin, Haoguang Li (LCS, Caen) pour avoir bien voulu diriger, aider ou subir l'incapable dans ses recherches post-doctorales.

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1 Curriculum vitae.

1. Curriculum vitae

1. Curriculum vitae

Arnaud TRAVERT

né le 23 décembre 1972 à Bayeux (14) Vie maritale, un enfant.

Laboratoire Catalyse et Spectrochimie

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1.1 PARCOURS PROFESSIONNEL

depuis 2000 Maître de Conférences.

Enseignement : UFR Sciences - Université de Caen

Recherche : Laboratoire Catalyse et Spectrochimie (LCS) – ENSICAEN

02/2000-12/2000 Post-doctorant. Schuit Institute of Catalysis, TU Eindhoven.

Modélisation de catalyseurs sulfures par DFT périodique - Etude par RMN de la mobilité d'alcanes adsorbés.

Directeur : Prof. R.A. van Santen.

10/1997-01/2000 Doctorant. Laboratoire Catalyse et Spectrochimie. Université de Caen - ISMRA.

Etude de l'acidité de Catalyseurs Sulfures Supportés.

Directeur : F. Maugé (DR).

1.2 DIPLOMES UNIVERSITAIRES.

2000 Doctorat (Spécialité Chimie des Matériaux) - Université de Caen

"Etude par Spectroscopie IR de l'acidité d'oxydes métalliques et de catalyseurs sulfures supportés - influence du sulfur d'hydrogène" - Dir. F. Maugé (DR CNRS)

1996 DEA Sciences des Matériaux - Université de Caen

1995 Maîtrise de Chimie - Université de Caen

1994 Licence de Chimie - Université de Caen

1993 DEUG Sciences B - Université de Caen

1991 Baccalauréat série D - Lycée A. Chartier (Bayeux)

1.3 THEMES DE RECHERCHE ACTUELS.

➤ Etude des propriétés acido-basiques d'oxydes et de sulfures métalliques.

- Spectroscopie IR de molécules sondes adsorbées et en conditions réactionnelles (*Operando*).
- Tests catalytiques.

➤ Application aux procédés de raffinage et de pétrochimie

- Hydrodésulfuration (HDS)
- Hydrodéoxygénation (HDO)
- Craquage catalytique en lit fluidisé (FCC)
- Valorisation de bio-alcools

1. Curriculum vitae

1.4 COLLABORATIONS ACADEMIQUES ET INDUSTRIELLES.

2011 - 2014 Michelin

Etude de l'interface silice – silane – polymère. Responsable scientifique : F. Thibault-Starzyk (LCS)

2010 - 2013 ANR CP2D 'Guerbet'. UCCS (U. Lille I), IRCELYON (U. Lyon), ARKEMA, LCS. Coordinateur F. Dumeignil (UCCS)

Valorisation de bio-alcools – Responsable Scientifique pour le LCS

2010 - 2013 Projet PIE 'Lignobocarb' – LACCO (Poitiers), LCS, UCCS (Lille) Coordinatrice S. Brunet (LACCO)

Recherche de nouveaux catalyseurs d'HDO - Responsable Scientifique pour le LCS

2009 Congé de Recherches, Centre de Recherches Grace Davison (Columbia, MD, USA) Etude de catalyseurs et d'additifs de craquage catalytique (FCC)

2009 - 2010 Consultant Scientifique. W.R. Grace & Co.-Conn.

2007-2011 ANR PNRB 'ECOHDOD'. LCS, UCCS (U. Lille I), LACCO (U. Poitiers), TOTAL. Coordinatrice F. Maugé (LCS)

Désoxygénation d'huiles issues de la pyrolyse de la biomasse ligno-cellulosique.

2003-2005 Université de St. Petersburg (Dept of Physics, Prof. A.A. Tsyganenko) : sondes de basicité.

2002 - 2010 Grace Davison (Columbia, MD, USA)

Mode d'action d'additifs de désulfuration en FCC. Co-responsable scientifique : F. Maugé (LCS)

2001-2011 UCCS, Université Lille I (Prof. E. Payen, Prof. J.-F. Paul) : modélisation de catalyseurs sulfures.

2002-2003 Action Intégrée Franco-Marocaine Ma/02/36. "Nouveaux matériaux catalytiques à base de phosphates apatitiques". Coordinateur J. Léglise (LCS)

1998-2000 LACCO, Université de Poitiers (Prof. G. Pérot). Caractérisation par spectroscopie IR de l'échange isotopique H-D par des catalyseurs sulfures.

1998 Dalian Institute of Chemical Physics, Chine (Prof. Can Li). Caractérisation de catalyseurs Sulfures par Spectroscopie Raman de Résonance.

1997-1998 Institut Français du Pétrole (Dr. S. Kasztelan). Caractérisation par spectroscopie IR de catalyseurs sulfures Mo/Al₂O₃

1.5 ORGANISATION DE COLLOQUES, ECOLES.

2006-2008 Membre du Bureau du GECat (co-organisation des Congrès GECat-DivCat de 2006 à 2008).

Organisation du GECat 2008, Hammamet, Tunisie

2001, 2003 Membre du comité d'organisation de la formation permanente "Spectroscopie IR pour l'étude des surfaces de Solides en Catalyse Hétérogène"

1.6 ENCADREMENT SCIENTIFIQUE

1.6.1 THESES.

Entre parenthèses (%encadrement moyen)

Franck Vilmin (40%) "Etude IR de Etude de l'interface silice – silane – polymère ». (2011-2014)

Lena Kondratieva (10%) "Etude IR de catalyseurs pour la désoxygénation de bio-huiles de seconde generation issue de la biomasse lingo-cellulosique". Soutenance prévue Décembre 2011

1. Curriculum vitae

Fatma Mahjoubi (70%) "Désulfuration des essences dans les conditions de FCC : Etude des mécanismes d'élimination du soufre par des additifs à base de vanadium." Thèse soutenue le 29 Janvier 2010.

Marc Antoine Lélias (20%) « Influence d'agents chélatants et des conditions de sulfuration sur la structure et l'activité de catalyseurs d'hydrotraitement. »

Fabien Can (50%), "Elimination du Soufre des Essences de FCC par des Additifs à Base d'Alumine et de Vanadium. Etude du mécanisme et identification des sites actifs." Thèse soutenue le 20 décembre 2004.

1.6.2 DEA, MASTER RECHERCHE.

Entre parenthèses (%encadrement moyen)

Najat Madri (100%) " Etude d'additifs de FCC pour la désulfuration des essences". Master Recherche Sciences des Matériaux, Juin 2005

Stéphane Caillot (100%) "Caractérisation de l'échange isotopique du d₄-thiophène sur catalyseur CoMo supporté sur SiO₂". DEA Sciences des Matériaux, Juin 2002

1.6.3 POST-DOCTORANTS.

Entre parenthèses (%encadrement moyen)

Haoguang Li (100%) « Etude operando du craquage d'alcane » 2011 – 2012 (12 mois)

Sergey Siroton (100%) «Valorisation de bio-alcools » 2011 – 2012 (12 mois)

Pawel Stelmachowski (100 %) «Valorisation de bio-alcools » 2010 – 2011 (10 mois)

Fatma Mahjoubi (100%) « Etude d'additifs Fe/P/ZSM-5 en FCC » 2010 – 2011 (8 mois)

1.6.4 MINI-PROJETS, STAGIAIRES.

Sidi Maouloud (M1 SMCO, avril-juin 2011) "Etude operando du craquage d'alcane »

Aude Ventura (L3 Chimie, juin 2007) "Modélisation de l'interaction de CO₂ avec des sites basiques"

J. Belnoue, I. Brazitlov et B. Dierre (ENSICAEN 2° Année, 2005) "Etude d'un catalyseur pour la destruction d'agents vésicants"

Diane Bauchart (ENSICAEN 2° Année, 2004) "Caractérisation de la basicité de phases sulfures supportées"

Antoine Daudin (ENSICAEN 3° Année, 2003) "sonde de basicité en liaison hydrogène impropre : CF₃H"

1.7 ENSEIGNEMENT, PARTICIPATION A L'INFORMATION SCIENTIFIQUE ET TECHNIQUE

Enseignement universitaire (service statutaire) :

Thermodynamique chimique (CM, TD, TP) : niveaux L1-L2 (UFR Science, IBFA)

Chimie Théorique (CM, TD) : niveaux L2 à M1 (IBFA, UFR Sciences),

Spectroscopie atomique et moléculaire (CM, TD) : niveaux L2-L3 (IBFA, UFR Sciences)

Cinétique et Catalyse (TP): niveau M1 (UFR Sciences)

Organisation de l'enseignement. Responsable du Master 1 Chimie – Quadrienal 2012 – 2015.

Formation permanente. Cours dans le cadre de la formation « Spectroscopie IR pour l'étude des surfaces de Solides en Catalyse Hétérogène" LCS - CNRS Formations (2001, 2003.)

Vulgarisation scientifique. Conférences dans des lycées de Basse-Normandie dans le cadre du GRES (Groupe de Réflexion sur L'Enseignement des Sciences,)

Rapporteur pour des revues scientifiques : Applied Catalysis A:General; Applied Catalysis B:Environmental; Catalysis Letters; Catalysis Today; Chemical Physics Letters; Fuel; Journal of the

1. Curriculum vitae

American Chemical Society; Journal of Catalysis; Journal of Molecular Structure: theochem; Journal of Physical Chemistry B; Surface Science.

1.8 CONSEILS ET COMITES

Depuis 2010 Membre du Bureau de la section de Chimie, Université de Caen

2006-2009 Membre du Bureau de GECat (Groupe d'Etudes en Catalyse)

2003-2008 Membre élu de la Commission de Spécialistes de la 31^o section de l'Université de Caen (2007 : 2nd vice-président).

Depuis 2003 Membre du CHS de l'Université de Caen.

2003-2006 Membre élu du Conseil Scientifique de l'ENSICAEN.

2002-2008 Membre élu du Conseil de Laboratoire.

1.9 PRODUCTION SCIENTIFIQUE

35 publications (26 revues à parution régulière, 9 actes de congrès)

1 coordination d'ouvrage collectif (Comptes-Rendus Chimie, Vol. 12, Juin-Juillet 2009)

32 communications dans des congrès internationaux (25 oraux dont 3 keynotes, 14 affiches)

13 communications dans des congrès nationaux (9 oraux, 4 affiches)

1 communication dans un congrès local (oral)

10 contributions à des séminaires et workshops (1 conférence invitée, 6 oraux, 3 affiches)

2 Liste des publications et communications

2.. Publications et communications

2.1 ARTICLES DANS DES REVUES A PARUTION REGULIERE.

(* Auteur correspondant)

A26. IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation. Popov, A.; Kondratieva, E.; Gilson, J.P.; Mariey, L.; **Travert, A.**; Maugé, F.*. *Catalysis Today* **2011**, 172, 132-135.

A25. Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study. Badawi, M.; Paul, J.F.; Cristol, S.; Payen, E.; Romero, Y.; Richard, F.; Brunet, S.; Lambert, D.; Portier, X.; Popov, A.; Kondratieva, E.; Goupil, J.M.; El Fallah, J.; Gilson, J.P.; Mariey, L.; **Travert, A.***; Maugé, F. *Journal of Catalysis*, **2011**, 282, 155-164

A24. Molecular Insight into the Adsorption of H₂S in the Flexible MIL-53(Cr) and Rigid MIL-47(V) MOFs : Infrared Spectroscopy Combined to Molecular Simulations. Vimont, A.*; Oliviero, L.; Leclerc, H.; **Travert, A.**; Serre, C.; Lavalley, J.-C.; Devic, T.; Ghoufi, A.; Maurin, G.; De Weireld, G.; Hamon, L.; Férey, G. *The Journal of Physical chemistry C*, **2011**, 115, 2047-2056

A23. Combined XRD and Infrared Studies of Pyridinium Species in (PyH)₃[PW₁₂O₄₀] Single Crystals. Pichon, C.; Mialane, P.; Marrot, J.; Binet, C.; Vimont, A.; **Travert, A.**; Lavalley, Jean-Claude, *Physical Chemistry Chemical Physics*, **2011**, 13, p322-327

A22 Bio-Oils Hydrodeoxygenation: Adsorption of Phenolic Molecules on Oxidic Catalyst Supports. Popov, A.; Kondratyeva, E.; **Travert, A.**; Gilson, J.-P.; Mariey, L. Goupil, J.-M.; Maugé, F. *The Journal of Physical chemistry C*, **2011**, 114(37), 15661-15670.

A21. Effect of EDTA addition on the structure and activity of the active phase of cobalt-molybdenum sulfide hydrotreatment catalysts. Lélías, M.A.; Le Guludec, E.; Mariey, L.; van Gestel, J.; **Travert, A.**; Oliviero, L.; Maugé, F. *Catalysis Today* **2010**, 150, 179-185

A20. Effect of NTA addition on the the structure and activity of the active phase of cobalt-molybdenum sulfide hydrotreating catalysts. Lélías, M.A.; Kooyman, P.J.; Mariey, L.; Oliviero, L.; **Travert, A.**; van Gestel, J.; van Veen, J.A.R.; Maugé, F. *Journal of Catalysis* **2009**, 267, 14-23.

A19. Evidence of CO₂ molecule acting as an electron acceptor on a nanoporous metal-benzenedicarboxylate Cr³⁺(OH)(O₂C-C₆H₄-CO₂). Vimont*, A.; **Travert, A.**; Bazin, P.; Lavalley, J.-C.; Daturi, M.; Serre, C.; Férey, G.; Bourrelly, S.; Llewellyn, P. *Chemical Communications* **2007** (31) 3291-3293.

A18. FCC gasoline sulfur reduction additives: Mechanism and active sites. Can, F.; **Travert*, A.**; Ruaux, V.; Gilson, J. P.; Mauge, F.; Hu, R.; Wormsbecher, R. F. *Journal of Catalysis* **2007**, 249 (1), 79-92.

A17. Towards the characterization of active phase of (Co)Mo sulfide catalysts under reaction conditions--Parallel between IR spectroscopy, HDS and HDN tests. Dujardin, C.; Lélías, M. A.; van Gestel, J.; **Travert, A.**; Duchet, J. C.; Maugé,* F. *Applied Catalysis A: General* **2007**, 322, 46-57.

A16. CO Adsorption on CoMo and NiMo Sulfide Catalysts: A Combined IR and DFT Study. **Travert*, A.**; Dujardin, C.; Mauge, F.; Veilly, E.; Cristol, S.; Paul, J. F.; Payen, E. *Journal of Physical Chemistry B* **2006**, 110 (3), 1261-1270.

A15. Comment on "Density Functional Theory Study of Triangular Molybdenum Sulfide Nanocluster and CO Adsorption on It". Lélías, M. A.; **Travert*, A.**; van Gestel, J.; Maugé, F. *Journal of Physical Chemistry B* **2006**, 110 (28), 14001-14003.

A14. Effect of the electronic properties of Mo sulfide phase on the hydrotreating activity of catalysts supported on Al₂O₃, Nb₂O₅ and Nb₂O₅/Al₂O₃ Rocha, A. S.; Faro*, A. C. J.; Oliviero, L.; Lélías, M. A.; **Travert, A.**; van Gestel, J.; Maugé, F. *Catalysis Letters* **2006**, 111 (1-2), 27-34.

A13. An example of misinterpretation of IR spectra of adsorbed species due to gas phase H₂O: Comment on "The surface acidity and characterization of Fe-montmorillonite probed by in situ FT-IR spectroscopy of adsorbed pyridine" [Appl. Catal. A 294 (2005) 156-160]. **Travert*, A.**; Vimont, A.; Lavalley, J.-C. *Applied Catalysis A: General* **2006**, 302 (2), 333-334.

A12. Relationship between infrared spectra and stoichiometry of pyridine-H₃PW₁₂O₄₀ salts using a new TGA-infrared coupling. Vimont*, A.; **Travert, A.**; Binet, C.; Pichon, C.; Mialane, P.; Secheresse, F.; Lavalley, J.-C. *Journal of Catalysis* **2006**, 241 (1), 221-224.

A11. Use of pyridine CH(D) vibrations for the study of Lewis acidity of metal oxides. **Travert*, A.**;

2.. Publications et communications

Vimont, A.; Sahibed-Dine, A.; Daturi, M.; Lavalley, J.-C. *Applied Catalysis A: General* **2006**, 307 (1), 98-107.

A10. Hydroprocessing of dibenzothiophene, 1-methylnaphthalene and quinoline over sulfided NiMo-hydroxyapatite-supported catalysts. Elazarifi, N.; Chaoui, M. A.; Ouassouli, A. E.; Ezzamarty, A.; **Travert, A.**; Leglise*, J.; Menorval, L.-C. d.; Moreau, C. *Catalysis Today* **2004**, 98 (1-2), 161-170.

A9. Evidence for discrepancy between surface Lewis acid strength and infrared spectra of adsorbed molecules: the case of borica-silica. **Travert*, A.**; Vimont, A.; Lavalley, J.-C.; Cuat Pascual, J. J.; Rodriguez Delgado, M.; Otero Arèan, C. *Journal of Physical Chemistry B* **2004**, 108, 16499-16507.

A8. FTIR study of unsupported molybdenum sulfide--in situ synthesis and surface properties characterization. Tsyganenko, A. A.; Can, F.; **Travert, A.**; Mauge*, F. *Applied Catalysis A: General* **2004**, 268 (1-2), 189-197.

A7. Hydrogen activation on Mo-based Sulfide Catalysts, a Periodic DFT Study. **Travert*, A.**; Nakamura, N.; van Santen, R. A.; Cristol, S.; Paul, J.-F.; Payen, E. *Journal of American Chemical Society* **2002**, 124, 7084-7092.

A6. Effect of hydrogen sulfide and methanethiol adsorption on acidic properties of metal oxides : an infrared study. **Travert, A.**; Manoilova, O. V.; Tsyganenko, A. A.; Mauge*, F.; Lavalley, J.-C. *Journal of Physical Chemistry B* **2002** 106 1350-1362.

A5. Parallel between infrared characterisation and ab initio calculations of CO adsorption on sulphided Mo catalysts. **Travert, A.**; Dujardin, C.; Mauge*, F.; Cristol, S.; Paul, J. F.; Payen, E.; Bougeard, D. *Catalysis Today* **2001**, 70 (1-3), 255-269.

A4. Correlation between activity and acidity on zeolites : a high temperature infrared study of adsorbed acetonitrile. Thibault-Starzyk*, F.; **Travert, A.**; Saussey, J.; Lavalley, J.-C. *Topics in Catalysis* **1998**, 6, 111-118.

A3. Deuterium Tracer Studies on Hydrotreating Catalysts. 2. Contribution of the Hydrogen of the Alumina Support to H-D Exchange. Thomas, C.; Vivier, L.; **Travert, A.**; Mauge, F.; Kasztelan, S.; Perot*, G. *Journal of Catalysis* **1998**, 179 (2), 495-502.

A2. Reactions of alcohols with hydrogen sulphide on zeolites. Part 7: the effect of Bronsted acidity of faujasite type zeolites on methanol hydrosulphurisation. Ziolk*, M.; Czyzniewska, J.; Kujawa, J.; **Travert, A.**; Mauge, F.; Lavalley, J. C. *Microporous and Mesoporous Materials* **1998**, 23 (1-2), 45-54.

A1. Use of but-1-yne as a probe for the characterization of the basicity of alkali exchanged zeolites. Lavalley*, J.-C.; Lamotte, J.; **Travert, A.**; Czyzniewska, J.; Ziolk, M. *Journal of the Chemical Society, Faraday Transactions* **1998**, 94 (2), 331-335.

2.2 ACTES DE CONGRES.

(* Auteur correspondant)

Ac9. Hidrodesoxigenación de biocombustibles – Efecto de moléculas fenólicas con catalizadores sulfurados. Mauge, F.* , A. Popov, E. Kondratieva, , L. Mariey, J.P. Gilson, **A. Travert SICAT Preprints 2010**

Ac8. Basic Properties of Supported Transition Metal Sulfides : combined DFT and infrared study. **Travert, A.** ; Mauge, F.; Paul, J.-F. *Preprint Papers - American Chemical Society, Division of Petroleum Chemistry* **2010** , 55, 17-20.

Ac7 Deactivation of Mo-based hydrodeoxygenation catalysts: the effect of water. Popov, A. ;Badawi, M. ; Kondratieva, E. ; Goupil, J.-M.; El Fallah, J. ; Mariey, L.; **Travert, A.** ; Mauge, F. ; Gilson, J.-P. ; Cristol, S. ; Paul, J.-F.; Payen, E. ; Portier, X. *Preprint Papers - American Chemical Society, Division of Petroleum Chemistry* **2009** , 54, 131-133.

Ac6. Catalyst made of NiMo sulfide supported on hydroxyapatite: Influence of Al addition on support properties and on the catalytic conversion of thiophene. El Azarifi, N.; El Ouassouli, A.; Lakhdar, M.; Ezzamarty, A.; Moreau, C.; **Travert, A.**; Leglise*, J. *Journal de Physique IV* **2005**, 123, 203-206.

Ac5. Sulfided catalysts based on apatite modified by adding zirconium ions: Characterization and catalytical behaviour. Ait Chaoui, M.; El Ouassouli, A.; Ezzamarty, A.; Lakhdar, M.; Moreau, C.; Leglise*, J.; **Travert, A.** *Journal de Physique IV* **2005**, 123, 319-322.

2.. Publications et communications

- Ac4.** Impacto del tratamiento con hidrogeno sobre los sitios de superficie de un catalizador CoMo sulfurado, estudio por espectroscopía infrarroja. Dujardin, C.; Ruaux, V.; van Gestel, J.; **Travert, A.**; Duchet, J. C.; Maugé*, F. *SICAT Preprints* **2004** 1470-1478.
- Ac3.** Influence of the support acidity on the sulfided phase properties. Maugé*, F.; Crepeau, G.; **Travert, A.**; Cseri, T. *ACS Preprint, Fuel Chemistry Division* **2003**, 48 (1), 131.
- Ac2.** Involvement of support hydrogen in the H₂-D₂ isotopic exchange on sulfide catalysts. Scaffidi, A.; Vivier*, L.; **Travert, A.**; Maugé, F.; Kasztelan, S.; Scott, C.; Pérot, G. *Studies in Surface Science and Catalysis* **2001**, 138, 31-36.
- Ac1.** IR study of hydrotreating catalysts in working conditions : comparison of acidity present on the sulfided phase and the support. **Travert, A.**; Maugé*, F. *Studies in Surface Science and Catalysis* **1999**, 127 269-277.

2.3 COMMUNICATIONS ORALES DANS DES CONGRES INTERNATIONAUX .

(Le nom de l'auteur présentant la communication est souligné)

- O28.** Basic Properties of Supported Transition Metal Sulfides : combined DFT and infrared study. Travert, A. ; Maugé, F.; Paul, J.-F. *ACS National Meeting*, Boston (USA) Aout **2010**.
- O27** Hidrodesoxigenación de biocombustibles – Efecto de moléculas fenólicas con catalizadores sulfurados. Maugé, F. , A. Popov, E. Kondratieva, , L. Mariey, J.P. Gilson, A. Travert. *CICAT*, Vina del Mar (Chili), Septiembre **2010**
- O26** Deactivation of Mo-based hydrodeoxygenation catalysts: the effect of water. Popov, A. ;Badawi, M. ; Kondratieva, E. ; Goupil, J.-M.; El Fallah, J. ; Mariey, L.; Travert, A. ; Maugé, F. ; Gilson, J.-P. ; Cristol, S. ; Paul, J.-F.; Payen, E. ; Portier, X. *ACS National Meeting*, Washington DC (USA) Aout **2009**.
- O25.** Deactivation of MoS₂-based hydrodeoxygenation catalysts: the effect of water. Popov, A; Badawi, M.; Kondratieva, E.; Goupil, J.M.; El Fallah, J.; Mariey, L.; Travert, A.; Maugé, F.; Gilson, J.P.; Cristol, S.; Paul, J.F.; Payen, E.; Portier X. *ISAHOF*, Ixtapa-Zihuatenejo (Mexique), Mai **2009**
- O24** IR study of oxygenates interaction with HDS catalysts for bio-oils processing. Popov, A. ; Kondratieva,E.; Goupil, J.M.; Mariey, L.; Travert, A.; Maugé, F. ; Gilson, J.P. *ISAHOF*, Ixtapa-Zihuatenejo (Mexique), Mai **2009**
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CS10 Mechanisms of FCC desulfurization additives. [séminaire invité] Travert, A. Instituto Mexicano del Petroleo Mexico (Mexique), Janvier **2011**

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3 Introduction Générale

Ce mémoire met en perspective les résultats marquants issus des recherches que j'ai réalisées depuis l'obtention de ma thèse de doctorat (Janvier 2000, Université de Caen). Ces travaux ont été menés au Schuit Institute of Catalysis (TU Eindhoven, Pays-Bas) à l'occasion d'un stage post-doctoral 2000 sous la direction du Professeur Rutger van Santen, au Laboratoire Catalyse et Spectrochimie (LCS) de l'ENSICAEN entre 2001 et 2008, ainsi qu'au centre de recherches Grace Davison (Columbia, MD, USA) de 2004 à 2009, en particulier lors d'un congé pour recherches en 2009.

Mes travaux ont essentiellement porté sur l'étude des propriétés superficielles d'oxydes et de sulfures métalliques supportés utilisés en vue d'applications catalytiques, en particulier pour la désulfuration des carburants fossiles par des catalyseurs d'hydrotraitement [A7, 8,10,14, **15, 17, 20, 21** ; Ac1-6, **8, 9**][†] ou des additifs de catalyseurs de craquage catalytique [A18]. Plus récemment, j'ai développé une activité de recherche visant à évaluer l'utilisation de catalyseurs d'hydrotraitement pour l'hydrodéoxygénation de bio-huiles en vue de la production de bio-carburants de seconde génération [A22, **25, 26**]. Enfin, j'ai également mené ou participé à des études plus 'fondamentales' (non liées à une application catalytique), en particulier l'étude de nouveaux aspects de la spectroscopie infrarouge de la pyridine adsorbée, l'une des sondes d'acidité les plus utilisées pour la caractérisation des surfaces [A9, 11, 12, 13, 23].

Dans ces études, j'ai principalement utilisé des méthodes spectroscopiques (spectroscopie IR *in situ* et *operando*), des méthodes de modélisation moléculaire (calculs ab initio et DFT) et des tests catalytiques (sur charges modèles ou réelles) afin de mettre en évidence des relations entre les spectres de vibration de molécules sondes adsorbées, la nature des sites d'adsorption et, le cas échéant, leur activité catalytique. A partir des relations structure - activité ainsi établies, l'objectif appliqué de ces études est d'aboutir à la définition des propriétés des sites de surface requis pour obtenir une activité catalytique optimale.

Je présenterais dans cette synthèse mes travaux les plus marquants menés dans les domaines de la production de carburants propres dans deux procédés de raffinage : l'hydrotraitement (hydrodésulfuration des coupes fossiles ou hydrodéoxygénation de bio-huiles) et le craquage catalytique en lit fluidisé (additifs de désulfuration).

Le Chapitre 4 portera sur l'étude de phases sulfures supportées (Mo, CoMo, NiMo). J'y montrerais en particulier comment l'utilisation combinée de la modélisation moléculaire et de la spectroscopie infrarouge de sondes adsorbées (CO en particulier) permet de mieux définir la nature des sites superficiels de ces phases sulfures et de mieux comprendre l'influence des promoteurs sur l'activité des catalyseurs d'hydrotraitement.

Le Chapitre 5 portera sur l'étude de deux types d'additifs de désulfuration en FCC par spectroscopie

[†] Les références A... et Ac... renvoient aux publications listées page 11 et suivantes. Les références en gras sont reproduites in extenso à la fin de manuscrit.

IR de molécules sondes adsorbées et des tests d'activité sur des charges modèles ou réelles. Je montrerais que ces additifs agissent en synergie avec le catalyseur de craquage, l'additif permettant un craquage efficace des composés soufrés aliphatiques produits par transfert d'hydrogène par le catalyseur de craquage.

Le Chapitre 6 décrira les premiers résultats des études que j'ai récemment initiées au laboratoire. Elles portent sur la quantification, l'identification et la thermodynamique d'espèces adsorbées sous flux à haute température, qu'il s'agisse de molécules sondes (CO₂ sur oxydes métalliques) ou de réactifs (alcanes dans des zéolithes). J'y détaillerais enfin mes projets de recherche en montrant notamment comment ces méthodologies pourraient être étendues à l'étude IR de réactions d'hydrotraitement en conditions *operando*.

4 Catalyseurs Sulfures

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4.1 INTRODUCTION

Le soufre constitue le troisième constituant du pétrole brut après le carbone et l'hydrogène avec une teneur variant de 0,1 à 8% en poids.¹ La teneur moyenne en soufre du pétrole extrait dans le monde - actuellement de 1,15%,² - est amenée à s'accroître en raison du déclin de la production de bruts doux, de l'accroissement de la part des pétroles sulfurés de Russie, Moyen-Orient, Afrique du Nord (Figure 4-1) ainsi que de l'augmentation prévue de la production de pétroles non-conventionnels : sables bitumineux (Canada) et liquéfiats de charbon (Chine).³

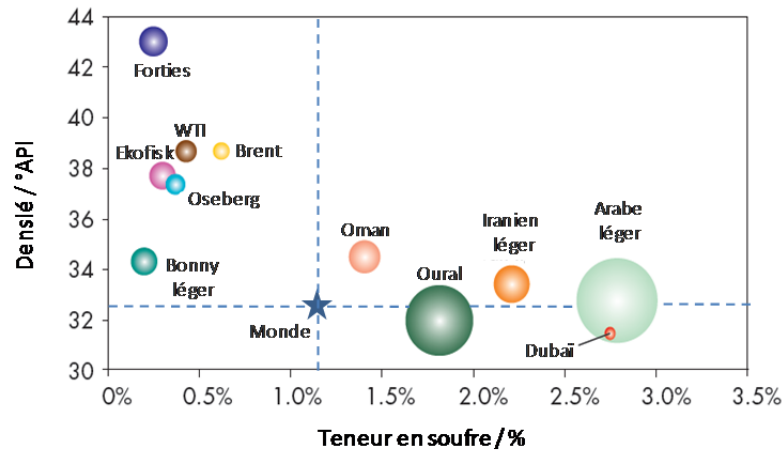


Figure 4-1 : Densité API et teneur en soufre de quelques pétroles bruts. La taille des symboles est proportionnelle à la production 2005. Adapté de [2-3].

Parallèlement, les teneurs maximales en soufre autorisées dans les carburants ont décliné exponentiellement ces dernières années (Figure 4-2). Si dans les années 80 la limitation de ces teneurs visait essentiellement à diminuer les rejets atmosphériques de dioxyde de soufre (SO₂) responsables des pluies acides, les limitations actuelles doivent permettre d'optimiser le fonctionnement des nouvelles générations de pots catalytiques des véhicules essence et diesel en limitant leur empoisonnement par les oxydes de soufre.⁴

En Europe, les teneurs maximales en soufre ont atteint 10 ppm en poids au 1er Janvier 2009 pour l'essence (Ultra Low Sulfur Gasoline, ULSG) et le gazole (Ultra Low Sulfur Diesel, ULSD).⁴ Des directives récentes imposent une norme similaire à compter du 31 décembre 2011 pour le gazole non-routier (contre 1000 ppm depuis 2008),⁵ et une réduction accrue des teneurs en soufre des combustibles marins.⁶ Aux Etats-Unis, une diminution des teneurs maximales en soufre est également à l'ordre du jour, avec la généralisation de l'ULSD (<15 ppm) pour le gazole routier et non-routier en 2010, et des gazoles locomotive et marine en 2012.² Enfin, il convient de noter que si les législations les plus strictes concernent essentiellement les pays de l'OCDE (soit ~ 55% de la demande mondiale de pétrole), la plupart des autres pays consommateurs (Amérique latine, Chine, Inde, Maghreb, Russie..) ont adopté des normes proches de celles qui prévalaient en Europe il y a une dizaine d'années (Figure 4-2). La quasi-généralisation de carburants à très basse teneur en soufre est donc certainement une question de temps.

4. Catalyseurs Sulfures.

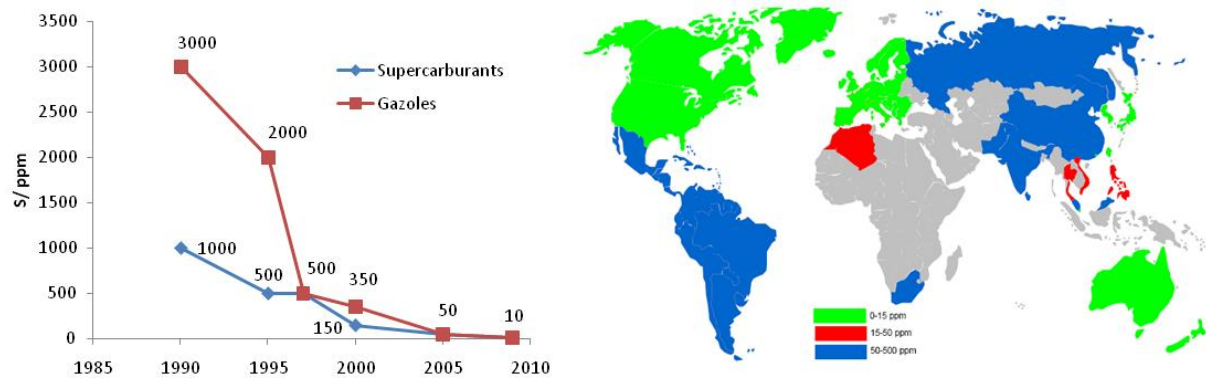
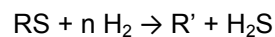


Figure 4-2. Gauche : Teneurs maximales en soufre des carburants commercialisés en France (Source UFIP). Droite : Teneurs maximales en soufre du gazole à l'horizon 2012.²

Le procédé de raffinage essentiellement employé pour réduire les teneurs en soufre des carburants est l'hydrodésulfuration (HDS), consistant à traiter la charge sous forte pression d'hydrogène (50-100 bars) à température élevée (200-400°C), le soufre étant éliminé sous forme de sulfure d'hydrogène :



Les catalyseurs d'hydrodésulfuration les plus utilisés consistent en des sulfures mixtes de métaux de transition (sulfures de Mo ou W promus par du Ni ou du Co) de taille nanométrique (1-5 nm), supportés sur un oxyde métallique de grande surface spécifique (typiquement, une alumine γ de 200 à 300 m²).

L'hydrodésulfuration est le procédé majeur d'élimination du soufre, tant en terme de volume de charges traitées (~ 50 Mbl/jour), de catalyseur consommé (~ 30 000 t/an) que de taux de conversion (jusqu'à 99,9%). L'effet combiné de la dégradation de la qualité des charges et de la demande croissante en carburants à basse teneur en soufre conduit à une augmentation massive et continue des capacités d'hydrodésulfuration des charges pétrolières: + 8 Mbl/jour sur la période 2007-2012, dont plus de la moitié est destinée à satisfaire aux régulations sur le gazole.² Des procédés alternatifs ou complémentaires à l'hydrotraitement ont été développés ces dernières années (c'est notamment le cas de la désulfuration en FCC que nous aborderons dans le chapitre 4).⁷⁻¹⁰

Pour l'heure, les efforts de recherche et développement ont principalement porté sur l'amélioration des procédés d'hydrodésulfuration. L'industrie du raffinage a ainsi pu satisfaire aux normes en agissant sur trois leviers principaux :

- la modification des variables des procédés existants (pression, température, vitesse spatiale, densité/volume du lit catalytique, ...),¹¹
- le développement de catalyseurs plus actifs : depuis 2000, l'activité spécifique des catalyseurs industriels conventionnels a été doublée.¹² On notera également l'apparition de formulations originales, telles que des sulfures massiques (Nebula,¹³) ou des catalyseurs sélectifs pour la désulfuration des essences,¹⁴
- la modification des schémas de procédés : amélioration d'unités existantes,¹¹ mise au point de nouveaux procédés d'hydrodésulfuration sélective des essences¹⁴ et de désulfuration poussée des gazoles⁹.

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Les recherches académiques conduites ces dernières années ont participé à ces progrès via plusieurs axes, notamment :

- l'optimisation des phases actives existantes (CoMo, NiMo) par l'utilisation de nouveaux précurseurs (hétéropolyanions, sulfures, ...) ou additifs (agents chélatants, dopants...) et la recherche de nouvelles phases actives (sulfures massiques, phosphures, nitrures, métaux nobles...),¹⁵
- l'utilisation de nouveaux supports (solides mésoporeux, oxydes mixtes, ...) et l'examen des interactions support-phase active,¹⁶
- la mise en évidence des mécanismes de réaction par des études cinétiques expérimentales ou de modélisation moléculaire,¹⁷
- la détermination de la structure de la phase active des catalyseurs 'classiques' (Mo, CoMo, NiMo) par des techniques d'imagerie,¹⁸ des méthodes spectroscopiques,¹⁹⁻²⁰ ou des études de modélisation moléculaire.^{17,21-23}

Ce dernier axe a constitué le champ principal de mes recherches sur les catalyseurs d'hydrodésulfuration. Mes travaux de thèse de doctorat ont essentiellement porté sur la caractérisation de l'acidité catalyseurs sulfures supportés par spectroscopie IR *in situ* et *operando*. Ils m'ont permis notamment de mettre en évidence l'influence de H₂S sur la génération de sites acides de Brønsted sur les supports oxydes [A6, Ac1] et les phases sulfures [Ac1] ainsi que sur le transport de l'hydrogène entre phase active et supports [A3, Ac2]. Par la suite, j'ai intégré le GdR Européen "Dynamique moléculaire quantique appliquée à la catalyse"[†] lors de mon stage post-doctoral en 2000 dans le groupe de Rutger van Santen (Université Technologique d'Eindhoven, NL). Dans ce cadre, j'ai contribué à la modélisation des faces (10 $\bar{1}$ 0) des phases MoS₂, CoMoS et NiMoS thermodynamiquement stables dans les conditions de l'hydrotraitement [A7]. J'ai ensuite modélisé l'activation de l'hydrogène moléculaire sur ces surfaces en collaboration avec le groupe de Chimie Théorique de l'UCCS (J.-F. Paul, S. Cristol, E. Payen - Université Lille 1) [A7]. Après mon intégration au LCS, j'ai poursuivi cette collaboration pour étudier l'adsorption de molécules sondes carbone sur ces surfaces, monoxyde de carbone [A5, A15, A16] ou chloroforme [Ac8] en combinant les approches théoriques (modélisation réalisée à Lille) et expérimentales (spectroscopie infrarouge réalisée à Caen). J'ai également contribué à des études menées spécifiquement au LCS visant à corrélérer l'activité de catalyseurs d'hydrotraitement avec les informations issues de l'adsorption de molécules sondes (nature et nombre de sites) [A10, 14, 17, 20, 21, Ac3, 5, 6].

Si les procédés d'hydrodésulfuration sont maintenant matures et permettent de produire des carburants propres d'origine fossile, les catalyseurs sulfures ont également connu un regain d'intérêt dans le domaine de la production de bio-carburants. La plupart des pays développés cherchent à accroître la production de biocarburants pour diversifier leurs bouquets énergétiques et réduire leurs émissions de CO₂. A ce titre, l'UE a pour objectif la réduction de 10% de ses émissions de gaz à effet de serre au 31 décembre 2020 en augmentant notamment la part des biocarburants dans la consommation des carburants routiers (essence et gazole). Elle impose également des critères de

[†] GdRE 1209. CNRS - Institut Français du Pétrole - Total - U. Vienne - T.U. Eindhoven.

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durabilité en limitant la conversion de zones naturelles dédiée à la production de biocarburants et en surveillant les impact éventuels sur la production agricole dédiée à l'alimentation,⁵ en particulier dans le cas des filières éthanol ou biodiesel existantes, basées sur la production de céréales et de plantes sucrières ou d'oléagineux.

Si les catalyseurs sulfures sont actuellement utilisés dans la filière bio-diesel (hydrotraitement d'huiles végétales en particulier), ils pourraient également trouver des applications pour la production de carburants de seconde génération basés biomasse ligno-cellulosique, pour lesquels deux voies de conversion thermochimique sont actuellement envisagées :²⁴

- gazéification de la biomasse en un gaz de synthèse (CO_2 , CO , H_2O , CH_4 , H_2) converti ensuite en alcools ou hydrocarbures par synthèse Fischer-Tropsch,
- liquéfaction de la biomasse par pyrolyse flash conduisant à une bio-huile.

Si la majorité des études actuellement conduites sur la voie gazéification considèrent des catalyseurs Fischer-Tropsch conventionnels à base de Co, les chercheurs de Dow Chemical et Union Carbide ont montré que des catalyseurs MoS_2 promus par des alcalins peuvent être utilisés pour la synthèse d'alcools à partir de gaz de synthèse.²⁵⁻²⁷ Si ces systèmes n'ont pas encore trouvé d'applications au-delà du stade pilote, ils font toujours l'objet d'études académiques.²⁸⁻²⁹

La voie liquéfaction, quant à elle, conduit à des huiles contenant des quantités importantes de composés oxygénés (jusqu'à 45% en poids) qui ne permettent pas leur incorporation dans le pool carburant (immiscibilité, corrosion, faible densité énergétique).³⁰⁻³¹ L'utilisation de ces huiles requiert donc le développement de procédés de désoxygénation, en particulier l'hydrotraitement (hydrodésoxygénation - HDO) par des catalyseurs sulfures classiques (CoMo, NiMo) empruntés à l'HDS en particulier.³²⁻³³ Néanmoins, leur utilisation en HDO de bio-huiles se heurte à un certain nombre de difficultés, en particulier une forte désactivation due à la formation de coke d'une part, et à l'eau produite lors des réactions d'HDO d'autre part.^{32,34}

Dans le but de mieux comprendre ces phénomènes de désactivation, j'ai donc plus récemment mis à profit mon expérience de la caractérisation IR des catalyseurs sulfures pour mieux comprendre ces phénomènes de désactivation induits par l'eau ou les précurseurs de coke [A22, **25**, **26**, Ac7,9].*

On trouvera des articles représentatifs de ces recherches reproduits *in extenso* en Annexe de ce manuscrit. Dans la suite de ce chapitre, je rappellerai l'essentiel des résultats obtenus lors de ces études en les mettant en perspective avec mes travaux de thèse et les développements récents du domaine.

* Travail réalisé dans le cadre du projet ANR-PNRB "ECOHDOD", LCS (ENSICAEN), UCCS (U. Lille 1), LACCO (U. Poitiers), TOTAL. Coordinatrice F. Maugé, LCS.

4. Catalyseurs Sulfures.

4.2 MODELISATION DES SURFACES ACTIVES

4.2.1 INTRODUCTION

A la fin des années 1990, la structure de ces catalyseurs était généralement décrite par le modèle de décoration de Topsøe³⁵⁻³⁶ dans lequel la phase active consiste en des feuillets de sulfure de molybdène MoS₂ au pourtour desquels sont localisés les atomes de promoteurs (Ni ou Co), formant une phase mixte CoMoS ou NiMoS (Figure 4-3). Il était généralement considéré que les sites catalytiques actifs en HDS consistent en des lacunes anioniques (sites CUS: Coordinatively Unsaturated sites) portées par le Mo ou le promoteur, associées à des groupements sulfhydriles -SH⁻ ou des anions sulfures S²⁻ voisins. Néanmoins, la structure de ces sites à l'échelle atomique n'était pas connue et sujette à de nombreuses spéculations. Bien que les lignes générales de ce modèle n'aient pas fondamentalement bougé, les développements récents des techniques d'imagerie (microscopie à effet tunnel – STM – et imagerie en champ sombre annulaire à grand angle – HAADF-STEM) et des méthodes de modélisation moléculaire (DFT périodique en particulier) ont permis de préciser considérablement la structure et l'environnement de ces sites.

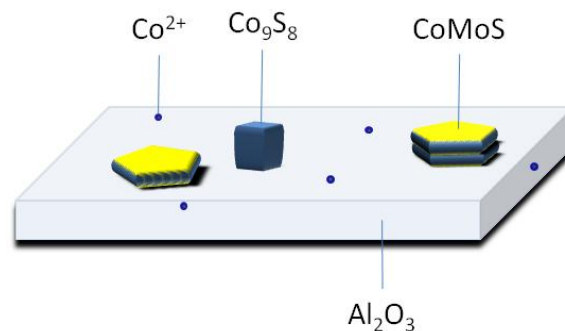


Figure 4-3 : modèle structural d'un catalyseur CoMo/Al₂O₃

Les modèles structuraux des catalyseurs sulfures CoMo ou NiMo sont basés sur la structure cristalline stable de MoS₂, consistant en un empilement de feuillets de symétrie hexagonale (P6₃/mmc). Dans ces feuillets, le molybdène est situé au centre d'un prisme hexagonal formé par les anions sulfure (Figure 4-4).

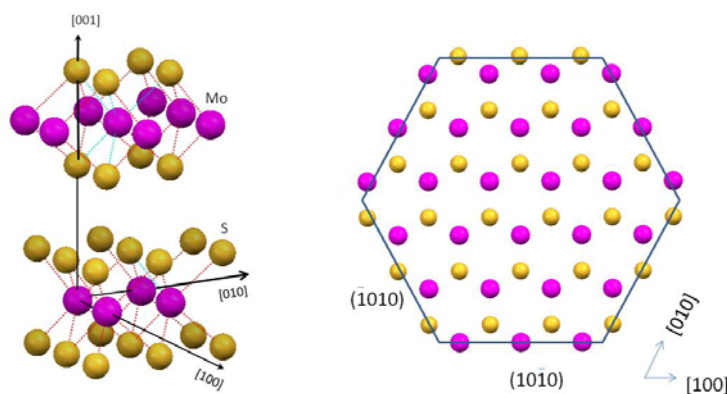


Figure 4-4 : Gauche : structure cristallographique du disulfure de molybdène. Droite : Plans cristallographiques exposés par clivage d'un cristal MoS₂

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Les feuillets MoS_2 interagissent par des interactions de van der Waals et le plan de clivage le plus simple d'un cristal est le plan basal (0001), exposant uniquement des anions soufre tri-coordinés. Ce plan est généralement considéré inactif du fait de l'impossibilité de la formation d'une lacune anionique dans les conditions de l'hydrotraitement. Cette vision d'un plan basal inerte doit toutefois être relativisée : il a depuis longtemps été montré que ces plans avaient une activité en isomérisation d'oléfines,³⁷ plus récemment, l'hydrogénation du thiophène suivie d'une ouverture de cycle sur le bord ce plan a été observée par STM en 2004.³⁸

Les surfaces perpendiculaires au plan basal, en revanche, sont susceptibles de présenter des lacunes anioniques. Le clivage d'un cristal le long de la direction (100) conduit à la formation de deux faces de densité atomique élevée (Figure 4-4) :

- la face $(10\bar{1}0)$, ou bord molybdène (bord M), présente des atomes de molybdène coordinés à quatre atomes de soufre,
- la face $(\bar{1}010)$, ou bord soufre (bord S), présente des paires d'anions soufre coordinés à deux atomes de molybdène

Telles quelles, ces deux surfaces sont non stœchiométriques relativement à MoS_2 . Sur le bord molybdène chaque atome métallique présente 2 liaisons pendantes $\text{Mo}\rightarrow(\text{S})$, ce qui conduit, - dans l'hypothèse où les charges formelles du Mo (+4) et du S (-2) sont conservées - à un excès de charge de $+4/3$ par atome de Mo.[†] De même, sur le bord soufre, chaque anion soufre présente une liaison pendante $\text{S}\rightarrow(\text{Mo})$, soit un excès de charge de $-2/3$ par atome de soufre. Ces surfaces 'idéales' sont donc a priori instables.

4.2.2 METHODOLOGIE

La détermination des surfaces stables dans les conditions de l'hydrotraitement est réalisée en construisant une cellule de travail (*supercell*) à partir de la maille de MoS_2 (Figure 4-5). Elle est constituée initialement de deux feuillets MoS_2 dans la direction x (001) et trois cellules élémentaires dans les deux autres directions. Les feuillets de MoS_2 sont clivés selon les surfaces (100) qui sont séparées, entre cellules adjacentes, par ~ 10 Å de vide de manière à isoler ces surfaces. Les feuillets de MoS_2 ainsi modélisés présentent alternativement des bords soufre (bord S) et des bords molybdène (bord M).

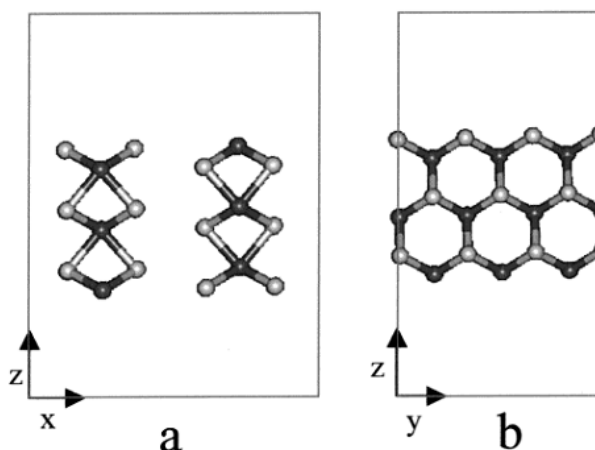
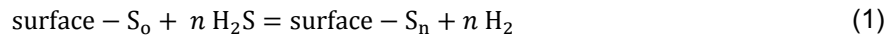


Figure 4-5 : représentation de la cellule de travail utilisée pour les calculs de DFT périodique (MoS_2 surface clivée) [A7].

[†] Ce calcul est basé sur les valences de Pauling. Dans ce modèle, la force de liaison électrostatique d'un cation (s_+) ou un anion (s_-) est donnée par le rapport de sa charge formelle (Q^\pm) à son nombre de coordination (n): $s^\pm = Q^\pm / n$. L'excès de charge sur un atome donné est donné par : $q^\pm = Q^\pm + \sum_i s_i^\pm$, où la somme porte sur les plus proches voisins. La structure la plus stable est celle qui minimise les excès de charge et/ou la charge de surface.

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L'approche utilisée pour déterminer le taux de couverture en soufre des bords consiste à considérer l'équilibre thermodynamique de la surface clivée avec une phase gaz (H_2/H_2S) représentatives des conditions d'hydrodésulfuration.³⁹⁻⁴² En excluant en première approximation la présence d'hydrogène adsorbé, le seul équilibre à considérer est la sulfuration/désulfuration de la surface sous une atmosphère H_2/H_2S :



où $\text{surface} - S_0$ représente la surface clivée 'nue' (référence) et $\text{surface} - S_n$ est la surface sulfurée (n atomes de soufre).

L'enthalpie libre de cette réaction est approximée par :

$$\Delta_r G = \Delta E^\circ + n\Delta\mu \quad (2)$$

où ΔE° est la différence des énergies électroniques des surfaces, calculées par une méthode de DFT périodique, et $\Delta\mu$ est différence des potentiels chimiques de H_2S et de H_2 dans les conditions expérimentales ($T, P(H_2S)/P(H_2)$) considérées.

Le choix des surfaces les plus stables est déterminé en fonction des populations de Boltzmann des surfaces considérées :

$$x_i = \exp\left(-\frac{\Delta_r G_i}{RT}\right) / \sum_j \exp\left(-\frac{\Delta_r G_j}{RT}\right) \quad (3)$$

La construction des surfaces promues (CoMo, NiMo) est réalisée suivant la méthodologie développée par Raybaud et al.⁴⁰ qui avaient montré que sur ces surfaces le promoteur est localisé en substitution d'un ou plusieurs atomes de Mo de bord. Les premières simulations DFT réalisées alors ne permettaient pas de déterminer clairement si la substitution du molybdène par le promoteur se faisait préférentiellement sur l'un ou l'autre type de bord (M ou S)^{40,43} et les études de caractérisation des phases promues, notamment par EXAFS, privilégiaient une localisation du promoteur sur le bord métallique $(10\bar{1}0)$.^{35,44-49} Nous avons donc, pour cette étude, uniquement étudié l'influence du promoteur et du taux de couverture en soufre des bords métalliques de MoS_2 qui était alors la plus étudiée. Les surfaces modèle ont donc été construites en substituant un, deux ou trois atomes de Mo de bord par le promoteur, conduisant à des surfaces promues substituées à 33, 67 et 100% par le promoteur Co ou Ni.

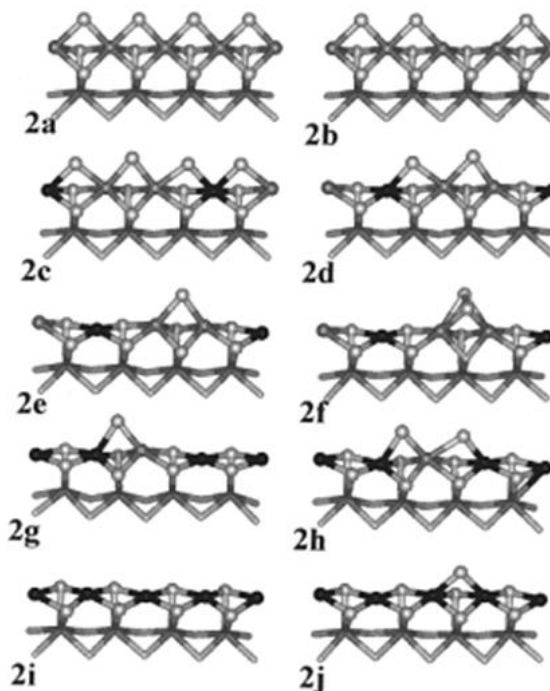
Les différentes configurations des surfaces étudiées ont été obtenues en augmentant progressivement le taux de couverture en soufre jusqu'à ce que l'évolution de leurs énergies indique qu'aucune surface stable ne serait obtenue en augmentant encore le taux de couverture en soufre.

Structure et énergie des surfaces : influence du promoteur.

Le Tableau ci-dessous regroupe les énergies et les populations des surfaces stables obtenues pour les différents taux de promotion étudiés. Les structures obtenues, représentées sur la Figure 4-6 sont généralement en bon accord avec les travaux antérieurs à cette étude.³⁹⁻⁴³

Tableau 4-1 : Energie et population des surfaces.^a

Pr/(Pr+Mo)	Structure	ΔE° eV	x
0.00	2a	-6,0	1×10^0
	2b	-4.7	8×10^{-6}
Co 0,33	2c	-3.8	4×10^{-4}
	2d	-3,6	8×10^{-2}
	2e	-3,1	9×10^{-1}
	2f	-3,4	5×10^{-3}
Co 0,66	2g	-1,2	9×10^{-1}
	2h	-1,3	1×10^{-4}
Co 1,00	2i	0,0	9×10^{-1}
	2j	-0,1	2×10^{-4}



^a Pr/(Pr+Mo), fraction atomique de promoteur, ΔE° énergie de la réaction (1), x population de Boltzmann.

Figure 4-6 : Structures des surfaces modèles [A7]

Les surfaces non-promues stables présentent essentiellement des ions Mo hexacoordinés et des atomes de soufre pontant (surface **2a**). La formation de lacunes anioniques par départ d'un atome de soufre sur ce bord (surface **2b**) est fortement défavorisée et la population de ces surfaces lacunaires est très faible dans les conditions de l'hydrotraitement ($\sim 10^{-5}$). La substitution du Mo par les promoteurs Co ou Ni conduit à la création de lacunes stables (sites CUS) portées par le promoteur lui-même ou un atome de molybdène voisin (Figures **2d - 2j**). La comparaison des énergies relatives de surfaces promues par le Co ou le Ni de structure identique, en accord avec les études précédentes, indique que la formation de lacunes anioniques est encore plus favorisée par le Ni que par le Co.

La formation de lacunes anioniques induites par la substitution du molybdène par le promoteur peut formellement être considérée comme résultant de la substitution d'une entité $[\text{MoS}]^{2+}$ par un ion Co^{2+} ou Ni^{2+} . Plus fondamentalement, la plus grande stabilité des lacunes anioniques sur les surfaces promues est due à la faible énergie de liaison promoteur-soufre comparée à la liaison molybdène-soufre. Byskov et al.⁴³ puis Raybaud et al.⁴⁰ ont montré que la diminution d'énergie de liaison est liée à l'abaissement de l'énergie des orbitales d du métal qui conduit, après liaison avec le soufre, à la formation d'états antiliants partiellement remplis. Nous avons pu illustrer ce phénomène par des cartes de différence de densité électronique entre une surface substituée par du cobalt d'une part et une

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surface non promue d'autre part. Ces cartes montrent que la substitution du molybdène par du cobalt (Figure 4-7a) conduit à une forte diminution de la densité électronique le long des liaisons métal-soufre de l'atome en substitution et augmentent la densité électronique des orbitales anti-liantes centrées sur le cobalt (orbitale 3d) et le soufre (orbitales 3p). A plus longue distance, on observe également une légère augmentation de la densité électronique autour des atomes de molybdène (orbitales 4d), probablement induite par les atomes de soufre pontant ces atomes et le cobalt en substitution. Cette augmentation de densité électronique avait déjà été rapportée dans des études plus anciennes par Harris et Chiannelli.⁵⁰ Enfin des effets similaires mais amplifiés sont observés lors de la substitution de deux atomes de molybdène par du cobalt (Figure 4-7b).

Ces résultats indiquent que les effets électroniques induits par le promoteur sont spatialement limités à sa première sphère de coordination et, dans une moindre mesure, sur les atomes de molybdène voisins. Par conséquent, la création de lacunes sur des surfaces partiellement substituées par le promoteur résulte d'une compétition entre cations voisins: le promoteur préférant une coordination quatre (configuration plan carré sur le bord M), l'incorporation de promoteur entraîne le départ d'ions sulfures de la sphère de coordination des ions métalliques de bord, conduisant à la création de sites coordinativement insaturés (Co_V , Co_{IV} , Ni_{IV} et Mo_V).

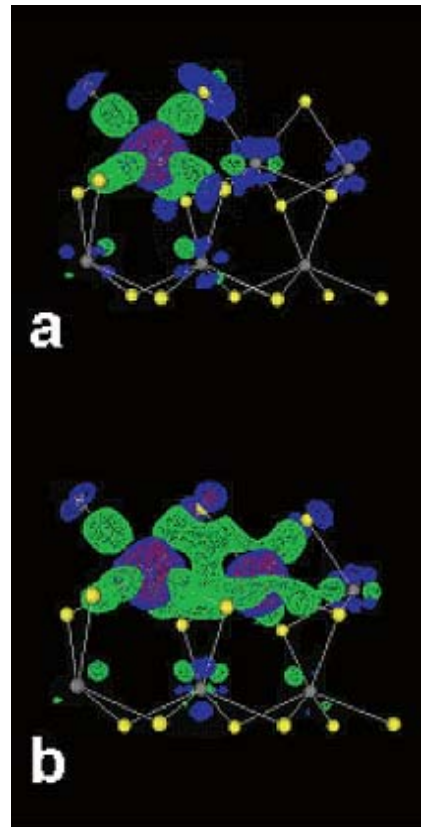


Figure 4-7 : Cartes de différences de densité électronique montrant l'effet de la substitution de molybdène par le cobalt. Vert : diminution , rouge-bleu : augmentation de densité électronique. (a) un atome substitué, (b) deux atomes substitués. [A7]

Mise en perspective avec les études ultérieures.

Bien que les conclusions essentielles de travail soient encore valides, la structure et la composition des surfaces stables déterminées par les calculs DFT ont été précisées ou modifiées par des études réalisées simultanément ou postérieurement à ce travail. En particulier, l'existence de lacunes anioniques ou d'hydrogène adsorbé sur les surfaces non promues, la stabilité relative des deux types de bord (M ou S) et la localisation du promoteur sur l'un ou l'autre de ces bords ont ou font encore l'objet de débats dans la communauté.

Formation de lacunes sur le bord M de MoS_2

En accord avec notre étude, la majeure partie des travaux réalisés sur les surfaces non promues a conclu que le bord métallique stable dans les conditions de l'hydrotraitement ne présente que des atomes de molybdène hexacoordinés (Figure 4-6, **2a**).^{39,41,43,51} Ce résultat était inattendu dans la mesure où l'existence de sites Mo coordinativement insaturés (CUS) stables était généralement admise et tous les mécanismes réactionnels proposés pour les réactions d'hydrotraitement sur MoS_2 considéraient que les sites actifs impliquaient des sites CUS.³⁵ Ces propositions semblaient en outre être confirmées par les bonnes corrélations qui sont obtenues entre la chimisorption de molécules

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sondes (O_2 , CO et NO en particulier)⁵²⁻⁵⁴ sur ces catalyseurs. Si nous verrons par la chimisorption de ces molécules de faible taille (CO, NH_3) permet de rendre compte de ces sites Mo hexacoordinés, il n'en reste pas moins que l'évaluation de la stabilité des sites CUS Mo est d'une importance capitale pour la compréhension du fonctionnement des catalyseurs sulfures Mo non promus. L'analyse de population que nous avons menée pour les surfaces non-promues indique que l'énergie requise pour la création d'une lacune (1,25 eV) implique une concentration très faible en lacunes à l'équilibre ($p = 10^{-5}$ - 10^{-6}). Dans cette hypothèse, les mécanismes de réaction sur ces surfaces requièrent la formation préalable d'une lacune qui constitue alors l'étape limitante des réactions d'HDS du thiophène⁵⁵ ou du (méthyl-)benzothiophène.⁵⁶

Néanmoins, dans cette étude, nous avons souligné que les valeurs des populations calculées sont très sensibles aux énergies relatives des surfaces. Dans un travail préliminaire (A7, supplementary material), nous avons montré que les énergies relatives de surfaces de composition et de structure identiques, calculées à l'aide du même logiciel (VASP⁵⁷) sont susceptibles de varier de $\delta E \sim 0,2$ eV selon les paramétrages utilisés (fonctionnelle, énergie de coupure, nombre de points k,...). Une variation de cet ordre de grandeur multiplie ou divise la constante d'équilibre entre deux surfaces par un facteur $\exp(\delta E/RT) \sim 30$ pour $T = 673$ K. A cette indétermination s'ajoutent l'influence des conditions expérimentales sur le potentiel chimique de la phase gaz (température, ratio H_2S/H_2 , autres composés de la charge non pris en compte) ainsi que l'influence possible du support sur la stabilité relative des surfaces.⁵⁸ En raison de la grande sensibilité des populations calculées aux variations d'enthalpie libre, nous avons noté que les structures présentant des populations de 10^1 - 10^2 étaient vraisemblablement présentes en proportion importante dans la mesure où ces valeurs sont relativement affectées par des changements d'énergie. De même, les structures présentant les populations les plus faibles ($p < 10^{-5}$) étaient considérées instables dans les conditions réactionnelles et certaines d'entre elles pouvaient être considérées comme transitoires ($p = 10^{-5}$ - 10^{-6}). Les populations intermédiaires ($p = 10^{-3}$ - 10^{-4}) étant très sensibles à de faibles variations d'énergies sont susceptibles d'atteindre quelques pourcents selon le potentiel chimique de phase gaz et les paramètres de calcul. Cette approche nous a ainsi permis de nuancer les conclusions relatives à la structure des surfaces stables et a été utilisée ultérieurement par le groupe de Nelson et al.^{51,59}

Si l'énergie de création d'une lacune sur le bord M que nous avons déterminée (1,25 eV) est en bon accord avec les résultats de Raybaud et al.³⁹ (1,26 eV) et Cristol et al.^{42,60} il est important de noter que d'autres études ont rapporté des valeurs sensiblement plus faibles pour des surfaces similaires. Dans une étude antérieure à ces travaux, Byskov et al.⁴³ avaient déterminé une valeur de 0,59 eV en utilisant une méthode similaire (DFT périodique, base d'onde planes), mais une cellule de travail plus petite (2 unités MoS_2 dans la direction z) qui ne permettait pas de prendre en compte les contraintes liées aux atomes de cœur du feuillet (A7, supplementary material). Ultérieurement, Schweiger, Raybaud et al.^{21,61} ont obtenu une valeur de $\sim 1,0$ eV pour des agrégats MoS_2 de grande taille (> 8 atomes de bords), soit une valeur significativement plus faible que celle obtenue par le même groupe dans le cas de feuillets continus (1,25 eV).³⁹ Sun et al.^{51,59}, en utilisant une cellule de travail moins étendue dans la direction y (2 Mo vs. 3 Mo pour notre étude) et un logiciel de DFT périodique utilisant une base d'orbitales (DMOL³) ont quant à eux déterminé une valeur de $\sim 0,65$ eV. Plus récemment, Cristol et al., en utilisant une cellule de travail plus longue dans la direction y (4 Mo) ont obtenu des

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énergies de 0,56 et 0,86 eV correspondant à la formation de deux types de lacunes ('longue' et 'courte', respectivement), dont la différence s'explique par la relaxation de la surface.⁶²

Il apparaît donc que l'énergie de formation d'une lacune sur le bord M est très sensible au modèle utilisé. La Figure 4-8 ci-contre représente les populations des bords M lacunaires correspondant aux différentes valeurs rapportées dans la littérature. Il apparaît que nos données, qui faisaient alors consensus en raison de qualité des modèles utilisés, conduisent à des populations très faibles. Les valeurs issues de modèles plus élaborés conduisent à des populations en bords lacunaires pouvant être importantes dans les conditions de travail de ces catalyseurs (jusqu'à 40%, soit ~ 1 lacune pour 10 Mo de bord). Le consensus encore récent sur l'absence de lacunes sur les bords M de MoS₂,^{17,21-22} est donc fortement remis en cause par ces études. A cet égard, dans une étude très récente, Prodhomme et al.⁶³ ont réexaminé en détail les surfaces stables de MoS₂ et ont confirmé que les lacunes anioniques sur le bord M sont effectivement stabilisées sous faible pression d'H₂S ($p_{H_2S}/p_{H_2} \leq 10^{-3}$).

Enfin, il convient d'ajouter que d'autres sites, à proximité du bord M, sont susceptibles de jouer un rôle catalytique. C'est le cas en particulier des sites lacunaires de coin pour lesquels Schweiger et al.⁶¹ et Wen et al.⁶⁴ ont déterminé des énergies de formation variant de 0,5 à -0,2 eV. Ces sites lacunaires devraient donc être relativement abondants dans les conditions de réaction (Figure 4-8), ce que semble confirmer une étude STM récente dans le cas de feuillets MoS₂ de petite taille.⁶⁵ Enfin, les observations par STM de Lauritsen et al.³⁸ mentionnées plus haut ont montré que les sites de 'rebord' (*brim sites*), localisés sur le plan basal à proximité des bords M présentent un caractère métallique et sont susceptibles de catalyser l'hydrogénation de composés thiophéniques.^{38,66}

Taux de couverture en hydrogène.

La méthode que nous avons utilisée pour déterminer les surfaces stables ne prend pas en compte l'adsorption dissociative de l'hydrogène sur ces surfaces qui peut conduire à la formation d'hydrures (Mo-H) ou de sulfhydriles (S-H). Les travaux précédents de Cristol et al.⁴¹⁻⁴² avaient en effet montré que l'adsorption dissociative de H₂ sur le bord M non promu est toujours endothermique ($\Delta E = 0,3 - 0,9$ eV), de sorte que la présence d'hydrogène adsorbé sur ces surfaces semblait très défavorisée dans les conditions de l'hydrotraitement ($\Delta_r G \sim 1,0 - 2,0$ eV).

Néanmoins, des études DFT ultérieures ont rapporté des énergies d'adsorption beaucoup plus faibles. En particulier, Bollinger et al.⁶⁷ ont obtenu une valeur de -0,60 eV pour la formation de deux groupements -SH de part et d'autre d'un atome de soufre pontant (Figure 4-9b, ci-après), de sorte

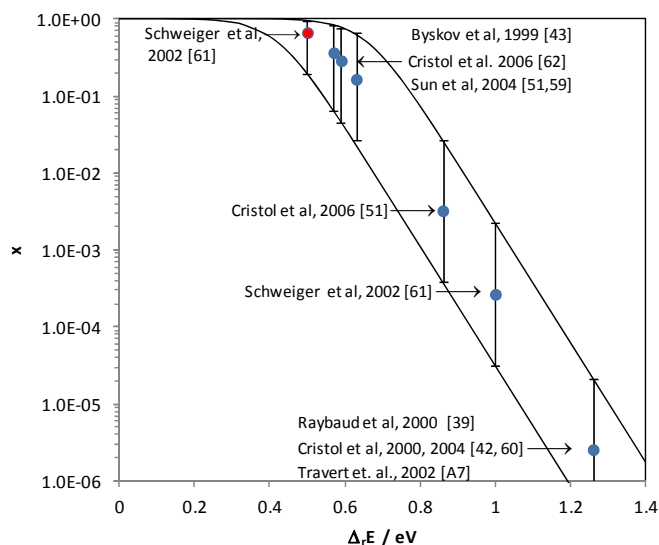


Figure 4-8 : Population des bords M lacunaires (x) en fonction de l'énergie de formation de la lacune (ΔE) à 673 K et $H_2S/H_2 = 0,1$ (courbe du bas) ou $H_2S/H_2 = 0,01$ (courbe du haut). (●) bord M; (●) coin.

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que cette surface est thermodynamiquement stable dans les conditions de l'hydrotraitement, ce qui a été confirmé très récemment par l'étude de Prodhomme et al.⁶³

Cette surface a été utilisée dans la plupart des études ultérieures publiées par le groupe Nørskov - Topsøe et la présence de groupements –SH stables entraîne des implications très importantes quant à la réactivité de ces surfaces car ces groupements pourraient notamment initier l'hydrogénation de cycles thiophéniques adsorbés sur les sites de 'rebord' (*brim sites*)⁶⁶ et seraient à l'origine de l'empoisonnement de ces catalyseurs par la pyridine via la formation d'ions pyridinium.⁶⁸⁻⁶⁹

Le désaccord entre ces études et nos hypothèses antérieures pourrait s'expliquer notamment par le fait que la cellule de travail utilisée dans nos premières études^{41-42,A7} ne comprend que trois atomes de soufre pontant, ce qui implique que contrairement au modèle de Bollinger et al. (Figure 4-9b), les deux groupements –SH formés sont nécessairement vicinaux et diminuent fortement l'ordre de liaison de l'atome de Mo auquel ils sont liés.[‡] En tout état de cause, les études DFT les plus récentes montrent que les bords M de MoS₂ sont susceptibles de présenter des groupements –SH qui n'ont pas été pris en compte dans notre étude.

Enfin, aucune étude à ma connaissance n'a explicitement étudié la thermodynamique de l'hydrogène sur les surfaces promues, certainement en raison du nombre très important de configurations qu'il serait nécessaire de prendre en compte pour obtenir un diagramme de stabilité réaliste. J'aborderais plus loin l'étude de l'adsorption de l'hydrogène que nous avons réalisé sur ces surfaces (p. 47 et suivantes). Notons ici que les énergies d'adsorption dissociative de H₂ sur ces surfaces sont sensiblement plus basses que celles obtenues sur les surfaces non promues, de sorte qu'il est possible que les surfaces promues soient susceptibles de présenter un taux de couverture en hydrogène (hydrures ou –SH) non négligeable.

Stabilités relatives des surfaces.

Au moment de ce travail, les stabilités relatives des bords promus ou non promus n'étaient pas encore clairement déterminées et le choix d'étudier le bord M était alors basé sur le fait que ce bord était privilégié dans les modèles structuraux des phases Co-Mo-S ou Ni-Mo-S publiés dans la littérature.^{35,44-49}

La première étude STM réalisée sur MoS₂,⁷⁰ publiée au moment de ce travail, avait montré que des catalyseurs modèles Mo/Au(111) sulfurés dans des conditions particulières (673K, H₂S, 10⁻⁶ bars), présentent essentiellement une morphologie triangulaire et des bords M (10 $\bar{1}0$) de structure similaire à la surface la plus stable déterminée par DFT (Figure 4-9). Néanmoins, les études expérimentales publiées ultérieurement ont permis de nuancer ce résultat. Le Tableau 4-2 ci-après présente les

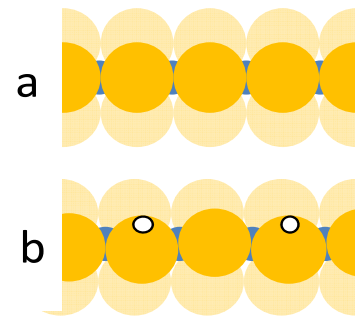


Figure 4-9 : Bord M stables dans les conditions d'HDS (A) non-hydrogéné, (Figure 4-6, 2a) ; (B) hydrogéné (Bollinger et al, 2003)

[‡] Une étude ultérieure de Sun et al. (*Catalysis Today* **2005**, 105, 36) a également rapporté une énergie d'adsorption intermédiaire pour la formation de groupements SH vicinaux (-0,18 et -0.29 eV) sur une surface de structure similaire, mais utilisant une méthode DFT différente.

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morphologies et les faces exposées de MoS₂ reportées depuis par STM ou HAADF-STEM.

Tableau 4-2 : Morphologie des phases MoS₂ observée par STM et HAADF-STEM.

Support	Technique	Sulfuration (T, P)	Morphologie	Bords exposés	Réf.
Au (111)	STM	673 K, H ₂ S, 1x10 ⁻⁹ bar	Triangle	M	70-71
Au (111)	STM	723 K, H ₂ S/H ₂ = 500, 2x10 ⁻⁹ bar	Triangle	M	72
Au (111)	STM	673 K, H ₂ S/H ₂ = 500, 1x10 ⁻⁹ bar	Triangle Hexagone tronqué (minoritaire)	M M, S	73
Au (111)	STM	723 K, H ₂ S/H ₂ = 0,07, 2x10 ⁻⁹ bar	Hexagone tronqué	M, S	72
Au (111)	STM	673 K, H ₂ S, 5x10 ⁻¹¹ bar	Triangle (> 1,5 nm) Triangle (< 1,5 nm)	M S	65
C (0001)	STM	1000 K, H ₂ S/ H ₂ = 500, 5x10 ⁻⁹ bar	Hexagone monofeuillet	M, S	74
C (0001)	STM	1200 K, H ₂ S/ H ₂ = 500, 5x10 ⁻⁹ bar	Hexagone multifeuillet	M, S	74
TiO₂ (110)	STM	900-950K, H ₂ S, ~5x10 ⁻⁹ bar	Plaquette allongée	M, S	75
Graphite	HAADF-STEM	1073 K, H ₂ S/H ₂ = 0,10, 1 bar	Hexagone tronqué	M, S	76-77

Il montre que les conditions de sulfuration et la nature du support conditionnent le type de bord exposé par MoS₂. En particulier, la présence d'hydrogène dans le mélange de sulfuration,^{72-73,76} une température de sulfuration plus élevée,^{72,74} et/ou l'utilisation d'autres supports (TiO₂ rutile et graphite)⁷⁴⁻⁷⁶ conduisent à stabiliser le bord S ($\bar{1}010$) et donc à des morphologies hexagonales tronquées ou hexagonales. Enfin, une étude récente montre qu'au dessous d'une taille critique de ~1,5 nm, les feuillets MoS₂ exposent uniquement le bord S, leur permettant ainsi de maintenir un rapport S/Mo inférieur à 3.⁶⁵ Notons que dans les conditions de cette expérience, le taux de couverture en soufre du bord M est deux fois plus élevé que celui de la surface stable en HDS (Figure 4-9), de sorte qu'a priori, ce type d'inversion n'est pas attendu pour des conditions de sulfuration plus classiques.

La modélisation DFT de MoS₂ par des feuillets continus entraîne la présence simultanée des deux types de bord sur un feuillet (Figure 4-5) et ne permettait donc pas de déterminer indépendamment leurs énergies. En revanche, en modélisant des feuillets triangulaires de MoS₂ présentant l'un ou l'autre type de bord, Schweiger, Raybaud et al.^{21,61} ont pu déterminer ces énergies. Leurs résultats confirment que le bord M est généralement plus stable que le bord S, mais que leur différence de stabilité tend à diminuer lorsque le potentiel chimique du soufre diminue (température ou pression en hydrogène plus élevée), de sorte que dans des conditions de sulfuration plus conventionnelles ou dans les conditions de l'hydrotraitement, ce modèle prévoit des morphologies hexagonales tronquées pour lesquelles les bords M sont prépondérants, en bon accord avec les observations expérimentales (Tableau 4-2).

Si ces études valident a posteriori notre choix d'étudier prioritairement le bord M des catalyseurs non promus, il convient de remarquer que l'utilisation d'un support oxyde (TiO₂ rutile) peut conduire à des feuillets présentant des bords M et S de longueur équivalente, possiblement due à la formation de liaisons covalentes entre le support et le plan basal de MoS₂.⁷⁵ Cette observation pose donc la question de la morphologie de MoS₂ sur les supports utilisés industriellement, en particulier l'alumine.

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Nous verrons plus loin que l'utilisation de CO permet de répondre en partie à cette question et confirme que dans ce cas également, les feuillets MoS₂ présentent principalement des bords M (p.68 et suivantes).

Localisation du promoteur.

Les observations STM (Tableau 4-3) et les modélisations DFT de catalyseurs promus publiées ultérieurement à ce travail ont en partie remis en cause le modèle structural des phases promues que nous avons utilisé.

Tableau 4-3 : Morphologie des phases promues Co-Mo-S et Ni-Mo-S observée par STM et HAADF-STEM.

Phase	Support	Technique	Sulfuration (T, P)	Morphologie	Bords exposés	Localisation promoteur	Ref
CoMoS	Au (111)	STM	673 K, H ₂ S, ~10 ⁻⁹ bar	Hexagone tronqué	M, S	S	71,73,78
CoMoS	Graphite	HAADF-STEM	1073 K H ₂ S/H ₂ = 0,1, 1 bar	Hexagone Dodécagone	M, S M, S, (11 $\bar{2}$ 0)		76
NiMoS	Au (111)	STM	673 – 773 K, H ₂ S, 1x10 ⁻⁹ bar	Hexagone Dodécagone	M S M, S, (11 $\bar{2}$ 0)	M, S M, S, (11 $\bar{2}$ 0)	73,78
NiMoS	Graphite	HAADF-STEM	1073 K, H ₂ S/H ₂ = 0,1, 1 bar	Hexagone Dodécagone	M S M, S, (11 $\bar{2}$ 0)		76

Les clichés STM de phases CoMoS/Au(111) montrent qu'en présence du promoteur, les feuillets MoS₂ adoptent une morphologie hexagonale tronquée après sulfuration à 673K sous H₂S pur,^{71,78-79} alors que dans les mêmes conditions, les feuillets non promus sont triangulaires, exposant exclusivement le bord M. Ces changements de morphologie s'expliquent par le fait que dans ces conditions de synthèse, le promoteur stabilise le bord S ($\bar{1}010$) par substitution complète des atomes de Mo de ce bord. Plus récemment, des observations similaires ont été rapportées par le même groupe dans le cas de phases MoS₂ sulfurées en présence de Fe et Cu.⁷⁸ Dans le cas des phases NiMoS/Au(111), un autre type de feuillet, de morphologie dodécagonale, est formé majoritairement.⁷⁹ Cette morphologie plus complexe reflète notamment l'affinité du promoteur Ni pour le bord à haut indice (11 $\bar{2}$ 0) qui n'avait, à ma connaissance, jamais été envisagé comme surface active possible pour ces catalyseurs. L'analyse des images STM de ce type de feuillet indique également que le Ni est présent sur les bords S (substitution complète ou partielle) et M (substitution partielle), de sorte que les atomes de Ni présentent une multiplicité d'environnements distincts et la structure des phases NiMoS apparaissait alors sensiblement plus complexe que les phases CoMoS.⁷⁹

Les analyses HAADF-STEM de phases NiMoS/C(graphite) et CoMoS/C(graphite) sulfurées à haute température (1073K) mais dans des conditions de pression plus conventionnelles (H₂S/H₂=0,1, P=1 bar) ont montré ultérieurement que ces deux types de phases promues sont susceptibles de présenter les bords à haut indice (11 $\bar{2}$ 0) qui ne sont pas observés dans le cas de feuillets MoS₂ sulfurés dans les mêmes conditions (Tableau 4-2 et Tableau 4-3).⁷⁶ Ce résultat permet d'établir que les deux promoteurs, Co et Ni peuvent être localisés sur ces bords. La résolution de ces clichés, néanmoins, ne permet pas de déterminer la composition des bords et de tirer des conclusions quant à la localisation du promoteur Co ou Ni sur les bords S et M. A cet égard, une étude très récente publiée par le même groupe montre qu'il est maintenant possible d'obtenir des clichés HAADF-STEM de

feuillet MoS_2 non promu à une résolution atomique.⁷⁷ Il est donc probable que dans un avenir proche, l'utilisation de cette technique permettra de déterminer si, dans des conditions de sulfuration plus conventionnelles, les promoteurs Co ou Ni sont également localisés sur les bords M des feuillets MoS_2 .

En l'absence de techniques expérimentales permettant de déterminer plus complètement la localisation des promoteurs, des études DFT ont cherché à évaluer les bords pour lesquels une substitution du Mo par le promoteur est thermodynamiquement favorisée. Schweiger et al. ont étendu la méthodologie qu'ils avaient mis au point dans le cas des feuillets non promu⁶¹ à l'étude de la stabilité des bords complètement substitués par du Co ou du Ni.⁸⁰ Ils ont pu ainsi montrer que dans les conditions de sulfuration conventionnelles de ces catalyseurs, seule la décoration complète des bords S par le cobalt est favorisée, les bords M stables restant non-promus dans ces conditions. Le Ni, en revanche, est susceptible de substituer complètement les deux types de bords. Les conclusions de cette première étude sont en bon accord avec les observations STM décrites plus haut (Tableau 4-3) et ont été confirmées ensuite par Sun et al. en utilisant une approche méthodologique alternative.⁵¹ Ces derniers ont en outre considéré le cas d'une substitution partielle des bords par le promoteur (50% de substitution) et ont montré que dans ce cas, les affinités des promoteurs Ni ou Co pour les bords M et S sont proches, de sorte que la substitution partielle des deux types de bord est thermodynamiquement possible.⁵¹ L'étude de ces surfaces partiellement substituées a ensuite été reprise et étendue par Krebs et al.⁸¹ qui ont confirmé que le cobalt tend à décorer complètement le bord S et partiellement le bord M des phases CoMoS dans les conditions de travail de ces catalyseurs. La promotion par le Ni, quant à elle peut conduire à la substitution complète ou partielle des deux types de bord.⁸¹

Les modèles structuraux des phases promues ont donc évolués sensiblement ces dernières années. Si le modèle de promotion sur le bord M que nous avons utilisé était en contradiction avec les premières études STM⁷¹ et a été critiqué lors de sa présentation devant la communauté en 2001 (MACS II, **O7**), il a plus récemment connu un regain d'intérêt au vue notamment des études DFT ultérieures.^{51,81} Nous verrons plus loin que l'adsorption de CO sur des phases promues supportées sur Al_2O_3 révèle la présence d'atomes de Mo de faible coordination au voisinage du promoteur (p. 68 et suivantes), ce qui constitue l'une des premières indication expérimentales de l'existence de bords partiellement substitués par le promoteur.^{A16} En comparant la composition de surface obtenue par XPS avec les modèles structuraux de Krebs et al.⁸¹, Gandubert et al. ont proposé que le ratio Co/Mo optimal pour l'hydrogénation du toluène conduit à maximiser le nombre de ces 'sites mixtes' Co-Mo sur le bord M de la phase Co-Mo-S.⁸² Ces sites seraient également actifs dans les réactions d'hydrogénation et de désulfuration en HDS sélective des essences.⁸³ Plus récemment, enfin, Okamoto et al.,⁸⁴ en examinant l'activité en HDS du thiophène de catalyseurs CoMo/SiO_2 synthétisés par dépôt contrôlé du Co sur des phases $\text{MoS}_2/\text{SiO}_2$ ont également proposé que la substitution du bord M par le Co conduit à des sites particulièrement actifs pour l'HDS.

Ces études récentes montrent donc que les surfaces promues que nous avons modélisées dans ce travail restent pertinentes au regard de l'état de l'art du domaine. Il convient toutefois de remarquer que ces questions sont encore loin d'être tranchées et que les bords S promu par le Co ou le Ni, dont l'existence est clairement établie, sont tout aussi légitimement considérés actifs dans des études de

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modélisation ou expérimentales.⁸⁴⁻⁸⁶ En l'absence d'études systématiques et plus complètes des propriétés catalytiques de ces surfaces 'concurrentes' (énergies d'adsorption, d'activation,...), il ne paraît pas encore possible de déterminer clairement les contributions de l'une ou l'autre de ces surfaces promues aux réactions d'hydrotraitement.

4.2.4 CONCLUSIONS

La modélisation des surfaces des phases sulfures par les méthodes de DFT, à laquelle a participé ce travail, a sans doute établi définitivement le modèle structural 'CoMoS' de proposé par Topsøe³⁵ et a profondément changé la manière de considérer ces systèmes catalytiques. En particulier, une grande partie des études expérimentales se réfèrent maintenant systématiquement à ces études.

Si l'ensemble des études DFT conduisent à des conclusions similaires sur des aspects essentiels de ces systèmes, tels que la nature des surfaces non promues ou l'effet du promoteur sur la création de lacunes anioniques, elles ont également donné lieu à des modèles divergents et posent de nouvelles questions quant à la nature des sites catalytiques des phases sulfures conventionnelles.

Ainsi, deux modèles clairement distincts sont actuellement proposés pour l'HDS par les phases MoS₂ : un modèle 'lacunaire' dans lequel le site actif (CUS) est préexistant⁶³ ou créé par le départ d'un atome de soufre sous l'effet de H₂,⁵⁵⁻⁵⁶ et permet l'adsorption puis la réaction du cycle thiophénique avec l'hydrogène adsorbé, et le modèle du 'site de rebord' (*brim edge*), pour lequel l'adsorption et la réaction sur le bord M se déroulent essentiellement sur le rebord du plan basal.^{38,66,69} En l'absence d'études comparant explicitement ces deux hypothèses ou de nouveaux résultats expérimentaux, il est encore difficile d'évaluer leur pertinence.

Le cas des surfaces promues est évidemment plus complexe en raison du nombre et de la variété des surfaces stables et des sites potentiellement actifs. A titre d'exemple, les surfaces promues de haut indice (11 $\bar{2}$ 0) pourraient, si un parallèle peut être établi avec les métaux,⁸⁷⁻⁸⁸ être particulièrement actives mais n'ont pas encore été modélisées à ma connaissance. Il est probable qu'à mesure que des données nouvelles issues d'études théoriques ou expérimentales seront produites, ces modèles s'affineront et permettront d'envisager notamment des approches micro-cinétiques des réactions d'hydrotraitement sur ces surfaces.²¹ De telles approches permettent déjà de rendre compte de la cinétique de réduction de surfaces non promues par TPR.⁸⁹⁻⁹⁰

Enfin, il est utile de rappeler que ces études DFT considèrent l'état thermodynamiquement stable de feuillet isolés. Dans le cas d'un catalyseur réel, la genèse de la phase sulfure fait intervenir une multitude d'étapes (imprégnation, séchage, calcination, sulfuration, mise en régime, ...) dont l'influence n'est pas prise en compte dans ces modèles. Il en est de même des interactions phase sulfure – support qui influencent clairement l'activité catalytique.^{15,§} L'adéquation de ces modèles et la précision avec laquelle ils peuvent décrire les phases supportées d'un catalyseur réel demeure donc une question récurrente. Je montrerais plus loin que l'adsorption de CO sur des catalyseurs supportés permet de répondre en partie à ces questions.

Je proposerais, dans la dernière partie de ce manuscrit, des stratégies expérimentales en conditions

[§] Notons ici que Raybaud et al. ont étudié les effets de support (Al₂O₃, TiO₂) sur MoS₂ et ont pu notamment proposer une explication de l'effet promoteur de TiO₂ (Applied Catal. A **2007**, 322, 76). Toutefois, en raison de la taille de ces calculs, la dimension des feuillets MoS₂ modélisés est sensiblement plus faible que celle qui est observée expérimentalement.

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operando qui devraient permettre d'obtenir de nouvelles informations sur la nature et l'activité des sites actifs de catalyseurs supportés. Ces études devraient permettre d'une part de discriminer les modèles 'lacunaire' et 'site de rebord' et d'autre part d'évaluer les activités intrinsèques des sites promus et non promus de ces catalyseurs.

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4.3 ACTIVATION DE L'HYDROGENE

4.3.1 INTRODUCTION

Après avoir défini la structure des bords M, nous avons cherché à mieux comprendre l'activation de l'hydrogène sur ces surfaces, étape indispensable aux réactions d'hydrotraitement. Au moment de ce travail, des études théoriques avaient déterminé des chemins de réaction pour l'HDS du thiophène ou du 4-méthylbenzothiophène en incluant de facto des espèces hydrogène actives (hydrures ou sulfhydriles) sur les surfaces étudiées.⁵⁵⁻⁵⁶

De nombreuses études expérimentales avaient montré la présence de groupements sulfhydriles par dosage chimique,⁹¹⁻⁹³ diffusion inélastique de neutrons,⁹⁴ adsorption de molécules sondes suivie par infrarouge⁹⁵⁻⁹⁶ [Ac1] ou plus récemment par STM.^{38,69} Au cours de mon travail de thèse, j'ai pu d'ailleurs montrer par spectroscopie IR operando que l'adsorption dissociative de H₂S sur des phases sulfures conduit à la création de groupements sulfhydriles acides [Ac1]. En revanche, aucune preuve expérimentale de la présence d'hydrures sur les sulfures de molybdène non promus ou promus par du Ni ou du Co n'a encore été apportée.

L'approche expérimentale la plus directe pour obtenir des informations sur l'activation de l'hydrogène sur ces catalyseurs consiste à étudier la cinétique des réactions d'échange isotopique H₂-D₂. L'étude de ces réactions a connu un regain d'intérêt à la fin des années 90, en particulier avec les travaux de Thomas et al. (LACCO, Poitiers),⁹⁷⁻⁹⁸ auxquels j'ai collaboré durant ma thèse [A3,Ac2] et les études de Lacroix et al.⁹⁹ (IRC, Lyon) et de Hensen et al. (TU Eindhoven).¹⁰⁰⁻¹⁰¹ Ces études montrent que l'activation de l'hydrogène par les phases sulfures a lieu à basse température (80-150°C) et que la promotion par le Co accélère fortement les réactions d'échange H₂-D₂,¹⁰¹ [Ac2]. En outre, le Co abaisse l'ordre en hydrogène de la réaction de 1 pour un catalyseur non promu à 0,5, ce qui indique un changement de l'étape limitante.¹⁰¹ En revanche, le Ni n'a pratiquement pas d'influence sur ces vitesses d'échange,⁹⁷ [Ac2] sauf dans le cas où ces catalyseurs sont pré-réduits sous hydrogène.⁹⁹ Dans tous les cas, l'effet des promoteurs sur la vitesse d'échange (multipliée par un facteur 2 à 3) est bien plus faible que celle qui est observée dans les réactions d'hydrotraitement, ce qui indique que l'activation de l'hydrogène n'est pas limitante pour ces réactions.

Ces études ont également montré que la mobilité des espèces H(D) formées sur la phase sulfure est importante dans la mesure où elles s'échangent également avec l'hydrogène du support [A3, Ac2].¹⁰⁰ Cet échange est accéléré par H₂S, qui augmente la densité de groupements sulfhydriles sur les bords de la phase sulfure¹⁰⁰ et le taux d'hydroxylation du support [A3,Ac2] favorisant ainsi la mobilité de l'hydrogène. Nous avons également montré les processus d'adsorption/désorption de H₂S sur le support et la phase sulfure contribue également à cette mobilité accrue, H₂S jouant le rôle de « molécule navette », facilitant le transport de l'hydrogène entre la phase active et le support [A3,Ac2]. La possibilité d'échanges entre H₂(D₂) et H₂S(D₂S) sur la phase sulfure indiquait en outre que l'hydrogène se dissocie hétérolytiquement sur la phase sulfure, conduisant à la formation de groupements -SH dont l'hydrogène peut s'échanger avec ceux issus de l'adsorption dissociative de H₂S.^{98,100}

Au moment de ce travail, néanmoins, la dissociation homolytique de H₂ sur des espèces disulfures S₂²⁻ conduisant à la formation de groupements -SH, ainsi qu'une dissociation hétérolytique sur des

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paires métal-soufre, conduisant à la formation d'un hydruure métallique M-H et un groupement –SH, étaient toutes deux considérées dans la littérature, dans la mesure où il était difficile de faire la part entre ces deux modes possibles d'activation.^{35,102}

Quelques études théoriques avaient été alors menées sur l'adsorption de l'hydrogène sur des sulfures métalliques, montrant que l'hydrogène est susceptible de se dissocier hétérolytiquement sur MoS₂,^{42,103} des particules NiS_x,¹⁰⁴ et RuS₂.¹⁰⁵ Au moment de ce travail, Byskov et al. avaient publié une étude sur la dissociation homolytique de l'hydrogène sur le bord S d'une phase Co-Mo-S.¹⁰⁶ La surface utilisée, néanmoins, n'était pas stable dans les conditions de l'hydrotraitement [A7].⁴⁰

Au vu de ces premières études aux conclusions parfois contradictoires, nous avons donc étudié de manière plus systématique l'activation de l'hydrogène sur les bords M stables non-promus ou promus par le Co en examinant l'adsorption moléculaire, la dissociation homolytique ou hétérolytique de H₂ et les chemins de diffusion de l'hydrogène atomique (protons ou hydruures) sur ces surfaces. Il est à noter que ce travail constitue l'une des toutes premières déterminations d'états de transition sur ces systèmes catalytiques.

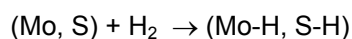
Cette étude, essentiellement limitée aux bords M des phases MoS₂ et CoMoS, a depuis été complétée par les travaux de Paul et Payen¹⁰⁷ et Sun et al.⁵⁹ qui ont en particulier étudié la dissociation de H₂ sur les bords S des phases non promues, ainsi que le bord M de la phase CoMoS pour cette dernière étude. Plus récemment, Prodhomme et al.⁶³ ont réexaminé en détail la dissociation de H₂ sur MoS₂. Ces derniers ont pu incorporer explicitement les effets entropiques et déterminer ainsi les profils d'énergie libre de ces réactions.

Les principaux résultats obtenus dans notre étude [A7] sont décrits ci-après et comparés avec ces travaux plus récents. Je montrerais dans quelle mesure ces résultats permettent d'expliquer l'effet du promoteur sur les réactions d'échange H₂-D₂.

4.3.2 RESULTATS ET DISCUSSION

Surfaces non promues

Les bords M stables de MoS₂ dans les conditions de travail de ces catalyseurs ne présentent pas de groupements disulfures S₂²⁻, qui ne sont stables sous très forte pression partielle de H₂S [A7].^{39,42,63} Par conséquent, les seuls sites disponibles pour l'activation de l'hydrogène sur ces surfaces sont les paires (Mo,S) qui conduisent à une dissociation hétérolytique :



La Figure 4-10a ci-contre représente la surface obtenue après dissociation sur la surface la plus stable ne présentant aucune lacune anionique. L'énergie d'adsorption obtenue pour cette configuration est endothermique (0,4 eV) et l'énergie d'activation obtenue est relativement élevée (1,0 eV). La Figure 4-11 ci-après compare le profil

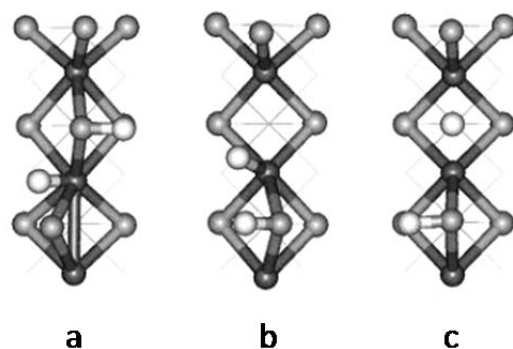


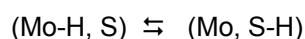
Figure 4-10 : Structure des surfaces non-promues après dissociation hétérolytique de H₂. (a) surface non-lacunaire, (b, c) surface lacunaire.

énergétique obtenu dans notre étude à ceux déterminés ultérieurement par Sun et al.⁵⁹ et Prodhomme et al.⁶³ Elle montre que l'énergie d'activation que nous avons déterminée est comparable à celle déterminée par Sun et al. (0,9 eV), mais sensiblement plus élevée que celle reportée par Prodhomme et al. (0,5 eV). De plus ces deux études conduisent à des énergies d'adsorption beaucoup plus faibles (-0,1 - -0,2 eV) que celle que nous avons déterminé (+0,4 eV).

Ces différences soulignent une fois de plus la sensibilité des énergies obtenues aux paramètres utilisés pour ces calculs.** Il est également intéressant de noter que la prise en compte des effets entropiques, discutés qualitativement dans notre étude [A7], conduit à une énergie libre d'activation élevée (+1,4 eV), une adsorption endergonique (+0,6 eV), et un profil qualitativement similaire à celui que nous avons déterminé, de sorte que les conclusions essentielles de notre travail ne sont pas sensiblement modifiées par ces nouvelles données. Elles montrent en particulier que les espèces hydrure et sulfhydryle formées après dissociation de H₂ sont thermodynamiquement instables.

Dans notre étude, nous avons également considéré la dissociation hétérolytique de H₂ sur la surface lacunaire de MoS₂ (Figure 4-6, **2b**). Dans ce cas, l'énergie d'activation et l'énergie d'adsorption obtenues pour la dissociation sur la paire Mo_v-S sont sensiblement plus faibles que précédemment (+0,5 et +0,10 eV). Cette différence s'explique essentiellement par la plus faible coordination du Mo, qui facilite notamment la formation de l'hydrure Mo_v-H (Figure 4-10b). Ce dernier est relativement mobile et migre facilement en position pontante entre deux atomes Mo_v, au centre de la lacune (Figure 10c). Conformément à ce que l'on pouvait attendre a priori, la dissociation de l'hydrogène sur une lacune est donc nettement facilitée. Dans la mesure où ces lacunes sont certainement présentes en quantités significatives dans les conditions de l'hydrotraitement (en particulier faible pression de H₂S, cf. p. 37 et suivantes), il est probable que ces sites jouent un rôle essentiel pour l'activation de H₂ sur ces bords, prépondérants dans ces conditions.

L'examen des chemins de diffusion de l'hydrogène montre que celle si se fait par sauts de l'hydrogène entre atomes de molybdène et soufre voisins :



Dans le cas de la surface la plus stable, non lacunaire, ces sauts sont pratiquement athermiques ($\pm 0,04$ eV) et présentent une énergie d'activation de 0,5 eV, sensiblement plus faible que l'énergie d'activation de dissociation sur ces surfaces. Dans le cas de la surface lacunaire (Figure 4-10b,c), le déplacement de l'hydrure vers un atome de soufre voisin est plus difficile ($E_a = 0,9$ eV), mais la

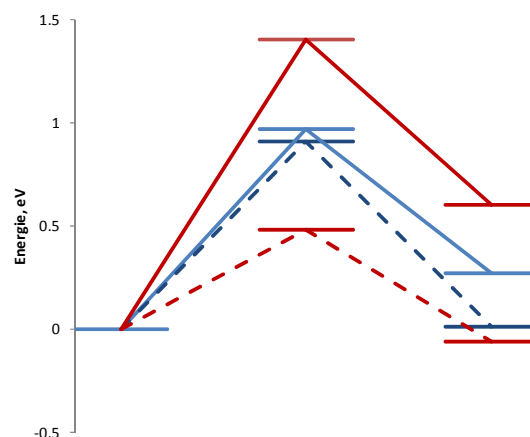


Figure 4-11 : Comparaison des profils d'énergie pour la dissociation de H₂ sur la surface non lacunaire. — notre étude; - - - Sun et al. ; - - - Prodhomme et al., énergie électronique ; — Prodhomme et al., énergie libre à 573K.

** L'origine possible de ces différences est brièvement analysée par Prodhomme et al., Supplementary Material. Il semble que l'énergie de coupure que nous avons utilisée (~200 eV, conforme à la valeur recommandée pour nos pseudopotentiels) n'assure pas une convergence suffisante.

diffusion du proton du groupement –SH est équivalente, en terme d'énergies d'activation, à celle obtenue pour la surface non-lacunaire, ce qui indique que la lacune voisine a peu d'influence sur la diffusion de ces espèces. Ces résultats montrent donc que la dissociation hétérolytique de l'hydrogène est limitante par rapport à la diffusion des hydrures ou des protons formés à la surface du bord M de MoS₂.

Ce résultat important est confirmé par les études ultérieures de Prodhomme et al. et Sun et al. qui ont rapporté des énergies d'activation un peu plus faibles ($E_a = 0,2 - 0,4$ eV) dans le sens direct de la réaction précédente (hydrure → sulfhydrile). En revanche, ces deux études indiquent que la formation de l'hydrure est favorisée par rapport à celle d'un groupement –SH, de sorte que l'énergie d'activation dans le sens indirect (sulfhydrile → hydrure) est plus élevée que dans le sens direct hydrure → sulfhydrile ($E_a = 0,5 - 0,7$ eV). Dans ces deux cas, néanmoins, la dissociation hétérolytique de H₂ reste limitante, en particulier lorsque les effets entropiques sont pris en compte.⁶³

Les études réalisées sur bord S le plus stable de MoS₂ dans les conditions de l'hydrotraitement,^{59,63,107} montrent que la dissociation hétérolytique de H₂ est athermique ou légèrement exothermique (0,02 - 0,2 eV) avec une énergie d'activation de l'ordre de 0,6 – 1,0 eV,^{63,107} soit des valeurs équivalentes à celles obtenues sur le bord M.

Ces études montrent en outre que la diffusion de l'hydrogène sur ces surfaces présente des énergies d'activation généralement plus élevées que sur le bord M : de 0,8 eV à 1,3 eV,^{59,107} pour le premier saut hydrure → sulfhydrile, et de ~0,4 eV à 0,9 eV,^{59,107} pour le processus inverse. Les espèces proton ou hydrure formées sur le bord S sont donc moins mobiles que sur le bord M et leur diffusion devient limitante par rapport à la dissociation de l'hydrogène.⁵⁹

Implication pour les échanges H₂-D₂

Les réactions d'échange H₂-D₂ se déroulent schématiquement en trois étapes élémentaires : (i) adsorption dissociative de H₂ et D₂ sur la surface, (ii) diffusion des espèces dissociées conduisant à la formation d'espèces voisines (Mo-H, S-D) ou (Mo-D, S-H) et (iii) désorption de ces espèces, conduisant à la formation de HD en phase gaz.

Les profils énergétiques obtenus sur le bord M montrent que la dissociation de l'hydrogène constitue l'étape limitante de cette série de réactions élémentaires, de sorte que l'échange H₂-D₂ sur ce bord est d'ordre premier en hydrogène, en bon accord avec l'ordre obtenu expérimentalement par Hensen et al. sur des catalyseurs Mo/C.¹⁰¹ Dans le cas du bord S, en revanche, la diffusion de l'hydrogène est limitante, ce qui implique un ordre 1/2 par rapport à l'hydrogène et indique que ce bord ne semble pas contribuer significativement aux réactions d'échanges H₂-D₂. Les résultats issus des études DFT permettent de soutenir cette interprétation des résultats expérimentaux par deux causes convergentes. D'une part l'énergie d'activation du premier saut hydrure → proton sur cette surface est l'une des plus élevées parmi l'ensemble des étapes examinées, de sorte que la constante de vitesse de cette étape pourrait être particulièrement faible. D'autre part, comme souligné par Sun et al.,⁵⁹ l'étude des stabilités relatives des bords M et S de ces surfaces montre que le bord S est largement minoritaire (cf. p. 40 et suivantes), ce qui a pour conséquence de réduire d'autant la contribution de cette surface à la réaction d'échange H₂-D₂. Notons enfin que l'étude de Prodhomme et al. conclue

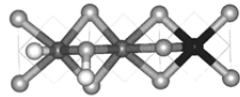
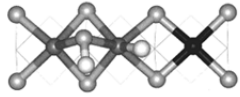
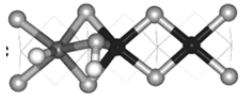


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également au rôle essentiel du bord M dans l'activation de l'hydrogène pour les réactions d'hydrotraitement.⁶³

Surfaces promues par le cobalt.

Les surfaces promues Co-Mo-S que nous avons obtenues présentent une variété importante de paires métal-soufre qui constituent autant de sites potentiels pour la dissociation hétérolytique de H₂ sur ces surfaces. Nous avons donc cherché à déterminer dans quelle mesure les caractéristiques structurales de ces sites (nature et sphère de coordination du métal, sphère de coordination du soufre) influent sur le profil énergétique de la dissociation de l'hydrogène. Le Tableau 4-4 ci-dessous présente les structures et les profils énergétiques typiques obtenus pour la dissociation de l'hydrogène sur ces surfaces.

Tableau 4-4 : Structure et énergies de dissociation de H₂ sur les surfaces promues Co-Mo-S^a

Site		E_{ads} / eV	$E_a(ads)/\text{eV}$	$E_a(des)/\text{eV}$
a	 MoV-S_{II} (MoV, MoVI)	0,51	0,79	0,28
b	 MoV-S_{II} (MoV, MoV)	0,44		
c	 MoV-S_{II} (MoV, CoV)	-0,08		
d	 CoV-S_{II} (MoVI, CoV)	-0,15	0,52	0,67
e	 CoV-S_{II} (MoV, CoV)	-0,55	0,34	0,91

(a) E_{ads} : énergie d'adsorption, $E_a(ads)$ Energie d'activation pour l'adsorption ; $E_a(des)$: Energie d'activation pour la désorption.

L'analyse détaillée des relations structure – énergie d'adsorption, que l'on trouvera dans la référence [A7], montre qu'elles s'interprètent qualitativement en considérant le principe de conservation de l'ordre de liaison (Bond Order Conservation) de Shustorovich.¹⁰⁸ La substitution du Mo par le Co conduit à un affaiblissement des liaisons métal-soufre de l'atome substitué (cf. p. 36 et suivante), ce qui a pour effet, toutes choses égales par ailleurs, de renforcer les liaisons soufre-métal de la seconde sphère de coordination du Co et d'augmenter la capacité du soufre lié au Co à accepter un proton (conservation de l'ordre de liaison du soufre). En retour, la formation d'un hydrure sur le métal de la seconde sphère de coordination est défavorisée (conservation de l'ordre de liaison du métal). Ces effets sont illustrés sur le schéma suivant, dans lequel l'épaisseur des liaisons pendantes reflète la capacité de l'atome à former une liaison avec l'hydrogène (hydrure ou proton).

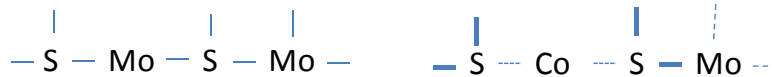


Schéma 4-1 : influence de la promotion sur les ordres de liaison.

Ainsi, l'adsorption dissociative de H_2 sur le site lacunaire **a** (voisin d'un atome de Co non représenté), conduit à une des énergies d'adsorption et d'activation plus élevées que dans le cas de la surface lacunaire non promue qui présente une structure similaire (Figure 4-10b) : $E_{ads} = 0,5$ vs. $0,1$ eV ; $E_a(ads) = 0,8$ vs. $0,5$ eV. Ces différences significatives résultent essentiellement de l'affaiblissement de la liaison Mo-H formée au voisinage du cobalt qui défavorise la dissociation de H_2 sur ce site.

La comparaison des énergies d'adsorption obtenues sur les sites **a** et **b**, qui diffèrent par le nombre de coordination de l'un des atomes de Mo lié au groupement sulfhydryle formé montre que ce paramètre n'a pas d'influence majeure sur la dissociation. En revanche, lorsque le soufre pontant est lié à un atome de Co, la dissociation de l'hydrogène est alors légèrement exothermique, qu'elle ait lieu sur une paire Mo-S (site **c**) ou Co-S (site **d**). Les énergies de formation des hydrures Mo_V-H et Co_V-H étant similaires ($\Delta E = \pm 0,04$ eV), la forte diminution d'énergie d'adsorption entre le site **b** d'une part, et les sites **c** et **d** d'autre part, est attribuée à la plus forte basicité du soufre lié à un atome de cobalt. Cet effet est amplifié lorsque l'atome de soufre pontant deux atomes de Co (site **e**), et conduit à une adsorption fortement exothermique ($-0,6$ eV), ce qui confirme le rôle important des paires Co-S dans la stabilisation des protons issus de la dissociation de H_2 .

L'énergie d'activation de la dissociation hétérolytique de l'hydrogène est d'autant plus basse que les espèces formées, hydrures et protons, sont stabilisés sur ces surfaces. Ceci est illustré sur la Figure 4-12A (ci-dessous) qui reporte l'évolution des énergies d'activation en fonction de l'énergie d'adsorption sur les sites des surfaces promues et non-promues étudiées dans ce travail.

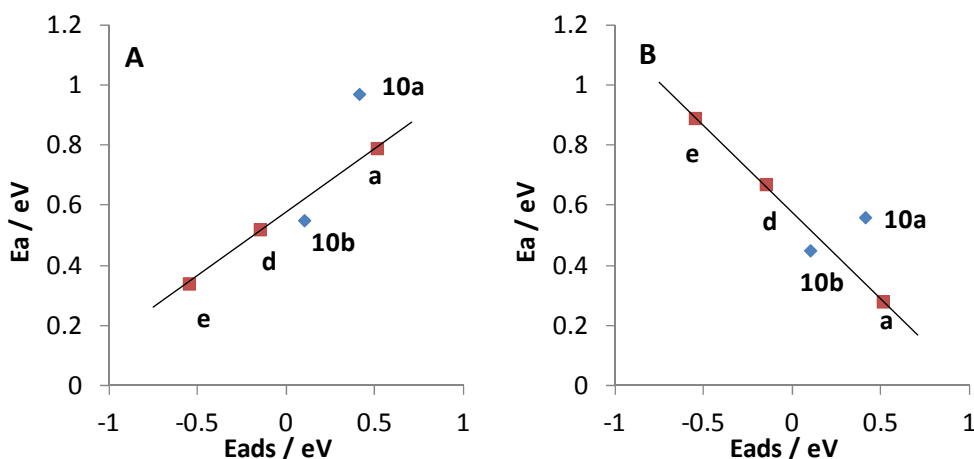


Figure 4-12 : Energies d'activation pour (A) l'adsorption dissociative et (B) la désorption associative en fonction de l'énergie d'adsorption. (■ surfaces promues ; ◆ surfaces non-promues). Les références a,d,e et 10a,10b correspondent aux structures du Tableau 4-4 et de la Figure 4-10, respectivement.

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L'évolution linéaire de l'énergie d'activation avec l'énergie d'adsorption indique l'existence d'une relation de type Evans – Brønsted – Polanyi, qui généralise les relations similaires reportées par Raybaud et al. pour les surfaces non promues, à partir de données de la littérature (incluant celles de la présente étude)⁸⁹⁻⁹⁰ ou de calculs plus récents.⁶³ Cette relation indique que l'état de transition de ces réactions élémentaires est stabilisé par les mêmes facteurs que ceux gouvernant l'énergie d'adsorption, en particulier la basicité du soufre des paires métal - soufre.

La Figure 4-13 ci-contre représente la géométrie d'états de transition typiques obtenus sur ces surfaces. La distance H-H est beaucoup plus élevée (typiquement 1,2 – 1,3 Å) que la distance intermoléculaire de l'hydrogène moléculaire adsorbé sur ces lacunes (0,8 – 0,9 Å) et la formation des liaisons M-H et S-H y est clairement apparente. La configuration de l'état de transition est donc plus proche de l'état final que de l'état initial, expliquant ainsi la corrélation obtenue entre l'énergie d'activation et l'énergie d'adsorption (Figure 4-12).

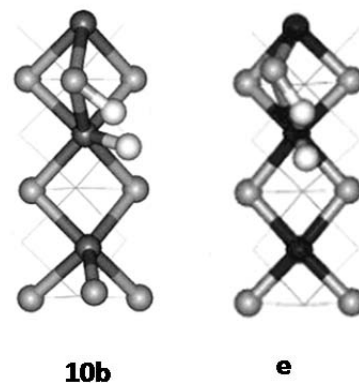
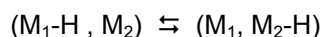


Figure 4-13 : Etats de transition pour la dissociation de H₂ sur la surface lacunaire (Figure 4-10b) et le site e (Tableau 4-4)

Les résultats obtenus dans notre étude indiquent donc que sur les surfaces promues, les paires cobalt-soufre diminuent sensiblement l'énergie d'activation de la dissociation de H₂ en stabilisant le proton sur l'atome de soufre pontant. A l'inverse, comme l'indique la Figure 4-12B, elles défavorisent évidemment la désorption des espèces dissociées, de sorte que dans la désorption de ces espèces devient limitante par rapport à l'adsorption dissociative, au contraire des bords M non-promus.

L'examen des chemins de diffusion de l'hydrogène sur ces surfaces nous a permis de mettre en évidence de nouveaux chemins de diffusion des espèces formées après dissociation, en particulier des sauts hydrure → hydrure entre deux atomes métalliques situés de part et d'autre d'une lacune anionique :



Ces sauts, directs ou via un atome de soufre tri-coordiné du plan basal, ont une énergie d'activation du même ordre de grandeur que celle observée sur les bords non promus (~ 0,3 eV), indiquant que ces espèces sont également mobiles sur bord promu par le Co. Notons ici que nous n'avons pas spécifiquement étudié la diffusion des protons formés sur ces surfaces. Les groupements SH correspondant sont particulièrement stables lorsqu'ils sont liés à un ou deux atomes de Co et l'énergie d'activation des sauts sulfhydrile → hydrure est sans doute sensiblement plus élevée pour les sulfhydriles liés au Co que pour ceux liés uniquement au Mo. Néanmoins, la vitesse globale de diffusion des espèces dissociées est a priori fixée par celle des espèces les plus mobiles, de sorte que l'on peut raisonnablement conclure que l'hydrogène est effectivement mobile sur ces surfaces

Notre étude, limitée au bord M des surfaces promues, a depuis été complétée par Sun et al.⁵⁹ qui ont étudié l'activation de l'hydrogène sur le bord S complètement substitué par le Co, correspondant au bord S le plus stable dans les conditions de réaction (cf. p.42 et suivantes). Leur étude montre également que par rapport au bord non-promu, la substitution du Mo par le Co diminue l'énergie

d'activation nécessaire à la dissociation de l'hydrogène sur ces surfaces et stabilise les protons sur les atomes de soufre pontant deux atomes de cobalt. En revanche, comme pour le bord non promu, la diffusion des espèces dissociées reste limitante sur cette surface ($E_a \sim 1,0$ eV).⁵⁹

Implication pour les échanges H_2-D_2

La comparaison des profils énergétiques obtenus sur les bords M non promu ou promu par le Co permet d'expliquer l'essentiel de l'effet promoteur du Co sur les échanges $H_2 - D_2$: augmentation de la vitesse d'échange d'un facteur 2 à 3 et diminution de l'ordre en hydrogène. La Figure 4-14 ci-dessous compare des profils énergétiques représentatifs obtenus pour l'adsorption dissociative, la diffusion des espèces dissociées et la désorption de l'hydrogène moléculaire sur ces surfaces.

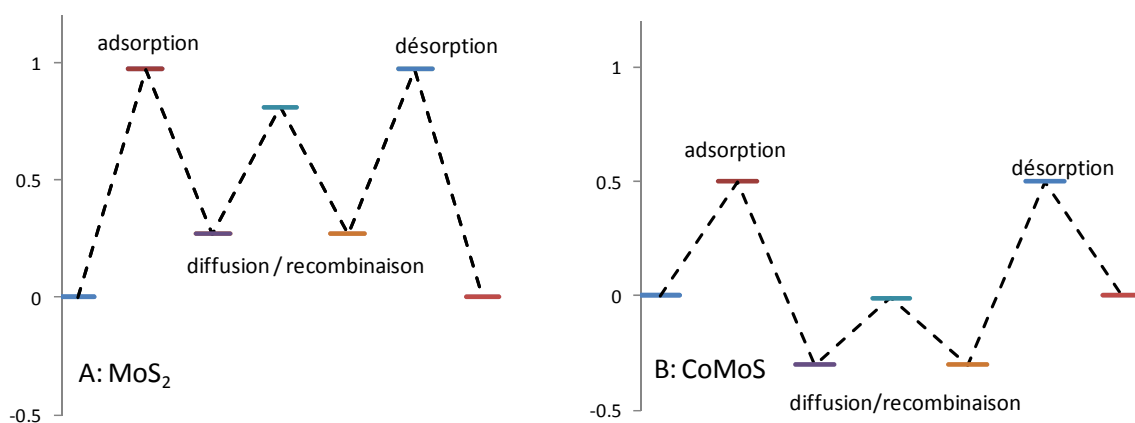


Figure 4-14 : profils énergétiques typiques pour les échanges H_2-D_2 sur les bords M non promu (A) ou promu par le Co (B).

Cette figure que la promotion par le Co conduit à abaisser sensiblement les énergies d'activation pour l'adsorption dissociative et la diffusion de l'hydrogène atomique sur ces surfaces, de sorte que la désorption de l'hydrogène moléculaire devient limitante et implique un ordre 1/2 pour la réaction globale d'échange $H_2 - D_2$, conformément aux observations expérimentales. Enfin, l'énergie d'activation obtenue pour l'étape de désorption sur le bord M n'est que légèrement plus faible (0,7-0,9 eV) que l'énergie d'activation de dissociation sur la surface la plus stable de MoS₂ (1,0 eV) qui constitue de l'étape limitante de la réaction d'échange sur la surface non-promue, expliquant ainsi l'effet positif mais limité du promoteur sur la vitesse globale d'échange H_2-D_2 .

Dans le cas du bord S, examiné par Sun et al.,⁵⁹ l'étape limitante est la diffusion de l'hydrogène sur ces surfaces, ce qui implique également à un ordre 1/2 et l'énergie d'activation correspondante est du même ordre de grandeur que celle que nous avons déterminée pour le bord M. Par conséquent, compte tenu des écarts d'énergie observés entre études différentes, il n'est pas encore possible de déterminer la contribution de chacun de ces types de bord à la réaction globale d'échange H_2-D_2 .

4.3.3 CONCLUSIONS

Les résultats obtenus dans cette étude nous ont permis de mieux comprendre les étapes élémentaires impliquées dans l'activation de l'hydrogène sur ces surfaces et de rationaliser la cinétique des réactions d'échange isotopique H_2-D_2 . Nous avons montré que le mode prépondérant de l'adsorption dissociative de H_2 est la dissociation hétérolytique sur les paires métal-soufre, qui constituent l'essentiel des sites de dissociation disponibles sur les surfaces stables dans les conditions de l'hydrotraitement.

Sur les surfaces non-promues, l'adsorption dissociative de l'hydrogène sur le bord M est limitante par rapport à la diffusion ou la désorption associative des espèces dissociées, ce qui explique l'ordre un en hydrogène des réactions d'échange $H_2 - D_2$. La comparaison de nos résultats avec les études ultérieures confirme en outre que le bord M joue un rôle majeur dans l'activation de l'hydrogène par ces catalyseurs. Les données numériques qui sont issues de notre travail (énergies d'adsorption et énergies d'activation) ont notamment été utilisées à l'Institut Français du Pétrole (IFPEN) en vue de simulations Monte-Carlo de la réduction de MoS_2 par l'hydrogène.⁸⁹⁻⁹⁰

Si le cobalt entraîne la création de nombreuses lacunes anioniques qui facilitent la l'étape de dissociation, l'effet promoteur du Co sur l'activation de l'hydrogène résulte essentiellement des paires Co-S qui stabilisent l'état de transition et le proton issu de la dissociation. Du fait de cette stabilisation, la désorption associative des espèces hydrure et proton devient l'étape déterminante des réactions d'échange H_2-D_2 , expliquant ainsi l'effet du promoteur sur l'abaissement de l'ordre en hydrogène. Enfin, les paires métal-soufre des surfaces partiellement promues étant sensiblement plus stables que celles de la surface complètement promue, nos résultats indiquent que les bords M partiellement promus par le Co devraient a priori être particulièrement actifs pour l'activation de l'hydrogène.

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4.4 PROPRIETES ACIDO-BASIQUES.

4.4.1 INTRODUCTION

L'étude précédente montre que l'effet promoteur du Co sur l'activation de l'hydrogène résulte en dernier ressort de modifications des propriétés acido-basiques de ces surfaces : création de lacunes anioniques et augmentation de la basicité du soufre. Le rôle majeur des propriétés acide-base des phases sulfures n'est évidemment pas limité à l'activation de l'hydrogène et a été reconnue de longue date pour les réactions d'hydrotraitement.³⁵ Néanmoins, la caractérisation de ces propriétés est généralement délicate, notamment parce que l'acido-basicité des supports classiquement utilisés, l'alumine en particulier, masquent généralement celle de la phase sulfure.¹⁰⁹ La caractérisation des sites acides ou basiques de la phase sulfure nécessite donc la mise en place de stratégies particulières visant à minimiser la contribution des sites du support.

Ainsi, en adsorbant la pyridine à haute température (400°C) sur des catalyseurs sulfures Mo/Al₂O₃ et CoMo/Al₂O₃, Topsøe et al.^{95,110} ont pu mettre en évidence la présence d'ions pyridinium ou pyridonium alors que ces mêmes expériences réalisées sur l'alumine seule montrent l'absence d'espèces protonées. Si cette étude est la première à avoir montré l'existence de sites acides sur la phase sulfure (-SH), il convient de noter que dans ces conditions, les phases sulfures conduisent également à l'apparition de nouvelles bandes attribuées à de la pyridone formée par l'intermédiaire de la phase sulfure.^{95,110} Dans le but de pallier à ces difficultés, Berhaut et al.¹¹¹ ont étudié les propriétés acides de catalyseurs supportés sur un support neutre SiO₂ et ont pu également mettre en évidence la présence de sites acides de Lewis et de Brønsted sur les phases sulfures (Co)Mo/SiO₂.

La caractérisation des propriétés acides de phases sulfures supportées a constitué également le cœur de mon travail de thèse. En particulier, j'ai pu clairement montrer en utilisant des méthodes de caractérisation in situ et operando que H₂S induit la création de sites acides de Brønsted sur le support et sur la phase sulfure [A6, Ac1]. En empoisonnant spécifiquement les sites de dissociation du support par de très faibles quantités d'eau (20 ppm), j'ai pu également montrer que l'acidité induite sur une phase promue CoMoS (Figure 4-15, ci-contre) est sensiblement plus importante que sur une phase non promue.

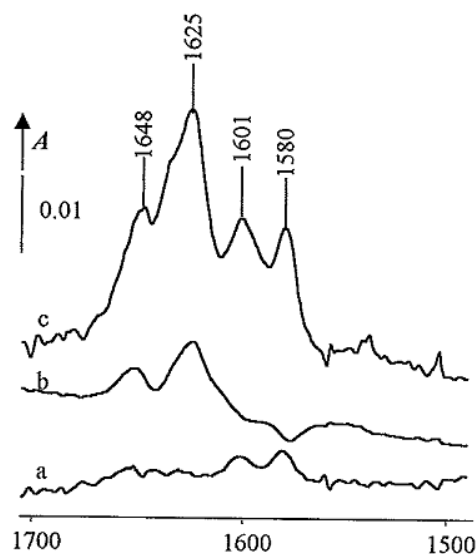


Figure 4-15 : Spectres IR des espèces lutidinium induites par adsorption de H₂S. (a) Al₂O₃ ; (b) Mo/Al₂O₃; (c) CoMo/Al₂O₃ (A.. Travert, Thèse de doctorat, Caen 2000)

Au moment de ce travail, les premières études DFT de Raybaud et al.⁴⁰ sur l'effet du promoteur sur la structure des phases sulfures n'étaient pas publiées et aucun travail théorique n'avait spécifiquement étudié les propriétés acido-basiques de ces catalyseurs, de sorte que l'interprétation des résultats des études de l'acidité des phases sulfures restait spéculative.

Dans le but de mieux comprendre ces résultats expérimentaux, j'ai donc étudié les propriétés acides des surfaces modélisées lors de mon stage post-doctoral [A7]. Par la suite, j'ai cherché à caractériser

4. Catalyseurs Sulfures.

la basicité de phases sulfures massiques [A8] ou de phases sulfures supportées [Ac8] par spectroscopie IR de sondes adsorbées, combinée à la modélisation des spectres IR de ses sondes, en collaboration avec J.F Paul (UCCS, Lille) [Ac8]. A ma connaissance, ces travaux constituent les premières caractérisations de la basicité de phases sulfures. Les principaux résultats de ces études sont présentés ci-après.

4.4.2 ACIDITE

Nous avons sondé les propriétés acides des surfaces stables en modélisant l'adsorption d'ammoniac sur les lacunes anioniques (sites acides de Lewis) et les groupements sulfhydriles obtenus après adsorption de l'hydrogène (sites acides de Brønsted). La Figure 4-16 ci-contre illustre l'adsorption de NH_3 sur le site Co_{IV} d'une surface partiellement promue par le Co (Figure 4-6, 2g).

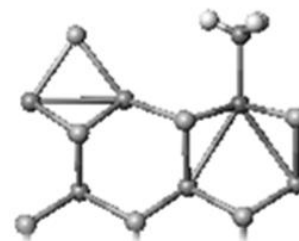


Figure 4-16 : adsorption d'ammoniac sur un site Co_{IV} .

Sites acides de Lewis

Le Tableau 4-5 ci-dessous reporte l'évolution des énergies d'adsorption et de la distance métal – azote pour la coordination de l'ammoniac selon la nature et la coordination en soufre du cation.

Tableau 4-5. Adsorption de NH_3 sur les sites acides de Lewis des bords M^a

Site de Lewis	$r_{M...N}$ / pm	Eads / eV
Mo_{VI}	235	-0,45
Mo_{V}	236	-0,99
Co_{V}	216	-0,17
Co_{IV}	209	-1,17
Ni_{IV}	227	-0,39

^a $r_{M...N}$, distance metal – azote, Eads, énergie d'adsorption $E_{\text{ads}} = E(\text{surface-NH}_3) - E(\text{surface}) - E(\text{NH}_3)$

Dans tous les cas envisagés, l'adsorption de l'ammoniac est exothermique, ce qui indique clairement le caractère acide de Lewis de ces sites superficiels, y compris la surface non promue la plus stable qui présente uniquement des atomes de Mo hexacoordinés (Mo_{VI}). Dans ce cas particulier, l'adsorption relativement forte de l'ammoniac résulte notamment de la petite taille de cette sonde. L'utilisation d'une sonde plus basique mais plus volumineuse, telle que la pyridine, conduit à une adsorption beaucoup plus faible sur ce type de site (- 0,03 eV).⁶⁸

La force de ces sites acides de Lewis dépend fortement de la nature du cation, puisque pour une coordination identique, l'énergie d'adsorption diminue selon l'ordre : $\text{Mo} > \text{Co} > \text{Ni}$, en bon accord avec l'évolution des énergies des liaisons métal-soufre déterminées pour ces métaux. Le second paramètre influençant la force de ces sites est le degré de coordination en soufre du cation qui, comme attendu, diminue significativement l'acidité de Lewis du cation.

En confrontant ces données issues de l'adsorption de l'ammoniac aux structures des surfaces

4. Catalyseurs Sulfures.

thermodynamiquement stables, il apparaît donc que l'ajout de promoteurs Co ou Ni augmentent non seulement le nombre de sites acides de Lewis via la formation de lacunes anioniques stables, mais également leur force, notamment en stabilisant les sites CUS Mo_v qui sont parmi les plus forts sur ces surfaces.

Cette influence du promoteur sur le nombre et la force des sites acides de Lewis est en bon accord avec les résultats expérimentaux de Berhaut et al. qui ont montré que des catalyseurs promus CoMo/SiO₂ présentent des sites acides de Lewis plus forts et plus nombreux qu'un catalyseur non promu Mo/SiO₂.¹¹¹

Sites acides de Brønsted

L'adsorption de l'ammoniac avec les sites acides de Brønsted (groupements –SH) des phases sulfures peut conduire à la formation d'un complexe en liaison hydrogène (-SH...NH₃) ou bien à la formation d'un ion ammonium par transfert du proton (-S⁻ ... NH₄⁺). Si cette dernière situation correspond exactement à la définition de l'acidité de Brønsted, elle conduit à l'apparition d'espèces chargées dont la modélisation par DFT périodique est plus délicate en raison des interactions à longue distance entre cellules voisines. Aussi, pour cette étude, nous avons uniquement étudié la structure et l'énergie des complexes en liaison hydrogène qui se sont révélés stables sur ces surfaces. Cette approche est similaire à l'utilisation de sondes d'acidité faibles en spectroscopie IR (CO par exemple), qui permet de définir la force des sites acides de Brønsted à partir de la force de la liaison hydrogène formée.¹¹²

Le Tableau 4-6 ci-dessous reporte les paramètres structuraux et les énergies d'adsorption obtenues pour la formation d'une liaison hydrogène entre l'ammoniac et les groupements sulfhydriles typiquement formés après adsorption de H₂ sur les bords M non promus ou promus par le Co.

Tableau 4-6 : Adsorption de NH₃ sur les groupements –SH des bords M.^a

Site	$\Delta r/r_0$	rH...N / pm	Eads / eV
(Mo,Mo)S-H	0,14	148	-0,47
(Co,Mo)S-H	0,08	160	-0,45
(Co,Co)S-H	0,06	170	-0,37

^a $\Delta r/r_0$ élongation de la liaison S-H sous l'effet de la liaison hydrogène ; rH...N distance hydrogène- azote ; Eads : énergie d'adsorption $E(\text{surface-NH}_3) - E(\text{surface}) - E(\text{NH}_3)$

L'adsorption de l'ammoniac sur ces groupements –SH est exothermique, indiquant le caractère fortement acide de ces sites. Il est à noter que les valeurs des énergies d'adsorption obtenues (0,4-0,5 eV) sont très fortes pour une liaison hydrogène (généralement inférieure à 0,3 eV,¹¹³), ce qui indique que l'état le plus stable pour l'adsorption de NH₃ sur ces sites est certainement la formation d'une paire d'ion après transfert du proton qui est sans doute faiblement activée, comme montré récemment dans le cas de la pyridine.⁶⁸

D'un point de vue énergétique et structural, les données du Tableau 4-6 indiquent que la force acide des groupements sulfhydriles augmente selon l'ordre : (Mo,Mo)S-H > (Mo,Co)S-H > (Co,Co)S-H.

Ces résultats montrent donc qu'en tant que ligand, le Co diminue sensiblement la force acide des

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groupements sulfhydriques, ou, en d'autres termes, augmente la basicité du soufre auquel il est lié. Ce dernier résultat est en bon accord avec l'effet stabilisateur du cobalt sur l'adsorption dissociative de l'hydrogène décrite précédemment. Du point de vue de l'acidité de Brønsted, le cobalt conduit à deux effets antagonistes : il stabilise les protons des groupements sulfhydriques, ce qui devrait conduire à une augmentation sensible de leur concentration dans les conditions de travail de ces catalyseurs, mais cette stabilisation est la diminue la force de ces sites. Au vue des énergies d'adsorption obtenues, néanmoins, ces sites restent acides, en particulier pour les surfaces partiellement promues sur lesquelles les atomes de soufre pontant une paire (Co, Mo) sont significativement plus stables que ceux pontant une paire (Co, Co) et conduisent à des sites de Brønsted (Co,Mo)S-H dont l'acidité reste proche de celle des groupements sulfhydriques des surfaces non promues (Mo,Mo)S-H.

Ces conclusions issues de la modélisation DFT sont en bon accord avec l'étude de Maternova⁹² qui a montré que la promotion par le cobalt conduit à une augmentation sensible du nombre de groupements -SH ainsi qu'avec les études plus récentes de Petit et al.⁹⁶ et Berhault et al.¹¹¹ qui indiquent que l'acidité de Brønsted d'une phase CoMo supportée sur SiO₂ ou Al₂O₃ est supérieure à celle d'une phase non promue. Enfin, la capacité des phases promues Co-Mo-S à produire un nombre important de sites acides de Brønsted par adsorption de H₂S [Ac1] s'explique par l'augmentation du nombre de lacunes anioniques qui sont a priori susceptibles de dissocier H₂S, conduisant à la formation de groupements -SH acides et plus stables que sur une phase non promue.

4.4.3 BASICITE

Si la présence de centres basiques est fréquemment invoquée dans les mécanismes des réactions d'hydrotraitement (dissociation de dihydrogène [A7], ruptures des liaisons C-N,¹¹⁴⁻¹¹⁵ ou C-S,¹¹⁶⁻¹¹⁷ ...), aucune étude à ma connaissance n'a caractérisé les propriétés basiques de phases sulfures supportées. L'une des causes probables de cette absence d'étude est la faible basicité des phases sulfures. En particulier, nous avons montré que la dissociation de l'hydrogène ou de H₂S conduit à la formation de groupements -SH acides [Ac1, A7], ce qui indique que les atomes de soufre acceptant les protons issus de la dissociation de ces molécules sont peu basiques.

Néanmoins, nous avons montré que le promoteur est susceptible d'accroître la basicité du soufre, ce qui influence notamment l'activation de l'hydrogène [A7] et des études mécanistiques on considéré que la basicité accrue du soufre pouvait en partie expliquer l'effet promoteur du cobalt sur la voie de désulfuration directe des dibenzothiophènes.¹¹⁶⁻¹¹⁷ Il est donc particulièrement important de caractériser l'acidité des phases sulfures en cherchant, dans la mesure du possible, à déterminer si la nature de la phase sulfure influence significativement cette basicité.

Dans un premier temps, j'ai cherché à caractériser les sites basiques de catalyseurs sulfures supportés sur Al₂O₃ en utilisant des sondes courantes de basicité (CO₂, CCl₄, pyrrole, ...). Les résultats obtenus montrent dans tous les cas que la basicité du support seul est au moins aussi importante que celles des catalyseurs sulfures supportés, indiquant que la basicité des phases sulfures supportées est sensiblement plus faible en nombre et en force que celle du support.

Adsorption de CO₂ et COS sur MoS₂ massive

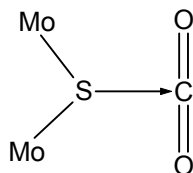
Dans le but de s'affranchir des effets de support, nous avons cherché à caractériser la basicité de MoS₂ massive dans une étude réalisée avec A. Tsyganenko (Université de Saint Petersburg, Russie) [A8] en caractérisant par spectroscopie IR l'adsorption des sondes acides (SO₂, CO₂ et COS). Utilisées pour la caractérisation des oxydes métalliques, ces sondes forment généralement des espèces fortement adsorbées (sulfites, (thio)hydrogénocarbonates et (thio)carbonates) révélant la présence d'hydroxyles ou d'oxygènes basiques.¹¹⁸

Dans le cas de MoS₂ massive, nous avons montré que ces sondes sont moléculairement adsorbées et interagissent faiblement avec la surface. Néanmoins, les fréquences de vibration observées sont significativement déplacées par rapport à la phase gaz (10-30 cm⁻¹), indiquant une interaction de ces sondes avec MoS₂.

La Figure 4-17 ci-contre montre les spectres obtenus dans le cas de l'adsorption de CO₂ et COS à basse température dans la région des vibrations d'élongation asymétrique ν₃ de ces molécules.

Les fréquences observées (2326-2331 cm⁻¹ et 2032-2038 cm⁻¹) sont significativement plus faibles que les fréquences de ces molécules en phases gaz (2349 et 2062 cm⁻¹, respectivement). Dans le cas de des oxydes métalliques, l'interaction de CO₂ avec des sites de Lewis (adsorption linéaire) conduit à une augmentation de cette fréquence.¹¹⁹ En revanche, les études de complexes de CO₂ en interaction avec des donneurs d'électrons¹²⁰⁻¹²²

(alcools, ou polymères fonctionnalisés,) montre que l'interaction de CO₂ avec un centre basique conduit à une diminution de cette fréquence, ce qui nous permet de conclure que les espèces CO₂ observées interagissent avec des centres basiques de la phase sulfure via l'atome de carbone selon :



Les déplacements en fréquence observés sont toutefois relativement faibles ($\Delta\nu_3 = -18 - -23$ cm⁻¹), indiquant une faible basicité du soufre.^{††}

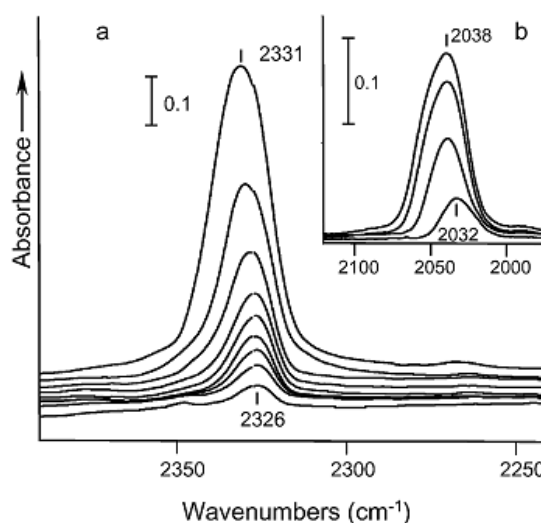


Figure 4-17 Spectres IR de (a) CO₂ et (b) COS après adsorption sur MoS₂ à basse température (77-100K)

^{††} Plus récemment, nous avons pu également mettre en évidence ce type d'interaction dans le cas de l'adsorption de CO₂ dans des solides hybrides organiques-inorganiques (MOF) [A19].

Adsorption de $CDCl_3$ sur ses phases sulfures supportées sur SiO_2 .

Dans une seconde étude [Ac8], j'ai cherché à caractériser la basicité de phases sulfures supportées sur SiO_2 , support ne présentant pas de basicité notable. Afin d'examiner l'influence éventuelle du métal sur la basicité du soufre, cette étude a été réalisée sur différentes phases sulfures RuS_2 , PtS , MoS_2 et $CoMoS$.

Nous avons choisi le chloroforme deutéré ($CDCl_3$), classiquement utilisé pour la caractérisation de la basicité d'oxydes métalliques.¹¹⁸ Il présente un groupement C-D acide et interagit par liaison hydrogène avec les centres basiques. La formation de ces liaisons hydrogènes se traduit par un abaissement de la fréquence $\nu(C-D)$ d'autant plus important que la basicité est forte.

La Figure 4-18 ci-contre montre les spectres obtenus dans la région des vibrations $\nu(C-D)$ après adsorption de $CDCl_3$ sur le support seul et la silice. Elle montre que la présence d'une phase sulfure (spectres b-e) conduit à une bande supplémentaire νCD à $\sim 2235\text{ cm}^{-1}$ qui caractérise l'interaction de $CDCl_2$ avec la phase sulfure. Dans tous ces cas, l'adsorption de $CDCl_3$ est totalement réversible (absence d'espèces dissociées).

Dans le but de déterminer plus précisément la nature de l'interaction conduisant à cette nouvelle bande, nous avons examiné l'influence du taux de couverture en soufre des catalyseurs Mo/SiO_2 et $CoMo/SiO_2$ par un traitement sous hydrogène à

400°C. La Figure 4-19 ci-contre montre que ce traitement a pour effet de diminuer l'intensité de cette bande à 2235 cm^{-1} au profit d'une bande à plus haut nombre d'ondes, vers 2255 cm^{-1} . En parallèle, l'adsorption de CO montre que le traitement sous H_2 conduit effectivement à une augmentation du nombre de sites CUS accessibles à CO, et donc à une diminution du taux de couverture en soufre des phases MoS_2 et $CoMoS$ (Figure Figure 4-19B). La comparaison des spectres νCO et νCD obtenus avant et après traitement sous hydrogène nous a ainsi permis d'attribuer la bande νCD à 2235 cm^{-1} à la formation de liaisons hydrogènes entre $CDCl_3$ et les atomes de soufre de bord de ces phases sulfures et la bande νCD à 2255 cm^{-1} au chloroforme coordonné aux sites CUS créés sous l'effet de traitement par H_2 :

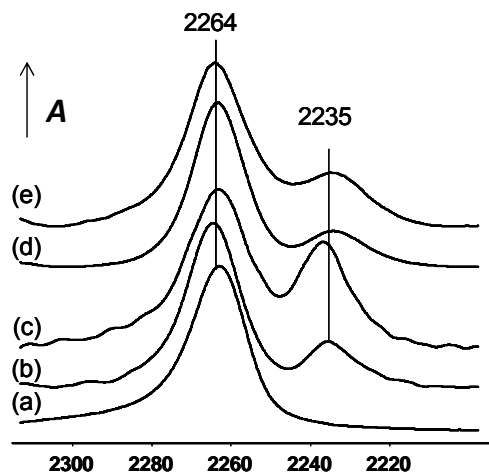
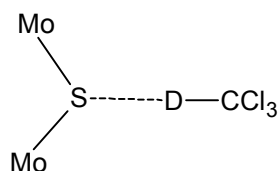
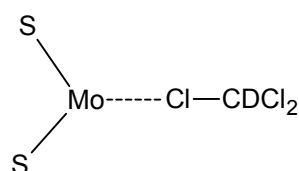


Figure 4-18 : Spectres IR après adsorption de $CDCl_3$ sur (a) SiO_2 , (b) Mo/SiO_2 , (c) $CoMo/SiO_2$, (d) Pd/SiO_2 , (e) Ru/SiO_2



$$\nu(CD) = 2235\text{ cm}^{-1}$$



$$\nu(CD) = 2255\text{ cm}^{-1}$$

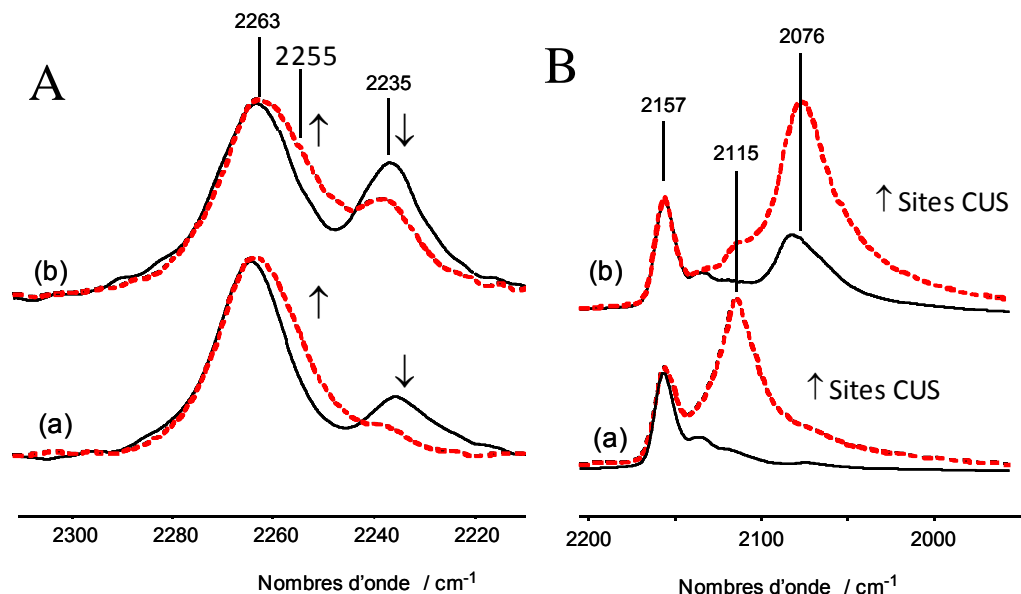


Figure 4-19 : Effet d'un traitement par l'hydrogène sur l'adsorption de (A) CDCl_3 et (B) CO sur (a) Mo/SiO_2 et (b) CoMo/SiO_2 . (— avant traitement, --- après traitement).

La modélisation de l'adsorption de CDCl_3 sur les bords stables de MoS_2 réalisés à l'UCCS permettent de confirmer l'attribution de la bande à 2235 cm^{-1} à la formation d'une liaison hydrogène avec le soufre de ces bords, les fréquences $\nu(\text{CD})$ calculées étant proches du déplacement ($\nu(\text{CD}) = 2330 - 2345 \text{ cm}^{-1}$ vs. 2335 cm^{-1}).

Si l'observation de cette bande $\nu(\text{CD})$ indique que les atomes de soufre de bord présentent un caractère basique, il convient toutefois de remarquer que le déplacement en fréquence de cette bande, $\Delta\nu \sim -30 \text{ cm}^{-1}$, est significativement plus faible que celui observé pour des solides modérément basiques. A titre d'exemple, des zéolithes basiques conduisent à un déplacement de $-40 - -60 \text{ cm}^{-1}$.¹²³ Néanmoins, en l'absence de travaux de références sur l'interaction de CDCl_3 avec des composés sulfurés, il est délicat de comparer directement ces fréquences. Nous avons donc étudié l'interaction de cette sonde avec des sulfures organiques en phase liquide (diméthylsulfure, dibutylsulfure et tetrahydrothiophène) et montré que les complexes formés avec ces molécules conduit à des fréquences $\nu(\text{CD})$ comparables à celle observée sur les phases sulfures étudiées ($2231 - 2236 \text{ cm}^{-1}$), indiquant une basicité du soufre comparable à celle de ces composés organiques dont l'affinité protonique est de l'ordre de 850 kJ mol^{-1} .

La nature de la phase sulfure (Mo, CoMo, Ru ou Pt) ne modifie pas sensiblement la position de la bande $\nu(\text{CD})$, ce qui semble indiquer que la basicité du soufre n'est pas sensiblement affectée par la nature de la phase sulfure. Il convient de noter, toutefois, que si CDCl_3 permet d'évaluer une basicité 'moyenne' de surface, cette sonde ne permet pas toujours de discriminer des différences modérées de basicité,^{118,124} de sorte que de nouvelles études sont nécessaires pour caractériser plus finement la basicité de phases sulfures supportées, par exemple en étudiant l'interaction de cette sonde avec des phases sulfures présentant des liaisons métal-soufre plus faibles (Rh_2S_3 , notamment) ou en utilisant une sonde acide plus forte, CF_3H par exemple [P9,10].

Notons ici que la caractérisation de la basicité du soufre par l'évaluation de la force de la liaison

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hydrogène formée avec un groupement X-H acide ne permet pas formellement d'évaluer son caractère basique au sens de Brønsted qui implique un transfert de proton. Toutefois, l'utilisation de sondes plus acides conduisant à un transfert complet du proton, tel que CH₃SH ne permet pas de caractériser isolément la basicité du soufre dans la mesure où la 'force' du site de dissociation (paire acide-base de Lewis), dépend à la fois de l'acidité du site CUS et de la basicité du soufre.

En l'état actuel, toutefois, les résultats obtenus indiquent clairement que la basicité de ces phases sulfures est faible, ce qui est en bon accord avec le fait que les groupements –SH issus de la dissociation de H₂ ou de H₂S présentent un caractère acide de Brønsted, comme montré par la modélisation moléculaire [A7],⁶⁸ la spectroscopie IR de sondes adsorbées [A1]^{95,110-111} ou plus récemment par STM.⁶⁸

4.4.4 CONCLUSIONS

L'étude des propriétés acides des bords M non promus ou promus par le Co ou le Ni nous a permis de rationaliser les conclusions issues des études de caractérisation des propriétés acides de catalyseurs sulfures supportés. Nous avons ainsi pu montrer que le promoteur augmente à la fois le nombre et la force acide de Lewis des lacunes anioniques de ces surfaces. La promotion partielle des surfaces stabilise les sites CUS Mo de basse coordination au voisinage du promoteur dont l'acidité est particulièrement élevée. Le promoteur Co a également pour effet de stabiliser les protons des groupements sulfhydriles sans pour autant neutraliser leur acidité de Brønsted. En particulier, les groupements –SH pontant une paire (Co,Mo) sur les surfaces partiellement promues sont stables et présentent une acidité élevée, relativement aux surfaces non promues ou complètement promues. Ces constatations suggèrent donc que les sites résultants de la promotion partielle du bord M pourraient jouer un rôle essentiel dans l'adsorption et l'activation des réactifs, composés thiophéniques en particulier, impliqués dans les réactions d'hydrotraitement, comme récemment proposé par Gandubert al. dans le cas du toluène.⁸²

La caractérisation expérimentale des propriétés basiques des phases sulfures s'avère plus délicate encore que celle de leurs propriétés acides. Néanmoins, nous avons pu, pour la première fois à notre connaissance, mettre en évidence le caractère electro-donneur du soufre de MoS₂ vis-à-vis de CO₂ (basicité au sens de Lewis), ainsi que la capacité du soufre de phases sulfures supportées à former des liaisons hydrogènes faibles avec le groupement C-H(D) du chloroforme. Si cette dernière interaction ne caractérise pas formellement la basicité au sens de Brønsted, elle permet néanmoins d'évaluer grossièrement la force de ces sites qui s'avère être faible et similaire à celle de sulfures organiques.

Si la basicité de ces phases sulfures est faible, il n'en reste pas moins que son étude reste un enjeu important : les propriétés basiques du soufre influent notablement sur la réactivité de ces surfaces, comme nous l'avons montré par une approche théorique dans le cas de l'activation de l'hydrogène. Ces premières études mériteraient donc certainement d'être poursuivies pour, dans la mesure du possible, mieux distinguer la basicité de différentes phases sulfures ou de sites basiques distincts. La difficulté majeure consistera en partie à définir une sonde 'optimale', suffisamment acide pour interagir plus fortement avec le soufre sans se dissocier à la surface.

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4.5 CO : SONDE DES PHASES SULFURES

4.5.1 INTRODUCTION

L'activité des catalyseurs d'hydrotraitement étant généralement liée à la présence de lacunes anioniques (sites CUS), de nombreuses études ont cherché à quantifier et caractériser ces sites par l'adsorption de molécules sondes, en particulier le dioxygène, le monoxyde d'azote et le monoxyde de carbone. Les deux premières sondes présentent l'avantage de s'adsorber spécifiquement sur la phase sulfure, ce qui facilite la quantification des sites par des méthodes volumétriques, mais sont également réactives et susceptibles d'oxyder la phase sulfure.¹²⁵ L'intérêt du monoxyde de carbone pour la caractérisation de catalyseurs sulfures a été montré pour la première fois au laboratoire par Bachelier et al.⁵³ qui ont pu établir des corrélations entre l'activité en HDS et la prise de CO de catalyseurs Mo/Al₂O₃ de teneurs variable.^{‡‡} L'adsorption de CO sur la phase sulfure de ces catalyseurs a été étudiée par spectroscopie IR par différents groupes¹²⁶⁻¹³¹ et conduit à des spectres similaires à celui présenté sur la Figure 4-20 ci-dessous, caractérisés par l'apparition d'un massif dissymétrique vers les bas nombres d'onde, composé d'une bande intense vers 2110 cm⁻¹ et d'un épaulement à 2070 cm⁻¹.

Ces fréquences, plus basses que celle de la phase gaz (2143 cm⁻¹) indiquent une rétrodonation des électrons d de la phase sulfure vers l'orbitale antiliante 2π* du monoxyde de carbone, ce qui a conduit les premiers groupes ayant réalisé ce type d'étude à proposer que les sites Mo conduisant à la bande à 2110 cm⁻¹ soient dans un état réduit (Mo^{δ+}, résultant de l'interaction entre des centres Mo⁰ et Mo⁴⁺,¹²⁶⁻¹²⁷ ou Mo²⁺,¹²⁸). L'épaulement à 2070 cm⁻¹ a été attribué à ces centres Mo dans un état plus réduit,¹²⁹ ou aux Mo de coin des feuillets MoS₂.¹³⁰ Le coefficient d'absorption intégré moyen de CO adsorbé sur la phase sulfure de catalyseurs non promus a été déterminé par Maugé et al.¹³¹ permettant ainsi l'étude quantitative de CO sur ce type de catalyseurs.

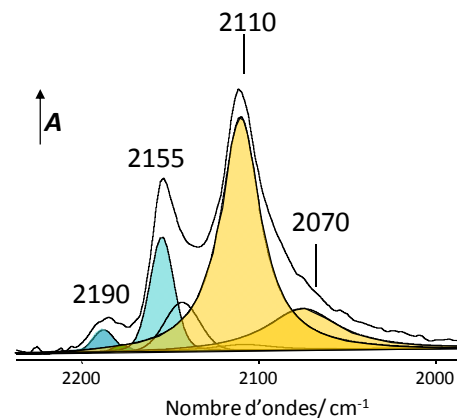


Figure 4-20 : Spectres IR après adsorption de CO sur un catalyseur Mo/Al₂O₃ (les bandes à 2190 et 2155 cm⁻¹ caractérisent l'adsorption sur le support).

Dans une étude en collaboration avec l'IFP réalisée au cours de ma thèse, j'ai pu ainsi montrer que sur une série de catalyseurs Mo/Al₂O₃ de teneurs variable (1 – 12%pds de Mo), le nombre de sites Mo détectés par CO représentent environ 70% du nombre total de sites de bord des feuillets MoS₂, tel que déterminé par l'utilisation du modèle géométrique de Kasztelan,¹³² combinée à la détermination des tailles des feuillets par microscopie électronique (Figure 4-21A), montrant que CO est un bon indicateur de la dispersion de ces phases sulfures.¹³³⁻¹³⁴ Dans une étude ultérieure [A17], nous avons également pu établir que le nombre de sites détectés par CO sur ces catalyseurs non promus est très bien corrélé avec les vitesses de réactions modèles, telles que l'HDS thiophène ou l'HDN de la 2,6-diméthylaniline.

‡‡ Pour minimiser l'adsorption sur le support, tout en maximisant l'adsorption sur la phase sulfure, ces expériences étaient réalisées à 0°C.

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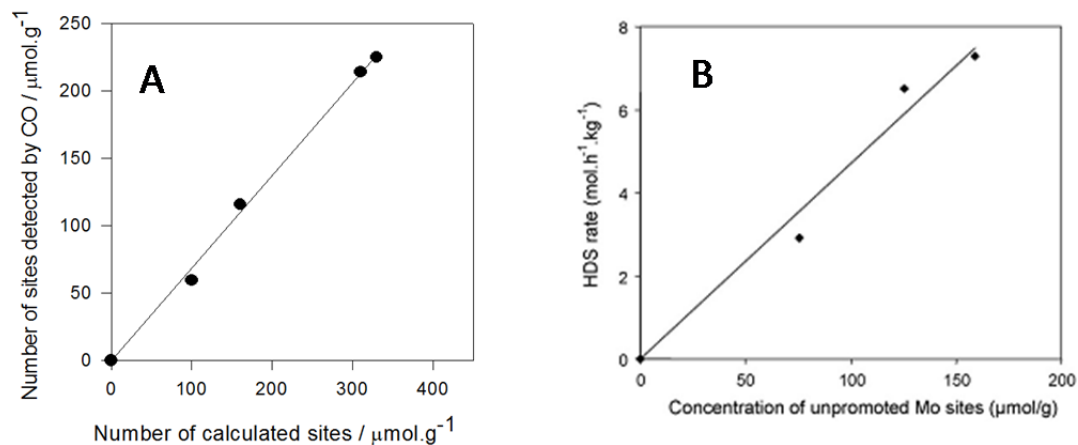


Figure 4-21. (A) Corrélation entre le nombre de sites détecté par CO et le nombre de Mo de bord déterminée pour une série de catalyseurs $\text{Mo/Al}_2\text{O}_3$ (A. Travert, Thèse de doctorat). (B) Corrélation entre la vitesse en HDS du thiophène et le nombre de sites détectés par CO sur une autre série de catalyseurs $\text{Mo/Al}_2\text{O}_3$ à teneur variable [A17]

L'ajout d'un promoteur, Co ou Ni, modifie fortement les spectres obtenus. Dans le cas des catalyseurs CoMo, l'adsorption de CO donne lieu à la diminution de la bande à 2110 cm^{-1} (sites Mo non promus) au profit d'une bande intense à $\sim 2070\text{ cm}^{-1}$ accompagnée d'un épaulement à plus bas nombres d'onde ($\sim 2055\text{ cm}^{-1}$).^{129,131,135} Ces changements sont illustrés sur Figure 4-22A qui montre les spectres obtenus après adsorption de CO sur une série de catalyseurs CoMo à teneur en Co variable.

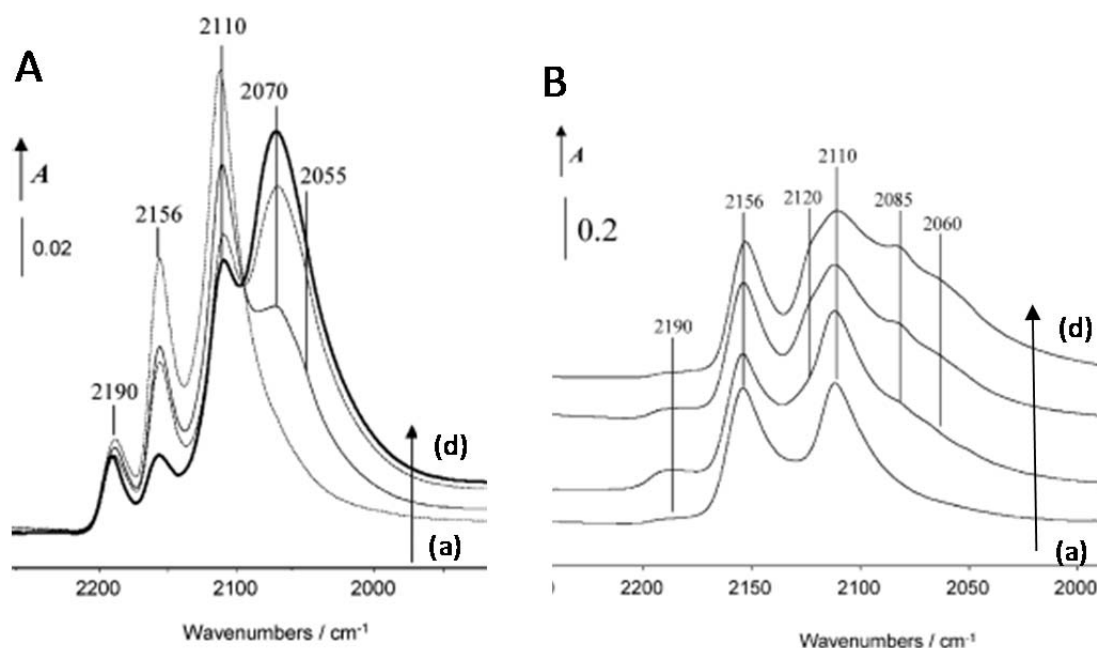


Figure 4-22. (A) Spectres IR après adsorption de CO sur (a) $\text{Mo/Al}_2\text{O}_3$ (8,7% Mo) et des catalyseurs CoMo contenant (b) 1,7, (c) 3,2 (d) 4,7 % Mo. [A16, A17]. (B) adsorption de CO sur (a) $\text{Mo/Al}_2\text{O}_3$ (8,7% Mo) et des catalyseurs NiMo contenant (b) 0,5, (c) 1,5 (d) 3,4 % Ni [A17].

La nature des sites (Mo ou Co) donnant lieu à cette nouvelle bande n'était pas clairement déterminée dans la mesure où (i) l'adsorption de CO sur des catalyseurs $\text{Mo/Al}_2\text{O}_3$ donne également lieu à une bande à 2070 cm^{-1} , mais d'intensité beaucoup plus faible (Figure 4-20) et où (ii) la possibilité de

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transferts électroniques du Co vers le Mo, montrée précédemment (p. 36 et suivante), peut a priori baisser la fréquence de la bande initialement à 2110 cm^{-1} sur les catalyseurs non promus en augmentant la rétrodonation des électrons d du Mo. Cette bande était donc attribuée à des sites dits 'de promotion', sans que leur nature (Co localisés au pourtour du feuillet MoS_2 ou Mo à proximité du Co) ait pu être clairement déterminée.

Dans le cas de la promotion par le Ni, la situation est plus complexe encore dans la mesure où de nouvelles bandes apparaissent à des nombres d'onde proches de celui des sites Mo non promus à 2110 cm^{-1} (Figure 4-22B), ce qui rend très difficile l'intégration de ces bandes et l'exploitation quantitative des spectres obtenus.

Dans le cas des catalyseurs CoMo, en revanche, des corrélations entre l'intensité de la bande correspondant aux sites de promotion et l'activité des catalyseurs correspondant en HDS du thiophène ont été établies par des groupes différents,^{128,136} montrant que ces sites sont effectivement à l'origine de l'effet promoteur du Co sur l'activité catalytique. Le coefficient d'absorption intégré moyen a également été déterminé par Maugé et al.,¹³¹ et permet d'étudier quantitativement l'influence des sites promus sur les vitesses de réaction.

La Figure 4-23 ci-contre illustre ce type de corrélation dans le cas de la série des catalyseurs (Co)Mo dont les spectres CO ont été décrits précédemment (Figure 4-22A). La pente de la droite obtenue permet d'estimer l'activité intrinsèque de ces sites promus qui s'est révélée sensiblement plus importante que celle des sites non-promus (d'un facteur ~ 30) dans le cas de l'HDS du thiophène à 673K [A17].

L'ensemble de ces études montre donc que l'utilisation de la molécule sonde CO permet de

rendre compte de manière très satisfaisante l'activité de catalyseurs sulfures non promus ou promus par le Co. Néanmoins, l'attribution des bandes $\nu(\text{CO})$ à des sites particuliers n'était pas déterminée. Aussi, j'ai entrepris des études visant à modéliser l'adsorption de CO sur des phases sulfure non promues (Mo) [A5] ou promues (CoMo, NiMo) [A17] en comparant les spectres obtenus sur des séries homogènes de catalyseurs sulfures (supports et méthodes de préparation identiques) aux fréquences $\nu(\text{CO})$ calculées par des méthodes de DFT périodique. Ces études, dont les résultats essentiels sont décrits ci-après, ont été réalisées en collaboration avec l'équipe d'Edmond Payen et Jean-François Paul (UCCS, Université Lille 1). Je montrerai que les résultats obtenus permettent de mieux décrire la structure des phases actives de ces catalyseurs supportés sur Al_2O_3 (nature des bords exposés et taux de substitution par le promoteur), ce que ne permettent pas, notamment, les études STM basées sur des catalyseurs modèles.

Pour clore ce chapitre, je décrirais de nouveaux exemples de l'utilisation de CO : caractérisation de phases sulfures préparées à l'aide d'agents chélatants [A20, A21] et étude de la désactivation de catalyseurs sulfures utilisés pour la déoxygenation de bio-huiles [A22, A25, A26, Ac7, Ac9].

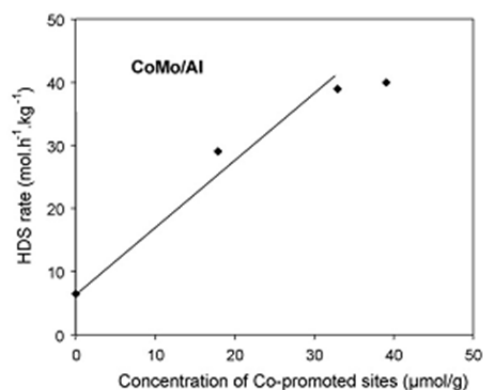





Figure 4-23 : Corrélation entre la vitesse en HDS du thiophène et le nombre de sites promus détectés par CO sur une série de catalyseurs (Co)Mo/ Al_2O_3 à teneur en Co variable [A17]

Catalyseurs non promus

Le Tableau 4-7 ci-dessous reporte les énergies d'adsorption et les fréquences $\nu(\text{CO})$ calculées pour l'adsorption de CO sur les surfaces de MoS₂ les plus stables pour une large gamme de rapports de pressions partielles PH₂S/PH₂.

Tableau 4-7 : Energies d'adsorption et fréquences de vibration de CO adsorbé sur les sites des surfaces stables de MoS₂ [A5, A17].

Bord	Site		Eads / eV	ν calc / cm ⁻¹	ν exp / cm ⁻¹
M	Mo _{VI}		0,1	2100	2110
S	Mo _{VI}		0,1	2060	2070
S	Mo _{IV}		0,7	2020	2000-2060

Comme déterminé précédemment, le bord M stable présente des atomes de molybdène hexacoordinés Mo_{VI}. La Figure 4-24 ci-contre représente la configuration stable obtenue pour l'adsorption de CO sur ce bord. Elle montre que CO s'adsorbe linéairement les sites Mo_{VI}, avec une énergie d'adsorption faible (0,1 eV) et un nombre d'onde de 2100 cm⁻¹, très proche du nombre d'onde de la bande principale observée à 2110 cm⁻¹ sur les catalyseurs non promus Mo/Al₂O₃, ce qui nous a conduit à attribuer cette bande à l'adsorption de CO sur le bord M de MoS₂.

La fréquence de cette bande, sensiblement plus faible que celle de la phase gaz (2143 cm⁻¹) indique une rétrodonation des électrons d du molybdène vers l'orbitale 2 π^* antiliante de CO. Ce phénomène est clairement mis en évidence par la carte de différence de densité ci-contre sur laquelle les anneaux sombres autour des atomes de carbone et d'oxygène indiquent le remplissage de l'orbitale 2 π^* . L'augmentation de densité électronique entre le carbone et le molybdène correspond, quant à elle, à la formation de la liaison σ C-Mo à partir de l'orbitale σ non liante de CO.

Notons ici qu'une étude théorique ultérieure à ce travail menée par Zeng et al. a proposé que la bande à 2110 cm⁻¹ soit due à la vibration asymétrique de dicarbonyles adsorbés sur les coins de MoS₂.¹³⁷ Outre le fait que cette attribution ne permet pas d'expliquer que la quantité de CO adsorbé sur un

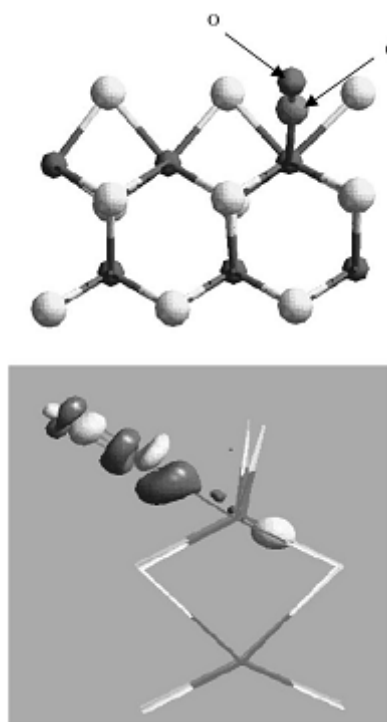


Figure 4-24 : Haut : adsorption de CO sur un site Mo_{VI} du bord M ; Bas : carte de différence de densité [A5].

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catalyseur non promu représente environ 70% des sites de bord, nous avons pu démontrer par l'utilisation de mélanges isotopiques $^{12}\text{CO}/^{13}\text{CO}$ que la bande à 2110 cm^{-1} correspond à un monocarbone [A15], ce qui conforte notre attribution de cette bande à l'adsorption de CO sur les bords M de MoS_2 .

L'adsorption de CO sur les sites Mo du bord S conduit à des fréquences beaucoup plus faibles ($2020 - 2060\text{ cm}^{-1}$). La diminution en fréquence par rapport à l'adsorption sur le bord M s'explique essentiellement par la meilleure accessibilité des sites Mo du bord S, moins écrantés par les atomes de soufre de surface, permettant un recouvrement plus important de l'orbitale $2\pi^*$ de CO avec les orbitales d du molybdène, augmentant ainsi la rétrodonation de ces électrons. Ces fréquences correspondant au pied de bas nombre d'onde du massif $\nu(\text{CO})$ (Figure 4-20), nous avons attribué la composante large observée à 2070 cm^{-1} à l'adsorption de CO sur le bord S de MoS_2 .

Si ces attributions permettent de rendre compte de l'essentiel des spectres expérimentaux, il convient toutefois de noter qu'elles n'expliquent pas complètement l'évolution des spectres de CO adsorbé sur des catalyseurs ayant subi un traitement sous hydrogène. La Figure 4-25 ci-contre montre l'influence d'un post-traitement d'un catalyseur $\text{Mo}/\text{Al}_2\text{O}_3$ sous hydrogène à température modérée (200°C) sur les spectres $\nu(\text{CO})$. Ce traitement conduit à une augmentation d'intensité et un déplacement de la bande initialement à 2110 cm^{-1} vers les bas nombres d'onde, ainsi qu'une augmentation de l'intensité des composantes à bas nombre d'onde. Les modèles de surface utilisés dans notre étude prévoient qu'après une sulfuration réalisée dans nos conditions,

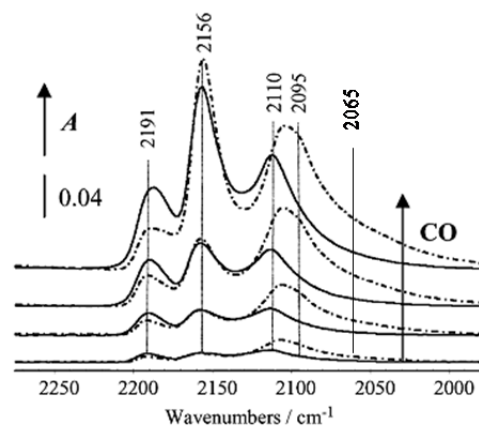


Figure 4-25 : Comparaison des spectres IR après adsorption de quantité croissantes de CO après sulfuration (—) et traitement par H_2 à 473K (---) [A5].

l'ensemble des sites Mo, qu'ils soient localisés sur le bord M ou S sont accessibles à CO et ne permettent donc pas de rendre compte de ces résultats de manière complètement satisfaisante. Il conviendrait donc de réexaminer l'adsorption de CO sur ces surfaces modèle en prenant notamment en compte la présence de groupements $-\text{SH}$ et de lacunes anioniques dont la stabilité a été montrée par des études théoriques plus récentes (cf. p.37 et suivantes). Nous montrerons que dans le cas des surfaces promues, l'adsorption de CO sur des sites Mo_V ou Mo_{IV} du bord M conduit à des fréquences basses ($2020-2080\text{ cm}^{-1}$), compatibles avec la position des composantes à bas nombre d'onde dont l'intensité augmente après traitement par H_2 . Il est donc possible que cette augmentation d'intensité soit due à la formation de lacunes anioniques sur le bord M sous l'effet de l'hydrogène. De même, l'apparition d'une composante à 2095 cm^{-1} , proche de la bande à 2110 cm^{-1} pourrait être due à la formation de groupement sulfhydriles sur le bord M (Figure 4-9B, p.40) qui pourraient diminuer la fréquence de vibration de CO adsorbé sur les sites Mo auxquels ils sont liés. Ces hypothèses, a priori compatibles avec nos observations expérimentales, mériteraient donc d'être vérifiées par de nouveaux calculs.

Ces réserves sur nos conclusions initiales, néanmoins, ne remettent pas fondamentalement en cause

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l'attribution de la bande principale à $2110 - 2095 \text{ cm}^{-1}$ à l'adsorption de CO sur les bords M de MoS_2 . Le fait que cette bande soit toujours beaucoup plus intense que la composante de bas nombre d'onde à 2070 cm^{-1} (bord S et lacunes) d'un facteur cinq environ, indique que les catalyseurs non promus supportés sur Al_2O_3 présentent majoritairement des bords M. Si les coefficients d'absorption de ces deux composantes ne sont pas déterminés individuellement, il est connu de le coefficient d'absorption de CO augmente fortement lorsque la fréquence diminue,^{131,138} de sorte que la proportion des sites de bord S est certainement plus faible que celle de l'intensité des bandes correspondantes.

Ces considérations impliquent donc que dans nos conditions de sulfuration, les cristallites MoS_2 supportées sur Al_2O_3 présentent les deux types bord M et S et une morphologie hexagonale tronquée présentant majoritairement des bords M. Ce résultat important est en accord avec notre étude de l'activation de l'hydrogène par MoS_2 qui nous a permis de montrer que les bords M sont essentiellement impliqués dans ces réactions. Les études théoriques de Schweiger et al.⁶¹ réalisée simultanément à ce travail et les observations ultérieures par STM de Lauritsen et al.⁷² ont également montré que les feuillets de MoS_2 présentent majoritairement des bords M dans des conditions de sulfuration proches de celle que nous avons utilisée. A cet égard, les résultats que nous avons obtenus dans cette étude permettent donc d'étendre ces conclusions à des catalyseurs supportés sur Al_2O_3 , support utilisé industriellement.

Catalyseurs promus

La promotion par le Co ou le Ni conduit à une variété importante de sites d'adsorption potentiels pour CO : sites Mo, Co ou Ni présentant différentes coordinations en soufre (cf. p.36 et suivantes). Nous avons donc cherché à déterminer dans quelle mesure les caractéristiques structurales de ces sites (type de bord, nature et coordination du métal) influence l'adsorption de CO (énergie d'adsorption et fréquence de vibration).

Phases CoMoS

Le Tableau 4-8 ci-après reporte les données obtenues pour des surfaces CoMoS complètement ou partiellement substituées par le Co.

Ces données montrent que l'adsorption de CO sur le Co conduit à des fréquences très similaires, $2075 \pm 8 \text{ cm}^{-1}$ indépendamment du type de bord (M ou S) et de l'environnement immédiat du Co (surface partiellement ou totalement substituée). Ces fréquences calculées sont proches de la bande expérimentalement observée à 2070 cm^{-1} , ce qui nous a conduits à attribuer cette bande à l'adsorption de CO sur des sites Co. En outre, les énergies d'adsorption obtenues sont beaucoup plus importantes (0,7 – 1,4 eV) que dans le cas de l'adsorption sur le bord M non promu (0,1 eV), ce qui est en bon accord avec la meilleure stabilité thermique de cette bande caractérisant les sites promus par rapport à la bande à 2110 cm^{-1} correspondant aux sites non-promus.¹³¹

Dans le cas des surfaces partiellement substituées, la promotion par le Co stabilise des sites Mo de basse coordination, Mo_V (bord M) et Mo_{IV} (bord M et S). La comparaison de ces fréquences avec celles des surfaces non promues montre qu'elles diminuent pratiquement linéairement avec la coordination du Mo : Mo_{VI} (2100 cm^{-1}) > Mo_V (2080 cm^{-1}) > Mo_{IV} ($2054\text{-}2040 \text{ cm}^{-1}$).

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Les sites Mo de coordination V conduisent à une fréquence proche de la bande expérimentalement observée à 2070 cm^{-1} et sont donc susceptibles de contribuer, avec les sites Co, à la formation de cette bande. Les fréquences obtenues pour les sites Mo de plus basse coordination (Mo_{IV}) présents sur l'un ou l'autre type de bord partiellement substitué sont quant à elles attribuées à l'épaulement à 2055 cm^{-1} observé sur les catalyseurs promus par le cobalt.

Tableau 4-8 : Energies d'adsorption et fréquences de vibration de CO adsorbé sur les sites des surfaces CoMoS complètement (100%) ou partiellement (25%) substituées [A17].

Bord	Site ^a	Eads / eV	ν calc / cm^{-1}	ν exp / cm^{-1}
M (100%)	Co_{IV}	1,4	2083	2070
S (100%)	Co_{IV}	0,7	2080	2070
M (25%)	Co_{IV}	1,0	2076	2070
M (25%)	Mo_{V}	1,1	2080	2070
M (25%)	Mo_{IV}	0,7	2054	2055
S (25%)	Co_{IV}	0,7	2068	2070
S (25%)	Mo_{IV}	0,7	2041	2055

(a) Atome bleu: Mo, noir: Co, jaune: S.

Le réexamen de l'influence du Co sur les spectres $\nu(\text{CO})$ permet, à la lumière de ces attributions, d'obtenir de nouvelles informations sur la structure de la phase CoMoS de catalyseurs supportés sur Al_2O_3 .

La diminution de la bande à 2110 cm^{-1} , caractéristique des bords M de la phase non promue est une indication forte de l'insertion du Co sur ces bords. A ce titre, il est important de noter que la bande à 2110 cm^{-1} est toujours présente, y compris sur des catalyseurs $\text{CoMo}/\text{Al}_2\text{O}_3$ commerciaux, comme illustré sur la Figure 4-26 ci-contre.^{§§}

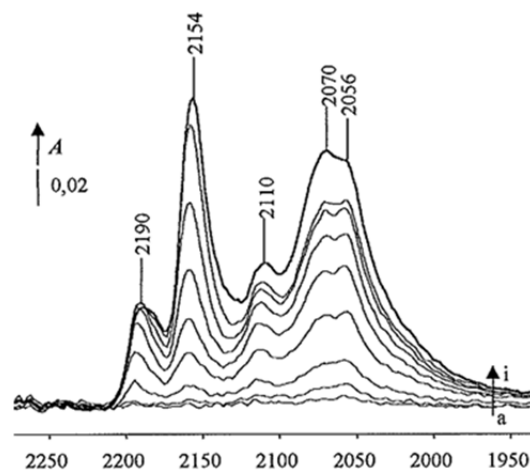


Figure 4-26 : Adsorption de CO sur catalyseur commercial (A. Travert, Thèse 2000).

^{§§} On trouvera des exemples plus récents de l'adsorption de CO réalisés au laboratoire sur des catalyseurs commerciaux ou de type industriel dans les travaux de C. Dujardin (Thèse de doctorat, Caen, 2002), M.-A. Lélias (Thèse de doctorat, Caen, 2008) et E. Le Guludec (Thèse de doctorat, Caen, 2011). Les spectres obtenus sont qualitativement similaires à ceux présentés ici.

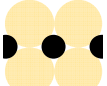

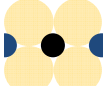




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Ces observations indiquent donc que l'insertion du Co sur ces bords n'est jamais complète, de sorte que ces bords partiellement substitués présentent des sites Mo de basse coordination, comme indiqué par la présence de l'épaule à $\sim 2055 \text{ cm}^{-1}$, également observé sur des catalyseurs commerciaux.

Phases NiMoS

L'examen des fréquences $\nu(\text{CO})$ obtenues sur les surfaces promues par le Ni, reportées dans le Tableau 4-9 ci-dessous conduit à des conclusions similaires à celles obtenues pour les phases CoMoS.

Tableau 4-9 : Energies d'adsorption et fréquences de vibration de CO adsorbé sur les sites des surfaces NiMoS complètement (100%) ou partiellement (25%) substitués [A17].

Bord	Site ^a	Eads / eV	ν calc / cm^{-1}	ν exp / cm^{-1}
M (100%)	Ni _{IV} 	1,3	2138	2120
S (100%)	Ni _{IV} 	0,6	2117	2120
S (100%)	Ni _{III} 	0,75	2101	2110
M (25%)	Ni _{IV} 	0,56	2100	2110
M (25%)	Mo _{VI} 	0,21	2050	2060 – 2040
M (25%)	Mo _V 	0,86	2022	2060-2040
S (25%)	Ni _{IV} 	0,40	2117	2120
S (25%)	Mo _{IV} 	0,62	2047	2060-2040

(a) Atome bleu: Mo, noir: Ni, jaune: S.

Pour ces surfaces, néanmoins, l'adsorption sur les sites Ni conduit à des fréquences significativement plus élevées ($2100 - 2138 \text{ cm}^{-1}$) que pour le Co ($2068-2083 \text{ cm}^{-1}$). Ces différences sont en bon accord avec les fréquences observées dans le cas des carbonyles de Ni et de Co.¹³⁹ Dans le cas présent, ces fréquences relativement élevées s'expliquent par la plus faible densité d'électrons d,⁴⁰ qui limitent la rétrodonation vers l'orbitale $2\pi^*$ de CO.

Ces fréquences plus élevées conduisent à un recouvrement important de ces bandes caractéristiques des sites Ni avec celle des sites Mo non promus à 2110 cm^{-1} , en bon accord avec les spectres expérimentaux qui montrent que le Ni entraîne l'apparition d'une composante à haut nombre (2120 cm^{-1}) d'onde qui recouvre en partie la bande à 2110 cm^{-1} (Figure 4-22B). D'un point de vue

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pratique, ce recouvrement important limite l'utilisation de CO pour déterminer le taux de promotion des phases NiMoS. A cet égard, l'utilisation de NO pourrait être plus appropriée, dans la mesure où cette sonde permet de distinguer plus clairement les sites de promotion induits par le Ni des sites Mo non promus.¹⁴⁰

A contrario, ces fréquences élevées permettent de mieux distinguer les bandes à bas nombre d'onde dues aux sites de Mo de basse coordination (2040 – 2060 cm^{-1}) qui indiquent que comme dans le cas des phases CoMoS, les surfaces NiMoS sont partiellement décorées par le promoteur.

Dans ces deux cas, la fréquence de CO adsorbé sur les sites Mo de basse coordination indique une rétrodonation accrue des électrons d du molybdène vers l'orbitale antiliante $2\pi^*$ de CO, due à une meilleure accessibilité d'une part et à l'augmentation de la densité en électrons d du fait de la basse coordination de ces sites,⁴⁰ d'autre part. Nous avons également montré que ces sites présentent également un caractère acide de Lewis accru (cf. p.58 et suivante).

Ces observations nous ont ainsi conduit à proposer que les sites Mo de basse coordination, combinant des propriétés donneuses et acceptrices d'électron et un faible encombrement stérique sont susceptibles de jouer un rôle important dans les réactions d'hydrotraitement. Cette proposition semble être confirmées par les travaux plus récent de Gandubert et al.⁸², menés à l'IFPEN, qui montrent que le taux de promotion optimal conduit à maximiser la concentration de sites « mixtes » constitués d'atomes de Co et de Mo au voisinage l'un de l'autre. Dans cette hypothèse, les bandes $\nu(\text{CO})$ observées à bas nombre d'onde sur les catalyseurs promus par le Ni ou le Co constituent la signature spectroscopique de ces sites mixtes.

4.5.3 EXEMPLES RECENTS D'UTILISATIONS DE LA SONDE CO.

Le travail décrit précédemment a constitué une avancée significative dans l'interprétation des spectres infrarouge de CO adsorbé sur les phases sulfures. Ces résultats sont maintenant utilisés par d'autres groupes dans le but d'examiner l'influence des méthodes de préparation ou de la nature du support sur la structure des phases sulfures.¹⁴¹⁻¹⁵⁶ Je présenterais ici des études récentes réalisées au laboratoire dans ce domaine en montrant l'intérêt, mais également les limites de la sonde CO pour l'évaluation du taux de promotion de catalyseurs sulfures préparés à l'aide d'agents chélatants (EDTA, NTA), connus pour améliorer sensiblement les performances catalytiques des catalyseurs sulfures [A20, A21].

Nos travaux sur l'adsorption de CO sont également utilisés dans le cadre d'études sur de nouvelles applications des catalyseurs sulfures, notamment pour mieux comprendre les réactions impliquées dans la synthèse Fischer-Tropsch sur MoS_2 ,¹⁵⁷⁻¹⁶¹ ou les phénomènes de désactivation induits par CO, produit de décarbonylation lors de l'hydrodéoxygénation des huiles végétales.^{83,162} J'illustrerais ici comment l'adsorption de CO suivi par spectroscopie IR permet de mieux comprendre les phénomènes de désactivation induits par l'eau ou les précurseurs de coke lors de l'hydrodéoxygénation de bio-huiles [A22, A25, A26, Ac7, Ac9].

Influence des agents chélatants sur la structure et l'activité de phases CoMoS.

Dans les études décrites en introduction à cette section, nous avons montré que les spectres de CO adsorbé sur la phase sulfure permettent de rendre compte de manière satisfaisante l'activité catalytique de catalyseurs non promus ou promus par le Co. Ces travaux portaient sur des catalyseurs Mo ou CoMo préparés de manière conventionnelle (imprégnation des précurseurs métalliques, séchage, calcination puis sulfuration). D'autres méthodes de préparation ont été développées pour améliorer les performances en hydrotraitement de ces catalyseurs. En particulier, l'utilisation d'agents chélatant tels que l'acide nitrilotriacétique (NTA),¹⁶³⁻¹⁶⁵ ou l'acide éthylène diamine tétraacétique (EDTA),¹⁶⁵⁻¹⁶⁶ permet généralement d'obtenir des catalyseurs plus actifs en HDS. L'origine de cette amélioration de l'activité catalytique, toutefois, ne fait pas l'objet d'un consensus dans la littérature. Ainsi, certaines études l'expliquent par la stabilité du complexe agent chélatant-promoteur, permettant une meilleure promotion des feuillets MoS₂,¹⁶⁷⁻¹⁷⁰ alors que d'autres concluent que ces préparations conduisent à la formation de phase CoMoS de type II, en plus faible interaction avec le support que dans le cas d'une préparation classique (phases de type I).¹⁷¹⁻¹⁷²

Dans le but de mieux comprendre l'influence de ces agents chélatants sur le nombre et la nature des sites de phases sulfures Mo et CoMo, nous avons entrepris des études visant notamment à corréliser les spectres $\nu(\text{CO})$ obtenus sur des catalyseurs préparés avec ou sans agent chélatant (NTA [A20] ou EDTA [A21]) avec leurs activités catalytiques en HDS du thiophène et en HDN de la 2,6-diméthylaniline (DMA).

La Figure 4-27 et la Figure 4-28 montrent l'évolution des activités catalytiques en HDS du thiophène et les spectres $\nu(\text{CO})$ obtenus pour des catalyseurs CoMo en fonction de la teneur en Co pour des catalyseurs CoMo préparés à partir d'un catalyseur Mo/Al₂O₃ (9%pds Mo), avec ou sans ajout d'EDTA. Dans ces deux cas, l'activité optimale est obtenue pour une teneur en cobalt de 3%pds environ. L'ajout d'EDTA conduit à des activités supérieures pour toutes les teneurs en Co. Cet effet, très important pour la plus faible teneur en Co (+56%) est plus modéré pour la teneur la plus élevée (+13%). Un effet promoteur de l'EDTA sur les activités en HDN de la DMA est également observé pour ces catalyseurs [A21].

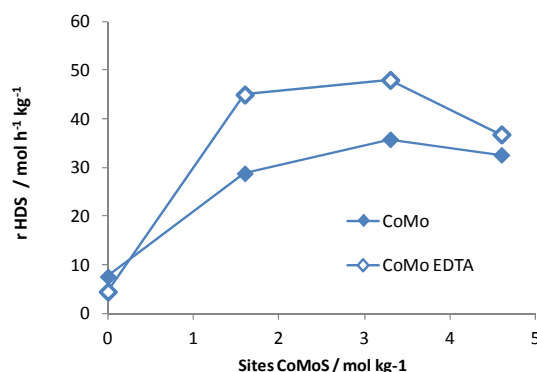


Figure 4-27 : Evolution de la vitesse en HDS du thiophène en fonction de la teneur en Co, avec (◇) ou sans (◆) EDTA [A21]

Les spectres $\nu(\text{CO})$ obtenus sur ces deux séries de catalyseurs sont qualitativement similaires et indiquent que l'augmentation de la teneur en Co conduit à la diminution du nombre de sites Mo non promus en faveur des sites promus. L'EDTA, néanmoins, conduit à des modifications importantes des intensités des bandes $\nu(\text{CO})$ observées.

Sur le support, l'EDTA conduit à une diminution des bandes caractéristiques de l'adsorption de CO sur les sites acides de Lewis Al³⁺ (2188 cm⁻¹) et les groupements OH (2156 cm⁻¹). Cette diminution résulte essentiellement de la présence d'espèces carboxylates résiduelles issues de la décomposition de l'EDTA sur le support [A21].

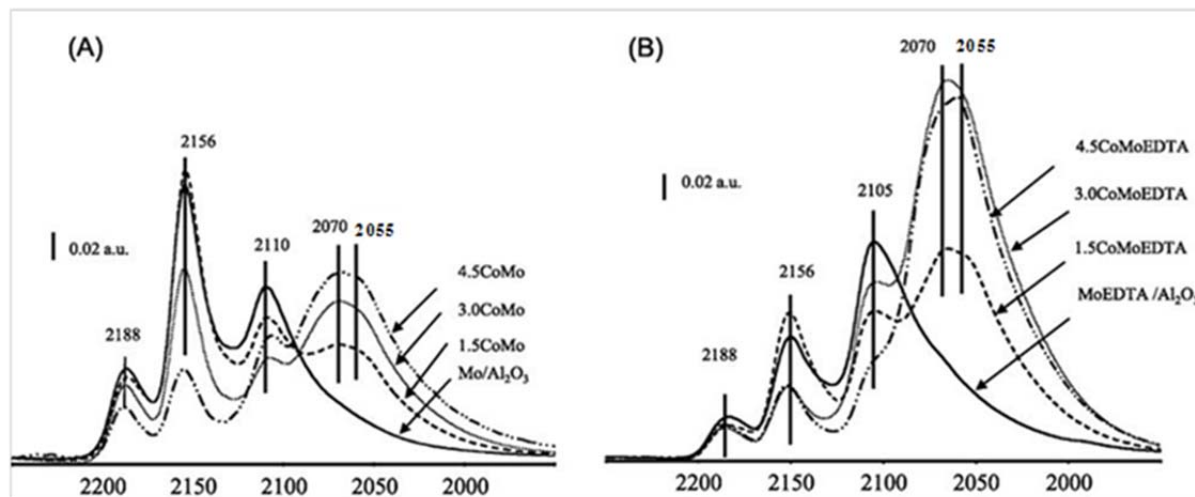


Figure 4-28 : Spectres IR obtenus après adsorption de CO à basse température sur des catalyseurs (Co)Mo/Al₂O₃ préparés (A) sans EDTA et (B) avec EDTA.

L'examen des bandes $\nu(\text{CO})$ obtenues sur la phase sulfure montre que l'ajout d'EDTA conduit à un léger déplacement de la bande $\nu(\text{CO})$ caractéristique des sites Mo non promus de 5 cm^{-1} vers les bas nombres d'onde ($2105\text{ vs. }2110\text{ cm}^{-1}$), alors que les fréquences des bandes caractéristiques des sites promus ($2070\text{ et }2055\text{ cm}^{-1}$) ne sont pas affectées. Surtout, l'EDTA conduit à une augmentation importante de l'intensité des bandes caractéristiques de l'adsorption sur la phase sulfure. Dans le cas des sites non promus ($2110\text{-}2105\text{ cm}^{-1}$), cette augmentation est essentiellement observée pour le catalyseur non promu (MoEDTA/Al₂O₃). Pour les catalyseurs promus, l'aire de cette bande, obtenue après décomposition des spectres, est similaire pour les deux séries de catalyseurs [A21], alors que l'intensité du massif caractérisant les sites promus est sensiblement plus importante pour les catalyseurs préparés avec l'EDTA.

L'étude réalisée avec le NTA [A22] ne sera pas détaillée ici mais conduit à des résultats similaires : augmentation de l'activité catalytique (HDS du thiophène ou HDN de la DMA) et de l'intensité des bandes caractéristiques des sites promus, sans modification notable de leurs fréquences.

Ces résultats concordants indiquent que l'utilisation d'un agent chélatant conduit à une augmentation importante du nombre de sites promus, augmentant ainsi l'activité de ces catalyseurs. Néanmoins, l'augmentation relative d'activité des catalyseurs préparés avec un agent chélatant est plus faible que celle du nombre de sites promus déterminé à partir de l'aire des bandes $\nu(\text{CO})$ correspondantes. Ce résultat est illustré sur la Figure 4-29 ci-contre, qui montre l'évolution de l'activité en HDS du thiophène des catalyseurs CoMo préparés avec ou sans EDTA en fonction du nombre de sites

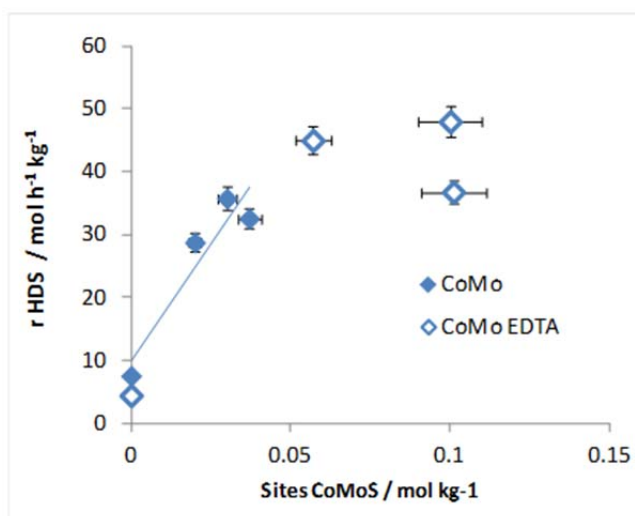


Figure 4-29 : Evolution de l'activité en HDS avec le nombre de sites promus déterminé par CO [A21]

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promus (CoMoS). Si une corrélation satisfaisante entre activité et nombre de sites est obtenue pour la série préparée sans EDTA, en bon accord avec nos études précédentes [A17], il apparaît clairement que l'activité des catalyseurs préparés avec EDTA, bien qu'améliorée, augmente moins rapidement que le nombre de sites promus déterminé par adsorption de CO. Nous avons constaté des évolutions similaires tant pour l'activité en HDN de la DMA de ces catalyseurs [A21], que pour les activités en HDS et HDN de catalyseurs préparés en présence de NTA [A20].

L'activité apparente des sites promus des catalyseurs préparés à l'aide d'un agent chélatant apparaît donc plus faible que celle des catalyseurs préparés classiquement. Pour quantifier plus précisément ces variations, nous avons déterminé les activités intrinsèques moyennes des sites promus CoMoS ($\overline{TOF}(\text{CoMoS})$) à l'aide de l'équation :

$$r = [\text{Mo}_{\text{np}}] \times \overline{TOF}(\text{Mo}_{\text{np}}) + [\text{CoMoS}] \times \overline{TOF}(\text{CoMoS})$$

Où r est la vitesse de la réaction considérée ; $[\text{Mo}_{\text{np}}]$ et $[\text{CoMoS}]$ sont les concentrations en sites non promus et promus déterminées à partir des aires des bandes $\nu(\text{CO})$ caractéristiques de ces sites (2110 cm^{-1} et $2070 - 2055 \text{ cm}^{-1}$) ; $\overline{TOF}(\text{Mo}_{\text{np}})$ et $\overline{TOF}(\text{CoMoS})$ sont les fréquences d'acte catalytique moyennes (*turnover frequencies*, TOF) de ces sites. Les activités intrinsèques des sites non-promus $\overline{TOF}(\text{Mo}_{\text{np}})$ sont déterminées à partir des corrélations obtenues pour des catalyseurs non-promus, que l'on suppose identiques pour les sites non-promus des catalyseurs CoMo/Al₂O₃ [A17].

Les Figure 4-30A et B ci-dessous reportent l'évolution des activités intrinsèques des sites CoMoS en HDS du thiophène et en HDN de la DMA (voie hydrogénation), pour les séries de catalyseurs CoMo/Al₂O₃ préparés avec ou sans agent chélatant (EDTA ou NTA). La Figure 4-30C et la Figure 4-30D reportent l'évolution de ces activités en fonction du taux de promotion, défini par le rapport du nombre de sites promus (CoMoS) sur le nombre de sites total ($\text{Mo}_{\text{np}} + \text{CoMoS}$).

Malgré une dispersion relativement élevée, liée notamment à l'incertitude sur la détermination des aires des bandes caractéristiques des sites promus et non promus, la Figure 4-30 montre que les activités intrinsèques moyennes des sites promus diminuent avec le taux de promotion de la phase sulfure. Ces résultats, concordants pour plusieurs séries de catalyseurs et deux réactions modèles de l'hydrotraitement, indiquent a priori un changement de la nature des sites promus.

Cette conclusion importante appelle néanmoins des commentaires d'ordre méthodologique. D'une part, le calcul du nombre de sites promus est basé sur l'utilisation du coefficient d'absorption moyen du massif $\nu(\text{CO})$ caractérisant les sites promus déterminé par Maugé et al.¹³¹ et l'examen des spectres obtenus sur ces catalyseurs indique que les intensités relatives des principales composantes de ce massif (bandes à 2070 et 2055 cm^{-1} sont susceptibles de changer avec la composition du catalyseur (voir par exemple la Figure 4-28). Malheureusement, le recouvrement de ces bandes est tel qu'il n'est pas possible de d'évaluer quantitativement ces intensités relatives. Le coefficient d'absorption de CO adsorbé sur ces phases sulfures étant sensible à la fréquence de vibration, la détermination du nombre de sites promus est certainement entachée par ces variations d'intensités relatives. Néanmoins, les écarts d'activité observés sont tels (facteur 3 à 4) qu'il paraît difficile de les expliquer par une variation du coefficient d'absorption moyen du massif $\nu(\text{CO})$.

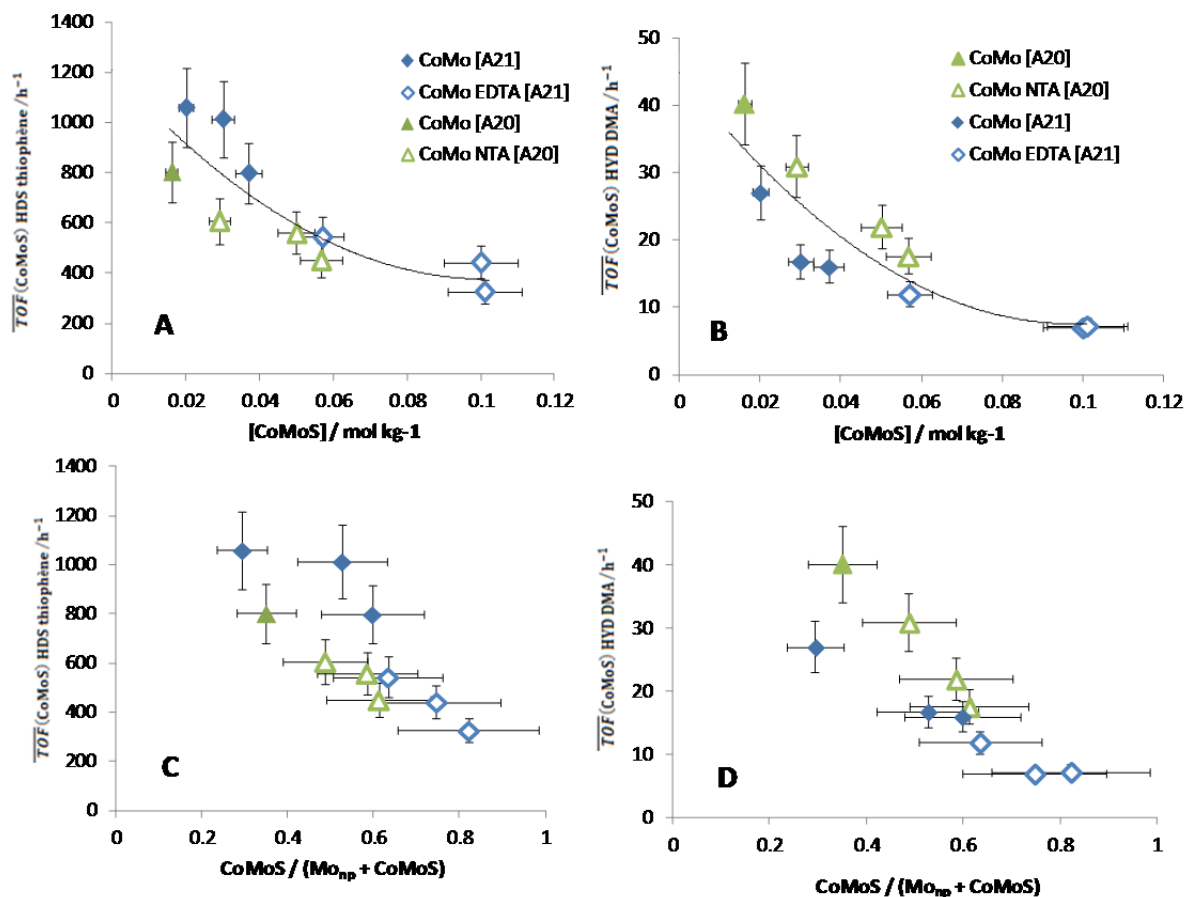


Figure 4-30 : Evolution des fréquences d'acte catalytique moyennes (\overline{TOF}) des sites promus (CoMoS) en HDS du thiophène et HDN de la DMA en fonction de (A,B) la concentration en sites promus et (C,D) du taux de promotion de la phase promue sur des catalyseurs CoMo/Al₂O₃ préparés avec ou sans agent chélatant.

D'autre part, en raison de l'incertitude sur la détermination des aires des bandes caractéristiques des sites promus, il est difficile de conclure quant à la variation de l'activité intrinsèque de ces sites pour les catalyseurs préparés en l'absence d'agent chélatant, en particulier pour l'HDS du thiophène. On observe néanmoins une diminution tendancielle de leurs activités intrinsèques en HDN de la DMA, réaction plus difficile que l'HDS du thiophène. Ceci indique donc que la qualité des sites promus de ces catalyseurs préparés de manière classique diminue également avec leur concentration.

Dans le cas des catalyseurs préparés avec un agent chélatant, la diminution des activités intrinsèques des sites promus est beaucoup plus nette pour les deux réactions et indique clairement un changement de la structure des sites promus. Nous avons considéré plusieurs hypothèses qui permettraient d'expliquer ce changement [A20, A21]: (i) formation d'une phase CoMoS de type II, favorisée par la présence de l'agent chélatant lors de la sulfuration de ces catalyseurs ; (ii) formation de sites « CoMoSN » par insertion d'azote issu de la décomposition de l'agent chélatant, (iii) formation d'agrégats CoS_x au pourtour des feuillets MoS₂.¹⁷³

Il est difficile de trancher entre ces hypothèses dans la mesure où (i) les phases de type II, en interaction plus faible avec le support, restent mal définies, (ii) l'adsorption de CO sur des phases mixtes nitrure CoMo donne lieu à des bandes proches de celles des phases sulfures,¹⁷⁴⁻¹⁷⁶ et (iii) l'adsorption de CO sur le Co donne lieu à des fréquences de vibration très proches (autour de 2070 cm⁻¹), peu sensibles à son environnement [A17].

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Néanmoins, si la structure du massif $\nu(\text{CO})$ caractéristique de l'adsorption sur les sites promus est relativement complexe, l'examen des spectres obtenus sur les catalyseurs préparés classiquement ou en présence d'agent chélatant ne permet pas d'affirmer que les sites promus soient de nature sensiblement différente pour ces deux types de catalyseurs. De même, la diminution des activités intrinsèques de ces sites avec leur concentration semble suivre une tendance générale (Figure 4-30).

Selon nos attributions, les sites promus correspondent d'une part à des centres Co (2070 cm^{-1}) et des centres Mo de basse coordination à proximité du Co (Mo_V , 2070 cm^{-1} et Mo_{IV} , 2055 cm^{-1}). En faisant l'hypothèse d'une distribution statistique des atomes de Co sur le pourtour des feuillets MoS_2 , l'augmentation de la teneur en Co devrait conduire à l'apparition progressive de sites Co vicinaux (paires, triplets, ...), ce qui entraîne une diminution de la fraction de sites Mo_V ou Mo_{IV} voisins du Co. La diminution progressive de l'activité intrinsèque moyenne observée pourrait donc s'expliquer par le fait que les sites Mo de basse coordination présentent une activité intrinsèque plus importante que celle des sites Co. Cette dernière hypothèse est confortée par les travaux décrits précédemment dans ce mémoire qui montrent que ces sites lacunaires présentent des caractéristiques favorables à l'activité catalytique (acidité de Lewis exacerbée, stabilisation de l'hydrogène, ...).

Ces considérations, en accord avec l'hypothèse (iii) de la formation de domaines CoS_x en pourtour des feuillets MoS_2 ,¹⁷³ vont également dans le sens de l'étude de Gandubert et al.⁸² qui montre également, dans le cas de l'hydrogénation du toluène, une diminution de l'activité intrinsèque des sites promus avec le taux de promotion des feuillets MoS_2 comme illustré sur la Figure 31 ci-contre, que les auteurs expliquent également par la diminution de fraction de sites mixtes Co-Mo.

En conclusion, l'ensemble de ces résultats

conduit à un modèle structural des phases CoMoS cohérent avec les résultats issus de leur modélisation par DFT, de leur caractérisation par adsorption de CO et de l'évaluation de leurs propriétés catalytiques dans des réactions modèles de l'hydrotraitement. Elles expliquent en particulier que l'activité optimale des catalyseurs CoMoS est obtenue pour une décoration partielle des feuillets MoS_2 qui permet de maximiser le nombre de sites promus les plus actifs (lacunes Mo ou sites mixtes CoMo). Selon ce modèle, l'utilisation d'agents chélatants ne conduit pas à la formation de sites particuliers, mais permet d'optimiser la décoration des feuillets MoS_2 , en particulier pour des teneurs en Co relativement faibles (Figure 4-27).

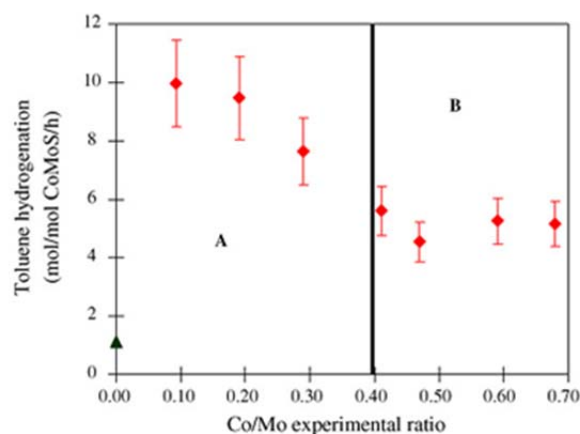


Figure 4-31 : Activité intrinsèque des sites CoMoS en hydrogénation du toluène en fonction du taux de promotion des feuillets MoS_2 (Gandubert et al. 2008)

Etude de l'interaction de composés phénoliques avec de catalyseurs sulfures

L'utilisation de catalyseurs sulfures pour la valorisation d'huiles de pyrolyse en bio-carburants de seconde génération se heurte à un certain nombre de difficultés, en particulier, une désactivation importante du catalyseur.^{32,34} Les raisons essentielles de cette désactivation invoquées dans la littérature sont la réoxydation de la phase sulfure, qui sera abordée dans la section suivante, et la formation de coke. Les travaux de Laurent et al.¹⁷⁴⁻¹⁷⁵ ont montré que cette dernière est fortement dépendante de l'acidité du support d'une part et de la nature de la charge d'autre part. En particulier, les composés phénoliques, présents en quantités significatives dans les bio-huiles (2-20 %pds),²⁴ jouent un rôle majeur dans la formation de coke sur ces catalyseurs.

Dans cette optique, nous avons étudié l'interaction de composés oxygénés avec différents supports oxydes, tels que la silice, l'alumine (pure ou dopée avec de alcalins ou des halogénures) ou la silice-alumine amorphe [A22]. Nous avons montré que les composés phénoliques interagissent principalement par liaison hydrogène avec la silice et s'adsorbent dissociativement sur les paires acide-base des oxydes à base d'alumine conduisant à la formation de phénates dès la température ambiante. L'étude quantitative des espèces irréversiblement adsorbées par un couplage IR – thermogravimétrie (AGIR,¹⁷⁶) nous a permis de montrer que l'adsorption du phénol dans les conditions de température typiques de l'HDO, conduit à l'empoisonnement de près des deux-tiers de la surface d'une alumine par les espèces phénate.

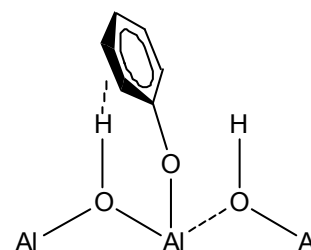


Schéma 4-2 : Espèce phénate sur Al_2O_3

Par la suite, nous avons examiné l'interaction du phénol avec des catalyseurs supportés Mo/Al_2O_3 et $CoMo/Al_2O_3$ [A26]. Alors que les espèces phénates formées sur les catalyseurs oxydes se distinguent clairement des espèces formées sur le support, l'examen des spectres obtenus sur les catalyseurs sulfure conduit à une diminution sensible du nombre d'espèces carboxylates formées, mais n'entraîne pas l'apparition d'espèces structurellement différentes de celles formées sur le support Al_2O_3 seul, comme l'illustre la Figure 4-32 ci-dessous dans le cas d'un catalyseur Mo/Al_2O_3 sulfuré.

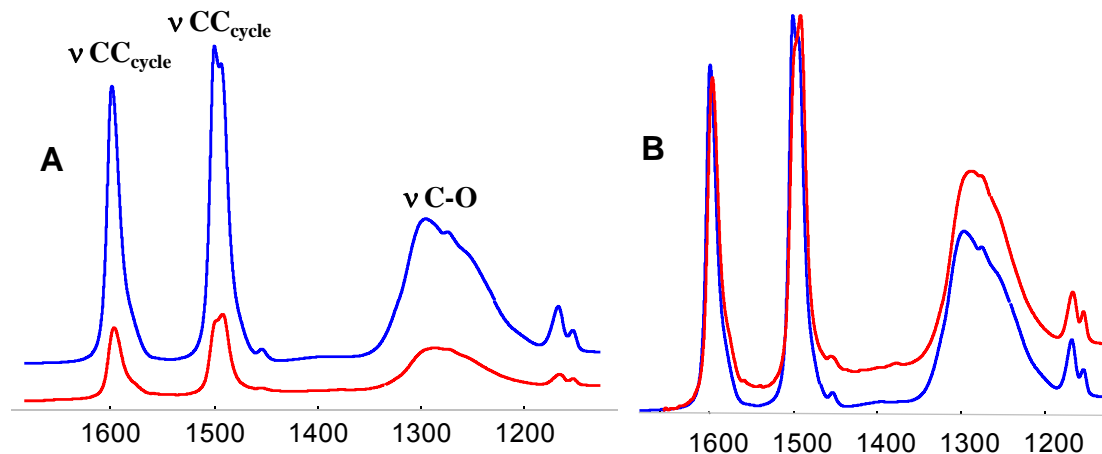


Figure 4-32. Spectres IR des espèces phénate formées sur (—) Al_2O_3 et (—) Mo/Al_2O_3 après adsorption du phénol à 673K. **A**: Intensités normalisées masse, **B**: Intensités normalisées à la hauteur de la bande la plus intense.

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Ces résultats suggèrent que la totalité des espèces phénolates sont localisées sur le support non recouvert par la phase active. Dans le but d'examiner l'influence de ces espèces sur le support, nous avons comparé les spectres $\nu(\text{CO})$ obtenus avant et après adsorption du phénol sur les catalyseurs sulfurés (Figure 4-33). Les spectres obtenus montrent que la présence de phénates diminue fortement l'intensité des bandes caractéristiques de l'adsorption sur le support (2190 et 2155 cm^{-1} , correspondant aux sites de Lewis et aux groupements hydroxyles). De manière plus surprenante, les quantités de CO adsorbé sur les sites de bord de la phase sulfure sont également plus faibles en présence de phénates et diminuent dans les mêmes proportions sur les sites promus et non promus, indiquant un empoisonnement non sélectif des sites de la phase sulfure. En l'absence d'indication de la formation de phénates sur la phase sulfure, nous concluons que cet empoisonnement résulte du blocage des sites de bord de la phase sulfure par les espèces phénates formées sur le support à proximité des feuilletts.

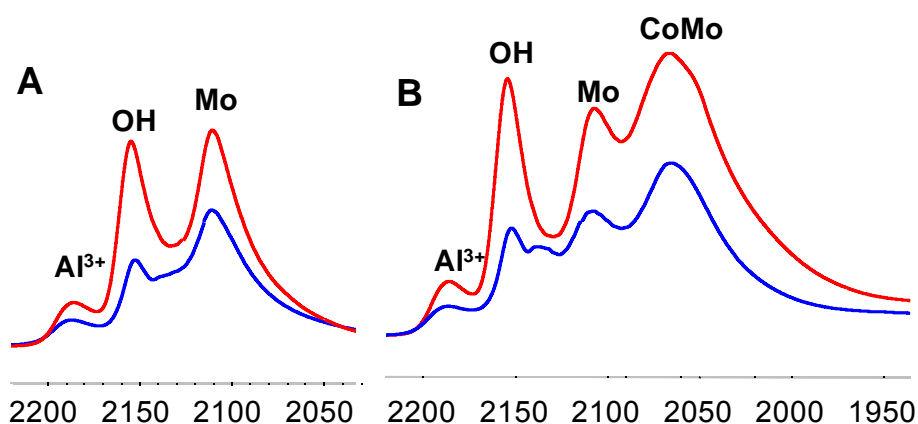


Figure 4-33 : Spectres IR de CO adsorbé sur (A) $\text{Mo}/\text{Al}_2\text{O}_3$ et (B) $\text{CoMo}/\text{Al}_2\text{O}_3$, en l'absence (—) ou en présence (---) d'espèces phénate sur le support.

Plus récemment, des expériences réalisées à différents taux de couverture en phénate nous ont permis de montrer que la quantité de sites accessibles diminue linéairement avec la quantité de phénates adsorbés sur le support, dans un rapport de 1 site empoisonné pour 5 espèces phénate environ. Les quantités d'espèces phénate formées dans nos conditions correspondent à un taux de carbone de l'ordre de 1% pour les catalyseurs sulfurés, soit des quantités sensiblement plus faibles que celles obtenues lors de l'HDO de composés phénoliques (typiquement 10%).¹⁷⁷ Notre étude ne permet donc pas d'affirmer que ce mécanisme d'empoisonnement indirect de la phase sulfure soit également valide dans le cas de la formation de coke en HDO des bio-huiles. Néanmoins, il est probable que les espèces phénates adsorbées sur le support soient les précurseurs des espèces polyaromatiques (coke). Il apparaît donc essentiel de moduler les propriétés superficielles des supports classiquement utilisés en vue de leur application en HDO en particulier en limitant le nombre ou la force des sites responsables de cette adsorption irréversible.

Influence de l'eau lors des réactions d'HDO

La seconde cause de la désactivation accrue des catalyseurs d'HDO est la réoxydation partielle de la phase sulfure par les composés oxygénés, plus particulièrement par l'eau formée en cours de réaction, comme l'ont montré des études réalisées sur des systèmes modèles ou pour l'HDO de charges réelles.¹⁷⁸⁻¹⁷⁹ Néanmoins, ni la nature de la phase oxysulfure (formation de sulfates, démixtion de la phase sulfure,..) ni la sensibilité relative à l'oxydation de différentes phases sulfures (e.g. Mo vs. CoMo) n'avaient été clairement déterminées. Nous avons donc étudié l'impact de l'eau (673 K) sur la stabilité de phases sulfures Mo et CoMo en collaboration avec les groupes de S. Brunet (LACCO, Poitiers) et J.-F. Paul (UCCS, Lille) [Ac7, A25].

En utilisant une méthodologie similaire à celle employée dans le cas des composés phénoliques, nous avons pu montrer qu'un traitement par H₂O à température de réaction (673 K) suivie d'une évacuation n'affecte pas les sites du support mais diminue sensiblement la quantité de sites de la phase sulfure de catalyseurs Mo/Al₂O₃ et CoMo/Al₂O₃ (Figure 4-34). La diminution d'intensité des bandes caractéristiques des sites non promus (2110 cm⁻¹) est sensiblement plus élevée (~ -60%) que celle des sites promus (2070 et 2155 cm⁻¹, ~ -30%). En outre, la resulfuration du catalyseur dans des conditions similaires à celles de la sulfuration initiale (673K, H₂S(10%)/H₂, 2h) montre que la diminution du nombre de sites promus est complètement réversible, alors qu'une fraction importante des sites non promus reste toujours empoisonnée après resulfuration (~ -50%).

Dans le but de mieux comprendre les phénomènes à l'origine de cet empoisonnement, nous avons caractérisé la morphologie des phases sulfures des ces catalyseurs par microscopie électronique (HRTEM) avant et après traitement par H₂O dans des conditions identiques à celles utilisées pour l'adsorption de CO. La Figure 4-35 ci-après montre la distribution des tailles des feuillettes MoS₂ obtenues. Dans le cas du catalyseur non promu, le traitement par H₂O conduit clairement à un déplacement de la distribution vers des tailles plus faibles, conduisant à une diminution sensible de la taille de ces feuillettes (1,6 nm vs. 2,3 nm). Dans le cas du catalyseur promu CoMo/Al₂O₃, la distribution des feuillettes est également déplacée vers les tailles plus faibles, mais dans des proportions beaucoup plus faibles, de sorte que la taille moyenne est bien moins affectée par le traitement par H₂O (2,4 vs. 2,6 nm).

L'influence de l'eau sur l'activité catalytique en HDO du 2-ethylphénol, réalisée au LACCO, montre que l'ajout d'eau au mélange réactionnel diminue l'activité de catalyseurs. Cette désactivation induite

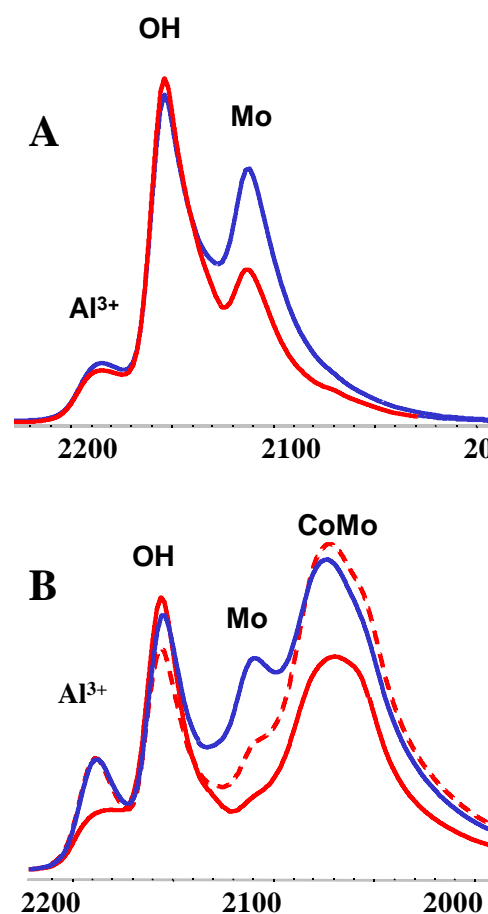


Figure 4-34 : Spectres IR après adsorption de CO sur **A** : Mo/Al₂O₃ et **B** : CoMo/Al₂O₃. (—) Avant traitement par H₂O, (—) Après traitement par H₂O, (- - -) Après resulfuration.

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par l'eau est réversible pour le catalyseur CoMo, mais partiellement irréversible pour le catalyseur non promu : l'activité obtenue lors des tests en absence d'eau ajoutée n'est pas totalement restaurée après que l'ajout d'eau dans le mélange réactionnel soit arrêté.

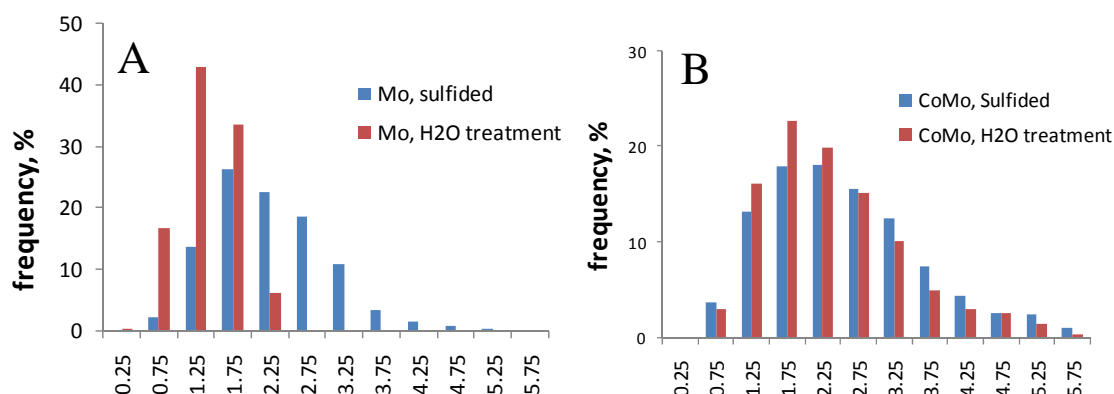
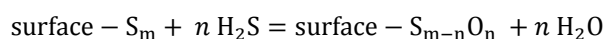


Figure 4-35 : Evolution de la distribution en taille des feuillets MoS₂ sous l'effet d'un traitement par H₂O à 673K. **A** Mo/Al₂O₃ ; **B** CoMo/Al₂O₃.

Ces résultats expérimentaux montrent donc de manière concordante que l'eau est susceptible d'affecter irréversiblement la structure et l'activité des phases MoS₂ non promues. La promotion par le Co, en revanche, stabilise la phase sulfure vis-à-vis de H₂O.

Dans le but d'interpréter ces résultats, des simulations DFT ont été entreprises à l'UCCS pour déterminer la structure thermodynamiquement stable des phases MoS₂ et CoMoS en présence d'eau, en utilisant une méthodologie similaire à celle employée dans le cas de l'hydrotraitement conventionnel (cf. p.34, [A7]). Dans ce cas, nous avons considéré les réactions d'échange soufre – oxygène sur ces surfaces :



où surface – S_m représente la surface stable en l'absence de H₂O, et surface – S_{m-n}O_n est la surface partiellement substituée par l'oxygène (*n* atomes d'oxygène).

La Figure 4-36 ci-après illustre l'évolution des énergies d'échange S-O en fonction de l'environnement de l'atome de soufre échangé. Elle montre que la substitution du Mo par le Co dans la sphère de coordination du soufre conduit à une augmentation significative de l'énergie de réaction, tant pour les atomes de soufre pontés de surface que pour les atomes de soufre tricoordinés sur le bord du plan basal.

Si ces résultats théoriques ne permettent pas de déterminer la cinétique d'échange, ils indiquent néanmoins que l'échange S-O est thermodynamiquement plus favorisé sur les surfaces non promues que sur les surfaces promues par le Co. Ils permettent de confirmer la plus grande sensibilité à l'eau des catalyseurs non promus par un échange oxygène-soufre sur le bord des feuillets, modifiant la structure des sites actifs de ces catalyseurs.

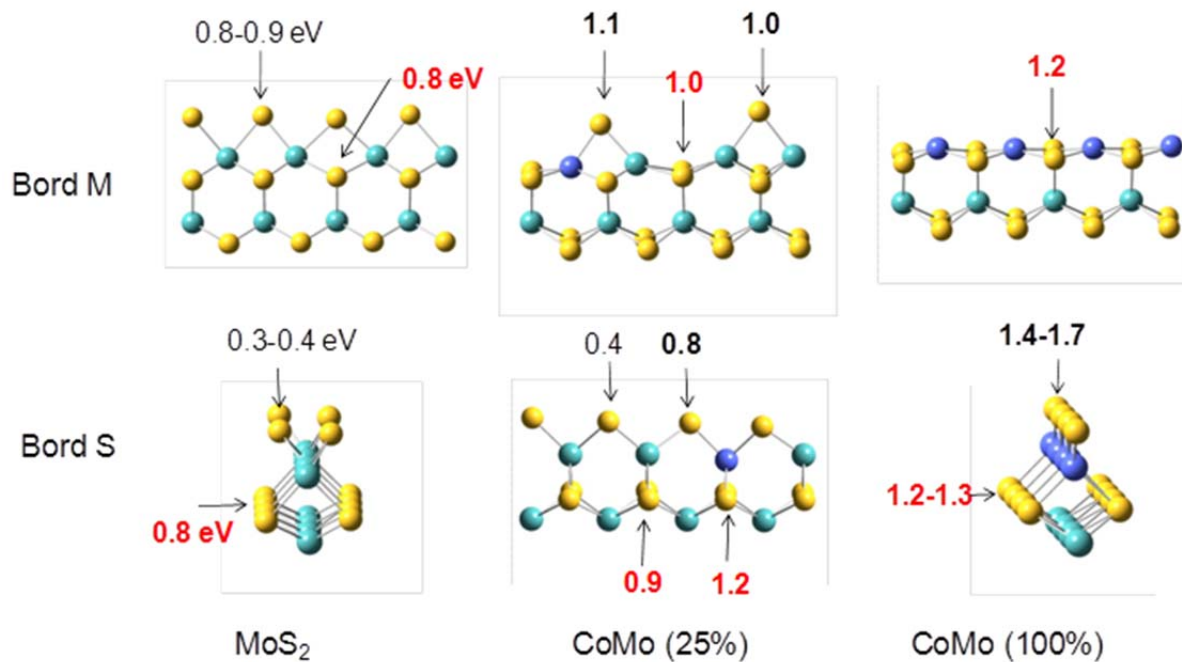


Figure 4-36. Energies d'échange S-O pour des surfaces non promues (MoS_2), partiellement substituées (CoMo 25%) ou complètement substituées (CoMo 100%) par le Co.

La diminution de la taille des feuillets de MoS_2 observée par HRTEM après traitement par H_2O peut s'expliquer par la formation d'une couche oxysulfure sur les bords de ces feuillets. En raison de la différence de longueur des liaisons Mo-O et Mo-S (0,19 vs. 0,23 Å, respectivement), la substitution S – O conduit à une distorsion des distances Mo – Mo au bord des feuillets, conduisant à une extinction des franges de diffraction dues à ces atomes de bord. La distance Mo-Mo dans MoS_2 étant de 0,3 nm, l'échange S-O sur toute la périphérie du feuillet devrait conduire à une diminution de la longueur des feuillets déterminée par HRTEM de $\sim 0,6$ nm, soit une valeur proche de celle déterminée expérimentalement ($\sim 0,8$ nm).

Dans le but d'expliquer la forte diminution des bandes $\nu(\text{CO})$ observée après traitement par H_2O , nous avons déterminé les énergies d'adsorption et les fréquences de vibration de CO adsorbé sur ces surfaces (Tableau ci-dessous).

Tableau 4-10 : Energies d'adsorption et fréquences de vibration de CO adsorbé sur le bord M de MoS_2 échangé ou non avec de l'oxygène.

Bord	Site	Eads / eV	$\nu(\text{CO}) / \text{cm}^{-1}$
Bord M non échangé	S-Mo-S	-0,57	2110
	S-Mo-O	-0,51	2167
Bord M échangé	O-Mo-O	-0,10	2183

Les échanges S-O conduisent à une diminution sensible des énergies d'adsorption et à une augmentation des fréquences $\nu(\text{CO})$. Ces effets peuvent être expliqués par la forte électronégativité de l'oxygène par rapport au soufre, qui conduit à une diminution de la rétrodonation des électrons d du

4. Catalyseurs Sulfures.

molybdène vers l'orbitale $2\pi^*$ de CO. Ces modifications des propriétés électroniques des sites Mo pourraient contribuer à la baisse sensible d'activité en HDO observée en présence d'eau.

Nos résultats montrent donc qu'en présence d'eau, les catalyseurs non promus Mo/Al₂O₃ subissent des réactions d'échange S-O qui modifient la nature des sites Mo de bord. Dans le cas des catalyseurs promus, nous avons pu montrer que le Co augmente non seulement l'activité intrinsèque en HDO (effet promoteur), mais stabilise également la phase active en limitant les échanges oxygène-soufre (effet de passivation).

4.5.4 CONCLUSIONS

Les travaux décrits ici nous ont permis d'attribuer les spectres $\nu(\text{CO})$ caractéristiques des phases sulfures supportées à base de molybdène sur la base des modèles structuraux développés par les études DFT des surfaces actives de ces phases.

Les spectres obtenus sur les catalyseurs non promus sont essentiellement caractérisés par une bande intense à 2110 cm⁻¹ attribuée à l'adsorption de CO sur les bords M des feuillets MoS₂, indiquant que ces phases supportées sur Al₂O₃ présentent majoritairement ce type de bord. Dans le cas des catalyseurs promus, CoMo ou NiMo, les spectres $\nu(\text{CO})$ présentent toujours la bande à 2110 cm⁻¹ caractéristique du Mo non-promu, ainsi que des épaulements à bas nombre d'onde, caractéristiques de sites Mo de basse coordination au voisinage du promoteur, montrant que la décoration des bords des feuillets MoS₂ par le promoteur n'est que partielle.

L'utilisation de la sonde CO nous a donc permis, outre d'évaluer la dispersion des phases sulfures, de préciser la structure de ces phases dans le cas de catalyseurs de type industriel.

L'étude de catalyseurs CoMo préparés à l'aide d'agents chélatants nous a permis, en examinant des gammes de taux de promotions plus larges, de montrer que l'activité moyenne des sites promus (sites Co et sites Mo à proximité du Co) diminue sensiblement avec le taux d'insertion du Co sur les bords des feuillets MoS₂. Ce résultat implique que les sites les plus actifs des phases CoMoS sont les sites sites mixtes CoMo, constitués de centres Mo de basse coordination voisins d'atomes de Co. Cette activité maximale peut a priori s'expliquer par les propriétés de ces sites : acidité de Lewis et rétrodonation d'électrons *d* élevée, permettant d'activer les réactifs adsorbés ; stabilisation de l'hydrogène sur le soufre pontant le promoteur, permettant d'hydrogéner ces réactifs.

Enfin, plus récemment, nous avons montré l'intérêt de l'utilisation de CO pour mieux comprendre les phénomènes de désactivation des catalyseurs sulfures utilisés en hydrodéoxygénation.

Nous avons ainsi montré que l'adsorption de composés phénoliques sur le support conduit à un blocage des sites actifs de la phase supportée. Ce résultat suggère que les espèces phénates adsorbées sur le support, possibles précurseurs de coke, pourraient jouer un rôle important dans la désactivation par le coke en HDO de bio-huiles.

Nous avons pu également préciser le rôle de l'eau dans la désactivation de ces catalyseurs. A température de réaction, l'eau conduit à l'échange d'une fraction importante des atomes de soufre de bord de MoS₂ par l'oxygène, conduisant à des sites peu ou pas actifs. La promotion par le cobalt

4. Catalyseurs Sulfures.

limite sensiblement ces échanges, montrant qu'en HDO le Co joue non seulement un rôle de promoteur, mais qu'il permet également de passiver la surface active vis-à-vis de l'eau produite durant la réaction.

Si l'ensemble de ces études montre l'intérêt de CO pour la caractérisation des catalyseurs sulfures, les conditions expérimentales de l'adsorption de CO (basse température et faible pression), nécessitent de figer l'état de surface de ces catalyseurs par un traitement sous vide. Je proposerais, dans la dernière partie de ce mémoire, d'utiliser cette sonde dans des conditions *operando*.

5 Additifs de Désulfuration pour le Craquage Catalytique.

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5.1 INTRODUCTION

La majeure partie du soufre contenu dans les essences (~80-90%) provient des coupes obtenues par craquage catalytique (*Fluid Catalytic Cracking*, FCC) qui contribuent pour ~30% de l'essence à la pompe.¹⁸⁰

Les composés soufrés principaux de ces coupes essence sont le thiophène, les alkylthiophènes légers et le benzothiophène, principalement concentrés dans la fraction la plus lourde de l'essence (Figure 5-1).¹⁸¹⁻¹⁸² Ces composés légers ne sont pas présents dans la charge initiale dont les teneurs en soufre varient généralement de 0,5 à 2,5%.¹⁸³ Lors du craquage catalytique, la majeure partie du soufre de la charge est convertie sous forme de H₂S et seule une fraction relativement faible du soufre initiale aboutit dans la coupe essence (2-5%).¹⁸⁰

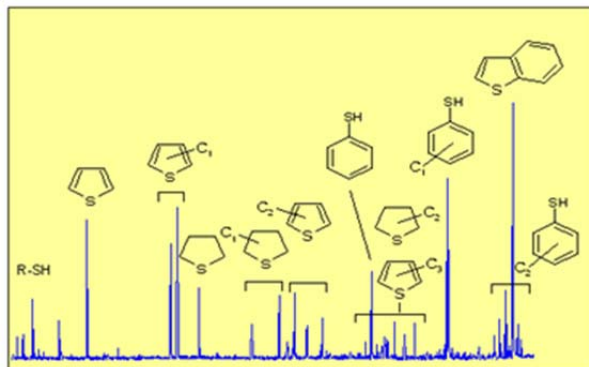


Figure 5-1 : Analyse chromatographique des espèces soufrées d'une essence de FCC typique (GC-AED) (E.T. Habib et al., 2001)

La Figure 5-2 ci-après schématise les principales voies de transformation des composés soufrés dans le *riser* de l'unité de FCC, établies par la littérature¹⁸⁴⁻¹⁸⁷ et les travaux décrits dans ce chapitre.

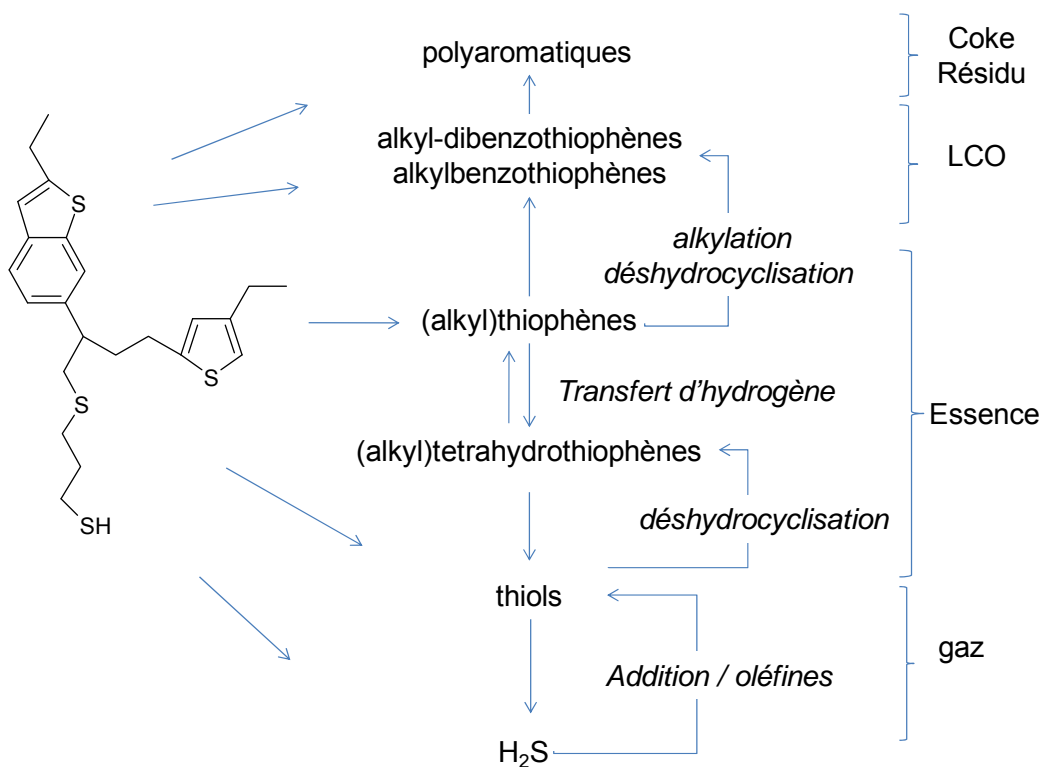


Figure 5-2 : Transformation des composés soufrés en FCC (F. Mahjoubi, Thèse de doctorat, Caen 2010)

Cette figure fait apparaître que les espèces thiophéniques sont formées par craquage des composés soufrés¹⁸⁴⁻¹⁸⁷ plus lourds, ou par recombinaison de H₂S avec les oléfines.¹⁸⁷ Une fois formée, ces espèces thiophéniques sont particulièrement stables.¹⁸⁶ Leur élimination de la coupe essence peut se faire soit par transformation en composés plus lourds (benzothiophènes et dibenzothiophènes aboutissant dans la coupe LCO), soit par craquage en hydrocarbures et H₂S. Cette dernière réaction, néanmoins, requiert une hydrogénation préalable du cycle thiophénique via des réactions de transfert d'hydrogène avec les hydrocarbures de la charge.^{184,188}

Certaines modifications des variables de l'unité de FCC permettent de réduire les quantités de soufre de l'essence provenant des unités de FCC, mais la plupart affectent généralement les rendements ou la qualité des produits : diminution du point de coupe de l'essence, diminution de la température de réaction, utilisation de catalyseurs à forte activité de transfert d'hydrogène,...^{180,189} Pour pallier à ces difficultés, la société Grace Davison a développé des additifs de réduction du soufre (GSR – *Gasoline Sulfur Reduction*), qui, ajoutés au catalyseur de craquage dans l'unité de FCC permettent de diminuer significativement les teneurs en soufre de l'essence de 10 à 40%, sans modifier sensiblement les rendements et la qualité des produits obtenus.¹⁹⁰⁻¹⁹⁴ L'utilisation de ces additifs permet aux raffineurs, toute chose égale par ailleurs, de traiter des charges plus lourdes, de diminuer la sévérité des hydrotraitements en amont ou en aval de l'unité de FCC (économie d'hydrogène, amélioration de l'indice d'octane), de mieux gérer les périodes d'arrêt de ces unités, ou d'augmenter le point de coupe de l'essence FCC (amélioration du rendement en essence).¹⁹⁵

Si ces additifs GSR sont maintenant utilisés dans plusieurs dizaines d'unités FCC, les mécanismes par lesquels ils permettent de réduire les teneurs en soufre des essences de FCC n'étaient pratiquement pas connus. Nous avons donc entrepris des études en partenariat avec la société Grace Davison dans le but de mieux comprendre les mécanismes de réduction du soufre par ces additifs. Ces travaux, décrits ci-après ont donné lieu à deux thèses de doctorat que j'ai co-encadrées au laboratoire (F. Can, 2004 ; F. Mahjoubi, 2010). Ils ont porté sur deux générations d'additifs, à base de zinc supporté sur alumine (Zn/Al₂O₃) [A18],¹⁹² et de vanadium.¹⁹⁴

5. Additifs de désulfuration en FCC.

5.2 ADDITIFS A BASE D'ALUMINE.

5.2.1 INTRODUCTION

La première génération d'additifs GSR est basée sur l'utilisation de solides acides de Lewis (Zn/Al_2O_3) ajoutés à hauteur de 10%pds au catalyseur de FCC. Des tests en microréacteurs réalisés par Grace Davison et d'autres groupes de recherche académiques ou industriels, ainsi que des tests en unités pilotes ont montré que ce type d'additif est susceptible de réduire la teneur en soufre de la coupe essence jusqu'à 40% sans affecter significativement les rendements, excepté une légère augmentation du coke et de l'hydrogène produits. Les espèces soufrées les plus affectées par ces additifs sont le thiophène et les alkylthiophènes légers, alors que les quantités de composés soufrés les plus lourds de la coupe essence, le benzothiophène en particulier, ne sont pas ou peu diminuées.

Les groupes ayant étudié la réactivité de ce type d'additifs ont émis plusieurs hypothèses quant à leur rôle dans l'élimination des composés thiophéniques :

- amélioration du transfert d'hydrogène vers les espèces thiophéniques,¹⁹⁶⁻¹⁹⁷
- augmentation de la vitesse de craquage des intermédiaires hydrogénés (tétrahydrothiophène),¹⁸⁸
- craquage des espèces thiophéniques fortement adsorbées sur ces additifs.¹⁹⁸⁻¹⁹⁹

Dans le but de déterminer plus précisément les mécanismes de réaction par lesquels ces additifs améliorent le craquage des composés thiophéniques, nous avons tout d'abord cherché à déterminer les rôles respectifs du catalyseur de craquage et de l'additif vis-à-vis de la décomposition de molécules soufrées en utilisant des charges modèles. Nous montrerons ainsi que l'additif permet essentiellement d'améliorer le craquage des intermédiaires hydrogénés, comme initialement proposé par Harding et al.¹⁸⁸ Dans un deuxième temps, nous avons cherché à déterminer la nature des sites superficiels impliqués dans ce craquage, tout d'abord en corrélant l'activité d'additifs présentant des gammes d'acido-basicité variables avec leurs propriétés superficielles, puis en étudiant cette réaction par spectroscopie IR operando. L'ensemble des résultats ainsi obtenu nous permettra finalement de proposer un mécanisme de craquage d'un intermédiaire hydrogéné type (tétrahydrothiophène) sur ces additifs.

5.2.2 ACTIVITE DE L'ADDITIF EN CRAQUAGE DE COMPOSES SOUFRES MODELES

Nous avons examiné dans un premier temps l'influence d'un additif Zn/Al_2O_3 sur le craquage de charges modèles (hexadécane et mélange hexadécane+héxylthiophène, 1%S) dans les conditions du FCC en réalisant des tests d'activité au centre de recherche de Grace Davison sur des bancs SCT-MAT (*Short Contact Time Microactivity Test*). En accord avec la littérature, ces premières expériences montrent clairement l'effet de l'additif sur les teneurs en soufre de la coupe essence (-26%) et LCO (-6%), comme indiqué sur la Figure 5-3 ci-après. On trouvera le détail des conversions et rendements obtenus dans la publication jointe en annexe [A18]

5. Additifs de désulfuration en FCC.

En raison de la nature de la charge utilisée (hexylthiophène), les quantités de thiophène et de tétrahydrothiophène (THT) produites en l'absence d'additif à une conversion typique du FCC (~ 65%) sont près de 50 fois plus élevées que pour une charge réelle (450 ppm S vs. 10 ppm S pour le THT), ce qui permet dans ce cas d'examiner plus précisément l'effet de l'additif sur ces composés.

En présence d'additif, la réduction du thiophène (-14%) est du même ordre de grandeur que celle des alkylthiophènes (-17%), alors que celle du tétrhydrothiophène est pratiquement complète (-99%). Cette diminution spectaculaire, qui ne peut pas être établie dans le cas d'une charge réelle en raison de la présence systématique de faibles concentrations de THT (5-10 ppm), indique que l'additif améliore le craquage de cet intermédiaire.

Néanmoins, la complexité des réactions mises en jeu dans le cas de ces charges est telle que l'analyse des rendements des produits de craquage et les composés soufrés ne permet pas d'établir complètement dans quelle mesure le craquage du THT par l'additif conduit à une diminution des espèces thiophéniques.

Dans le but d'exalter les effets de l'additif sur la charge hydrocarbonée et les composés soufrés, nous avons donc étudié le craquage de molécules modèles plus simples (méthylcyclohexane (MCHA) et thiophène) sur un système catalytique modèle (zéolithe HY et Al_2O_3), sous flux, en réacteur piston. Ces simplifications nous ont notamment permis de nous affranchir de l'effet déshydrogénant du Zn (augmentation du coke et de H_2) et d'examiner plus précisément l'influence de l'additif sur les réactions de transfert d'hydrogène entre la charge et les composés soufrés.

En accord avec la littérature,¹⁸⁶ nous avons pu établir que le thiophène seul est très peu réactif, tant sur la zéolithe (conversion <1%) que sur l'additif (conversion nulle). De même, l'additif seul est inactif vis-à-vis du MCHA et du thiophène, pris seuls ou en mélange. Ce dernier résultat montre donc que l'additif n'a d'effet sur les composés soufrés qu'en présence de la zéolithe et de la charge hydrocarbonée. Le Tableau 5-1 ci-après compare les conversions et sélectivité obtenues pour le craquage du MCHA ou du mélange MCHA + thiophène (10 %pds de S) en l'absence ou en présence de l'additif.

Dans le cas de la zéolithe seule, l'ajout de thiophène conduit à une diminution sensible de la conversion du MCHA en raison de la compétition à l'adsorption de ces deux réactifs. En revanche, une quantité significative du thiophène est convertie en présence de MCHA (~35%), alors qu'il ne l'est pratiquement pas en absence de MCHA (<1%). Ces résultats sont en accord avec les études de Yu et al. qui rapportent une désulfuration significative du thiophène en présence d'oléfines.²⁰⁰ Les produits soufrés principalement obtenus sont le THT et H_2S . En outre, la conversion accrue du thiophène

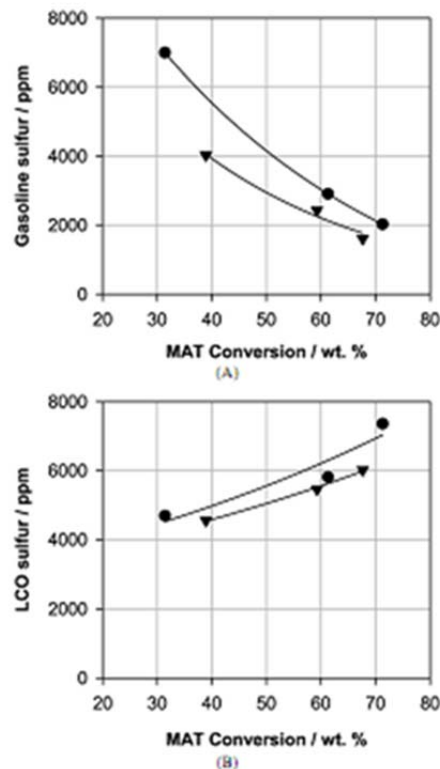


Figure 5-3 : Influence de l'additif $\text{Zn}/\text{Al}_2\text{O}_3$ sur les teneurs des coupes essence et LCO obtenues par craquage d'une charge modèle hexadécane + hexylthiophène [A18].

5. Additifs de désulfuration en FCC.

s'accompagne d'une déshydrogénation plus importante du MCHA, essentiellement liée à la formation de toluène, dont les rendements sont plus que doublés en présence de thiophène.

Tableau 5-1 : Conversions et distributions des produits pour le craquage de charges modèles (MCHA et MCHA + thiophène) en l'absence ou en présence d'additif Zn/Al₂O₃.^a (F. Can, Thèse de Doctorat, 2004)

Charge : Catalyseur :	MCHA HY	MCHA + Thiophène HY	MCHA + Thiophène HY + Additif
Conversion MCHA (%)	46,9	37,6	42,9
Conversion Thiophène (%)	-	34,3	43,7
Distribution massique (%)			
Isomérisation	8,9	7,2	5,8
Craquage	16,1	8,8	11,6
C3-C4	8,9	5,1	8,2
C5	3,0	1,8	1,6
C6	2,2	0,9	0,8
CHA	2,0	1,1	1,2
Déshydrogénation	24,3	33,1	40,5
Toluène	6,2	12,6	20,7
Xylène	12,0	13,3	13,1
Triméthylbenzène	6,1	7,1	6,1
Tétrahydrothiophène	-	6,1	1,3

(a) 450°C, 1 atm, temps de contact sur la zéolithe: MCHA : 7 g h mol⁻¹, thiophène 17,5 g h mol⁻¹.

Ces résultats nous permettent de conclure, en accord avec la littérature,^{184,188} que le craquage du thiophène nécessite une hydrogénation préalable du cycle thiophénique via les réactions de transfert d'hydrogène avec la charge hydrocarbonée, comme illustré ci-dessous dans le cas des molécules modèles utilisées dans nos expériences.

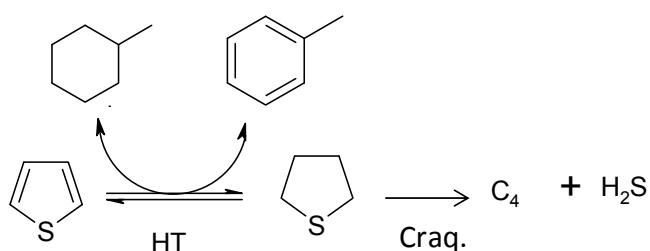


Schéma 5-1 : désulfuration du thiophène en présence de MCHA.

La comparaison des deux dernières colonnes du Tableau 5-1 permet d'évaluer l'influence de l'additif sur le craquage de la charge (MCHA + thiophène). Elle montre que l'additif conduit à une augmentation significative de la conversion du thiophène et de la déshydrogénation de MCHA, exclusivement liée à la production accrue de toluène.

L'additif seul étant totalement inactif vis-à-vis du MCHA ou du thiophène, les variations d'activité observées résultent nécessairement de l'action de l'additif sur un intermédiaire de la réaction. En

5. Additifs de désulfuration en FCC.

particulier, les quantités de THT produits en présence de l'additif diminuent sensiblement (Tableau 5-1), en bon accord avec les résultats obtenus en SCT-MAT dans le cas de charges plus complexes. Nous avons donc examiné la réactivité du THT pur sur la zéolithe HY et l'additif séparément. Les conversions et sélectivités obtenues sont rapportées dans le Tableau suivant.

Tableau 5-2 : Conversion et sélectivités pour la réaction du THT sur HY et Al_2O_3 .^a

	HY	Al_2O_3
Conversion (%)	50	58
Sélectivités (%)		
C ₄	35	95
Thiophène	60	5
dihydrothiophènes	5	0

(a) 450°C, temps de contact 3,2 g h mol⁻¹.

Il apparaît que tant la zéolithe que l'additif sont actifs pour la conversion du THT, mais présentent des sélectivités très différentes. Ainsi, en accord avec l'étude de Leflaive et al.¹⁸⁷ dans le cas d'un catalyseur de FCC équilibré, la zéolithe présente une activité importante en déshydrogénation du THT, conduisant essentiellement à la formation de thiophène. Ce résultat montre que pour une zéolithe seule, le craquage du THT en H₂S et hydrocarbures est fortement limitée par les réactions parallèles de déshydrogénation. L'additif, en revanche, est beaucoup plus actif pour le craquage du THT, conduisant essentiellement à la formation de butadiène et H₂S :

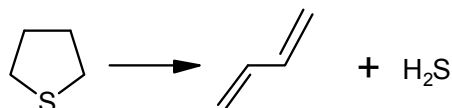


Schéma 5-2 : décomposition du butadiène et de H₂S sur Al_2O_3

L'ensemble de ces résultats catalytiques nous a ainsi permis de proposer un mécanisme en deux étapes expliquant la désulfuration accrue des composés thiophéniques en présence de l'additif :

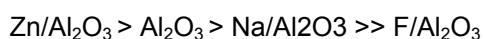
- hydrogénation du cycle thiophénique par le catalyseur de craquage via les réactions de transfert d'hydrogène avec la charge hydrocarbonée
- décomposition sélective de l'intermédiaire hydrogéné (THT) par l'additif.

L'additif agit ainsi en synergie avec le catalyseur de craquage et la dernière étape permet de déplacer les équilibres d'hydrogénation/deshydrogénation des cycles thiophéniques dans la zéolithe, favorisant le craquage de ces composés réfractaires en FCC.

5.2.3 INFLUENCE DES PROPRIETES ACIDO-BASIQUE DE L'ADDITIF SUR LE CRAQUAGE DU THT

Dans le but d'identifier les sites superficiels de l'additif impliqués dans la réaction de craquage du THT, étape clé de la désulfuration des composés thiophéniques par ces additifs, nous avons cherché à corrélérer les performances catalytiques en craquage du THT d'alumines dopées ou non par du sodium, du zinc et du fluor avec leurs propriétés acido-basiques déterminées par adsorption de molécules sondes (CO, pyridine, CO₂).

Dans tous les cas, la seule réaction observée sur ces additifs est le craquage du tétrahydrothiophène en butadiène et H₂S (Schéma 5-2), les dihydrothiophènes étant généralement observés à l'état de traces [A18]. Pour une alumine donnée, l'activité initiale en craquage du THT de ces additifs varie selon de classement :



Ce résultat confirme l'effet promoteur du zinc, qui entre dans la composition des additifs commerciaux, sur leur activité en désulfuration. Le sodium, en revanche, diminue sensiblement l'activité de ces additifs. Ce résultat est en accord avec les observations réalisées dans les unités de FCC qui montrent que l'accumulation de sodium sur ces additifs diminue leur activité en désulfuration. Ceci confirme donc que l'examen de la réaction de craquage du THT est pertinent pour l'évaluation de leurs performances en désulfuration. Enfin, l'ajout de fluor, utilisé dans cette étude pour exalter l'acidité de surface, diminue très fortement l'activité catalytique et conduit en outre à la production accrue de produits déshydrogénés (dihydrothiophènes et thiophène).

On trouvera l'analyse détaillée des propriétés acide-base de ces additifs déterminée par adsorption de molécules sondes dans l'article reproduit in extenso à la fin de ce manuscrit [A18]. En accord avec la littérature, nous avons montré que l'incorporation de sodium, zinc ou fluor modifie sensiblement ces propriétés. Ainsi, le sodium empoisonne préférentiellement les sites acide de Lewis forts de l'alumine,²⁰¹ alors que de zinc,^{199,202-203} et le fluor,²⁰⁴⁻²⁰⁶ au contraire, augmentent la quantité de ces sites. Enfin, alors que le zinc et le sodium ont peu d'influence sur la basicité de surface, le fluor conduit à une diminution très forte du nombre de ces sites.

Dans le but de déterminer la nature des sites actifs en craquage du THT, nous avons cherché à établir des corrélations entre la vitesse de craquage et le nombre de sites acides ou basiques de ces additifs (Figure 5-4).

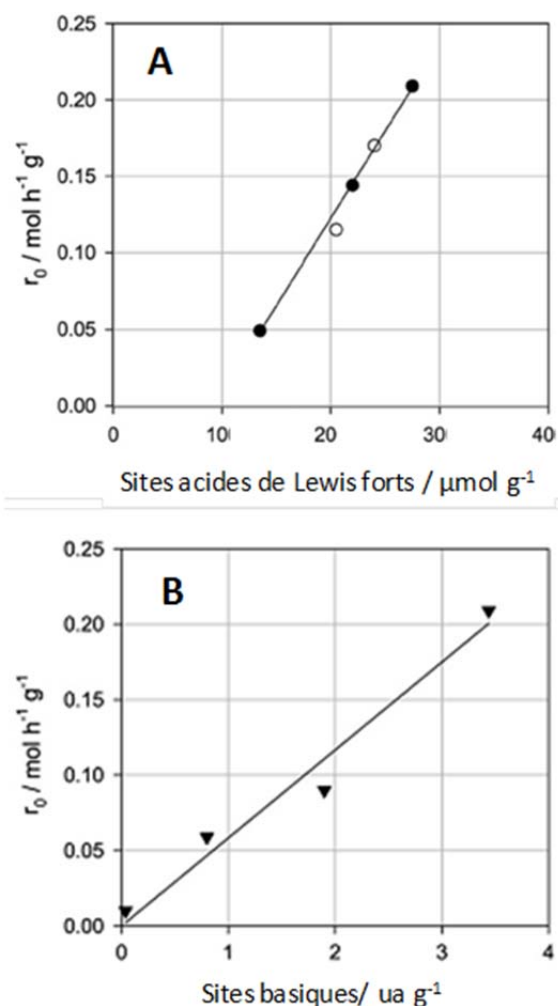


Figure 5-4 : A : vitesse initiale de craquage du THT en fonction du nombre de sites acide de Lewis forts : (o) (Na)/Al₂O₃ et (•) (Zn)/Al₂O₃. B : en fonction du nombre de sites basiques (▼) (F)/Al₂O₃ [A18]

Dans le cas des alumines pures ou modifiées par le sodium et le zinc (Figure 5-4A), nous avons obtenu une corrélation très satisfaisante de leurs activités avec leurs concentrations en sites acides de Lewis forts, tels que déterminés par la pyridine (sites Al^{3+} tétraédriques). Cette corrélation, obtenue pour des alumines différentes, indique que ces sites sont vraisemblablement directement impliqués dans la réaction de craquage du THT.

Dans le cas des additifs modifiés par le fluor, en revanche, cette corrélation n'est plus valable : le fluor augmente le nombre et la force de ces sites mais conduit à une diminution très importante de l'activité, indiquant que d'autres facteurs influent sur l'activité de ces additifs. Dans le cas de cette série de catalyseurs, en revanche, nous avons pu établir une corrélation très claire entre le nombre de sites basiques déterminé par adsorption de CO_2 et l'activité en craquage du THT (Figure 5-4B), indiquant que la baisse d'activité observée en présence de fluor est probablement liée à la diminution du nombre d'oxygènes basiques induite par le fluor.

En l'absence d'une corrélation unique entre activité et acidité ou basicité, nous avons, dans des études ultérieures, cherché à corréler ces activités avec le nombre de paires acide-base de Lewis déterminé par adsorption dissociative de sondes acides. Nous avons pu obtenir une corrélation satisfaisante avec le nombre d'espèces thiolates formées par dissociation de CH_3SH avec l'activité des additifs à base de Zn et de F, mais pas pour les deux additifs les plus chargés en Na... Cette absence de corrélation universelle souligne la complexité de ces surfaces et indique que plusieurs types de sites acide-base (par exemple de forces différentes) sont vraisemblablement impliqués dans cette réaction.

Dans tous les cas, les corrélations structure-activité que nous avons obtenues montrent qu'une acidité de Lewis forte est une condition nécessaire mais non suffisante pour obtenir une bonne activité en décomposition du THT, et que des sites basiques sont également requis. Ces considérations nous ont ainsi conduit à proposer que les sites actifs en craquage du THT soient les paires acide-base de Lewis (Al_{IV}^{3+}, O^{2-}).

5.2.4 ETUDE OPERANDO DU CRAQUAGE DU THT

Implication des sites basiques

Dans le but d'obtenir des informations supplémentaires sur les sites impliqués dans le craquage du THT, nous avons étudié l'évolution des spectres IR de surface durant la réaction en conditions *operando*. La Figure 5-5 ci-après montre les spectres différence obtenus lors de premières minutes de la réaction (pendant moins avant la réaction).

Ces spectres montrent une perturbation des groupements hydroxyles de surface (bande négative à 3745 cm^{-1} et bande large à 3600 cm^{-1}), ainsi que l'augmentation progressive de bandes $\nu(CH)$ à $2960\text{--}2850\text{ cm}^{-1}$ et de deux bandes intenses à 1560 et 1450 cm^{-1} . Ces bandes restent présentes après balayage du catalyseur par un gaz neutre après réaction, indiquant qu'elles correspondent à des espèces irréversiblement adsorbées qui s'accumulent à la surface au cours de la réaction. En réalisant des expériences similaires sur des surfaces préalablement échangées à ^{18}O , nous avons pu attribuer les bandes intenses à 1560 et 1450 cm^{-1} à des vibrations $\nu(C=O)$ caractéristiques d'espèces

carboxylates, similaires à celles formées par des oléfines sur Al_2O_3 à haute température.²⁰⁷⁻²¹⁰

Des spectres similaires étant obtenus par adsorption du butadiène à ces températures, ces observations nous ont conduit à proposer que les carboxylates formés lors du craquage du THT soient produits par réaction du butadiène – produit de la réaction – sur les oxygènes basiques de ces surfaces.

Notons ici qu'en raison des conditions de réaction utilisées ici, ces spectres ne sont certainement pas représentatifs de la surface de ces additifs dans l'unité de FCC, en raison notamment du très faible temps de contact de ces catalyseurs avec la charge (quelques secondes).

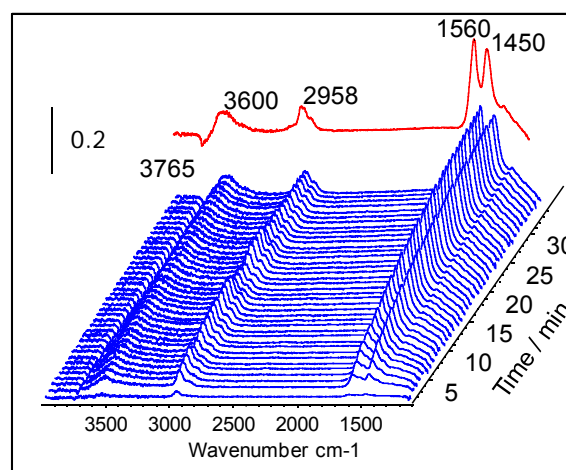


Figure 5-5 : Spectres bleus : spectres IR enregistrés durant la réaction de craquage du THT en conditions *operando*. Spectre rouge : après réaction et balayage sous He.

Néanmoins, l'examen de l'influence de ces espèces superficielles sur l'activité est susceptible de donner des indications indirectes sur les sites impliqués dans le craquage du THT. En effet, dans nos conditions, les additifs se désactivent régulièrement au cours du temps, indiquant un empoisonnement progressif de la surface [A18].

La Figure 5-6 ci-contre montre l'évolution de la vitesse de réaction en fonction de l'intensité des bandes $\nu(\text{C}=\text{O})$ caractéristiques des espèces carboxylates formées au cours de la réaction. La corrélation obtenue indique clairement que ces espèces sont directement responsables de la baisse d'activité observée.

Bien que le mode de formation de ces espèces ne soit pas encore élucidé (formation d'un complexe allylique sur des paires $(\text{Al}^{3+}, \text{O}^{2-})$,²⁰⁹ ou des hydroxyles basiques,²⁰⁸), leur formation conduit à l'empoisonnement d'oxygènes basiques de surface, ions O^{2-} ou groupements OH basiques. La diminution linéaire de l'activité avec le nombre d'espèces formées constitue donc une autre indication de la participation de centres basiques à la réaction de craquage du THT par ces additifs.

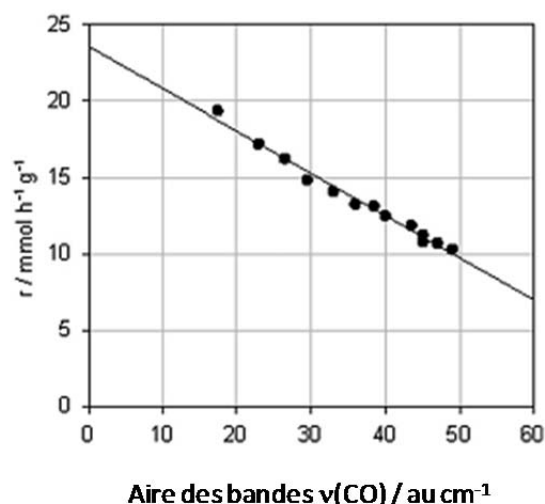


Figure 5-6 : Evolution de l'activité au cours du temps en fonction de l'aire des bandes carboxylate.

Implication des sites acide de Lewis

Dans le but de vérifier la participation des sites acide de Lewis forts en condition *operando*, nous avons réalisé des expériences en pré-adsorbant de la pyridine à température de réaction. Les spectres obtenus avant réaction, représentés sur la Figure 5-7A ci-après indiquent que dans ces conditions, les seules espèces pyridine adsorbées sont coordonnées sur les sites de Lewis les plus forts de l'additif (bande ν_8 à 1625 cm^{-1}).

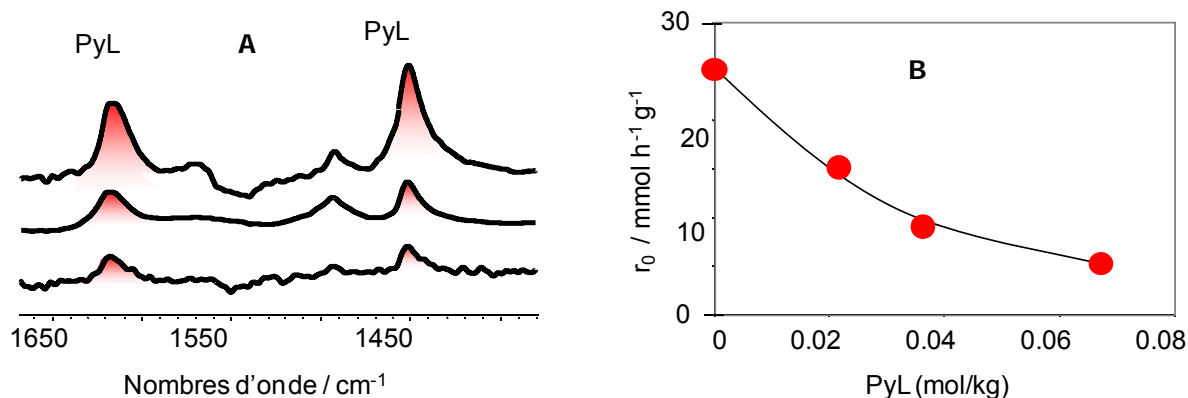


Figure 5-7 : A Spectres IR obtenus après préadsorption de pyridine ; B vitesses de réaction initiales en fonction du nombre de sites de Lewis empoisonnés par la pyridine.

La Figure 5-7B montre l'évolution de la vitesse initiale de craquage en fonction des quantités de pyridine coordonnée déterminées à partir de l'intensité des bandes IR obtenues avant réaction. Le fait que la vitesse diminue avec la quantité de pyridine coordonnée indique que les sites de Lewis correspondant (Al_{IV}^{3+}) sont directement impliqués dans cette réaction, en accord avec les corrélations structure-activité décrites précédemment. On notera toutefois que cette diminution n'est pas linéaire, ce qui pourrait indiquer que les sites de Lewis forts sondés par la pyridine ne sont pas homogènes et pourraient présenter des activités intrinsèques variables.

Proposition de mécanisme

L'ensemble des résultats obtenus (corrélations structure – activité et étude *operando*) nous a permis de montrer l'implication des sites acides et basiques de surface dans la réaction de craquage du THT. Cette réaction présentant des similarités avec la déshydratation des alcools par les oxydes métalliques (implication de sites acides et basiques, influence du sodium,...), nous avons proposé un mécanisme de craquage par éliminations E_2 successives sur des paires acide-base de Lewis, similaire au mécanisme généralement admis pour la déshydratation des alcools²¹¹⁻²¹⁵ (Schéma 5-3).

Les sites actifs les sites actifs sont des couples acide-base de Lewis pour lesquels le centre acide (Al) est un ion Al^{3+} tétraédrique (Al_{IV}^{3+}) et le centre basique (O) un anion O^{2-} de surface ou un groupement hydroxyle basique OH^- .

La coordination du soufre sur le centre acide de Lewis permet de polariser la liaison C-S et facilite l'abstraction du proton en β par le centre basique voisin. Ce mécanisme rend donc compte de la sensibilité importante de cette réaction aux variations des propriétés acido-basiques des additifs.

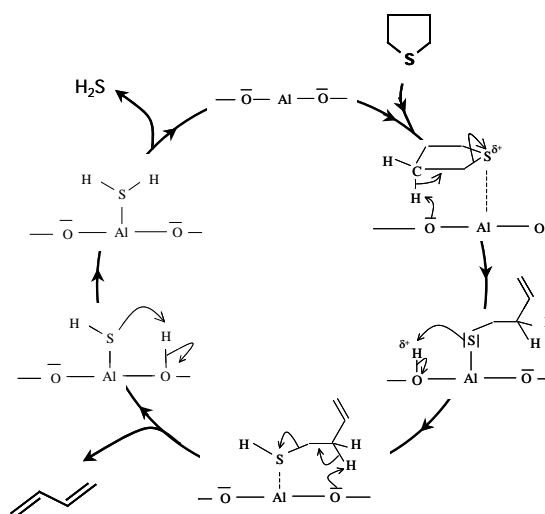


Schéma 5-3 : Mécanisme de craquage du THT

5. Additifs de désulfuration en FCC.

5.3 ADDITIFS A BASE DE VANADIUM

5.3.1 INTRODUCTION

Lors du craquage catalytique de charges lourdes, des métaux provenant de la charge sont déposés sur le catalyseur et affectent l'activité catalytique et la sélectivité. En particulier, le vanadium et le nickel et sont connus pour leurs propriétés déshydrogénantes (augmentation du coke et de H₂).²¹⁶ En outre, le vanadium a généralement un effet important sur la désactivation du catalyseur de craquage et accélère la destruction du réseau zéolithique lors de la phase de régénération du catalyseur. Cet effet s'explique par la formation d'acide vanadique dans le régénérateur (H₃VO₄) qui permet une redispersion du vanadium sur le lit catalytique et catalyse l'hydrolyse de la structure,²¹⁷⁻²¹⁸ en particulier en présence de sodium.²¹⁹⁻²²⁰

Néanmoins, les études de l'impact de ces métaux sur les composés soufrés montrent qu'ils conduisent à une diminution importante des teneurs en soufre de la coupe essence, en particulier dans le cas du vanadium.²²¹⁻²²³ Le développement de catalyseurs de craquage plus résistants au vanadium, a ainsi permis la mise au point d'additifs de désulfuration à base de vanadium.^{194,224-225}

Ces additifs consistent généralement en du vanadium supporté sur un oxyde de grande surface spécifique (SiO₂ ou Al₂O₃) et incorporé à hauteur de 0,1-0,5 %pds de vanadium.^{194,226} Lorsque le catalyseur de FCC est vapotraité en présence de ces additifs, le vanadium est redispersé à un état d'oxydation élevé (+V) sur l'ensemble du lit catalytique et permet alors d'obtenir des réductions des teneurs en soufre de l'essence de 30 à 50%.^{194,226} En revanche, une réduction préalable du vanadium ne conduit plus à une réduction significative des teneurs en soufre,^{194,223} indiquant que le vanadium actif pour la réduction du soufre est à l'état d'oxydation +V.

Au début de nos études, les mécanismes par lesquels le vanadium réduit les teneurs en soufre de la coupe essence n'étaient pas connus et sujets à spéculation. Ainsi, pour Myrstad et al. le vanadium agirait sur les mêmes intermédiaires que les additifs Zn/Al₂O₃.²²¹ Pour Lappas et al., néanmoins, le vanadium affecterait principalement les précurseurs des composés soufrés de la coupe essence et favoriserait l'alkylation et la cyclisation des alkylthiophène de la coupe essence, conduisant à un accroissement de la teneur en soufre de la coupe LCO,²²³ ou du coke.²²⁷

Les travaux décrits ici ont pour objectif de déterminer les mécanismes par lesquels le vanadium permet de diminuer les teneurs en soufre de la coupe essence.

Dans ce but, nous avons d'abord cherché à établir un bilan en soufre sur l'ensemble des coupes produites en FCC : gaz, essence, LCO, résidus et coke pour le craquage de charges réelles ou modèles dans des gammes de conversion typiques du FCC. Ce travail, le premier à notre connaissance, nous permettra de montrer que le vanadium favorise essentiellement l'élimination du soufre sous forme de H₂S en phase gaz.

Par la suite, nous examinerons l'influence de l'additif sur la réactivité de molécules soufrées modèles (dipentylsulfure et hexylthiophène) ajoutées à un gazoil hydrotraité. Cette étude nous permettra de montrer que le vanadium accélère les vitesses de rupture des liaisons carbone-soufre aliphatiques et d'estimer le nombre de rotation (TON) du vanadium pour ces réactions.

Enfin, nous examinerons la structure des espèces vanadium et leur interaction avec les sites de la

zéolithe par photoluminescence et spectroscopie IR.

L'ensemble des résultats ainsi obtenu nous permettra finalement de proposer un mécanisme de craquage radicalaire des liaisons carbone-soufre dans lequel le vanadium joue le rôle d'initiateur.

5.3.2 VOIES D'ÉLIMINATION DU SOUFRE PAR LES ADDITIFS AU VANADIUM

Bilan matière sur le soufre

Nous avons pu déterminer les bilans en soufre des coupes obtenues par craquage de charges réelles ou modèles, en l'absence ou en présence d'additif. Les résultats étant qualitativement similaires dans tous les cas, nous présenterons ici les résultats obtenus dans le cas d'une charge réelle typique du FCC contenant 1%pds de soufre.

La Figure 5-8 ci-dessous représente l'évolution des rendements en gaz, essence, LCO, coke et résidu en fonction de la conversion obtenue sur une zéolithe USY commerciale (CBV-600) vapotraitée en l'absence ou en présence de vanadium. Dans la gamme de conversion examinée, les rendements sont très proches pour les deux catalyseurs, à l'exception d'une légère augmentation du coke au détriment de l'essence dans le cas du catalyseur au vanadium, en accord avec la littérature.²¹⁶ Nous avons également pu mettre en évidence une légère augmentation des alcanes légers (méthane et éthane en particulier) en présence de vanadium.

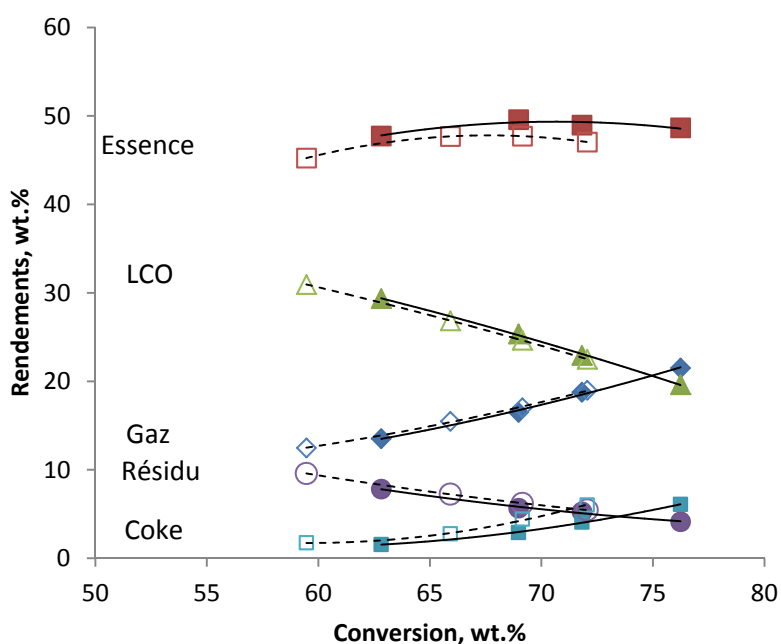


Figure 5-8 : Evolution des rendements des produits de craquage (gaz, essence, LCO, résidu et coke) en fonction de la conversion sur USY (symboles pleins, lignes continues) et USY+0.5%V (symboles ouverts, ligne pointillée)

Dans le but d'établir un bilan matière sur le soufre, nous avons déterminé les teneurs en soufre des différentes coupes obtenues. L'évolution de la distribution du soufre de la charge (10 000 ppm) dans ces coupes est représentée sur la Figure 5-9 ci-contre. Elle montre que le soufre de la charge aboutit essentiellement en phase gaz sous forme de H₂S (de 20 à 40% selon la conversion) ainsi que dans

5. Additifs de désulfuration en FCC.

les coupes les plus lourdes : LCO (25-40%) et résidus (20-40%). Une fraction beaucoup plus faible du soufre de la charge aboutit dans la coupe essence (de 1 à 3%) ou le coke (de 2 à 5%) Les distributions obtenues ici sont compatibles avec les distributions du soufre observées dans les unités industrielles,¹⁸⁰ Ceci montre que les catalyseurs modèles et conditions utilisées ici reproduisent correctement la transformation des espèces sulfurées dans la partie réactionnelle (riser) d'une unité de FCC.

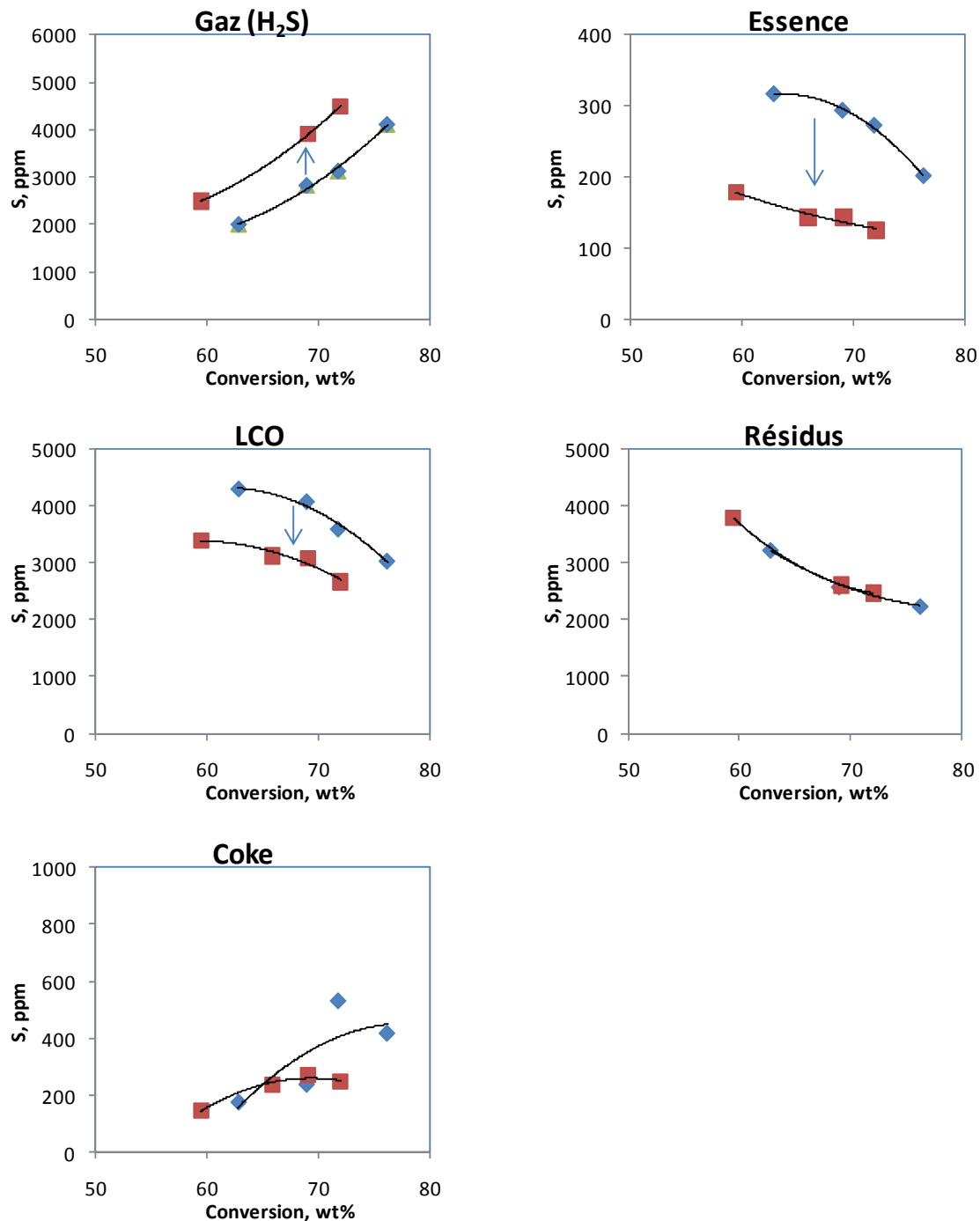


Figure 5-9: Distribution du soufre en fonction de la conversion dans les différentes coupes obtenues sur USY (◆) et USY+0,5%V (■).

Ces expériences montrent également que le vanadium a pour effet principal d'augmenter la production de H₂S, seul produit détecté en phase gaz, de 30% environ, au détriment des coupes essences et LCO. Les quantités de soufre restant adsorbée sur le catalyseur et attribuées au coke sont délicates à mesurer en raison des faibles teneurs en coke après réaction (moins de 5 %pds). Néanmoins, elles ne semblent pas significativement affectées et, en tout état de cause, ne sont pas plus importantes sur le catalyseur au vanadium. Les quantités de soufre restant dans les produits lourds (résidu) sont identiques pour les deux catalyseurs.

Ces résultats montrent donc très clairement que dans la gamme de conversion étudiée, typique de la pratique industrielle, le vanadium a pour effet d'améliorer l'élimination des composés soufrés des produits liquides (essence et LCO), conduisant à un accroissement de la production de H₂S.

Influence du vanadium sur les composés soufrés de la coupe essence

Le vanadium conduit à une diminution importante du soufre dans l'essence et le LCO de 50% et 20% respectivement à 70 % de conversion.

La Figure 5-10 ci-après détaille la distribution des composés soufrés dans la coupe essence obtenue en l'absence ou en présence de vanadium. Elle montre que le vanadium a pour effet d'abaisser sensiblement les teneurs de tous les composés soufrés de l'essence, des mercaptans au benzothiophène. On note toutefois que ces diminutions sont particulièrement importantes pour le tetrahydrothiophène et les alkylthiophènes, des méthylthiophène (C1-Thiophènes) aux C4-Thiophènes, ainsi que les thiophénols (thiols aromatiques).

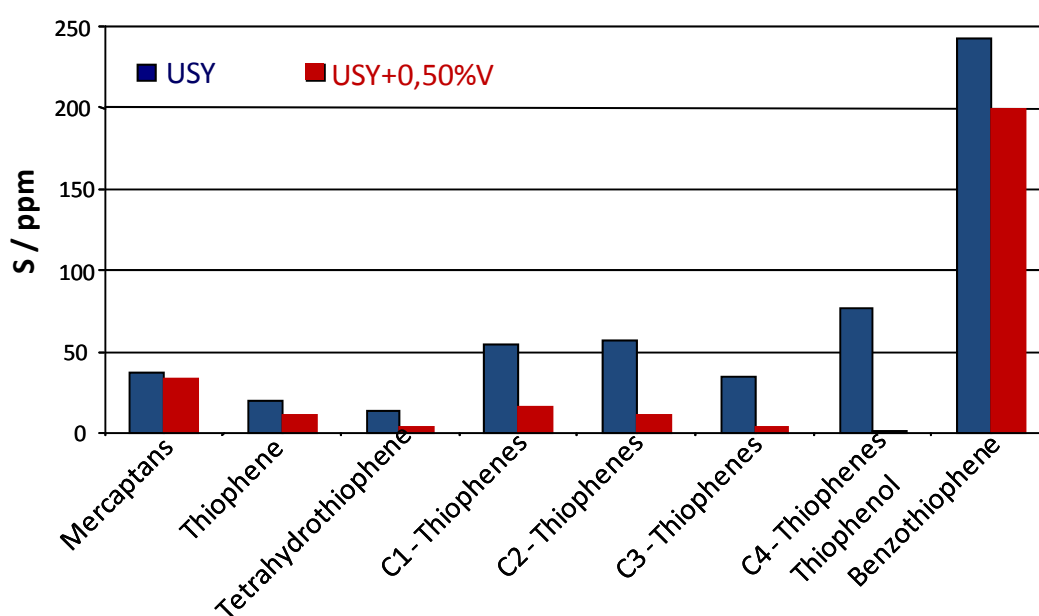


Figure 5-10: Distribution des grandes classes de composés soufrés de la coupe essence obtenus sur USY et USY+0,5%V à 70% de conversion.

Influence du vanadium sur la conversion de molécules modèles.

Nous nous intéressons ici à la transformation de composés soufrés modèles ajoutées à hauteur de 1% pds de soufre à un gasoil hydrotraité (0,035 pds% de soufre). Dans ces conditions, le soufre provenant de la charge hydrotraitée peut être pratiquement négligé, et cette dernière peut être considérée comme une matrice hydrocarbonée assez représentative d'une charge légère de FCC. Ces tests ont été réalisés en utilisant un catalyseur et un additif au vanadium commerciaux.

Les tests réalisés avec des charges additivées avec du benzothiophène ou du dibenzothiophène ne montrent pas de différences significatives des teneurs en soufre des produits liquides (essence et LCO) en l'absence ou en présence de l'additif indiquant que le vanadium n'a pas d'influence sensible sur la transformation de ces composés. En revanche, nous avons pu mettre en évidence un effet important de l'additif sur la transformation de composés aliphatiques (dipentylsulfure) et thiophéniques (hexylthiophène).

Transformation du dipentylsulfure.

Les tests réalisés à faible conversion nous ont permis de détecter des quantités mesurables de dipentylsulfure et de pentanethiol, l'un des produits primaires de craquage du dipentylsulfure. En parallèle, l'analyse des produits hydrocarbonés de l'essence fait apparaître une augmentation significative des pentènes et du *n*-pentane, formés par craquage du dipentylsulfure (pentène-1), suivie d'une hydrogénation (*n*-pentane) ou d'une isomérisation (autres pentènes).

La Figure 5-11 suivante rapporte l'évolution des quantités de dipentylsulfure, pentanethiol, H₂S et de l'ensemble des autres produits soufrés des coupes essence et LCO en fonction du rapport catalyseur/charge (C/O – *Cat to Oil*). Ces derniers ont été regroupés à part pour la lisibilité de la figure.

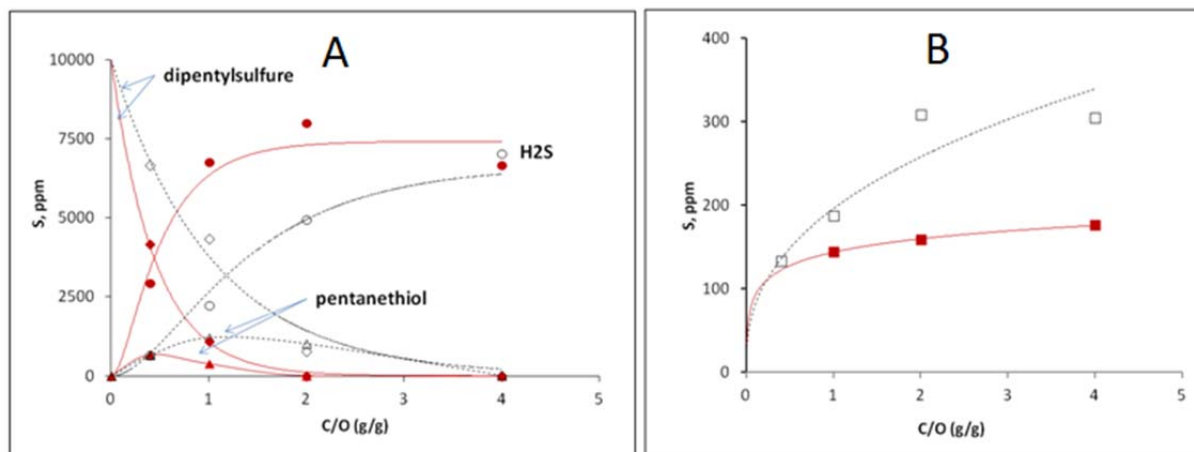


Figure 5-11 : **A** : Evolution des quantités de dipentylsulfure, pentanethiol et H₂S en fonction du rapport catalyseur/charge. **B** : autres produits soufrés, pour le catalyseur de référence (symboles ouverts, lignes pointillées) et le catalyseur au vanadium (symboles fermés, lignes continues).

Il apparaît clairement sur cette figure que le dipentylsulfure est converti en pentanethiol, qui apparaît comme un intermédiaire, puis en H₂S qui apparaît comme un produit secondaire. La présence de vanadium conduit très clairement à une augmentation de la vitesse de disparition du dipentylsulfure

ainsi que du pentanethiol, conduisant à une production accrue de H₂S. Les autres produits soufrés des coupes essence et LCO apparaissent également dès les très faibles rapports catalyseur/charge puis se stabilisent en présence de vanadium, lorsque la quasi-totalité du dipentylsulfure a été convertie. En l'absence de vanadium, en revanche, les quantités produites augmentent jusqu'à consommation totale du dipentylsulfure.

Afin de quantifier l'effet du vanadium sur la disparition du pentanethiol, nous avons modélisé la transformation du dipentylsulfure en utilisant un schéma cinétique simple obéissant à une loi du premier ordre:

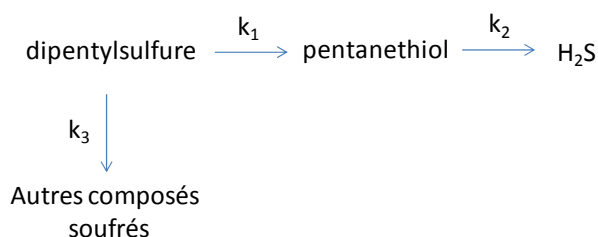


Schéma 5-4 : modèle cinétique de la transformation du dipentylsulfure

Les constantes de vitesse ont été optimisées en minimisant l'écart entre les concentrations de soufre calculées et les valeurs expérimentales par une méthode de régression non linéaire. Les courbes de la Figure 5-11 correspondent aux prévisions du modèle après optimisation des constantes de vitesse. Il apparaît que les concentrations expérimentales sont reproduites de manière satisfaisante, justifiant la validité de ce modèle simple.

Les trois constantes de vitesses optimisées pour le catalyseur référence (Cat) et le mélange (Cat + V) sont indiquées dans le Tableau 5-3. Le rapport des constantes de vitesse obtenues pour la fraction du catalyseur chargé au vanadium à celles du catalyseur de référence sont indiquées dans la dernière colonne du tableau.

Tableau 5-3 : Constantes de vitesses optimisées

	Cat (référence)	Cat + V	$k_i(\text{Cat})/k_i(\text{Cat} + \text{V})$
k_1 / s^{-1}	10	30	3,0
k_2 / s^{-1}	32	130	4,0
k_3 / s^{-1}	5	6	1,2

Les constantes de vitesse de craquage du pentanethiol (k_2) sont 3 à 5 fois supérieures aux constantes de vitesse de craquage du dipentylsulfure (k_1), indiquant que cet intermédiaire est beaucoup plus réactif que le dipentylsulfure. Il apparaît également que l'ajout de vanadium augmente considérablement les vitesses de craquage de ces composés aliphatiques, d'un facteur 3 à 4. Enfin, le vanadium augmente également la constante de vitesse k_3 , correspondant à la transformation du dipentylsulfure en composés (benzo)thiophéniques. Cette augmentation rend bien compte de l'effet déshydrogénant du vanadium. L'accroissement de cette constante de vitesse est néanmoins

5. Additifs de désulfuration en FCC.

beaucoup plus faible que l'augmentation des vitesses de craquage du dipentylsulfure et du pentanethiol.

Afin de déterminer si l'action du vanadium sur la désulfuration du dipentylsulfure est catalytique, nous avons estimé le nombre de rotation (TON, *Turn Over Number*) pour ces réactions en déterminant les quantités de dipentylsulfure éliminé ($\Delta C_{10}S$) et de H_2S produit (ΔH_2S) par l'action du vanadium.

La figure ci-contre représente l'évolution des rapports de ces quantités produites ou éliminées à la quantité de vanadium présente dans le lit catalytique pour tous les rapports C/O testés.

Ces ratios sont maximaux aux plus faibles temps de contact. En supposant que tous les atomes de vanadium sont actifs en désulfuration et en prenant en compte la participation du vanadium à l'élimination du pentanethiol, chaque atome de vanadium participe en moyenne à la rupture d'une douzaine de liaisons carbone-soufre aliphatiques.

Notons enfin que ces ratios représentent la quantité minimale de molécules de dipentylsulfure éliminées par atome de vanadium effectivement actif en désulfuration dans la mesure où même en l'absence de soufre, une fraction importante du vanadium est réduite au contact de la charge.

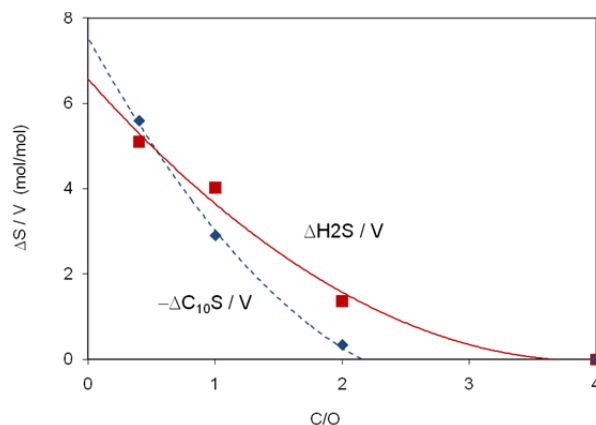


Figure 5-12 : Evolution des ratios molaires dipentylsulfure éliminé/vanadium ($\Delta C_{10}S/V$) et H_2S produit/vanadium (ΔH_2S) en fonction du rapport catalyseur/charge

Transformation de l'hexylthiophène.

Les tests réalisés à faible conversion nous permettent de détecter des quantités mesurables d'hexylthiophène. L'analyse des chromatogrammes nous a également permis de mettre en évidence des pics correspondants vraisemblablement à des intermédiaires de réaction. La Figure 5-13 suivante rapporte l'évolution des quantités d'hexylthiophène, d'intermédiaires, de H_2S et de l'ensemble des autres produits soufrés des coupes essence et LCO.

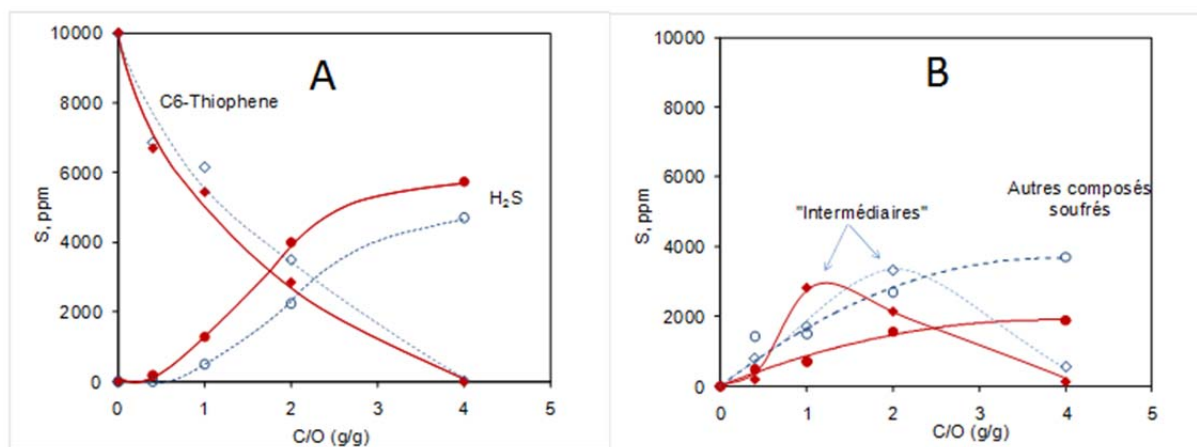


Figure 5-13 : Gauche : Evolution des quantités d'hexylthiophène et de H_2S en fonction du rapport catalyseur/charge. Droite : Evolution des rendements en « intermédiaires » et en autres produits soufrés des coupes essence et LCO pour le catalyseur de référence (symboles ouverts, lignes pointillées) et le catalyseur au vanadium (symboles fermés, lignes continues).

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Il apparaît clairement sur cette figure que la présence de vanadium ne conduit pas à une diminution très importante de l'hexylthiophène. Pour les rapports C/O les plus faibles, sa conversion est pratiquement identique en l'absence ou en présence de vanadium.

De même, les quantités de H₂S produites pour le plus petit rapport C/O sont très faibles en regard de la conversion de l'hexylthiophène, mais pour des rapports C/O plus importants, le vanadium conduit à une très nette augmentation de l'H₂S produit.

Les produits intermédiaires, en revanche, sont clairement affectés par la présence de vanadium : leur rendement maximal est plus faible et il est obtenu pour un temps de contact plus court sur le catalyseur au vanadium, indiquant qu'ils sont convertis plus rapidement en présence de vanadium. Bien qu'ils n'aient pas été identifiés, ces composés sont éludés dans la gamme des méthylbenzothiophènes, un peu après l'hexylthiophène. Le mécanisme de désulfuration généralement admis faisant intervenir des intermédiaires tetrahydrothiophéniques, nous attribuons ces pics à des intermédiaires hydrogénés, notamment les produits tetrahydrogénés des alkylthiophènes lourds.

Ces observations contrastent avec la transformation du dipentylsulfure pour laquelle le vanadium augmente très fortement la conversion dès les plus faibles rapports C/O montre clairement que le vanadium n'affecte pratiquement pas les premières étapes de transformation de l'hexylthiophène.

La Figure 5-14A ci-après montre l'évolution des quantités de H₂S produit par l'action du vanadium (ΔH_2S). Ces quantités n'augmentent fortement qu'au-delà du rapport C/O = 1, correspondant approximativement au maximum de rendement des intermédiaires. La Figure 5-14B présente également l'évolution du ratio des quantités de H₂S produites sous l'effet du vanadium à la quantité de vanadium présente dans le lit catalytique. Ce ratio présente un maximum pour des rapports C/O compris entre 1 et 2, lorsque les quantités de produits intermédiaires sont maximales.

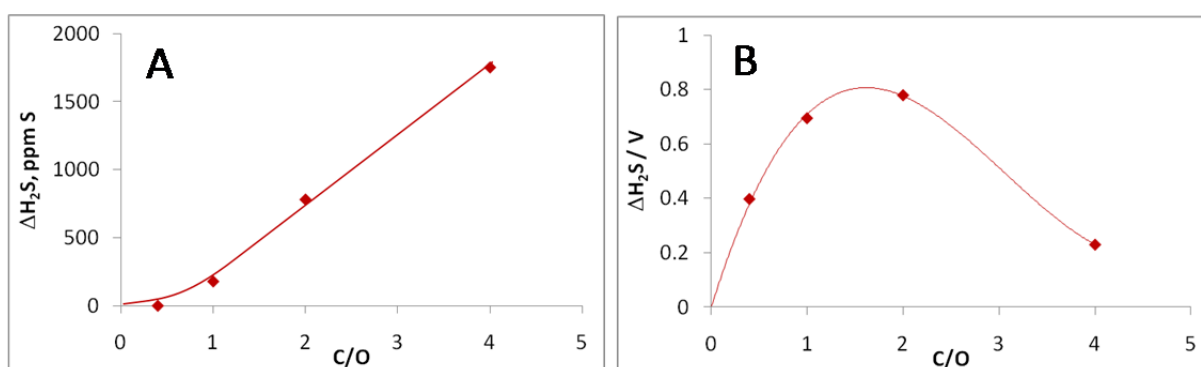


Figure 5-14 : **A** : Quantité de H₂S produite sous l'effet du vanadium (ΔH_2S). **B** : Evolution du rapport molaire $\Delta H_2S/V$ en fonction du rapport catalyseur/charge

L'ensemble de ces données montre clairement que le vanadium a pour effet principal de désulfurer plus efficacement une partie de ces intermédiaires hydrogénés, conduisant à l'augmentation de la quantité de H₂S produite et à la diminution concomitante des autres produits soufrés présents dans les coupes essence et LCO.

Ces résultats sont en bon accord avec les conclusions de l'étude de la transformation du dipentylsulfure qui avait montré que le vanadium accélère très fortement les vitesses de rupture des liaisons C-S aliphatiques.

5.3.3 CARACTERISATION DE L'INTERACTION DU VANADIUM AVEC LES ZEOLITHES

La caractérisation du vanadium et de son interaction avec la phase active du catalyseur de craquage (zéolithe) s'est avérée particulièrement difficile en raison notamment des faibles quantités de vanadium (0,1-0,5 %pds).

Néanmoins, nous avons pu montrer par spectroscopie IR que le vanadium est susceptible d'interagir avec tous les types de sites accessibles dans ces catalyseurs (groupements silanols, hydroxyles zéolithiques et sites acides de Lewis) sans montrer d'interaction préférentielle avec l'un ou l'autre de ces sites : le vanadium apparaît donc uniformément distribué et très dispersé sur ces catalyseurs.

La caractérisation du vanadium par photoluminescence (réalisée en collaboration avec G. Costentin, LRS, Paris VI), nous a permis de confirmer la dispersion importante du vanadium dans la zéolithe. La comparaison des spectres obtenus (Figure 5-15A) avec la littérature,²²⁸⁻²³⁰ nous a permis de montrer que les espèces vanadyles sont sous forme tétraédrique (Figure 5-15B).

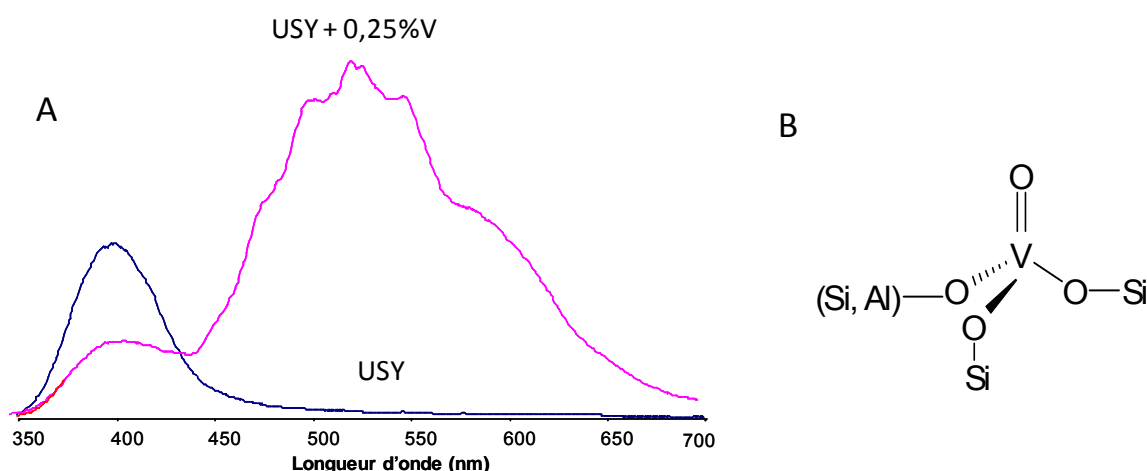


Figure 5-15. **A** Spectres de photoluminescence d'une zéolithe USY en l'absence ou en présence de vanadium. **B** Structure des espèces vanadyles supportées sur une zéolithe USY.

L'étude de systèmes catalytiques proches de ceux fonctionnant en FCC (zéolithe mélangée à une matrice et vapotraitée) a aussi été menée. Dans ce cas, le vapotraitement conduit à une diminution très marquée du nombre de groupements hydroxyles acides et de sites acides de Brønsted et de Lewis, accrue en présence de vanadium. En revanche, le vapotraitement accroît la dispersion du vanadium, confirmant la très forte mobilité du vanadium en conditions hydrothermales.

5.3.4 PROPOSITION DE MECANISME

L'ensemble des résultats obtenus montre que le vanadium conduit à une diminution importante des composés soufrés de la coupe essence en accélérant les ruptures des liaisons carbone-soufre aliphatiques. Ceci a notamment pour effet d'ouvrir les cycles tétrahydrothiophéniques et donc de limiter leur déshydrogénation en composés thiophéniques réfractaires au craquage ; d'éliminer efficacement les thiols formés par l'ouverture de ces cycles et de limiter la recombinaison de H₂S avec les oléfines, par re-craquage des thiols formés. Le problème posé ici est de déterminer de quelle manière le vanadium est susceptible d'accélérer ces réactions de rupture carbone-soufre.

Il est très clair que ni les caractérisations, ni les tests d'activités sur charge réelles ou charges modèles ne permettent de conclure à une modification importante de l'acidité qui permettrait de favoriser ces réactions: le vanadium conduit au contraire à une baisse de l'acidité (Brønsted et Lewis) et ne conduit ni à une activité en craquage plus élevée, ni à des sélectivités sensiblement différentes. La seule influence sensible du vanadium sur la conversion de la charge hydrocarbonée est l'augmentation du coke et de l'hydrogène ainsi que des hydrocarbures les plus légers, C₁ et C₂ en particulier.

Cette augmentation des hydrocarbures légers est surprenante. Le craquage catalytique est en effet connu pour être très peu sélectif en ces produits légers, au contraire du craquage thermique qui s'en distingue notamment par une sélectivité accrue en C₁, C₂. La voie principale de formation de méthane et d'éthane par une voie acide est le craquage protolytique d'un alcane, faisant intervenir un ion carbonium. Néanmoins, le vanadium ne conduit pas à une exaltation de l'acidité telle qu'elle pourrait favoriser la voie de craquage protolytique.

Au contraire du craquage catalytique, le craquage thermique fait intervenir des radicaux libres (CH₃· ou R-CH₂·) qui ont une stabilité plus importante et la formation accrue en hydrocarbures légers, C₁-C₂, est généralement considérée comme la signature de réactions radicalaires. Dans l'hypothèse où l'augmentation des C₁, C₂ sous l'effet du vanadium est également une signature de réactions radicalaires, nous sommes amenés à conclure que le vanadium favorise l'initiation de radicaux libres. Le vanadium, initialement à l'état d'oxydation 5+, est en effet susceptible de donner lieu à des transferts d'électrons et de se réduire à l'état 4+ ou 3+, au cours du craquage.²³¹ Cette réduction implique le transfert d'un électron d'une molécule de la charge vers le vanadium et rend possible la formation de radicaux. Un tel transfert pourrait se faire, par exemple, par abstraction d'un atome d'hydrogène :

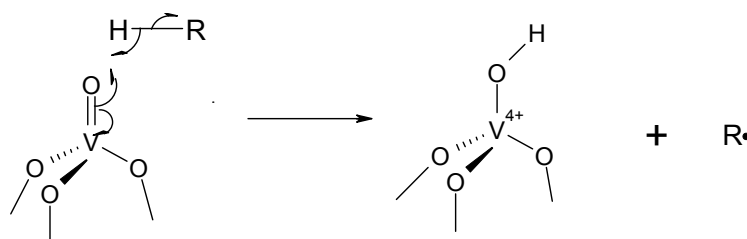


Schéma 5-5 : Abstraction d'hydrogène par un groupement vanadyle

5. Additifs de désulfuration en FCC.

Les radicaux ainsi formés sont ensuite susceptibles de se propager et d'initier des réactions de craquage radicalaire, expliquant ainsi la formation accrue de méthane et d'éthane qui est systématiquement observée en présence de vanadium.

Les molécules soufrées aliphatiques sont également susceptibles de former des radicaux libres relativement stables. Dans le cas des thiols aliphatiques, en particulier, l'abstraction d'hydrogène se fait préférentiellement sur le soufre ou sur l'atome de carbone en position alpha par rapport au soufre.²³² Pour un composé tétrahydrothiophénique, l'abstraction d'un atome d'hydrogène conduit à la formation d'un radical en alpha du soufre (Schéma 5-6). Ce radical est susceptible de conduire à la rupture de la liaison carbone-soufre en beta, conduisant à la formation d'une thione. Ce composé, peu stable, peut s'hydrogéner ensuite rapidement en thiol par des réactions de transfert d'hydrogène. Alternativement, le radical peut être déplacé position beta et conduire à la formation d'un thiol après rupture de la liaison carbone-soufre et réhydrogénation (Schéma 5-6).

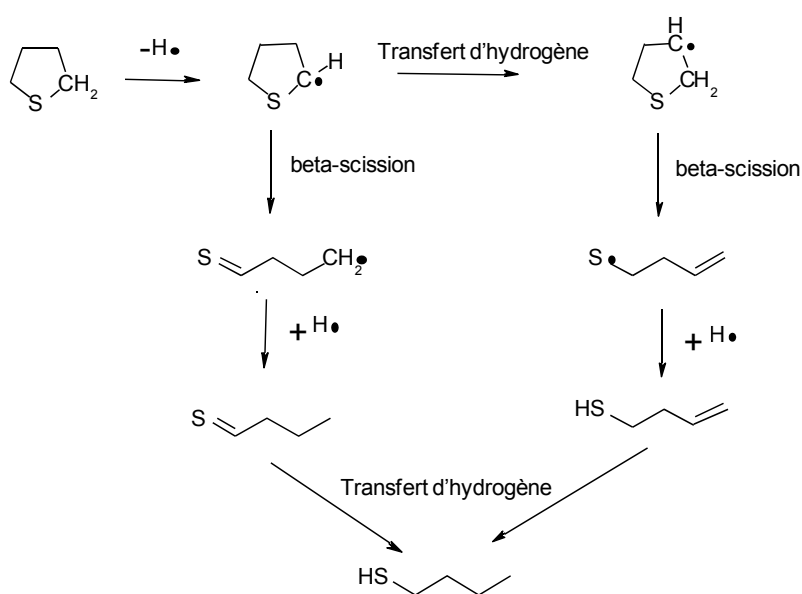
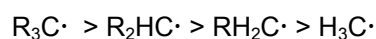


Schéma 5-6 : rupture de liaison carbone soufre par beta scission radicalaire

La stabilité relative des radicaux est similaire à celle des carbocations et augmente avec le degré de substitution :

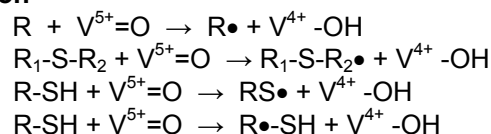


On s'attend donc à ce que la formation de radicaux soit favorisée pour des tétrahydrothiophènes substitués, ce qui peut expliquer le fait que le vanadium favorise l'élimination des thiophènes les plus lourds de la coupe essence (C2-C4-thiophènes).

Enfin, ces mécanismes permettent également d'expliquer l'action 'catalytique' du vanadium sur la rupture des liaisons carbone-soufre. Dans le cas du craquage du dipentylsulfure, nous avons en effet montré, que chaque atome de vanadium est susceptible d'induire la rupture d'une douzaine de liaisons carbone-soufre. La quantité de vanadium effectivement actif constituant vraisemblablement une fraction du vanadium total, le nombre d'actes catalytiques par atome de vanadium est vraisemblablement beaucoup plus élevé.

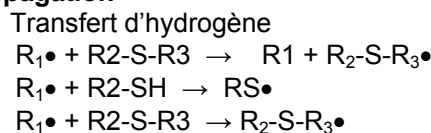
Un mécanisme radicalaire permet d'envisager des réactions en chaînes, expliquant le nombre élevé des ruptures de liaisons carbone-soufre par le vanadium comme indiqué ci-après :

Initiation



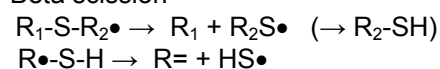
...

Propagation



...

Beta scission



...

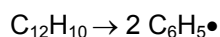
Terminaison



...

Influence d'un initiateur de radicaux sur l'élimination du soufre

Dans le but de conforter ces hypothèses, nous avons examiné l'influence d'un initiateur de radicaux ajouté à la charge. Nous avons choisi le biphenyle qui se décompose thermiquement en radicaux phényle à des températures typiques des conditions du FCC :²³³



La Figure 5-16 ci-contre compare les teneurs en soufre des produits liquide (essence et LCO) obtenus après craquage de la charge hydrotraitée additivée de dipentylsulfure en l'absence de vanadium et de biphenyle (référence), en présence de biphenyle (référence + biphenyl) ou en présence d'un additif au vanadium (référence + V). Les quantités de biphenyle ajoutées ont été ajustées pour correspondre à la quantité de vanadium et restent faibles au regard de la quantité de charge (0,3 %pds).

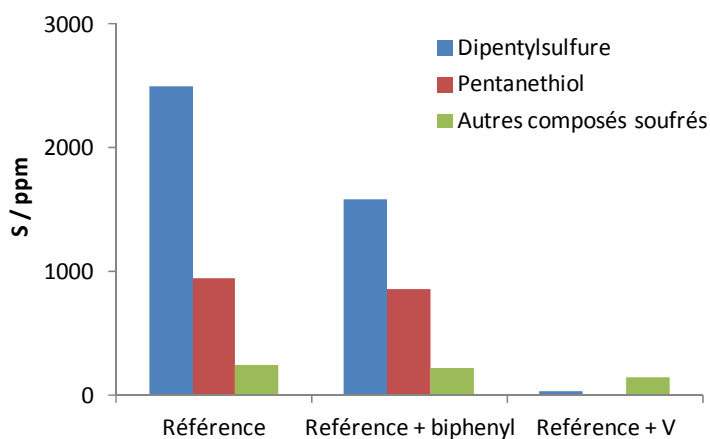


Figure 5-16 : influence d'un initiateur de radicaux sur les teneurs en soufre des produits liquides (essence et LCO) à isoconversion de la charge (30%).

Les résultats obtenus montrent donc que l'ajout de biphenyle conduit à une diminution significative du dipentylsulfure et, dans une moindre mesure, du pentanethiol. Ces résultats montrent donc que l'ajout d'un initiateur de radicaux améliore sensiblement le craquage de ces composés soufrés aliphatiques

et conforte donc le mécanisme proposé. Notons enfin qu'à teneurs équivalentes, néanmoins, le vanadium est beaucoup plus efficace pour l'élimination des composés soufrés, ce qui pourrait s'expliquer par le fait que le rendement en radicaux phényles est probablement faible dans nos conditions, en raison notamment de son craquage par le catalyseur de FCC.

5.4 CONCLUSIONS

Les études présentées dans ce chapitre nous ont permis de montrer que l'élimination des composés thiophéniques par les additifs GSR résulte d'une synergie entre le catalyseur de FCC permettant d'hydrogéner les cycles thiophéniques par des réactions de transfert d'hydrogène, et l'additif qui améliore les vitesses de craquage des composés hydrogénés ainsi formés.

Les mécanismes de craquage des composés soufrés aliphatiques, néanmoins, sont très différents pour les deux familles d'additifs étudiées.

Les additifs Zn/Al_2O_3 conduisent au craquage des liaisons carbone-soufre par des réactions d'élimination catalysées par des paires acide-base de Lewis. Ces additifs présentent donc une activité optimale pour des propriétés acido-basique équilibrées : centres acides de Lewis forts et basicité modérée.

Les additifs au vanadium sont également très efficaces en craquage des liaisons métal-soufre aliphatiques. Dans ce cas, néanmoins, les réactions de craquage des liaisons métal-soufre sont vraisemblablement radicalaires, le vanadium jouant le rôle d'initiateur de radicaux.

Ces différences de mécanisme (acide-base vs. redox) permettent, dans une certaine mesure, d'expliquer les différences de sélectivité de ces additifs pour les composés soufrés de la coupe essence. La sélectivité relativement faible des additifs Zn/Al_2O_3 pour les composés thiophéniques les plus lourds (C_3 - C_4 -thiophènes) pourrait s'expliquer par l'encombrement stérique des intermédiaires hydrogénés. Dans le cas des additifs au vanadium, au contraire, les radicaux formés à partir de ces intermédiaires sont a priori plus stables, expliquant ainsi la bonne sélectivité de ces additifs sur l'ensemble de la coupe essence.

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6.1 INTRODUCTION

J'ai récemment initié au laboratoire de nouvelles études visant à quantifier des espèces adsorbées sous flux à haute température par spectroscopie IR dans le but de déterminer leurs constantes thermodynamiques (enthalpie et entropie d'adsorption).

Appliquées à l'adsorption de molécules sondes d'acidité ou de basicité, ces travaux doivent permettre de définir quantitativement la distribution en force des sites d'adsorption, acides ou basiques. Dans le cas de réactifs et pour une réaction élémentaire, la détermination des constantes d'adsorption sur les sites actifs en conditions *operando* permet d'accéder aux constantes cinétiques intrinsèques de la réaction.

Dans ce chapitre, je décrirais les premiers résultats de ces nouvelles études. Je présenterais d'abord une nouvelle méthodologie permettant de quantifier et de déterminer les paramètres d'adsorption d'espèces distinctes simultanément adsorbées et son application à l'adsorption de CO₂ sur ZrO₂.^{***}

Je montrerais ensuite comment l'étude *operando* du craquage monomoléculaire d'un alcane (propane) par des zéolithes acides (H-ZSM-5) permet pour la première fois à ma connaissance de déterminer *directement* les paramètres intrinsèques de cette réaction.

Enfin, je décrirais mes nouveaux projets de recherche, en montrant notamment comment ces méthodologies pourraient être étendues à l'étude IR de réactions d'hydrotraitement en conditions *operando*.

6.2 DEVELOPPEMENT D'UNE METHODE DE TRAITEMENT DES ISOTHERMES SPECTROSCOPIQUES

6.2.1 INTRODUCTION

L'hétérogénéité en nature et force des sites superficiels de catalyseurs ou d'adsorbants est une caractéristique fondamentale qui doit être prise en compte l'étude des mécanismes d'adsorption et de réaction sur ces surfaces. Les approches visant à caractériser ces propriétés consistent en l'étude de l'adsorption de molécules sondes.²³⁴⁻²³⁸ Alors que les méthodes volumétriques, gravimétriques ou calorimétriques donnent des informations quantitatives en termes de nombre et distribution en force des sites d'adsorption, elles n'informent pas sur la structure moléculaire des espèces adsorbées. Les méthodes spectroscopiques, infrarouge en particulier, présentent le défaut opposé: elles donnent des informations essentielles sur la nature des sites mais sont peu précises d'un point de vue quantitatif (nombre et force de ces sites), en particulier lorsque ces espèces sont adsorbées sur des sites distincts. Dans ce cas, les spectres IR sont généralement complexes et la détermination des intensités des bandes caractéristiques des espèces adsorbées est généralement difficile, ne permettant qu'une analyse qualitative de leurs stabilités.

^{***} Ce travail a été réalisé dans le cadre du projet ANR Guerbet (programme CP2D), UCCS (Lille), IRCELYON (Lyon), LCS (Caen) et Arkema (Lyon), Coordinateur F. Dumeignil, UCCS.

Un exemple typique de cette situation est la caractérisation par spectroscopie IR de la basicité d'oxydes métalliques par adsorption de CO_2 . La Figure 6-1 ci-contre présente les spectres obtenus après adsorption et désorption de CO_2 à températures croissantes sur une zircone monoclinique. Elle conduit à la formation de différentes espèces caractérisées par des bandes $\nu(\text{CO}_3)$ multiples dans la zone $1200\text{-}1800\text{ cm}^{-1}$, dont le recouvrement important rend difficile l'évaluation des intensités individuelle et la caractérisation quantitative de leurs stabilités thermiques : hydrogénocarbonates (HC), carbonates bidentés (C_2 , C_2') ou polydentés (C_3), et carbonates pontés (BC – *bridged carbonates*) dont les structures typiques proposées dans la littérature,^{118,239} sont représentées sur le Schéma 6-1 ci-dessous.

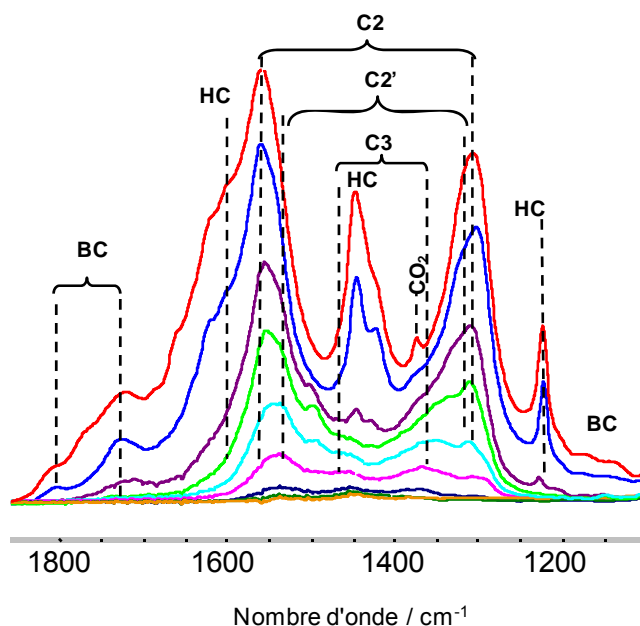


Figure 6-1 : Spectres IR obtenus après adsorption de CO_2 sur ZrO_2 à température ambiante suivie d'une évacuation à température croissante ($50\text{-}400^\circ\text{C}$)

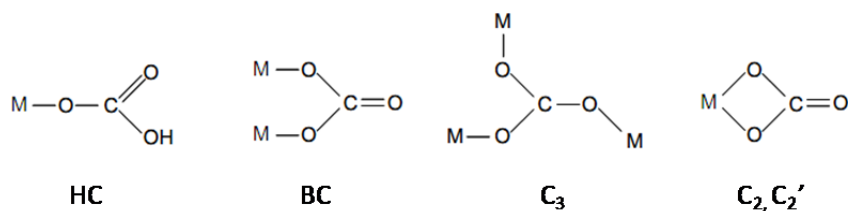


Schéma 6-1 : structure de espèces carbonates formées sur un oxyde métallique.

Dans le but de caractériser quantitativement les espèces adsorbées, un nouvel appareillage a été développé au laboratoire, consistant à coupler une cellule IR à une balance thermogravimétrique (AGIR – Analyse Gravimétrique et Infrarouge), permettant de déterminer simultanément la prise de masse de l'échantillon et les spectres IR des espèces adsorbées.¹⁷⁶

Nous avons utilisé ce nouveau système pour déterminer simultanément les isothermes d'adsorption par gravimétrie et spectroscopie infrarouge du CO_2 et développé une méthode de traitement de ces isothermes pour quantifier et déterminer la stabilité thermodynamique des espèces formées.

6.2.2 PRINCIPE DE LA METHODE ET RESULTATS

La Figure 6-2A ci-après montre les spectres obtenus après adsorption de CO₂ sur ZrO₂ sous pressions variables (1×10^{-3} – 3×10^{-1} bars) à 300°C. La Figure 6-2B représente l'isotherme correspondant.

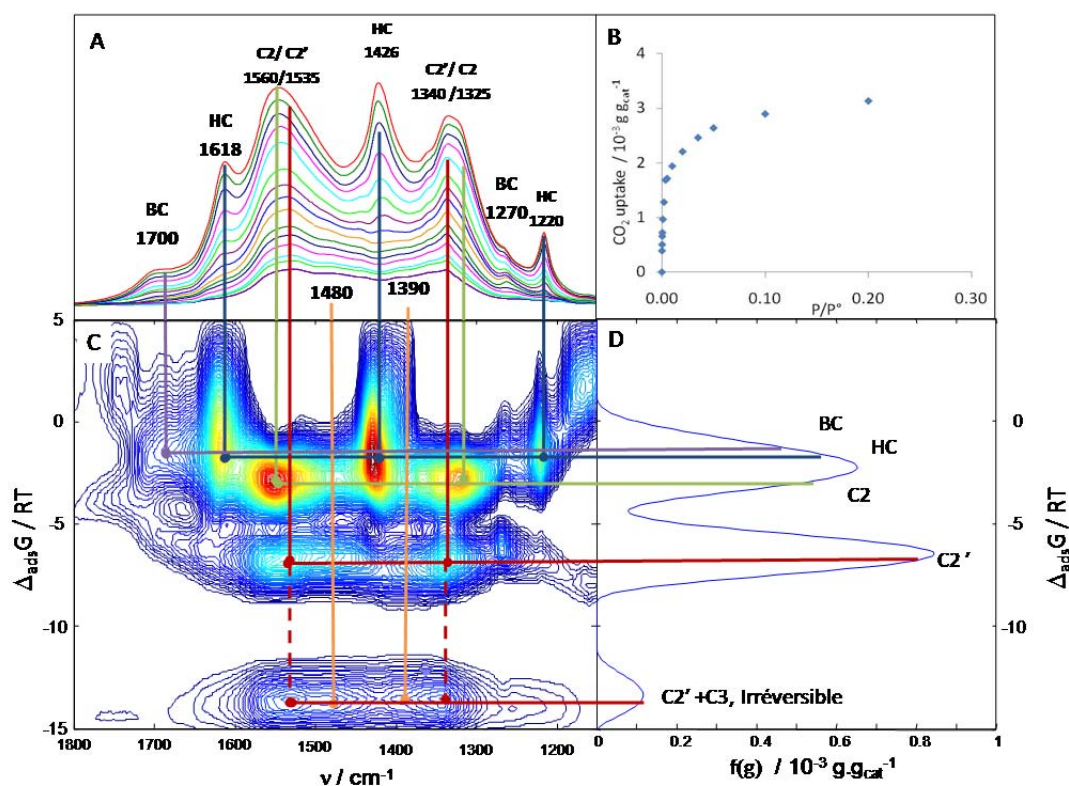


Figure 6-2 : **A.** spectres IR obtenus après adsorption de CO₂ sur ZrO₂ at 300°C, $P = 10^{-4}$ – 0.3 bars. **B.** Isotherme gravimétrique. **C.** fonction de distribution $f(v,g)$ obtenue à partir des spectres IR. **D.** fonction de distribution $f(g)$ obtenue à partir de l'isotherme gravimétrique.

La méthodologie que nous avons développée consiste à déterminer les énergies libres d'adsorption $\Delta_{ads}G$ des espèces individuelles en considérant que chacune d'entre elles contribue à un isotherme de Langmuir généralisé. Pour l'isotherme gravimétrique, la prise de masse à la pression p est donnée par :

$$a(p) = \int_{g_{min}}^{g_{max}} \theta(p, g) f(g) dg \quad (1)$$

où $\theta(p, g)$ est le taux de couverture d'un type de site donné, $f(g)$ est la fonction de distribution en énergie des sites d'adsorption, et $g = \Delta_{ads}G/RT$ est l'enthalpie libre réduite d'adsorption.

L'inversion de cette équation intégrale permet d'accéder à la distribution $f(g)$ des sites d'adsorption. La résolution numérique de cette équation nécessite l'utilisation d'une procédure de régularisation en raison de son caractère mal posé : une erreur faible sur la mesure de $a(p)$ est susceptible de conduire à une variation importante de la solution (g) .

De tels problèmes d'inversion ont été résolus dans le cas d'isothermes d'adsorption,²⁴⁰⁻²⁴¹ ou de spectres de désorption en température programmée.²⁴² Dans le cas de l'adsorption de CO₂, l'application de ces procédures d'inversion à l'isotherme gravimétrique (Figure 6-2B) conduit à la fonction de distribution en enthalpie libre $f(g)$ représentée sur la Figure 6-2D. Elle montre que les sites d'adsorption présentent trois gammes d'énergie. L'intégration des trois pics obtenus permet en outre de quantifier directement ces sites. Néanmoins, à partir des seules données thermogravimétriques, il est difficile d'attribuer ces sites à une ou plusieurs espèces particulières sans connaissance préalable des interactions adsorbat-surface.

L'originalité de notre approche consiste à inverser de la même manière les isothermes spectroscopiques $a(\nu, p)$ (intensité à une fréquence et pression données) obtenus à partir des spectres IR. Cette inversion conduit à une fonction de distribution bidimensionnelle $f(\nu, g)$ représentée sur la Figure 6-2C, dont les composantes correspondent aux bandes IR des espèces adsorbées résolues en nombre d'onde (ν) et en énergie libre d'adsorption (g).

L'examen de cette carte montre que la plupart des espèces identifiées sur les spectres IR sont maintenant séparées en énergie libre d'adsorption, dans l'ordre :



Ce classement est en bon accord avec les études qualitatives de ces spectres rapportées dans la littérature. L'intérêt de la méthode d'inversion développée ici est de caractériser thermodynamiquement ces stabilités. Néanmoins, il convient de noter que les énergies obtenues pour les espèces irréversiblement adsorbées ($g = -14$) n'a pas de sens physique dans la mesure où notre modèle postule une adsorption réversible.

La comparaison des deux fonctions de distribution obtenues montre que les pics obtenus à partir de l'isotherme gravimétrique peuvent être attribués, par ordre croissant d'énergie (i) aux espèces BC, HC et C₂, (ii) aux espèces C₂' et (iii) aux espèces irréversiblement adsorbées dans nos conditions (C₃+C₂'), respectivement. Les espèces BC, HC et C₂' ayant des énergies d'adsorption proches, leurs contributions respective à la distribution obtenues à partir de l'isotherme gravimétrique n'est pas résolue, comme l'est la projection des composantes de la distribution $f(\nu, g)$ sur l'axe des énergies.

Les quantités de sites conduisant à l'adsorption de ces espèces, obtenues par intégration de la distribution $f(g)$ sont reportées dans le Tableau 6-1 ci-après. La quantité totale de sites d'adsorption obtenue (1.5 $\mu\text{mol m}^{-2}$) est proche de celles reportées dans la littérature (1.2 – 2.8 $\mu\text{mol m}^{-2}$).

En réalisant ces expériences à différentes températures (250 – 350°C), nous avons pu déterminer les enthalpies et entropies d'adsorption pour les principales espèces observées à partir de la relation de van't Hoff (Figure 6-3). Les valeurs ainsi obtenues sont reportées dans le Tableau 6-1 ci-après. Les valeurs d'enthalpie obtenues sont comprises dans la gamme des chaleurs d'adsorption moyennes de CO₂ sur ZrO₂ reportées dans la littérature, de 160 à 30 kJ mol⁻¹ selon le taux de couverture.

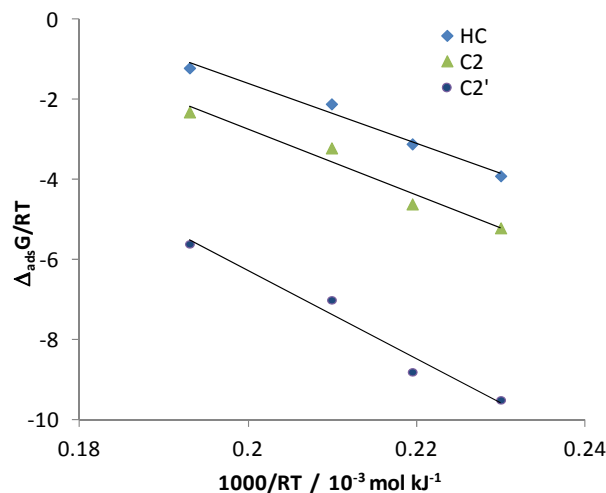


Figure 6-3 : Graphe de van't Hoff des 'énergies libre d'adsorption obtenu par inversion des isothermesw spectroscopiques obtenus à différentes températures (250-350°C

Tableau 6-1 : Quantification et thermodynamique des espèces CO₂ adsorbées sur ZrO₂

	Q / μmol m ⁻²	Δ _{ads} H / kJ mol ⁻¹	Δ _{ads} S / J K ⁻¹ mol ⁻¹
BC	} 0.68 ± 0.14	N/D	N/D
HC		-75 ± 7	-112 ± 10
C ₂		-84 ± 8	-118 ± 15
C ₂ '	0.70 ± 0.14	-112 ± 8	-135 ± 18
C ₃	0.13 ± 0.02	N/D	N/D

6.2.3 CONCLUSION

La méthodologie présentée ici permet de caractériser l'hétérogénéité de surface en termes de nature, nombre et force des sites d'adsorption de manière beaucoup plus complète que par les méthodes habituellement utilisées.

Par rapport aux études spectroscopiques classiques, la distribution bidimensionnelle $f(v, g)$ permet d'améliorer la résolution spectrale de bandes caractéristiques d'espèces distinctes en les séparant selon la stabilité relative de ces espèces. Elle permet également de quantifier la stabilité de ces espèces en terme de constante d'adsorption (ou enthalpie libre) et, en réalisant ces expériences à températures variables, d'accéder aux enthalpies et entropies d'adsorption de ces espèces. De ce point de vue, elle constitue une avancée majeure dans le traitement de spectres IR complexes d'espèces adsorbées.

Comparé aux méthodes quantitatives classiques (volumétrie, thermogravimétrie, calorimétrie), la

méthodologie présentée ici permet d'identifier, de quantifier et de déterminer des paramètres d'adsorption d'espèces distinctes, alors que les méthodes existantes ne donnent aucune indication sur la nature des espèces formées par adsorption et ne permettent généralement d'obtenir que des quantités moyennées sur plusieurs types d'espèces.

Enfin, il est important de noter que la méthode d'inversion des spectres présentée ici n'est pas limitée à une spectroscopie ou un processus physique particulier et devrait être applicable à d'autres données spectroscopiques dans le cas où les intensités spectrales sont liées à la variable expérimentale (pression, température, temps, ...) par une dépendance fonctionnelle simple. Elle pourrait notamment être utilisée pour la caractérisation d'autres processus tels que la désorption en température programmée, ou la cinétique de formation d'espèces superficielles (coke par exemple).

6.3 ETUDE OPERANDO DU CRAQUAGE MONOMOLECULAIRE D'ALCANES PAR DES ZEOLITHES ACIDES.

6.3.1 INTRODUCTION

Bien que le craquage monomoléculaire des alcanes par des zéolithes acides ait été assez largement étudié, les paramètres gouvernant l'activité d'une zéolithe ou la réactivité d'alcanes de structures différentes ne sont toujours pas bien compris, en particulier parce que la vitesse de craquage résulte de la combinaison de paramètres cinétiques (constante de vitesse de craquage k de l'alcane sur les sites acides) et thermodynamiques (constante d'adsorption K_{ads} de l'alcane) : ²⁴³⁻²⁴⁷

$$r = k K_{ads} P \quad (1)$$

avec :

$$k = A \exp\left(-\frac{E_{act}}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (2)$$

$$K_{ads} = \exp\left(\frac{\Delta_{ads} S}{R}\right) \exp\left(-\frac{\Delta_{ads} H}{RT}\right) \quad (3)$$

La détermination expérimentale de la vitesse de craquage monomoléculaire d'un alcane à température variable permet de déterminer des constantes de vitesses et des énergies d'activation apparentes données par :

$$k_{app} = k K_{ads} \quad \text{et} \quad E_{app} = E_{act} + \Delta_{ads} H \quad (3)$$

Alors que les vitesses de craquage augmentent très fortement avec la longueur de l'alcane et sont sensibles à la structure de la zéolithe (H-Y < H-BEA < H-MOR < H-ZSM-5 < H-FER), de nombreuses études ont montré que les énergies d'activation E_{act} , obtenues à partir des énergies d'activation apparentes E_{app} et de la mesure des chaleurs d'adsorption $\Delta_{ads} H$ sont pratiquement indépendantes de la structure de la zéolithe ou de l'alcane considéré. ²⁴³⁻²⁴⁸ Deux hypothèses ont été émises pour expliquer les différences de vitesses observées :

- variations de la constante d'équilibre K_{ads} et donc du taux de couverture des sites acides par l'alcane dans les pores de la zéolithe, ²⁴³⁻²⁴⁵ ce qui implique que la constante de vitesse intrinsèque k soit indépendante de la structure de la zéolithe ou de l'alcane.
- variations de l'entropie d'activation ΔS^\ddagger , et donc du facteur pré-exponentiel. ²⁴⁶⁻²⁴⁷

Cette dernière hypothèse, émise par Bhan et al. en 2008 résulte de l'observation que l'augmentation de l'enthalpie d'adsorption $\Delta_{ads} H$ d'alcanes de taille croissante s'accompagne généralement d'une diminution de l'entropie d'adsorption $\Delta_{ads} S$. ²⁴⁹

La comparaison des entropies d'adsorption reportées dans littérature est souvent difficile en raison de définitions différentes de l'état standard notamment. Néanmoins, il nous a été possible de généraliser cette relation en considérant les enthalpies et entropies d'adsorption relatives au *n*-hexane, presque systématiquement examiné dans ces études. ^{245,249-253}

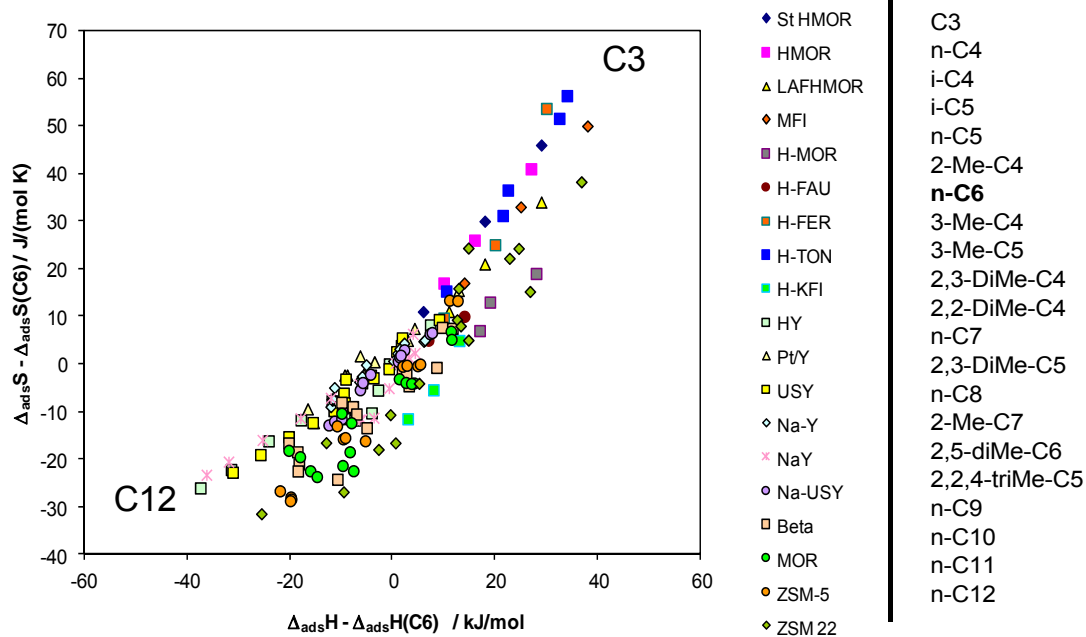


Figure 6-4 : Entropies et enthalpies d'adsorption relatives au *n*-hexane calculées à partir des données de la littérature.^{245,249-253}

La Figure 6-4 ci-dessus illustre ce phénomène de compensation pour l'adsorption d'alcane linéaires ou branchés dans de nombreuses zéolithes. Il s'explique qualitativement par le fait que plus l'enthalpie d'adsorption augmente, moins l'alcane adsorbé est mobile dans la zéolithe. La contribution de l'enthalpie d'adsorption diminuant avec la température (Eqn. 3), la compensation enthalpie-entropie tend à niveler les constantes d'adsorption calculées à température de réaction (800 K). La Figure 6-5 ci-après reporte les constantes d'adsorption relatives au *n*-hexane calculées à 300K et 800K à partir des données précédentes en fonction de l'enthalpie d'adsorption $\Delta_r H$ des alcanes considérés. Elle montre qu'à basse température, la constante d'adsorption augmente pratiquement exponentiellement avec l'enthalpie d'adsorption. A 800 K, en revanche, les constantes d'adsorption présentent une gamme de valeurs beaucoup plus resserrée. Ainsi, sur une zéolithe H-ZSM-5, la constante d'adsorption du propane relative au *n*-hexane est de $\sim 1 \cdot 10^{-4}$ à 300 K, contre 1,3 à 800 K, indiquant que dans les conditions de réaction, les concentrations de propane et d'hexane sont similaires et ne permettent pas d'expliquer la réactivité beaucoup plus importante de l'hexane (deux ordres de grandeur environ). Les études de simulation de l'adsorption de *n*-alcane dans des zéolithes confirment également qu'à haute température, les constantes d'adsorption de ces composés varient faiblement avec leur taille.²⁵⁴⁻²⁵⁵ L'hypothèse selon laquelle l'activité intrinsèque en craquage monomoléculaire est essentiellement gouvernée par l'entropie d'activation semble donc maintenant faire consensus.^{246-247,255}

Il est important de noter, néanmoins, qu'aucune étude à ma connaissance n'a permis de déterminer expérimentalement le taux de couverture des sites actifs dans les conditions de réaction. C'est dans ce but que j'ai initié une étude visant à déterminer la réactivité intrinsèque d'alcane dans des zéolithes par spectroscopie IR operando. Les premiers résultats obtenus pour le craquage du propane dans des zéolithes H-ZSM-5 sont présentés ici.

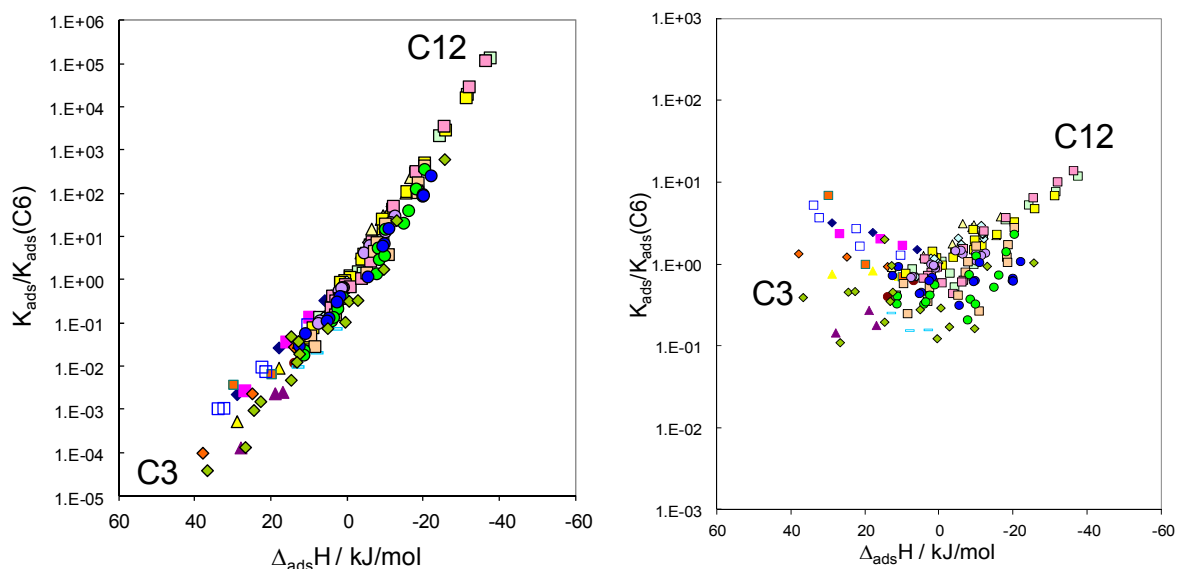
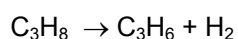
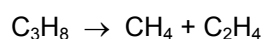


Figure 6-5 : Constantes d'adsorption relatives au n-hexane à 300 K et 800 K

6.3.2 RESULTATS

Le craquage mono-moléculaire du propane a été réalisé dans une cellule-réacteur [Ac1] sous flux, à température, pression et temps de contact variables (400 - 475°C, 0,1 – 1 bar, 0 – 0,1 s g μmol⁻¹) dans des conditions différentielles sur trois zéolithes H-ZSM-5 (Si/Al = 27, 29, et 75). Dans ces conditions, outre le propane, seuls le méthane, l'éthylène (en quantités équimolaires) et le propène sont détectés, indiquant l'absence de réactions secondaires de condensation.

En accord avec la littérature, le propane subit donc une réaction de craquage et une réaction de déshydrogénation :



La figure suivante montre à titre d'exemple l'évolution des rendements craquage et déshydrogénation, en fonction du temps de contact pour les cinq pressions étudiées à 475°C sur l'une des zéolithes étudiées. Les vitesses des réactions sont déterminées par la pente des droites obtenues. Les énergies d'activation apparentes, obtenues à partir des vitesses déterminées entre 400°C et 475°C sont très proches pour les trois zéolithes étudiées : $152,2 \pm 1,6$ kJ/mol et $118,8 \pm 3,2$ kJ/mol pour le craquage et le déshydrogénation, respectivement. Les valeurs obtenues sont cohérentes avec les résultats précédemment publiés sur des systèmes catalytiques similaires.²⁴³

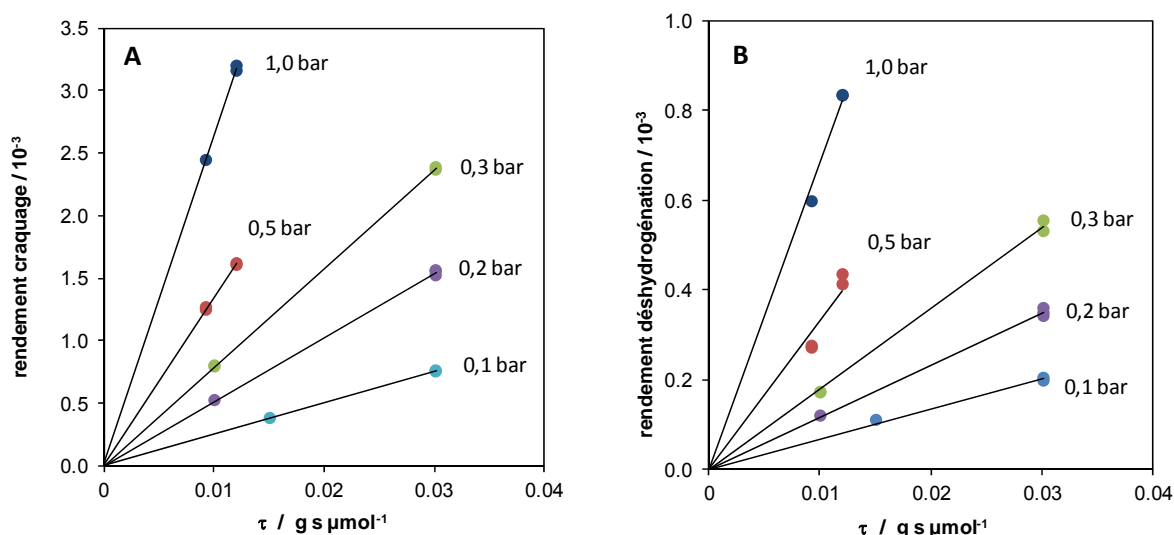


Figure 6-6 : Rendements en produits de craquage (A) et deshydrogénation (B) du propane en fonction du temps de contact et de la pression à 450°C (H-ZSM-5 Si/Al = 29)

L'originalité de l'étude présentée ici réside en la détermination simultanée des spectres IR de la zéolithe en cours de réaction. Dans nos conditions expérimentales, il ne nous a pas été possible d'identifier des bandes caractéristiques des espèces propane adsorbées en raison notamment de la contribution importante de la phase gaz.

Néanmoins, nous avons pu caractériser la perturbation par le propane des hydroxyles acide pontés de ces zéolithes, caractérisés par une bande à 3600 cm^{-1} . La Figure 6-8 ci-après montre les spectres différence (pendant moins avant la réaction) obtenus pour une pression de 0,3 bar de propane aux différentes températures et temps de contact étudiés. Ces spectres différence montrent que ces hydroxyles acides forment une liaison hydrogène avec le propane ou les produits de réaction, conduisant à l'apparition d'une bande large vers 3530 cm^{-1} .

Outre que le déplacement en fréquence de cette bande est compatible avec l'adsorption d'un alcane, on constate également que la perturbation est pratiquement indépendante du temps de contact utilisé car les spectres IR sont pratiquement superposables à une température donnée. L'augmentation du temps de contact conduisant à une augmentation sensible de la conversion (Figure 6-5), ceci indique que la perturbation des OH est essentiellement due à l'adsorption du propane et l'adsorption des produits de réaction peut être négligée dans nos conditions, ce qui s'explique par les très faibles

conversions du propane.

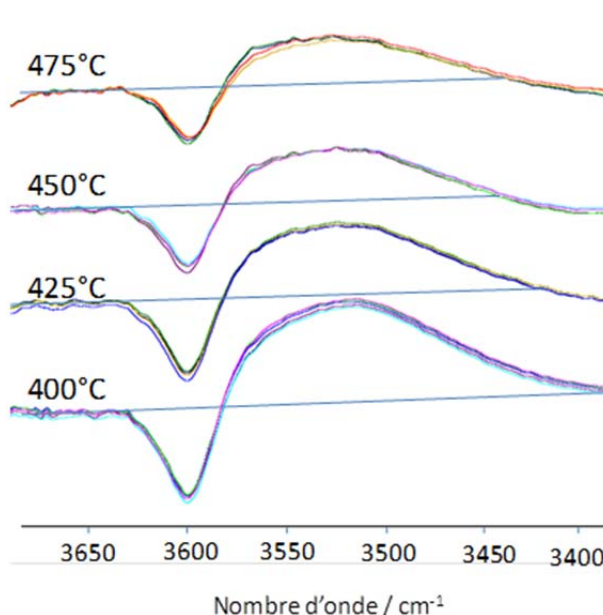


Figure 6-7 : spectres différences pendant moins avant la réaction de craquage du propane (0,3 bars) à différentes températures et temps de contact.

A partir de l'intégration de la bande négative à 3600 cm^{-1} , il nous a été possible de quantifier le nombre d'hydroxyles pontés en liaison hydrogène avec le propane à l'aide du coefficient d'extinction molaire des OH pontés des zéolithes H-ZSM-5 précédemment déterminée au laboratoire $\epsilon(\text{OH})=3,5\text{ cm}\mu\text{mol}^{-1}$.²⁵⁶

La Figure 6-8 suivante reporte l'évolution des vitesses de réaction déterminées précédemment en fonction du nombre d'OH pontés en liaison hydrogène déterminés par spectroscopie infrarouge. On constate, pour chacune des températures étudiées et pour les deux réactions un bon accord entre l'évolution de la vitesse et le nombre d'OH en liaison hydrogène avec le réactif propane. La pente des droites obtenues nous permet alors de déterminer les vitesses et les paramètres de réaction intrinsèques (E_a , ΔH^\ddagger , ΔS^\ddagger) pour les réactions de craquage et de déshydrogénation du propane aux températures étudiées.

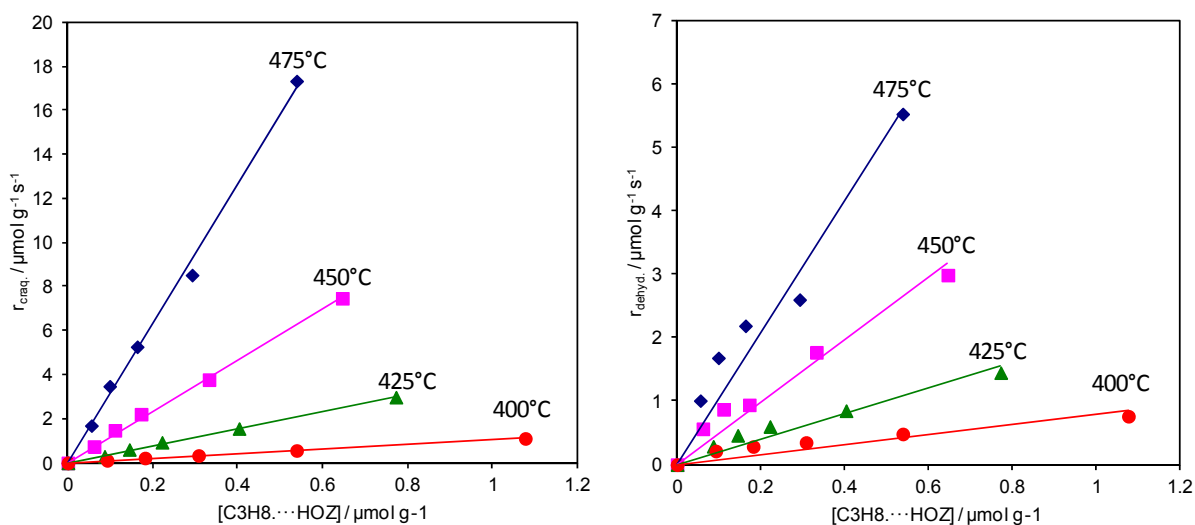


Figure 6-8 : Evolution des vitesses de craquage et de déshydrogénation du propane sur zéolithe H-ZSM-5 (Si/Al = 29) en fonction du nombre d'hydroxyles pontés en liaison hydrogène avec le propane

Le Tableau 6-2 ci-dessous reporte les paramètres obtenus pour la réaction de craquage du propane sur les trois zéolithes testées. Les valeurs obtenues sont très proches pour les trois échantillons et comparables aux valeurs estimées dans la littérature, ce qui conforte les résultats obtenus dans notre étude.

Tableau 6-2 : Paramètres cinétiques intrinsèques de la réaction de craquage du propane sur H-ZSM-5

Si/Al	$E_a / \text{kJ mol}^{-1}$	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J mol}^{-1} \text{K}^{-1}$
27	181	175	-102
29	183	177	-96
75	178	172	-104

6.3.3 CONCLUSIONS

L'étude du craquage du propane sur H-ZSM-5 permet, pour la première fois à ma connaissance, de déterminer le taux de couverture des sites actifs (hydroxyles pontés) en conditions de réaction, permettant ainsi de déterminer de manière directe les paramètres intrinsèques de réaction.

Cette étude est actuellement poursuivie pour le n-hexane. La comparaison des paramètres obtenus pour ces molécules nous permettra, le cas échéant de vérifier si les différences de réactivité de ces alcanes sont liées à des variations du taux de couverture, comme initialement proposé dans la littérature ou, selon les études plus récentes, à des changements de l'entropie d'activation.

6.4 PROJETS DE RECHERCHE

6.4.1 CATALYSEURS SULFURES

Amélioration de la résolution des spectres $\nu(\text{CO})$

La caractérisation par CO des catalyseurs sulfures Mo, CoMo ou NiMo permet d'obtenir des informations essentielles quant à la structure des phases et sites actifs de ces catalyseurs. Néanmoins, l'analyse des spectres obtenus sur les catalyseurs promus est complexe en raison du recouvrement important des bandes caractéristiques de l'adsorption sur le promoteur (Co ou Ni) et les sites Mo de basse coordination.

J'envisage d'appliquer la méthodologie d'inversion des isothermes spectroscopiques récemment développée aux spectres $\nu(\text{CO})$ obtenus sur ces phases sulfures. Cette étude devrait permettre d'une part de mieux différencier les sites de promotion de ces catalyseurs, et de déterminer les énergies d'adsorption de CO sur ces sites. Ces données devraient permettre à terme d'affiner nos conclusions quant à la structure des phases promues et de mieux comprendre les phénomènes d'inhibition de l'activité de catalyseurs sulfures liés à l'adsorption de CO lors de l'hydrodéoxygénation d'huiles végétales ou de bio-huiles.^{83,162}

Etude operando de réactions d'hydrotraitement

L'étude par spectroscopie operando de réactions d'hydrotraitement a fait l'objet de peu de travaux,²⁵⁷⁻²⁵⁸ [Ac1]. Ces études sont généralement difficile en raison des très faibles concentrations superficielles des espèces actives (réactif, intermédiaire ou produit) et de la présence d'espèces spectatrices parfois fortement adsorbées sur le support. En outre, contrairement aux zéolithes par exemple, les sites actifs de ces catalyseurs ne sont pas directement visibles par spectroscopie IR. Néanmoins, l'utilisation de sondes 'poison' spécifiques peut permettre déterminer la nature des sites actifs. Ainsi, durant ma thèse, j'ai pu montrer que l'isomérisation d'oléfines sur une phase sulfure est catalysée par des groupements acides –SH en empoisonnant de ces sites par la lutidine en conditions operando [Ac1].

J'envisage d'utiliser des méthodologies similaires dans le cas de réactions d'HDS. L'utilisation de la pyridine ou de la lutidine en cours de réaction devrait permettre, pour des catalyseurs supportés sur SiO_2 de distinguer l'adsorption de ces sondes basiques sur les sites CUS de celle sur les groupements –SH acides. Dans le cas de phases molybdène non promus, en particulier, ces études devraient nous permettre de déterminer si, comme il était généralement admis, l'empoisonnement de la phase active est dû à la coordination de ces sondes sur les sites CUS ou, comme proposé plus récemment, par les groupements sulfhydriles.⁶⁸⁻⁶⁹ Cette étude devrait donc apporter des informations essentielles quant au rôle catalytique de ces deux types de sites.

L'utilisation de monoxyde de carbone, qui conduit à un empoisonnement réversible des sites CUS de la phase sulfure,⁸³ devrait permettre de corréler les variations d'activité observées avec le nombre et la nature des sites (promus ou non promus) empoisonnés par CO durant la réaction. Cette étude devrait permettre d'estimer les activités intrinsèques des sites actifs pour l'HDS de molécules simples (sulfures aliphatiques, thiophène,...).

Hydrodéoxygénation de biohuiles

Les études sur l'utilisation de catalyseurs sulfures pour l'hydrodéoxygénation de bio-huiles seront poursuivies avec nos partenaires académiques (Lille, Poitiers, Lyon) et un nouveau partenaire industriel (Valagro) dans le but de développer de nouvelles formulations de catalyseurs d'HDO dans le cadre d'un nouveau projet ANR en cours d'évaluation (HDO-2G, programme BioME). Ma contribution à ce projet consistera notamment à caractériser de nouvelles phases sulfures à base de Mo ou de W promues par d'autres éléments de transition que le Ni ou le Co et à établir des relations structure – activité en HDO de molécules modèles ou de bio-huiles. En étendant à ces nouvelles phases les méthodes utilisées dans le cas de phases conventionnelles, ces travaux devraient permettre, d'un point de vue plus fondamental, de mieux comprendre les effets de promotion/dépromotion induits par l'ajout de métaux de transition aux phases non promues.

6.4.2 CATALYSEURS DE CRAQUAGE

Etude operando du craquage monomoléculaire

L'étude du craquage monomoléculaire d'alcane par spectroscopie IR *operando* permet d'accéder de distinguer la cinétique intrinsèque de la réaction des phénomènes d'adsorption et donc déterminer de manière directe les paramètres intrinsèques de la réaction (énergie et entropie d'activation).

J'envisage d'étendre cette étude à d'autres classes d'hydrocarbures (alcane branchés et oléfines notamment) et d'autres types de zéolithes (H-Y, H-MOR, H-FER) dans le but d'établir les paramètres structuraux gouvernant la réactivité de ces molécules (taille des pores, environnement de la liaison C-C, ...). Le craquage monomoléculaire de ces composés constituant l'initiation du craquage catalytique, les données issues de ce travail devraient permettre de mieux comprendre cette étape essentielle et pourraient être utilisées, par exemple en vue de la modélisation microcinétique du craquage catalytique.

Recherche d'alternatives aux terres rares

Les phases actives des catalyseurs de craquage actuels (zéolithes USY) est généralement échangée avec des terres rares, le lanthane en particulier, dans le but d'améliorer leur résistance à la désalumination lors de l'étape de régénération du catalyseur.²⁵⁹ La Chine, détenant actuellement le quasi-monopole (95%) de la production mondiale de terre rares, a récemment restreint de manière drastique ses exportations, provoquant une augmentation spectaculaire du coût de ces éléments.²⁶⁰⁻²⁶¹ Dans le but de pallier à ces difficultés, les fabricants de catalyseurs de FCC développent de nouvelles formulations sans terres rares.²⁶² Dans le cadre d'un contrat industriel en partenariat avec la société Grace Davison, je conduirais une étude visant à mieux comprendre comment ces nouvelles formulations influence la structure et l'activité des catalyseurs de FCC.

6.4.3 AUTRES APPLICATIONS

Valorisation des bio-alcools par condensation de Guerbet

Je participe actuellement au projet ANR Guerbet,^{†††} qui vise à développer de nouvelles formulations catalytiques pour la condensation d'alcools légers par la réaction de Guerbet. Nous avons, dans la première phase de ce projet, développé une nouvelle méthode de caractérisation de la basicité par adsorption de CO₂ (section 6.2) et caractérisé les propriétés acido-basique d'oxydes métalliques en vue d'établir des relations structure activité qui devraient permettre à terme de déterminer la nature et la force des sites requis pour obtenir une activité optimale.

Dans la seconde phase de ce projet, nous étudierons cette réaction par spectroscopie IR operando. Cette étude devra permettre de caractériser l'état de la surface dans les conditions de la réaction et d'identifier les espèces superficielles (spectateurs, intermédiaires, poisons) dans le but de proposer des mécanismes pour cette réaction encore peu connue.

Etude des interfaces silice – silane – polymère

La méthode d'inversion des spectres IR d'espèces adsorbées en vue d'obtenir leur spéciation et leur stabilité (section 6.2) doit être applicable à de nombreuses problématiques liées à l'adsorption. Dans le cadre d'une thèse réalisée en partenariat avec la société Michelin, nous chercherons à caractériser l'interaction de silanes et d'hydrocarbures modèles avec la silice dans le but de mieux comprendre l'interaction de la charge silice avec les polymères lors de la fabrication de pneumatiques.

Dans ce but, nous utiliserons la méthodologie TG-IR ainsi que des méthodes chimométriques pour caractériser l'adsorption de composés modèles (silanes et (poly)butadiènes) seuls ou en mélange sur la silice, dans le but de déterminer la nature et les distributions en énergie d'adsorption des espèces superficielles. Cette méthode sera ensuite étendue à l'étude de la cinétique de l'adsorption et des réactions de surface entre ces composés et la silice, dont les mécanismes sont encore peu connus. Cette étude devrait également nous permettre de développer des méthodes de traitement de données spectroscopiques pour la détermination des paramètres thermodynamiques et cinétiques gouvernant la réactivité d'espèces superficielles.

^{†††} Programme CP2D, UCCS (Lille), IRCELYON (Lyon), LCS (Caen) et Arkema (Lyon), Coordinateur F. Dumeignil, UCCS.

7 Conclusion Générale

Les recherches que j'ai menées à l'issue de mon travail de thèse m'ont permis d'acquérir des compétences dans des méthodes d'étude variées (modélisation moléculaire *ab initio*, caractérisations spectroscopiques, tests sur charges modèles ou réelles) de catalyseurs utilisés dans deux procédés de raffinage de premier plan, l'hydrotraitement et le craquage catalytique en lit fluidisé.

Les études réalisées sur les catalyseurs d'hydrotraitement permettent de mieux comprendre l'influence des promoteurs sur la structure et les propriétés des sites actifs des phases sulfures supportées. En particulier, elles fournissent des résultats concordants qui montrent que la substitution partielle des bords de MoS₂ conduit à la création des sites lacunaires constitués de centres Mo de basse coordination voisins d'atomes de Co. Ces sites présentent des activités intrinsèques élevées en HDS ou HDN de molécules modèles, qui peuvent en partie être expliquées par les propriétés particulières de ces sites vis-à-vis de l'adsorption et de l'activation des réactifs : synergie entre propriétés acceptrices (acidité de Lewis) et donneuses (rétrodonation d'électrons d) permettant d'activer les réactifs adsorbés, activation et stabilisation de l'hydrogène conduisant à la formation de groupements –SH acides permettant d'hydrogéner ces réactifs. L'étude de réactions d'hydrotraitement par spectroscopie IR *operando* devrait à terme nous permettre d'évaluer plus précisément l'activité catalytique 'intrinsèque' de ces sites.

Plus récemment, nous avons appliqué ces méthodes à l'étude de la désactivation de catalyseurs sulfures en HDO par les composés phénoliques – précurseurs de coke – et l'eau formée lors de la réaction. Ces travaux nous ont conduits à proposer des mécanismes de désactivation originaux : adsorption de composés phénoliques sur le support conduisant un blocage des sites actifs de la phase supportée ; échange par l'oxygène des atomes de soufre de bord par l'oxygène, conduisant à des sites peu ou pas actifs. Dans ce dernier cas, nous avons également montré le double rôle de Co en HDO, promoteur de l'activité catalytique et agent de passivation de la surface vis-à-vis de l'eau. Ces travaux seront poursuivis pour l'évaluation de nouvelles phases sulfure mixtes.

L'étude de la désulfuration en FCC par les deux familles d'additifs utilisés commercialement (acide de Lewis supporté – Zn/Al₂O₃ – et vanadium) nous a permis de montrer qu'ils agissent en synergie avec le catalyseur de craquage, l'additif accélérant les réactions de rupture des liaisons C-S des composés soufrés aliphatiques produits par transfert d'hydrogène par le catalyseur de craquage. Les mécanismes de rupture C-S sont néanmoins très différents : mécanisme d'élimination sur des paires acide-base pour les additifs Zn/Al₂O₃ vs. scissions radicalaires pour les additifs au vanadium, ce dernier jouant le rôle d'initiateur. Ces différences de mécanisme (acide-base vs. redox) permettent notamment d'expliquer une grande partie des phénomènes observés sur charge réelles.

Plus récemment, j'ai initié des études portant sur la quantification, l'identification et la thermodynamique d'espèces adsorbées sous flux à haute température. J'ai notamment développé une méthode de traitement des spectres IR d'espèces adsorbées permettant la spéciation de ces espèces en fonction de leur énergie d'adsorption. L'application de cette méthodologie à l'adsorption de molécules sondes devrait permettre d'établir des échelles quantitatives d'acidité ou de basicité par

8. Références.

spectroscopie (nombre et distribution en force des sites). Elle sera également étendue à d'autres processus (cinétique d'adsorption et de transformation des espèces superficielles).

Enfin, l'étude par spectroscopie IR *operando* du craquage monomoléculaire d'alcane sur H-ZSM-5 nous a permis de déterminer le taux de couverture des sites actifs (hydroxyles pontés) par le réactif en conditions de réaction, permettant ainsi de déterminer de manière directe les paramètres intrinsèques de réaction. L'extension de ce travail à d'autres hydrocarbures et zéolithes devraient nous permettre de déterminer les paramètres structuraux gouvernant la réactivité intrinsèque de ces molécules.

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[A7] Hydrogen activation on Mo-based Sulfide Catalysts, a Periodic DFT Study.

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Journal of American Chemical Society **2002**, 124, 7084-7092.

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[A17]. Towards the characterization of active phase of (Co)Mo sulfide catalysts under reaction conditions--Parallel between IR spectroscopy, HDS and HDN tests.

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[A21] Effect of EDTA addition on the structure and activity of the active phase of cobalt-molybdenum sulfide hydrotreatment catalysts. Lélías, M.A. ; Le Guludec, E. ; Mariey, L. ; van Gestel, J. ; Travert, A. ; Oliviero, L.; Mauge, F.*

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[A20] Effect of NTA addition on the the structure and activity of the active phase of cobalt-molybdenum sulfide hydrotreating catalysts. Lélías, M.A.; Kooyman, P.J. ; Mariey, L. ; Oliviero, L. ; Travert, A. ; van Gestel, J. ; van Veen, J.A.R. ; Mauge, F. *Journal of Catalysis* **2009**, 267, 14-23.

[A26]. IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation.

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Catalysis Today **2011**, 172, 132-135.

[A25] Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study.

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[A18] FCC gasoline sulfur reduction additives: Mechanism and active sites.

Can, F.; Travert*, A.; Ruaux, V.; Gilson, J. P.; Mauge, F.; Hu, R.; Wormsbecher, R. F.

Journal of Catalysis **2007**, 249 (1), 79-92.

Hydrogen Activation on Mo-Based Sulfide Catalysts, a Periodic DFT Study

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Abstract: Hydrogen adsorption on Mo–S, Co–Mo–S, and Ni–Mo–S (10 $\bar{1}0$) surfaces has been modeled by means of periodic DFT calculations taking into account the gaseous surrounding of these catalysts in working conditions. On the stable Mo–S surface, only six-fold coordinated Mo cations are present, whereas substitution by Co or Ni leads to the creation of stable coordinatively unsaturated sites. On the stable MoS₂ surface, hydrogen dissociation is always endothermic and presents a high activation barrier. On Co–Mo–S surfaces, the ability to dissociate H₂ depends on the nature of the metal atom and the sulfur coordination environment. As an adsorption center, Co strongly favors molecular hydrogen activation as compared to the Mo atoms. Co also increases the ability of its sulfur atom ligands to bind hydrogen. Investigation of surface acidity using ammonia as a probe molecule confirms the crucial role of sulfur basicity on hydrogen activation on these surfaces. As a result, Co–Mo–S surfaces present Co–S sites for which the dissociation of hydrogen is exothermic and weakly activated. On Ni–Mo–S surfaces, Ni–S pairs are not stable and do not provide for an efficient way for hydrogen activation. These theoretical results are in good agreement with recent experimental studies of H₂–D₂ exchange reactions.

1. Introduction

Hydrotreating covers a variety of catalytic hydrogenation processes that aim at reducing the heteroatom content of petroleum feedstocks.¹ More stringent environmental regulations have urged refiners on the improvement of the hydrodesulfurization processes, one possible approach being the development of better catalysts. The vast majority of hydrotreating catalysts used nowadays consists of mixed CoMo or NiMo sulfides highly dispersed on high surface area carriers such as alumina. It is well known that both mixed sulfides exhibit a much higher activity (1 order of magnitude) than the corresponding monometallic Mo catalysts, an increase which is often referred to as the *promoting effect* of Co or Ni on Mo-based catalysts. Despite the intense research effort in the domain during the past decades, the molecular basis of the promoting effect is still controversial.

Under the hydrotreating reaction conditions, the thermodynamically stable monometallic Mo sulfide phase is molybdenite,²

the structure of which consists of the stacking of MoS₂ sheets of hexagonal symmetry.³ It is generally concluded that the active phase of supported Mo catalysts is similar and consists of small MoS₂ particles (few nanometers), whose active sites are coordinatively unsaturated (CUS) molybdenum atoms located at the edge of MoS₂ crystallites. On this basis, several models have been proposed that explain the synergetic effect between Co (Ni) and Mo.

Thus, in the “remote-control” model, Delmon et al.⁴ have considered the existence of two distinct sulfide phases on the working catalyst. The sulfide phase which is formed by the promoter (e.g., Co₉S₈) would activate hydrogen which would then spill-over toward the MoS₂ phase, that would maintain a fraction of surface Mo in coordinative unsaturation (active for hydrogenation) and form –SH groups that would be active for hydrogenolysis.

On the other hand, the existence of a direct contact between Co (Ni) sulfide species and MoS₂ has been demonstrated by many spectroscopic techniques.^{5–8} The question that arised from

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these experimental studies is whether the active sites resulting from this contact belong to Co or Mo species.

By measuring the intrinsic HDS activity of highly dispersed Co/C and CoMo/C catalysts, Vissers et al. did not observe significant activity differences between both catalysts.⁹ This finding led the authors to propose a dispersion model where MoS₂ would act as a secondary support for Co sulfide particles that would be active by themselves. More recently, however, new HDS activity measurements together with H₂-D₂ exchange experiments carried out on similar systems have made this model questionable.¹⁰

By now, it is generally believed that the promotor effect results essentially from specific modifications of the MoS₂ surface induced by the promotor. The precise origin of the promoting effect, however, is still not understood insofar as promoted systems do not form a phase in the crystallographic sense, and little is known about their structures at the molecular scale; usual spectroscopic techniques only give indirect information, whereas the very first surface science studies of these materials have only appeared recently.¹¹ On the other hand, recent developments in periodic density functional theory (DFT) calculations have recently made possible realistic theoretical investigations of these systems.¹²⁻²¹ Technical aspects of these calculations will be discussed in the next section.

The first periodical DFT calculations on Mo-based sulfide catalysts were carried out by Byskov et al.¹²⁻¹⁴ Thus, using Mo₂S₄ chains as a model for unpromoted Mo catalysts, they could show that substitution of Mo by promotor atoms such as Co or Ni leads to a significant decrease of the binding energies of exposed sulfur atoms and leads to the creation of stable sulfur vacancies.¹³ More recently, using a larger model, Raybaud et al. have performed a thorough study of the structure of MoS₂ surfaces^{15,16} and promoted Mo catalysts.¹⁷ The use of a thermodynamical approach to take into account the gaseous H₂S/H₂ surroundings of the working catalysts has made possible the determination of their sulfur coverages.¹⁶⁻²¹ Although these last computed surface structures showed important differences with

the earlier studies of Byskov et al., the striking conclusion of these calculations is similar; substitution of Mo by Co or Ni leads to the appearance of CUS sites that are stable under hydrotreating conditions.

Now that many aspects of the surface structures of Mo-based catalysts are well defined within this theoretical framework, it becomes possible to carry out mechanistic studies of hydrotreating reactions. At this time, the reaction pathways for the HDS of thiophene¹⁵ and 4-methylbenzothiophene^{18,21} on MoS₂ surfaces have been computed. In these studies, however, the formation and the nature of active hydrogen species (e.g., hydrides and sulfhydryl groups) were not computed as a part of the reaction scheme but were assumed de facto as little is known about the actual nature of these species.

Using silver salts, Maternová²² has been able to demonstrate and to titrate sulfhydryl groups (-SH) on Mo and CoMo sulfided catalysts, nonsupported or supported on Al₂O₃. Miciuckiewicz et al. and Stuchlý et al. have further used this method on similar systems.²³ Some of these studies gave evidences of correlations of the catalytic activity and the amount of titrated -SH species. They showed that these sulfhydryls could either play an important role in hydrotreating reactions or be a measure for the sulfide phase dispersion.

Spectroscopic evidence for the presence of these -SH groups, however, is still scarce. Direct observations were obtained by inelastic neutron scattering by Wright et al.²⁴ and more recently by Sundberg et al.²⁵ on bulk and alumina-supported MoS₂ catalysts. A spectral peak at ca. 600 cm⁻¹ has been assigned to a MoSH deformation mode. Other spectroscopic studies have only reported indirect evidence for the presence of -SH groups. Thus, analyzing FTIR spectra of (Co)Mo/Al₂O₃ catalysts, Topsøe et al. have ascribed the perturbation of the support hydroxyl groups to hydrogen bonding with acidic -SH groups.²⁶ They could further confirm this acidity using FTIR spectroscopy of pyridine adsorbed at high temperature.²⁷ More recently, Maugé et al. demonstrated an increase in Brønsted acidity related to the sulfided phase on similar catalytic systems^{28,29} and could further find evidence that H₂S adsorption leads to an important increase in the Brønsted acidity of the sulfide phase.^{28,30} Finally, the presence of -SH groups on Mo-based catalysts is now well recognized. This is not the case, however, for hydride species. Still, no experimental evidence for such species has been provided on MoS₂ catalysts, although such species have been found on other sulfide phases such as RuS₂.³¹

Another approach to get more insight into hydrogen activation over sulfided catalysts is the study of H₂-D₂ exchanges. Thomas et al. have studied this reaction in the case of unsupported and alumina-supported catalyst,³²⁻³⁵ whereas Hensen et al. have investigated the case of sulfides supported on carbon.³⁶ Both

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studies have led to similar conclusions. First, on these systems, the HD exchange reaction readily occurs at relatively low temperatures (353–423 K) through the sulfide phase. Moreover, there are strong indications that H₂ dissociation is heterolytic since an initial exchange occurs between H₂(D₂) and D₂S(H₂S). The mobility of hydrogen species is important, since in all cases an exchange of the hydrogen with the support has been observed, though different explanations for this mobility have been proposed by these groups. Finally, both groups have also studied the influence of the promotor on the rate of the exchange reaction. It has been shown by Thomas et al. that NiMo catalysts do not present a significant difference in activity as compared to a nonpromoted catalyst,³³ whereas a strong accelerating effect of the Co has been observed.³⁵ Similar results were obtained on (Co)Mo/C by Hensen et al. who could also show an important difference in the reaction order in H₂ and D₂ for Mo and CoMo catalysts that they have ascribed to a change in the rate-limiting step of the H₂–D₂ exchange reaction on these catalysts.³⁶

As for theoretical investigations of hydrogen activation by metal sulfides, they show that hydrogen can dissociate heterolytically on MoS₂,³⁷ NiS_x particles,³⁸ and RuS₂,³⁹ leading to the formation of a metal hydride and a sulfhydryl group. More recently, Cristol et al. have reinvestigated H₂ adsorption on MoS₂ surfaces by periodical DFT studies and could show that hydrogen species are metastable on these surfaces, the least unstable configuration being the heterolytic dissociation of hydrogen on a metal–sulfur pair.¹⁹

Hydrogen adsorption on Co–Mo–S surfaces has been studied by Byskov et al. who have shown that atomic hydrogen adsorption is more stable on sulfur than on Mo or on Co atoms. Accordingly, this group has exclusively studied the homolytic dissociation of hydrogen on sulfur dimers, which is exothermic and for which activation energies have been computed.¹⁴ More recent studies, however, have shown that such dimers are not stable in hydrotreatment conditions.^{16,17,19} In view of the importance of heterolytic dissociation demonstrated by most of the recent experimental studies,^{32–36} it seems particularly important to reconsider hydrogen adsorption on the stable surfaces.

The aim of the present study is to investigate, using periodical DFT calculations, hydrogen activation on the (1010) surfaces of nonpromoted and promoted MoS₂ crystallites. In the following, we first describe the theoretical methods and the models we have used throughout the present study. The energetics and structures of the model surfaces prior to H₂ adsorption are discussed and briefly compared with the results published recently in this field.^{12–21} To get more insight in surface properties that are relevant for heterolytic dissociation of hydrogen, we report an investigation of the acid–base properties

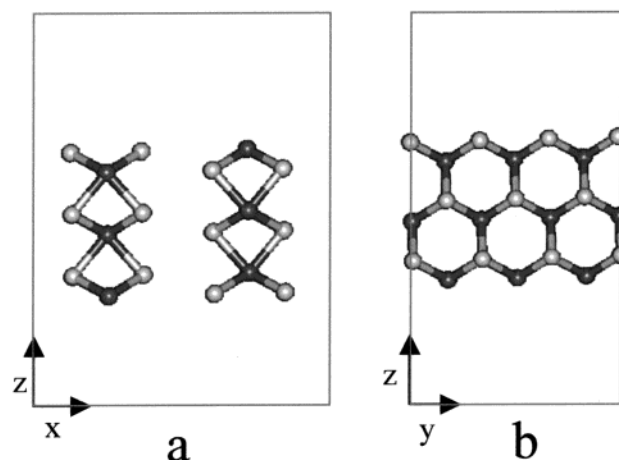


Figure 1. Representation of the supercell used for calculations, showing the axes. Dark circles, Mo atoms; light circles, S atoms.

of these surfaces. We then describe in detail the molecular adsorption of H₂, its dissociation, and the surface diffusion of atomic species. These theoretical results are finally compared with experimental studies of the H₂–D₂ exchange reactions.

2. Theoretical Methods

For our calculations, we have used the Vienna ab initio simulation program (VASP)⁴⁴ based on the density functional theory.⁴⁰ Exchange–correlation was treated using the functional of Perdew and Zunger⁴¹ and corrected for nonlocal effects using the generalized gradient approximation (GGA) of Perdew et al.⁴² The wave functions were expanded in plane waves, and the ionic cores were modeled by ultrasoft pseudopotentials (US-PP).⁴³ The solution of the Kohn–Sham equations was improved self-consistently until a difference lower than 10^{−4} eV was obtained between successive iterations. All of the ions were fully relaxed using a conjugate-gradient algorithm until all exact Hellmann–Feynman forces acting on ions are smaller than 2 × 10^{−2} eV Å^{−1}. For more details about the code, we refer the reader to other studies.⁴⁴

The supercell used in the present study is shown in Figure 1. It contains two MoS₂ layers along the *x* direction (stacking), three Mo rows along the *y* direction, and three rows along the *z* direction. In this axis system, the (100) MoS₂ active surface is represented by the upper layers parallel to the *xy* plane, and it exhibits alternative rows of exposed molybdenum atoms and sulfur atoms which are commonly called molybdenum edges (or Mo edges) and sulfur edges (or S edges). Geometries were fully relaxed using the G point and a cutoff energy of 200 eV for the study of S, H₂S, and H₂ adsorption and 300 eV to describe NH₃ adsorption. The validity of the relative energies was further checked by single point calculations at this geometry using two *k*-points in the *y* direction. These settings ensure an accuracy of ca. 0.2 eV for the relative energies of the surfaces prior to hydrogen adsorption and better than 0.1 eV on the adsorption energies of hydrogen. For more details on the computation parameters and convergence checks, we refer the reader to the Supporting Information.

For the construction of promoted surfaces, we have followed the work of Raybaud et al. who have extensively studied the energetics and structures of promoted catalysts, showing that the most favorable location of Co is for the substitution of exposed Mo atoms of the metal

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(44) (a) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558; *Phys. Rev. B* **1994**, *49*, 14221. (b) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *6*, 15; *Phys. Rev. B* **1996**, *54*, 11169. (c) <http://cms.mpi.univie.ac.at/vasp/>.

edge of MoS₂ (100) surface.¹⁷ Accordingly, we have built our surfaces by substituting from one to three molybdenum atoms of this edge, leading to metal edges presenting 0, 33, 66, and 100% Co and 33% Ni. As for the sulfur edge, we have used the most stable one under hydrotreating conditions which present a sulfur coverage of 50% (one sulfur atom per exposed molybdenum atom).^{16,19}

To determine the sulfur coverages and the structure of the metallic edges, we have followed the same approach as Cristol et al.¹⁹ by considering the thermodynamic equilibrium of these surfaces with H₂S and H₂ in the gas phase. The relative energies of the surfaces as a function of the S coverage are obtained from the energetics of the following reaction:



where surface-S₀ stands for the naked metallic edge (no S atom), and surface-S_n stands for the sulfided metallic edge (*n* sulfur atoms). The Gibbs energy of this reaction allows one to determine the stable surfaces in various experimental conditions:

$$\Delta_r G = \mu(\text{surface-S}_n) - \mu(\text{surface-S}_0) - n(\mu(\text{H}_2\text{S}) - \mu(\text{H}_2))$$

which is approximated by

$$\Delta_r G = \Delta E^\circ - n\Delta\mu$$

ΔE° is the difference between the electronic energies of the considered surfaces that are provided by VASP. $\Delta\mu$ is the difference between hydrogen sulfide and dihydrogen chemical potentials:

$$\Delta\mu(T, P_{\text{H}_2\text{S}}, P_{\text{H}_2}) = \Delta\mu^\circ(T) + RT \ln \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}}$$

$\Delta\mu^\circ(T)$ has been evaluated using the computed electronic energies and rotational momenta (rigid body approximation) and the experimental vibration frequencies. In typical conditions of hydrotreatment (673 K and $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 0.01$), $\Delta\mu = -5.04$ eV molecule⁻¹. In sulfiding conditions (673 K, $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 0.10$), $\Delta\mu = -4.90$ eV molecule⁻¹.

It should be noted that the thermodynamical approach we used does not take into account the total pressure, but only the $P(\text{H}_2\text{S})/P(\text{H}_2)$ ratio. A more advanced approach,⁴⁵ taking into account the total pressure, has shown that surface structures under large excess of hydrogen – conditions which correspond to the present surfaces – are poorly affected by the total pressure.

Finally, the (100) surfaces that are relevant under given experimental conditions are obtained by computing their Boltzmann population:

$$x_i = \frac{\exp(-\Delta_r G_i/RT)}{\sum_j \exp(-\Delta_r G_j/RT)}$$

Following this, the acidic properties of the surfaces and the interactions of hydrogen with various adsorption sites have been considered, molecular adsorption as well as homolytic and heterolytic dissociation. Typical reaction pathways for hydrogen dissociation and diffusion on the surface were computed using the nudged elastic band method.⁴⁶ We successively present and discuss these results in the following sections.

3. Thermodynamically Stable Surfaces before H₂ Adsorption

In the present study, we have investigated the various surface configurations by progressively increasing the sulfur coverage

Table 1. Energetics of (10 $\bar{1}$ 0) Sulfide Surfaces^a

Pr/ (Pr + Mo)	<i>n</i> S	structure	$\Delta E/\text{eV cell}^{-1}$	$\Delta_r G/\text{eV cell}^{-1}$	x_i
0.00	0		0.00	0.00	1.73×10^{-32}
	1		-2.51	-1.93	4.37×10^{-18}
	2	2b	-4.73	-3.57	8.17×10^{-6}
	3	2a	-5.99	-4.25	$1.00 \times 10^{+0}$
Co 0.33	4		-5.53	-3.21	1.80×10^{-8}
	0		0.00	0.00	9.39×10^{-20}
	1	2e	-3.12	-2.54	9.10×10^{-1}
	2	2d	-3.56	-2.40	8.44×10^{-2}
Co 0.66	2	2f	-3.39	-2.23	4.95×10^{-3}
	3	2c	-3.82	-2.08	3.66×10^{-4}
	3		-3.60	-1.87	9.02×10^{-6}
	4		-3.48	-1.17	5.05×10^{-11}
Co 1.00	0		0.00	0.00	1.11×10^{-5}
	1	2g	-1.24	-0.66	$0.99 \times 10^{+0}$
	2		0.55	1.12	4.18×10^{-14}
Ni 0.33	1	2h	-1.31	-0.15	1.43×10^{-4}
	2		-1.41	0.33	3.78×10^{-8}
	0	2i	0.00	0.00	0.99×10^{-1}
Ni 1.00	1	2j	-0.07	0.51	1.60×10^{-4}
	2		-0.22	0.94	9.60×10^{-8}
Ni 0.33	0		0.00	0.00	7.79×10^{-20}
	1		-3.16	-2.55	$0.99 \times 10^{+0}$
	2		-3.27	-2.23	3.96×10^{-3}

^a Pr/(Mo + Pr), atomic fraction of promotor atom on the metallic edge; *n*S, number of sulfur atoms adsorbed on the metallic edge; structure, refers to Figure 2; ΔE , electronic energy difference for reaction 1 per unit cell; $\Delta_r G$, Gibbs energy difference for reaction 1 per unit cell 673 K, H₂S/H₂ = 0.1; x_i , Boltzmann population.

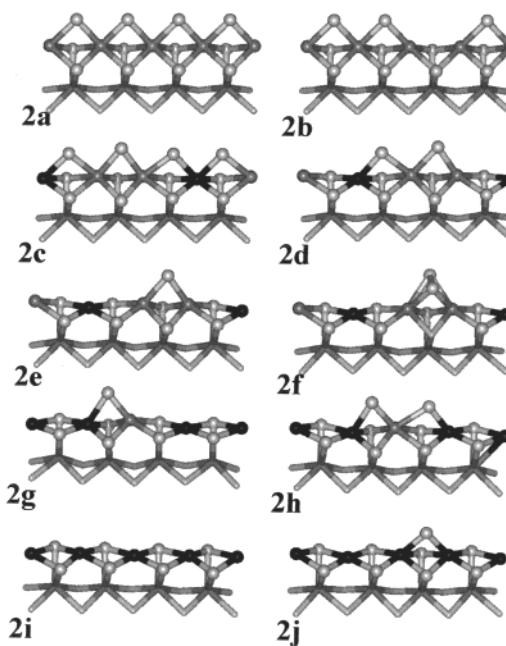


Figure 2. Representation of the stable (10 $\bar{1}$ 0) surfaces under sulfiding conditions (673 K, H₂S/H₂ = 0.1). Dark gray circles, Mo; light gray circles, S; black circles, Co.

of each of the three promoted surfaces and stopping once the evolution of the energies of these surfaces as a function of the sulfur coverage clearly showed that higher sulfur coverages would not lead to more stable surfaces. The energetics and the structures of the most stable surfaces are reported in Table 1 and Figure 2, respectively. Whenever it was possible, we have compared these results with the data recently published by Raybaud et al.,^{16,17} and we generally found a good agreement.

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(46) (a) Mills, G.; Jónsson, H. *Phys. Rev. Lett.* **1994**, *72*, 1124. (b) Mills, G.; Jónsson, H.; Schenter, G. K. *Surf. Sci.* **1995**, *324*, 305. (c) Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9978.

For a detailed structural and electronic structure analysis of these surfaces, we refer the reader to these studies.^{16,17}

The Gibbs energy variations and Boltzmann populations have been computed for “sulfiding conditions”, at 673 K with a H₂S/H₂ ratio of 0.1. The surfaces presenting computed populations in the range 10⁻¹–10⁻⁴ are represented in Figure 2.

Before going into more details, we stress here that because of (i) the uncertainty of the relative energies ΔE of the surfaces, (ii) the influence of temperature and H₂S/H₂ ratio variations on chemical potential of the gas phase, and (iii) the absence of experimental data on the actual Co contents of the metal edges of promoted catalysts, care should be taken with the surface populations that are reported in this table, since in particular these values are very sensitive to slight variations of the Gibbs energies. Therefore, these values are reported to give an indication of the relative stabilities of the surface sites that such surfaces may exhibit. Accordingly, we consider that the structures presenting a computed Boltzmann population on the order of 10⁻¹–10⁻² are likely to be present in large amounts, since these values are usually poorly affected by slight variations in the energies. Similarly, the structures presenting the lowest Boltzmann populations ($x_i < 10^{-5}$) are unlikely to be stable under hydrotreating conditions, although some of them might be considered as “transient” surface species that can appear locally during the reaction, especially when x_i is on the order of 10⁻⁵–10⁻⁶. Last, structures presenting an intermediate Boltzmann population (10⁻³–10⁻⁴) are sensitive to slight variations in the energies, so that their “actual” population can reach a few percents according to the chemical potential of the gas phase or the details of calculation settings. Therefore, such structures could be relevant for catalysis, since “unstable” sites are presumably more reactive.

Unpromoted MoS₂ Molybdenum Edge. The sulfur coverage of unpromoted MoS₂ (100) surfaces has been extensively studied by Raybaud et al.^{16,17} and Cristol et al.¹⁹ Both studies show that under the working conditions of these catalysts, the most stable metallic edge presents only bridging sulfur atoms with six-fold coordinated molybdenum atoms, as shown in Figure 2a. For further comparison, we have reported in Table 1 the energetics of four unpromoted surfaces studied by Cristol et al.¹⁹ The cost in electronic energy to remove one sulfur atom from this surface is 1.26 eV and leads to the creation of two Mo CUS sites (five-fold coordinated Mo atoms, Figure 2b). When the chemical potential of the gas phase is taken into account, the energy cost is lowered to 0.68 eV. To remove one sulfur atom is still thermodynamically unfavorable, even in the case of very low H₂S/H₂ ratios. As a result, the population of such sites is particularly low, ca. 10⁻⁵.

These observations have lead Cristol et al. to conclude that these CUS sites, which are required for hydrotreating reactions, can only appear transitorily in the course of the reaction.^{19,21} It should be noted that although such a conclusion was a priori unexpected, these theoretical results are in good agreement with experimental data derived from EXAFS, TPR, and IR spectroscopy studies.^{19,20}

Co–Mo–S Surfaces. For a substitution of 33% of Mo by Co, the most stable surface – before thermodynamics corrections – presents a sulfur coverage of 50% (Figure 2c). This is similar to the unpromoted surface. In that case, however, the energy required to remove one sulfur atom is much lower (0.3

eV instead of 1.2 eV). Consequently, when the effect of the temperature and of the H₂S/H₂ gas phase is taken into account, the most stable surfaces present sulfur vacancies, and the 50% covered surface is not the most stable anymore ($x_i = 3.6 \times 10^{-4}$). The surface most stable in hydrotreating conditions ($x_i = 0.91$) is the 17%-covered one with a sulfur atom bridging two Mo atoms (Figure 2e). Two other surfaces presenting a S coverage of 33% are also present in these conditions. The first one ($x_i = 8.44 \times 10^{-2}$, Figure 2d) presents two two-fold coordinated sulfur atoms bridging two Mo atoms, on one hand, and a Mo and a Co atom, on the other hand. The second one ($x_i = 4.95 \times 10^{-3}$, Figure 2f) presents two two-fold coordinated sulfur atoms forming a S–S bridge.

Similar trends are observed for higher Co–Mo substitution ratios. For 66% substitution, the most stable surface before thermodynamics corrections is also 50%-covered by sulfur, and the energy required to remove one S atom is 0.1 eV, 3 times lower than in the previous case (33% Co). As result, when the gas phase is taken into account, this surface is not thermodynamically stable ($x_i = 3.78 \times 10^{-8}$), and the predominant surface presents a sulfur coverage of 17%, with a sulfur atom bridging one Co and one Mo atom ($x_i = 0.99$, Figure 2g). A second surface, presenting a sulfur coverage of 33%, is much less stable ($x_i = 1.43 \times 10^{-4}$, Figure 2h) but might appear in nonnegligible amount, for example, in sulfur-rich conditions. Finally, when the metallic edge is fully substituted by cobalt, two surfaces may appear. The most stable surface is not covered at all by sulfur and presents only four-fold coordinated Co atoms ($x_i = 0.99$, Figure 2i), whereas a second structure with sulfur atoms bridging two cobalt atoms is likely to appear in sulfur-rich conditions ($x_i = 1.60 \times 10^{-4}$, Figure 2j).

Ni–Mo–S Surfaces. To compare the effect of Ni and Co, we have investigated Ni-promoted surfaces for a surface substitution ratio of 33% Ni. The structure of these surfaces is similar to the Co case (Figure 2c–f). As for the energetics (Table 1), the most stable surface is also 17%-covered by sulfur, but it is significantly more abundant ($x_i > 0.99$) than the corresponding CoMo surface (Figure 2c, $x_i = 0.91$). The relative energy of this surface with respect to the naked surface is the same as in the unpromoted and the Co cases (–2.5 eV). On the other hand, the surface presenting a sulfur atom bridging one Mo and one Ni atom has a lower stability than the analogous Co–Mo–S surface depicted in Figure 2d, which may be ascribed to the lower stability of Ni–S bonds as compared to Co–S bonds. Therefore, the influence of Ni on the surface structure is essentially similar to the Co case, the formation of Ni–S bonds being even less favorable than Co–S bonds.

Influence of the Promotor on Surface Structure. Finally, the striking difference with the unpromoted case is that Mo substitution by Co or Ni leads to the creation of CUS sites and sulfur dimers that are stable under the working conditions of these catalysts. This result is in good agreement with the previous studies of Byskov et al.¹³ and Raybaud et al.¹⁷ who have provided detailed explanations on the electronic origin of this effect of the promotor atom on the surface structure. From an elementary chemical point of view, one can consider a [MoS]²⁺ unit on the stable MoS₂ surface to be replaced by a Co²⁺ or Ni²⁺, hence maintaining charge neutrality. From a structural point of view, the promoted surfaces may be considered as resulting from a balance between the sulfur

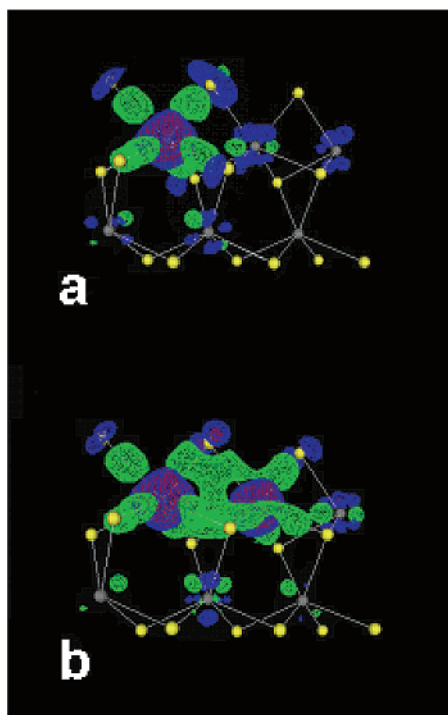


Figure 3. Electron density difference maps showing the effect of Mo substitution by Co on the (1010) surface. Green zones, electron density depletion; red and blue zones, electron density accumulation. (a) One Mo atom substituted, (b) two Mo atoms substituted.

coordination of the exposed molybdenum atoms that tend to be six-fold coordinated and the sulfur coordination of cobalt or nickel atoms that tend to be four-fold coordinated when the sulfur potential of the gas phase is taken into account.

In Figure 3 are reported electron density difference maps that clearly illustrate the effect of the substitution of one (Figure 3a) and two (Figure 3b) Mo atoms by cobalt atoms on the most stable MoS₂ surface (Figure 2a). Schematically, substitution of one Mo by Co (Figure 3a) leads to a withdrawing of electrons from the metal–sulfur bonding states (green zones) and an increase of electron density in the metal–sulfur antibonding orbitals shown by the important electron density around the Co atom and the ring around the bridging sulfur atoms (blue zones). Besides, a small increase in electron density is also observed around the neighboring Mo atoms (d states), that could be induced by the sulfur atoms of the Mo-coordination sphere that bridge the cobalt atom. Harris and Chianelli have already reported such an increase for cluster calculations.⁴² Similar but amplified effects are observed for a higher substitution ratio (Figure 3b). The electron withdrawal from Co–S–Co bonding states, on one hand, and the increase in electron density around the sulfur atom bridging two Co atoms, on the other hand, are more important than in the case of the sulfur atoms bridging one Co and one Mo atom. Finally, these electronic modifications are rather local since they only occur in the first (sulfur atoms) and second (metal atoms) coordination sphere of the Co atoms.

Influence of the Promotor on Surface Acidity. To probe the acidic properties of the stable surfaces presented in Figure 2, we have monitored their interaction with ammonia. In Table 2 are reported adsorption energies and selected structural data for NH₃ coordination on Mo, Co, and Ni cations presenting different sulfur coordinations.

Table 2. NH₃ Adsorption on Lewis Acid Sites of (1010) Surfaces^a

cation	<i>r</i> M–N/Å	Δ <i>E</i> /eV
Mo _{VI}	2.35	−0.45
Mo _V	2.36	−0.99
Co _V	2.16	−0.17
Co _{IV}	2.09	−1.17
Ni _V	2.27	−0.39

^a *r*M–N, metal–nitrogen distance; Δ*E*, difference in electronic energies, Δ*E* = *E*(surface–NH₃) – *E*(surface) – *E*(NH₃).

Whatever the nature of the metal ion and its coordination environment, NH₃ adsorption is always exothermic, hence demonstrating the acidic character of these surface sites. The strength of the acid–base interaction is strongly dependent on the nature of the cation, since for an identical sulfur coordination the adsorption energies decrease according to the ranking Mo > Co > Ni.

For a given coordination, this ranking is the same as the one of metal–sulfur bond strengths. On the other hand, the second factor governing the Lewis acid strength of these cations is their sulfur coordination which, as it increases, tends to decrease their Lewis acidity, as could be expected from straightforward application of the bond order conservation principle.⁴⁷

Finally, in view of the data reported in Table 2, on one hand, and the surface structures that we have derived from thermodynamical calculations (Figure 2), on the other hand, it clearly appears that Co and Ni promoters also enhance the surface Lewis acidity by inducing the creation of stable Mo CUS sites which are among the strongest ones on these surfaces.

This effect of Co on the Lewis acidity of the surface is in excellent agreement with the work of Berhault et al. who have shown by FTIR spectroscopy that after sulfidation, CoMo/SiO₂ catalysts present stronger Lewis acid sites as compared to a Mo/SiO₂ catalyst.²⁹

4. Hydrogen Adsorption

The stable sulfide surfaces represented on Figure 2 present many potential adsorption sites for dissociation of hydrogen, either homolytic on sulfur dimers or heterolytic on metal–sulfur pairs. We have investigated several configurations for typical cases, on the basis of the local environment of the dissociation site. In the following, the heterolytic dissociation sites are denoted according to the coordination number of the molybdenum atom, the coordination of the sulfur atom, and the atoms to which it is bound, for example, Mo_X–S_{II}(Mo_X, Mo_Y). The structures and the energetics of the resulting surfaces are reported in Figures 4–8 and Table 3, respectively.

Unpromoted Surfaces. As previously shown by Cristol et al.,¹⁹ hydrogen dissociation on the Mo edge of the most stable surface (Figure 2a) is always endothermic whatever the final geometry considered. The less unfavorable reaction (Δ*E* = +0.27 eV) corresponds to hydrogen dissociation on a six-fold coordinated Mo and a sulfur bridging two six-fold coordinated molybdenum atoms, that is denoted by Mo_{VI}–S_{II}(Mo_{VI}, Mo_{VI}). The resulting surface presents a Mo–H and a S–H group (Figure 4a). The endothermicity of hydrogen dissociation on this surface may be explained considering that the molybdenum edge of the surface does not present any unsaturated Mo atom.

(47) (a) Shustorovich, E. *Surf. Sci. Rep.* **1986**, *6*, 1. (b) Shustorovich, E. *Adv. Catal.* **1990**, *37*, 101.

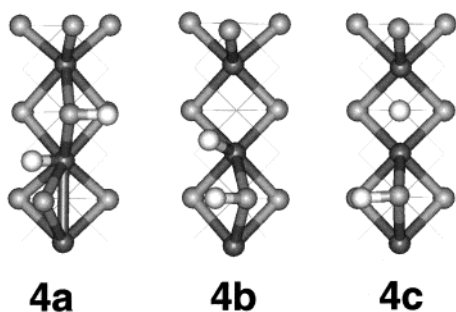


Figure 4. Representation of unpromoted ($10\bar{1}0$) MoS_2 surfaces after heterolytic addition of hydrogen. Dark circles, Mo; light circles, S; white circles, H.

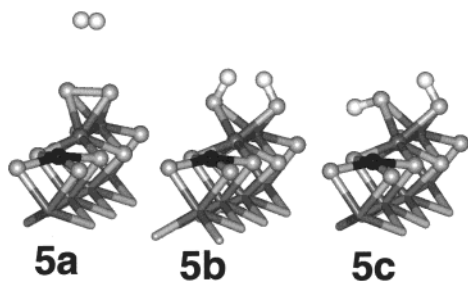


Figure 5. Representation of stable configurations of ($10\bar{1}0$) Co–Mo–S surfaces after homolytic addition of hydrogen. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H.

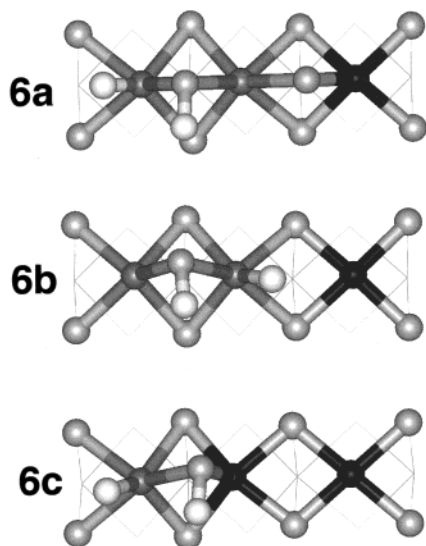


Figure 6. Representation of Co–Mo–S ($10\bar{1}0$) surfaces after heterolytic addition of hydrogen on Mo–S pairs. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H.

Two stable geometries were found for the addition of hydrogen to the $\text{Mo}_V\text{--S}_{II}(\text{Mo}_V, \text{Mo}_{VI})$ site of the defective surface (Figure 2b). The first one leads to the formation of one S–H and one Mo–H group and is endothermic by +0.1 eV (Figure 4b). For the second one (Figure 4c), the hydride connects two Mo atoms in a bridging position, within the Mo plane. Evidently, such a position was impossible on the previous surface because of the presence of a bridging sulfur atom. This adsorption mode is slightly exothermic (–0.10 eV). However, considering (i) the large translation entropy loss occurring during the adsorption reaction and (ii) the low population of such sites, the number of hydrogen atoms on the surface in equilibrium with the gas phase should be very small.

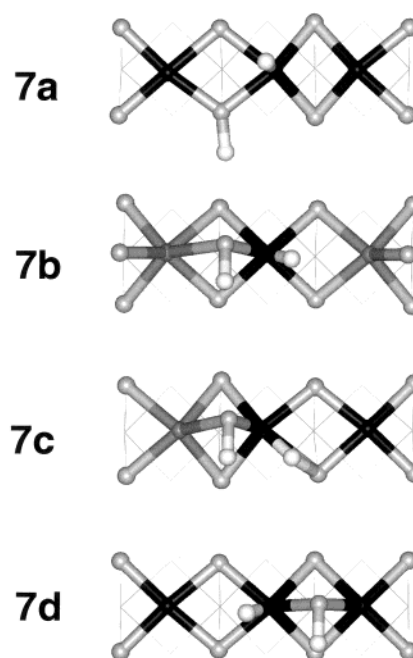


Figure 7. Representation of Co–Mo–S ($10\bar{1}0$) surfaces after heterolytic addition of hydrogen on Co–S pairs. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H.

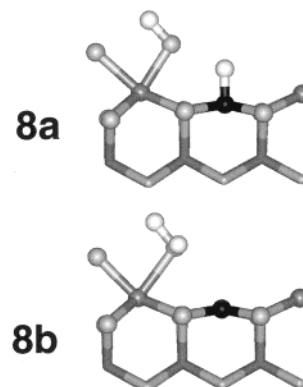


Figure 8. Representation of Ni–Mo–S ($10\bar{1}0$) surfaces after heterolytic addition of hydrogen on Ni–S pairs. Dark gray circles, Mo; light gray circles, S; black circles, Ni; white circles, H.

Any other adsorption geometry is endothermic. Thus, heterolytic dissociation on a $\text{Mo}_{VI}\text{--S}_{II}(\text{Mo}_V, \text{Mo}_{VI})$ site of the defective surface (Figure 2b) is endothermic by +0.49 eV. Interestingly, this value is slightly increased as compared to the heterolytic addition on the most stable surface (+0.27 eV), which can be understood in terms of the bond order conservation model; removing one sulfur atom from the surface induces an increase of the neighboring Mo–S bonds strength (the $\text{Mo}_{VI}\text{--S}_{II}$ distance is decreased from 2.51 to 2.43 Å), that in turn reduces the ability of these S and Mo atoms to form new bonds with hydrogen.

Promoted Surfaces. Homolytic Dissociation on Sulfur Dimers. Among the various surfaces that we have investigated, only one presents a stable sulfur dimer (Figure 2f) that may lead to homolytic dissociation, resulting in the reduction of the sulfur dimer. Three stable configurations for hydrogen interaction with this dimer are reported in Figure 5.

The molecular adsorption of hydrogen (Figure 5a) is athermic (+0.03 eV), and neither the hydrogen bond length nor the

sulfur–sulfur distance is significantly modified upon adsorption, revealing a weak interaction. On the other hand, two configurations were found stable for homolytic dissociation. The first one (Figure 5b) is also athermic (+0.01 eV), which could be ascribed to steric constraints between the two protons that are separated only by 1.77 Å. The second configuration (Figure 5c), however, is clearly exothermic (−0.19 eV). Similar results were obtained in the case of H₂ dissociation on the same kind of sulfur dimer on an unpromoted surface.⁴⁸ Byskov et al.¹⁴ have reported activation energies on the order of 0.6 eV for such a dissociation.

Heterolytic Dissociation on Mo–S Pairs. In Figure 6 are represented three stable configurations for the heterolytic dissociation of hydrogen on molybdenum–sulfur pairs.

The first case (Figure 6a) corresponds to the heterolytic dissociation of H₂ on a five-fold coordinated Mo and a sulfur bridging two molybdenum atoms, five- and six-fold coordinated, that is denoted by Mo_V–S_{II}(Mo_V, Mo_{V1}). In this case, the dissociation is clearly endothermic, by +0.51 eV. It is interesting to note that it is even more endothermic than in the case of the unpromoted MoS₂ surface for hydrogen dissociation on a Mo CUS site presenting the same local environment, except for the substitution of a Mo by a Co at the neighboring dissociation site. Such a difference may be explained in the following way: replacement of Mo by Co reduces the metal–sulfur bond energy, which in turn enhances neighboring S–Mo bonds. As a consequence, the bonding of H to Mo weakens, and hence the thermodynamics of H₂ dissociation become less favorable.

The second case, Mo_V–S_{II}(Mo_V, Mo_V), is very similar (Figure 6b), except that the second molybdenum atom to which the sulfur atom is bound is also five-fold coordinated instead of six-fold. The dissociation energy is still endothermic (+0.44 eV) and very close to the dissociation energy computed for the previous case.

The third case we have investigated is depicted in Figure 6c. It corresponds to H₂ heterolytic dissociation on a Mo_V–S_{II}(Mo_V, Co_V) site. It strongly differs from the previous ones, in that the sulfur atom is bridging a molybdenum and a cobalt atom. In that case, the dissociation energy is significantly different and is slightly exothermic (−0.08 eV). Because the cobalt atom tends to increase the electron density around the bridging sulfur (Figure 3), we mainly ascribe this exothermicity to the ability of the bridging sulfur atom to bind the proton, that would result from this higher electron density, which is bonding for hydrogen (p-like orbitals, Figure 3).

Heterolytic Dissociation on Co–S Pairs. Four configurations for the heterolytic dissociation of hydrogen on cobalt–sulfur pairs are represented in Figure 7.

The first surface (Figure 7a) corresponds to the most stable surface for full substitution of molybdenum by cobalt. In that case, the only possibility for heterolytic dissociation is on a site formed by a four-fold coordinated Co atom and a three-fold coordinated sulfur of the basal plane. The dissociation is athermic, which is due to the low energy of the resulting S–H bond, as the sulfur atom is four-fold-coordinated. Hydrogen bonding of the proton with the second MoS₂ sheet might stabilize this species, the two closest sulfur atoms being at 2.76 and 2.97 Å from the proton.

Table 3. Energetics of Heterolytic Dissociation of H₂ on (10 $\bar{1}$ 0) Sulfide Surfaces^a

structure	dissociation site	ΔE /eV	$E_{\text{act}}(\text{ads})$ /eV	$E_{\text{act}}(\text{des})$ /eV
4a	Mo _{V1} –S _{II} (Mo _{V1} , Mo _{V1})	0.41	0.97	0.56
	Mo _{V1} –S _{II} (Mo _V , Mo _{V1})	0.49		
4b	Mo _V –S _{II} (Mo _V , Mo _{V1})	0.10	0.55	0.45
4c	Mo _V –S _{II} (Mo _V , Mo _{V1})	−0.10		
6a	Mo _V –S _{II} (Mo _V , Mo _{V1})	0.51	0.79	0.28
6b	Mo _V –S _{II} (Mo _V , Mo _V)	0.44		
6c	Mo _V –S _{II} (Mo _V , Co _V)	−0.08		
7a	Co _{IV} –S _{III} (Co _{IV} , Co _{IV} , Mo _{V1})	0.04		
7b	Co _V –S _{II} (Co _V , Mo _{V1})	−0.15	0.52	0.67
7c	Co _V –S _{II} (Co _V , Mo _V)	0.51		
7d	Co _V –S _{II} (Co _V , Co _V)	−0.55	0.34	0.91
8a	Ni _V –S _{II} (Ni _V , Mo _V)	0.50		

^a ΔE , difference in electronic energies, $\Delta E = E(\text{surface-H}_2) - E(\text{surface}) - E(\text{H}_2)$; $E_{\text{act}}(\text{ads})$, activation energy for H₂ dissociation; $E_{\text{act}}(\text{des})$, activation energy for the desorption of dissociated species.

The second case, Co_V–S_{II}(Co_V, Mo_{V1}), corresponds to the dissociation on a cobalt atom and a sulfur atom bridging one cobalt and one molybdenum atom (Figure 7b). The dissociation is exothermic (−0.15 eV), and it differs by 0.66 eV as compared to the heterolytic dissociation on the Mo_V–S_{II}(Mo_V, Mo_{V1}) site on the same surface (Figure 6a). The coordination of the sulfur atom to the cobalt may explain this difference for a large part, since in the case of molybdenum–sulfur pairs, this could lower the dissociation energy by ca. 0.5 eV. The relative stabilities of hydride species (Co–H vs Mo–H) should also be considered in the energetic balance, but we will show later that their bond energy is similar (section 6).

The third case (Figure 7c) corresponds to the dissociation on a Co_V–S_{II}(Co_V, Mo_V) site. The dissociation is clearly exothermic (−0.51 eV). In this case, the “hydride” species is bridging the cobalt and one sulfur atom of the basal plane. This particular configuration has to be related to an important distortion of the surface around the dissociation site that is already present before hydrogen adsorption (Figure 2f). A similar geometry for this site has also been reported by Raybaud et al.¹⁷

Finally, the fourth case (Figure 7d) corresponds to the dissociation on the Co_V–S_{II}(Co_V, Co_V) site that is also present on the surfaces fully substituted by Co (Figure 2i). The dissociation on this site is the most exothermic with respect to all the previous cases and is −0.55 eV. The energy difference with the dissociation on the Co_V–S_{II}(Co_V, Mo_{V1}) is around 0.4 eV. Interestingly, this value is similar to the difference in energy for the dissociation on Mo_V–S_{II}(Mo_V, Mo_V) and Mo_V–S_{II}(Mo_V, Co_V) sites, respectively. As previously, we may consider that the coordination environment of the sulfur atom that is bridging to two cobalt atoms causes this large energy difference.

Finally, at this stage of the study, considering only the local environment of the dissociation site and discarding the particular case of Figure 7b, simple energy differences between various configurations show that substitution of one molybdenum atom by one cobalt leads to (i) a decrease in the stability of Mo–H species and (ii) a higher proton affinity of sulfur atoms bridging one or two Co atoms.

Heterolytic Dissociation on Ni–S Pairs. Figure 8a reports a stable configuration that has been obtained for heterolytic dissociation of hydrogen on the Ni_V–S_{II}(Ni_V, Mo_{V1}) site. The dissociation on this site is slightly endothermic, by ca. 0.06 eV,

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Table 4. NH₃ Adsorption on –SH Groups of (10 $\bar{1}$ 0) Surfaces^a

	$rS-H\text{\AA}$	$rS-H\cdots NH_3\text{\AA}$	$\Delta r/r_0$	$rH\cdots N\text{\AA}$	$\Delta E/eV$
(Mo,Mo)S–H	1.363	1.55	0.137	1.48	–0.47
(Co,Mo)S–H	1.361	1.47	0.080	1.60	–0.49
(Co,Co)S–H	1.369	1.45	0.059	1.70	–0.37

^a $rS-H$, sulfur–hydrogen bond length before NH₃ adsorption; $rS-H\cdots NH_3$, sulfur–hydrogen bond length after NH₃ adsorption; $\Delta r/r_0$, S–H bond length extension upon adsorption; $rH\cdots N$, hydrogen–nitrogen bond length; ΔE , difference in electronic energies, $\Delta E = E(\text{surface-NH}_3) - E(\text{surface}) - E(\text{NH}_3)$.

and leads to the cleavage of the Ni–S bond, resulting in the formation of a monodentate –SH group and a Ni_{IV} hydride species. The second stable configuration for the addition of H₂ on this site is represented in Figure 8b and corresponds to the formation of H₂S, which is an exothermic process (–0.5 eV). Evidently, this case strongly differs from the dissociation on the analogous site Co_V–S_{II}(Co_V, Mo_{VI}) which was exothermic and for which the Co–S bond remained stable after dissociation (Figure 5c). To a first approximation, this difference may be ascribed to the much lower stability of Ni–S bonds as compared to Co–S bonds that we have mentioned previously.

Brønsted Acidity of the Resulting Surfaces. To check quantitatively the aforementioned variation of the sulfur basicity according to its coordination environment, we have monitored the interaction of the sulfhydryl groups with ammonia. Table 4 reports selected structural data and adsorption energies for the hydrogen bonding of NH₃ with three –SH groups selected according to the coordination environment of the sulfur atom.

The adsorption of ammonia on these –SH groups is clearly exothermic, on the order of 0.4–0.5 eV, indicating that such groups present a Brønsted acidic character. On an energetic basis, one can make a clear distinction between the SH group bridging two Mo atoms, on one hand, and those bridging one or two cobalt atoms, on the other hand, the latter being less acidic than the former one. On a structural point of view, it is interesting to look at the S–H bond extension that occurs upon hydrogen bonding with ammonia, since it is a usual indicator for Brønsted acidity. This bond stretching varies according to the ranking (Mo,Mo)S–H > (Mo,Co)S–H > (Co,Co)S–H.

This clearly suggests that as a ligand of surface sulfur atoms, Co decreases the Brønsted acid strength of sulfhydryl groups or, otherwise stated, increases the sulfur basicity. This trend is in excellent agreement with the strong variations in H₂ dissociation energies on the various metal–sulfur pairs previously described.

5. Reaction Paths for Heterolytic Dissociation of Hydrogen

Unpromoted Surfaces. The geometry of the transition state (TS) leading to the heterolytic dissociation of H₂ on the Mo_{VI}–S_{II}(Mo_{VI}–Mo_{VI}) site of the unpromoted surface is reported in Figure 9a. The activation energy of the elementary reaction is 0.97 eV. As the reaction is endothermic (+0.41 eV), the barrier associated to the reverse reaction is much smaller (0.56 eV). The final geometry of the elementary step does not match exactly the geometry of the most stable adsorption mode (Figure 4a). To get this stable situation, one of the hydrogen atoms must jump from one side of the metallic edge to the other one. However, as this displacement does not include the breaking or the formation of bonds, it is reasonable to assume that this elementary step has a low activation energy.

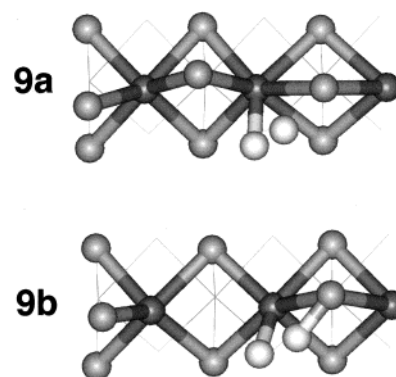


Figure 9. Representation of the transition states for the heterolytic addition of hydrogen on unpromoted MoS₂ (10 $\bar{1}$ 0) surfaces. Dark gray circles, Mo; light gray circles, S; white circles, H.

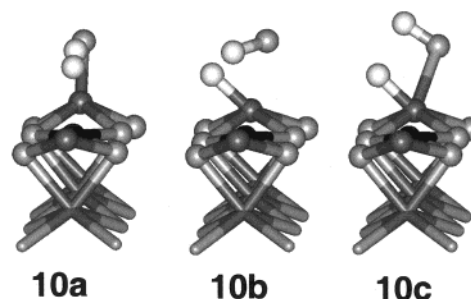


Figure 10. Representation of (a) initial state, (b) transition state, and (c) final state for the heterolytic addition of hydrogen on a Mo–S pair of the Co–Mo–S (10 $\bar{1}$ 0) surface. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H.

The TS leading to H₂ addition on the Mo_V–S_{II}(Mo_V, Mo_{VI}) site of the unpromoted defective surface is depicted in Figure 9b. Starting from the physisorption mode, the computed activation energy is 0.55 eV for the formation of one S–H and one Mo–H group (Figure 4b). The migration of the hydride to the more stable bridging position (Figure 4b) is very easy ($E_a = 0.05$ eV).

Promoted Surfaces. In Figure 10 are reported three snapshots of the minimum energy reaction path for the dissociation on Mo_V–S_{II}(Mo_V, Mo_{VI}), which is the most endothermic on the promoted surfaces.

The first image (Figure 10a) corresponds to the molecular adsorption of hydrogen that is almost athermic. The hydrogen bond length is 0.79 Å that has to be compared with 0.75 Å for the free molecule. The TS (Figure 10b) is located at 0.79 eV above the molecular adsorption. The important extension of the molybdenum–sulfur bonds that is a consequence of hydrogen dissociation may significantly contribute to this energy. Figure 10c represents the final state of the elementary reaction.

Figure 11 reports six snapshots and the energy diagram of the minimum energy reaction path for the dissociation on the Co_V–S_{II}(Co_V, Co_V) site, which is the most endothermic case of hydrogen dissociation on these surfaces. The energy diagram for this path is plotted as function of the H–H distance. The first image (Figure 11a) clearly shows that the configuration for molecular adsorption of H₂ on this site is quite different from the previous case. First, the hydrogen bond length is much higher (0.86 vs 0.79 Å), showing that as an adsorption center, cobalt favors activation of molecular hydrogen. Second, a surface reconstruction occurs upon molecular adsorption, which leads to an important displacement of the bridging sulfur atom

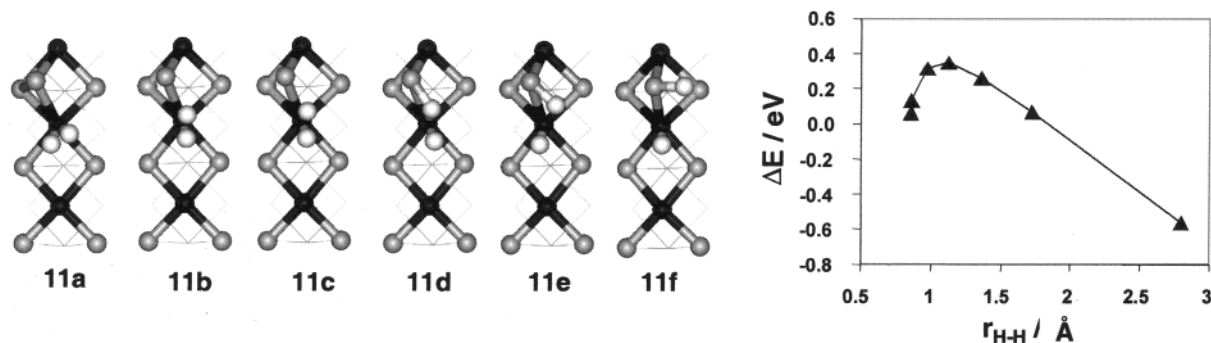


Figure 11. Snapshots of the minimum energy reaction path for the heterolytic addition of hydrogen on a Co–S pair of the Co–Mo–S ($10\bar{1}0$) surface. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H. Graph: Energy diagram as a function of the H–H distance.

that now forms a sulfur bridge with a sulfur atom of the basal plane. This molecular adsorption is slightly exothermic, +0.06 eV. The reaction pathway is straightforward. First, the hydrogen molecule undergoes a slight rotation, and the bridging sulfur comes back in the molybdenum plane; this leads simultaneously to an extension of the H–H distance and a reduction of the hydrogen–bridging sulfur distance. The dissociation then occurs, and the stable dissociated state is finally reached. The activation energy for this dissociation is 0.34 eV, which is much lower than in the previous cases. Such a low activation barrier may be ascribed to the effect of cobalt that (i) directly favors the activation of molecular hydrogen and (ii) increases sulfur reactivity and flexibility.

6. Surface Diffusion of Dissociated Species

Several pathways for the surface diffusion of dissociated species were computed, for displacements from metal atom to metal atom, as well as from sulfur to metal. Figures 12 and 13 report snapshots of the diffusion paths on unpromoted and Co promoted surfaces, respectively.

Unpromoted Surfaces. Once the hydrogen molecules have been dissociated on the most stable molybdenum edge (Figure 12a), the activation energies for the diffusion are relatively small. The migration of one hydrogen from one Mo_{VI} atom to an S_{II} atom is almost athermic (+0.04 eV, Figure 12a–c), showing that the energies associated to the Mo–H and to the S–H bonds are close. This is in good agreement with a previous study¹⁹ where it was shown that the energies associated with the formation of two –SH groups, on one hand, and one –SH and one Mo–H group, on the other hand, are similar, within 0.1 eV.

The activation energy for this diffusion step is 0.54 eV, and the direct reaction is as easy as the reverse one. We have been looking for an elementary diffusion of the hydride species directly from one Mo atom to a second one. Whatever the computational technique used, however, we have not been able to determine a direct reaction, and an S–H intermediate group has always been created.

The diffusion of hydrogen on the defective surface may be decomposed into two parts. In the first part, we have investigated the diffusion of hydrogen atoms between fully coordinated atoms (i.e., Mo_{VI} and S_{II}). The activation energy of the diffusion from the S atom to the Mo one is 0.39 and 0.25 eV for the reverse reaction (Figure 12d–f). These two values match the values calculated on the most stable surface, showing that the electronic influence of the vacancy on this surface has a small spatial

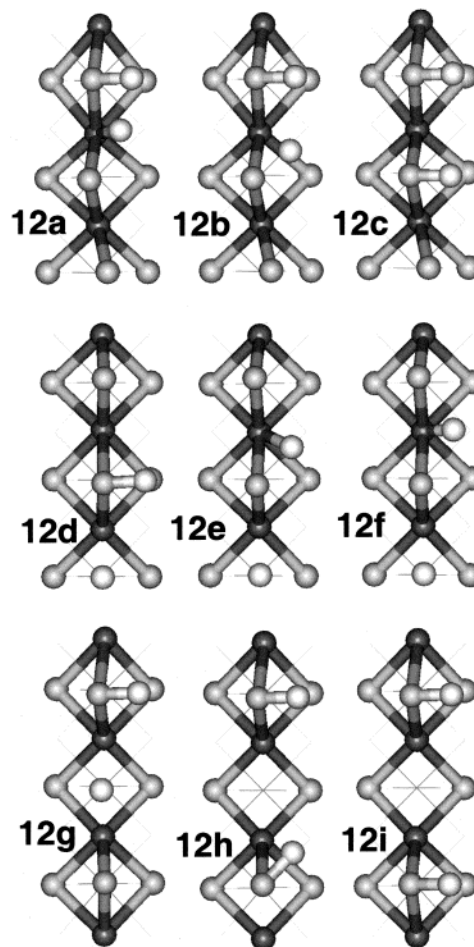


Figure 12. Representation of initial states (left), transition states (middle), and final states (right) for hydrogen diffusion on the unpromoted MoS_2 ($10\bar{1}0$) surface. Dark gray circles, Mo; light gray circles, S; white circles, H.

extension. In the second part, we have investigated the diffusion of the hydrogen originating from the bridging position between two Mo's. The activation for this displacement to the next sulfur atom is 0.93 eV (Figure 12g–i). This important activation energy is even larger than the desorption activation energy (0.72 eV). Taking into account the small number of such vacancies on these surfaces, however, such pathways should have a very small influence on the overall diffusion on MoS_2 surfaces.

Promoted Surfaces. Figure 13a corresponds to the diffusion of a hydride species from the five-fold coordinated Co atom that is involved in the heterolytic dissociation on the $\text{Co}_{\text{V}}-\text{S}_{\text{II}}$ -

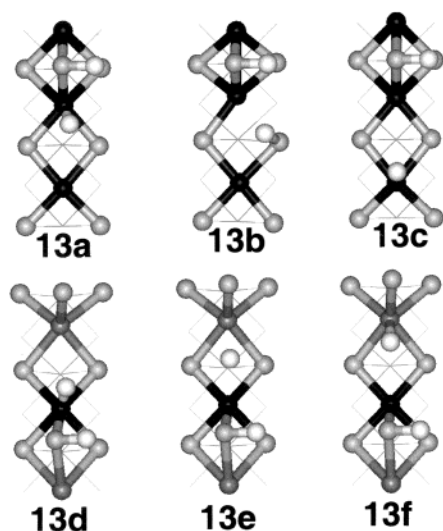


Figure 13. Representation of initial states (left), transition states (middle), and final states (right) for hydrogen diffusion on the Co–Mo–S ($10\bar{1}0$) surface. Dark gray circles, Mo; light gray circles, S; black circles, Co; white circles, H.

(Co_V , Co_V) site to the vicinal four-fold coordinated Co atom. In this case, hydrogen diffuses via the three-fold coordinated sulfur atom of the basal plane that bridges the two cobalt atoms. This process is weakly activated by 0.29 eV, and both initial and final configurations are of similar energy, showing that Co_V and Co_{IV} hydride species have a similar stability. Figure 13b depicts the reaction path for the diffusion of a hydride species from a Co_V to a Mo_V center. In this case, the hydride species does not diffuse via a three-fold coordinated bridging sulfur atom but is directly transferred from the Co_V atom to the Mo_V atom. This can be explained by the shorter distance (1.70 Å vs 2.35 Å) that the hydride has to cross from the initial to the final states of the elementary process. This hydride “hopping” has a similar activation energy as in the previous case, and, interestingly, the energy difference between the initial and the final state is on the order of 0.04 eV. From this, we deduce that $\text{Co}_V\text{--H}$ and $\text{Mo}_V\text{--H}$ species have a similar stability since the initial and final configurations (Figure 13d–f) only differ by the nature of the metal atom to which the hydride species is bound. This similar stability clearly shows that the nature of the hydride species that is formed after H_2 dissociation is not likely responsible for the important changes in the dissociation energy of hydrogen on Mo–S and Co–S pairs. These are on the order of 0.5 eV. Hence, the energetic balance for hydrogen heterolytic dissociation is mainly governed by the stability of the resulting –SH groups as mentioned before.

7. Implications for the $\text{H}_2\text{--D}_2$ Exchange Reaction and Hydrotreating Reactions

The $\text{H}_2\text{--D}_2$ exchange reaction consists of three elementary steps: (i) H_2 and D_2 adsorb dissociatively on the catalyst, (ii) the dissociated species diffuse over the surface so that two isotopic species can meet, and finally (iii) recombinative desorption occurs, leading to the formation of HD species in the gas phase.

In the case of the unpromoted ($10\bar{1}0$) MoS_2 stable surface, we have shown that the activation energies for the heterolytic dissociation of hydrogen are on the order of 1.0 eV. This is in all cases much higher than either the desorption (ca. 0.6 eV) or

the diffusion of dissociated species (ca. 0.3–0.4 eV). Therefore, the rate-limiting step of this exchange reaction is the dissociation of dihydrogen and dideuterium on the surface. This implies that the overall rate of reaction is proportional to the amount of H_2 and D_2 present in the gas phase, or, in other words, it is first order in H_2 and D_2 .

For the promoted surfaces we have shown that when the dissociation occurs on Co–S pairs, desorption of dissociated species is in most cases much more difficult (up to 0.9 eV) than either the dissociation (as low as 0.3 eV) or the diffusion (ca. 0.3 eV). Therefore, in this case, the rate-limiting step for the H–D exchange reaction is the recombinative desorption of dissociated species. This implies that the overall rate is proportional to the amount of dissociated species, that is, half order in H_2 and D_2 .

This change in the rate-limiting step of the H–D exchange reaction which is predicted by our theoretical results on the nonpromoted MoS_2 and promoted Co– MoS_2 ($10\bar{1}0$) surfaces is in excellent agreement with the experimental kinetic data reported by Hensen et al. in the case of Mo/C and CoMo/C catalysts,³⁶ thus demonstrating the crucial role of Co–S pairs in hydrogen activation on promoted catalysts.

For NiMo sulfide catalysts, the activity data reported by Thomas et al. show that the Ni promotor does not significantly change the activity of these catalysts in the H–D exchange reaction.³³ Our theoretical calculations have shown that Ni–S pairs are not very stable on these surfaces. Even when such sites are present on these surfaces, they do not provide an efficient way for hydrogen activation. This would lead to the cleavage of the Ni–S bond and possibly to the departure of the sulfur atom from the surface under the form of H_2S , the latter resulting in a more stable surface (Table 1). Therefore, according to our calculations, the only stable heterolytic dissociation sites of hydrogen on the ($10\bar{1}0$) Ni–Mo–S surface are Mo–S(Mo,Mo) pairs that, as shown by our calculations on Co–Mo–S surfaces, would essentially behave in a similar way as the Mo–S pairs of unpromoted MoS_2 surfaces. This hypothesis would explain, at least in part, the experimental results of Thomas et al.³³

Finally, the present theoretical results as well as the previous experimental studies^{34,36,37} clearly show that Ni and Co have a very different effect on the activation of hydrogen on Mo-based catalysts.

It is well known that NiMo and CoMo catalysts present significant differences of activity and selectivity in hydrotreating reactions. In particular, NiMo catalysts are usually more active and selective for hydrogenation reactions. From this, one may be tempted to conclude that NiMo catalysts are more efficient for hydrogen activation than are CoMo catalysts. Our calculations together with H_2/D_2 studies, however, clearly show that this is not the case. Obviously, hydrotreating reactions are complex processes where, besides hydrogen activation, many parameters have to be taken into account: adsorption of the reacting molecule, hydride or proton attack, and competitive adsorption with products (hydrocarbons, H_2S , NH_3 , ...). In view of the present results, it is clear that hydrogen activation is not the rate-limiting step for these reactions. The computed activation energies for hydrogen dissociation are low, which is in good agreement with experimental H_2/D_2 experiments that show that H_2 dissociation readily occurs at low temperatures. Actually,

to the best of our knowledge, no recent kinetic study has ever shown that hydrogen dissociation could be the rate-limiting step of these reactions.

On the other hand, our calculations show that the nature of the promotor has a strong influence on the configuration and the adsorptive properties of these surfaces. Therefore, the activation of the reacting molecule or reaction inhibition by H_2S and NH_3 might strongly differ on these surfaces and could partly explain the differences in the promotional behavior of Co and Ni in hydrotreating reactions.

8. Conclusions

This contribution reports a theoretical investigation of hydrogen adsorption on Mo-based sulfide catalysts. The main results may be summarized as follows. At working conditions of these catalysts, on the stable Mo–S surface, only six-fold coordinated Mo cations are present. Substitution by Co or Ni leads to the creation of stable CUS sites on the working conditions of these catalysts. On the MoS_2 surface, hydrogen presents a high activation barrier, and the resulting dissociated species are metastable. On CoMoS surfaces, the ability to dissociate H_2 is dependent on the nature of the metal atom and the sulfur coordination environment. As an adsorption center, Co strongly favors molecular hydrogen activation as compared to Mo atoms. As a ligand of S atoms, Co increases their basicity. As a result, CoMoS surfaces present Co–S sites for which the

dissociation is exothermic and weakly activated, hence demonstrating the crucial role of Co–S pairs in hydrogen activation over CoMo catalysts. On Ni–Mo–S surfaces, Ni–S pairs are not stable and do not provide an efficient way for hydrogen activation. Finally, these theoretical results are in good agreement with the recent experimental studies of H_2 – D_2 exchange reactions, showing again the validity of this theoretical approach that provides a realistic description of these catalytic systems.

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Supporting Information Available: Comparative study of supercells and discussion of calculation parameters affecting surface structures and energies (PDF). Typical output file (279 ko), showing calculation parameters and convergence for structure **2g**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Parallel between infrared characterisation and ab initio calculations of CO adsorption on sulphided Mo catalysts

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Abstract

Carbon monoxide adsorption on sulphided Mo catalysts has been investigated by means of IR spectroscopy and DFT ab initio calculations. IR experiments show that CO adsorption on the sulphide phase of Mo/Al₂O₃ catalysts gives rise to various $\nu(\text{CO})$ bands, the intensities of which are strongly modified when post-treatment of the catalyst with H₂ or H₂S is performed before CO adsorption, therefore, revealing strong modifications in the nature and the number of sites present on the sulphide phase. Ab initio periodic DFT calculations allow to define two types of edges for MoS₂, which sulphur coverage and structure depend on the H₂/H₂S ratio in the surrounding atmosphere. Adsorption energies and stretching wavenumber of CO adsorbed on the various sites of these surfaces were computed, providing the possibility to compare for the first time results from theoretical calculations and spectroscopic measurements on these systems. A novel attribution of the main IR features of CO adsorbed on MoS₂ is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectroscopy; Density functional theory; Carbon monoxide; Hydrotreating catalysts

1. Introduction

Improvement in the hydrodesulphurisation (HDS) of the petroleum feedstocks has been driven by the need to produce clean fuels based on the pressing requirement for environmental protection. HDS is generally performed with Mo-based catalysts, the active phase of which consists of molybdenum disulphide nanocrystallites well dispersed on an alumina support. Molybdenum disulphide is a highly anisotropic material and it is now well admitted that the Mo coordinative unsaturated sites (CUSs) located at the edges

of these nanocrystallites play a major role in the adsorption and the activation of the reactants. Although a considerable amount of research has been made on these systems, an accurate description of these sites is still lacking. A convenient way to characterise such sites is the use of probe molecule adsorption. In this way, oxygen and nitrogen monoxide were found particularly well suited, because they specifically adsorb on the sulphide phase. NO presents the additional advantage to be easily detected by IR spectroscopy, providing informations on the nature and the amount of the different sites on which it is anchored. However, it has been recognised on time that NO as well as O₂ lead to a partial oxidation of the sulphide, even at very low temperatures [1]. The reliability of these

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methods may therefore be questioned: experimental parameters as the adsorption temperature or the contact time of the probe with the surface are expected to strongly influence the oxidation state of the sulphide phase and accordingly the interaction of the probe with the surface. Indeed, many disagreements are found in the literature on the IR observations of NO adsorbed on sulphided Mo catalysts [2].

On the other hand, carbon monoxide that is otherwise widely used for the IR characterisation of metal oxides and supported metals, has been more scarcely employed in the case of sulphided catalysts. Its worth, however, has been demonstrated by several studies among which Lavalley's group brought major contributions. Indeed, recognising the oxidant behaviour of probes such as O₂, Bachelier et al. [3] firstly proposed the use of carbon monoxide as an alternative probe. The totally reversible adsorption of CO on the sulphide phase was demonstrated and some correlations were obtained between the CO uptake and HDS activities of Mo-based catalysts [3]. The first IR observations of CO adsorption on sulphided Mo catalysts were reported by Peri [4], showing a broad band at ca. 2100 cm⁻¹ characteristic of CO adsorbed on the sulphide phase. Apart from this main feature, Bachelier et al. [5] could also evidence the presence of a weak component at ca. 2070 cm⁻¹, further reported by Müller et al. [6]. Last, by means of CO–NO co-adsorption experiments, Qin et al. [7] were able to distinguish another component in the broad band at ca. 2090 cm⁻¹. In spite of the complexity of the spectrum in that spectral range, Maugé and Lavalley [8] determined its mean extinction coefficient, allowing therefore quantitative evaluation of the amount of sites on sulphided Mo/Al₂O₃ catalyst, which they correlated with their activities. A quantitative relationship was further obtained with the number of Mo atoms located at the edge of the sulphide crystallites as determined by HREM measurements [9,10].

Therefore, the sites probed by CO are likely to play an important role in hydrotreating catalysis. In this respect, IR spectroscopy of adsorbed CO could significantly improve our knowledge of the active surface of sulphided Mo catalysts. However, the interpretation of the IR spectra is not straightforward and, on the basis of qualitative arguments, most of workers were in trouble to give a precise attribution of the observed $\nu(\text{CO})$ bands. Accordingly, Peri [4]

defined the CUS sites responsible for CO adsorption as Mo^{δ+} sites resulting from the interaction of Mo⁰ with Mo⁴⁺ centres, this interpretation being later adopted by Zaki et al. [11]. On the other hand, Bachelier et al. [5] proposed that the main feature at 2100 cm⁻¹ correspond to the adsorption on reduced Mo^{x+} centres, whereas the component at 2070 cm⁻¹ would be due to the adsorption on more reduced Mo atoms. In the same time, Delgado et al. [12] proposed for these species a formal oxidation state of +2, which would result from the reduction of surface Mo during the sulpho-reduction. Last, Müller et al. [6] attributed the component at 2070 cm⁻¹ to Mo atoms located on the corner of the sulphide crystallites.

Finally, the nature and the location of the sites on which CO adsorb is still under debate and IR spectroscopy — as a single technique — is unlikely to provide an answer. Modelling of these nanocrystallites is one possible approach to get a better insight into the nature of the sites. The recent development of new molecular modelling techniques, especially DFT, now allows one to define more and more realistic sulphide surfaces. Raybaud et al. [13] published an ab initio investigation of the structural and electronic properties of the clean MoS₂ (0 1 0) edge surface using the Vienna ab initio simulation program (VASP). These authors showed that the as-cleaved (1 0 0) edge surface remains stable in vacuum up to temperatures of $T = 700$ K [14]. The sulphur coverage of the MoS₂ edge surfaces, which depends on the operating conditions through the relative chemical potential of H₂ and H₂S in the surrounding atmosphere, was later developed [15,16]. These works allowed the calculation of different edge surfaces, the domains of existence of which are defined by the H₂ pressure and the H₂/H₂S ratio.

The aim of the present work is to use molecular modelling techniques to assign the stretching frequencies of CO adsorbed on an unpromoted MoS₂ catalyst. We will first present FTIR experiments in which the distribution of the Mo sites is varied by the pre-treatments of the sulphided sample. Then the MoS₂ (1 0 0) stable surfaces and the stretching frequencies of CO adsorbed on these surfaces deduced from the calculations will be presented. We will finally compare both the methods of investigation and discuss the attribution of the IR bands in relation with our model.

2. Experimental

2.1. IR spectroscopy

2.1.1. Catalysts

Two Mo/Al₂O₃ samples, 8Mo and 9Mo, containing, respectively, 8 and 9 wt.% molybdenum were prepared by impregnation of the alumina support ($S_{\text{BET}} = 220 \text{ m}^2 \text{ g}^{-1}$) with an ammonium heptamolybdate solution, followed by drying and calcination at 773 K. Before introduction in the IR cell, the oxide precursors so obtained were grounded, pressed into self-supported wafers (ca. 5 mg cm^{-2}).

2.1.2. Sulphidation

The sulphidation was carried out in situ in the IR cell according to the following procedure. After out gassing at 523 K, the catalysts were contacted with 100 Torr (1 Torr = 133.3 N m^{-2}) of a H₂S/H₂ (15/85) mixture and heated at a rate of 10 K min^{-1} up to 673 K and further maintained at this temperature. The sulphidation was followed by an evacuation of 10 min at the same temperature. The sulphidation–evacuation cycle was repeated three times, the duration of sulphidation being, respectively, 1.5, 12 and 1.5 h. The last evacuation was performed up to a residual pressure of 2×10^{-6} Torr. The catalysts treated in such a way will be named “sulphided catalysts” in the following parts and will be denoted as 8Mo(S) and 9Mo(S).

A set of experiments was also performed on the 9Mo sample after an ex situ pre-sulphidation. In this case, the oxide precursor was sulphided under a flow of H₂S/H₂ (15/85) mixture at 623 K, further ground and pressed into a self-supported pellet in the laboratory atmosphere before introduction in the IR cell. This catalyst will be denoted as 9Mo(exS).

2.1.3. Post-treatments

The sulphided 8Mo(S) and 9Mo(S) catalysts were subjected to various post-treatments before or between CO adsorption experiments.

1. *Hydrogen treatments.* The 8Mo(S) catalyst was evacuated at 673 K and further cooled down to the reduction temperature (473, 573 and 673 K). Then, the catalyst was contacted with 250 Torr H₂ during 30 min at the chosen temperature followed by an evacuation of 10 min at the same temperature.

Two reduction–evacuation cycles were done in order to remove the H₂S formed upon reduction. The last evacuation was performed up to a residual pressure of 6×10^{-6} Torr. The solids will be denoted as Mo(SR-T), where T is the temperature of reduction.

2. *H₂S treatments.* Another set of experiments was performed on 9Mo(S) and consisted in the following sequence. After in situ sulphidation of the catalyst, successive calibrated doses of H₂S were introduced at room temperature (RT). After each H₂S dose, the catalyst was cooled down to 100 K and characterised by CO adsorption. Before introducing the following H₂S dose at RT, the cell was maintained under dynamic vacuum from 100 up to 673 K in order to completely desorb CO. Then, the catalyst was re-sulphided at 673 K for 30 min, degassed up to a residual pressure of 5×10^{-6} Torr was reached and further cooled down at RT, allowing the introduction of another dose of H₂S in the cell. We have checked that these successive treatments did not modify the catalyst surface state before the introduction of a given dose of H₂S.

2.1.4. CO adsorption

The adsorption of CO has then been characterised by FTIR. Before IR characterisation, the catalysts were contacted with 0.5 Torr of He at RT, for a better thermal contact at low temperature, and further cooled down to 100 K. Small calibrated doses of CO were introduced in the IR cell up to an equilibrium pressure of 1 Torr. CO was further evacuated at low temperature ($P = 1 \times 10^{-4}$ Torr). FTIR spectra were recorded in 256 scans after each CO introduction using a 60SX Nicolet FTIR spectrometer with a resolution of 4 cm^{-1} .

In all these experiments, CO as well as H₂ and He were purified by trapping in liquid nitrogen before contact with the catalyst. H₂S was purified by distillation at low temperature (77–160 K).

2.2. Computational techniques

The periodic DFT calculations were performed with the VASP [17–20], based on plane waves that allows a good description of the MoS₂ surface, by using large supercells ($9.48 \times 12.294 \times 20 \text{ \AA}^3$). Fig. 1 shows the cell that has been used for the calculations. As shown in a previous study [14,15], such a model containing

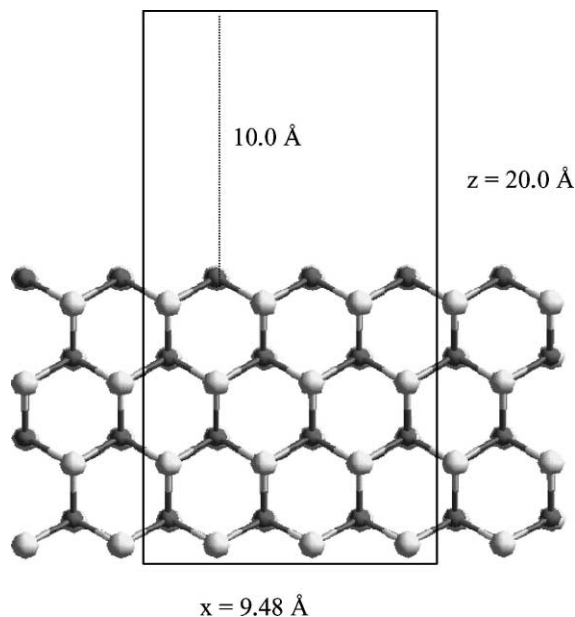


Fig. 1. Representation of the supercell used for calculations, showing the axes. Dark circles: Mo; light circles: S.

two layers along the y -direction, three rows in the x -direction and four in the z -direction is suitable to give a good description of the structural and adsorption properties of the (100) MoS₂ surface. All over this work, we used a cut-off energy of $E_{\text{cut}} = 300$ eV,

a Methfessel–Paxton [21] smearing with $\sigma = 0.1$ eV and Γ point for Brillouin zone integration. The two upper rows and the adsorbed molecules were allowed to relax during the calculation, while the two lower ones were kept fixed at the bulk geometry. In order to compute reliable adsorption energies, the non-local functional using generalised gradient corrections (GGA) of Perdew et al. [22,23] was applied. The CO vibration frequencies were calculated by numerical differentiation of the force matrix. In order to reduce the computation time, we computed only the part of the matrix corresponding to the three or six atoms closest to CO. As isotopic substitution suggests that the CO stretching vibration mode is only very weakly coupled with the vibrations of the surface, this approximation should not induce important systematic errors. All the calculated frequencies are scaled by 1.02, a factor used to fit calculated and experimental CO stretching vibration of the free CO molecule.

3. Results

3.1. IR characterisation of CO adsorption

3.1.1. Sulphided catalyst

The IR spectra of CO adsorbed on sulphided 8Mo catalyst are presented in Fig. 2. Three main bands at

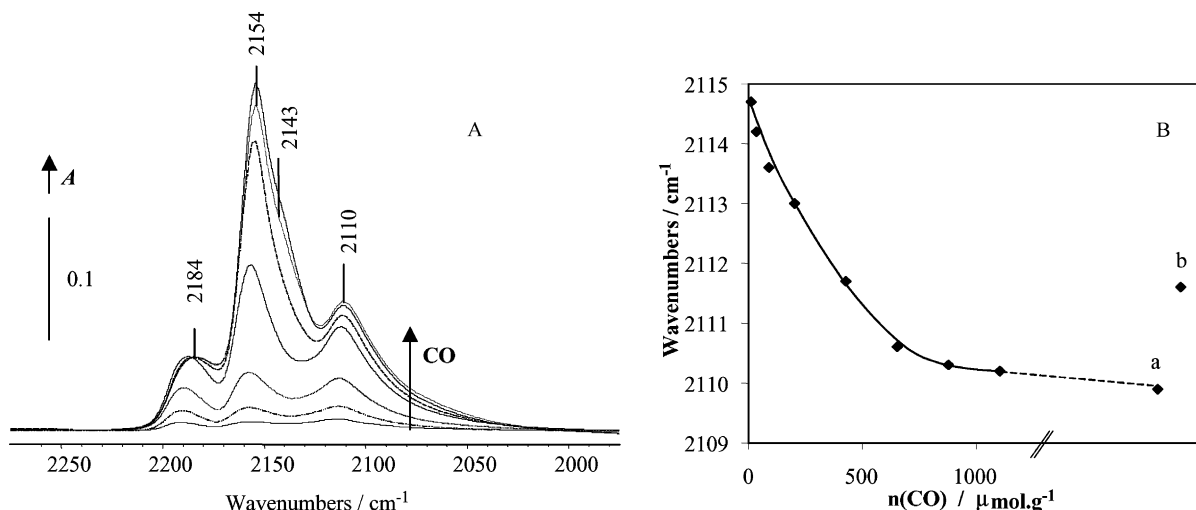


Fig. 2. (A) IR spectra of increasing doses of CO adsorbed at 100 K on sulphided 8Mo(S) catalyst. (B) Variation of the wavenumber of CO/Mo band versus the CO doses (a: 1 Torr of CO at equilibrium; b: CO evacuated up to $P = 2 \times 10^{-5}$ Torr).

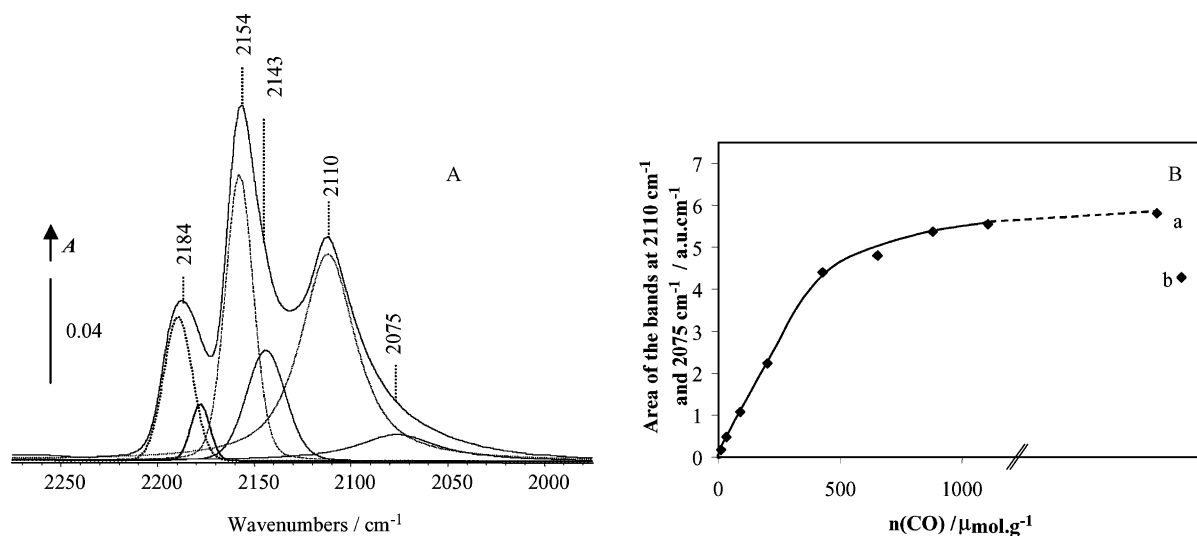


Fig. 3. (A) Decomposition of the IR spectra for $429 \mu\text{mol g}^{-1}$ of CO adsorbed at 100 K on sulphided 8Mo(S) catalyst. (B) Variation of the area of CO/Mo bands at 2110 and 2075 cm^{-1} versus CO doses (a: 1 Torr of CO at equilibrium; b: CO evacuated up to $P = 2 \times 10^{-5}$ Torr).

2184 , 2154 and 2110 cm^{-1} are observed, the intensity of which increases with the amount of CO introduced. From previous studies [6,8], these bands can be attributed, respectively, to coordination of CO on Lewis acid sites of the alumina support, CO in hydrogen bonding with the support hydroxyl groups and to CO in interaction with the edges of the MoS_2 nanocrystallites. At high CO uptake, a shoulder at 2143 cm^{-1} , corresponding to physisorbed CO, appears. Upon degassing at 100 K, a strong decrease of the intensity of the band characterising physisorbed CO and CO interacting with the support is noticed. By evacuation at 295 K, all the CO bands are eliminated except a small shoulder at ca. 2075 cm^{-1} [5].

A careful analysis of the spectra shows that the band characteristic of CO adsorbed on the disulphide crystallites shifts with the increase of the CO uptake. Introduction of the first dose of CO leads to the appearance of a main band at 2115 cm^{-1} with a shoulder at 2126 cm^{-1} . The wavenumber at the maximum of the predominant band shifts from 2115 to 2110 cm^{-1} for 1 Torr CO at equilibrium and slightly increases up to 2112 cm^{-1} after evacuation (Fig. 2B). In order to obtain more accurate information about the sites characterised by this band, decomposition of the spectra obtained after introduction of various CO doses was performed. The decomposition of the

spectrum corresponding to an intermediate CO dose is reported in Fig. 3A. The asymmetry of the band at 2110 cm^{-1} required generating a weak band at ca. 2075 cm^{-1} to correctly fit the experimental spectrum. The presence of such a low wavenumber $\nu(\text{CO})$ band has already been reported by Bachelier et al. [5] and more recently by Müller et al. [6]. Its absorbance is weak, indicating that the corresponding number of adsorbed CO molecules should be low as the molar extinction coefficient usually increases as the $\nu(\text{CO})$ wavenumber decreases. Thus after sulphidation, the 8Mo(S) catalyst presents mainly Mo sites corresponding to the 2110 cm^{-1} band.

Decomposition of the spectra recorded at various CO coverages shows that the area of bands characterising Mo sites are maximum from ca. $500 \mu\text{mol g}^{-1}$ (Fig. 3B), a value that correspond to the saturation of the sites. After introduction of 1 Torr CO at equilibrium, the area of these bands remains very close to the values measured at saturation.

3.1.2. Effect of H_2S adsorption on sulphided catalyst

The effect of the introduction of increasing doses of H_2S at RT on the CO adsorption spectra of 9Mo(S) catalyst is presented in Fig. 4A and B.

H_2S pre-adsorption leads to a decrease of the intensity of the bands characterising CO coordinated

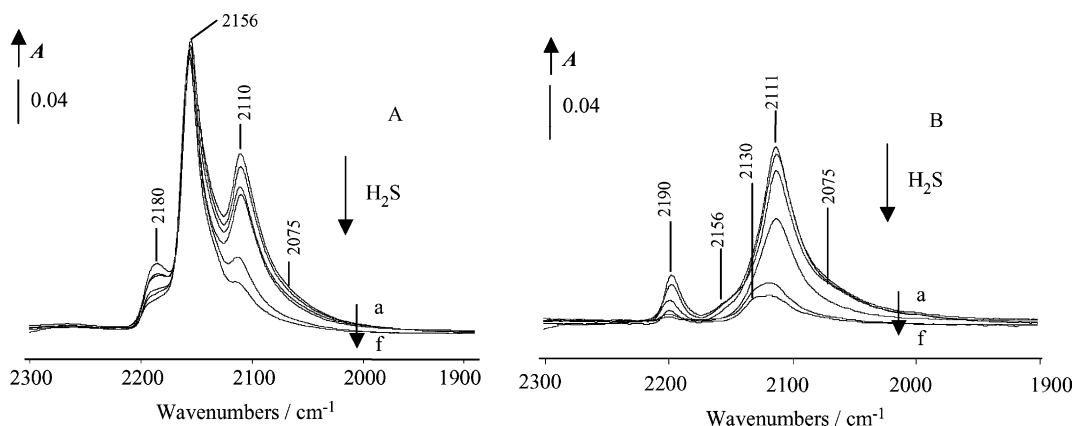


Fig. 4. IR spectra of CO adsorbed at 100 K after introduction of increasing doses of H_2S at RT (a, b, c, d, e = 0, 40, 50, 96, $240 \mu\text{mol g}^{-1}$, respectively; f = 5 Torr at equilibrium) on sulphided 9Mo(S) catalyst: (A) 1 Torr of CO at equilibrium; (B) CO evacuated up to $P = 2 \times 10^{-5}$ Torr.

on the support and to a slight increase of the high frequency side of the band at 2155 cm^{-1} (H-bonded CO). A careful analysis of alumina hydroxyl bands (not presented here) shows the creation of some new acidic OH groups due to H_2S dissociative adsorption. As for CO in interaction with the MoS_2 slabs, an important decrease in the intensity of the band at 2110 cm^{-1} as well as of the shoulder at 2075 cm^{-1} is observed. No preferential variation of these bands with the adsorption of H_2S could be noticed. At high H_2S coverage, the intensity of the 2110 cm^{-1} band is very weak and after CO evacuation at ca. 100 K, a shoulder is observed at 2130 cm^{-1} (Fig. 4B). One cannot consider that this band originates from H_2S introduction as it could be present before its introduction and be hidden by the intense band at 2110 cm^{-1} . Moreover, it should be noted that a small band at such a high wavenumber can also be noticed when a few amount of CO is adsorbed on the 8Mo(S) catalyst.

Finally, the global decrease in the intensity of the $\nu(\text{CO}/\text{MoS}_2)$ massif after H_2S pre-adsorption indicates a partial poisoning of the sites of MoS_2 edges by sulphur species.

3.1.3. Effect of an ex situ pre-sulphidation

CO adsorption has been performed after in situ re-sulphidation of an ex situ pre-sulphided catalyst. Surprisingly, CO adsorption on the 9Mo(exS) reveals a very low number of Mo sites (Fig. 5), whereas the various adsorption mode on the support are not mod-

ified by the sample preparation. The comparison of the spectra of CO adsorbed on 9Mo(S) and 9Mo(exS) catalysts points out that the Mo sites giving rise to the band at 2110 cm^{-1} are preferentially poisoned, while those corresponding to the $\nu(\text{CO})$ shoulder at ca. 2065 cm^{-1} do not seem to be affected by this treatment. This shows that once they are poisoned by such a treatment, the Mo sites giving rise to the band at 2110 cm^{-1} cannot be restored by a re-sulphidation. Such deep modifications of the catalyst by air contact have already been reported [24].

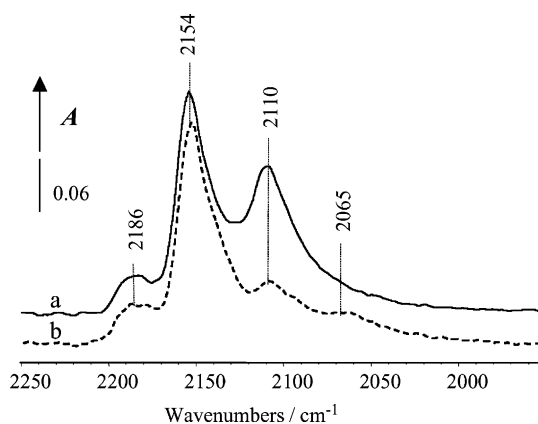


Fig. 5. Comparison of the IR spectra of 1 Torr CO at equilibrium at 100 K adsorbed on 9Mo catalyst either directly sulphided in the IR cell (a) or pre-sulphided ex situ and re-sulphided in the IR cell (b).

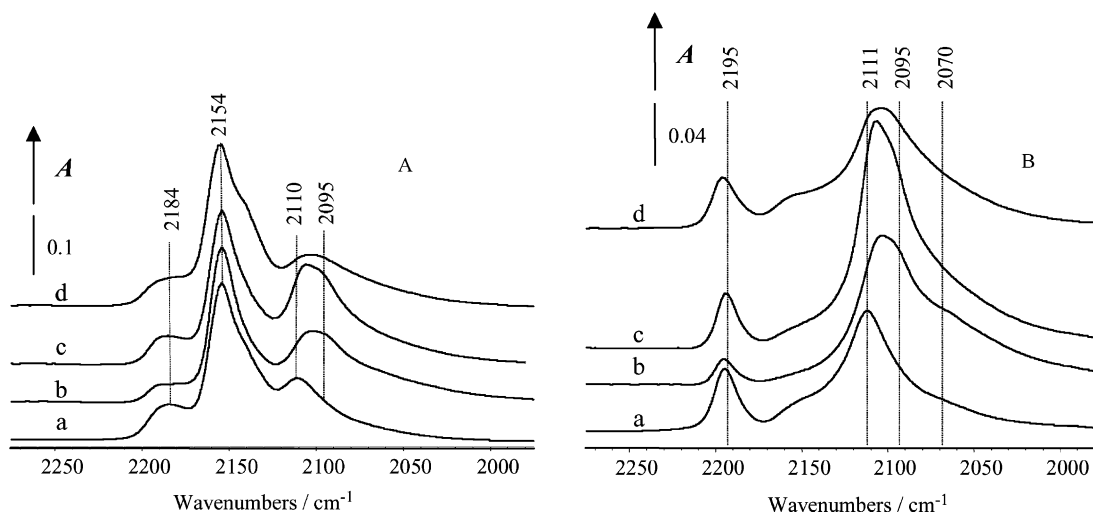


Fig. 6. IR spectra of CO adsorbed at 100 K after various treatment of 8Mo catalyst. (A) 1 Torr of CO at equilibrium; (B) CO evacuated up to $P = 2 \times 10^{-5}$ Torr (a: sulphided catalyst; b: a + H₂ treatment at 473 K; c: b + H₂ treatment at 573 K; d: b + H₂ treatment at 673 K).

Such a selective poisoning clearly confirms the presence of two kinds of edge sites on the MoS₂ slabs giving rise to $\nu(\text{CO})$ bands at 2110 cm⁻¹ (strong) and at a wavenumber lower than 2080 cm⁻¹ (weak).

3.1.4. Effect of a hydrogen treatment

The $\nu(\text{CO})$ spectra obtained after a hydrogen treatment of the 8Mo(S) catalyst are presented in Fig. 6A and B. A strong increase in the intensity of the bands characterising CO adsorption on the sulphide phase is observed up to a reduction temperature of 573 K. Indeed, the corresponding band area is more than twice higher after post-reduction at 573 K than after sulphidation. By contrast, as already reported by Müller et al. [6], intensity of these $\nu(\text{CO})$ bands is strongly decreased after reduction of the catalyst at 673 K.

Besides these variations of intensities, changes in the shape of the $\nu(\text{CO}/\text{MoS}_2)$ massif are also observed. To analyse precisely these modifications induced by reduction, spectra corresponding to introduction of the various CO doses on 8Mo(S) and 8Mo(SR-473) are compared in Fig. 7A. They provide evidence for a decrease in the number of Lewis acid sites of the support upon reduction ($\nu(\text{CO}) = 2191 \text{ cm}^{-1}$) as well as an increase in the number of OH groups ($\nu(\text{CO}) = 2156 \text{ cm}^{-1}$). The band characteristic of the adsorption on the MoS₂ crystallites is also affected. In particular, the maximum of the massif initially present

at 2110 cm⁻¹ on the sulphided sample is shifted to 2105 cm⁻¹, whereas a shoulder at ca. 2095 cm⁻¹ and a broad feature centred at ca. 2055 cm⁻¹ develop after reduction. One should note that the shift of the maximum of the massif towards lower wavenumbers after reduction cannot be related to a modification of the CO coverage, since it is observed even for the first CO doses. Thus, the increase of the $\nu(\text{CO}/\text{MoS}_2)$ massif area as well as the occurrence of new bands shows the creation of new Mo sites upon reduction.

To compare the effect of reduction temperature, the difference between spectra (1 Torr of CO at equilibrium) obtained after successive treatments have been computed and are presented in Fig. 7B. Spectrum 7B-a shows that reduction at 473 K leads to appearance of a band at ca. 2095 cm⁻¹ with a shoulder at 2105 cm⁻¹, and a broad, low wavenumber feature presenting a maximum at ca. 2055 cm⁻¹ with a tail extending down to 2020–2000 cm⁻¹. Spectrum 7B-b shows that reduction at 573 K — compared to reduction at 473 K — induces an increase in the number of sites characterised by the bands at 2095 and 2105 cm⁻¹. A slight increase in intensity is also observed at ca. 2075 cm⁻¹, whereas in contrast with the previous spectrum, no significant variation of absorbance at lower wavenumbers is observed between reduction at 473 and 573 K. The negative intensity of the spectra difference presented Fig. 7B-c indicates that reduction at 673 K

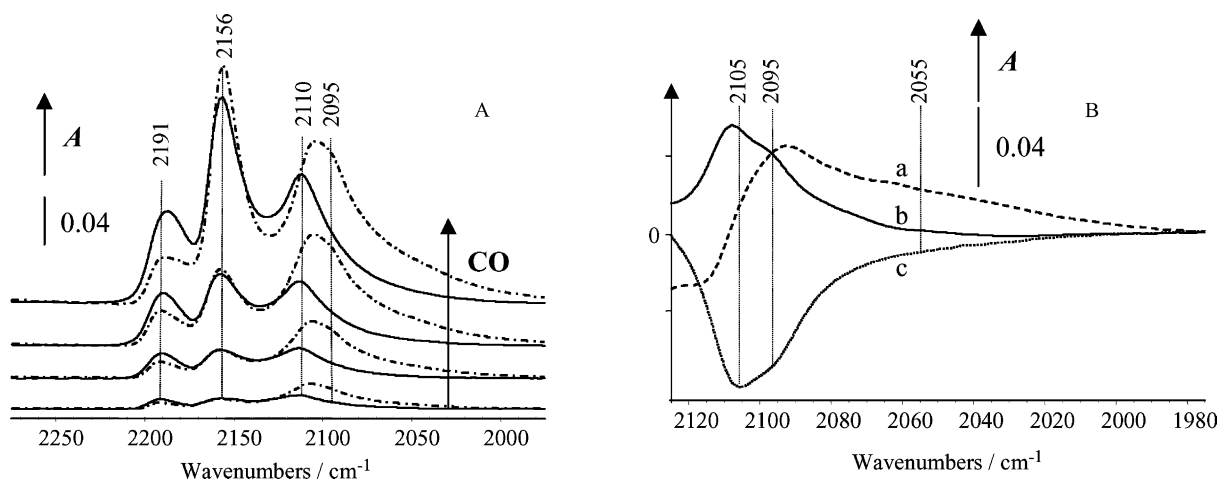


Fig. 7. (A) Comparison of IR spectra of increasing small calibrated CO doses adsorbed at 100 K on 8Mo catalyst either sulphided (—) or sulphided and reduced at 473 K (-----). (B) Difference between spectra corresponding to adsorption of 1 Torr CO at equilibrium at 100 K for two successive treatments of 8Mo catalyst (a: reduced at 473 K minus sulphided; b: reduced at 573 K minus reduced at 473 K; c: reduced at 673 K minus reduced at 573 K).

induces a decrease in the number of sites characterised by bands at 2105 and at 2095 cm⁻¹, the disappearance of the band at 2105 cm⁻¹ being more marked.

Decomposition of the spectra of the reduced catalysts was also performed. It appeared that the $\nu(\text{CO}/\text{MoS}_2)$ massif could not be correctly fitted with only the two bands at ca. 2110 and ca. 2055 cm⁻¹ which were adequate in the case of the sulphided catalyst. In particular, a third band at ca. 2095 cm⁻¹ had to be introduced, confirming the creation of new sites upon reduction. However, although some trends in the variation of the number of sites appear, no quantitative analysis of these modifications can be performed at present, since the molar extinction coefficient of the individual $\nu(\text{CO})$ bands is not known.

Finally, from the analysis of the spectral range characteristic of the adsorption on the MoS₂ edges, several $\nu(\text{CO})$ components can be distinguished as follows:

1. An intense band at ca. 2110 cm⁻¹ present on sulphided catalyst, which increases in intensity and undergoes a slight downward shift upon reduction.
2. A band at ca. 2130 cm⁻¹ which can only be noticed when very small amount of CO are present on Mo edge sites or when large amounts of H₂S are pre-adsorbed.
3. A band at ca. 2095 cm⁻¹ which develops only after reduction of the catalyst.

4. A broad, low wavenumber feature below 2080 cm⁻¹ that is partly present on freshly sulphided catalysts, increases in intensity upon reduction (below 673 K) and spreads at wavenumbers as low as 2000–2020 cm⁻¹. This feature seemingly includes several components that, however, cannot be resolved due to their broadness.

3.2. DFT calculation

3.2.1. Sulphur coverage of the MoS₂ crystallites

Fig. 8A is a representation of the perfect (100) crystal showing alternative rows of molybdenum and sulphur atoms. Therefore, surface of a perfect MoS₂ crystal presents rows of sulphur atoms (called sulphur edge, S edge) or of molybdenum atoms (called molybdenum edge, Mo edge). This perfect surface will be denoted [6–0] as there are six sulphur atoms on the sulphur edge and no sulphur atom on the molybdenum edge. However, the exact nature of the surface stable under the HDS conditions will be defined by the chemical potential of the different species present in the gas surrounding atmosphere. Indeed in previous studies [15,16], it has been shown that the number of sulphur atoms present on the edges of the crystallites is dependent on the H₂/H₂S molar ratio and only three surfaces are thermodynamically stable

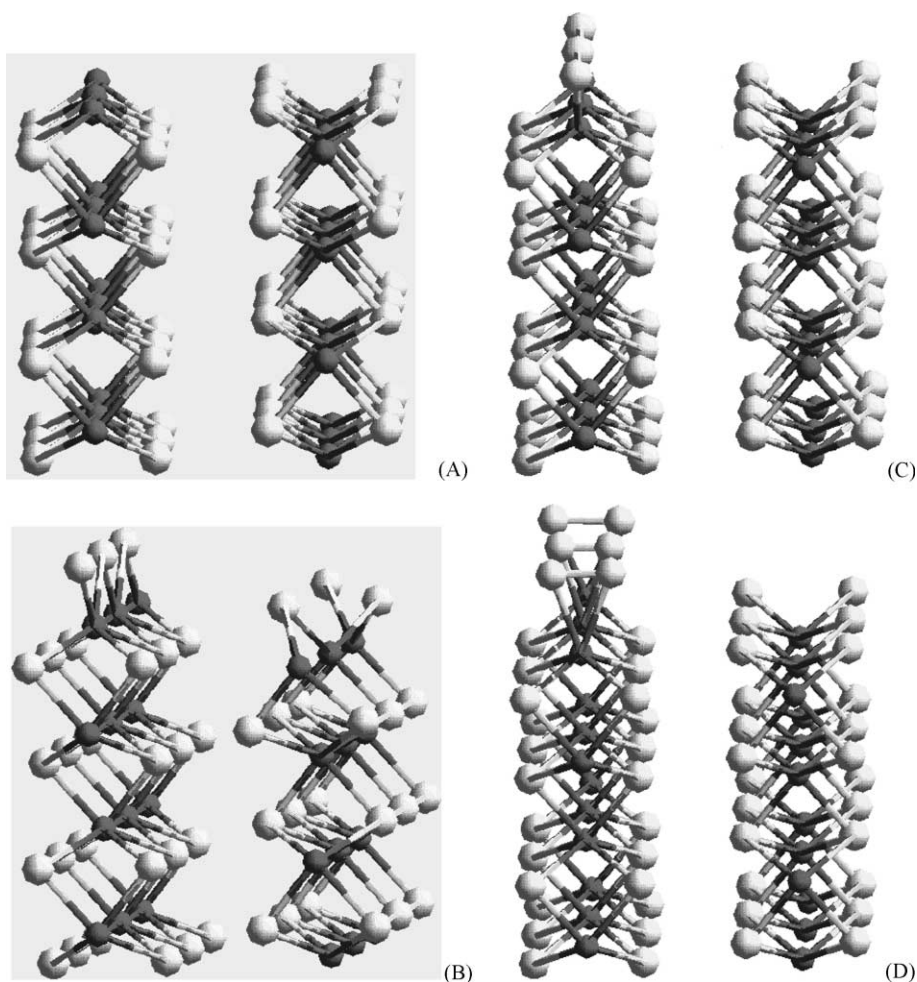


Fig. 8. Representation of the surface modification with the H_2/H_2S partial pressure: (A) perfect (100) MoS_2 surface [6-0]; (B) surface [3-3], stable surface when $H_2/H_2S > 20$; (C) surface [6-3], stable surface when $10^{-4} < H_2/H_2S < 20$; (D) surface [6-6], stable surface when $H_2/H_2S < 10^{-4}$.

within the H_2/H_2S partial pressure ratio defining the zone of stability of MoS_2 . These various surfaces, named as above according to the number of sulphur atoms present on each edge are shown in Fig. 8B–D according to their H_2/H_2S domain of stability.

In reductive conditions (hydrogen rich atmosphere: $H_2/H_2S > 20$) the stable surface is the [3-3] one (Fig. 8B). The coordinations of the molybdenum atoms on the sulphur edge and on the molybdenum edge are, respectively, 4 (Mo_{4c}) and 6 (Mo_{6c}). The terminal sulphur atoms are in bridging position between two molybdenum atoms on both edges but the Mo–S

distances are similar to the distance in the crystal (2.40 Å). Considering only the coordination numbers, we can suppose that CO adsorption on the sulphur edge will be favoured in a H_2 -rich environment.

Decreasing the partial pressure ratio under 20 induces a modification of the surface, the stable one being now the [6-3] one (Fig. 8C). The coordination of the molybdenum atoms of the sulphur edge is increased from 4 to 6, while the geometry of the molybdenum edge does not change. In these conditions, the geometry of the sulphur edge is similar to the geometry of the perfect (100) surface with four bridging sulphur

atoms in a plane above the surface molybdenum atoms. The coordination of Mo on both edges is now 6 which means that there is no more unsaturated site (CUS) on the edges of the crystallite. However, CO adsorption could still be possible on both edges but this adsorption will produce 7-fold coordinated molybdenum atoms.

A second transformation occurs upon decreasing the H_2/H_2S ratio ($H_2/H_2S < 1/10^{-4}$) and in these H_2S -rich conditions, the stable surface is the [6–6] one (Fig. 8D). The geometry of the sulphur edge does not change, whereas the number of sulphur atoms on the molybdenum edge is increased even if the coordination number of the molybdenum does not change (Mo_{6c}). The bridging sulphur atoms shift to a $\mu 1$ position. So the terminal sulphur are now bounded to only one molybdenum atom.

3.2.2. CO adsorption

The post-treatments of the catalysts before CO adsorption were chosen to correspond to the three zones of stability of the MoS_2 edge surfaces. The catalyst should thus expose three different edge surfaces. The adsorption energies of CO on each of these surfaces have been computed and are reported in Table 1.

In the intermediate range of partial pressure ratio, which approximately corresponds to the sulphiding conditions, we have to consider that the crystallites exhibit the [6–3] surface configuration that does not present any CUS site. A top adsorption on the molybdenum edge is possible, but the energy is very weak ($E_{ads} = 0.1$ eV). Fig. 9A is a representation of the optimised structure in which CO interacts with a single Mo atom. In Fig. 9B are represented the iso-surfaces of the electronic density variation induced by the

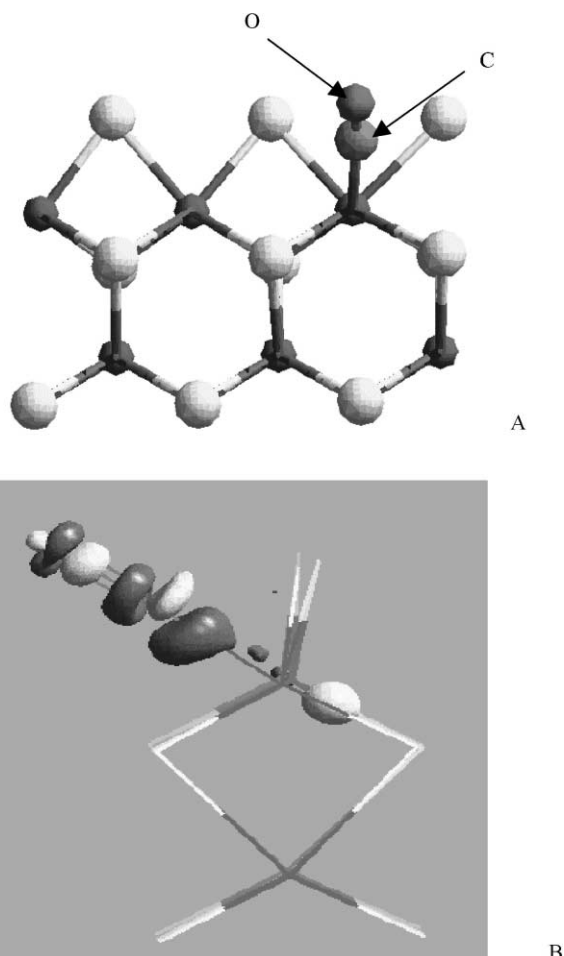


Fig. 9. Optimised configuration for one CO molecule adsorbed on the molybdenum edge [X–3]: (A) adsorption geometry; (B) electron density variation induced by the CO adsorption.

Table 1
Comparison of the calculated properties of CO adsorbed on the various stable MoS_2 edges^a

Edge	Surface	Mo coordination	E_{ads} (eV)	$\nu(CO)$ (cm^{-1})	$\Delta\nu$ (cm^{-1}) ^b	D_{Mo-C} (Å)	D_{C-O} (Å)
Molybdenum	[X–3]	6	0.1	2080	60	1.15	2.08
	[X–6]	6	NA ^c	–	–	–	–
Sulphur	[6–X]	6	0.1	2040	100	1.16	2.06
	[3–X]: 1 CO/cell	4	0.7	2000	140	1.16	2.05
	[3–X]: 2 CO/cell	4	0.7	1995/2035	115	1.16	2.05
	[3–X]: 2 CO/Mo/cell	4	0.7	1965/2015	125	1.16	2.05

^a The calculated free CO stretching vibration is 2143 cm^{-1} .

^b Difference between the calculated stretching wavenumber of the free CO molecule and the adsorbed one.

^c No adsorption.

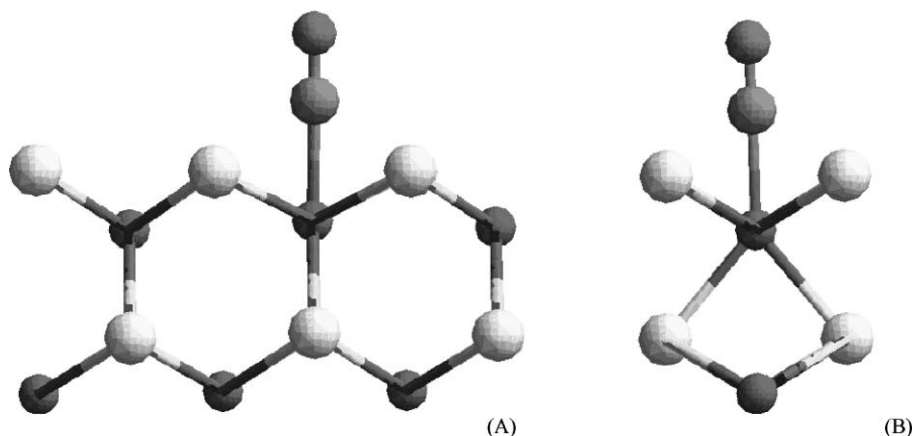


Fig. 10. Optimised configuration for one CO molecule adsorbed on the sulphided sulphur edge [6-X]: (A) front view; (B) side view.

adsorption. The important increase in this density (dark region) between the carbon and the molybdenum reflects the formation of the Mo–C bond. This is the result of electron transfer from both the non-bonding σ CO orbital and the molybdenum in direct interaction with the CO molecule. The back-donation into the π^* CO orbital is shown by the two dark rings around the carbon and oxygen atoms. Attempts have also been made to adsorb a CO molecule in a bridging position between two Mo atoms. Whatever the starting configuration, the final geometry always corresponds to the aforementioned top adsorption. Moreover, it appears that only one CO molecule can adsorb per unit cell. Indeed, attempts to adsorb two CO molecules on two vicinal Mo atoms in the cell were performed, but a destabilisation occurs for this configuration since the adsorption energy of the second molecule is negative (-0.2 eV) even if a minimum can be reached. Thus, only one adsorption mode is possible on the [6–3] molybdenum edge for which the stretching wavenumber is calculated at 2080 cm^{-1} . By comparison with the $\nu(\text{CO})$ wavenumber of the free molecule, a downward shift of 60 cm^{-1} is obtained upon adsorption on this edge.

A top adsorption is also possible on the sulphur edge of the [6–3] surface configuration with an adsorption energy of 0.1 eV similar to the one obtained with the Mo edge. However, the Mo–C distance is shorter (2.06 versus 2.08 \AA) than on the molybdenum edge and the C–O distance longer (1.16 versus 1.15 \AA). The $\nu(\text{CO})$ wavenumber is now calculated at

2040 cm^{-1} , a value that is in agreement with the C–O distance. The CO molecule is perpendicular to the surface as shown in Fig. 10 that gives the geometry after optimisation. This orientation may allow an important overlap: (i) between the non-bonding CO orbital and the first empty surface state, which is mainly d_{z^2} type orbital located on the Mo [14]; (ii) between the empty π^* CO orbital and the last occupied surface states. On the other hand, the distance between the four sulphur atoms and the carbon (2.56 \AA) induces repulsion and lowers the binding energy.

In conditions corresponding to high hydrogen amount, the stable surface configuration is the [3–3] one. The molybdenum edge is the same as on the previous surface and the same CO adsorption mode is therefore obtained. The difference is found on the sulphur edge where three sulphur atoms are removed, creating CUS sites (Mo_{4c} atoms). As a consequence, CO adsorption is much stronger ($E_{\text{ads}} = 0.7$ eV) and the computed stretching frequency shifts towards lower wavenumbers (2000 cm^{-1}), e.g. a shift of 80 cm^{-1} by comparison with CO adsorbed on the molybdenum edge. A representation of the optimised structure is given in Fig. 11. An important difference between the molybdenum edge and the reduced sulphur edge is the number of CO molecules that can adsorb per unit cell on the later edge. Indeed as shown in Fig. 11, two CO molecules can adsorb per unit cell on two vicinal Mo atoms (Fig. 11A and B) or on the same one (Fig. 11C). Whatever the adsorption mode, e.g. mono- or dicarbonyl, the adsorption energy per

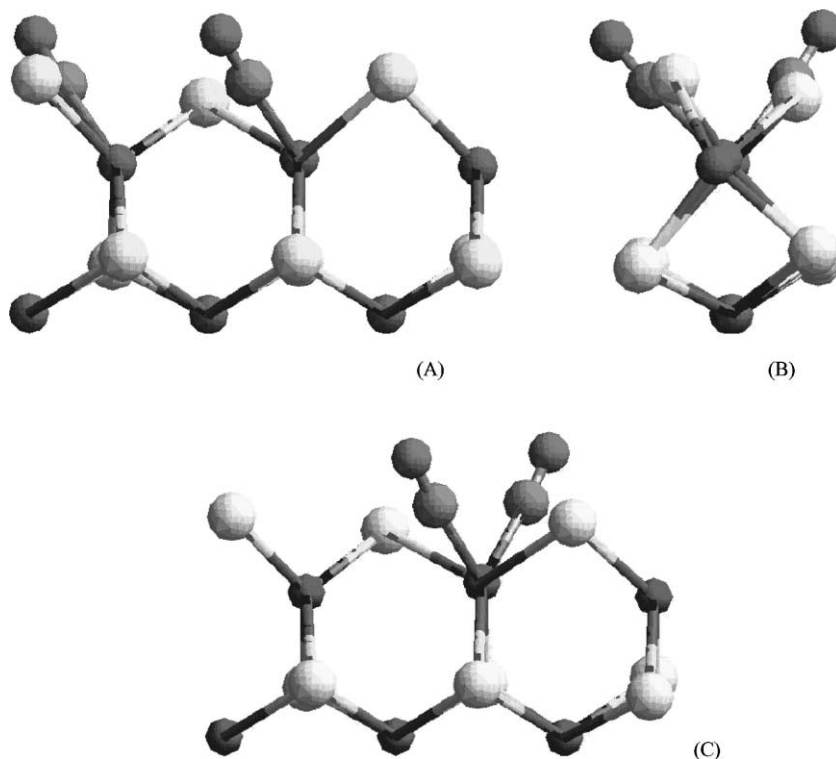


Fig. 11. Optimised configuration for two CO molecules adsorbed on two different molybdenum atoms of the reduced sulphur edge [3–X]: (A) front view; (B) side view; (C) front view of two CO molecules adsorbed on the same molybdenum atom of the reduced sulphur edge [3–X].

CO molecule is the same and corresponds to the value obtained for the adsorption on the Mo edge. The maximum number of CO molecules that can adsorb on this sulphur edge is thus higher than the number that can adsorb on a molybdenum edge and lies between 2-fold and 4-fold the latter one according to the CO uptake. The calculation of the $\nu(\text{CO})$ stretching wavenumber gives the two $\nu(\text{CO})$ values at 2035 and 1995 cm^{-1} for the dicarbonyl geometry (Fig. 11C) and at 2015 and 1965 cm^{-1} for CO adsorbed on vicinal Mo atoms (Fig. 11A and B). The possibility of various mode of adsorptions on this edge can thus be described as a distribution of sites that should induce a broadening of the IR band.

The last stable surface configuration that we have to consider is the [6–6] one that only exist in H₂S-rich conditions. Both edge has 6-fold coordinated Mo atoms, but adsorption of CO can only proceed on the sulphur edge as described above for the [6–3] sulphur

edge surface. Indeed, calculations show that CO adsorption on the molybdenum edge is a very endothermic reaction. This is ascribed to the steric hindrance in the direction of the unoccupied orbitals that is much more important and precludes CO adsorption.

4. Discussion

From experimental results, CO adsorption on MoS₂ slabs gives rise at least to four $\nu(\text{CO})$ bands: (i) a band at 2110–2100 cm^{-1} which is already observed on the sulphided catalyst; (ii) a weak one at ca. 2130 cm^{-1} observed at very low CO coverage or in the case of a partial poisoning of the Mo sites by H₂S; (iii) a band at 2100–2095 cm^{-1} which appears after reduction of the sulphided phase; (iv) a broad feature at 2075–2020 cm^{-1} which is already present after sulphidation and develops under reductive treatment. The

question, which evidently arises, is to which specific sites of the MoS₂ slabs correspond these $\nu(\text{CO})$ bands.

The downwards shift of the $\nu(\text{CO})$ wavenumber as compared with the gas phase, observed upon adsorption on MoS₂-based catalysts, has led to a lot of discussions about the oxidation degree of the Mo sites. It is generally proposed that the shift of the CO stretching mode is due to a lower oxidation degree of the Mo atom that would present an oxidation degree of +2 or even lower [4–6,11,12]. However, direct evidences of these lower oxidation degrees have never been given by XPS. This discrepancy could be related to the fact that XPS characterised both bulk and surface Mo, whereas CO adsorption specifically probes surface Mo atoms. Molybdenum is a very versatile element, which can adopt many oxidation states and coordination. Even if the question of the oxidation degree of the Mo edges still exists, another way to interpret the shift is to consider the probe molecule as a ligand that interacts with Mo atoms of the edge, the coordination of which depends on the surrounding atmosphere.

Taking into account the crystallographic structure of the MoS₂ crystallites, two types of edge were considered, i.e. the sulphur edge and the molybdenum edge. CO adsorption may proceed on both the edges. The appearance of mainly one symmetrical $\nu(\text{CO})$ band (2110 cm⁻¹) with a tail at lower wavenumbers (ca. 2075 cm⁻¹) on the sulphided molybdenum catalysts allows one to deduce that CO is essentially adsorbed on two kinds of Mo site after such a treatment. Calculation shows that, in sulphiding conditions, the stable configuration exhibits [6–3] surface according to our nomenclature. In this configuration, the Mo sites of the molybdenum edges, which are Mo_{6c} ones, can adsorb CO as schematically represented in Fig. 9A. Calculations show that this adsorption configuration induces a shift towards low wavenumber of 60 cm⁻¹ compared to the frequency of the free CO molecule. The band observed at 2110 cm⁻¹ can be assigned to the $\nu(\text{CO})$ vibration of molecules adsorbed on these molybdenum sites (Mo_{6c}) of the molybdenum edges, since it presents a downwards shift of 30 cm⁻¹, which is in rather good agreement with calculations. This attribution is also in accordance with the low value of the calculated adsorption energy as this band disappears by outgassing the catalyst at RT.

On the other hand, the tail observed at low wavenumbers (ca. 2075 cm⁻¹) could be due to CO

adsorbed on the sulphur edge of the [6–3] surface since in this case, the calculated $\nu(\text{CO})$ shift is 40 cm⁻¹ with respect to CO adsorption on the Mo edge, which nicely corresponds to the experimental shift. However, it should be noted that the thermal stability of this species is higher than that giving rise to the band at 2110 cm⁻¹, although calculations indicate the same adsorption energy for both sites (see Table 1).

Qualitative agreement between experiments and calculation are also obtained upon increasing the sulphur coverage of the MoS₂ slabs. Indeed, H₂S introduction on the sulphided catalyst, progressively hinders CO adsorption in agreement with our DFT calculations that show that in rich sulphur atmosphere, both molybdenum and sulphur edge sites are saturated. Calculation showed that adsorption on the molybdenum edge (Mo_{6c}) is not possible, whereas adsorption on the sulphur edge may occur as discussed above.

If a reductive treatment is performed on the sulphided catalyst, modifications of the spectra of adsorbed CO are evidenced that should be assigned to the creation of new Mo sites. An augmentation and a broadening of the low wavenumber features around 2075–2050 cm⁻¹ occur as already reported, and a band at 2100–2095 cm⁻¹, never quoted in the literature, appears. It should be mentioned that previous studies do not report metallic Mo to be formed after such reductive treatments [4]. Calculation indicates that upon reduction, the surface transforms into a [3–3] one, where the molybdenum edge remains unchanged in agreement with the persistence of the band at 2110 cm⁻¹. On the sulphur edge, Mo_{4c} are formed on which CO adsorption may also proceed. An increase in the CO uptake after reduction is therefore expected. From our DFT calculations, the band characteristic of CO adsorbed on these Mo sites should be observed at lower wavenumber than for CO adsorption on molybdenum edge. A wavenumber decrease of at least 115 cm⁻¹ depending on the adsorption configuration is calculated. Taking into account calculated CO wavenumber shift, the bands at 2055–2020 cm⁻¹ could be assigned to CO adsorption on the reduced sulphur edges. Moreover, the absence of intensity variation of this band upon degassing at 100 K (Fig. 6) is in agreement with the high adsorption energy (0.7 eV) of CO on these sites. Calculations indicate that various configurations of adsorption are possible on this kind of edges, e.g. monocarbonyl on vicinal Mo atoms and/or

dicarbonyl adsorption configuration. This could explain the broadness of the low wavenumber features.

In a previous study [6], the low wavenumber band which develops after reduction of the catalyst was attributed to CO adsorption on corner sites. Indeed, the authors envisage that corner sites present a lower sulphur coordination number than edge ones. However, our calculations show that the coordination number of surface sites is difficult to presume because strong reorganisation of the surface occurs when sulphur atoms are eliminated. Therefore, modelisation of corner sites should be done to confirm or infer such attribution. At this stage of our investigation, we consider that this low wavenumber $\nu(\text{CO})$ corresponds to CO in interaction with Mo atoms of lower coordination, mainly arising upon reduction.

Experiments performed on an ex situ sulphided catalyst show that an irreversible poisoning of the Mo sites occurred. It is interesting to note that the sensitivity of the 2110 cm^{-1} band to air contact is higher than the $2050\text{--}2075\text{ cm}^{-1}$ one. From the previous attribution, one can consider that the metallic edge sites of the [6–3] surface are more easily poisoned by laboratory atmosphere than the sulphur edge.

Some sites remain however unidentified. Indeed the high wavenumber band at 2130 cm^{-1} , which is observed when few amounts of CO are adsorbed on the sulphided catalyst, is not attributed. Moreover, the reduction also leads to the appearance of a band at 2095 cm^{-1} . Its wavenumber very close to that of CO adsorbed on the Mo_{6c} sites of metallic edges (2110 cm^{-1}) discards its attribution to adsorption on reduced sulphur edge sites (Mo_{4c}). An intermediate coordination of Mo (Mo_{5c}) has to be considered and calculations are in progress to interpret this band.

5. Conclusion

This paper reported an investigation of carbon monoxide adsorption on sulphided Mo catalysts by means of IR spectroscopy and ab initio calculations. Both techniques show that the surface state of the sulphided phase is strongly modified by post-treatment with H_2 or H_2S . The parallel between experimental and calculated results on MoS_2 allowed us to attribute the main $\nu(\text{CO})$ bands. Results may be summarised as follows:

- After sulphidation, $\nu(\text{CO})$ spectra mainly consist in: (i) an intense band at ca. 2110 cm^{-1} ; (ii) a tail at lower wavenumbers. These bands are, respectively, attributed to CO adsorption on: (i) 6-fold coordinated Mo of the molybdenum edge and (ii) 6-fold coordinated Mo of the sulphur edge of MoS_2 crystallites exhibiting [6–3] surfaces.
- After a reductive treatment, new features appear: (i) below 2080 cm^{-1} , the tail of $\nu(\text{CO})$ band develops and spreads down to $2000\text{--}2020\text{ cm}^{-1}$; (ii) a band at 2095 cm^{-1} develops. These features are attributed to CO adsorption on: (i) 4-fold coordinated Mo of the reduced sulphur edge under the form of mono- or dicarbonyl species; (ii) possibly 5-fold coordinated Mo atoms.
- A weak, hardly visible band at ca. 2130 cm^{-1} could not be attributed with our model.

Finally, this first confrontation of results issued from experiments and theoretical calculations allows a better understanding of the surface-site configuration, by the way it confirms that the calculated surfaces are suitable for surface modelisation.

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CO Adsorption on CoMo and NiMo Sulfide Catalysts: A Combined IR and DFT Study

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Experimental IR spectra of carbon monoxide adsorbed on a series of Mo/Al₂O₃, CoMo/Al₂O₃, and NiMo/Al₂O₃ sulfided catalysts have been compared to ab initio DFT calculations of CO adsorption on CoMo and NiMo model surfaces. This approach allows the main IR features of CO adsorbed on the sulfide phase to be assigned with an uncertainty of 15 cm⁻¹. On the CoMo system, the band at 2070 cm⁻¹ is specific of the promotion by Co and is assigned to CO interacting either with a Co atom or with a Mo atom adjacent to a Co atom. On the NiMo system, CO adsorption on Ni centers of the promoted phase leads to a high-wavenumber band at ~2120 cm⁻¹ that strongly overlaps the band at 2110 cm⁻¹ characteristic of nonpromoted Mo sites. For NiMo and CoMo catalysts, broad shoulders at low wavenumbers (below 2060 cm⁻¹) are characteristic of Mo centers adjacent to promoter atoms, indicating a partial decoration of the MoS₂ edges by the promoter.

1. Introduction

Mo-based sulfide catalysts are widely used in hydrotreatment processes that aim at reducing the heteroatom content (sulfur, nitrogen, and metals) of petroleum feedstocks.¹ The active phases of conventional hydrotreating catalysts consist of mixed sulfide nanosized particles (Co–Mo–S or Ni–Mo–S) supported on high specific surface area alumina. It is accepted that these particles are basically made of MoS₂ sheets, the promoter atoms (Co or Ni) being localized on their (100) edges.¹ The catalytic activity of these catalysts in hydrotreating reactions such as hydrodesulfurization (HDS) is usually related to anionic vacancies (coordinatively unsaturated sites, CUS) located on these edges. An accurate description of these sites, however, is still missing. A convenient way to characterize these vacancies is the use of probe molecules, the adsorption mode of which is characterized by IR vibrational spectroscopy. Nitrogen monoxide and carbon monoxide have been mostly employed as probe molecules of the CUS of the sulfide-based catalysts. Upon adsorption, specific IR features are observed, providing information on the adsorption mode and indirectly on the nature of the sites. The amount of the different sites on which they adsorb can be assessed through the absorbance. Nitrogen monoxide has been the most employed since it presents the advantage to be strongly adsorbed on the sulfide phase (see, e.g., ref 2 for a recent application). However a partial oxidation of the sulfide phase may occur, even at very low temperatures.³ The reliability of this probe may therefore be questioned, and many disagreements are found in the literature on the IR observations of NO adsorbed on sulfide catalysts.⁴

Carbon monoxide has been less used to characterize sulfide catalysts although no undesired reaction between the sulfide phase and CO occurs if the adsorption is performed at low temperature. On sulfided Mo/Al₂O₃ catalysts, a strong band at ~2110 cm⁻¹ is observed together with a weak, broad component

at ~2070 cm⁻¹.^{5–7} Both bands characterize CO adsorption on the edge sites of the MoS₂ slabs, these sites being considered as active sites since linear correlations have been established between the intensity of these bands and HDS catalytic activities of these Mo/Al₂O₃ catalysts.⁸ Infrared spectra of CO adsorbed on the sulfided promoted CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are much more complex and do not result from a simple combination of the spectra obtained on the corresponding monometallic catalysts. New bands and intensity changes occur, demonstrating the formation of specific “promoted” sites to the detriment of “nonpromoted” Mo sites. Thus, in the case of CoMo/Al₂O₃ catalysts, a strong band at ~2070 cm⁻¹ appears while the intensity of the band at 2110 cm⁻¹ characteristic of nonpromoted Mo sites decreases. The intensity of the new band at 2070 cm⁻¹ is also directly correlated to the HDS catalytic activity,⁹ which allows the authors to propose that adsorption proceeds on catalytic sites. However, the exact nature of these promoted sites is not yet clearly established since the corresponding $\nu(\text{CO})$ band is located at an intermediate frequency, between those corresponding to the adsorption on nonpromoted Mo and on Co sites. Similar questions arise in the case of NiMo/Al₂O₃ catalysts.

Hence, the question of the nature and location of the sites on which CO adsorbs is still under debate, and IR spectroscopy alone is unlikely to provide an answer. Molecular modeling of these nanocrystallites is one possible approach to get a better insight into the nature of the sites. The recent development of computational techniques, especially periodic DFT methods, currently allows more realistic sulfide surfaces to be studied (see ref 10 and references therein). In a previous study,¹¹ we have investigated the adsorption of CO molecules on a series of nonpromoted Mo sulfide catalysts. Comparison of experimental spectra and theoretical calculations showed that the CO stretching frequency is not only sensitive to the coordination number of the Mo centers but also to the location of the Mo center on which CO is adsorbed. These results obtained through a periodic approach¹¹ are in agreement with recently published

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data in which the authors have carried out DFT calculations with MoS_x clusters containing different Mo/S ratios.¹²

The aim of the present work is to specify the structure and the nature of CO adsorption sites on Co–Mo–S and Ni–Mo–S phases. For this purpose, a study combining infrared spectroscopy and periodic DFT calculations was carried out. In the following, we first describe the experimental and theoretical methods used in this work. IR experiments in which CO was adsorbed on a series of sulfided CoMo and NiMo catalysts are then presented. After a brief description of the CoMo and NiMo (100) model surfaces, we describe in detail the adsorption of CO on the various CUS sites available on these model surfaces. These theoretical results are finally compared with experimental spectra, and an assignment of the observed IR bands is proposed.

2. Experimental Section

Monometallic $\text{Mo}/\text{Al}_2\text{O}_3$ (8.7 wt % Mo), $\text{Co}/\text{Al}_2\text{O}_3$ (3.4 wt % Co), and $\text{Ni}/\text{Al}_2\text{O}_3$ (3.0 wt % Ni) catalysts were prepared by pore-filling impregnation of a γ -alumina support ($258 \text{ m}^2 \text{ g}^{-1}$, $0.66 \text{ cm}^3 \cdot \text{g}^{-1}$) with ammonium heptamolybdate, cobalt nitrate, and nickel nitrate solutions, respectively. The samples were dried at 393 K overnight and calcined at 773 K for 3 h. The series of CoMo and NiMo catalysts were prepared by impregnation of the molybdenum catalyst with cobalt nitrate and nickel nitrate solutions, respectively. They were further dried and calcined at 773 K for 3 h. The catalysts contained 1.7, 3.2, and 4.7 wt % cobalt (CoMo series) and 0.5, 1.5, and 3.4 wt % nickel (NiMo series) as determined by elemental analysis performed at the Service Central d'Analyse (CNRS, Vernaison, France). For the infrared study, the catalyst was ground, pressed into self-supported wafers ($\sim 5 \text{ mg} \cdot \text{cm}^{-2}$, $\varnothing = 1.6 \text{ cm}$) and placed into the IR cell. Prior to sulfidation, the catalyst was dried in situ at atmospheric pressure at 423 K under N_2 and cooled to 298 K. It was then sulfided with 10% H_2S in H_2 (30 mL/min) with a heating rate of 3 K/min up to 623 K. After 2 h of sulfiding at 623 K, the catalyst was flushed with N_2 for 0.25 h, and the temperature was decreased to 298 K. The sulfide catalyst was rapidly evacuated at 573 K and finally cooled to 100 K for CO adsorption. The catalyst was then contacted with increasing amounts of CO up to an equilibrium pressure of 133 Pa. IR spectra of adsorbed CO were recorded with a Nicolet Magna 550 IR spectrometer equipped with an MCT detector. For comparison, all the spectra were normalized to a disk of $5 \text{ mg} \cdot \text{cm}^{-2}$ of sulfided catalyst.

3. Computational Techniques

The calculations were performed using the VASP (Vienna ab initio simulation package) software^{13–15} based on the density functional theory.^{16,17} The electron–ion interactions were modeled by ultrasoft pseudopotentials (US-PP).^{18,19} To compute reliable adsorption energies, the nonlocal functional using generalized gradient approximations (GGA) proposed by Perdew and co-workers was applied^{20,21} and the wave function was expanded over a planewaves basis set with an energy cutoff of 300 eV. The solution of the Kohn–Sham equation was improved self-consistently until a difference between successive iterations lower than 10^{-4} eV in electronic energy was reached. A Methfessel–Paxton²² smearing with $\sigma = 0.1$ eV was applied in order to compute the band occupation, and all calculations were carried out with Γ point integration as a consequence of the large size of the cell (i.e., $12.64 \times 20.0 \times 6.15 \text{ \AA}^3$).

Figure 1 shows the supercell used in the present study, which contains four Mo rows along the x direction, four rows along the y direction and one MoS_2 layer along the z direction. The

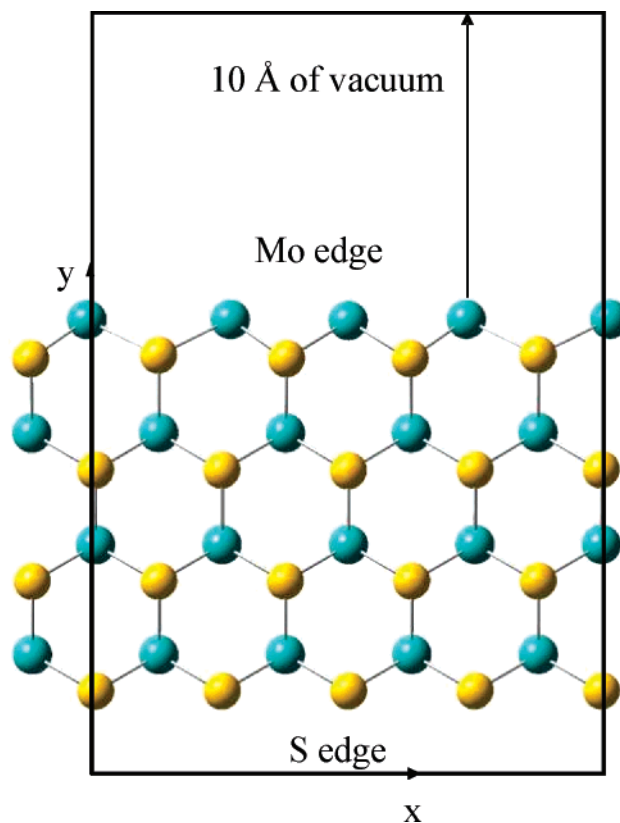


Figure 1. Representation of the supercell used for calculations; x and y correspond to the Cartesian axes. Yellow circles, S atoms; light blue circles, Mo atoms.

MoS_2 (100) plane represents the active surface of the catalyst and exhibits alternative edges of molybdenum atoms and sulfur atoms, called “molybdenum edge” (M-edge) and “sulfur edge” (S-edge), respectively.²³ As we take into account one layer in our calculations, each model represents either a molybdenum edge or a sulfur edge. With this setting, the stacking order of crystalline MoS_2 is not taken into account. However, since vicinal slabs interact only via van der Waals forces, the electronic properties of the MoS_2 sheets are well described in this model. Moreover, interactions between CO molecules of vicinal cells are negligible since CO is a very small molecule. The optimization of the atomic positions was performed using a conjugate gradient minimization of the total energy, until all exact Hellmann–Feynman forces acting on ions were smaller than $3 \times 10^{-2} \text{ eV} \cdot \text{\AA}^{-1}$. Only the two upper rows of the MoS_2 slab were included in this optimization; the two lower ones were frozen in the bulk geometry. The localization of the promoter atoms has been previously studied by DFT calculations.^{24,25} These results indicated that the promoter is preferentially located on the edge of the particles in substitutions of the Mo atoms, in agreement with recent atomically resolved STM images.²⁶

As previously shown,^{27,28} the sulfur coverage of the two types of MoS_2 edges, i.e., the molybdenum and the sulfur edges, depends on the $\text{H}_2/\text{H}_2\text{S}$ partial pressure ratio in the surrounding atmosphere. The determination of the sulfur coverage of the edges was performed by considering the thermodynamic equilibrium between the surfaces and the surrounding atmosphere. Extended details on the methodology are reported in the work of Cristol et al.²⁸

The CO vibration frequencies were calculated by numerical differentiation of the force matrix. The CO stretching vibrational mode being very weakly coupled with the vibration of the surface, only the part of the matrix corresponding to the atoms

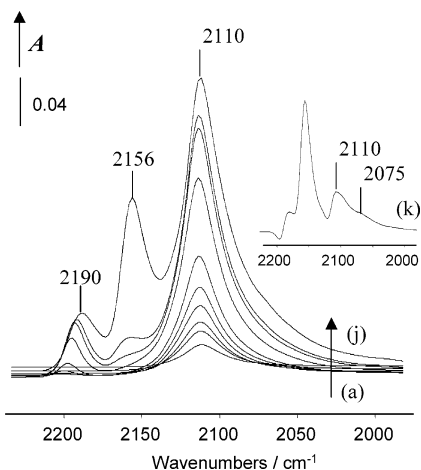


Figure 2. IR spectra of CO adsorbed (100 K) on sulfided Mo/Al₂O₃ catalyst (8.7 wt % Mo). Spectra a–i: doses of 20, 60, 130, 230, 390, 650, 1170, 1960, and 3000 μ mol of CO per g of catalyst. Spectrum j: 133 Pa of CO at equilibrium. Inset, spectrum k: difference between spectra j and i: (k) = (j) – (i).

closest to CO was taken into account in the diagonalization process. All the calculated CO stretching frequencies are scaled by a factor of 1.03, determined to obtain the best fit between the experimental and calculated wavenumbers. It should be mentioned that a slightly different scaling factor was used in our previous work¹¹ because of differences in the unit cell size that changed the basis set.

4. Results

4.1. IR Characterization of CO Adsorption.

4.1.1. Mo/Al₂O₃. Spectra obtained after introduction of increasing amounts of CO on the sulfide Mo/Al₂O₃ catalyst are presented in Figure 2. The first doses of CO lead to the appearance of an intense, symmetrical band at 2110 cm⁻¹ characteristic of CO adsorption on the sulfide phase noted ν -(CO/Mo).^{5–7} As the coverage increases, other bands appear at 2190 cm⁻¹ and 2156 cm⁻¹. They are due to CO adsorption on the Al₂O₃ support and correspond respectively to coordination on Al³⁺ Lewis acid sites and hydrogen bonding with the surface hydroxyl groups. At the highest coverage, a shoulder is observed at 2075 cm⁻¹, on the low-wavenumber side of the intense ν -(CO/Mo) band. This shoulder, which is better evidenced on difference spectra between successive CO doses (inset of Figure 2), is also characteristic of CO adsorption on the sulfide phase.

4.1.2. Co/Al₂O₃. Figure 3 shows the spectra obtained after CO adsorption on the sulfide Co/Al₂O₃ catalyst. In addition to the bands due to CO adsorption on the support (2190 and 2156 cm⁻¹), a sharp band at 2094 cm⁻¹ and a broad shoulder below 2070 cm⁻¹ are observed, which correspond to adsorption on the sulfide phase.

4.1.3. CoMo/Al₂O₃. Spectra obtained after introduction of increasing amounts of CO on the sulfide CoMo/Al₂O₃ catalyst are presented in Figure 4. At low CO coverage, two bands appear at 2110 and 2070 cm⁻¹ together with a shoulder at 2055 cm⁻¹ that are characteristic of the adsorption on the sulfide phase. Upon increasing the CO coverage, bands corresponding to adsorption on the support (2200–2190 and 2156 cm⁻¹) appear, whereas the intensity of the aforementioned bands at 2110, 2070, and 2055 cm⁻¹ continue to increase. Figure 4B compares the spectra obtained after CO adsorption at equilibrium (133 Pa) on Mo/Al₂O₃ and CoMo/Al₂O₃ catalysts with increasing Co content. It shows that the presence of Co leads to the appearance of the band at 2070 cm⁻¹ and of the shoulder at

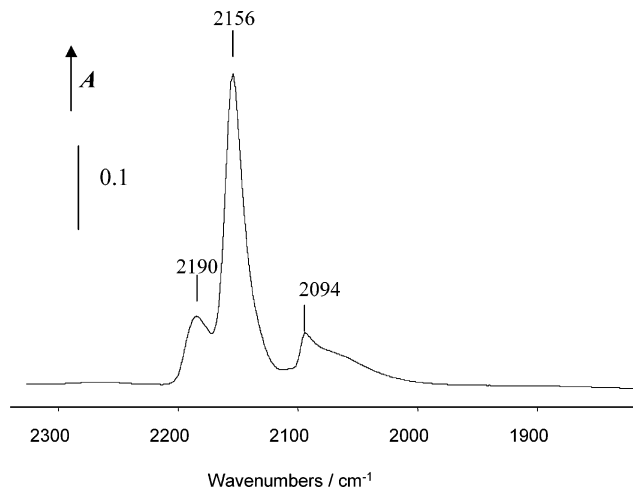


Figure 3. CO adsorption (133 Pa, 100 K) on sulfided Co/Al₂O₃ catalyst (3.4 wt % Co).

2055 cm⁻¹ to the detriment of the band at 2110 cm⁻¹. Hence, the promoted phase presents at least two characteristic sites induced by the presence of cobalt, leading to a main band at 2070 cm⁻¹ and a shoulder at 2055 cm⁻¹. These bands are due to CO adsorption on either Mo or Co centers different from those obtained on sulfided monometallic Mo/Al₂O₃ and Co/Al₂O₃ catalysts.

4.1.4. Ni/Al₂O₃. Spectra obtained after introduction of CO on the sulfided Ni/Al₂O₃ catalyst (spectra not shown) present, in addition to the bands due to CO adsorption on the support, a single asymmetric band at \sim 2092 cm⁻¹, close to that observed on sulfided Co/Al₂O₃. This band reflects CO adsorption on the sulfide Ni phase.

4.1.5. NiMo/Al₂O₃. Spectra obtained after introduction of CO on sulfided NiMo/Al₂O₃ catalysts are shown in Figure 5. In addition to the bands due to CO adsorption on the support (2200–2190 and 2156 cm⁻¹), four bands at \sim 2120, 2110, 2085, and 2060–2045 cm⁻¹ due to CO adsorption on the sulfide phase are detected. The comparison of the spectra obtained after CO adsorption on the series of sulfide NiMo/Al₂O₃ catalysts shows that, by contrast with the CoMo series of catalysts (Figure 4B), increasing the promoter content does not lead to an apparent decrease of the intensity of the band at 2110 cm⁻¹ (nonpromoted Mo sites). On the other hand, an increase in the intensity of the bands at 2120, 2085, and 2060–2045 cm⁻¹ is observed as the promoter content increases. These bands were not observed on monometallic catalysts and could be considered as due to CO adsorption on “promoted” sites, either Mo or Ni centers.

4.2. Periodic DFT Calculations.

4.2.1. Surface Structures. The (100) surface of a perfect MoS₂ crystal (Figure 6A) presents rows of molybdenum atoms (M-edge) or of sulfur atoms (S-edge). The structure of the stable surface is defined by the chemical potential of the various species present in the surrounding atmosphere. In particular, sulfur coverage of these surfaces drastically depends on the H₂/H₂S molar ratio.^{27,28} In the present work, the M-edge and the S-edge were treated separately. In the following, we will present the structures of these two edges in sulfiding conditions (i.e., H₂/H₂S ratio around 10). Indeed, in the case of promoted systems, it has been shown^{24,25} that the surface structure is the same in sulfiding and reducing conditions.

4.2.1.1. Nonpromoted Surface. The thermodynamic stability of (100) MoS₂ surfaces was investigated in previous studies.^{23,28} Stable surfaces in reducing (hydrogen-rich atmosphere, H₂/H₂S > 10) and sulfiding conditions (H₂/H₂S \sim 10) are shown in

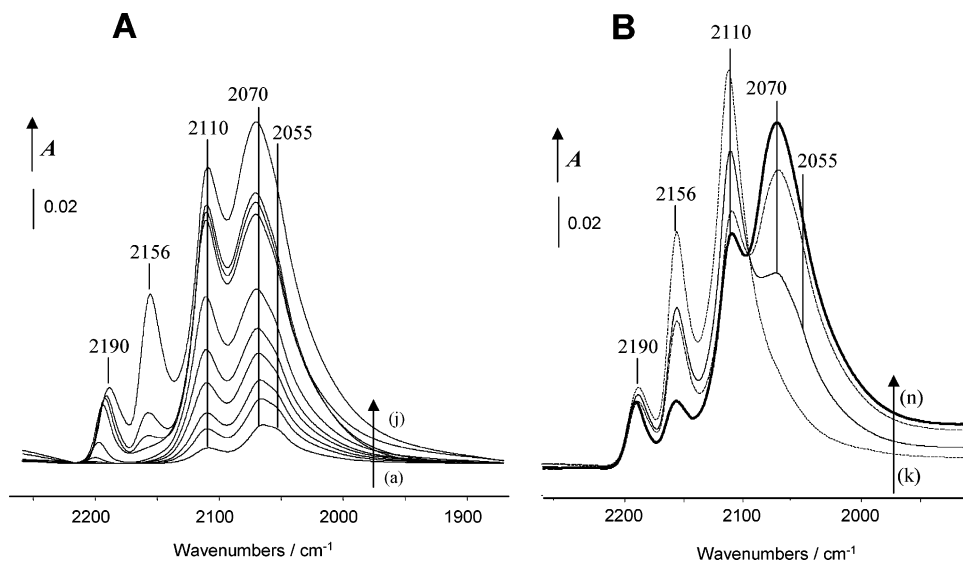


Figure 4. (A) IR spectra of CO adsorbed (100 K) on sulfided CoMo/Al₂O₃ catalyst (3.2 wt % Co, 8.7 wt % Mo). Spectra a–i: doses of 20, 70, 140, 250, 420, 700, 1260, 2100, and 3230 μ mol of CO per g of catalyst. Spectrum j: 133 Pa of CO at equilibrium. (B) IR spectra of CO adsorbed on Mo/Al₂O₃ catalyst (k) and CoMo/Al₂O₃ catalysts containing 1.7 (l), 3.2 (m), and 4.7 (n) wt % Co.

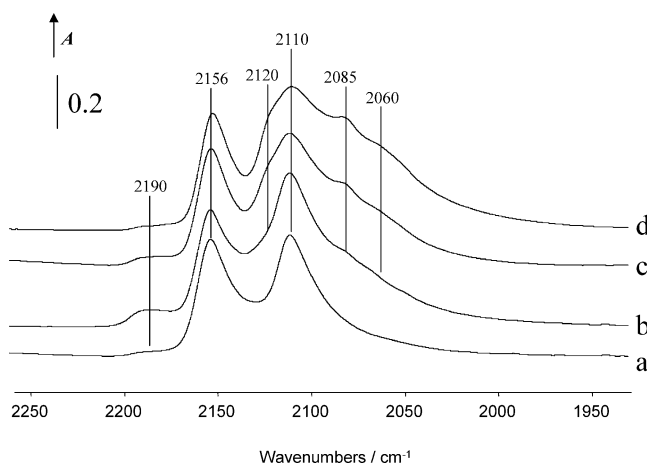


Figure 5. IR spectra of CO adsorbed on sulfided (Ni)Mo/Al₂O₃ catalysts (133 Pa, 100 K). (a) Mo/Al₂O₃ (8.7 wt % Mo); (b–d) NiMo/Al₂O₃ containing 0.5, 1.5, and 3.4 wt % Ni, respectively.

Figure 6, parts B and C, respectively. The M-edge is not very sensitive to the H₂/H₂S ratio. Indeed, in both conditions, this edge exhibits 6-fold coordinated Mo atoms (Mo_{6c}) in a trigonal prismatic environment and terminal sulfur atoms bridging successive Mo_{6c} atoms. Conversely, the structure of the S-edge changes with modifications of the H₂/H₂S ratio. In sulfiding conditions, Mo atoms are 6-fold coordinated (Mo_{6c}), in a trigonal prismatic environment similar to that of the bulk one. In reducing conditions, the sulfur coverage of this edge decreases, and Mo atoms become 4-fold tetrahedrally coordinated (Mo_{4c}). The remaining bridging sulfur atoms are positioned alternatively on both sides of the molybdenum plane, forming a zigzag chain.

4.2.1.2. Promoted Surfaces. Two degrees of substitution were investigated, corresponding to the two limits of our model: partial substitution in which one Mo atom at the edge is substituted by one promoter atom (25% substitution) and full substitution in which all surface molybdenum atoms are substituted by promoter atoms (100% substitution). Recent theoretical studies^{25,29} have shown that Co and Ni substitution are thermodynamically favored on the S-edge and M-edge, respectively. It is worth noting, however, that these studies do not exclude alternative locations (Co on the M-edge and Ni on the S-edge), although such location should be less abundant.²⁵

Moreover, our experimental work is carried out on alumina-supported catalysts, and many parameters such as the kinetics of the formation of the active phases during the sulfidation or sulfide–support interactions play an important role regarding the final structure of the sulfide phase. Hence, both edges have been considered in this study.

4.2.1.3. Promotion by Cobalt Atoms. As shown in previous studies,^{23,24} for the fully Co-substituted edge, only one configuration of the fully Co-substituted edges is stable under either reducing (H₂/H₂S > 10) or sulfiding (H₂/H₂S ~ 10) conditions (Figure 7). All cobalt atoms are 4-fold coordinated on both edges. On the M-edge, their environment is almost square planar and alternate Co–Co distances (3.23 and 2.83 Å) are observed (Figure 7B). On the S-edge, Co atoms are tetrahedrally coordinated with the S atoms lying in the plane of metallic atoms.

For 25% substitution of Mo by Co atoms, only one surface is stable for H₂/H₂S molar ratio larger than 10 (Figure 8), corresponding to both sulfiding and reducing conditions. The M-edge exhibits only one sulfur atom bridging two Mo atoms, leading to two 5-fold (Mo_{5c}) and one 4-fold (Mo_{4c}) coordinated molybdenum atoms. The Co atom is, again, 4-fold coordinated (Co_{4c}); however its environment is no longer square planar. Indeed, an important surface reconstruction occurs, and one of the sulfur atoms initially just below the surface moves above the plane of the metallic atoms. This rearrangement leads to vicinal Co_{4c} and Mo_{4c} atoms in a tetrahedral environment. The partially substituted S-edge exhibits the zigzag configuration of the S atoms, as in the case of the nonpromoted catalyst in reducing conditions. It is worth noting that on the sulfur edge, for all the Co substitution ratios (0%, 25%, and 100%), both Co and Mo atoms are 4-fold coordinated in a tetrahedral environment.

4.2.1.4. Promotion by Nickel Atoms. The substitution of all the Mo atoms by Ni on the M-edge leads to the same stable surface as the one obtained with total substitution by Co. The Ni atoms are 4-fold coordinated in a square planar environment (Figure 9). Conversely, the structure of the fully substituted S-edge differs from those calculated for the nonpromoted or for Co-promoted edges since only three sulfur atoms are present. In that case the sulfur edge exposes two 3-fold coordinated Ni_{3c} atoms and two 4-fold coordinated Ni_{4c} atoms (Figure 9).

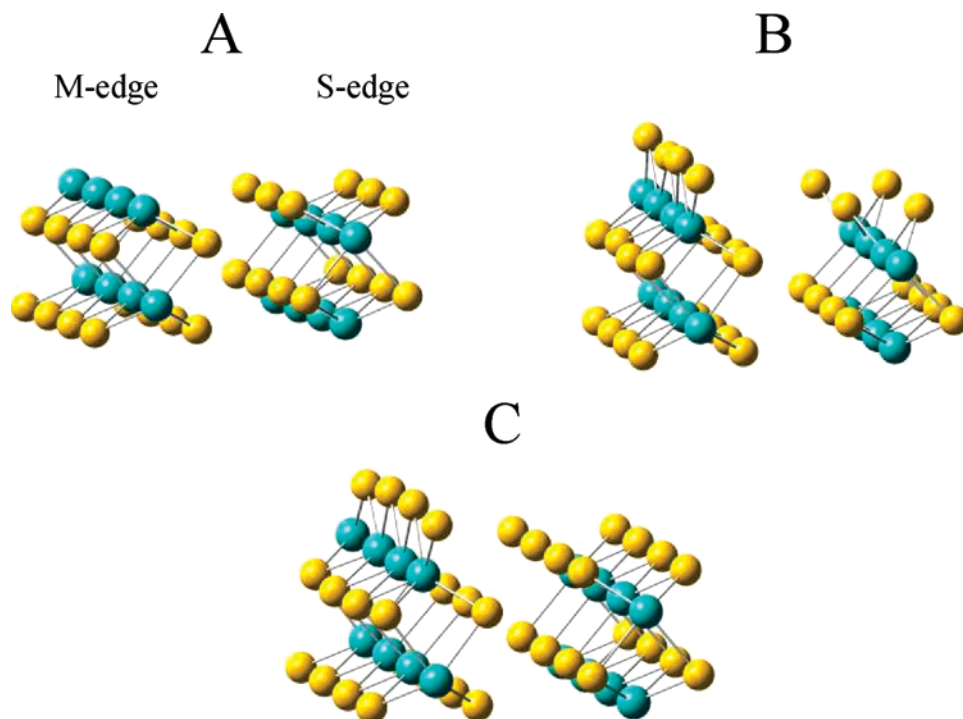


Figure 6. Representation of the MoS₂ edges for various H₂/H₂S partial pressure: (A) perfect (100) plane; (B) stable surfaces in reducing condition; (C) stable surfaces in sulfiding conditions. For each representation, the M-edge is on the left, the S-edge is on the right. Yellow circles, S atoms; light blue circles, Mo atoms.

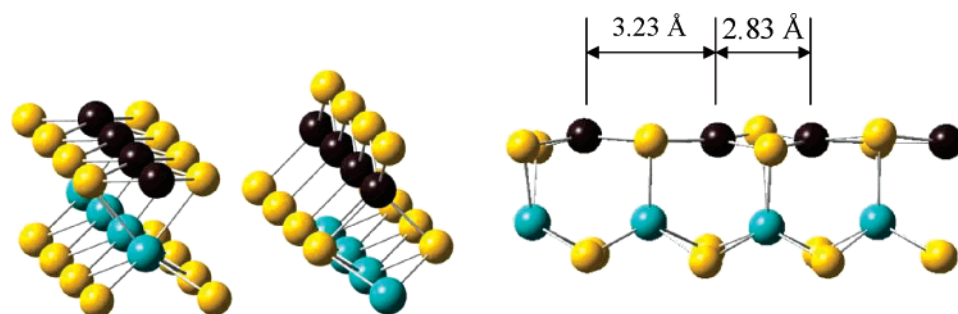


Figure 7. Representation of the stable fully Co-promoted surfaces (M-edge is on the left, S-edge is on the right). Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Co atoms.

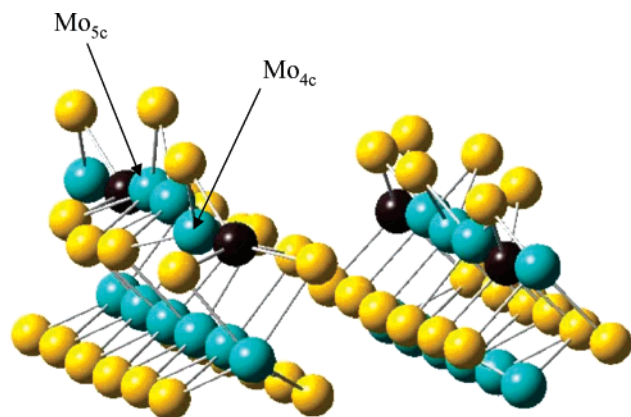


Figure 8. Representation of the stable 25% Co-promoted surfaces (M-edge is on the left, S-edge is on the right). Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Co atoms.

For a partial substitution, the stable M-edge surface presents 4-fold square planar Ni_{4c} atom adjacent to two 5-fold coordinated Mo_{5c} atoms, the last Mo atom of the unit cell remaining 6-fold coordinated (Figure 10). The sulfur edge adopts a geometry similar to that of pure MoS₂ in a reductive environ-

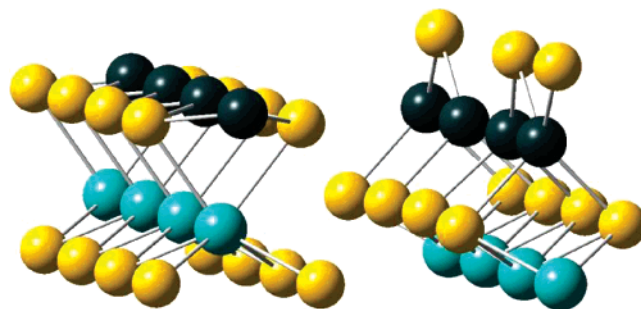


Figure 9. Representation of the stable fully Ni-promoted surfaces (the M-edge is on the left, the S-edge is on the right). Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Ni atoms.

ment (zigzag configuration). As for the partially promoted CoMo surface, this edge presents Mo_{4c} and Ni_{4c} in a tetrahedral environment.

4.2.2. CO Adsorption. Calculated properties of CO adsorbed on the various stable surfaces of the Co- and Ni-promoted catalysts are described below and summarized in Tables 1 and 2. It should be noted at first that there is no general correlation between adsorption energy and CO stretching frequencies.

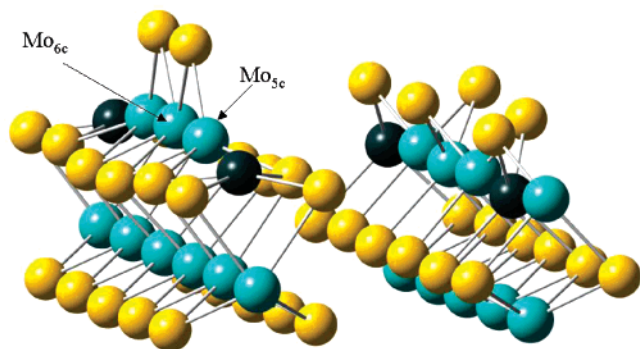


Figure 10. Representation of the stable 25% Ni-promoted surfaces (M-edge is on the left, S-edge is on the right). Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Ni atoms.

TABLE 1: Calculated Properties of CO Adsorbed on the Co-Promoted MoS₂ Edge

degree of promotion	edge type	metal coordination	E_{ads} (eV)	$\nu(\text{CO})$ calcd (cm ⁻¹)	$\nu(\text{CO})$ exptl (cm ⁻¹)
100%	M	Co _{4c}	1.40	2083	2070
	S	Co _{4c}	0.70	2080	2070
25%	M	Co _{4c}	0.97	2076	2070
	M	Mo _{4c}	1.30	2054	2055
	M	Mo _{5c}	1.07	2080	2070
	S	Co _{4c}	0.71	2065	2070
	S	Mo _{4c}	0.66	2041	2055
0%	Mo	Mo _{6c}	0.1	2100	2110
	S	Mo _{6c} (Mo _{4c}) ^a	0.1 (0.7) ^a	2060 (2020) ^a	2075

^a Only in an H₂S-poor atmosphere, H₂/H₂S > 20 (see ref 11).

TABLE 2: Calculated Properties of CO Adsorbed on the Ni-Promoted MoS₂ Edge

degree of promotion	edge type	metal coordination	E_{ads} (eV)	$\nu(\text{CO})$ calcd (cm ⁻¹)	$\nu(\text{CO})$ exptl (cm ⁻¹)
100%	M	Ni _{4c}	1.30	2138	2120
	S	Ni _{4c}	0.65	2117	2120
	S	Ni _{3c}	0.75	2101	2110
25%	M	Ni _{4c}	0.56	2100	2110
	M	Mo _{5c}	0.86	2022	2060–2040
	M	Mo _{6c}	0.21	2050	2060–2040
	S	Ni _{4c}	0.40	2117	2120
	S	Mo _{4c}	0.62	2047	2060–2040
0%	M	Mo _{6c}	0.1	2100	2110
	S	Mo _{6c} (Mo _{4c}) ^a	0.1 (0.7) ^a	2060 (2020) ^a	2075

^a Only in an H₂S-poor atmosphere, H₂/H₂S > 20 (see ref 11).

Indeed, CO adsorption has been studied on various cations (Mo, Co, Ni), and the position of the d band differs for each cation. Variations of coordinative environments (number of S ligands and geometries) also change the steric repulsion between the molecule and the surface with small effect on the back-donation. Thus, a general correlation cannot be expected within so different systems.

4.2.2.1. CO Adsorption on the Nonpromoted Mo-Edge. We summarize here the main results concerning CO adsorption on nonpromoted MoS₂ presented previously in ref 11, taking into account the new scaling factor (1.03 vs 1.02) for the computed frequencies. On the M-edge, only Mo_{6c} are present in the conditions we are interested in. The computed CO stretching wavenumber is 2100 cm⁻¹ with a low adsorption energy (0.1 eV). On the sulfur edge, two types of Mo sites are available, depending on the surrounding atmosphere. In a sulfur atmosphere (H₂/H₂S molar ratio lower than 20), CO adsorption on Mo_{6c} is weak (0.1 eV) and the calculated wavenumber $\nu(\text{CO})$

is 2060 cm⁻¹. In more reductive conditions, the surface molybdenum atoms are tetrahedrally coordinated and CO adsorption on these lower coordinated Mo sites is stronger (0.7 eV) and leads to a lower wavenumber (2020 cm⁻¹) for the CO stretching vibration.

4.2.2.2. CO Adsorption on the Fully Co-Substituted Edge. Co atoms on the two edges are all 4-fold coordinated. On the M-edge, CO adsorbs on top position (Figure 11A), the adsorption energy being very high (1.4 eV) due to the square planar configuration of Co atoms (Table 1). The stretching wavenumber of CO is calculated at 2083 cm⁻¹, and the Co–C and the C–O distances are 1.76 and 1.16 Å, respectively. CO adsorption on the S-edge (Figure 11B) leads to a wavenumber (2080 cm⁻¹) similar to the one obtained on the M-edge, although the adsorption energy is half (0.7 eV). The C–O bond length is similar for adsorption on both edges (1.16 Å), whereas the Co–C bond length is larger on the S-edge (1.81 vs 1.76 Å).

4.2.2.3. CO Adsorption on the Partially Co-Substituted Edge. Three different surface sites are available on the partially substituted M-edge for CO adsorption (Mo_{5c}, Mo_{4c}, Co_{4c}). CO adsorption on Co_{4c} is weaker (0.97 eV) than in the case of a fully substituted surface (1.40 eV), because of the pseudo-tetrahedral coordination of Co (Figure 12A), which weakens the Co–C bond. However this steric repulsion does not affect the calculated stretching wavenumber (2076 cm⁻¹), which is similar to the CO stretching wavenumbers calculated on the fully substituted surface: 2083 cm⁻¹ on the M-edge and 2080 cm⁻¹ on the S-edge. CO adsorption on Mo_{5c} centers (Figure 12B) is strong (1.07 eV) and leads to a $\nu(\text{CO})$ wavenumber computed at 2080 cm⁻¹, close to the frequency calculated for the adsorption on the Co_{4c}. Finally, a third $\nu(\text{CO})$ value of 2054 cm⁻¹ is obtained for the adsorption on the Mo_{4c} with an adsorption energy of 1.30 eV. On the sulfur edge, CO adsorbs on tetrahedral Co_{4c} and Mo_{4c} centers with similar adsorption energies (0.71 and 0.66 eV, respectively). The $\nu(\text{CO})$ stretching wavenumber for the adsorption on Co_{4c} (2065 cm⁻¹) is lower than the one obtained on the totally substituted S-edge (2080 cm⁻¹). On the other hand, the wavenumber calculated for the adsorption on Mo_{4c} in the vicinity of Co_{4c} (2041 cm⁻¹, Figure 12C) is about 20 cm⁻¹ greater than on the nonpromoted S-edge. The presence of Co as promoter, for all the Co-substitution degrees (0%, 25%, or 100%), does not affect the CO adsorption energy on 4-fold coordinated metallic atoms of the sulfur edge (about 0.7 eV).

4.2.2.4. CO Adsorption on the Fully Ni-Substituted Edge. The M-edge of this surface exposes 4-fold coordinated, square planar Ni atoms (Figure 9). The CO molecule adsorbs in a top position on Ni, with Ni–C and C–O bond lengths of 1.80 and 1.15 Å, respectively (Figure 13A). The adsorption energy (1.30 eV) is almost as large as the one obtained on the fully substituted CoMo M-edge (1.40 eV), and the $\nu(\text{CO})$ wavenumber is calculated at 2138 cm⁻¹. The sulfur edge, presenting one sulfur vacancy, exposes 4-fold and 3-fold coordinated Ni atoms. The adsorption energies on both sites are close to 0.7 eV (0.75 eV on Ni_{3c} (Figure 13B) and 0.65 eV on Ni_{4c}). These values are similar to those obtained on the nonpromoted and Co-promoted sulfur edge. The $\nu(\text{CO})$ wavenumber is computed at 2101 cm⁻¹ for adsorption on Ni_{3c} and 2117 cm⁻¹ for adsorption on Ni_{4c}. The C–O bond lengths are equivalent (1.15 Å) and the Ni–C distances are similar (1.78 Å on Ni_{3c} and 1.79 Å on Ni_{4c}).

4.2.2.5. CO Adsorption on the Partially Ni-Substituted Edge. The partially Ni-substituted M-edge exposes bridging S atoms that are not observed on the corresponding CoMo surface

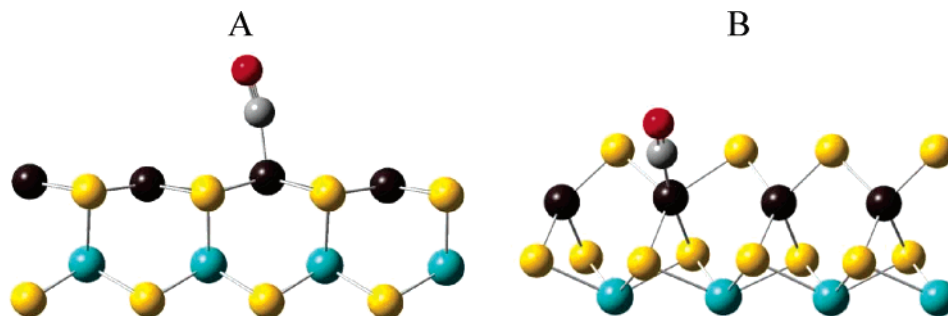


Figure 11. Adsorption geometries of CO molecule on the 100% Co-substituted catalyst: (A) M-edge; (B) S-edge. Yellow circles, S atoms; light blue circles, Mo; dark circles, Co atoms; gray circles, C atoms; red circles, O atoms.

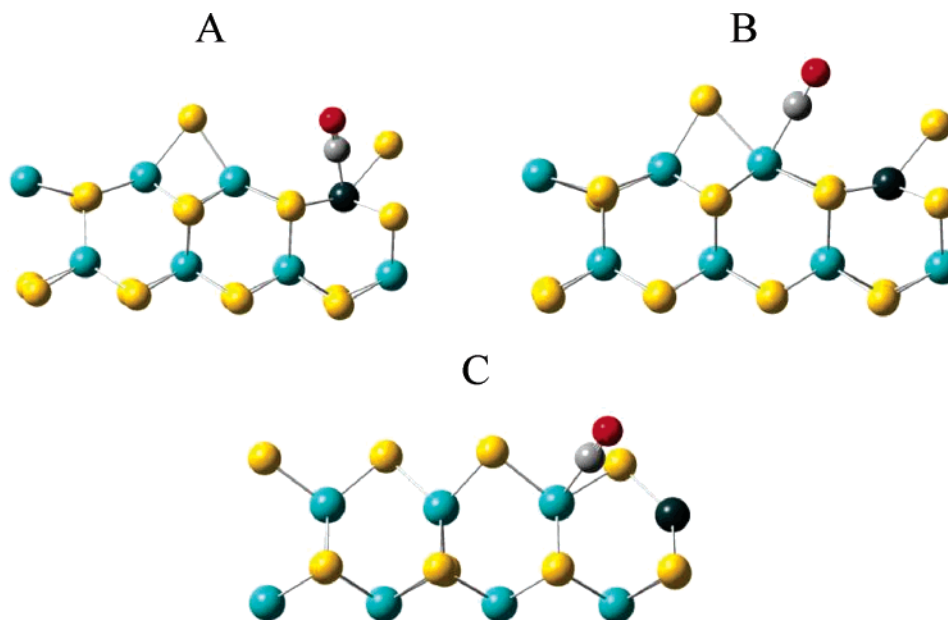


Figure 12. Adsorption geometries of CO molecule on the 25% Co-substituted catalyst: (A) M-edge Co_{4c} ; (B) M-edge Mo_{5c} ; (C) S-edge Mo_{4c} . Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Co atoms; gray circles, C atoms; red circles, O atoms.

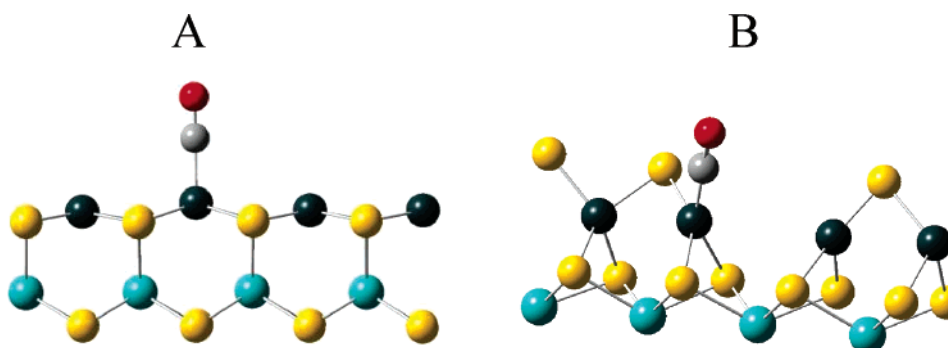


Figure 13. Adsorption geometries of CO molecule on the 100% Ni-substituted catalyst: (A) M-edge; (B) S-edge. Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Ni atoms; gray circles, C atoms; red circles, O atoms.

(Figure 10). The Ni promoter atom is square planar 4-fold coordinated. As in the case of the fully substituted M-edge, the CO molecule adsorbs in a top position on this site (Figure 14A), but with a much lower adsorption energy (0.56 vs 1.30 eV). This lower adsorption energy can be explained by the presence of the steric hindrance due to the two vicinal bridging S atoms on the surface. As a consequence, the Ni–C distance (1.85 Å) is longer than the Ni–C distance (1.80 Å) when the surface does not exhibit bridging S atoms. This steric hindrance disfavors σ donation, and the corresponding calculated $\nu(\text{CO})$ stretching wavenumber is 2100 cm^{-1} , downward shifted by 38 cm^{-1} with respect to that of CO adsorbed on a Ni_{4c} site of the

fully substituted M-edge. On Mo_{6c} , CO adsorbs with an adsorption energy of 0.21 eV, leading to a stretching CO wavenumber of 2050 cm^{-1} . In agreement with its lower coordination number, Mo_{5c} leads to a stronger adsorption (0.86 eV) and a lower stretching frequency (2022 cm^{-1}). The stable sulfur edge exhibits Ni_{4c} and Mo_{4c} atoms with sulfur atoms in a zigzag configuration described previously. CO adsorption on Ni_{4c} (Figure 14B) is slightly weaker (0.40 eV) than on the fully substituted surface (0.65 eV) and leads to a $\nu(\text{CO})$ stretching wavenumber of 2047 cm^{-1} . CO adsorption on Mo_{4c} adjacent to the Ni_{4c} center is exothermic (0.62 eV) and leads to a stretching frequency of 2047 cm^{-1} . A similar value (2041 cm^{-1})

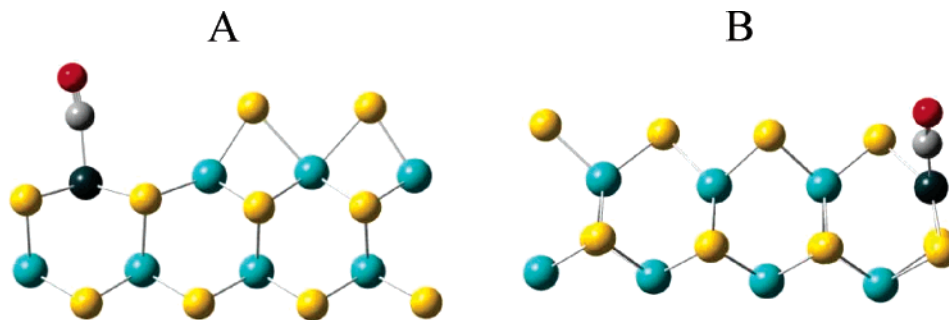


Figure 14. Adsorption geometries of CO molecule on the 25% Ni-substituted catalyst: (A) M-edge Ni_{4c}; (B) S-edge Ni_{4c}. Yellow circles, S atoms; light blue circles, Mo atoms; dark circles, Ni atoms; gray circles, C atoms; red circles, O atoms.

was obtained for the adsorption on Mo_{4c} belonging to the sulfur edge partially promoted by Co.

5. Discussion

5.1. Assignment of Experimental IR Spectra.

5.1.1. CO Adsorption on Mo Catalysts. CO adsorption on the sulfide phase of Mo/Al₂O₃ catalysts gives rise to a sharp band at 2110 cm⁻¹ and a broad shoulder at ~2070 cm⁻¹ extending toward low wavenumbers (Figure 2). Based on our calculations, we previously assigned the band at 2110 cm⁻¹ to CO adsorption on Mo_{6c} centers located on the M-edge of nonpromoted MoS₂ (computed at 2100 cm⁻¹) and the shoulder at ~2070 cm⁻¹ to CO adsorption on Mo centers of the sulfur edge (computed at 2060 and 2020 cm⁻¹).¹¹ Recently, based on cluster DFT Calculations, Zeng et al. have assigned the band at 2110 cm⁻¹ to the symmetric stretching mode of a dicarbonyl species adsorbed on a corner of triangular MoS₂ cluster.³⁰ However, experimental spectra clearly show that the band at 2110 cm⁻¹ cannot be due to a dicarbonyl species. Indeed this band already appears at the lowest CO coverages and is very symmetric (Figure 2), whereas dicarbonyl species should give rise to a doublet of bands corresponding to antisymmetric and symmetric stretching modes.

5.1.2. CO Adsorption on CoMo Catalysts. The main feature of CO spectra obtained on CoMo catalysts is the intense band at 2070 cm⁻¹, which intensity increases with the Co content. On the basis of our calculations, several assignments are possible: CO adsorption on (i) Co_{4c} of the fully substituted edges (2080 and 2083 cm⁻¹), (ii) Co_{4c} of the partially substituted S-edge (2065 cm⁻¹), and (iii) Co_{4c} and Mo_{5c} adjacent to a cobalt atom of the partially substituted M-edge (2076 and 2080 cm⁻¹). Accordingly, the band at 2070 cm⁻¹ is clearly related to the CoMoS phase and probably corresponds to several types of adsorption sites since it can be related to CO adsorbed on cobalt on both edges of the sulfide slabs and on a molybdenum atom close to a cobalt atom on the M-edge of the crystallites.

A shoulder at ~2055 cm⁻¹, was also detected on the promoted phase. According to the computed wavenumber, this band is assigned to the adsorption on Mo_{4c} on the partially substituted edges (M-edge, 2054 cm⁻¹; S-edge, 2041 cm⁻¹). Thus, this band is characteristic of 4-fold coordinated Mo centers adjacent to Co atoms on partially substituted edges.

5.1.3. CO Adsorption on NiMo Catalysts. CO adsorption on the sulfide phase of NiMo catalysts gives rise to four characteristic ν (CO) bands at 2120, 2110, 2085, and 2060 cm⁻¹ (Figure 5). The band at the highest wavenumber (2120 cm⁻¹) is assigned to CO adsorption on the fully substituted M-edge. Calculations indicate a top adsorption of CO with a high adsorption energy on these sites (1.3 eV). A weak back-donation from the surface to the CO molecule explains this high ν (CO) wavenumber

computed at 2138 cm⁻¹. An alternative assignment is an adsorption on the Ni atoms of the sulfur edge of the partially substituted surfaces (calculated at 2117 cm⁻¹) with a smaller adsorption energy (0.40 eV). Thus, in any case, this band at high wavenumber corresponds to CO adsorption on Ni centers of the NiMoS phase.

The band at 2110 cm⁻¹ has been assigned to CO adsorption on the nonpromoted M-edge. In the case of the NiMo surface, however, CO adsorption on Ni_{3c} of the fully substituted S-edge and Ni_{4c} of the partially substituted M-edge can also contribute to this band as the corresponding computed wavenumbers are 2101 and 2100 cm⁻¹. Such a contribution can explain the constant intensity of this band with increasing Ni content (Figure 5).

The band at 2085 cm⁻¹ is close to that observed when CO is adsorbed on a pure nickel sulfide phase,³¹ and our calculations do not allow any alternative assignment. We have therefore to consider the formation of NiS_x particles to the detriment of NiMoS phases.

Finally, the broad band toward 2060 cm⁻¹ is assigned to CO adsorption on Mo sites of the partially Ni-substituted edges. Indeed, values computed between 2022 and 2050 cm⁻¹ were obtained for CO adsorbed on Mo centers adjacent to Ni atoms. Thus, on Ni-promoted catalysts, it appears possible to distinguish CO adsorption on Ni sites from that on Mo sites in the vicinity of Ni atoms.

5.2. Structure of Supported Sulfide Phases in View of ν (CO) Spectra.

All experimental and computed CO frequencies are in agreement within 15 cm⁻¹. This is considered reasonable in view of the complexity of these catalytic systems. In this section, we examine to which extent experimental ν (CO) spectra can provide insight into the structure of Al₂O₃-supported Mo, CoMo, and NiMo sulfide phases.

On nonpromoted catalysts, the CO stretching frequency is sensitive to the nature of the edge (S- or M-edge) on which it adsorbs. Experimental spectra essentially show a sharp band at 2110 cm⁻¹ (M-edge) with a broad, ill-defined shoulder at ~2070 cm⁻¹ (S-edge), which indicates that supported MoS₂ crystallites expose both types of edges after sulfidation. This is in agreement with recent STM investigations of gold-supported MoS₂ clusters³² that showed hexagonally truncated morphologies after sulfidation in similar conditions (7% H₂S in H₂ at 723 K).

Compared to nonpromoted catalysts, the salient IR features of CO adsorbed on CoMo/Al₂O₃ catalysts is the decrease of the band at 2110 cm⁻¹ (nonpromoted M-edge) in favor of broad bands at 2070 and ~2055 cm⁻¹ (sh). The decrease in intensity of the band characteristic of nonpromoted M-edge at 2110 cm⁻¹ is a strong indication of cobalt insertion on the M-edge and is in agreement with recent computational studies showing that

partial substitution of this edge by Co is thermodynamically stable.²⁵ An alternative explanation for this intensity decrease could be a change of the morphology of the MoS₂ slabs. Indeed, Co insertion in the sulfur edge could induce the preferential formation of this type of edge to the detriment of nonpromoted M-edges. Such morphology changes have been proposed from DFT calculations²⁹ and have been observed on gold-supported model catalysts.³²

Our assignments show that adsorption on both the Co and Mo centers contribute to the bands at 2070 and 2055 cm⁻¹. For all the surfaces taken into consideration, the Co centers are 4-fold coordinated and CO adsorption on these sites gives rise to close stretching wavenumbers, computed between 2083 and 2065 cm⁻¹, accounting for the band observed at 2070 cm⁻¹. Thus, it appears that CO is neither sensitive to the location (S- or M-edge) nor to the coordinative environment (square planar or tetrahedral) of the Co centers. By contrast, CO adsorption on Mo centers leads to a wider range of stretching wavenumbers. Insertion of Co on the M-edge induces a decrease of the coordination number of vicinal Mo atoms from 6 on nonpromoted surface to 5 or 4 on promoted surfaces. The corresponding computed CO stretching wavenumbers decrease with coordination: Mo_{6c} (2100 cm⁻¹) > Mo_{5c} (2080 cm⁻¹) > Mo_{4c} (2054 cm⁻¹).

CO adsorption on tetrahedral Mo_{4c} centers of the S-edge also leads to low stretching wavenumbers (2020 and 2041 cm⁻¹, Table 1). CO adsorption on these various 4-fold coordinated Mo centers accounts for the shoulder observed at ~2055 cm⁻¹. It is worth mentioning that this shoulder as well as the band at 2110 cm⁻¹ is observed on all the CoMo catalysts studied in the present work, even for those with the highest Co loadings. Similar observations have been made in the case of commercial CoMo/Al₂O₃ catalysts.³³ According to our assignments, this indicates that the edges of MoS₂ sulfide particles are partially substituted by Co, leading to low-coordinated Mo sites adjacent to Co sites.

On the M-edge, the decrease of the Mo coordination increases the filled d density of states at the Fermi level²⁴ and thus favors back-donation into the antibonding 2π* CO orbital, leading to a decrease of the CO stretching frequency. It should be noted that lowering the coordination of the Mo centers also increases their acceptor properties,^{24,34} which favors σ donation from CO. Because of the synergy between σ donation and π* back-donation,³⁵ much higher adsorption energies are observed as the Mo coordination decreases (Table 1). These low-coordination sites combining donor and acceptor properties are not sterically hindered and could thus be particularly reactive.

On NiMo surfaces, CO adsorption on Ni centers gives rise to higher wavenumbers (bands at 2120–2110 cm⁻¹, computed at 2138–2100 cm⁻¹) as compared to the adsorption on Co centers (band at 2070 cm⁻¹, computed at 2083–2065 cm⁻¹). This difference is consistent with the ν(CO) frequencies of Ni and Co carbonyl complexes.³⁶ The high wavenumber of CO adsorbed on Ni centers of promoted surfaces can be explained by a lower density of states at the Fermi level compared to that of Co,²⁴ which limits the back-donation from the last occupied surface states to the empty 2π* CO orbital. On the other hand, the assessment of the degree of promotion of NiMo catalysts, as performed for CoMo catalysts, is difficult because of the strong overlap of the bands due to CO adsorption on Ni centers with the bands due to CO adsorption on unpromoted Mo sites (2110 cm⁻¹). In this respect, it is worth mentioning that the use of NO as a probe molecule could be more appropriate for NiMo catalysts, since it allows Ni-promoted sites to be

distinguished from nonpromoted Mo sites.³⁷ Finally, as for CoMo surfaces, partial substitution of Mo atoms of the M-edge by the promoter lowers the coordination number of adjacent Mo atoms. CO adsorption on these sites leads to low (CO) wavenumbers and results in the appearance of a broad shoulder at ~2060 cm⁻¹ which is observed even on the catalysts presenting the highest Ni loadings. As for CoMo/Al₂O₃ catalysts, this indicates a partial decoration of the edges of MoS₂ crystallites by the promoter.

6. Conclusions

This contribution reports a combined theoretical and infrared investigation of CO adsorption on sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts. Comparison of the experimental ν(CO) spectra with the computed stretching frequencies of CO adsorbed on model surfaces allows us to propose an assignment for the new bands that appear on the promoted catalysts. The main results can be summarized as follows:

Nonpromoted Mo/Al₂O₃ shows a sharp ν(CO) band at 2110 cm⁻¹ assigned to 6-fold coordinated Mo centers of the M-edge and a weak shoulder at ~2075 cm⁻¹ assigned to Mo centers of the S-edge of MoS₂, showing that Al₂O₃-supported MoS₂ crystallites exhibit both types of edges. CoMo/Al₂O₃ catalysts are characterized by a broad band at 2070 cm⁻¹ and a shoulder at ~2055 cm⁻¹ that are specific of the promotion. The band at 2070 cm⁻¹ is assigned to CO interacting either with a Co atom or with a 5-fold coordinated Mo atom adjacent to a Co. The shoulder at ~2055 cm⁻¹ is assigned to CO adsorption on 4-fold coordinated Mo sites adjacent to Co. On NiMo/Al₂O₃ catalysts, CO adsorption on Ni centers leads to high-wavenumber bands at ~2120 cm⁻¹ strongly overlapped with the band at 2110 cm⁻¹ characteristic of nonpromoted Mo sites. A broad shoulder at lower wavenumbers (~2060 cm⁻¹) is characteristic of CO adsorption on 4-fold coordinated Mo centers adjacent to promoter atoms.

Finally, for both promoted systems, the simultaneous presence of the band at 2110 cm⁻¹ (nonpromoted Mo sites) and of the shoulder at low wavenumber (2055–2060 cm⁻¹, 4-fold coordinated Mo sites) is a strong indication of a partial decoration of the MoS₂ edges by the promoter.

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Basic Properties of Supported Transition Metal Sulfides.

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Introduction

The catalytic activity of transition metal sulfides in hydrotreating reactions such as hydrodesulfurization (HDS) is usually related to their anionic vacancies (coordinatively unsaturated sites, CUS).¹ The structure and properties of these sites have been studied in-depth using chemisorption of probe molecules – in particular infrared spectroscopy of NO² and CO,³ as well as *ab initio* or DFT modeling techniques.^{4,5} By now, a clearer picture of these CUS sites has emerged from these studies, notably for Mo-based catalysts. Comparatively, little is known on the properties of sulfur atoms of the sulfide phase which are expected to play a key role in hydrogenation reactions (H₂ dissociation leading to SH groups, hydrogenation of adspecies...).

The aim of the present work was to specify the basic properties of supported sulfide phases. For this purpose, a series of supported sulfided phases (Mo, CoMo, Ru and Pt) was characterized using pyrrole (C₄H₄NH) and deuteriated chloroform (CDCl₃) as a probe molecules,⁶ before and after sulfur removal by a hydrogen treatment. The sulfur basicity was assessed by comparing the corresponding infrared spectra with those obtained for solutions of CDCl₃ in organic sulfides: dimethyl disulfide (DMDS), dibutyl sulfide (DBS) and tetrahydrothiophène (THT). Finally, DFT calculations were carried out to model CDCl₃ adsorption on MoS₂ compared with the experimental IR spectra.

Experimental and Theoretical Methods

Catalysts were obtained by pore-filling impregnation of a γ -Al₂O₃ (258 m²/g) and SiO₂ (350 m²/g) supports with solutions of the appropriate salts. The samples were dried at 393 K overnight and calcined at 773 K for 3 h. The metal contents as determined by elemental analysis were 8.0 wt.% for Mo/Al₂O₃; 9.5 wt.% (Mo/Al₂O₃); 1.1 (Co) and 9.5 wt.% (Mo) for CoMo/Al₂O₃ ; 7.2 wt.% (Mo/SiO₂); 7.5 wt.% (Ru/SiO₂) and 11 wt.% (Pt/SiO₂).

Sulfidation was carried out in situ under flow of H₂S (100%) for Ru/SiO₂ or a H₂S/H₂ (10/90) mixture for the other catalysts at 623 K followed by evacuation. Adsorption of CDCl₃ was carried out at room temperature (RT). Calibrated doses of CDCl₃ were introduced in the IR cell up to an equilibrium pressure of 5 mbars. Adsorption of CO was carried out at low temperature (100 K) up to an equilibrium pressure of 1 mbar.

The IR spectra of CDCl₃/organic sulfide solutions were recorded using an ATR cell.

The DFT calculations were performed using the VASP software based on periodic density functional theory using the exchange correlation functional of Perdew and Zunger and a plane wave basis set. The calculations were performed using a 5 k points mesh, a cutoff energy of 550 eV and a convergence criterion 10⁻⁶ eV. The supercell contains two MoS₂ layers, four elementary MoS₂ units in the direction parallel to the surface and four in the direction perpendicular to the (100) surface, with a vacuum layer of 10 Å on top of it.

Results and discussion

Pyrrole adsorption. On Al₂O₃ and Mo/Al₂O₃ pyrrole adsorption leads to the appearance of broad and complex band in the 3600 – 2500 cm⁻¹ range, mainly resulting from the formation of pyrrolate species (C₄H₄N⁻) by dissociative adsorption of pyrrole on Al₂O₃.⁶ The spectra obtained on Mo/Al₂O₃ did not show specific infrared bands that could result from pyrrole adsorption on the sulfide phase.

On SiO₂, pyrrole adsorption leads to a decrease of free SiOH groups and to the appearance of a broad ν OH band centered at 3500 cm⁻¹. The pyrrole ν NH vibration is located at 3474 cm⁻¹, close from that observed in diluted solution. These features are assigned to the formation of hydrogen bond from free silanol groups to the pyrrolic ring. No distinct features could be observed on the Mo/SiO₂ catalyst.

Chloroform adsorption. Adsorption of CDCl₃ on sulfided Al₂O₃ leads to a strong and broad ν CD band extending from 2250 to 2200 cm⁻¹. This band characterizes the formation of hydrogen bonds between CDCl₃ and the basic sites of the Al₂O₃ support (Cl₃CD \cdots O²⁻). Besides, however, supplementary bands characterizing CHCl₃ and formate species readily appeared. The latter species remained upon evacuation, which indicates that in our conditions CDCl₃ strongly reacts with the Al₂O₃ support. The possibility of chlorine deposition on the surface prevents a relevant assessment of basicity by CDCl₃ on Al₂O₃-based catalysts to be made.

The infrared spectra obtained upon CDCl₃ adsorption on SiO₂ and SiO₂ supported sulfide phase are reported on Figure 1. On all catalysts, CDCl₃ adsorption leads to a perturbation of the ν OH band of free silanol groups (3742 cm⁻¹) and to the appearance of a broad ν (OH) band centered at 3680 cm⁻¹. The ν OH frequency shift is close from that observed upon CCl₄ adsorption on SiO₂ and indicates the formation of a SiOH \cdots Cl hydrogen bond. This assignment is in agreement with the position of the ν CD band observed on SiO₂ (2264 cm⁻¹, Figure 1B, spectrum a) which is close from that observed in the gas phase. This clearly shows that CDCl₃ does not form CD \cdots OH(Si) or CD \cdots O²⁻ hydrogen bonds with the silica support.

Figure 1B shows that CDCl₃ adsorption on all supported sulfide catalysts (spectra b-e) leads to a supplementary ν CD band at ~2235 cm⁻¹. This band is not observed on pure SiO₂ and characterizes the interaction of CDCl₃ with the sulfided phase.

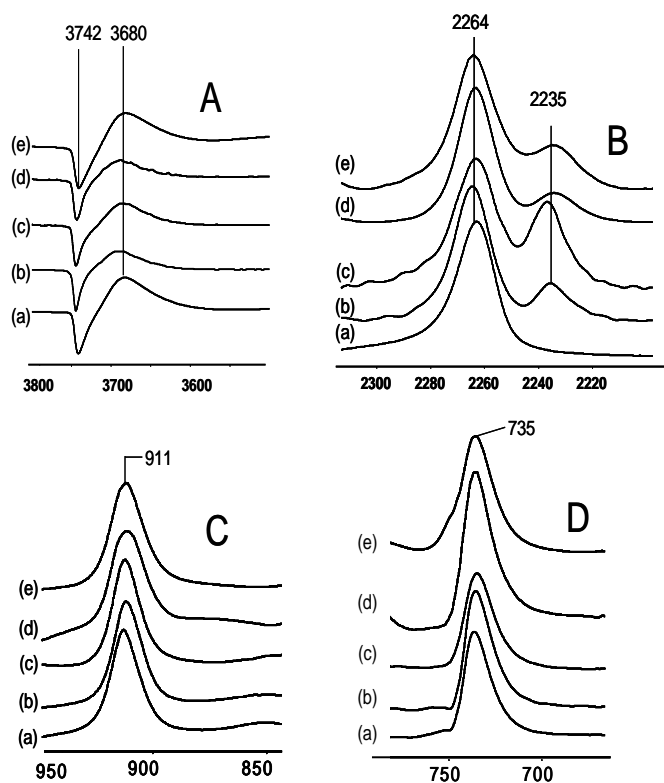


Figure 1 : Adsorption of CDCl_3 (5 mbars at equilibrium) on (a) SiO_2 ; (b) Mo/SiO_2 ; (c) CoMo/SiO_2 ; (d) Ru/SiO_2 ; (e) Pt/SiO_2 . A: νOH vibration; B: νCD vibration; C: δCD vibration ; D: $\nu_{\text{as}}\text{CCl}_3$ vibration

The appearance of this band (2235 cm^{-1}) is totally reversible: CDCl_3 desorption upon evacuation at room temperature leads to the complete disappearance of this band.

Figures 3C and 3D show the IR spectra recorded in the δCD and νCCl vibration ranges, respectively. No strong differences between the spectra obtained on SiO_2 and on SiO_2 supported catalysts are observed. Moreover, no supplementary bands were observed on these catalysts, showing that in our conditions, no dissociative adsorption of CDCl_3 occurs on the sulfide phase.

Hence, the νCD band observed at 2235 cm^{-1} is related to the molecular adsorption of CDCl_3 on the supported phase of these catalysts. Similar experiments carried out on the oxidic form of these catalysts did not lead to the appearance of this band led and the IR spectra were almost identical to that observed on SiO_2 . This allows one to exclude the assignment of the band at 2235 cm^{-1} to the adsorption of CDCl_3 on an oxysulfide phase. Thus, considering an adsorption on a fully sulfided phase, the band at 2235 cm^{-1} could result from either an interaction with the CUS sites or the formation of a hydrogen bond with the sulfur atoms of the sulfide phase.

Influence of sulfur coverage. Hydrogen treatments at 400°C (100 mbars, 1h) were carried out on Mo/SiO_2 and CoMo/SiO_2 in order to reduce the sulfur coverage of the sulfide phase⁷ and to examine its influence on the adsorption of CDCl_3 .

Figure 2 (left) shows the νCO spectra obtained after CO adsorption at low temperature (100 K) on Mo/SiO_2 and CoMo/SiO_2 before and after the hydrogen treatment. The band at 2157 cm^{-1} corresponds to CO adsorbed on the silanol groups

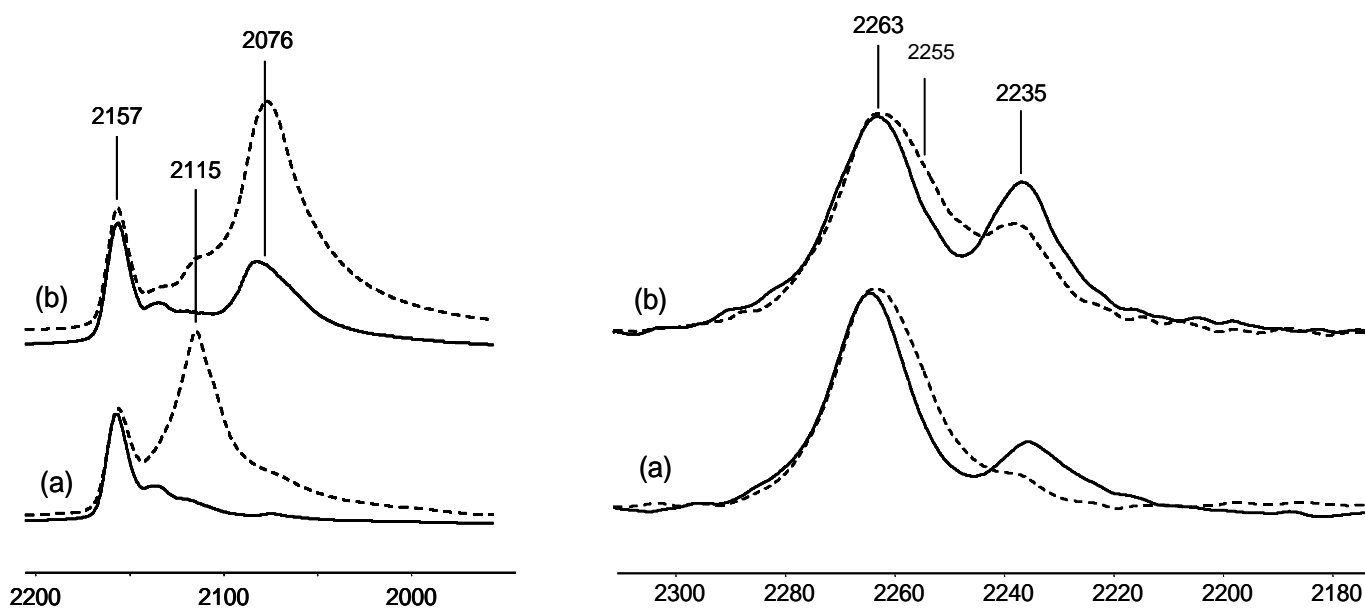
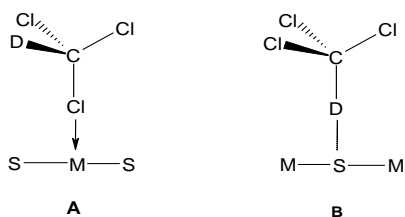


Figure 2 : Left : CO adsorption (1 mbar at equilibrium) on (a) Mo/SiO_2 and (b) CoMo/SiO_2 before (full lines) and after (dotted lines) H_2 treatment at 623K . Right : CDCl_3 adsorption (5 mbar at equilibrium) on (a) Mo/SiO_2 and (b) CoMo/SiO_2 .

of the support. The bands at 2115 and 2076 cm^{-1} are assigned to CO adsorbed on non-promoted Mo sites and promoted Co or Mo sites, respectively.³ These spectra clearly show a strong increase of the amount of CUS sites after the hydrogen treatment due to a decrease of the sulfur coverage of the edges of (Co)MoS₂ phases. Figure 4 (right) shows the corresponding vCD spectra obtained CDCl₃ on the same catalysts. It clearly appears that the hydrogen-treatment leads to a strong decrease of the band at 2235 cm^{-1} and to the appearance of a new vCD component at 2255 cm^{-1} . This component increases with the number of CUS sites and its position close from that observed in the gas phase ($\Delta\nu = -9 \text{ cm}^{-1}$). It is thus assigned to CDCl₃ adsorbed through one of its chlorine atoms on the CUS sites of the sulfide phase (Scheme 1A). On the other hand, the strong decrease of the intensity of the band at 2235 cm^{-1} allows to discard the assignment of this band to CDCl₃ adsorbed on CUS sites. This band is thus assigned to CDCl₃ adsorbed on sulfur atoms of the sulfide phase through hydrogen bond (Scheme 1B)



Scheme 1

Interaction of CDCl₃ with organic sulfides. While several studies have reported the adsorption of CDCl₃ on metal oxides or its interaction with oxygenated compounds through the formation of hydrogen bonds,⁹ to our knowledge no study have characterized its interaction with sulfur atoms. In order to ascertain our assignment of the band at 2135 cm^{-1} , we have carried out a study of CDCl₃ with organic sulfides: dimethyldisulfide (DMDS), tetrahydrothiophène (THT) and dibutylsulfide (DBS). To this aim, IR spectra of CDCl₃ / organic sulfide solutions were recorded (not shown). In the presence of these molecules, we have evidenced the formation of a vCD band resulting from the formation of a hydrogen bond with this compounds at a frequency close from that observed on the sulfide catalysts: 2236 cm^{-1} for DMDS, 2232 cm^{-1} for THT and 2231 cm^{-1} for DMS. No such a band was observed in CDCl₃/alkane solutions, indicating that it results from the formation of a hydrogen bond with sulfur atom (CCl₃D \cdots S).

DFT Calculations. DFT calculations were carried out to model CDCl₃ adsorption on MoS₂. The starting surfaces were chosen as the stable MoS₂ edges obtained in our experimental conditions,^{3,7} the M-edge consisting in 6-fold coordinated Mo atoms bridged with surface S atoms (M-edge, 4S), the S-edge consisting in tetrahedrally coordinated Mo atoms with either disulfide groups at high sulfur coverage (S-edge, 8S) or

bridged sulfur atoms lying alternatively on both sides of the Mo plane at low sulfur coverage (S-edge, 4S).

Figure 3 shows the adsorption geometry of CDCl₃ on the M-edge (4S) which is the dominating MoS₂ surface in our conditions of sulfidation.⁷ It clearly evidences the formation of a hydrogen bond of CDCl₃ with a sulfur atom of this edge. Similar adsorption geometries were found on the two other MoS₂ surfaces.

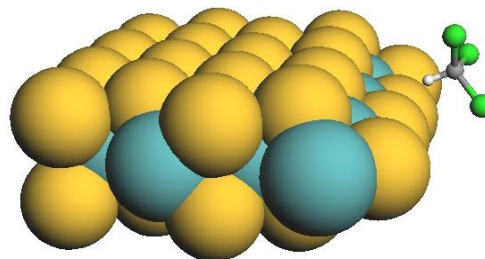


Figure 3: interaction of CDCl₃ with the M-edge (4S) of MoS₂

Table 1 reports the computed $\Delta\nu_{\text{CD}}$ frequency shifts ($\Delta\nu_{\text{CD}} = \nu_{\text{CD}_{\text{ads}}} - \nu_{\text{CD}_{\text{gas}}}$) and the sulfur-deuterium distances obtained for the various surfaces. These values clearly show that CDCl₃ forms hydrogen bonds with these surfaces, leading to ν (C-D) frequency shifts of 30-45 cm^{-1} , very close to those experimentally observed ($\Delta\nu_{\text{CD}} = 31 \text{ cm}^{-1}$).

Table 1. Computed CDCl₃ adsorption Energies, vCD vibration frequencies and CD \cdots S distances on MoS₂ edges.

MoS ₂ Edge	$\Delta\nu_{\text{CD}} / \text{cm}^{-1}$	$r(\text{D}\cdots\text{S}) / \text{pm}$
M-edge, 4S	-32	253
S-edge, 8S	-43	265
S-edge, 4S	-29	271

Assessment of sulfide phase basicity. The probe molecules used in this study, pyrrole (C₄H₄NH) and deuterated chloroform (CDCl₃) are classically used to characterize the basicity of metal oxides.⁶ They present an N-H (or C-D) group of similar acidity, with deprotonation energies of 1500 and 1496 kJ mol^{-1} , respectively. They interact by hydrogen bond with basic centers, leading to a downward shift of the ν_{NH} (or ν_{CD}) frequencies which increases with the strength of the basic center.

These molecules adsorb dissociatively and non-dissociatively on Al₂O₃ and Al₂O₃ supported catalysts, leading to complex spectra and preventing any precise assessment of the supported sulfide phase basicity. Moreover, in the case of CDCl₃, chlorine deposition on the Al₂O₃ alumina support lead to strong modifications of the surface which in turn is likely to change the acid-base properties of the sulfide phase.⁸ In any

case, however, Al₂O₃-supported catalysts did not present significantly higher basicity than Al₂O₃, indicating that the basicity of the sulfide phase is much lower than that of Al₂O₃.

The dissociation on the support could be avoided by using SiO₂-supported catalysts. In the case of pyrrole, however, the formation of SiOH... pyrrole hydrogen bonds leads to a broad νOH band which overlaps the νN-H band. This might explain why no clear differences were found between SiO₂ and SiO₂ supported catalysts.

Silanol groups also lead to hydrogen bond formation with the chlorine atoms of CDCl₃. In this case, however, the νCD vibration is located at a much lower frequency and does not overlap with other absorption bands. Moreover, CDCl₃ adsorbs non-dissociatively and reversibly on SiO₂ supported catalysts, thus allowing a reliable evaluation of the basicity of the sulfide phase.

CDCl₃ was found to form a hydrogen bond with the sulfur atoms of the sulfided phases, leading to a downward shift of ~ -31 cm⁻¹. Surprisingly, the nature of the sulfide phase (Mo, CoMo, Ru or Pt) does not significantly affect position of the ν(C-D) band indicating that sulfur basicity is not strongly affected by variations in sulfur-metal bond energies.⁹ It should be noted, however, that CDCl₃ is not very selective with respect to moderate changes in sulfur basicity:⁶ further work is certainly needed to characterize more finely the basicity these systems.

In any case, the νCD frequency shift observed on these catalysts clearly indicates that the sulfur atoms of the sulfide phase present a basic character which is confirmed by our DFT calculations. This frequency shift (31 cm⁻¹) is lower than that observed on classical basic catalysts. Thus, CDCl₃ adsorption on basic zeolites (NaY, KY, RbY and CsY) leads to νCD in the order of 40-60 cm⁻¹.¹⁰

Finally, the νCD band shift obtained on the supported sulfide phases is comparable to that observed for organic sulfides in solution, indicating that the basicity of these metal sulfides is close from that of these compounds which proton affinity lies in the range of 845±30 kJ mol⁻¹ (DMDS: 815 kJ mol⁻¹, THT: 849 kJ mol⁻¹ and DBS: 872 kJ mol⁻¹). These values indicate that sulfur basicity is weak. Such a weak basicity indicates that the dissociation of hydrogen on these surfaces should lead to acidic -SH groups, as suggested by DFT calculations¹¹ and previously observed by infrared spectroscopy^{12,13} and recent STM studies.¹⁴

Conclusions.

This study reports the first characterization of the basic properties of supported sulfide phases (Mo, CoMo, Ru and Pt). While no basic sites are detected on the SiO₂ support alone, CDCl₃ adsorption on supported catalysts leads to the formation of a (C-D...S) hydrogen bond which is clearly evidenced by a new νC-D band, downward shifted by ~31 cm⁻¹ as compared to the gas phase. The formation of the hydrogen bond was confirmed by comparing these IR spectra with those obtained in CDCl₃-organic sulfide solutions and by modeling CDCl₃ by DFT, leading to computed νCD frequency shifts of 25-40 cm⁻¹, consistent with those experimentally observed.

Such a νCD band indicates that the metal sulfides examined in the present study present a rather weak basicity and should lead to acid -SH groups upon hydrogen dissociation.

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Towards the characterization of active phase of (Co)Mo sulfide catalysts under reaction conditions—Parallel between IR spectroscopy, HDS and HDN tests

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Abstract

A series of sulfided (Co)Mo/Al catalysts was examined using IR spectroscopy of CO adsorption ($T_{\text{ads}} \sim 100$ K), thiophene hydrodesulfurization and 2,6-dimethylaniline hydrodenitrogenation. Spectroscopic analysis after treatments at H_2S partial pressures and temperatures close to the working conditions allows one to establish relationship between the nature, environment and concentration of sulfide phase sites and their catalytic functionalities. Unpromoted and Co-promoted edge sites do not exhibit the same sensitivity towards change in $\text{H}_2\text{S}/\text{H}_2$ partial pressure ratio. The Mo sites created in low $\text{H}_2\text{S}/\text{H}_2$ conditions present functionalities different from those formed in sulfiding conditions. By contrast, the Co-promoted sites are easily created even in sulfiding conditions and the sites generated in high or low $\text{H}_2\text{S}/\text{H}_2$ conditions possess the same environment as well as the same reactivity. Note that CoMo catalysts prepared by classical impregnation always exhibit an incomplete promotion of the MoS_2 slabs even when containing high Co/Co + Mo ratio.

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Keywords: Sulfide catalysts; IR spectroscopy; CO adsorption; Hydrodesulfurization; Hydrodenitrogenation; Hydrogen treatment

1. Introduction

Due to the implementation of more stringent specifications in sulfur content for diesel oil and gasoline, hydrodesulfurization (HDS) becomes a key process of the refinery [1]. HDS catalysts generally consist of small MoS_2 crystallites well dispersed on an alumina support with Co present in different forms. Cobalt is present as cobalt sulfide and as spinel in the alumina lattice but the active form is attributed to coordinatively unsaturated cobalt atoms located on the edges of the MoS_2 nano-slabs (called promoted phase or CoMoS phase). Optimum activity should be obtained for catalysts presenting the maximum of cobalt atoms located on these edges. Maximum activity is generally given for an atomic ratio of Co/Co + Mo of about 0.3 [1]. However, for catalysts presenting similar Co and Mo content, catalyst activity can strongly differ.

As a matter of fact, the preparation method or sulfidation procedure can strongly affect the Co distribution between its active and inactive forms [2–5]. Consequently, a characterization tool able to distinguish the Co-promoted Mo sites from the unpromoted Mo sites and to assess the amount of Co in the promoted phase appears crucial to develop new catalysts, to choose optimum conditions for catalyst activation and to reach a better knowledge at the molecular scale of the HDS catalysts.

Only few methods permit to attain such information. For example, Mössbauer spectroscopy allows one to distinguish the cobalt in its distinct phases but does not inform on the presence of unpromoted Mo sites [6]. From the slab size measurement of the MoS_2 particles by transmission electron microscopy (TEM) and considering a symmetrical hexagonal shape of the slabs [7], the concentration of Mo edge atoms can be estimated. However, no information about the degree of promotion of the MoS_2 edges can be obtained. Moreover, some authors claim that an important amount of active MoS_2 crystallites is undetectable by TEM due to their position towards the electron beam or due to their size lower than 1 nm [8,9]. Adsorbing probe molecules by IR spectroscopy appears to be a powerful method by giving rise to signals specific for unpromoted and promoted Mo sites

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[10–12]. Nitrogen monoxide and carbon monoxide have been mostly employed as probe molecules of the sites of the sulfide-based catalysts. Upon adsorption, specific IR features are observed, providing information on the adsorption mode and indirectly on the nature of the sites. The amount of the different sites on which they adsorb, can be assessed through the absorbance. Nitrogen monoxide has been the most employed since it presents the advantage to be strongly adsorbed on the sulfide phase. However a partial oxidation of the sulfide phase may occur, even at very low temperatures [13]. Reliability of this probe may therefore be questioned and many disagreements are found in the literature on the IR observations of NO adsorbed on sulfide catalysts [14,15]. CO appears to be a milder probe. No decomposition of the probe is reported if CO adsorption on the catalyst is performed at very low temperature. Correlation between chemisorption of carbon monoxide on promoted sites and HDS activity confirms the relevance of this probe [11,16]. Moreover, such method allows analysis of the surface treated in conditions close to the working ones. This is a meaningful advantage since the catalytic properties of the sulfided phase were found drastically dependent on the H₂S/H₂ partial pressure [17–19]. It is generally reported that H₂S addition decreases the catalytic activities. However, the effect of H₂S on the active site of the sulfide phase is not yet clearly established. Moreover, with respect to the deep HDS processes, the effect of very low H₂S/H₂ partial pressure on the nature, the amount and on the functionalities of the sulfide phase sites has also to be clarified.

The aim of the present study is to determine the nature, the environment and the concentration of sulfide phase sites in relation with their catalytic activity. Catalytic properties of a series of Mo/Al₂O₃ (with Mo loadings of 5–12 wt.%) and CoMo/Al₂O₃ catalysts (with Co loadings of 0–4.7 wt.%) were examined in thiophene hydrodesulfurization and 2,6-dimethylaniline decomposition. This latter reaction occurs according to three parallel routes representative of the various functions of the catalysts (Schemes 1 and 2 in reference [18]). Moreover, this reaction allows the measurement of catalyst performances even in absence of H₂S. Surface sites of the series of (Co)Mo catalysts were examined using IR spectroscopy of adsorbed CO ($T_{\text{ads}} = 100$ K). In view of understanding the sensitivity of activity and selectivity of sulfide catalysts towards H₂S partial pressure [18], reaction conditions were simulated by performing IR characterizations either after sulfidation, or after a subsequent H₂-treatment at a moderate temperature.

2. Experimental

2.1. Catalyst preparation

The alumina supported Mo-catalysts were prepared by pore-filling impregnation of a γ -alumina (AX300, Criterion, 258 m²/g, 0.66 cm³/g) with an ammonium heptamolybdate solution. Samples were dried at 383 K overnight and calcined at 773 K for 3 h. The catalysts were denoted Mo₄/Al, Mo₉/Al and Mo₁₂/Al for Mo contents of 4.2, 9.8 and 11.9 wt.% Mo, respectively. The CoMo/Al₂O₃ catalysts were prepared by impregnation of

the molybdenum catalyst (Mo₉/Al) with a cobalt nitrate solution, drying and finally calcination at 773 K for 3 h. Catalysts containing 1.6, 3.1 and 4.7 wt.% Co were prepared, and denoted Co₁Mo₉/Al, Co₃Mo₉/Al and Co₅Mo₉/Al, respectively.

A silica supported molybdenum catalyst (Mo₇Si, 7.2 wt.% Mo) was prepared by impregnation of a silica support (Degussa Aerosil 200) according to the previous procedure except that final calcination was performed at 623 K.

2.2. IR spectroscopy of adsorbed CO

The oxidic catalysts were pressed into self-supported wafers (disc of 2 cm² and about 10 mg) and placed into the IR cell. Two different activation procedures were applied: (i) a sulfidation under H₂S/H₂ flow or (ii) a sulfidation under H₂S/H₂ flow followed by a post-treatment under pure H₂ flow. For the first procedure, the catalyst was dried at 423 K under N₂ flow (30 mL/min) during 0.5 h, and cooled down to 298 K. The catalyst was then sulfided at atmospheric pressure with a flow of H₂S (10%)/H₂ (30 mL/min) at a rate of 3 K/min up to 623 K. After 2 h sulfiding at 623 K, the catalyst was flushed with N₂ for 0.25 h at 623 K and cooled down to 298 K. For the second type of activation, after performing the sulfidation following the previous procedure, the nitrogen flush was followed by a post-treatment under hydrogen (30 mL/min) at 573 K for 2 h. At the end of this treatment, the catalyst was cooled down under flowing N₂. After these two types of activation, the catalyst was evacuated up to 573 K (10 K/min) until a residual pressure of 6×10^{-3} Pa and finally cooled down to 100 K for CO adsorption.

CO adsorption was performed by introduction of small calibrated amounts of CO and finally with 133 Pa CO at equilibrium with the catalyst pellet. IR spectra of adsorbed CO were recorded with a Nicolet Magna 550 FT-IR spectrometer equipped with a MCT detector. All spectra were normalised to a disc of 5 mg cm⁻². The concentration of sulfide phase sites is evaluated after decomposition of the $\nu(\text{CO})$ envelope for a dose corresponding to the saturation (133 Pa of CO) and taking into account the molar extinction coefficients of CO adsorbed on sites determined previously, i.e. for unpromoted Mo sites $\epsilon_{\text{Mo}} = 16 \pm 4$ cm μmol^{-1} and for promoted sites $\epsilon_{\text{CoMoS}} = 43 \pm 12$ cm μmol^{-1} [20].

2.3. Activity measurement for thiophene HDS and 2,6-dimethylaniline HDN

Before HDS activity measurements, the oxidic catalysts (0.2–0.5 mm) were sulfided in the reactor at a rate of 3 K/min up to 673 K under a flow of H₂S (10%)/H₂ at atmospheric pressure during 2 h before the test. The thiophene conversion was measured at 673 K and atmospheric pressure with a thiophene partial pressure of 8 kPa in a mixture of hydrogen (91.2 kPa) and H₂S (2.1 kPa). Thiophene and its products, dihydrothiophene, tetrahydrothiophene, butenes and butane were analysed by on-line gas chromatography. Thiophene activity was measured for low conversion ($f_{\text{Thio}} < 5\%$) at a

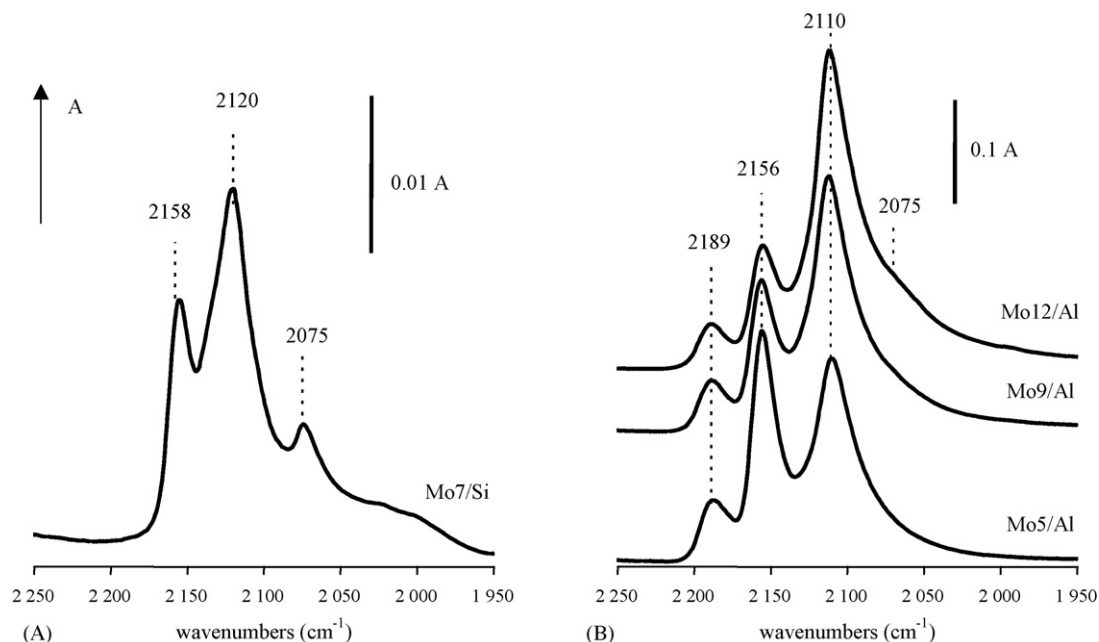


Fig. 1. IR spectra of CO adsorbed ($T \sim 100$ K, $P = 133$ Pa) on sulfide Mo catalysts supported on silica (A) and on alumina (B).

given contact time W/F_{Thio} . The HDS rate was obtained by $r_{\text{Thio}} = f_{\text{Thio}}/(W/F_{\text{Thio}}^0)$.

The activity measurements for 2,6-dimethylaniline HDN were performed at 573 K under 4 MPa total pressure, the H_2S partial pressure being varied between 0 and 56 kPa. More details about the reaction conditions are given in Ref. [18].

3. Results

3.1. CO adsorption on the Mo sulfide catalysts

On the sulfided Mo_7/Si catalyst, CO adsorption gives rise to three bands at 2158 cm^{-1} , 2120 cm^{-1} and 2075 cm^{-1} (Fig. 1A). The band at 2158 cm^{-1} corresponds to the interaction of CO with silanol groups. The two bands at 2120 cm^{-1} and 2075 cm^{-1} characterize CO adsorption on unpromoted Mo sites of the sulfide phase.

Fig. 1B compares CO adsorption on sulfided Mo/Al catalysts with different Mo loading. The main band at 2110 cm^{-1} is characteristic of CO in interaction with Mo sites while the bands at 2189 cm^{-1} and 2156 cm^{-1} are specific

of CO adsorption on Al^{3+} vacancies and hydroxyl groups of alumina [20]. The intensity of the band at 2110 cm^{-1} increases with Mo loading. At the same time, the bands characteristic of the alumina decrease indicating a higher coverage of the support by the sulfide phase. For the highest Mo loading (Mo_{12}/Al), a shoulder at 2075 cm^{-1} is clearly detected. Compared to the silica supported Mo-catalyst, the wavenumber of the main band related to the Mo sites on Mo/Al catalysts is shifted towards a lower value whereas that of the shoulder is not significantly affected. For all the Mo/Al catalysts, the area of the band of CO in interaction with Mo sites was measured after elimination of the contribution of CO in interaction with the support. The concentration of Mo sites adsorbing CO reported in Table 1 was calculated taking into account the corresponding molar extinction coefficient value, ϵ_{Mo} [20].

3.2. CO adsorption on cobalt-promoted molybdenum sulfide catalysts

Spectra of CO adsorbed on the series of CoMo_9/Al catalysts are presented in Fig. 2. In agreement with previous studies

Table 1
Effect of the H_2 post-treatment on the concentration of Mo sites of the sulfide Mo/Al catalysts. Comparison between the number of Mo edge sites determined from CO adsorption and that expected from HREM and calculation [7,25]

Catalysts	Mo (wt%)	Concentration of CO adsorbed on unpromoted Mo sites (mmol/g)		Calculated concentration of edge Mo atoms (mmol/g)	Percentage of edge site detected by CO^a
		After sulfidation (mmol/g)	After H_2 post-treatment (mmol/g)		
Mo_4/Al	4.2	0.075	0.167 (2.3 ^b)	0.184	91
Mo_9/Al	9.8	0.126	0.287 (2.3 ^b)	0.389	74
Mo_{12}/Al	11.9	0.159	0.291 (1.8 ^b)	0.402	72

^a $100 \times (\text{concentration of unpromoted Mo sites detected after } \text{H}_2\text{-treatment})/(\text{concentration of edge Mo obtained from HREM and calculation})$.

^b In parentheses: $(\text{concentration of unpromoted Mo sites detected after } \text{H}_2\text{-treatment})/(\text{concentration of unpromoted Mo sites detected after sulfidation})$.

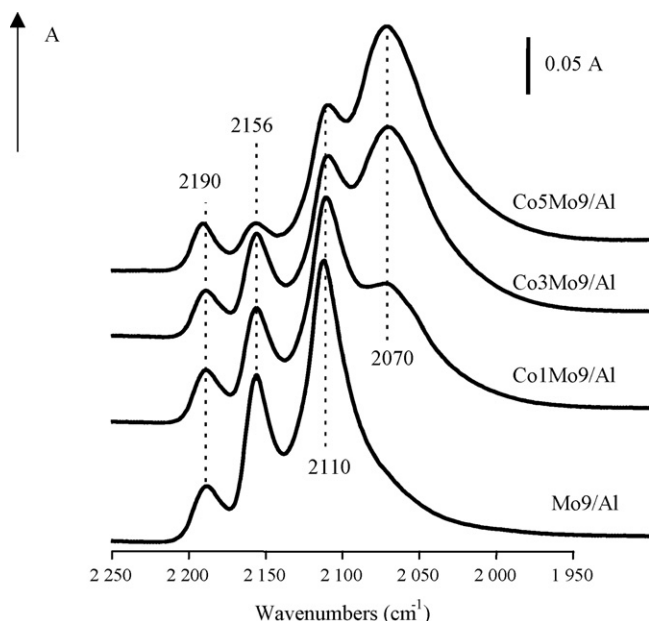


Fig. 2. IR spectra of CO adsorbed ($T \sim 100$ K, $P = 133$ Pa) on sulfide (Co)Mo catalysts supported on alumina.

[11,20], Co addition leads to the appearance of a new band situated at 2070 cm^{-1} at the expense of the band characteristic of unpromoted Mo sites (2110 cm^{-1}). CO adsorption on pure $\text{Co}/\text{Al}_2\text{O}_3$ catalyst (3 wt.% Co) sulfided in flow conditions gives rise to a band at 2094 cm^{-1} with a low intensity shoulder at 2056 cm^{-1} . Hence, the band at 2070 cm^{-1} observed on CoMo catalysts can be assigned to Co-promoted Mo sites, as proposed previously [11]. The intensity of this band characteristic of Co-promoted sites increases with the Co content up to 3.1 wt.% Co. Supplementary addition of Co does not increase the band intensity. Note that even for the highest Co loading of this series, i.e. for an atomic ratio $\text{Co}/(\text{Co} + \text{Mo})$ of 0.48, the band at 2110 cm^{-1} is still detected indicating that, in this series of CoMo catalysts, promotion of the MoS_2 slab by Co is never complete. Compared to corresponding Mo catalyst, the presence of Co leads also to a decrease of the bands related to the support. This diminution becomes more pronounced at higher Co loading and is likely due to an increasing amount of cobalt spinel or cobalt sulfide phase [1]. After elimination of the contribution of CO in interaction with the support, the IR spectrum corresponding to CO in interaction with the sulfide phase sites is decomposed into two components characterizing

Co-promoted and unpromoted Mo sites. Their concentrations were calculated for each sulfide catalyst taking into account the corresponding molar extinction coefficients, ϵ_{Mo} and ϵ_{CoMoS} (Table 2) [20].

3.3. Effect of H_2 post-treatment on Mo/Al and CoMo/Al catalysts

Spectra of CO adsorbed on sulfide or on H_2 -treated (Co)Mo catalysts are presented on Fig. 3A. Fig. 3B presents the difference between these spectra for each catalyst. This illustrates specifically the changes due to the H_2 -treatment.

On the Mo_9/Al catalyst, H_2 -treatment increases the intensity of the band characteristic of Mo sulfide sites. A new band at 2098 cm^{-1} appears, as evidenced in Fig. 3A and more clearly in Fig. 3B. The post-treatment leads also to the creation of supplementary Al^{3+} vacancies and hydroxyl groups. One explanation for this latter effect could be that $\text{Al}-\text{O}-\text{Al}$ bridges are broken during the H_2 -treatment, which leads to the creation of new Al^{3+} vacancies and hydroxyl groups. On all the Mo-catalysts, similar modifications are observed after H_2 -treatment. The amount of Mo sites increases by a factor 2.3 (Table 1), except on Mo_{12}/Al where the increase is somewhat smaller. Note that the effect of the H_2 -treatment is completely reversible, since if the H_2 -treated catalyst is resulfided by $\text{H}_2\text{S}/\text{H}_2$ at 573 K during 2 h, the CO signal is similar to that obtained directly after sulfidation, in particular the band at 2098 cm^{-1} totally disappeared (spectra not shown).

For CoMo catalysts, H_2 -treatment also leads to an increase of the concentration of sites on the sulfide phase (Fig. 3). The amount of unpromoted Mo sites increases by a factor of about 1.8 whatever the Co content, i.e. a factor slightly lower than the value of 2.3 observed on pure Mo_9 catalyst (Tables 1 and 2). Fig. 3B points out that the increase of the amount of unpromoted sites is mainly due to the creation of Mo sites characterized by the band at 2098 cm^{-1} . Regarding the concentration of promoted sites created by the H_2 -treatment, Fig. 3B and Table 2 reveal that it is clearly smaller than that of unpromoted ones. In fact, the amount of promoted sites increases only by a factor 1.3. This factor falls down to 1.1 for the catalyst containing the highest Co content. On sulfided $\text{Co}_1\text{Mo}_9/\text{Al}$, it can be observed that the H_2 -treatment increases the intensity of the band at 2070 cm^{-1} . No new band characteristic of promoted sites in a different environment could be detected. For the catalysts containing the highest

Table 2

Effect of H_2 post-treatment on the concentration of unpromoted and promoted Mo sites of sulfide Mo/Al and CoMo/Al as detected from CO adsorption

Catalysts	Amount of sites detected after sulfidation (mmol/g)			Amount of sites detected after H_2 -treatment (mmol/g)			Percentage of (Co-promoted sites)/(total Co)
	Unpromoted	Co-promoted	Total	Unpromoted ^a	Co-promoted	Total	
Mo_9/Al	0.126	–	0.126	0.287 (2.3 ^b)	–	0.287	–
$\text{Co}_1\text{Mo}_9/\text{Al}$	0.100	0.018	0.118	0.174 (1.7 ^b)	0.024 (1.3 ^b)	0.198	14
$\text{Co}_3\text{Mo}_9/\text{Al}$	0.077	0.033	0.110	0.145 (1.9 ^b)	0.044 (1.3 ^b)	0.189	9
$\text{Co}_5\text{Mo}_9/\text{Al}$	0.074	0.039	0.113	0.121 (1.6 ^b)	0.043 (1.1 ^b)	0.164	6

^a The molar extinction coefficient of the band at 2098 cm^{-1} is considered equal to that of the band at 2110 cm^{-1} .

^b In parentheses: (concentration of [un]promoted sites detected after H_2 -treatment)/(concentration of [un]promoted sites detected after sulfidation).

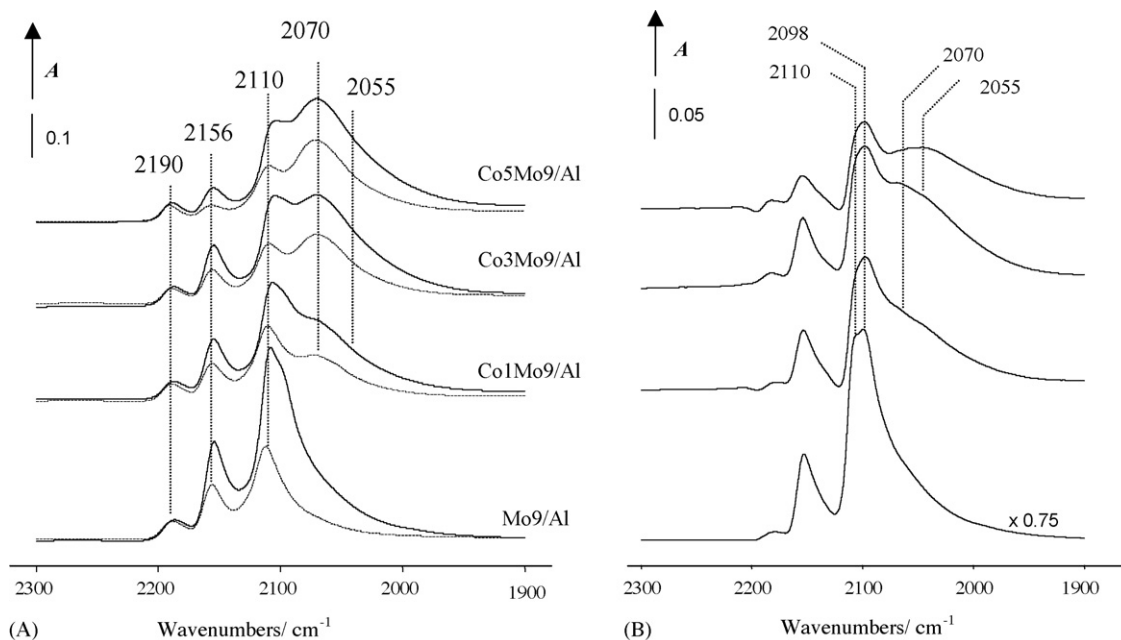


Fig. 3. Effect of H_2 post-treatment at 573 K on CO adsorption on sulfide Mo/Al and CoMo/Al catalysts. (A) IR spectrum of CO adsorbed ($T = 100$ K, $P = 133$ Pa) on the Co_xMo_9/Al catalyst after sulfidation (dotted line); after sulfidation and H_2 -treatment (full line). (B) Difference between IR spectra of CO adsorbed (after sulfidation and H_2 post-treatment) minus (after sulfidation) for Mo/Al and CoMo/Al.

amount of Co, sites characterized by a broad low intensity band at 2055 cm^{-1} appear after the H_2 -treatment. As observed on Mo samples, the post-treatment also leads to an increase of the number of Al^{3+} vacancies and hydroxyl groups on the support of CoMo catalysts.

3.4. Thiophene HDS activity

On the Mo/Al series, the thiophene HDS rate increases almost linearly with the molybdenum content up to 12 wt.% Mo (Fig. 4A). On the CoMo series, an increase of the rate is observed up to about 2 wt.% Co while the activity stays almost constant until 4.7 wt.% Co (Fig. 4B). Thus, the maximum of HDS activity is obtained for a Co amount which corresponds to an atomic $Co/(Co + Mo)$ ratio of 0.28. This corresponds to the value often reported in the literature [21]. The agreement

between results obtained on this series of catalysts and those reported in the literature was a way to check the quality of the present preparations.

3.5. 2,6-Dimethylaniline HDN activity

The reaction network of DMA decomposition presents four parallel routes (Scheme 1) [18]. For HYD and HYG routes, DMA is firstly dearomatized and the formed dihydro-intermediate reacts via two different pathways: (i) through an hydrogenation–elimination route leading to the formation of dimethylcyclohexenes and -anes (HYD route), or (ii) via an NH_3 elimination leading to the formation of xylene (HYG route). DMA can also react through a direct carbon–nitrogen bond cleavage leading to the formation of xylene (DDN route). Thus, xylene can be formed through two different pathways

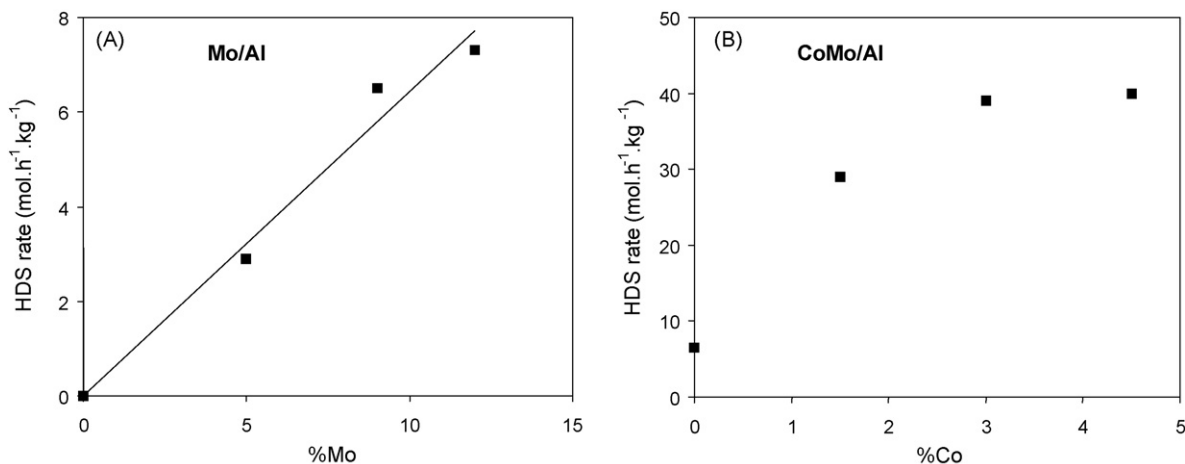
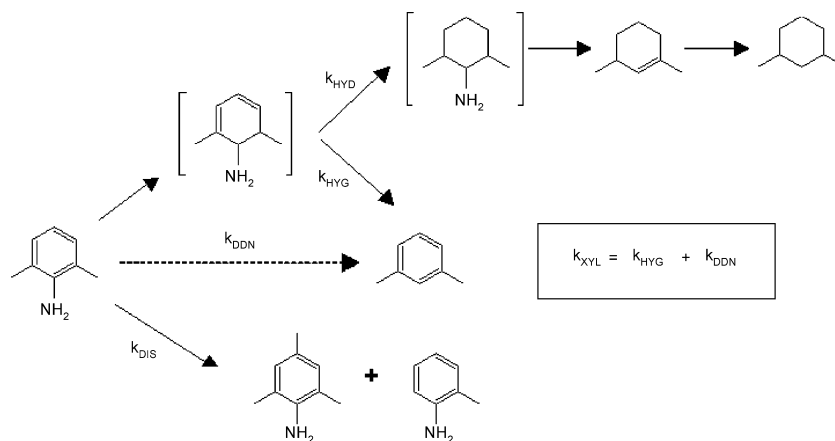


Fig. 4. Variation of the thiophene HDS activity for the series of sulfide Mo/Al (A) and CoMo/Al catalysts (B).



Scheme 1. Reaction network of 2,6-dimethylaniline decomposition.

(called the XYL route, $\text{XYL} = \text{HYG} + \text{DDN}$). Finally, disproportionation of DMA can also occur leading to the formation of 2-methylaniline and 2,4,6-trimethylaniline (DIS route).

The effect of $\text{H}_2\text{S}/\text{H}_2$ partial pressure on the various routes of DMA decomposition was examined on the series of (Co)Mo/Al catalysts characterized by IR spectroscopy in the previous section. Fig. 5 evidences that the effect of $\text{H}_2\text{S}/\text{H}_2$ partial pressure strongly depends on the nature of the sulfide phase and on the considered route.

With respect to HYD route, the hydrogenation activity of Mo/Al catalysts linearly increases with the Mo content. On the CoMo/Al catalysts, activity for HYD routes increases up to 3 wt.% Co and then remains constant. The sensitivity towards H_2S partial pressure is strongly different on Mo and CoMo

catalysts. Thus, the HYD activity of Mo/Al catalysts is almost insensitive to the PH_2S variation, whereas HYD activity of CoMo/Al is clearly enhanced in absence of H_2S . This indicates that both Co-promoted and unpromoted Mo sites are active for HYD route. However, this highlights that the sensitivity of these two types of sites towards $\text{H}_2\text{S}/\text{H}_2$ partial pressure is strongly different.

The effect of variation of H_2S partial pressure on the XYL activity of Co(Mo) catalysts was discussed in our previous paper [18]. In the absence of H_2S , XYL formation is strongly enhanced, specially on unpromoted catalysts. Increasing the cobalt content markedly decreases this effect. This indicates the role of highly sulfur-depleted unpromoted Mo sites for this route.

Finally, the disproportionation rate constant (not shown) increases both with Mo and Co amount. In absence of H_2S , a

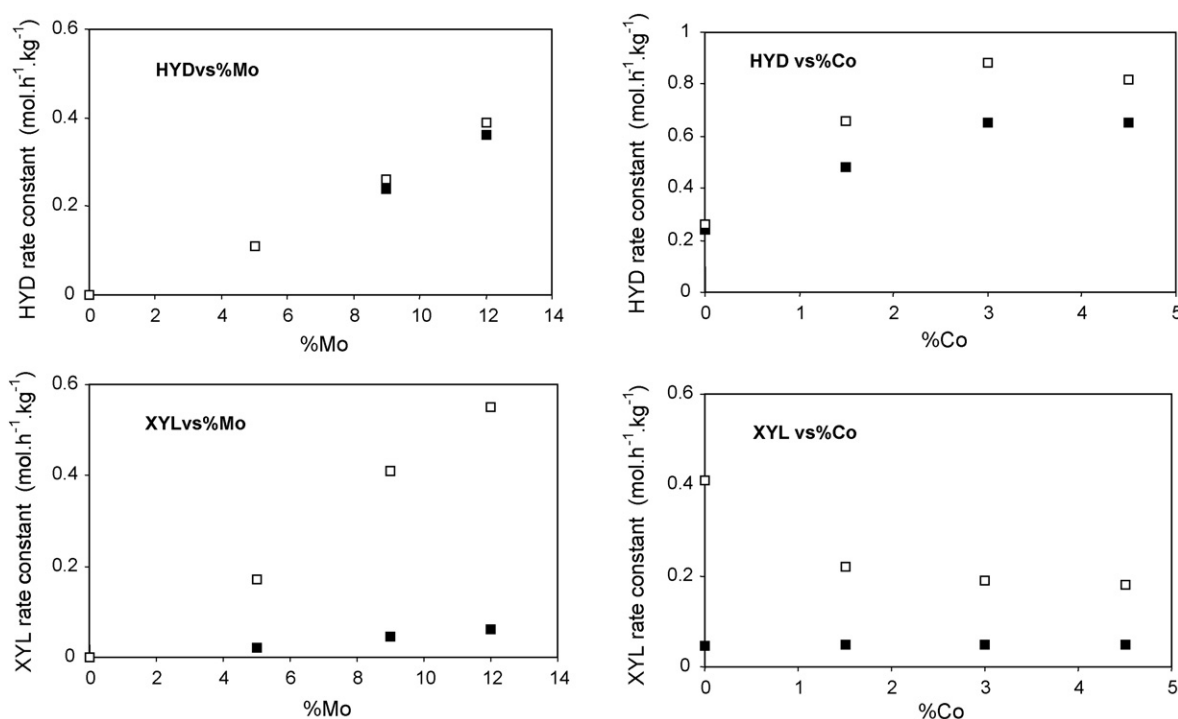


Fig. 5. Variation of the activity of 2,6-dimethylaniline decomposition for the different routes for the series of sulfide Mo/Al and CoMo/Al catalysts. Activity measured in presence (full symbol) or in absence of H_2S (open symbol).

decrease of DIS activity is observed on the whole series of catalysts.

4. Discussion

4.1. Environment of the MoS₂ edge sites

In order to assign more accurately the bands specific of the sulfide phase, spectra of CO adsorption on Mo/Al and Mo/Si catalysts are compared. On the Mo/Si catalyst, CO in interaction with the sulfide phase gives rise to two bands: a main band at 2120 cm⁻¹ and a smaller one at 2075 cm⁻¹, both being characteristic of CO adsorption on molybdenum atoms located on the MoS₂ edges. On the Mo/Al catalysts, two bands are also evidenced at 2110 cm⁻¹ and 2075 cm⁻¹. The observation of these two bands reveals the presence of at least two distinct Mo sites on the sulfide slab. Three assignments can be considered to explain these two bands. They can account for CO adsorption on: (i) edge and corner sites; (ii) slabs with different stacking; (iii) Mo- and S-edge sites of the MoS₂ slab.

Müller et al. [22] reported the presence of two bands for CO adsorbed on MoS₂. These authors proposed that the high wavenumber band (located at 2105 cm⁻¹ in their study) is characteristic of CO in interaction with Mo sites located on the edges of the MoS₂ slab, whereas the low wavenumber band located at 2075 cm⁻¹ is due to CO in interaction with sites located on the corners of the MoS₂ slab. This interpretation is issued from what is observed when CO is adsorbed on metal particles [23]. With such an assignment, the intensity ratio between these two bands would be an indication of the dispersion of the MoS₂ phase and the lower the MoS₂ slab size, the higher the intensity ratio between the bands at 2075 cm⁻¹ and at 2110 (2120) cm⁻¹ is expected. However, several experimental observations are not consistent with such an attribution. Indeed, previous TEM studies report the smaller size of Mo sulfide phase when deposited on alumina instead of silica, whereas this ratio is highest on Mo/Si [24]. Note that the present study confirms the higher dispersion of Mo sulfide phase when supported on alumina since CO uptake on Mo sites is clearly greater on Mo/Al than on Mo/Si (Fig. 1). In addition for Mo/Al catalysts, an increase of the slab size is reported for increasing Mo content [25], while Fig. 1 shows a small augmentation of the intensity ratio between the band at 2075 cm⁻¹ and at 2110 cm⁻¹ with Mo loading. Therefore, contradiction between the dispersions deduced taking into account the assignment of the CO bands to corner and edge sites and the observed dispersions, allows us to discard this first proposal.

The second hypothesis considers that the CO wavenumber is sensitive to slab stacking. TEM analysis presented in the literature shows that, on Mo/Al, the mean stacking of MoS₂ slabs is around 1.5, while on Mo/Si, MoS₂ slabs present a higher stacking [24]. Hence, the band at 2075 cm⁻¹ could be related to the presence of stacked slabs while the high wavenumber band would correspond to CO adsorbed on edges of MoS₂ presenting a low stacking. Recent study shows that CO adsorption on bulk

MoS₂ gives rise to a broad band at 2100–2080 cm⁻¹ [26]. Thus, the stacking of MoS₂ could account for the band at 2075 cm⁻¹.

The third hypothesis takes into account the hexagonal shape of the MoS₂ slab which allows distinguishing two types of crystallographic edge planes: the (10 $\bar{1}$ 0) and the ($\bar{1}$ 010) planes called respectively the molybdenum and the sulfur edges [27]. DFT calculation was applied to determine the configurations of these two surfaces according to the H₂S/H₂ environment [28]. Moreover, the wavenumbers of CO adsorbed on the two MoS₂ edges in different configurations were recently calculated by DFT [29,30]. These studies reveal that CO frequency is affected by the type of edge. Hence, CO adsorbed on the S-edge should give rise to a band at lower wavenumber than when adsorbed on the Mo-edge. The shift between the calculated wavenumbers for CO adsorbed on Mo- or S-edge ($\Delta = 40$ cm⁻¹) is very close to the experimental one ($\Delta = 35$ cm⁻¹ on Mo/Al, and $\Delta = 45$ cm⁻¹ on Mo/Si). Thus, the nature of the MoS₂ edges can be considered to explain the presence of the two CO bands. The band detected at 2075 cm⁻¹ on Mo/Al and on Mo/Si could be assigned to CO in interaction with Mo atoms on the S-edge while the band at 2110–2120 cm⁻¹ could correspond to CO adsorbed on Mo atoms on the Mo-edge. These observations highlight the great sensitivity of the Mo sites to their environment.

4.2. Effect of H₂-treatment on the MoS₂ sites

On the Mo/Al catalysts, H₂-treatment at 573 K eliminates sulfur atoms from the MoS₂ edge slabs which strongly increases the amount of accessible Mo sites to CO. This increase reaches a factor of 2.3 for Mo₅/Al and Mo₉/Al (Table 1, values in parentheses). It is somewhat smaller for high Mo containing catalysts (1.8 for Mo₁₂/Al). This could indicate that the size of the MoS₂ slab slightly decreases its reducibility. The augmentation of the amount of CO adsorbed is mainly related to the appearance of a new CO/Mo band near 2098 cm⁻¹ (Fig. 3B). As mentioned previously, the effect of the H₂-treatment is completely reversible. Thus, this new band should be characteristic of more sulfur-depleted Mo sites than the Mo sites characterized by the band at 2110 cm⁻¹.

4.3. Promoting effect of cobalt

On Co-promoted catalysts, CO adsorption shows that for increasing amount of Co, the concentration of unpromoted Mo sites diminishes while in parallel new Co-promoted sites are generated (Fig. 2 and Table 2). On sulfided catalysts, quantitative analysis presented in Fig. 6A shows that the sum of the amount of unpromoted and promoted sites stays almost constant in the whole series of (Co)Mo catalysts. This indicates that on catalysts prepared by classical impregnation, the creation of one promoted site makes inaccessible about one unpromoted molybdenum site. Such a result is in complete agreement with the decoration model proposed earlier by Topsøe et al. [1].

It is surprising that the Co₃Mo₉/Al and Co₅Mo₉/Al catalysts that present the maximum amount of Co atoms in

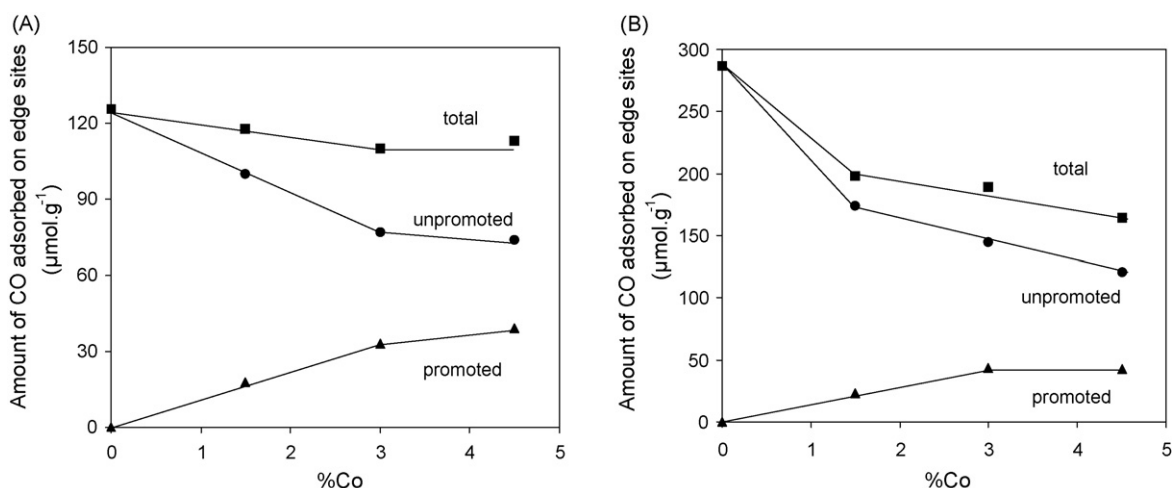


Fig. 6. Variation of the concentration of Co-promoted and unpromoted Mo sites for the series of sulfide CoMo/Al catalysts: (A) after sulfidation; (B) after H_2 -treatment.

promotion as well as the maximum thiophene HDS activity, still possess a large amount of unpromoted Mo sites (Figs. 2 and 6A). Increasing the atomic ratio $\text{Co}/(\text{Co} + \text{Mo})$ above 0.36 barely enhances the amount of Co-promoted sites. In parallel, that of unpromoted Mo sites almost does not decrease. Thus, from to a certain $\text{Co}/(\text{Co} + \text{Mo})$ ratio, supplementary Co atoms do not significantly anchor on the MoS_2 edges. Incomplete promotion of the MoS_2 slabs is not specific of the present preparation, since the same observation was done on industrial catalysts [31]. Moreover, presence of unpromoted Mo sites detected by CO on the present series of CoMo catalysts, is consistent with reactivity results obtained for DMA decomposition. Indeed, the non-zero activity for XYL formation measured in the absence of H_2S on the high Co-containing CoMo catalysts (Fig. 5) can be related to the incomplete MoS_2 slabs decoration [18]. It should be mentioned that a more complete promotion of the MoS_2 slabs can be obtained by chelating agent addition [32] or using cobalt carbonyl nitrosyl as precursor [16].

In fact, the difficulty to completely decorate the MoS_2 slab, even using high Co loading, suggests that not all the edge sites of the MoS_2 slabs are equivalent for Co anchoring. DFT calculations also point to that Co anchorage does not present the same stability on all the edge sites [33]: Co atoms are more stable on S-edge than on Mo-edge of MoS_2 . If we consider that the two CO/Mo bands characterize CO in interaction with the different MoS_2 edges, the decrease of the 2110 cm^{-1} band when the catalyst is promoted by Co, reveals that the anchorage of Co atoms on this Mo-edge is possible. Note that another interpretation of this decrease could be a change of morphology of the sulfide slab. The appearance of the CO band at 2070 cm^{-1} specific of Co-promoted sites prevents any conclusion from the IR spectra regarding the anchorage of Co on S-edge. In a previous work [30], we showed that the frequency of CO adsorbed on Co is not very sensitive to the location of Co, thus, preventing a direct determination of the edge-type of Co location by CO adsorption.

4.4. Effect of H_2 -treatment on the CoMo catalysts

On the CoMo/Al as well as on Mo/Al, the H_2 -treatment leads to the creation of highly sulfur-depleted unpromoted Mo sites (band at 2098 cm^{-1}) (Fig. 3). Thus, unpromoted Mo sites on the $\text{Co}_x\text{Mo}_9/\text{Al}$ catalysts behave similarly towards H_2 than those on Mo_9/Al catalysts, except that the relative increase of unpromoted Mo sites is somewhat smaller (factor ~ 1.8 (Table 2) instead of 2.3 (Table 1)). On the other hand, H_2 -treatment enhances the amount of Co-promoted sites but does not lead to the appearance of a new band. This suggests that the environment of Co-promoted sites is not modified by this reductive treatment. Moreover, for the whole series of CoMo catalyst, the relative increase of Co-promoted sites by H_2 -treatment is clearly smaller than that of unpromoted Mo sites (respectively, 1.3 instead ~ 1.8 ; Table 2). These results suggest that most of the Co-promoted sites are already created by sulfidation treatment whereas unpromoted molybdenum sites are more difficult to be created.

These observations can be compared to previous temperature programmed reduction (TPR) results [34–38]. In TPR patterns, three temperature domains are distinguished. The low temperature peak, whose maximum appears at about 473 K, is related to non-stoichiometric sulfur elimination (i.e. sulfur retained on the surface during the sulfidation process), the intermediate temperature peak characterizes the removal of edge sulfur anions, while the high temperature peak is ascribed to basal sulfur anion elimination. Previous papers agree to show that Co addition is beneficial for elimination of basal sulfur atoms. However, few studies compared lability of edge sulfur atoms of Mo and CoMo catalysts. Berhaut et al. report a TPR analysis of (Co)Mo phases supported on silica [38]. This study confirms that Co addition strongly increases the sulfide phase reducibility in the high temperature domain (T_r higher than 620 K). By contrast, for T_r below 620 K, the amount of sulfur eliminated from the CoMo sulfide phase is smaller than on the Mo sulfide phase. Hence, mild temperature reduction creates more edge vacancies on MoS_2 slabs than on CoMo sulfide

phase. Consequently, the IR results on sulfide Mo and CoMo catalysts after H₂-treatment at 623 K are in agreement with TPR analysis.

Recent DFT calculations show the influence of H₂S/H₂ ratio on the configuration of unpromoted and Co-promoted edges [28,30,39]. These papers report that, on unpromoted Mo edge, the removal of sulfur atoms is thermodynamically unfavourable even at low H₂S/H₂ pressure ratio and that in sulfiding conditions, the stable surface presents only six-fold-coordinated Mo atoms. By contrast on CoMoS surface, the energy requires to remove one sulfur atom is much lower and decreases when the promotion degree increases. Even in sulfur-rich conditions, the most stable Co-promoted surface presents a lower sulfur coverage as compared to unpromoted surface. This explains why a mild H₂-treatment leads to a relative increase of Co-promoted sites lower than that of unpromoted Mo sites.

4.5. Determination of the edge site concentration

In this section, the amount of edge sites detected by CO after H₂-treatment is compared to that detected by other methods. Da Silva previously calculated the concentration of edge sites of the MoS₂ slabs for a series of sulfided Mo/Al catalysts from the mean MoS₂ slab size measured by HREM, using the geometrical model developed by Kastzelan et al. [7], and taking into account the Mo fraction in the sulfided state determined by XPS [40]. Since these Mo catalysts were prepared and sulfided in similar conditions than those used in the present work (sulfidation at 623 K under a flow of H₂S (15%)/H₂ at atmospheric pressure), we take into account the characteristics obtained by Da Silva to calculate the amount of edge sites on our series of Mo catalysts. Thus, considering that the fraction of Mo in the sulfide state is about 85% and that the MoS₂ slab size is 2.2 nm, 2.6 nm and 2.9 nm, respectively, for Mo₅/Al, Mo₉/Al and Mo₁₂/Al catalysts, the concentration of Mo edge sites was calculated and compared to that determined from CO adsorption (Table 1). Table 1 shows that there is a good agreement between the concentrations of edge Mo atoms calculated and those determined from CO adsorbed on the

H₂-treated Mo catalysts since from 91 to 72% of the edge atoms are detected by CO (Table 1).

Table 2 shows the total amount of edge sites (unpromoted and Co-promoted) on Co_xMo₉/Al catalysts after sulfidation and H₂-treatment. As previously mentioned, the total amount of edge sites detected after sulfidation is constant over the whole series of Co_xMo₉/Al catalysts (Fig. 6A). By contrast, on H₂-treated catalysts, it appears that Co addition decreases the total amount of edge sites detected by CO (Table 2). This decrease appears to be related to a much smaller concentration of accessible unpromoted Mo sites on CoMo catalysts than expected (Fig. 6B).

With respect to the Co-promoted sites, it is worth mentioning that only a very small fraction of the total cobalt atoms present in the samples are located in promotion position (amount lower than 15%, Table 2, last column). It should be mentioned that, even considering the important uncertainty ($\pm 25\%$) on the molar extinction coefficient of the CO in interaction with Co-promoted sites, the amount of detected Co-promoted sites stays low. Moreover, this result is supported by the observation of unpromoted Mo sites on CoMo catalysts whatever the Co content. It should be mentioned that other preparation methods like the CVD of Co(CO)₃NO [20] or the addition of chelating agents [32] allow one to improve the fraction of “active” cobalt of the CoMo catalysts.

These results show that only a small percentage of Co loaded onto the catalysts ends up in promoted position. Simple calculation of the maximum amount of Co atoms, that can be anchored on the edge sites, can be done taking into account: (i) the total amount of Co atoms present in the catalyst; (ii) the concentration of potential edge sites deduced from HREM and geometrical model; (iii) the anchoring of one cobalt on one Mo site. For Co₃Mo₉/Al, the edge sites can accommodate, at the maximum, 75% of the total amount of Co atoms present in the catalyst. Consequently, this calculation supports also the idea that not all the Co atoms can be located in promoted sites. However, previous Mössbauer analysis indicates that the amount of Co-in-alumina and Co₉S₈ is very low on CoMo catalysts prepared in a similar way [41,42]. Hence, the presence of small CoS_x clusters

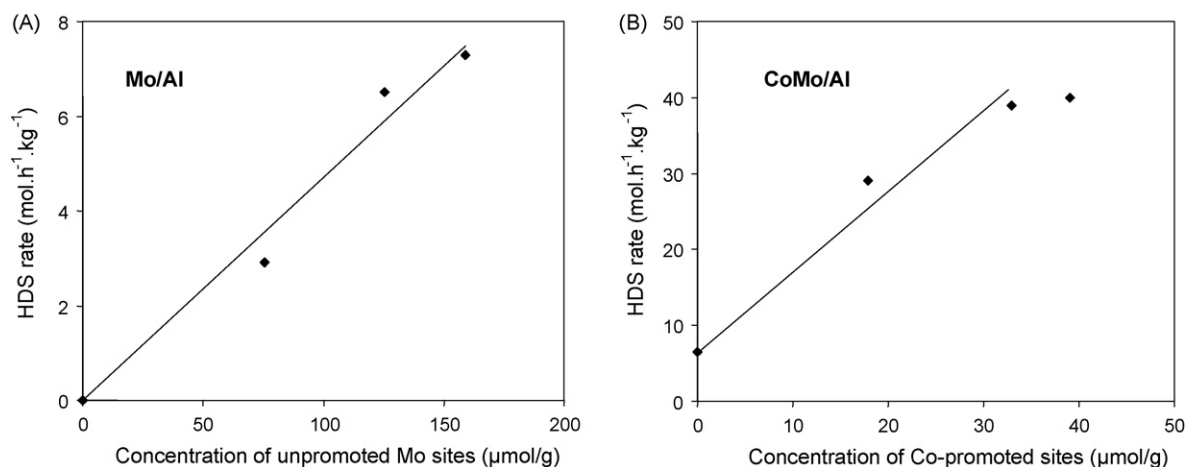
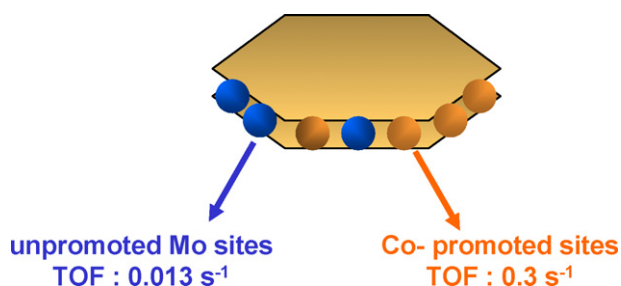


Fig. 7. Variation of the HDS activity vs. the concentration of unpromoted sites (A) and of Co-promoted sites (B) for the series of sulfide Mo/Al and CoMo/Al catalysts, respectively.



Scheme 2. Schematic representation of a MoS_2 slab with incomplete promotion by Co. Turn over frequency of unpromoted and Co-promoted edge sites of the MoS_2 slab for thiophene HDS.

located on the edge sites or on the basal planes of the MoS_2 particles can be proposed. A close proposal was previously done by Ledoux et al. [43]. This would make consistent IR and Mössbauer results. Indeed, such a model could account for both the low amount of chemisorption sites specific of Co in interaction with Mo and the absence of significant amount of Co in alumina and large particles of Co_9S_8 .

4.6. Structure–activity relationship

In order to identify the nature of active sites, surface sites and catalytic performances are examined in parallel. Thiophene HDS activity and concentration of surface sites detected by CO on sulfided Mo and CoMo/Al catalysts are compared in Fig. 7. On Mo/Al catalysts, a linear relationship appears between the rate for thiophene HDS and the amount of CO molecules adsorbed on unpromoted Mo sites. On the $\text{Co}_x\text{Mo}_9/\text{Al}$ catalysts, HDS activity increases with the concentration of Co-promoted sites. On CoMo catalysts, both unpromoted Mo sites and Co-promoted sites contribute to the catalytic activity. Hence, combination between the amount of each type of sites determined spectroscopically and the activity for Mo and CoMo catalysts allows one to evaluate separately the activity of these two types of sulfided sites. Thus, relationship between activity and amount of sites allows us to calculate the turn over frequency (TOF) of unpromoted and Co-promoted sites for the

HDS reaction. Thus, the values of the TOF for thiophene HDS of unpromoted and Co-promoted sites are equal to 0.013 s^{-1} and 0.3 s^{-1} , respectively (Scheme 2). It should be underlined that in this calculation only the edge atoms are considered, conversely to usual calculations, which improperly consider the total amount of Co and Mo. These TOF values confirm the strong enhancement of HDS activity on Co-promoted sites compared to unpromoted Mo sites. In a general fashion, the promotion factor is defined as the ratio between the activity of the optimised CoMo catalyst and that of the corresponding Mo catalyst. Hence, the promotion factor determined from the ratio of the rates on Mo_9/Al and $\text{Co}_3\text{Mo}_9/\text{Al}$ catalysts is about 4. On the other hand, defining the promotion factor by the ratio of the TOF values for Co-promoted and unpromoted sites, a promotion factor of about 23 is calculated. This value is significantly greater than the promotion factor of ~ 4 . Such difference results from the presence of an important fraction of unpromoted sites in the $\text{Co}_3\text{Mo}_9/\text{Al}$ catalysts.

Similar combined analysis was done for DMA reaction. In this case, additional information can be obtained, since HDN reaction enables one to measure the activity and selectivity of the catalysts in presence or in absence of H_2S . Activity for DMA hydrogenation route strongly depends on the Mo as well as on the Co content (Fig. 5). Sensitivity towards H_2S partial pressure is different on Mo and CoMo catalysts. Indeed, hydrogenation activity of Mo/Al catalysts is barely affected by the H_2S partial pressure whereas it is clearly increased on CoMo catalysts. As shown in Fig. 8A, a linear relationship between the hydrogenation rate measured in presence of H_2S and the concentration of unpromoted sites detected on Mo/Al sulfide catalysts appears. By contrast, the correlation is not so good when HYD activity measured in absence of H_2S is compared to the amount of Mo site detected after H_2 -treatment. Whereas the HYD activity is almost unaffected by the absence of H_2S , the H_2 -treatment increases the amount of sites characterized by the band at 2098 cm^{-1} . Hence, this suggests that these newly created Mo sites are not active for the hydrogenation reaction. However, it should be mentioned that these sites were found active for xylene formation [18].

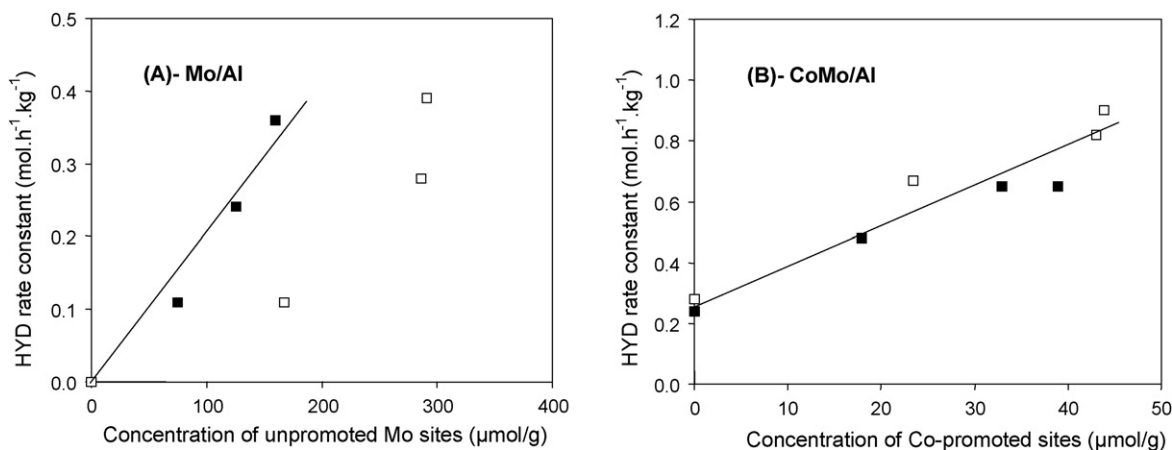


Fig. 8. (A) Rate of HYD route of 2,6-dimethylaniline HDN for Mo/Al catalysts vs. concentration of unpromoted sites; (B) rate of HYD route of 2,6-dimethylaniline HDN for $\text{Co}_x\text{Mo}_9/\text{Al}$ catalysts vs. concentration of Co-promoted sites. Full symbols correspond to activity measured in presence of H_2S and concentration of sites detected after sulfidation; open symbols correspond to activity measured in absence of H_2S and concentration of sites detected after H_2 -treatment.

With respect to the CoMo/Al catalysts, a linear relationship is obtained between the hydrogenation rate measured in presence of H₂S and the amount of sites detected after sulfidation, on one hand, and the activity measured in the absence of H₂S and the concentration of Co-promoted sites detected after H₂-treatment, on the other hand (Fig. 8B). Hence, it appears that the Co-promoted sites created by H₂-treatment are as active in hydrogenation as those detected on sulfided catalysts. This is in agreement with the absence of significant modifications of the environment of Co-promoted sites detected by CO after sulfidation or H₂-treatment.

As previously, TOF for hydrogenation route can be calculated for unpromoted and Co-promoted sites. TOF reaches 16.2 h⁻¹ for the Co-promoted sites, while for unpromoted sites it is 1.5 h⁻¹ considering the unpromoted sites detected after sulfidation. The promotion factor for HYD is equal to 11, a value in the same order of magnitude than that calculated for thiophene HDS.

5. Conclusion

This contribution reports a parallel between IR spectroscopy of CO adsorption ($T_{\text{ads}} \sim 100$ K) and activity and selectivity in thiophene HDS and 2,6-dimethylaniline HDN of a series of sulfided (Co)Mo/Al catalysts. The salient features highlighted in the present study are as follows:

- (i) CoMo catalysts prepared by impregnation always exhibit an incomplete promotion of the MoS₂ slabs, even for those containing a high Co/Co + Mo atomic ratio. This underlines that development of improved hydrotreatment catalysts is still possible.
- (ii) Combination between spectroscopic and catalytic data allows one to determine an intrinsic activity for unpromoted and Co-promoted sites, where only edge atoms are considered in the calculation. The relative activity of unpromoted and Co-promoted sites differs by one order of magnitude.
- (iii) In the temperature domain that corresponds to hydrotreatment reaction, unpromoted and Co-promoted edge sites do not present the same sensitivity towards H₂S partial pressure. The Mo sites created at low H₂S partial pressure are highly sulfur-depleted and present functionalities different than those formed in sulfiding conditions. By contrast, the Co-promoted sites are easily created even in sulfiding conditions and the sites generated in high or low H₂S/H₂ conditions present the same environment as well as the same reactivity.
- (iv) The presence of small clusters of CoS_x located on the edge sites or on the basal planes is proposed to account for the low amount of chemisorption sites specific of Co-promoted compared to the total cobalt content of the catalysts.
- (v) This study emphasizes the potentiality of IR spectroscopy of CO adsorption for discriminating nature, environment of the sulfide phase sites as well as for assessing their amount and that for H₂S/H₂ partial pressure close to the working conditions.

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Effect of EDTA addition on the structure and activity of the active phase of cobalt–molybdenum sulfide hydrotreatment catalysts

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ABSTRACT

Two series of (Co)Mo/Al₂O₃ catalysts were compared: one set was prepared with a constant amount of Mo, and various amounts of Co (from 0 to 4.5%), the second one containing the same amount of metals, but with ethylene diamino tetraacetic acid (EDTA) addition (27 wt%). The sulfided catalysts were characterized by IR spectroscopy of adsorbed CO. IR reveals that EDTA leads to a strong increase in the concentration of Co-promoted sites. EDTA has also a significant positive effect on thiophene hydrodesulfurization at atmospheric pressure, and 2,6-dimethylaniline hydrodenitrogenation at high pressure. Combination of spectroscopic and activity data shows that EDTA chiefly increases the amount of promoted sites having lower average intrinsic activities. This decrease in intrinsic activity should be due to a change of the site structure. Two models can be proposed to account for EDTA effect on the site structure such as the formation of type II slabs or that of nitrogeno-sulfide Co-promoted sites, “CoMoSN”.

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1. Introduction

The presence of sulfur as impurity in fuels poisons catalytic converters and generates polluting emissions. Drastic regulations are thus set up to limit the sulfur content of fuels. Hydrotreatment is the most largely used process to remove sulfur from oil streams. Hydrotreating catalysts are generally described as small MoS₂ crystallites promoted by cobalt (or nickel), dispersed on alumina-based support [1,2]. For CoMo catalysts, Co atoms anchored on the edges of the MoS₂ slabs generate active sites (CoMoS sites), whereas cobalt can also be present as CoS_x phase or as spinel in the support [3]. Several preparation methods have been developed in order to improve the performances of CoMo hydrotreating catalysts. Among them, addition during catalyst synthesis of chelating agents like nitrilo triacetic acid (NTA), ethylene diamino tetraacetic acid (EDTA), and cyclohexane diamine tetraacetic acid (CyDTA) has been studied [4–17]. In these studies, an increase of hydrodesulfurization (HDS) activity of CoMo catalyst was reported upon addition of chelating agent although the extent of increase could strongly differ. The origin of the beneficial effect of chelating agent addition is generally explained by an increase of the promotion of the sulfide phase by Co [9] due to either a decrease of cobalt loss by diffusion in the support or a limitation of CoS_x

particle growth [13]. Such modification has been explained by the stability of the promoter–chelating agent complex at high temperature towards the H₂S/H₂ mixture [6]. Similarly, de Jong et al. [5] and Coulier et al. [10,11] have shown that NTA delays the sulfidation of cobalt to temperatures at which MoS₂ is already formed. However, IR analysis of the sulfide phase formed on supported sulfide NTA-catalysts did not confirm this conclusion [16]. Another proposal, alternative to the increase of promotion and made by van Veen et al., is the formation of the type II CoMoS phase [4].

Thus from literature, it appears that chelating agents have a role on the concentration of active sites but could also change their structure and thus their intrinsic activity. In this study, in order to determine more precisely the role of one of these chelating agents, namely EDTA, on the structure and activity of CoMo/Al₂O₃ catalysts, both catalytic tests and spectroscopic analysis were performed.

Two series of catalysts were then compared: one series was prepared with a constant amount of Mo, and various amounts of Co (from 0 to 4.5 wt%), the second one containing the same amount of metals, but in which EDTA was introduced (27 wt%). Taking into account the previous studies [4,16], the chelating agent was added together with the metal precursors during the pore-volume impregnation. After drying, the catalyst was directly sulfided (without calcination step). The effect of EDTA was studied in two catalytic tests: HDS of thiophene, which is commonly used to rapidly evaluate the catalyst performances, and hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA) that enables to

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evaluate the various catalytic functions of the catalysts [18]. The nature and amount of sulfide phase of both sets of catalysts were characterized by IR spectroscopy of adsorbed CO [19,20]. Then, the effect of EDTA on the active phase structure was discussed.

2. Experimental

2.1. Catalyst preparation

The catalysts (Table 1) were prepared by pore-volume impregnation of a γ -alumina ($S_{\text{BET}} = 258 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.66 \text{ cm}^3 \text{ g}^{-1}$). The γ - Al_2O_3 support was calcined at 773 K for 3 h before impregnation. The $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst (8.7 wt% Mo) was prepared by impregnation of the γ - Al_2O_3 support with a $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Aldrich) solution. The sample was dried at 393 K for 5 h and calcined at 773 K for 3 h.

Two series of $\text{CoMo}/\text{Al}_2\text{O}_3$ (1.5–4.5 wt% Co) catalysts with and without chelating agent were prepared. The first series of $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts (without chelating agent) was prepared by impregnation of the calcined $\text{Mo}/\text{Al}_2\text{O}_3$ with a cobalt nitrate (Aldrich) solution, drying, and finally calcination at 773 K for 3 h with a heating rate of 3 K min^{-1} . The catalysts of this series are designated as X.XCoMo where X.X corresponds to the Co content (1.5–4.5 wt%).

The second series with chelating agent was prepared by contacting the calcined $\text{Mo}/\text{Al}_2\text{O}_3$ with a solution containing cobalt nitrate (Aldrich) and EDTA. The amount of EDTA in each catalyst was chosen to be constant, i.e. 27 wt% EDTA, and exceeds the full complexation of Co. Before sulfidation, the catalysts prepared with EDTA were not calcined but only dried at 393 K for 5 h, in order to keep the chelating agent in its initial form [15]. These catalysts are designated as X.XCoMoEDTA, where X.X corresponds to the percentage of Co in the EDTA-free catalyst (1.5–4.5 wt%). The $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst was also contacted with EDTA in absence of cobalt salt. The obtained catalyst is named $\text{MoEDTA}/\text{Al}_2\text{O}_3$.

Table 1 reports the catalyst composition measured by AAS before sulfidation. Note that the molar ratio between Co and Mo is almost the same in the two series after sulfidation which is expected to totally eliminate EDTA. Upon sulfidation, the loss of catalyst weight due to EDTA elimination, water desorption and precursor decomposition was measured experimentally. In the following, weight of catalyst referred to the weight of catalyst after sulfidation.

2.2. Catalytic tests

The catalysts were tested by means of two reactions: hydrodesulfurization (HDS) of thiophene and hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA).

2.2.1. Thiophene hydrodesulfurization

The thiophene HDS activity test was carried out in a flow micro-reactor working at atmospheric pressure and 623 K. Appropriate amounts of catalyst (about 20 mg) were used in order to keep the

conversion lower than 5%. Before the reaction, the catalysts were sulfided *in situ* with 30 mL min^{-1} of $\text{H}_2\text{S}/\text{H}_2$ (10 vol%) at 623 K (heating rate of 3 K min^{-1}) for 30 min.

Thiophene was introduced into the reactor by flowing hydrogen (70 mL min^{-1}) through a thiophene saturator maintained at 291 K and mixed to 20 mL min^{-1} of $\text{H}_2\text{S}/\text{H}_2$ (10 vol%). Products were analyzed on-line by using a Varian gas chromatograph equipped with a flame ionization detector (FID) and CPSIL-5CB capillary column. The specific reaction rate was calculated as $r_{\text{HDS}} = (F/w)X$, where F/w is the molar flow rate of reactant per mass of catalyst (after sulfidation) and X is the thiophene conversion.

2.2.2. 2,6-Dimethylaniline hydrodenitrogenation

The 2,6-dimethylaniline HDN activity test was carried out in a stainless steel flow reactor (Sotalem) at 4 MPa and 573 K. Around 0.35–0.40 g of catalyst was first sulfided *in situ* under 60 mL min^{-1} of $\text{H}_2\text{S}/\text{H}_2$ (10 vol%) at 4 MPa up to 623 K with a temperature ramp of 3 K min^{-1} and maintained 2 h at 623 K. Thereafter, the catalyst was cooled under $\text{H}_2\text{S}/\text{H}_2$ to the reaction temperature and the H_2S content adjusted at 1.4% in hydrogen. The liquid feed (10 vol% 2,6-dimethylaniline, reactant; 80% heptane, solvent; and 10% decane, internal standard) was introduced by an HPLC pump and vaporized in the $\text{H}_2\text{S}/\text{H}_2$ stream. The reaction products were condensed at the reactor exit and the liquid was analyzed with a Varian gas chromatograph equipped with a CPSIL-5CB capillary column and a FID detector.

The partial pressure of 2,6-dimethylaniline was kept constant at 13 kPa for all experiments. Reaction conditions at steady state were varied by changing the contact time (55 – 250 h g mol^{-1}) at 56 or 0 kPa of H_2S . We determined the reaction orders in 2,6-dimethylaniline for the hydrogenation (HYD), xylene (XYL) and disproportionation (DIS) reaction pathways as zero, zero and 0.4 respectively [18]. In this work, we report the activities for HYD and XYL expressed by the rate constant ($\text{mol h}^{-1} \text{ kg}^{-1}$) where the mass of catalyst was corrected for the weight loss due to sulfidation.

2.3. IR spectroscopy of adsorbed CO

2.3.1. IR experiments

The samples were ground and pressed to obtain a wafer (area 2 cm^2 , mass about 10 mg, but precisely weighted) before introduction in the IR cell. The spectra were recorded on a Fourier Transform IR spectrometer from Thermo Optek with a MCT detector. Spectra were recorded with 256 scans using a resolution of 4 cm^{-1} . All the spectra presented in this paper are normalized to a disc of 5 mg cm^{-2} of sulfided catalyst.

2.3.2. Standard sulfidation procedure

A standard sulfidation was carried out *in situ* in the IR cell, according to the following procedure. The disc was sulfided under a flow of $\text{H}_2\text{S}/\text{H}_2$ (10/90) at 30 mL min^{-1} , with a heating rate of 10 K min^{-1} up to 543 K, and then maintained at this temperature for 30 min. The temperature was then raised to 623 K and maintained during 1.5 h. At this temperature, the $\text{H}_2\text{S}/\text{H}_2$ flow was stopped and replaced by a flow of N_2 at 30 mL min^{-1} for 30 min. Then, the sample was cooled down to room temperature under N_2 . Afterward, an evacuation was performed from RT to 573 K (with a rate of 10 K min^{-1}) and maintained at 573 K until reaching a pressure of 10^{-3} Pa . Finally, the sample was cooled down to liquid nitrogen temperature before CO introduction.

2.3.3. H_2 post-treatment procedure

In some cases after standard sulfidation, the sample was submitted to a H_2 post-treatment in order to mimic the working conditions for HDN of DMA without H_2S . Thus, after the evacuation at 573 K (described in the previous section), a first pressure of

Table 1
Composition of the as-prepared (Co)Mo/ Al_2O_3 catalysts (before sulfidation) measured by AAS.

Catalysts	Co (wt%)	Mo (wt%)	EDTA (wt%)	EDTA/(Co + Mo) molar ratio
$\text{Mo}/\text{Al}_2\text{O}_3$	0.0	9	0	0
1.5CoMo	1.6	8.9	0	0
3.0CoMo	3.3	8.5	0	0
4.5CoMo	4.6	8.2	0	0
$\text{MoEDTA}/\text{Al}_2\text{O}_3$	0.0	6.6	27	0.82
1.5CoMoEDTA	1.3	6.6	27	0.69
3.0CoMoEDTA	2.6	6.2	27	0.62
4.5CoMoEDTA	3.5	5.9	27	0.58

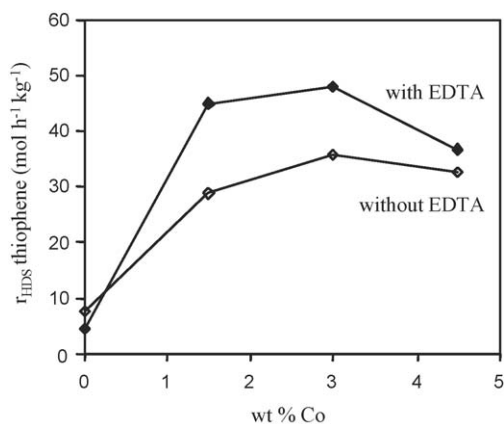


Fig. 1. Influence of Co amount and EDTA addition on the thiophene HDS activity of (Co)Mo/Al₂O₃ catalysts.

13.3 kPa of H₂ was introduced in the IR cell. After 30 min of H₂ at 573 K, the cell was evacuated under secondary vacuum, and the catalyst was contacted with a second pressure of 13.3 kPa of H₂ during 30 min. The cell was evacuated under secondary vacuum at 573 K, and cooled down to liquid nitrogen temperature.

2.3.4. Procedure for CO adsorption

Before CO introduction, a reference spectrum of the activated catalyst was recorded at liquid nitrogen temperature. Then, small calibrated doses of CO were introduced in the IR cell. Finally an equilibrium pressure of 133 Pa was established. A spectrum was taken after each CO introduction. All the CO spectra presented correspond to difference spectra, i.e. spectrum after CO adsorption minus reference spectrum.

3. Results

3.1. Catalytic activity

3.1.1. Hydrodesulfurization of thiophene

The thiophene HDS activities of both series of catalysts as a function of the Co content are reported in Fig. 1.

For the reference catalysts (without EDTA), the HDS activity increases with Co amount reaching a maximum for 3 wt% Co and slightly decreases at higher loading. This result is in agreement with literature [21].

EDTA addition decreases the HDS activity of the unpromoted Mo/Al₂O₃ catalyst (–41%), whereas the activity of CoMo catalysts is strongly increased. The beneficial effect of EDTA is maximum for the lowest Co loading and decreases for higher Co loading (1.5CoMoEDTA +56%; 3.0CoMoEDTA +34%; 4.5CoMoEDTA +13%).

However, the highest HDS activity is still observed for the 3.0CoMoEDTA catalyst. The positive effect of EDTA on the activity of CoMo catalysts as well as its order of magnitude is in agreement with previous studies [7]. However, the negative effect of EDTA on the Mo/Al₂O₃ catalyst activity is surprising since a positive effect was previously reported [12].

3.1.2. Decomposition of 2,6-dimethylaniline

3.1.2.1. Influence of Co amount and EDTA presence on HYD route. The HYD activity versus Co amount, with or without EDTA, measured in presence (A) and in absence of H₂S (B), is presented in Fig. 2. On the two catalyst series (with and without EDTA), an increase of the HYD activity with the Co content is observed both in presence and in absence of H₂S. In all cases, the increase is the most important for the first Co addition (from 0 to 1.5 wt%). EDTA addition has a beneficial effect on HYD activity whatever the Co amount. The activity increase is close to 30% for all the (Co)Mo catalysts. In particular, EDTA has also a positive effect on the HYD activity of the Mo/Al₂O₃ catalyst conversely to what was observed on the thiophene test.

3.1.2.2. Influence of Co amount and EDTA presence on XYL route. Fig. 3A shows that the activities for the XYL formation measured in presence of H₂S strongly increase with the amount of Co. Moreover, the presence of EDTA has a beneficial effect on the XYL activities. Fig. 3B shows a general decrease of the XYL activities with the amount of Co in absence of H₂S. As in presence of H₂S, the presence of EDTA has a beneficial effect whatever the catalysts although this effect is maximum for the Mo/Al₂O₃ catalyst. Whatever the catalysts, the XYL activities measured in presence of H₂S are always smaller than the activities measured in absence of H₂S.

3.1.2.3. Comparison between activity for HYD and XYL routes. The rate constants for the xylene formation route (XYL) obtained in presence or in absence of H₂S are plotted as a function of hydrogenation rate constants (HYD) measured under the same conditions for the two sets of catalysts (Fig. 4A and B).

In presence of H₂S (Fig. 4A), a linear relationship can be drawn between the two rate constants for the different catalysts that contain or not EDTA. This is in agreement with the DMA reaction scheme which shows a common dearomatized intermediate for the HYD and XYL routes. In agreement with previous work of van Gestel et al. [18], the straight line intercepts the ordinate at a positive value, which is attributed to an extra, but constant, xylene formation route (DDN route), independent of dearomatization. The presence of chelating agent increases in the same extent the HYD and XYL activities for all the catalysts including the unpromoted one. Thus, an increase of the activity due to an increase of the number of active sites could be envisaged in this case. However,

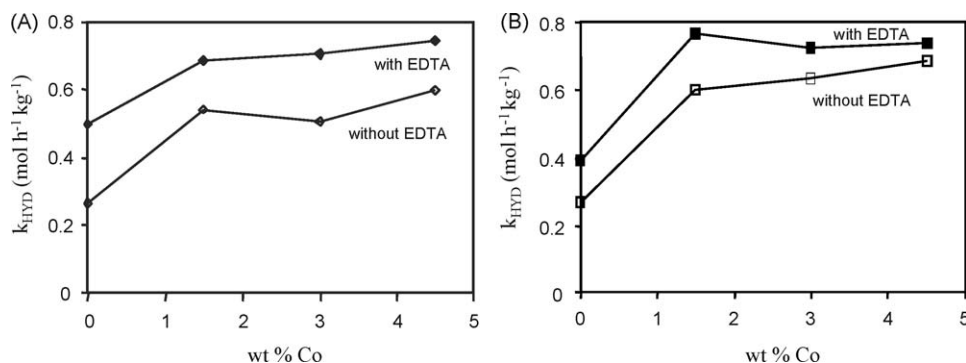


Fig. 2. HDN of DMA: HYD activity of the (Co)Mo/Al₂O₃ catalysts with and without EDTA. [A] Activity measured in presence of H₂S (56 kPa); [B] activity measured in absence of H₂S.

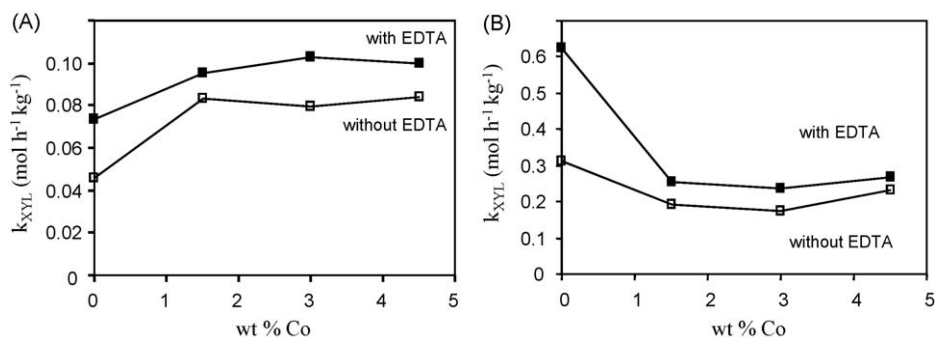


Fig. 3. HDN of DMA: XYL activity of (Co)Mo/Al₂O₃ catalysts with and without EDTA. [A] Activity measured in presence of H₂S (56 kPa); [B] activity measured in absence of H₂S.

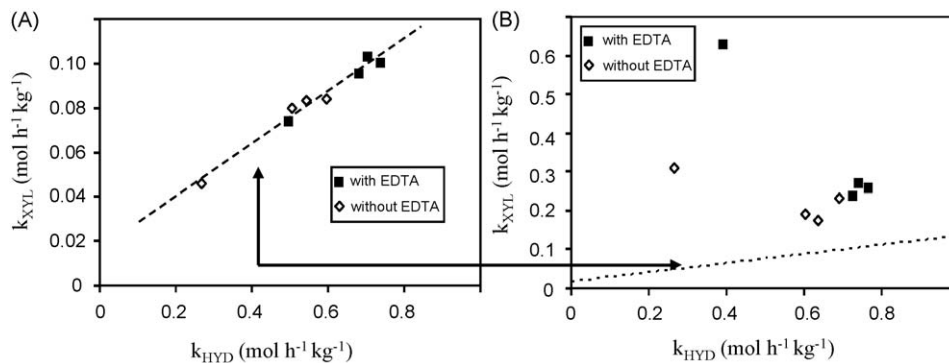


Fig. 4. HDN of DMA: XYL versus HYD activity of the (Co)Mo/Al₂O₃ catalysts with and without EDTA [A] activity measured in presence of H₂S (56 kPa); [B] activity measured in absence of H₂S (the dotted line corresponds to XYL versus HYD in presence of H₂S).

Fig. 4B points out that, in absence of H₂S, there is no linear relationship between the two rate constants anymore: the XYL rate constant decreases when HYD rate increases. The chelating agent enhances this effect.

3.1.2.4. Influence of Co amount and EDTA presence on DDN route. A previous work [18] has shown that, in presence of H₂S, xylene (XYL) is mainly formed by NH₃ elimination from dearomatized DMA (HYG). This elimination could occur after substitution of the amino group to form a thiol as proposed by Zhao and Prins [22]. By contrast, in absence of H₂S, xylene formation is strongly increased. In this case, xylene is formed by both NH₃ elimination from dearomatized DMA (HYG) and by direct carbon–nitrogen bond cleavage (DDN) (i.e., XYL = HYG + DDN). Comparison of the xylene formation in presence and in absence of H₂S allows one to calculate the DDN activity.

Fig. 5 presents the DDN activity plotted as a function of the amount of Co present on the catalysts prepared with and without EDTA. On the two series, DDN activity decreases with the addition of Co. This result is in agreement with the above mentioned study which related the DDN activity to the presence of highly unsaturated unpromoted MoS₂ sites. However, it should be mentioned that the presence of EDTA increases the activity for DDN both on Mo and Co-promoted catalysts.

3.2. Nature and concentration of the sulfide phase sites—IR spectroscopy of CO

3.2.1. Unpromoted catalysts

IR spectroscopy experiments of CO adsorbed at low temperature are performed on *in situ* sulfided catalysts. Fig. 6A represents the IR spectra of CO adsorbed on the sulfided Mo/Al₂O₃ and MoEDTA/Al₂O₃ catalysts (133 Pa at equilibrium). They are typical of Mo/Al₂O₃ catalysts [20] and can be decomposed in four main

bands: two of them (2188 and 2156 cm⁻¹) are attributed to the alumina sites (alumina Lewis and Br  nsted sites respectively), the band near 2110 cm⁻¹ is attributed to the adsorption of CO on the molybdenum edge of MoS₂ sites and the last one, a broad band at ≈ 2068 cm⁻¹ is attributed to CO adsorbed on the sulfur edge of MoS₂ slab [23]. A decrease of the amount of CO adsorbed on the alumina sites is observed when the catalyst is prepared in presence of EDTA. This can be accounted by the presence of carboxylate species observed by IR spectroscopy (see Fig. 6B) on the MoEDTA/Al₂O₃ catalyst just after the sulfidation. Thus, although most of the chelating agent has decomposed during the sulfidation step, carboxylate species are still present on the support after the sulfidation. Concerning the adsorption of CO on the sulfide phase itself, a downward shift of the maximum of absorbance of about 5 cm⁻¹ is observed for MoEDTA/Al₂O₃ as compared to Mo/Al₂O₃. The third spectrum in Fig. 6A represents the difference between

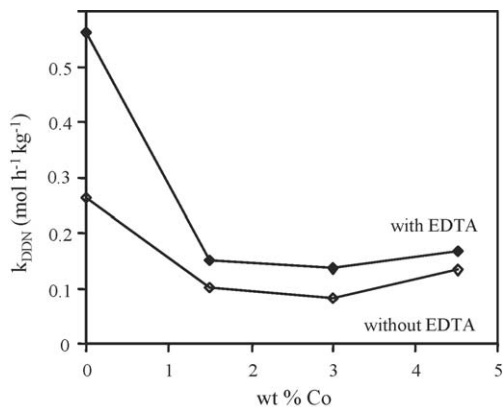


Fig. 5. HDN of DMA: activity for the DDN route of the (Co)Mo/Al₂O₃ catalysts with and without EDTA.

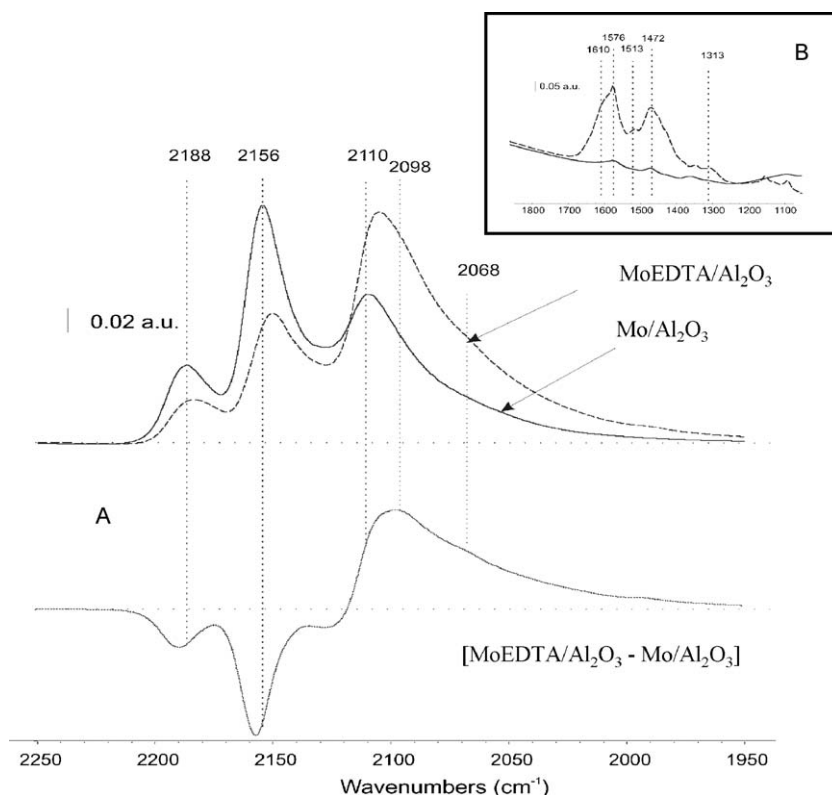


Fig. 6. IR spectra of [A] CO adsorbed on sulfided Mo/Al₂O₃ and MoEDTA/Al₂O₃ catalysts; [B] sulfided Mo/Al₂O₃ and MoEDTA/Al₂O₃ catalysts.

spectra of the two Mo catalysts: [MoEDTA/Al₂O₃]-[Mo/Al₂O₃]. This subtraction allows us to highlight the evolution of sulfide phase sites due to the use of EDTA. Two positive bands are observable, at 2068 cm⁻¹ and at 2098 cm⁻¹. This latest band was already observed after a H₂ treatment by Dujardin et al. [21] and was attributed to unsaturated MoS₂ sites which were proposed to be responsible of the extra DDN activity in the DMA HDN test in absence of H₂S.

3.2.2. Co-promoted catalysts

The IR spectra of CO adsorbed at low temperature on the two sets of sulfided catalysts are presented in Fig. 7.

They are composed of five main bands. The two bands at 2188 and 2156 cm⁻¹ are attributed to CO in interaction with alumina sites. The band around 2110 cm⁻¹ is due to CO in interaction with

MoS₂ sites and the two low wavenumber bands to CO adsorbed on CoMoS sites. More precisely, the bands at 2070 and 2060 cm⁻¹ are respectively attributed to fourfold coordinated Co sites and fivefold coordinated Mo sites in the vicinity of Co [23]. In both series, increasing Co content does not lead to any band shift but only to an increase of band intensity due to CO/CoMoS at the expense of bands due to CO/Mo. Addition of EDTA leads to a downward shift of the CO/Mo band (-5 cm⁻¹), as observed on the pure Mo catalyst, whereas no shift of the CO/CoMoS band is noted. Regarding the catalysts sulfided and H₂ post-treated, similar band positions are observed while the intensities of the CO/sulfide bands are markedly increased.

The quantification of the different sites was performed using CO/MoS₂ and CO/CoMoS molar absorption coefficient previously reported [20]. The evolutions of the total concentration of sites, MoS₂ sites and CoMoS sites versus the amount of Co on the H₂ post-

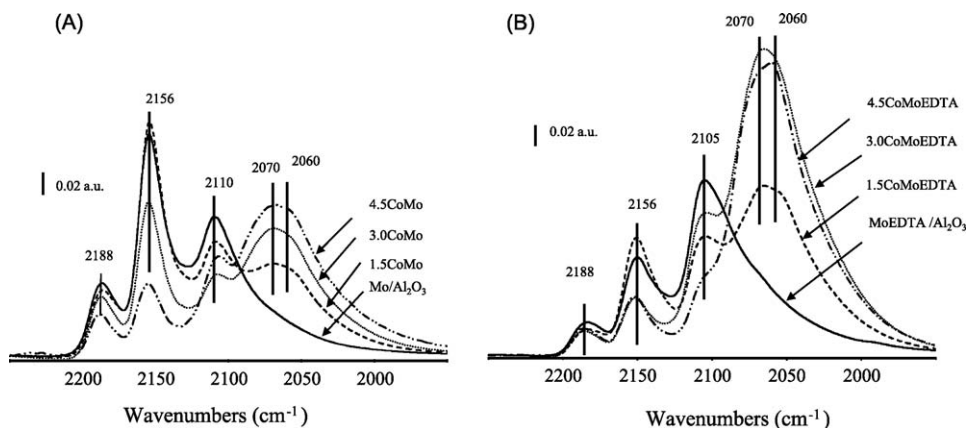


Fig. 7. IR spectra of CO adsorbed on (Co)Mo/Al₂O₃ and (Co)MoEDTA/Al₂O₃ catalysts.

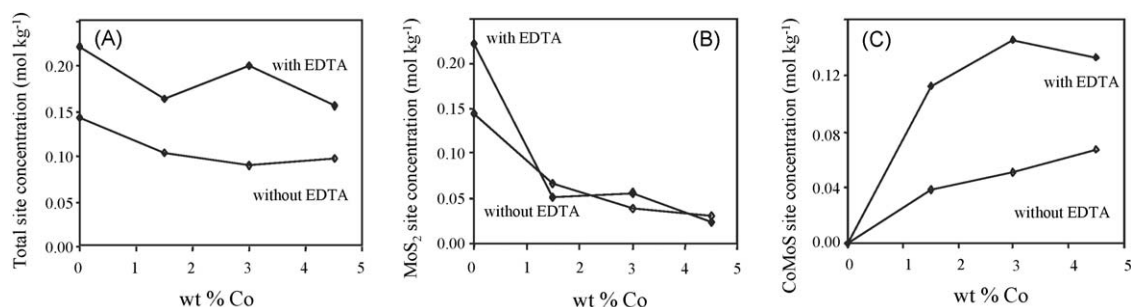


Fig. 8. Concentration of sites determined by CO adsorption after sulfidation and H₂ post-treatment. [A] Total sites, [B] MoS₂ sites and [C] CoMoS sites.

treated catalysts are presented in Fig. 8A, B and C, respectively. Similar trends are observed on sulfided catalysts.

For both series a slight decrease of the total amount of sites is observed for increasing Co content. However, the concentration of total sites is 50% higher when the catalyst is prepared with EDTA.

For MoS₂ sites, the effect of EDTA is mostly distinguishable for the unpromoted catalyst: the MoEDTA/Al₂O₃ catalyst has a 1.5-fold higher amount of MoS₂ sites (Fig. 8B). Concerning the promoted catalysts, EDTA seems to have no effect on the amount of unpromoted Mo sites.

As expected, the concentration of CoMoS sites increases with Co content whether the catalysts were prepared with EDTA or not (Fig. 8C). In the absence of chelating agent, this increase is proportional to the amount of Co, whereas for EDTA catalysts, a maximum is observed at 3 wt% Co content. This difference between the two series could indicate that the maximum of Co which can be anchored to the MoS₂ slabs is reached when the catalyst is prepared with EDTA. Moreover, it can be noticed that the EDTA catalysts have always a larger amount of CoMoS than the catalysts without EDTA: for each amount of Co, the concentration of CoMoS sites is at least multiplied by 2.

In conclusion, the presence of EDTA on CoMo catalysts increases the amount of CoMoS sites without modifying the amount of unpromoted MoS₂ sites, thus the total number of sites increases with EDTA.

4. Discussion

From a comparison between catalytic tests and IR characterization results, we aim to determine whether addition of EDTA has only an effect on the concentration of active sites or also an effect on their intrinsic activities, i.e. on the structure of active sites.

4.1. Site concentrations and HDS of thiophene and HYD of DMA activity

Figs. 9 and 10 show the evolutions of activity for HDS of thiophene and HYD of DMA versus the amount of CoMoS sites on the two series of catalysts, with or without EDTA, respectively. For series of (Co)Mo catalysts supported on Al₂O₃, correlations between activity and concentration of MoS₂ and CoMoS sites were previously reported by Dujardin et al. both in the HDS of thiophene and the HYD of DMA in presence of H₂S [21]. These correlations have allowed the TOF values to be determined for both types of sites in these two reactions (Table 2). In this previous work, it was supposed that activity of MoS₂ sites was independent of the one of CoMoS: i.e. that the TOF value for MoS₂ sites was the same on a Mo/Al₂O₃ series and a CoMo/Al₂O₃ series. The good correlation obtained for CoMoS site concentration and activity validated this hypothesis.

In the same way, in this study, we have first estimated the TOF value for MoS₂ sites from the activity of Mo/Al₂O₃ without EDTA.

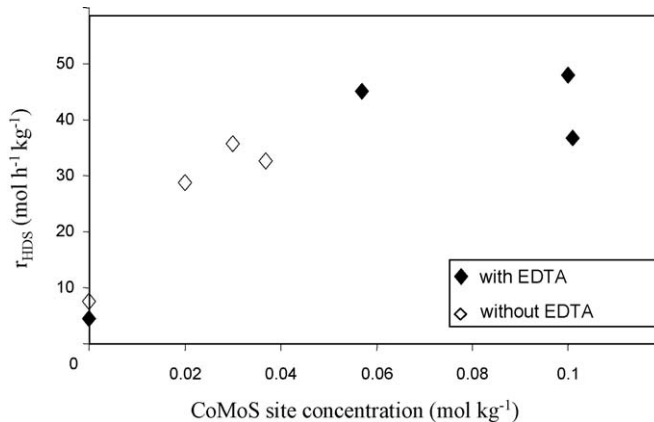


Fig. 9. Comparison between IR results and thiophene HDS activity.

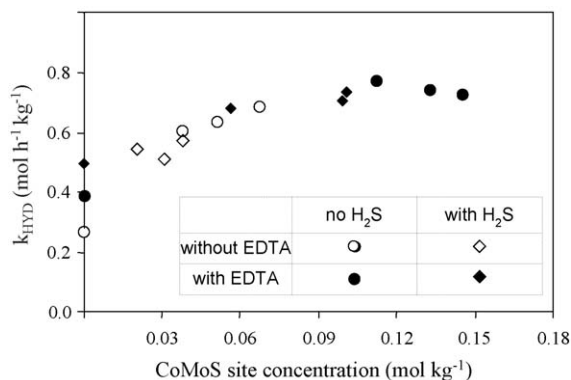


Fig. 10. Comparison between IR results and DMA HYD activity.

Then for the CoMo catalysts, the activity of CoMoS sites was estimated by subtracting from the total activity of CoMo catalysts the activity of MoS₂ sites obtained by multiplying the TOF value of MoS₂ by the concentration in MoS₂ sites. The resulting HDS and HYD activities of DMA showed satisfactorily linear correlations (not shown) with the CoMoS site concentrations ($R^2 > 0.9$) in the absence of EDTA and presence of H₂S.

Moreover, the TOF values obtained for CoMoS sites are in the same order of magnitude than the ones reported by Dujardin et al.

Table 2

TOF of CoMoS sites for thiophene HDS and HYD of DMA of CoMo/Al₂O₃ catalysts without EDTA.

Catalyst series	TOF HDS (h ⁻¹) [reaction 7]	TOF HYD (h ⁻¹) with H ₂ S
Dujardin, 2007	1080 [673 K]	16
This work	880 [623 K]	13

taking into account the change in reaction temperature (673 K in [21] and 623 K in this study) for thiophene HDS (Table 2). Thus, it can be concluded that for the series without EDTA, the catalytic activity is well explained by the concentration of CoMoS and MoS₂ sites.

In contrast, for the catalyst series with EDTA, no good linear relationship was obtained whatever the activity test: the increase of concentration of CoMoS sites does not lead to activity as high as expected from the TOF values in absence of EDTA. It has to be mentioned that for the EDTA series, calculations were done either considering that MoS₂ sites have the same intrinsic activity with or without EDTA or with TOF for MoS₂ calculated from MoEDTA/Al₂O₃ activity results. None of these options give satisfying results. Thus it appears that the nature of CoMoS sites is somewhat modified by EDTA addition. Accordingly, EDTA would essentially increase the concentration of CoMoS promoted sites to the detriment of their intrinsic activities.

4.2. Site concentrations and DDN route of DMA HDN

The activity for the DDN route of DMA HDN has been previously attributed to highly unsaturated MoS₂ sites [18]. On the Mo/Al₂O₃ catalyst, EDTA addition not only leads to an increase of MoS₂ site concentration (Fig. 8) but also increases the amount of unsaturated MoS₂ sites characterized by a band at 2098 cm⁻¹ (Fig. 6), thus explaining the strong increase of the DDN activity in HDN of DMA (Fig. 5).

The CoMo catalysts prepared with EDTA present an extra DDN activity – similar for the three Co levels – as compared to the catalysts prepared without EDTA. The concentrations of MoS₂ sites determined by IR spectroscopy being similar with or without EDTA (Fig. 8), the extra DDN activity could account for a higher intrinsic activity of unpromoted Mo sites. IR spectra in Fig. 7 show that EDTA addition leads to a downward shift of the band assigned to unpromoted sites (2105 cm⁻¹ vs. 2110 cm⁻¹), which could be accounted by the increase of unsaturated sites (2098 cm⁻¹, Fig. 6), active for DDN. The strong overlap of these bands with those due to CoMoS sites, however, prevents any assessment of these sites (Fig. 7).

Alternatively, assuming CoMoS sites present a much lower DDN activity as compared to unpromoted Mo sites, the small extra DDN activity observed for CoMoEDTA catalysts could be due to the strong increase of CoMoS sites induced by EDTA.

4.3. Influence of EDTA on the structure of sulfide sites

Addition of EDTA clearly increases the amount of CoMoS sites, which leads to a marked enhancement of the HDS and HDN activity of the catalysts. However, the results presented in the previous section does not allow to calculate a TOF in presence of EDTA. Moreover, DDN results suggests a change in sulfide site structure. These observations can be interpreted as the formation of new types of sites. Two models are tentatively proposed:

- EDTA could favor the formation of sulfide slabs of type II instead of type I. Note that type II sites are generally considered as more active than type I. However, this is not in contradiction if we consider that the amount of CoMoS sites has been overestimated in the present study (because of the use of absorption coefficient for 'conventional' CoMoS sites) and thus that the TOF value has been underestimated.
- EDTA leads to the formation of "CoMoSN" sites. The interaction between Co and EDTA leads to the insertion of some nitrogen into

the sulfide slab which could generate some nitrogeno-sulfide Co-promoted sites at the edges of the MoS₂ slabs.

Similar models were proposed to account for the effect of other chelating agents such as NTA, on the structure of the sulfide sites [17].

5. Conclusion

IR spectroscopy reveals that on unpromoted Mo/Al₂O₃ catalysts, EDTA increases the amount of Mo-edge unpromoted sites (2110 cm⁻¹) and, in a larger extent, unsaturated Mo sites (2098 cm⁻¹) active for the DMA DDN route. These findings account for the much higher activity of Mo/Al₂O₃ prepared with EDTA towards all DMA HDN routes. Surprisingly, these changes are not reflected in thiophene HDS for which activity is decreased by addition of EDTA.

For promoted CoMo catalysts, EDTA addition also leads to a change in unpromoted Mo sites distribution (Mo-edge vs. unsaturated), without affecting much their total amount. Consequently, CoMo catalysts prepared with EDTA present a limited extra DDN activity as compared to catalysts prepared without EDTA.

More strikingly, EDTA also leads to a strong increase of promoted CoMoS sites and significant increase in thiophene HDS (up to 1.6×) and DMA HDN (HYD up to 1.4×) activities. The relative increase of catalytic activities, however, is somewhat lower than that expected from the increase of CoMoS sites, suggesting that EDTA chiefly increases the amount of promoted sites having lower average intrinsic activities. This should be due to a change in the structure of promoted sites.

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Effect of NTA addition on the structure and activity of the active phase of cobalt-molybdenum sulfide hydrotreating catalysts

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Carbon monoxide

ABSTRACT

CoMoS catalysts with constant Co and Mo contents were prepared with different amounts of nitrilo triacetic acid (NTA) chelating agent. NTA has a marked positive effect on the catalyst activity for gas-phase reactions such as atmospheric pressure thiophene hydrodesulfurization (HDS) and high-pressure 2,6-dimethyl aniline hydrodenitrogenation, whereas no effect is found for liquid-phase dibenzothiophene HDS. Transmission electron microscopy analysis shows that NTA has no effect on MoS₂ slab size and stacking, while infrared spectroscopy of adsorbed CO reveals a strong increase in the amount of Co-promoted sites. Comparison of activity and spectroscopic data implies that increase of Co-promoted sites accounts for the catalytic activity enhancement, but it also provides evidences for the creation of different kinds of sites on the NTA catalysts. Various possibilities (type II CoMoS phase, Co clusters, or CoMoSN) are discussed.

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1. Introduction

To limit polluting emissions and preserve the catalytic converter from poisoning, more drastic regulations have been issued to limit the sulfur content in fuels. Hydrotreatment is the most widely used process to remove sulfur from oils. Hydrotreating catalysts are generally composed of small MoS₂ crystallites promoted by cobalt (or nickel) dispersed on alumina-based supports [1]. The anchoring of Co atoms on the edges of the MoS₂ slabs (CoMoS sites) accounts for the creation of active sites, whereas cobalt can also be present as a separate CoS_x phase or as spinel in the support [2]. By comparing catalytic data and sulfide slab size measured by transmission electron microscopy (TEM), Kastzellan et al. proposed a hexagonal shape for the sulfide slabs of alumina-supported CoMo catalysts [3]. This geometrical model has been largely used as a base for quantification of the amount of edge sites [4]. Recent scanning tunneling microscopy (STM) observations of sulfide slabs deposited on flat gold surfaces show that unpromoted Mo sulfide slabs are triangular, whereas after Co deposition the sulfide slabs

become hexagonal [5]. Further investigations also differentiated two types of CoMoS phase, called type I and type II [1,3–5], which are distinguishable by their sulfidation degree and by differences in their interaction with the carrier. The CoMoS phase of type II, with lower interaction with the support, is generally the most active one.

Several preparation routes were developed in order to improve the performance of hydrotreating catalysts. In 1986, a patent from Shell was the first to describe the use of chelating agents such as nitrilo triacetic acid (NTA) to improve the catalytic performances of CoMo and NiMo catalysts [6]. NTA [8–10] is still the most widely used chelating agent along with ethylene diamine tetraacetic acid (EDTA) [7,8] and cyclohexane diamine tetraacetic acid (CyDTA) [5,8–12]. An increase of thiophene hydrodesulfurization (HDS) activity is generally reported when these chelating agents are present during catalyst preparation, although the extent of increase differs strongly between different publications. For HDS of dibenzothiophene (DBT), a test performed in more drastic conditions (under high pressure and in the liquid phase), Hiroshima et al. [9] have shown an activity increase when the CoMo/Al₂O₃ catalysts are prepared using EDTA or CyDTA, whereas no influence of NTA addition was observed. Van Veen et al. [10] even found a slight decrease of the DBT HDS activity of NiMo/Al₂O₃ catalyst when NTA was added. It appears that a ratio of NTA/metal close

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to one [11] and the absence of a calcination step before sulfidation are key points to obtain more active catalysts, but the activation stage and catalytic test conditions can also affect the effect of chelating agent addition.

To specify the effect of chelating agents on the sulfide slab structure, various studies were undertaken. Hensen et al. [12] as well as Okamoto et al. [13] used TEM to study the effect of NTA on Mo/Al₂O₃ catalysts. They both found an increase of the length and stacking of the MoS₂ slabs. For CoMo/Al₂O₃ catalysts, Gonzalez-Cortés et al. [7] showed that the addition of EDTA also induces an increase of the average slab length. These results are in contradiction with those reported by Hiroshima et al. [9], who used extended X-ray absorption fine structure in order to compare the dispersion of Mo on a CoMo/Al₂O₃ catalyst with or without NTA and concluded that Mo dispersion was independent of the presence of the chelating agent.

Shimizu et al. [8] used infrared (IR) spectroscopy of adsorbed NO on sulfided CoMo catalysts prepared with or without chelating agents such as NTA and EDTA in order to determine the promotion of the sulfide phase by Co. They showed that catalysts with or without chelating agents have comparable total numbers of sites, but have more exposed Co atoms when prepared with a chelating agent. Kubota et al. [14] followed the chelating agent effect using EXAFS and showed that NTA induces, after sulfidation, a decrease of the quantity of Co in inactive form.

Hence, the effect of chelating agent on the dispersion and nature of the sulfide phase in the presence of chelating agent seems controversial. Different hypotheses are reported to explain the origin of the effect of chelating agent addition. Medici et al. [15] attribute the positive influence of chelating agent to the stability of the promoter-chelating agent complex at high temperature toward the H₂S/H₂ mixture. Similarly, de Jong et al. [16] and Coulter et al. [17,18] used model catalysts to study the effect of NTA on the sulfidation temperatures of the different metals, and concluded that NTA delays the sulfidation of cobalt to temperatures at which MoS₂ is already formed. However, IR analysis of the sulfide phase formed on supported sulfide catalysts does not confirm this conclusion [11]. Another proposal based on Mössbauer results is that NTA favors the formation of type II CoMoS [19,20].

Hence, the literature shows some discrepancies concerning chelating agent effect, but the various types of preparations and the different methods of sulfidation used hamper understanding the effect of chelating agent on the formation and structure of the sulfide phase.

The objective of the present study is to determine the role of NTA on the change of activity and functionalities of the catalysts more systematically, and to relate these changes to the structure and concentration of active sites.

To this aim, a set of NTA–CoMo/Al₂O₃ catalysts with constant Co and Mo contents and increasing NTA amount was studied. Taking into account the previous studies, the chelating agent was added together with the metals during the incipient wetness impregnation. After drying, the catalyst was directly sulfided (without calcination step). The effect of NTA was tested in three different catalytic tests: thiophene HDS, which is commonly used for a rapid evaluation of the catalytic performance, HDS of dibenzothiophene (DBT), which is currently used in both industrial and academic laboratories as a representative test for HDS of diesel, and 2,6-dimethylaniline (DMA) decomposition which enables evaluation of the various catalytic functions [21]. Note that thiophene HDS and DMA HDN are gas-phase reactions, while DBT HDS is carried out in the liquid phase. The structure as well as the nature and amount of sulfide phase of the NTA catalysts was characterized using IR spectroscopy of CO adsorption [22,23] and HREM.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by pore-volume impregnation of a γ -alumina ($S_{\text{BET}} = 258 \text{ m}^2 \text{ g}^{-1}$; $V_{\text{porous}} = 0.66 \text{ cm}^3 \text{ g}^{-1}$) according to the procedure developed by van Veen et al. [20]. The NTA was introduced together with the metallic precursors. Different solutions containing cobalt(II)nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck), ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Merck), and NTA ($[\text{C}_2\text{H}_3\text{O}_2]_3\text{N}$, Acros Organics) were prepared in order to obtain catalysts containing 2.1 wt% Co, 10 wt% Mo, and various amounts of chelating agent (0, 0.25, 0.9, and 1.2 mol of NTA/mol of metal (Co + Mo)). The solution was added to the carrier and shaken vigorously. Subsequently the preparation was put on a roller bank for 30 min and dried indirectly with the help of a hair dryer at 393 K for 1 h. Before sulfidation, the catalysts were not calcined but only dried at 393 K in order to keep the chelating agent in its initial form. The catalysts are denoted as CoMox.xxNTA, where x.xx is the molar ratio NTA/(Co + Mo).

2.2. Weight of the working catalyst

The weight of the working catalyst was experimentally determined in order to take into account the important mass loss that occurs during sulfidation stage, i.e. water elimination, molybdenum and cobalt precursors sulfidation, and NTA decomposition [24]. The weight loss upon sulfidation (according to the thiophene test procedure) is compared to the amount of NTA introduced in the catalysts (Fig. 1). The weight loss determined experimentally is generally greater than that expected considering only the NTA decomposition (dotted line). These discrepancies decrease when the NTA amount increases. This indicates a lower moisture content on the NTA-containing catalysts and suggests that the presence of NTA on the alumina support hinders water adsorption. In all the following sections, the weight of the catalysts is the weight of the sulfided catalysts.

2.3. Thiophene hydrodesulfurization

The thiophene HDS activity test was carried out in a flow micro-reactor working at atmospheric pressure and 623 K. Appropriate amounts of catalysts (about 20 mg) were used in order to keep the conversion lower than 5%. Before the reaction, the catalysts

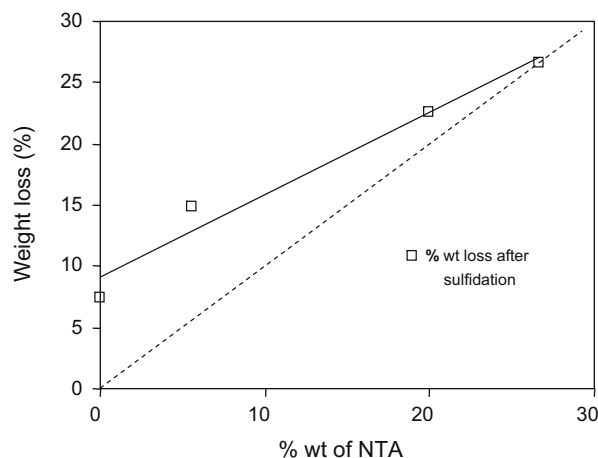


Fig. 1. Catalyst weight loss measured after sulfidation of the different NTA catalysts. The dotted line corresponds to the expected weight loss only due to NTA decomposition.

were sulfided *in situ* with 30 mL min⁻¹ of H₂S/H₂ (10 vol%) at 623 K (heating rate of 3 K/min) for 30 min.

Thiophene was introduced into the reactor by flowing hydrogen (70 mL min⁻¹) through a thiophene saturator maintained at 291 K and mixed into 20 mL min⁻¹ of H₂S/H₂ (10 vol%). Products were analyzed on-line using a Varian gas chromatograph equipped with a flame ionization detector (FID) and CPSIL-5CB capillary column. The specific rate was calculated as $r_{\text{HDS}} = (F/m)X$, where F/m is the molar flow rate of reactant per gram of catalyst and X is the thiophene conversion.

2.4. Dibenzothiophene hydrodesulfurization

High-pressure liquid-phase DBT HDS measurements [10] were performed in a 6-parallel nanoflow reactor system. About 400 mg of catalyst (diluted with 1.2 g of SiC) was sulfided *in situ*. First, the catalyst was wetted with a mixture of hexadecane and 3 wt% of di-tertiononyl pentasulfide (TNPS) with a flow of 0.75 mL h⁻¹ before a flow of 135 mL h⁻¹ of H₂ was added. The catalysts were heated to 373 K, and the pressure was raised to 3.5 MPa. Then, the temperature was raised to 553 K with a rate of 0.33 K/min, and maintained for 5 h. Then it was raised again to 613 K with a rate of 0.33 K/min, and maintained for 24 h. Finally, the reactor was cooled down to 473 K in 2 h.

The feed was a mixture of DBT (5.00 wt%), marker paraffin (C₁₂) (1.72 wt%), and hexadecane (93.28 wt%). The flow of the feed was 0.75 mL h⁻¹ and the flow of H₂ was 2.25 mL min⁻¹. Activity was measured at 493 K, 503 K, 518 K, and 533 K for periods of 20 h. The products (biphenyl, cyclohexylbenzene, and unreacted dibenzothiophene) were analyzed with a Carlo Erba Instrument ICU 600 gas chromatograph equipped with a FID.

2.5. 2,6-Dimethylaniline hydrodenitrogenation

The 2,6-dimethylaniline HDN activity test was carried out in a stainless steel reactor (Sotelem) at 4 MPa and 573 K. Around 0.35–0.40 g of catalyst was first sulfided *in situ* under 60 mL min⁻¹ of H₂S/H₂ (10 vol%) at 4 MPa at 623 K for 2 h (temperature ramp 3 K/min). Thereafter, the catalyst was cooled under H₂S/H₂ to the reaction temperature, and the H₂S content adjusted to 1.4% in hydrogen. The liquid feed (10 vol% 2,6-dimethylaniline, reactant; 80% heptane, solvent; and 10% decane, internal standard) was introduced using an HPLC pump and vaporized in the H₂S/H₂ stream. The reaction products were condensed at the reactor exit, and the liquid was analyzed using a Varian gas chromatograph equipped with a CPSIL-5CB capillary column and a FID detector.

The partial pressure of 2,6-dimethylaniline was kept constant at 13 kPa for all experiments. Reaction conditions at steady state were varied by changing the contact time (55–250 h g mol⁻¹) at 56 or 0 kPa of H₂S. We determined the reaction orders in 2,6-dimethylaniline for the hydrogenation (HYD), xylene (XYL), and disproportionation (DIS) routes as 0.0, 0.0, and 0.4, respectively [21]. Activities are expressed by the initial rates, i.e. reaction rates at zero conversion (mol h⁻¹ kg⁻¹).

2.6. IR spectroscopy of adsorbed CO

2.6.1. IR experiments

Before introduction into the IR cell, the samples were ground and pressed to obtain a wafer (area 2 cm², mass about 10 mg, but precisely weighed). The spectra were recorded using a Fourier Transform IR spectrometer from Thermo Optek using a MCT detector. Spectra were recorded with 256 scans at a resolution of 4 cm⁻¹. All the spectra presented in this paper are normalized to a disc of 5 mg cm⁻² of sulfided catalyst.

2.6.2. Standard sulfidation procedure

A standard sulfidation was carried out *in situ* in the IR cell according to the following procedure. The disc was sulfided under a flow of H₂S/H₂ (10/90) at 30 mL min⁻¹, with a heating rate of 10 K/min up to 543 K, and then maintained at this temperature for 30 min. The temperature was then raised to 623 K and maintained for 2 h. After 1 h30 at this temperature, the H₂S/H₂ flow was stopped and replaced by a flow of N₂ at 30 mL min⁻¹ for 30 min. Then, the sample was cooled down to room temperature under N₂. Afterward, an evacuation was performed from RT to 573 K (with a rate of 10 K/min) and maintained at 573 K until a pressure of 10⁻³ Pa was reached. Finally, the sample was cooled down to liquid nitrogen temperature before CO introduction.

2.6.3. H₂ post-treatment procedure

In some cases after standard sulfidation, the sample was submitted to a H₂ post-treatment. Thus, after standard sulfidation at 623 K, N₂ flush and evacuation at 573 K (described in the previous section), a first dose of 13.3 kPa of H₂ was introduced into the IR cell. After 30 min of H₂-contact at 573 K, the cell was evacuated, and the catalyst was contacted with a second dose of 13.3 kPa of H₂ for 30 min. The cell was evacuated under secondary vacuum at 573 K, and cooled down to liquid nitrogen temperature.

2.6.4. Procedure for CO adsorption

Before CO introduction, a reference spectrum of the activated catalysts was recorded at 100 K. Then, small calibrated doses of CO were introduced until an equilibrium pressure of 133 Pa was established. A spectrum was taken after each CO introduction. All the CO spectra presented correspond to difference spectra, i.e. spectrum after CO adsorption minus reference spectrum.

2.6.5. Spectral analysis

The concentration of each type of sites was calculated using spectral decomposition. For sulfided CoMo, the CO adsorption zone of the spectrum was fitted using five Gaussian curves corresponding to: CUS Al³⁺ (2186 cm⁻¹), Al–OH (2153 cm⁻¹), MoS₂ sites (2109 cm⁻¹), and CoMoS sites (2064 and 2028 cm⁻¹). The area of each band was then obtained using the fitting procedure of the OMNIC software. For all catalysts, the wavenumber of the band maximum and width at half height of the bands were kept in fixed limits. The detailed procedure with all the parameters used is given as [Supplementary material on-line \(http://www.elsevier.com.chimie.gate.inist.fr\)](http://www.elsevier.com.chimie.gate.inist.fr).

Calculation of the site concentrations was then done using the molar extinction coefficient determined previously ($\epsilon_{\text{MoCUS}} = 16 \pm 4 \mu\text{mol}^{-1} \text{cm}$ and $\epsilon_{\text{CoMoS}} = 43 \pm 12 \mu\text{mol}^{-1} \text{cm}$) [22].

2.7. Transmission electron microscopy

Quasi *in situ* high-resolution transmission electron microscopy (HREM) was performed using a Philips CM30T equipped with an LaB6 filament operated at 300 kV. To avoid detrimental exposure to air [25], sulfided catalysts were unloaded from the sulfidation reactor in a nitrogen glovebox. They were packed air-tight and transported to an argon glovebox near the microscopes, where they were mounted on Quantifoil® microgrid carbon film-covered metal TEM grids. A few drops of a suspension of ground catalyst in dry *n*-hexane were put on the TEM grid and left to dry inside the glovebox. Grids were transferred to the TEM using a specially developed protective-atmosphere transfer TEM holder [26].

Different procedures of sulfidation were used: (i) gas phase under 1 bar of H₂S/H₂; (ii) liquid phase under 40 bars in the presence of TNPS and heptane (same procedure as used for sulfidation in the DBT test); and (iii) gas phase under 40 bars of H₂S/H₂, this sulfidation was only performed on the catalyst without NTA.

Slab length and stacking degree distributions of sulfide slabs were determined manually by measuring at least 300 slabs per sample from the TEM images. Average slab length and fraction of Mo at the edges of the slabs were calculated from the slab length distributions, assuming MoS₂ crystallites of hexagonal morphology [3,12].

3. Results

3.1. Catalytic activity of the NTA catalysts

3.1.1. Hydrodesulfurization of thiophene

Thiophene HDS shows that NTA addition leads to a marked increase of the HDS activity of the CoMo/Al₂O₃ catalyst (by a factor of ~2.6) (Fig. 2). The literature generally reports a beneficial effect of NTA addition in thiophene HDS although the extent of this positive effect is lower than that measured in the present work [27].

3.1.2. Hydrodesulfurization of dibenzothiophene

In the case of HDS of DBT, the addition of NTA does not modify the conversion or the selectivity whatever be the temperature of reaction (493–530 K).

3.1.3. Hydrodenitrogenation of 2,6-dimethylaniline

As shown previously [21], DMA is decomposed according to four parallel routes: dearomatization followed by (ia) hydrogenation – elimination to dimethylcyclohexenes and dimethylcyclohexanes (HYD) or (ib) NH₃ elimination to *m*-xylene (HYG), (ii) direct NH₃ elimination from DMA to *m*-xylene (DDN) (mainly observed in the absence of H₂S), and (iii) disproportionation of DMA to 2-methylaniline and 2,4,6-trimethylaniline (DIS). In the discussion, we will refer to XYL activity as the formation of xylene by both the HYG and DDN routes. To explore the full potentialities of the catalysts, the HDN test was performed either in the presence or in the absence of H₂S.

3.1.3.1. Effect of NTA on HYD activity. Fig. 3A shows that the HYD activity of the catalysts increases with the amount of NTA. This augmentation is less important than that measured for thiophene HDS. Indeed, the HYD activity measured in the presence of H₂S is increased by a factor of ~1.5 for the highest NTA loadings. The HYD activities are increased by the absence of H₂S, and the extent of this augmentation is independent of the NTA amount (except in the absence of NTA where no increase is observed in the absence of H₂S) (Fig. 3A).

3.1.3.2. Effect of NTA on XYL activity. Fig. 3B shows that the XYL activity increases upon NTA addition. However, the influence of

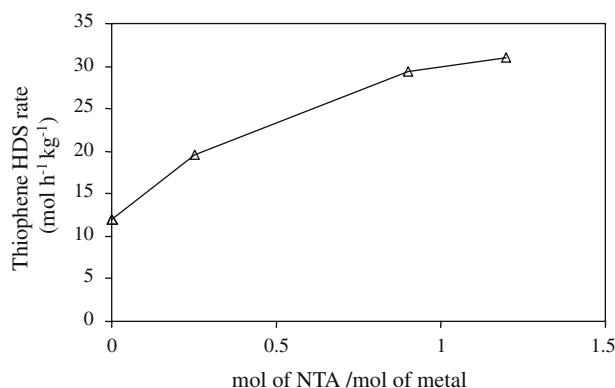


Fig. 2. Thiophene HDS activity of the various NTA catalysts.

H₂S partial pressure is markedly dependent on the level of NTA present. The calculated ratio between the XYL activities measured in the absence and in the presence of H₂S strongly increases with the NTA content: the ratio is 1.3 for the catalyst without NTA, and it increases up to 2.8 for the highest NTA loadings.

3.1.3.3. Comparison between HYD and XYL activities. Fig. 4 shows that the influence of H₂S partial pressure differs significantly for the XYL and HYD routes, and for catalysts with and without NTA. In the presence of H₂S, a linear relationship is found between the XYL and HYD routes (increase of both routes by a factor of ~1.5) suggesting that under these conditions HYD and XYL proceed via the same intermediate [21]. By contrast, without H₂S the XYL activity increases more strongly than the HYD activity when increasing the NTA amount, and no linear relationship appears between the two routes (Fig. 4).

3.1.3.4. Effect of NTA on DDN route. As reported previously [24,28], the strong increase of the XYL/HYD ratio in the absence of H₂S was assigned to a second route for xylene formation, DDN. Hence, from the total XYL formed in the absence of H₂S and taking into account the ratio HYD/XYL measured in the presence of H₂S, the additional xylene formed via the DDN route in the absence of H₂S can be calculated. Fig. 5 shows that the DDN activity increases linearly with NTA content.

3.1.4. Comparison of the NTA effect in the different catalytic tests

Addition of NTA to the CoMo/Al₂O₃ catalyst leads to an increase of the thiophene HDS activity as well as of DMA HDN. The thiophene activity can be increased by a factor of 2.6, while this factor amounts to about 1.5 for the HYD and XYL routes in the presence of H₂S. In the absence of H₂S, a strong DDN activity is developed, which increases with NTA content.

A linear relationship exists between thiophene HDS activity and HYD activity in the presence of H₂S (Fig. 6). This indicates that, on this set of catalysts, thiophene HDS and DMA HYD probe the same type of sites. This activity enhancement provides evidence for an increase of the amount of CoMoS sites with NTA addition.

As shown previously [21], the DDN route, i.e. the direct ammonia elimination (without previous hydrogenation), requires highly unsaturated unpromoted Mo sites. Hence, the increase of the DDN route observed on NTA-containing catalysts is surprising. Indeed, the increased concentration of Co-promoted sites with NTA addition indicated by DMA HYD and thiophene HDS should lead to a diminution of the amount of unpromoted Mo sites, and consequently to a decrease of the DDN activity. A reverse trend is observed that indicates the development of new types of sites on NTA catalysts.

For DBT HDS (not shown), NTA addition does not lead to any activity increase. Note that the absence of any positive effect in HDS of DBT has been reported already by van Veen et al. for NTA addition to NiMo/Al₂O₃ catalysts [10]. It should be mentioned that the sulfidation procedures used for DBT HDS and DMA or thiophene tests are completely different. The sulfiding agent TNPS used in DBT HDS might mask any effect of NTA by leading to a high promotion level even in the absence of NTA. On the other hand, it has been reported already that NTA only promotes HDS and HDN in the gas phase but not in the liquid phase [28].

3.2. Nature and concentration of the sulfide-phase sites of the NTA catalysts

3.2.1. Residual organic species after sulfidation

IR spectra presented in Fig. 7 show bands at 1608, 1580, 1471, and 1300 cm⁻¹ to be present after sulfidation of the NTA catalysts at 623 K. The intensity of the three latter bands increases with the

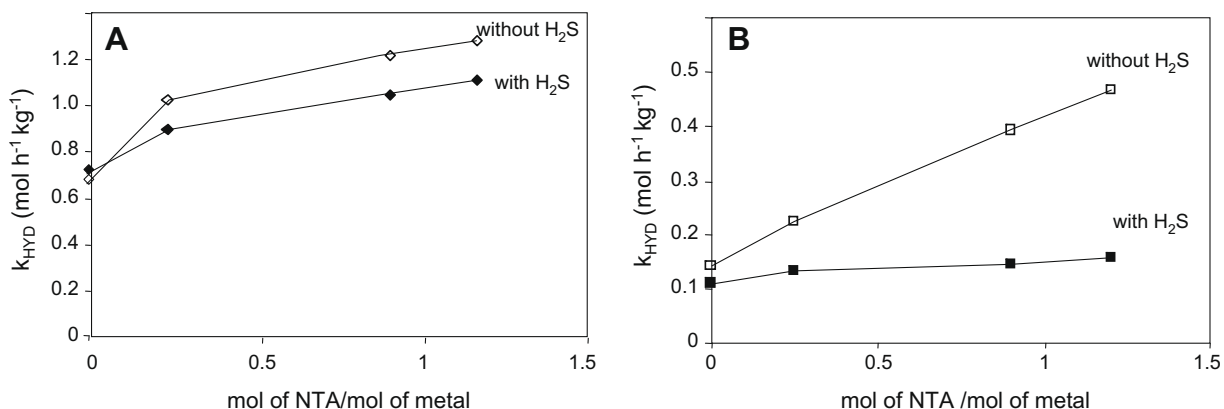


Fig. 3. HDN activity of the various NTA catalysts measured in the presence of H₂S (56 kPa) or in the absence of H₂S: (A) HYD activity; (B) XYL activity.

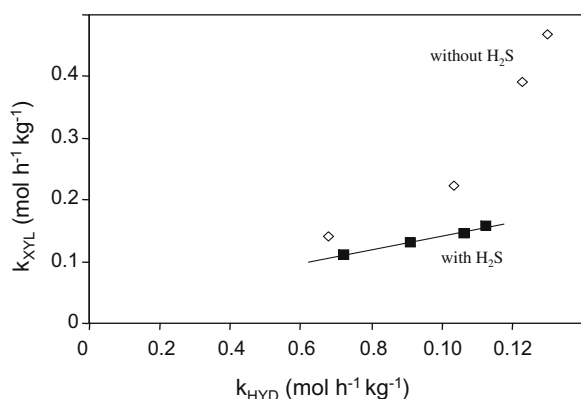


Fig. 4. Relationship between XYL and HYD activities measured in the presence and in the absence of H₂S.

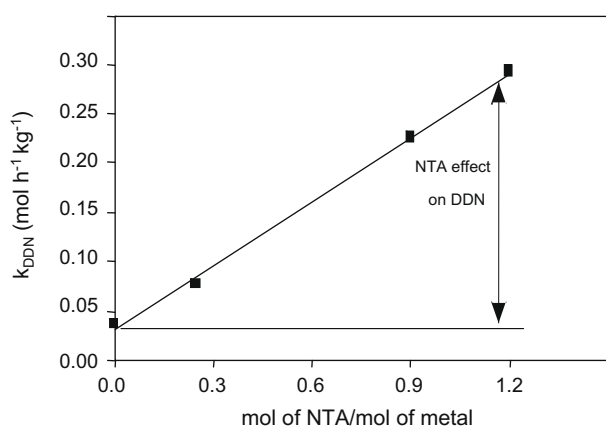


Fig. 5. Rate constant of the DDN route of the various NTA catalysts measured in the absence of H₂S.

NTA amount. The 1608 cm^{-1} band is more specifically observed on the catalysts containing the highest amount of NTA. These bands are close to those observed after treatment of NTA deposited on pure Al_2O_3 under vacuum at 623 K (see inset Fig. 7). These species can correspond to carboxylate adsorbed on Lewis acid sites of alumina. Thus, some residual organic fragments issued from NTA decomposition are still present on the alumina surface after sulfidation of the NTA catalysts at 623 K. Note that these species are still observed after sulfidation followed by H₂ treatment at 523 K.

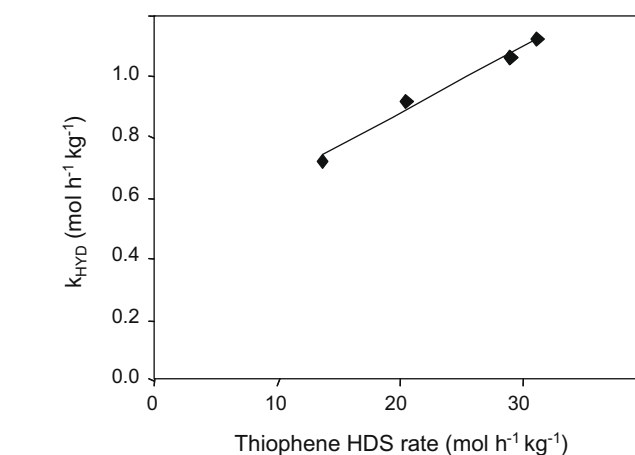


Fig. 6. Comparison between the rate constants for HYD route of DMA decomposition measured in the presence of 56 kPa H₂S and for thiophene HDS.

3.2.2. CO adsorption on sulfide phase

In order to determine the NTA effect on the nature and amount of the sulfide sites, IR analysis of CO adsorption was performed on sulfided as well as on H₂ post-treated NTA catalysts (in order to mimic the atmosphere of DMA decomposition without H₂S).

IR spectroscopy of CO adsorbed on sulfided CoMo catalysts (not presented) shows a band at $\sim 2070 \text{ cm}^{-1}$ characterizing CoMoS sites and one at $\sim 2110 \text{ cm}^{-1}$ associated to unpromoted Mo sites [22,29]. After H₂ treatment, similar types of sulfide sites are detected (Fig. 8). Just as after sulfidation, no noticeable band shift due to NTA addition can be evidenced after H₂ treatment.

On sulfided catalysts as well as on H₂-treated ones (Fig. 9A and B), CO adsorption shows that NTA addition, up to 0.9 mol NTA/mol metal, strongly increases the concentration of Co-promoted sites. For the highest NTA content (1.2 mol NTA/mol metal), the amount of CoMoS sites stays almost constant. The amount of unpromoted Mo sites is not significantly modified by NTA addition. Hence, the degree of promotion of the sulfide phase (PD, i.e. concentration of CoMoS sites over concentration of (CoMoS + Mo sites)) is multiplied by 1.4 by NTA addition (Table 1 – increased from 0.43 to 0.61). It should be noted that the total amount of sulfide-phase sites detected by CO increases with the NTA content.

The ratio between the amount of sites detected after H₂ treatment and after sulfidation is presented in Table 1 (values in parentheses). H₂ treatment strongly increases the CO uptake on the sulfide phase. Indeed, H₂ treatment eliminates some sulfur atoms via H₂S formation, creating supplementary CUS on the sulfide phase. Note that for CoMoS sites this ratio decreases significantly

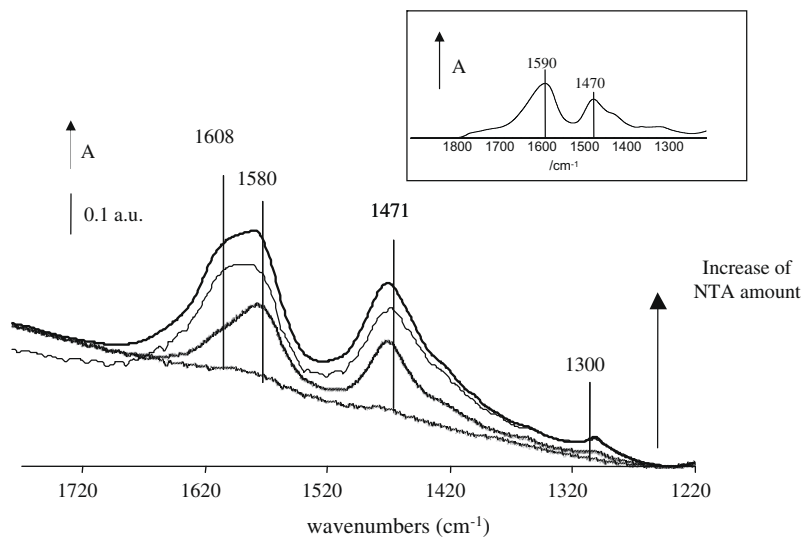


Fig. 7. IR spectra of the various NTA catalysts after sulfidation at 623 K. Inset: NTA–Al₂O₃ after sulfidation at 623 K.

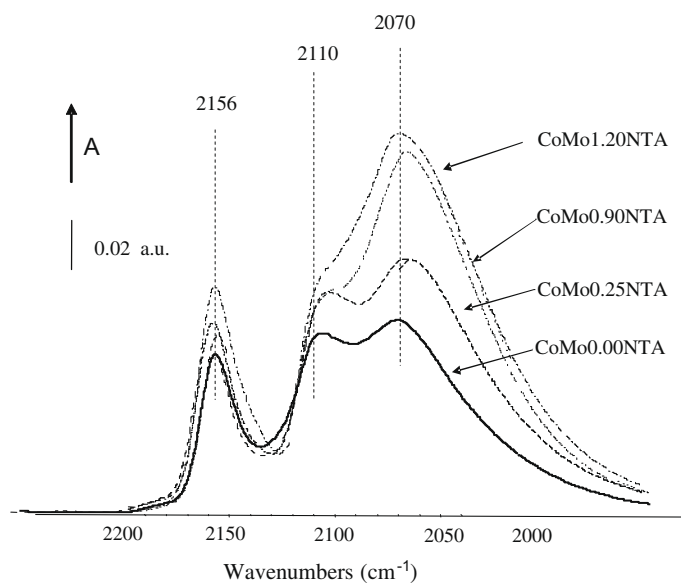


Fig. 8. IR spectra of CO adsorbed on the NTA catalysts after H₂ post-treatment.

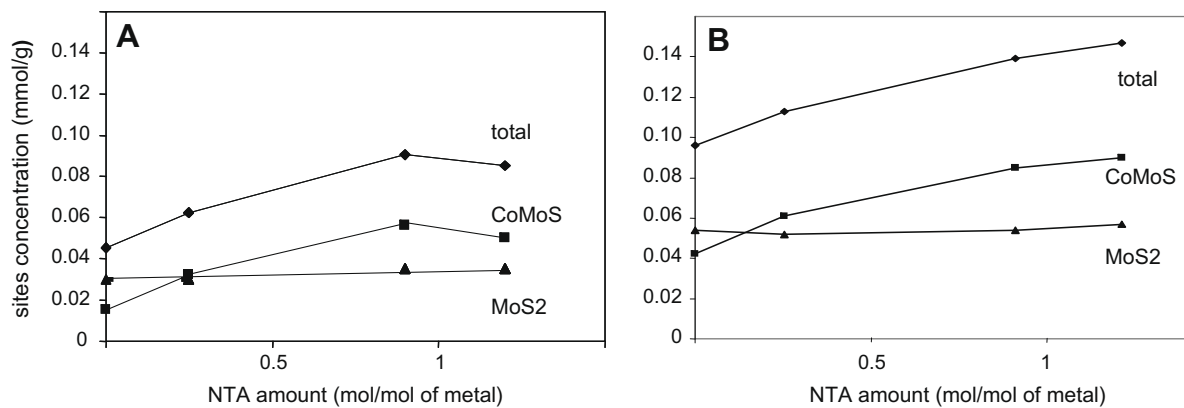


Fig. 9. Variation of the amount of Mo, CoMoS, and total sites with the amount of NTA. (A) Sulfidated catalysts. (B) Sulfidated catalysts after H₂ treatment.

Table 1Amount of promoted, unpromoted Mo, and total sites, and promotion degree determined from CO adsorption after H₂ treatment of the sulfided catalysts.

Catalyst	<i>n</i> MoS ₂ sites (�mol/g)	<i>n</i> CoMoS sites (�mol/g)	<i>n</i> total sites (�mol/g)	Promotion degree ^a
CoMo0.00NTA	54 (1.8)**	42 (2.6)	96	0.43
CoMo0.25NTA	52 (1.7)	61 (2.1)	113	0.54
CoMo0.90NTA	54 (1.5)	85 (1.5)	139	0.61
CoMo1.20NTA	57 (1.6)	90 (1.8)	147	0.61

^a Promotion degree = $n(\text{CoMoS sites})/n(\text{total sites})$.^{**} In parenthesis – H₂ treatment effect calculated from $n(\text{sites after H}_2 \text{ treatment})/n(\text{sites after sulfidation})$.

when NTA is added, as it goes from 2.6 on CoMo0.00NTA to 1.8 on CoMo1.20NTA.

To sum up, addition of NTA strongly increases the amount of CoMoS sites (by a factor of ~2). Maximum of promoted sites is obtained for an amount of 0.9 mol NTA per mol of metal. In addition, different points suggest some changes in the environment of the sulfide sites with NTA, as an increase of the total amount of sulfide-phase sites and the modifications of the extent of the H₂ effect.

3.3. Effect of NTA addition and sulfidation pressure on the morphology of sulfide phase

In order to determine the effect of NTA on the dispersion and stacking of the sulfide phase, the sulfided NTA catalysts were characterized using quasi *in situ* TEM. Different procedures of sulfidation were used: (i) gas phase under 0.1 MPa of H₂S/H₂; (ii) liquid phase under 4 MPa in the presence of TNPS and hexadecane; and (iii) gas phase under 4 MPa of H₂S/H₂. These different procedures

mimic the various sulfidation conditions used in the different reactivity tests.

The length and the stacking distributions of the sulfide phase obtained after atmospheric pressure sulfidation are presented in Fig. 10A. For all the NTA catalysts, the average length is about 2.6 nm and the stacking is about 2. NTA addition has a negligible effect on the distributions of length and stacking.

The morphology of the NTA catalysts sulfided in the liquid phase is presented in Fig. 10B. As observed previously, NTA addition hardly induces differences in the average values and in the distributions of the slab length and stacking. However, this sulfidation procedure clearly increases the average length of the sulfide slabs compared to the atmospheric pressure sulfidation (3.6 instead of 2.6 nm), whereas the stacking is not modified (about 2).

In order to discriminate the influence of the sulfidation pressure from that of the sulfiding agent, the morphology of the CoMo0.00NTA catalysts sulfided under high pressure and TNPS was compared to that obtained after sulfidation under high pressure

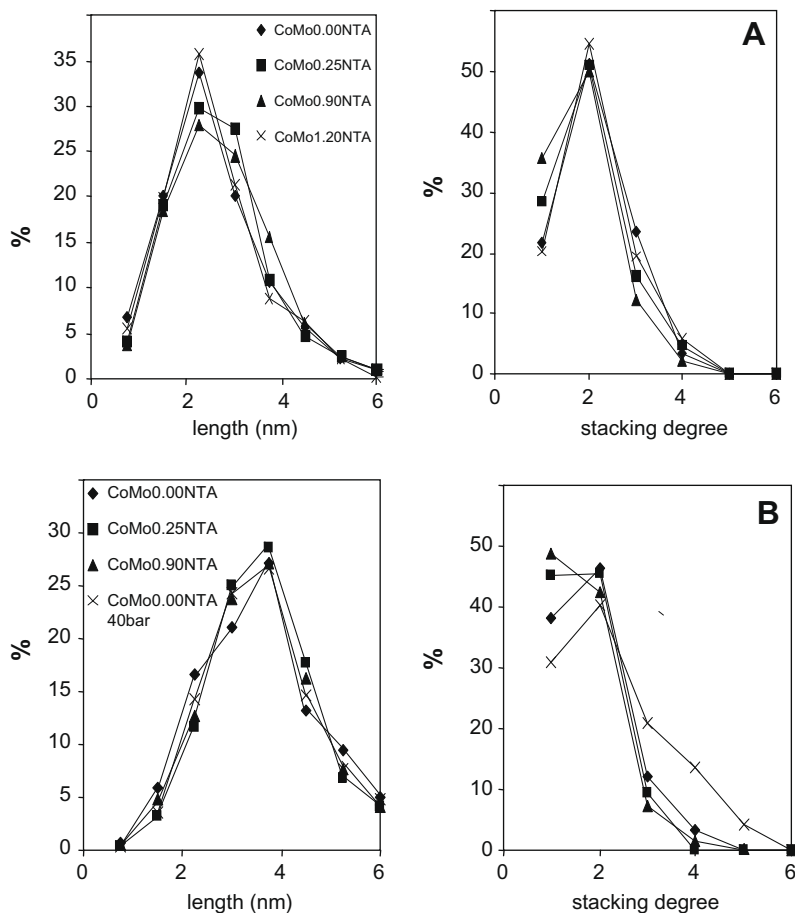


Fig. 10. TEM analysis of the morphology of the sulfided NTA catalysts – (A) Sulfidation under 1 bar H₂S/H₂. (B) Sulfidation under 40 bars of TNPS and heptane (for all the catalysts) or under 40 bars of H₂S/H₂ (for CoMo0.00NTA).

and H_2S/H_2 . Fig. 10B shows that the sulfidation pressure is the main parameter which affects the dispersion of the slabs. Indeed, using of a gas-phase sulfidation instead of a liquid-phase sulfidation (both at 4 MPa) does not change the average slab length. Note that the change of sulfiding agent leads to some modifications in the stacking, i.e. the average slab stacking reaches 2.5 in the case of H_2S instead of 2 for TNPS.

In conclusion, the sulfidation procedure (pressure and sulfiding agent) significantly influences the morphology of the sulfide phase. Increasing the pressure leads to longer slabs, but it hardly changes the stacking. Changing the sulfiding conditions (liquid phase vs. gas phase) can change the stacking. However, for similar procedures of sulfidation, NTA addition modifies neither the length nor the stacking of the slabs.

4. Discussion

4.1. Influence of NTA on the catalytic activity

4.1.1. Effect of NTA on the active sites for thiophene HDS

Comparison of thiophene HDS activity of the various NTA catalysts to the concentration of CoMoS sites measured after sulfidation (Fig. 11) reveals a linear relationship between the HDS activity and the amount of CoMoS sites. Hence, these results confirm that mainly the Co-promoted sites are responsible for the HDS activity.

4.1.2. Effect of NTA on the active sites for DMA hydrogenation

A similar comparison was plotted for the DMA reaction. For the HDN reaction, activity was measured in the presence or in the absence of H_2S . In parallel, site concentrations were determined on sulfided catalysts and on H_2 -treated catalysts. Fig. 12 compares the hydrogenation rate measured in the presence of H_2S to the concentration of CoMoS sites detected after sulfidation (full symbols), and the hydrogenation rate measured in the absence of H_2S to the concentration of CoMoS sites detected after H_2 treatment (open symbols).

As shown in Fig. 12, a good correlation appears between the hydrogenation rate and the concentration of CoMoS sites (except for CoMo0.00NTA in the absence of H_2S). Note that the Co-pro-

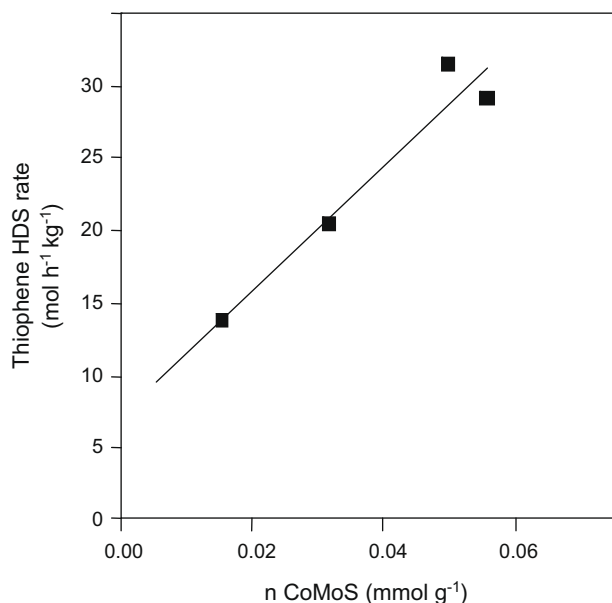


Fig. 11. Comparison between the thiophene HDS activity and the concentration of CoMoS sites.

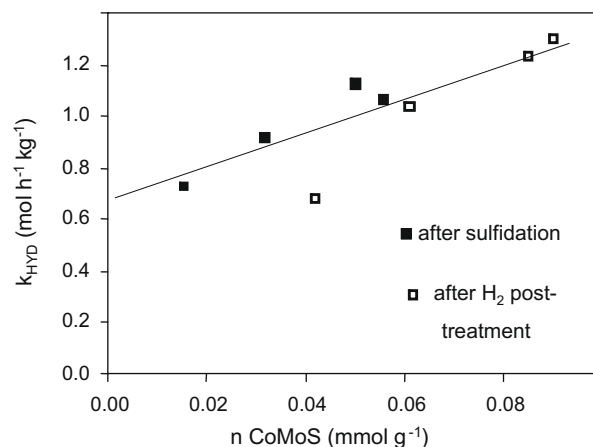


Fig. 12. Comparison between HYD activity route of DMA decomposition and concentration of CoMoS sites of NTA catalysts. Full symbol: activity measured in the presence of H_2S and concentration of sites detected after sulfidation. Open symbols: activity measured in the absence of H_2S and concentration of sites detected after H_2 treatment.

moted sites created by H_2 treatment have the same intrinsic activity in hydrogenation as those detected on sulfided catalysts. These results are in agreement with previous observations on a series of CoMo catalysts without NTA [30]. This indicates the absence of important changes in the environment of Co-promoted sites on sulfided catalysts by H_2 treatment. Hence, these results confirm that mainly the Co-promoted sites are responsible for the hydrogenation route of the DMA decomposition.

4.1.3. Effect of NTA on the active sites for DMA DDN route

NTA has been shown to increase the xylene formation via the DDN route (activity multiplied by a factor of 8). The active sites for the DDN route were thought to be highly unsaturated unpromoted Mo sites [30]. However, in the present study the concentration of unpromoted Mo sites stays almost constant when NTA is added. Moreover, a parallel appears between the concentration of Co-promoted sites and the DDN rate constant, even if the relationship is not linear (Fig. 13).

4.2. Influence of NTA on the nature of active sites

Even if previous section shows very good agreements between activity and amount of Co-promoted sites increases, one cannot exclude that NTA addition changes the nature of active sites. Only a quantitative analysis of catalytic and spectroscopic data could allow to answer this point. Hence, TOFs of the unpromoted and promoted NTA catalyst sites are calculated and compared to previous results obtained on CoMo series without NTA [30].

4.2.1. Effect of NTA on the nature of active sites for thiophene HDS

On the NTA series, the amount of unpromoted Mo sites is almost unchanged by chelating agent addition. Thus, an extrapolation of the line presented in Fig. 11 should correspond to the HDS activity of a pure Mo catalyst. The intercept is about $7 \text{ mol h}^{-1} \text{ kg}^{-1}$. Therefore, the turn over frequency (TOF) value for Mo sites is about 230 h^{-1} . From the slope of the line relating HDS activity and amount of CoMoS sites, the TOF of these sites is equal to 435 h^{-1} . The values reported by Dujardin in [30] were 47 h^{-1} for Mo sites and 1080 h^{-1} for CoMoS sites. Although the thiophene HDS activities were measured at 673 K by Dujardin and at 623 K in this study, there is obviously a discrepancy between the two sets of results. Indeed, the effect of Co-promotion is markedly lower on the NTA series.

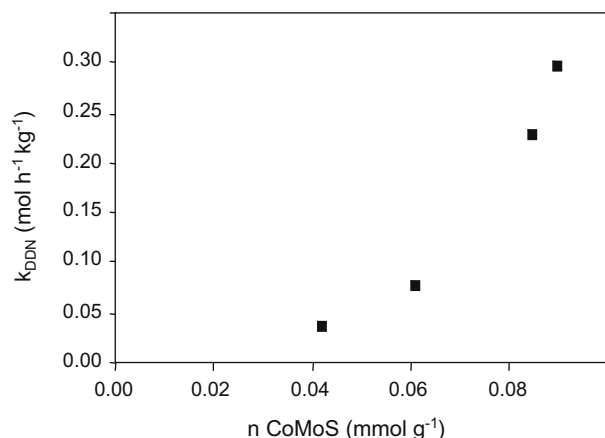


Fig. 13. DDN rate constant versus the concentration of CoMoS sites of the NTA catalysts.

4.2.2. Effect of NTA on the nature of active sites for DMA hydrogenation

The relation between HYD activity (in mol h⁻¹ kg⁻¹) and concentration of CoMoS sites (in mmol g⁻¹) in Fig. 12 can be written as $k_{\text{HYD}} = 7n_{\text{CoMoS}} + 0.67$. This means that the TOF of the Co-promoted sites for the hydrogenation route of DMA amounts to 7 h⁻¹ and that of the unpromoted Mo sites amounts to about 16 h⁻¹. The higher TOF value for the unpromoted sites as compared to the Co-promoted sites is highly unrealistic.

TOF values obtained by Dujardin et al. [30] were 16 h⁻¹ and 1.5 h⁻¹, respectively, for CoMoS and Mo sites. These values are obtained at the same conditions for DMA test and using the same temperature of sulfidation before IR experiment but with a different protocol. Thus, for the series of CoMo/Al₂O₃ catalysts without additive [25], a more realistic factor of about 10 was found between the TOF values of promoted and unpromoted sites.

In the current study the unexpected relative values for the TOF of promoted and unpromoted sites can probably be explained by an artifact in the estimation of the concentration of sites. For this calculation, the same values for the molar extinction coefficients for the two types of sites have been used as in the work of Dujardin et al. [30]. The discrepancy in the TOFs obtained using the same molar extinction coefficients indicates that these values change upon addition of NTA. Therefore, from the combination of spectroscopic data and activity tests, we can conclude that the nature of the active sites is modified on NTA catalysts.

4.2.3. Effect of NTA on the nature of active sites for DMA DDN route

As described above, a change in the nature of Mo sites upon NTA addition could lead to an underestimation of their concentration. This could be proposed to explain the strong increase of DDN activity on NTA catalysts (factor of 8 for the highest NTA loading with respect to the NTA-free catalyst), whereas no change in the concentration of Mo sites is measured. If we consider a change of

the CO/Mo molar extinction coefficient, it would mean that a factor of 8 is also needed, which seems not to be very probable.

The second hypothesis is related to the creation of a new type of Co-promoted sites. As suggested by Fig. 13, Co-promoted sites in a specific environment could be active for xylene formation via the DDN route.

4.3. Active sites on NTA catalysts

Activity and spectroscopic results show that the presence of NTA increases the amount of Co-promoted sites, leading to a marked enhancement of the catalytic activity in thiophene HDS and DMA HDN. However, some data also show that structural changes in the sulfide-phase sites occur with NTA. One can quote: (i) the increase of the total amount of adsorption sites detected by CO without change of dispersion of sulfide slab, (ii) the modification of sulfide site sensitivity to H₂ treatment evidenced from IR results, (iii) the HDS and HYD TOF values, and (iv) the increase of DDN activity with promotion degree increase. To sum up, some of the experimental data obtained on the NTA catalysts cannot be explained using only the decoration model, and activity results as well as quantitative IR data strongly suggest that formation of a new type of sites also occurs on the NTA catalysts. The change of concentration of the active sites as the only factor determining the activity increase must be excluded in view of the unrealistic TOF values. Thus, at least a part of the CoMoS sites must have been modified by NTA addition. However, we cannot specify which of the two features, i.e. increase of concentration or the change of quality of the CoMoS sites, is the major phenomenon that accounts for the increase of catalytic activity with NTA addition.

In fact, it should be noticed that quantification of the number of sites by IR spectroscopy of adsorbed CO on sulfide catalysts is rather delicate. Firstly, it is difficult to determine CO molar absorption coefficients for CoMo sulfide catalysts due to the simultaneous CO adsorption on both unpromoted and promoted sites. Secondly, different types of adsorption sites can give rise to the same CO frequency, and their absorption coefficients can be different. As shown in the Table 2, CO adsorbed on nitride or sulfide Mo catalysts can be difficult to discriminate. Nevertheless, the combination of CO adsorption with different reactivity tests gives useful information about the sulfide catalyst structure, via the TOF values.

For the modification of the CoMoS site quality, different possibilities can be considered.

4.3.1. Type II CoMoS phase

As mentioned in the introduction part, the presence of NTA, which decreases the interaction between the sulfide phase *in statu nascendi* and the subjacent carrier, could lead to the preferential formation of type II sulfide slabs. This proposal is strongly supported by the recent M ossbauer/XAS/DBT HDS study by Dugulan on similar catalysts [31]. Formation of type II sulfide phase could account both for the high performance of the NTA catalysts and for their modified behavior compared to conventional catalysts. Indeed, the presence of organic entities on the alumina surface could

Table 2
Comparison of the wavenumbers of CO adsorbed on various nitride catalysts.

Catalysts	Reference	Procedure of <i>in situ</i> activation	CO adsorption conditions	$\nu(\text{CO})$ (in cm ⁻¹) and proposed assignment
Mo ₂ N/Al ₂ O ₃	Aegerter et al. [32]	Catalyst activated under H ₂ at 750 K and evacuated at 673 K	CO adsorption at 130 K	2199 (Al ³⁺), 2165 (Mo), 2100 sh (Mo)
Mo ₂ N/Al ₂ O ₃ Reduced and passivated	Yang et al. [33,34]	<i>In situ</i> synthesis under NH ₃ flow at 873 K for 1 h	CO adsorption at 298 K	2200s (NCO), 2140–2090 sh (Mo ³⁺ (CO) ₂), 2045 sh (Mo ⁶⁺)
CoMoN _x /Al ₂ O ₃	Yang et al. [34] Wu et al. [36,35]	<i>In situ</i> synthesis under NH ₃ flow at 773 K for 1 h and evacuation at 773 K	CO adsorption at 298 K – contact during 10 min	2200 (NCO), 2155 w, 2060 (Co ⁶⁺), 2025 (Mo ⁶⁺)

modify the interaction sulfide phase/support without changing the stacking. A XAS study would be necessary to confirm this point.

4.3.2. Small Co clusters on the edges of sulfide slab

The presence of NTA, changing the interaction between Co and Mo as well as with alumina, could favor the growth of Co particles around the MoS₂ slabs. The presence of small CoS_x entities on the MoS₂ edge of conventional CoMo catalysts, which has already been proposed in the literature [32], could account for the increased Co-MoS site concentration in the absence of a decrease of Mo site concentration and increase of sulfide-phase dispersion.

4.3.3. Formation of “(Co)MoSN”

The interaction between Co and nitrilo triacetic acid could lead to the insertion of some nitrogen in the sulfide slab and form some nitrogeno-sulfide sites as “CoMoSN” and “MoSN” at the edges of the MoS₂ slab. Data are available indicating the high activity of pure MoN and CoMoN catalysts, but also their high sensitivity to H₂S atmosphere [33–37]. One can estimate that the amount of N present as “CoMoSN” sites on the catalysts should be relatively low. This means that evidence of the interaction between Co and N would be difficult to discriminate from the interaction between Co and S using spectroscopic tools such as XPS and EXAFS. Unfortunately, IR spectroscopy of CO adsorption cannot detect such species as it has been shown that the $\nu(\text{CO})$ bands on nitride and sulfide phases appear at almost the same wavenumbers (Table 2). The determination of the activity of pure nitride catalysts in the HYD and DDN routes for DMA decomposition could be a way to establish the formation of such “CoMoSN” species.

5. Conclusion

The addition of NTA to CoMo/alumina catalysts leads to a significant increase of thiophene HDS ($\times 2.6$) and DMA HDN (HYD $\times 1.9$) activities. By contrast, no effect is observed for liquid-phase DBT HDS, which shows the importance of the sulfidation and/or reaction conditions to obtain a positive NTA effect.

Increasing the amount of NTA in the CoMo catalysts progressively increases the spectral contribution of Co-promoted sites in the CO(ad)/IR measurements, up to an optimum for one mole of NTA for one mole of metals. A good correlation is observed between the rate of thiophene HDS and of DMA HYD, and this IR spectral contribution, suggesting that NTA significantly increases the total amount of Co-promoted sites.

However, there are strong indications that not only the number but also the quality of the Co-promoted sites changes upon addition of NTA. Firstly, while the TEM data show that the MoS₂ dispersion is not affected by NTA, no concomitant decrease in the number of unpromoted sites is observed in the CO(ad)/IR spectra. Secondly, parallel between catalytic and spectroscopic data shows unrealistic TOF. And thirdly, $k(\text{DDN})$ in the HDN of DMA increases more than proportionally with the increase of the spectral contribution of Co-promoted sites.

Three possibilities are considered to account for this change in CoMoS site quality: (i) increased formation of type II CoMoS slabs, (ii) formation of small Co(S) clusters on the edges of MoS₂ slabs, and (iii) formation of the so-called “CoMoSN” sites. Although, in view of the wider literature, (i) appears to be the most likely explanation, the combined body of our data does not allow discounting the other two.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.07.006.

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IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation

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ABSTRACT

The adsorption of phenol on supported sulfide CoMo catalysts and on oxides is investigated using IR spectroscopy. On silica, phenol mainly interacts via hydrogen-bonding, whereas on alumina it dissociates on the acid–base pairs of this oxide leading to the formation of strongly adsorbed phenolates species. On a sulfided CoMo catalyst supported on alumina, phenol dissociates on the support but does not interact strongly with the sulfide phase. The accessibility of the various sites of the catalyst after phenol contact is investigated by CO adsorption monitored by IR spectroscopy. As expected, phenolate formation decreases the accessibility of support sites. In addition, a decrease of the sulfide site accessibility is also observed. This is indicative of an indirect poisoning of the sulfide edge sites by phenolate species anchored on the support and in the vicinity of sulfide slabs. Consequently, decreasing the amount or strength of the acid–base paired sites of the support should be a way to limit deactivation.

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1. Introduction

In order to develop sustainable transportation fuels, the contribution of biomass derived feedstocks is set to grow above today's levels. For ethical reasons, the use of raw materials not competing with the food production chain should be the most preferred route. One option is to produce biofuels by pyrolysis of organic waste and lignocellulosic plant material (i.e. second generation biomass). Since these pyrolytic oils contain very large quantities of oxygenated compounds (up to 40 wt% O), their hydrodeoxygenation (HDO) is a way to produce stable fuels [1,2]. Hydroprocessing catalysts like the supported sulfided ((Co,Ni)Mo) catalysts used in the hydrodesulfurization (HDS) of oil fractions could be good candidates if their deactivation can be limited under HDO conditions [3–8]. The high concentration of phenolic compounds found in pyrolytic oils (2–20 wt%) was related to the fast deactivation observed during their HDO on the supported sulfided catalysts used in pioneering studies [3]. Our goal is to identify the cause of catalyst deactivation during HDO of phenolic compounds in order to better define the design rules of effective HDO catalysts.

We report the use of infrared (IR) spectroscopy to determine the adsorption modes of phenol on (i) oxides with different acid–base properties like alumina and silica, they are the supports commonly

proposed for hydroprocessing catalysts, (ii) alumina supported sulfided CoMo catalysts. In addition, the accessibility of the catalysts sites after phenol adsorption is monitored by IR spectroscopy of adsorbed CO.

2. Experimental

2.1. Materials

The silica sample is an Ultrasil 7000 (from Evonik) with a surface area of 173 m² g⁻¹. The alumina is a CatapalC (from Grace Davison) with a surface area of 292 m² g⁻¹. The CoMo/Al₂O₃ catalyst (9.2% Mo to 4.2% Co) is prepared by a classical impregnation using heptamolybdate ammonium and cobalt nitrate deposition on alumina (from Sasol) with a surface area of 255 m² g⁻¹. Phenol is supplied by Prolabo (purity 99.5%).

2.2. Infrared spectroscopy

Each sample is pressed into a self-supported disc (~10 mg, 2 cm²). The disc is introduced in the infrared cell for in situ sulfidation. The sample is first dried under an Ar flow (30 ml/min) for 0.5 h at 423 K and, then cooled down to 298 K. The catalyst is then sulfided under an H₂S (10%)/H₂ (30 ml/min) flow up to 623 K (ramp of 3 K/min). After 1 h of sulfidation at 623 K, the sample is evacuated at the same temperature.

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After activation in the IR cell, calibrated doses (from 0.015 μmol to 0.775 μmol) of phenol are introduced stepwise on the oxides and the sulfide catalyst. The final equilibrium pressure in the infrared cell is set to 20 Pa. Afterwards, the cell is evacuated at 298 K for 15 min. In another set of experiments, a phenol pressure of 20 Pa is introduced directly on the samples at 623 K, followed by evacuation at the same temperature for 15 min.

In order to evaluate the interaction of phenol with the sulfide phase, CO is adsorbed before and after phenol introduction. Again, calibrated doses of CO are introduced on the sample, at $\sim 100\text{K}$, followed by a desorption stage from 100 K up to 298 K.

The infrared spectra are recorded with a FT-IR spectrometer Nicolet Magna AEM equipped with a MCT detector (64 scans, resolution 4 cm^{-1} , “zero filling” 1 level). All the spectra are normalized to a mass of 5 mg cm^{-2} .

3. Results and discussion

3.1. Phenol adsorption on silica

Fig. 1 shows the adsorption of phenol on silica at 298 K (spectrum a). Table 1 reports assignments based on work reported elsewhere [9,10]. The adsorption of phenol on silica leads to bands at 1599 cm^{-1} (with a shoulder at $\sim 1606\text{ cm}^{-1}$) and 1500 cm^{-1} assigned to $\nu(\text{CC})$ ring vibrations. Bands at 1474 and 1360 cm^{-1} contain a significant contribution of $\delta(\text{OH})$ vibration ($\sim 20\%$). Note that the band at 1474 cm^{-1} is generally attributed to $\nu(\text{CC})$ ring

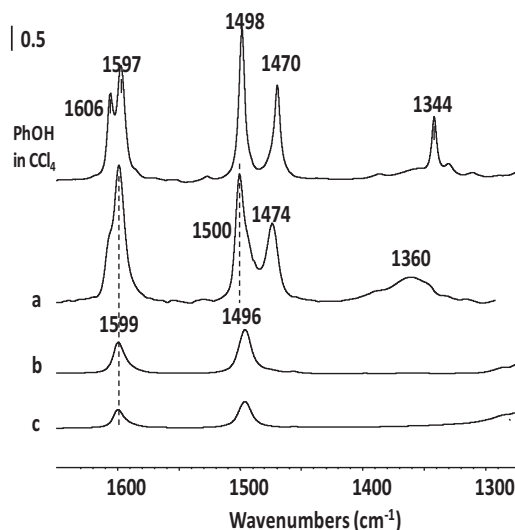


Fig. 1. Infrared spectra of phenol adsorbed on silica. Equilibrium pressure of 20 Pa at room temperature (a); after evacuation at 373 K (b), and 673 K (c). Comparison with phenol in CCl_4 .

Table 1

Assignments of the IR bands of liquid phenol.

Assignment	Phenol
$\nu(\text{OH})$	3610
$\nu(\text{CHring})$	3074–3021
$\nu(\text{CH}_3)$	–
$\nu(\text{CCring})$	1608
$\nu(\text{CCring})$	1600
$\nu(\text{CCring})$	1502
$\nu(\text{CCring}) + \delta(\text{OH})^a$	1473 ^a
$\delta(\text{CH}_3)$	–
$\nu(\text{CCring}) + \delta(\text{OH})$, polymer	1362
$\nu(\text{CCring}) + \delta(\text{OH})$, monomer	1344
X-sensitive ($\nu(\text{CCring}) + \nu(\text{CO})$)	1259

^a Assignment based on experiments with deuterated molecules.

vibrations [9,10]. However, this mode includes a $\delta(\text{OH})$ contribution ($\sim 15\%$), also observed (not shown) on the spectra recorded with deuterated phenol (OD position). These characteristic $\delta(\text{OH})$ vibrations highlight the presence of molecular phenol. After evacuation at 373 K (spectrum b), an important part of the perturbed SiO–H bands disappears along with those at 1474 and 1360 cm^{-1} . However, the bands characteristic of $\nu(\text{CC})$ ring vibrations at 1599 cm^{-1} and 1496 cm^{-1} remain. They are still present even after evacuation at 673–723 K (spectrum c). The νOH region of silica shows that the band at 3745 cm^{-1} (silanol groups) shifts to lower wavenumbers, giving rise to two broad components at 3620 and 3490 cm^{-1} . Evacuation at 373 K almost completely removes, these perturbed SiOH groups.

The IR spectrum of phenol adsorbed on silica indicates a hydrogen bonded interaction (Fig. 1). This is substantiated by: (i) the presence of phenol $\delta(\text{OH})$ bands and the shift of the 1344 cm^{-1} band to 1360 cm^{-1} with a broadening and splitting into several components, (ii) a decrease of the SiOH band intensity with the appearance of several new bands corresponding to perturbed SiOH bands, (iii) the restoration of a significant fraction of the silanol band after evacuation at 373 K. In conclusion, at room temperature, the predominant adsorption mode of phenol on silica is hydrogen bonding.

3.2. Phenol adsorption on alumina

The infrared spectrum of phenol adsorbed on alumina (Fig. 2a) presents bands at ~ 1597 , 1498/1492 cm^{-1} , characteristic of aromatic ring vibrations. For small amounts of phenol adsorbed (not presented here), the $\delta(\text{OH})$ bands at ~ 1470 and $\sim 1340\text{ cm}^{-1}$ are not observed. With increasing phenol coverage, only a shoulder appears at $\sim 1470\text{ cm}^{-1}$ (spectrum a) and disappears after evacuation at 373 K (spectrum b). A multi-component $\nu(\text{CO})$ broad band (1300 to 1230 cm^{-1}) develops also [2,3]. These observations are similar for the two alumina sources (Grace Davison and Sasol).

Fig. 2 shows that the interaction of phenol with alumina leads to the formation of phenolate species. Indeed, bands corresponding to aromatic rings (1597 and 1498/1492 cm^{-1}), and to $\nu(\text{CO})$ vibrations (1295/1250 cm^{-1}) appear, while those characteristic of $\delta(\text{OH})$ groups (at ~ 1470 and $\sim 1340\text{ cm}^{-1}$) are absent, except at high coverage and with a very low intensity (spectrum a). The presence of two different components in the $\nu(\text{CO})$ band (1498/1492 and 1295/1250 cm^{-1}) suggests the formation of two phenolates, mono- and bi-dentate, as illustrated in Fig. 3.

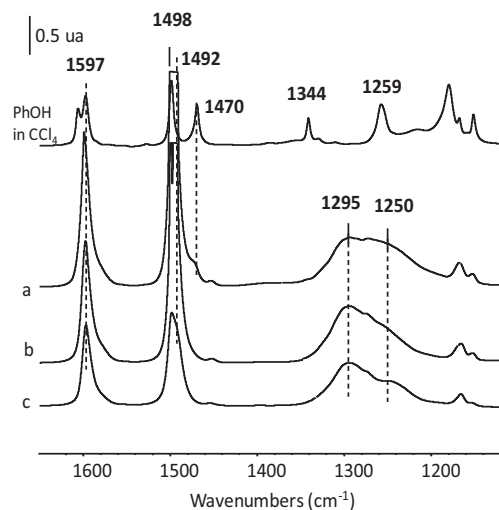


Fig. 2. Infrared spectra of phenol adsorbed on alumina. Equilibrium pressure of 20 Pa at room temperature (a); after evacuation at 373 K (b), and 673 K (c). Comparison with phenol in CCl_4 .

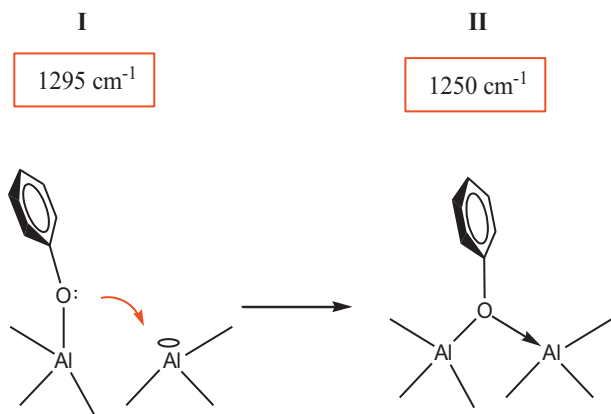


Fig. 3. Structure of phenolates species on alumina.

3.3. Phenol adsorption on a sulfided catalyst

Phenol was adsorbed on sulfided CoMo/Al₂O₃ at 623 K (Fig. 4). The spectra display the same main bands positioned at 1597 cm⁻¹, 1498/1492 cm⁻¹ (ν (CC) ring vibrations) and 1296/1245 cm⁻¹ (ν (CO) vibrations) as observed on alumina alone. The absence of bands at ~1470 and ~1340 cm⁻¹, characteristic of a δ (OH) vibration, indicates the formation of phenolate species on alumina alone. Moreover, the normalization of the spectra to the most intense band (see Fig. 4 insert) confirms the similarity in the ν (CO) region between the two samples. This indicates that there is no structural difference between the phenolate species formed on sulfided CoMo/Al₂O₃ and on pure alumina. However, the adsorption bands of phenol are clearly less intense (about 30–40%) on the sulfided CoMo/Al₂O₃ catalyst than on pure alumina. This implies that the phenolate species on the sulfided catalyst are located on the fraction of alumina support not covered by the sulfided phase and not on the sulfide phase, as described in Fig. 5. Two additional shoulders at 1564 and 1450 cm⁻¹, not present on alumina alone, appear on the sulfided CoMo/Al₂O₃ catalysts. They are absent after phenol

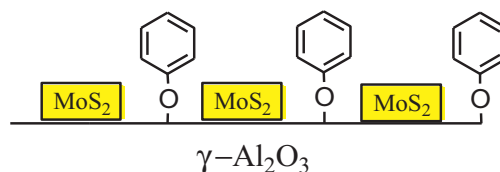


Fig. 5. Phenol interaction on sulfided CoMo/Al₂O₃.

adsorption at RT on the sulfided catalyst and indicate that phenol reacts with the sulfide phase at high temperature.

3.4. Phenol and CO co-adsorption on the sulfided catalyst

On sulfided CoMo/Al₂O₃, CO adsorption is characterized by bands at 2188, 2156, 2110, 2070 and 2055 cm⁻¹ (Fig. 6). The band at 2188 cm⁻¹ corresponds to the interaction of CO with Lewis acid sites of alumina (LAS – Al³⁺) and the one at 2156 cm⁻¹ to its interaction with hydroxyl groups. The other bands characterize the sulfide phase. The one at 2110 cm⁻¹ is due to the adsorption of CO on non-promoted Mo sites, while those at 2070 and 2055 cm⁻¹ belong to CO on Co promoted sites [11].

CO adsorption on sulfided catalysts in interaction with phenol shows a significant decrease in the accessibility of the support sites. The intensity decrease of the band of CO adsorbed on LAS is expected, since the formation of phenolates on alumina involves Al³⁺ sites. In addition, phenolate formation on the alumina support should indirectly perturb OH groups and therefore limit the interaction CO/OH (decrease of the band at 2110 cm⁻¹).

The IR spectra also show a decrease in the accessibility of the sulfide phase: both bands characteristic of CO adsorption on Co-promoted and unpromoted sulfide sites decrease. Since the analysis of the spectra does not indicate any interaction of phenol with sulfide phase (Fig. 4), we propose that the presence of phenolate species in the vicinity of the support prevents the access of CO to the sulfide phase sites. The carbonaceous species, formed in addition to the phenolates species, in the static conditions reported here should not be considered as poisons because they are not detected

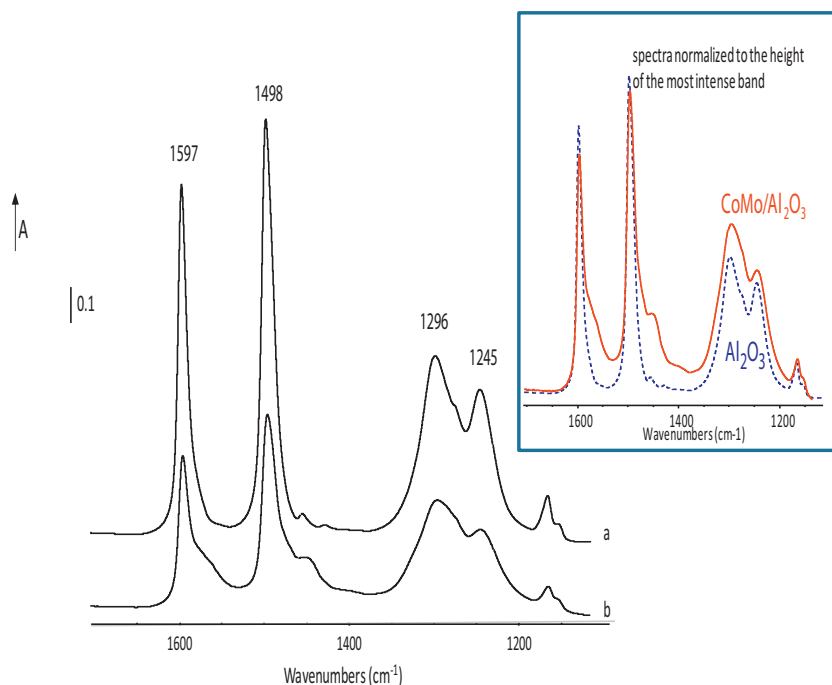


Fig. 4. Infrared spectra of phenol adsorbed on alumina (a) and sulfided CoMo/Al₂O₃ (b) after adsorption of 20 Pa of phenol followed by evacuation at 673 K.

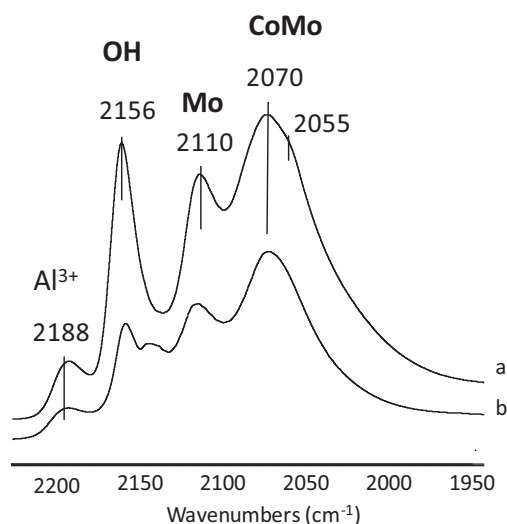


Fig. 6. Infrared spectra of CO adsorbed on sulfided CoMo/Al₂O₃, before adsorption of phenol (a), and after adsorption and desorption of phenol at 623 K (b).

on used catalysts tested under flow conditions of HDO of model molecules [12].

4. Conclusion

The adsorption mode of phenol on oxides such as silica or alumina is related to their acid–base properties. On silica, phenol interacts mainly via hydrogen-bonding, whereas on alumina it dissociates on acid–base pairs leading to the formation of strongly adsorbed phenolates species. On a sulfided CoMo catalyst supported on alumina, phenol dissociates on the support but does not strongly interact with the sulfide phase. As expected, the accessibility of support sites is decreased after phenol adsorption. Moreover,

a decrease of the accessibility of the sulfide sites is also observed; it is accounted by an indirect poisoning of the sulfide edge sites by phenolate species anchored on the support and in the close vicinity of sulfide slabs. As a practical consequence, a modulation (i.e. decrease) of the amount or strength of the acid–base pairs of the alumina support could be a way to limit deactivation by phenol. Recent results obtained using more complex phenolic compounds such as guaiacol, lead to similar conclusions [12]. This study is one of the first steps in the rational design of more efficient and stable HDO catalysts of pyrolytic oils. However, each step from a fundamental understanding of materials to a working catalyst with real feedstocks should be monitored by catalytic testing with model and synthetic feedstocks in order to validate the pertinence of all spectroscopic characterizations.

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Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study

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ABSTRACT

We report the study of the impact of water on the stability of Mo and CoMo sulfide catalysts in hydrodeoxygenation of phenolic compounds. The presence of water at reaction temperature leads to an additional deactivation of the catalyst, which is fully reversible on the CoMo catalyst, but partly irreversible on non-promoted Mo catalyst. IR and HRTEM characterizations as well as DFT simulations confirm the higher sensitivity of unpromoted MoS₂ toward water and show that large amounts of water at reaction temperature lead to the exchange of an important fraction of edge sulfur atoms on non-promoted MoS₂ catalysts, hence changing the nature of the active sites. For Co-promoted catalyst, the extent of water poisoning is much lower and reversible because Co atoms prevent sulfur–oxygen exchanges. Hence, in HDO conditions, Co does not only increase the intrinsic activity of the catalyst (promotion effect) but also stabilizes the active phase in the presence of water (passivation effect).

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1. Introduction

The European Union, the United States and many countries are promoting the use of non-edible lignocellulosic materials to produce biofuels to lower the consumption of fossil fuels and the emission of carbon dioxide without competing with a growing global demand for agricultural commodities [1]. Some green fuels, such as diesel, could be based on liquids derived from pyrolysis of lignocellulosic biomass. However, the bio-oil fraction produced by pyrolysis contains large amounts of oxygenated compounds (up to 45 wt.%) [2–4]. These molecules present multiple functions like aldehyde, ketone, acids and alcohols. High oxygen content leads to deleterious properties such as high viscosity, thermal and chemical instability as well as lower heating values than fossil sources [3–5]. The later was explained by the fact that combustion of oxygenated compounds is much less exothermic than that of hydrocarbons [6]. Hence, upgrading of bio-oils is mandatory to obtain usable fuels. Catalytic hydrodeoxygenation (HDO), a variant of hydroprocessing, refers to treatment of the feed under high

temperature and hydrogen pressure to lower the oxygen content of the feedstock. Oxygen is removed as water or carbon oxides.

Sulfided hydrotreating catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ appear to be good candidates for HDO processing [3–10]. They are well-known catalysts and are extensively used in commercial hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes; fundamental studies (in-depth experimental and theoretical investigations) greatly contributed to the understanding of their mode of action [7,11–18]. It is now well accepted that their active sites are located on the edges of MoS₂ nanocrystallites corresponding to the (1 0 0) edge planes of their layered structure [7,13,16]. This crystallographic (1 0 0) plane exhibits alternate rows of sulfur- (hereafter called S, or sulfur edge) and molybdenum-terminated layers (hereafter called M or molybdenum-edge) [13,16].

Lignocellulose is composed of cellulose (~40 wt.%), hemicellulose (~25 wt.%), lignin (~25 wt.%), extractives and inorganics (~10 wt.%). Lignin consists of aryl ether units connected by ether and alkyl bonds, and the cleavage of those bonds yields monomeric phenols and methoxyphenols [19]. Consequently, pyrolytic oils derived from such feedstocks contain a large amount of phenolic compounds, up to ~30% of the total oxygenated compounds

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[6,20,21]. Over sulfide-based catalyst, alkyl-phenols follow two main deoxygenation routes: one involves hydrogenation before C—O cleavage (HYD route) and the second one is a direct C—O bond cleavage (direct deoxygenation or DDO route) [22–31].

The stability of the sulfided catalysts in the presence of large amounts of oxygenated compounds and water is critical and may lead to modifications of the structure of the active edges of the sulfide phase [3,32]. Sulfided hydrotreating catalysts usually undergo a continuous deactivation caused by coke formation or partial reoxidation of the sulfide phase [3,4]. Water is known to have a slight inhibiting effect on the hydrodeoxygenation rate of phenolic compounds [23,33,34] or real feeds [35], which were related to a weak interaction between water and active sites at high temperature. Such an effect was also explained by the formation of a sulfate layer covering the active phase and reducing the catalytic activity [22]. However, water can also have a slight promoting effect in reactions such as HDN reactions [36].

The aim of the present study is to investigate the influence of water on the structure and activity of MoS₂-based sulfide catalysts using CO adsorption monitored by infrared spectroscopy (IR), high-resolution transmission electron microscopy (HRTEM), periodic density functional (DFT) calculations and catalytic activity measurements in HDO of 2-ethylphenol. Such a study will lead to a better understanding of sulfide catalysts and their active sites in working HDO conditions.

2. Materials and methods

2.1. Materials

The Mo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts were prepared by conventional incipient wetness impregnation and supplied by TOTAL. Their chemical composition and textural properties are given in Table 1.

2.2. IR spectroscopy

For the infrared (IR) study, the catalysts were grounded and pressed into self-supported wafers. After introduction in a low temperature IR cell, sulfidation was carried out in situ under a flow of H₂S/H₂ (10/90) at 623 K during 2 h and followed by an evacuation during 1 h at the same temperature. CO was adsorbed on the sample cooled at 100 K. Small calibrated doses of CO were introduced in the IR cell up to an equilibrium pressure of 1 Torr. The sample was further evacuated from low temperature to 623 K. Subsequent water treatment (4.5 Torr of H₂O at equilibrium) was carried out at 623 K for 2 h and followed by evacuation at 623 K for 1 h. CO adsorption was repeated in the same conditions than previously described.

2.3. HRTEM analysis

Before HRTEM analysis, the catalysts were sulfided in the same conditions as for IR experiments. A fraction of the sulfided sample was contacted with water at 623 K during 16 h and followed by evacuation at 623 K for 1 h. A blank experiment was also done

Table 1
Chemical composition, BET surface area and pore volume of the catalysts.

	Mo/ γ -Al ₂ O ₃	CoMo/ γ -Al ₂ O ₃
BET area (m ² /g)	251	255
Pore volume (cm ³ /g)	0.70	0.64
Mo (wt.%)	9.9	9.2
Co (wt.%)	–	4.2

where the sulfided catalyst was heated (without water) in the closed cell at 623 K during 18 h and evacuated at 623 K for 1 h. After these various treatments, the samples were transferred under Ar in a glove box, gently crushed under Ar and stored under Ar before microscopic analysis. A drop of a suspension of the solid sample in *n*-butanol was deposited on a 300 mesh “holey carbon film” grid and dried at 298 K under argon flow before introducing in the high vacuum chamber of the microscope. HRTEM was performed on a JEOL 2010. The field emission gun was operated at 300 kV. For each sample, stacking degrees and lengths of ~1000 MoS₂ crystallites were measured.

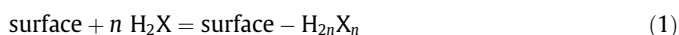
2.4. Computational settings

The density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) [37] using the generalized gradient corrections proposed by Perdew et al. [38]. The wavefunction is expanded in a plane wave basis set, and the electron–ion interactions are described using the projector augmented plane wave (PAW) method [39]. The solution of the Kohn–Sham equations was improved self-consistently until a difference lower than 10^{−5} eV was obtained between successive iterations. The calculations were performed with a cutoff energy of 450 eV and a Methfessel–Paxton smearing with $\sigma = 0.1$ eV. Throughout this work, we used the large super cell (1.2641 × 1.2294 × 2.0000 nm³) shown in Fig. 1. It contains four elementary MoS₂ units in the *x* direction, four in the *z* direction and two layers along the *y*-axis. A *k*-point mesh (3, 1, 1) was chosen to give an accurate sampling of the Brillouin zone. A vacuum layer of 1 nm is located above the MoS₂ slab in the *z* direction in order to avoid interactions between slabs. The two upper rows were allowed to relax until forces acting on ions are smaller than 3 × 10^{−2} eV Å^{−1}. The two lower were kept fixed to simulate bulk constraints. Previous studies [16,17,40,41] showed that this model is suitable to predict the electronic and structural properties of the MoS₂ surface.

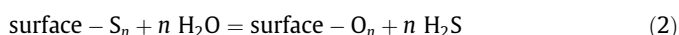
2.5. Thermodynamic treatment

Influence of the gas phase composition (H₂O vs. H₂S pressure) was taken into account by considering two reactions:

Adsorption of *n* H₂X species (X = O or S) on the surface:



and S—O exchange reaction:



Gibbs free energy of Reaction (2), for example, was computed according to:

$$\Delta_r G = \mu(\text{surface} - \text{O}_n) - \mu(\text{surface} - \text{S}_n) + n(\mu(\text{H}_2\text{S}) - \mu(\text{H}_2\text{O}))$$

Assuming that the difference between the chemical potential of solid phases can be approximated by the difference in their electronic energy [42] led to:

$$\Delta_r G = \Delta_r G^0 + n RT \ln 10 \log P(\text{H}_2\text{S})/P(\text{H}_2)$$

where

$$\Delta_r G^0 = \Delta E_n + \Delta \mu^0(T)$$

and

$$\Delta E_n = E(\text{surface} - \text{O}_n) - E(\text{surface} - \text{S}_n) - n E(\text{H}_2\text{O}) + n E(\text{H}_2\text{S})$$

ΔE_n being the electronic energy contribution to the S—O exchange reaction.

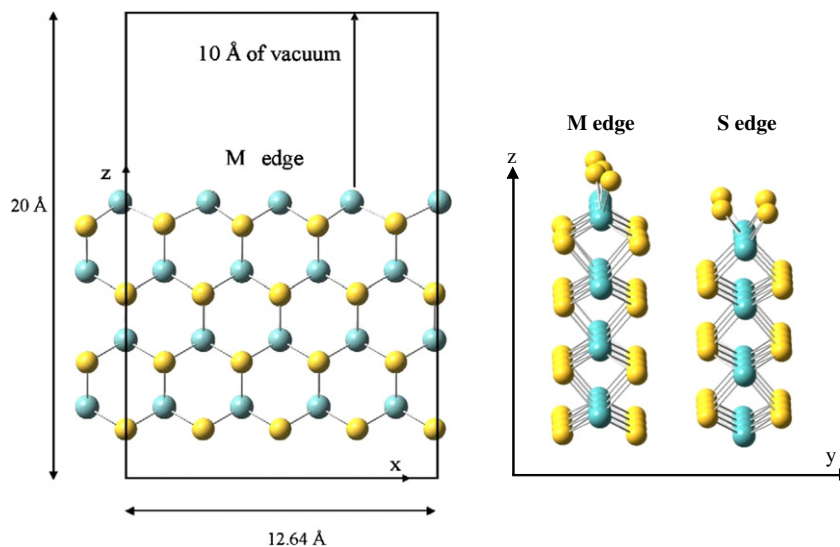


Fig. 1. On the left, cell showing the perfect MoS₂ (1 0 0) surface. On the right, cell showing the stable MoS₂ surface when $0.05 < \text{H}_2\text{S}/\text{H}_2 < 10,000$ [40,41] that will be used as reference. Molybdenum atoms are in blue, sulfur atoms are in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The gas phase molecules chemical potentials $\mu^0(T)$ were computed according to statistical thermodynamic equations for ideal gas [42,43]. The most stable surface is then the one presenting the lowest Gibbs free energy. The calculations were performed at $T = 623$ K, which corresponds to the working temperature of the catalyst and $\text{H}_2\text{S}/\text{H}_2$ partial pressure ratios between 10^{-4} and 10^2 .

2.6. Activity measurements

The particle size of the catalysts was in the range of 250–315 μm . The catalysts were diluted in carborundum to keep the volume of the catalyst bed constant. In order to obtain comparable conversions, 50 mg of promoted catalyst or 100 mg of unpromoted catalyst were used.

All the catalysts were sulfided in situ into a high-pressure dynamic flow reactor (length: 40 cm; inner diameter: 1.25 cm) using a mixture of 5.8 wt.% dimethyldisulfide (DMDS) in toluene, under 4.0 MPa of total pressure (Table 2). The sulfiding mixture was injected at a starting temperature of 423 K. After 1 h, the temperature was raised to 623 K at a rate of 5 K/min and it was maintained at this temperature for 14 h. The temperature was then lowered to the reaction temperature (613 K).

The catalytic test was carried out less than 7 MPa of total pressure using 2-ethylphenol (2-EtPh) as oxygenated model compound diluted in toluene. Its partial pressure was fixed to 49 kPa. DMDS was added to the feed to generate 30 kPa of H_2S during the reaction in order to preserve the sulfide state of the catalyst. The partial pressure of hydrogen was kept constant at 5.75 MPa by changing the partial pressure of the solvent (Table 2). Methylcyclohexane obtained from toluene hydrogenation was observed in very low quantities: less than 1 mol% whatever the contact time used.

The reactor effluents were condensed and liquid samples periodically collected and analyzed with a Varian 3300 chromatograph equipped with a DB1 capillary column (length: 30 m; inside diameter: 0.50 mm; film thickness: 0.25 μm) and a flame ionization

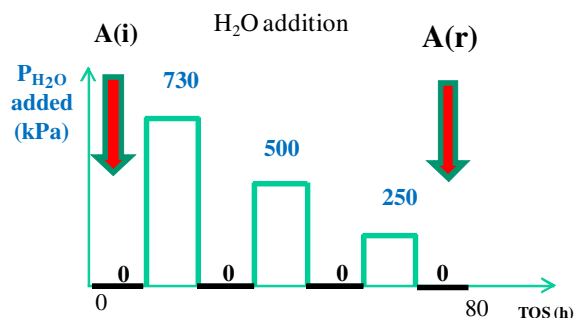


Fig. 2. Evolution of water partial pressure during 2-ethylphenol HDO reaction.

detector. The oven temperature was programmed from 328 K (maintained for 5 min) to 448 K (4 K/min). The products were identified by using GC/MS analysis (Finnigan INCOS 500) and by co-injection of commercial samples provided by Aldrich. Gaseous products were not found except for methane, which was produced by DMDS decomposition.

The model oxygenated feed and water were injected separately by using two pumps. Various model feeds were used in order to keep constant the partial pressures of 2-EtPh, H_2S and H_2 .

The experimental procedure to study the impact of water addition on 2-EtPh deoxygenation is depicted in Fig. 2 and described later:

Step 1: Hydrodeoxygenation of 2-EtPh was carried out without water. Conversions were kept lower than 20% in order to measure the activity (A_i). The activities were measured after stabilization of the catalyst. Contact times of 1.04 min and 2.3 min were used for unpromoted and promoted catalysts, respectively.

Table 2

Partial pressures of the various compounds in sulfidation and reaction conditions.

	P_{total} (MPa)	P_{H_2} (MPa)	P_{toluene} (MPa)	$P_{2\text{-EtPh}}$ (kPa)	$P_{\text{H}_2\text{S}}$ (kPa)	P_{CH_4} (kPa)	$P_{\text{H}_2\text{O}}$ (kPa)	$\text{H}_2\text{O}/\text{H}_2\text{S}$ ratio
Sulfidation conditions	4	2.67	1.07	–	129	129	–	–
Reaction conditions	7	5.75	0.39–1.14	49	30	30	250–730	8.3–24.3

Step 2: Water was injected at in the feed for 8 h at various pressures (730, 500 and 250 kPa, successively).

After each step 2, step 1 conditions were reestablished for 6 h in order to quantify the degree of catalyst deactivation. The final HDO rate (A_f) was measured at the end of this procedure.

2.7. XPS and elemental analysis of spent catalysts

Chemical analysis of carbon and sulfur was carried out after testing and was obtained by using an elementary analyzer (NA2100 analyzer, CE instruments). Prior analysis, the catalysts were washed with dichloromethane during 24 h under reflux and dried at 110 °C for 24 h in order to remove physisorbed hydrocarbons.

For the XPS analysis, the reactor was cooled down after the reaction, flushed with argon and transferred in a glove box in order to avoid any air oxidation. XPS spectra were recorded using an Axis Ultra DLD system (Kratos Analytical – UK), monochromatic Al K α X-ray radiation ($h\nu = 10,476$ eV). The samples are analyzed at a 90° take-off angle, and the hydrocarbon component of the C 1s spectrum (285.0 eV) is used as calibration of the energy scale. Fitting of the XPS spectra is performed using CasaXPS processing software.

3. Results

3.1. IR study

Fig. S1 (Supplementary information) shows the IR spectra of CO adsorbed on Mo/Al₂O₃ and CoMo/Al₂O₃ sulfide catalysts after sulfidation. As described in previous studies [44,45], adsorption on the freshly sulfided catalysts leads to the appearance of bands at 2190 and 2155 cm⁻¹ corresponding to CO interacting with Lewis acid sites (Al³⁺) and acidic AlO–H groups of the uncovered alumina support. On the Mo/Al₂O₃ (Fig. S1A), a main band at 2110 cm⁻¹ is detected that characterizes Mo edge sites of the sulfided MoS₂ slab. On the CoMo/Al₂O₃ catalyst in addition to this band, two bands at 2072 cm⁻¹ and at 2055 cm⁻¹ (shoulder) are observed (Fig. S1A). They correspond to promoted sites in various environments [44]. Addition of small doses of water over the sulfide catalysts at 298 K leads to a progressive poisoning of the acidic sites of the alumina support (spectra not shown). In these conditions, a subsequent adsorption of CO shows that water does not interact significantly with the sulfide phase sites. A decrease in the number of these sites is only observed when large amounts of water are in contact with the catalyst [46]. Hence, in mild conditions (small partial pressure of water at 295 K), water preferentially adsorbs on the oxide support than on the sulfide phase.

Table 3

Effect of the posttreatments with H₂O and H₂S on the variation of CO uptake on the various sulfided sites of (Co)Mo catalysts.

Catalysts	Mo/ Al ₂ O ₃	CoMo/Al ₂ O ₃	
ν CO frequency (cm ⁻¹)	2110	2110	2072, 2055
After water treatment at 623 K	-45%	-72%	-28%
After water treatment and resulfidation at 623 K	-	-54%	+6%

Adsorption of CO on Mo/Al₂O₃ and CoMo/Al₂O₃ sulfide catalysts after water treatment at high temperature leads to spectra showing similar bands as after sulfidation (Fig. S1), but with different intensities. Fig. 3 compares the spectra obtained before and after water treatment at 623 K on sulfided (Co)Mo/Al₂O₃ and shows that the CO uptake by the sulfide sites strongly decreases after water treatment. Such a decrease is observed for both Mo and CoMo catalysts. On the CoMo catalyst, water treatment has not the same impact on non-promoted Mo sites (2110 cm⁻¹) and promoted sites (2072–2055 cm⁻¹); the decrease in the intensity of the CO band characterizing the non-promoted Mo sites is significantly larger (-72 ± 14%) than that of promoted sites (-28 ± 7%), as shown in Table 3. An intermediate decrease is observed on the non-promoted Mo/Al₂O₃ catalyst (~-45%).

In order to check the reversibility of the water poisoning, a resulfiding treatment was carried out on the CoMo catalyst under the same conditions as for the initial sulfidation (623 K, H₂S/H₂ 10/90, 2 h). Fig. 3b and Table 3 clearly show that such a treatment leads to the complete regeneration of the promoted CoMoS sites, while the non-promoted sites are still strongly poisoned after resulfidation (-54%, Fig. 3 and Table 3).

Finally, IR and Raman analysis of the water treated samples did not reveal the presence of $\nu(\text{Mo}=\text{O})$ bands, indicating that no oxidic entities (MoO₃ or oxomolybdate species) were formed after such a treatment.

3.2. HRTEM analysis

HRTEM micrographs of sulfided (Co)Mo/Al₂O₃ catalysts present black thread-like fringes as observed in previous HRTEM studies that correspond to the MoS₂ slabs [47,48]. An example of TEM image is presented in the Supplementary information (Fig. S2). After water treatment at 623 K, no major changes in the aspect and repartition of the sulfide slabs were noted. To compare quantitatively the distribution of slabs length and stacking before and after water treatment, statistical analyses were made based on the analysis of about 50 images and 1000 slabs located in various parts of

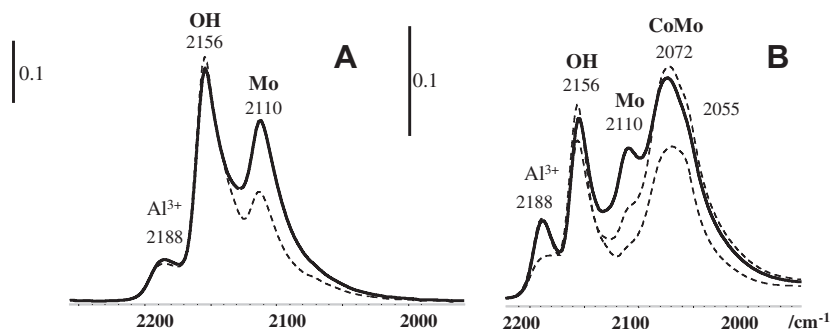


Fig. 3. IR spectra of CO adsorbed on sulfided catalysts after sulfidation (line), after water treatment at 623 K (dashed line), after resulfidation at 623 K (dotted dashed line) – A – Mo/Al₂O₃; B – CoMo/Al₂O₃.

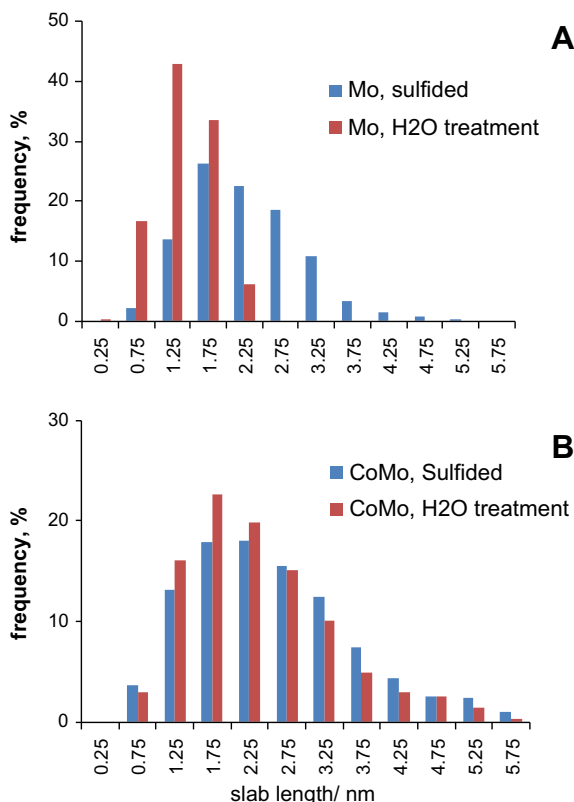


Fig. 4. HRTEM analysis of the effect of water treatment on the slab length of sulfided (Co)Mo/Al₂O₃ catalysts – A – Mo/Al₂O₃; B – CoMo/Al₂O₃ – blue bars: after sulfidation; red bars: after sulfidation and water treatment at 623 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the same sample. The sulfide slab length and stacking distribution for Mo and CoMo catalysts are presented in Fig. 4 and Table 4.

After sulfidation and in the absence of water treatment, the average slab length of the sulfide slabs is close for Mo and CoMo catalysts (2.4 and 2.6 nm, respectively).

After water treatment of the sulfided Mo catalyst, the slabs length distribution is clearly shifted toward lower slab lengths, resulting in the decrease of the average slab length from 2.4 to 1.6 nm (Table 4). The average stacking is not significantly changed on this sample. In addition, no MoO₃ crystallites were detected after water treatment.

The size of the sulfide slabs of the CoMo catalyst appear much less affected by the water treatment: no effect on stacking can be detected from the change of the average values, whereas the average sulfide slab length decreases from 2.6 to 2.4 nm after water treatment. Although this difference is small, a chi-square (χ^2) test

Table 4
Effect of water treatment on the average slab length (*L*) and stacking (*n*) of sulfided slabs of (Co)Mo/Al₂O₃.

Treatment	Mo/Al ₂ O ₃		CoMo/Al ₂ O ₃	
	<i>L</i> (nm)	<i>n</i>	<i>L</i> (nm)	<i>n</i>
Sulfidation by H ₂ S/H ₂ at 623 K	2.4	1.4	2.6	1.0
Sulfidation by H ₂ S/H ₂ at 623 K followed by water treatment at 623 K	1.6	1.1	2.4	1.1
Sulfidation by DMDS at 623 K	-	-	2.4	1.3
Sulfidation by DMDS at 623 K followed by standard HDO test	-	-	2.3	1.2

used to compare the length distribution before and after water treatment showed a statistically significant difference between both distributions ($p < 0.01$). In order to confirm the low sensitivity of CoMo catalysts to water, a HRTEM analysis of CoMo/Al₂O₃ catalyst was performed after the sulfidation procedure used in catalytic test as well as after HDO test of 2-ethylphenol (Table 4). Similar average slab length and stacking are measured before and after the HDO test.

In conclusion, although water treatment leads to a decrease in the average slab length for both catalysts, the non-promoted Mo/Al₂O₃ catalyst is much more sensitive to water than CoMo/Al₂O₃.

3.3. DFT calculations

3.3.1. Stability of the MoS₂ phase

The stability of non-promoted MoS₂ surfaces under typical hydrotreating conditions has been widely studied and reviewed in the last years [16–18,40,41,49]. In presence of H₂ and H₂S, the most stable surface [16,40,41], which will be used as reference, is presented in Fig. 1. The molybdenum-edge is covered with sulfur atoms, yielding sixfold coordinated Mo edge atoms [17,40]. Within the same partial pressure and temperature range, the sulfur edge is reduced: half-sulfur atoms are removed from the surface leading to fourfold coordinated molybdenum atoms.

Water can adsorb on unsaturated molybdenum sites of the surface or lead to sulfur–oxygen atom exchanges, hence strongly modifying the surface state. In a previous work [32], we investigated the effect of water on the stability of the two types of edges considering only sulfur–oxygen (S–O) exchanges. In the present study, we report in addition the adsorption of H₂S and H₂O on the molybdenum phase in order to get a more complete view of MoS₂ stability under HDO conditions.

On the M-edge (Table 5), neither adsorption of H₂O (or H₂S) nor S–O exchange lead to stable surfaces in the partial pressure range investigated in this study ($10^{-4} < P(\text{H}_2\text{X}) < 10^2$, with X = O or S). The M-edge is fully covered by S atoms, and Mo atoms remain sixfold coordinated.

On the opposite, the presence of water in the gas phase induces surface modification of the S-edge (Fig. 5). On this edge, H₂O and H₂S adsorption are dissociative and less endothermic as compared to the M-edge (Table 5). The values of H₂O and H₂S adsorption Gibbs free energies indicate that stable adsorption should occur under high partial pressure. Interestingly, H₂O adsorption is more difficult than H₂S adsorption on the S-edge. Finally, Gibbs free energy calculations demonstrate that exchange of the sulfur atoms located on the edge by oxygen atoms is possible for water partial

Table 5
MoS₂ ΔG^0 (eV) calculated at 350 °C (corresponding to the $\Delta E + \Delta\mu^0(T)$ term) for the three following reactions: (1) adsorption of *n* H₂O molecules, (2) adsorption of *n* H₂S molecules, (3) *n* S–O exchanges – the free energy reaction is divided by *n*.

Reaction	Number of reactions <i>n</i>	M-edge	S-edge
(1) H ₂ O adsorption	1	1.00 (molecular)	0.64 (dissociative)
	2	1.09 (molecular)	0.60 (dissociative)
(2) H ₂ S adsorption	1	1.29 (molecular)	0.25 (dissociative)
	2	1.44 (molecular)	0.20 (dissociative)
(3) S–O exchange	1	0.62	0.21
	2	0.55	0.24
	4	0.60	0.26

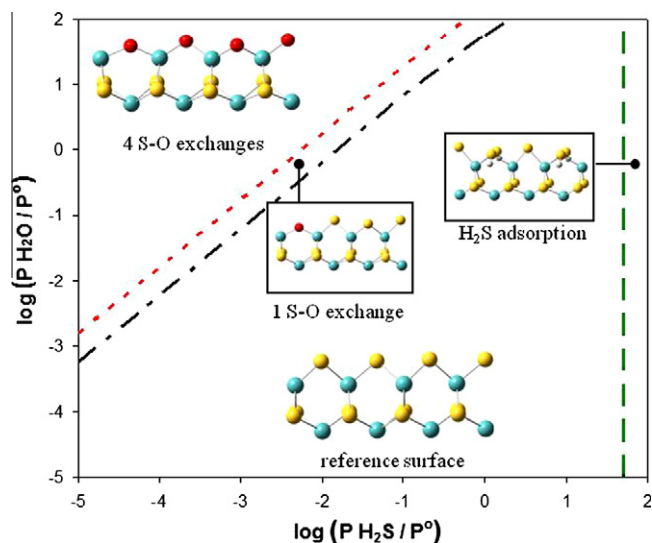


Fig. 5. Stability diagram of the thermodynamic stable surfaces of the MoS₂ S-edge under HDO conditions as a function of $\log(P(\text{H}_2\text{S})/P^0)$ and $\log(P(\text{H}_2\text{O})/P^0)$.

pressure greater than 40 times the H₂S partial pressure. It is worth noting that this exchange could occur even at low total H₂O/H₂S pressure.

Taking into account both reactions and thermodynamic corrections, the diagram shown Fig. 5 can be built, which shows that several types of surfaces are stable in the HDO conditions: the fully sulfided edge with fourfold coordinated molybdenum atoms (reference surface); at high H₂S partial pressure ($\log(P(\text{H}_2\text{S})/P^0) > 1.7$) and whatever H₂O partial pressure, H₂S dissociative adsorption is possible, leading to the formation of S–H groups on the surface; for lower H₂S partial pressures ($\log(P(\text{H}_2\text{S})/P^0) < 1.7$), the increase in H₂O partial pressure can lead to the exchanges of one (or more) sulfur atoms (one exchange for $P(\text{H}_2\text{O})/P(\text{H}_2\text{S}) > 40$; full exchange for $P(\text{H}_2\text{O})/P(\text{H}_2\text{S}) > 200$). These surfaces are then oxygenated, but the formal oxidation state and the coordination of the Mo atoms are kept constant.

The stability diagram (Fig. 5) shows that it is essential to keep a partial pressure in H₂S during the HDO process in order to avoid the desulfurization of the catalyst, which is consistent with experimental observations [27]. However, the amount of H₂S to be added in the feed need to be controlled otherwise, it leads to H₂S adsorption on the MoS₂ catalyst and will inhibit the HDO reactions [10,23,25].

3.3.2. CoMoS phases

The addition of promoter atoms such as cobalt or nickel on the catalyst increases its activity [7,12,31,50,51]. The evolution of the surface stoichiometry as a function of the partial pressures in H₂O and H₂S will be the key parameter to improve our understanding of the reaction. Based on STM observations [52,53], it was proposed that the Co atoms are mostly localized on the S-edge. However, IR experiments [44,54] suggest that a part of the Co atoms, in the case of high Co/Mo ratio, is also located on the M-edge. According to DFT studies [17,53,55,56], the S-edge is supposed to be fully promoted, while the M-edge is only partially substituted. In order to be able to describe the experimental Co/Mo ratio, we performed a systematic study of the promoter effect on the surface stability in presence of water.

Similarly to the results described on the non-promoted system, the addition of water is not favored on the promoted surface (Table 6). This result is valid for both edges and for molecular or

Table 6

CoMoS ΔG^0 (eV) calculated at 350 °C for the three following reactions: (1) adsorption of n H₂O molecules, (2) adsorption of n H₂S molecules.

Reaction	Promotion degree (%)	M-edge	S-edge
(1) H ₂ O adsorption	25	0.70 (dissociative)	0.35 (molecular)
	50	0.32 (molecular)	0.30 (molecular)
	100	0.50 (molecular)	1.28 (molecular)
(2) H ₂ S adsorption	25	0.95 (dissociative)	0.54 (dissociative)
	50	0.44 (molecular)	0.35 (dissociative)
	100	0.29 (molecular)	1.19 (dissociative)

Table 7

CoMoS ΔG^0 (eV) calculated at 350 °C for n S–O exchange reactions – the Gibbs free energy is divided by n .

Promotion degree	Number of reactions n	M-edge	S-edge
25%	1	0.68	0.12
	2	0.69	0.15
	4	0.72	0.37
50%	1	0.12 (top)	0.23
	2	0.13 (top)	0.31
	4	0.41 (basal)	0.37
100%	1	0.96	0.86
	2	0.90	0.81
	4	0.95	0.86

dissociative adsorptions. It can be noticed that adsorption energies are the most endothermic for the fully promoted edges.

The S–O exchange energies are reported in Table 7. On the M-edge, the substitution of one Mo atom by one Co (25% promoted M-edge) leads to the formation of fivefold coordinated atoms as already mentioned [16,18], but the addition of water or the S–O exchange remains not favored. The same conclusion occurs for the fully promoted M-edge. On the opposite, the S–O exchange is possible on the 50% promoted M-edge as soon as $P(\text{H}_2\text{O})/P(\text{H}_2\text{S})$ is greater than 10 (Fig. 6). The terminal Mo–S bond is easily transformed in a Mo–O one in presence of water in the gas phase. However, this exchange does not change the coordination of the Co atom, which would be the adsorption site of the reactive molecules.

The results on the S-edge show that addition of promoter Co atoms will stabilize the sulfide phase, almost stable under HDO conditions. The presence of traces of sulfur in the feedstock should be enough to get a stable catalyst. Fig. 7 summarizes the calculations on the S-edge surface stability giving the number of exchanged atoms depending on the promotion degree and reaction conditions.

3.4. Hydrodeoxygenation of 2-ethylphenol

Some of us reported previously [31] that the 2-EtPh transformation over (Co)Mo/Al₂O₃ sulfided catalysts follows three pathways (Scheme 1). The first one called the hydrogenation route (HYD) leads to the production of 1-ethylcyclohexene, 3-ethylcyclohexene and ethylcyclohexane. The second route, the direct deoxygenation (DDO), leads to the formation of ethylbenzene. In the present experimental conditions, ethylbenzene is not hydrogenated into ethylcyclohexane, indicating that these two routes are parallel. A third pathway (ACI) which involves mainly the acidic sites of the

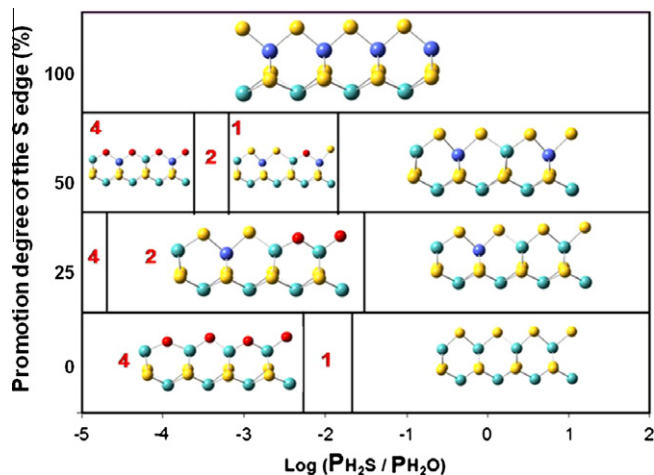


Fig. 6. Stability diagram of the thermodynamic stable surfaces of the M-edges of CoMoS and MoS₂ phases under HDO conditions – the number in red indicates the number of sulfur–oxygen exchanges as a function of the promotion degree and log ($P(\text{H}_2\text{S})/P(\text{H}_2\text{O})$). Color code: Co in dark blue, Mo in light blue, S in yellow, O in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

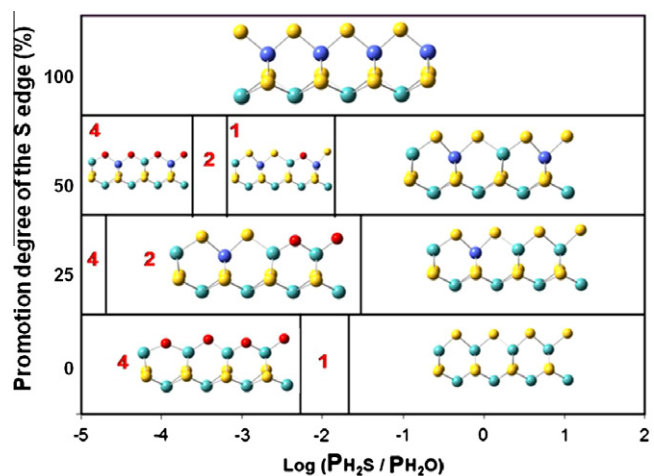


Fig. 7. Stability diagram of the thermodynamic stable surfaces of the S-edges of CoMoS and MoS₂ phases under HDO conditions – the number in red indicates the number of sulfur–oxygen exchanges as a function of the promotion degree and log ($P(\text{H}_2\text{S})/P(\text{H}_2\text{O})$). Color code: Co in dark blue, Mo in light, S in yellow, O in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

alumina support leads to the formation of oxygenated compounds by isomerization and disproportionation reactions (phenol, diethylphenols and 3-ethylphenol). These oxygenated compounds are further deoxygenated and produce benzene, cyclohexane, cyclohexene diethylbenzenes and diethylcyclohexanes.

In the presence of 30 kPa of H₂S in the feed (and in absence of added water - step 1 conditions), the Co-promoted sulfide catalyst is three times more active in deoxygenation than the unpromoted catalyst (Fig. 8a). In fact, both the activities for the HYD and DDO pathways are greater over the CoMo/Al₂O₃ (Fig. 8b–c) than over Mo/Al₂O₃ catalyst. The DDO activity is markedly improved in presence of cobalt. The DOD/HYD ratio increases from 0.26 for unpromoted catalyst to 0.85 for CoMo catalyst. In these conditions (step 1), the deoxygenated products represented about 80% of the total compounds over the CoMo catalyst and about 58% over the non-promoted catalyst. Consequently, the amount of water

generated by the HDO reaction is 4.9 kPa for the unpromoted catalyst and 7.8 kPa for the promoted catalyst.

To determine the effect of water on the stability and selectivity of the sulfided catalysts, quantities of water (between 250 kPa and 730 kPa) larger than that formed during the HDO reaction were introduced on the catalyst (step 2 conditions). Thus, one can consider that the partial pressure of water is constant on the two catalysts irrespective of the time on stream. It should be mentioned that large amounts of water can be typically found during the HDO of bio-oils [4] and that the partial pressures used in the present study are in the range of those used in previous studies (see, e.g., [33,34]). The activity-time profiles for the HYD and DDO routes on the Mo catalyst are reported Fig. S2 in the Supplementary information. It clearly evidence a fast decrease in the HYD activity in the presence of water as well as a fast recovery (about as fast as the initial decrease), which is only partly reversible. Fig. 8a shows the effect of water addition on the steady-state HDO activity for Mo and CoMo catalysts. This causes a decrease in activity of the two catalysts. The activity drop is independent of the added water partial pressure. Over the unpromoted catalyst, the HDO activity (Fig. 8a) is reduced by about 2.2 times, whereas over the Co-promoted catalyst, the HDO activity is only decreased by a factor of 1.3.

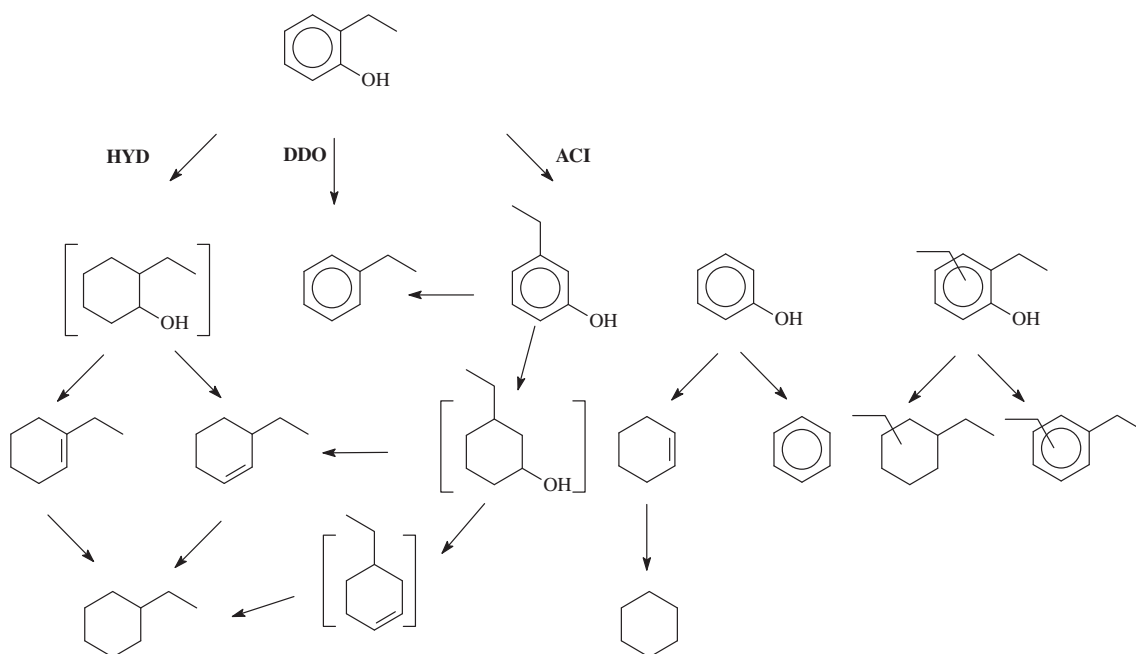
The effect of water addition is different for the two 2-EtPh deoxygenation pathways. For unpromoted and promoted catalysts, the HYD pathway is most sensitive to water addition than the DDO route (Fig. 8b and c). Indeed, the HYD activity drops by a factor about 3 for the Mo catalyst and by a factor of 1.3 on the CoMo catalyst. By contrast, the DDO pathway appears almost insensitive to water addition on the two catalysts. Such a difference leads to a marked improvement of the DDO/HYD selectivity when water is added. The ratio is increased from 0.26 to 0.81 for the unpromoted catalyst and from 0.85 to 1.11 for the promoted catalyst. This improvement of the DDO over the HYD activity reduces the H₂ consumption with only a small penalty in overall HDO activity.

In the last step, the test conditions are set to their initial values in order to estimate the catalyst sensitivity to water addition. For the various routes, the activity ratios (A_r/A_i) (A_r : residual activity, A_i : activity in step 1) are presented in Table 8. For the unpromoted catalyst, the initial HDO activity is not totally recovered. Indeed, for the Mo catalyst, the (A_r/A_i) ratio is equal to 0.75, mainly due to an irreversible loss of activity in the HYD route. In the absence of water, this ratio is 0.96 after the same time on stream (80 h), indicating a moderate deactivation in the absence of water, likely due to coke and/or water produced during the reaction. By contrast, over the Co-promoted catalyst, the (A_r/A_i) ratio is 0.91 for HDO vs. 0.93 after the same time on stream in absence of added water. The activities in both deoxygenation routes are equally recovered. These catalytic results show that the catalyst stability under a water cover is improved by the presence of the cobalt that also acts as promoter.

3.5. Chemical and XPS analysis of spent catalysts

Chemical analysis of sulfur was carried out on the Mo catalyst after catalytic testing for the same time on stream, in the presence or the absence of added water. The sulfur content was similar in both cases within the precision of the method (4.9 ± 0.2 wt.%).

Quasi in situ XPS analysis of Mo and CoMo catalysts was also carried out. The corresponding spectra are reported in Fig. S4 of the Supplementary information section and elemental surface composition from XPS is reported in Table 9. Fig. S4 shows that the Mo 3d XPS spectra of the spent catalysts with or without added water are nearly superimposable, indicating that no significant change of the Mo oxidation state occurs during the water treatment. Similarly, Table 9 indicates that no significant change in



Scheme 1. Transformation of 2-ethylphenol over sulfided Mo-based catalysts.

the amount of sulfide molybdenum (Mo(IV)) and sulfur (S(-II)) occurs after the water treatment, within the uncertainty due to the deconvolution of the XPS spectra. Hence, no significant oxidation of the sulfide phase could be evidenced by any of the characterization techniques used in the present study (TEM, IR, Raman, XPS, elemental analysis).

4. Discussion

For both the Mo and CoMo catalysts, an inhibition upon H₂O addition is observed in the deoxygenation of 2-EtPh. Nevertheless, the Mo catalyst is much more sensitive to water addition than CoMo. The results also show that water affects much more the HYD than the DDO pathway. This strongly suggests that different types of active sites are involved in these two routes, as already proposed by several authors for deoxygenation of phenolic compounds [24,25]. Similar proposals were already proposed for HDS of dibenzothiophenic compounds, which are also desulfurized by two parallel ways (namely DDS and HYD routes) [57] and for HDN reactions [58].

The effect of water addition on the HDO activity is almost completely reversible on the CoMo catalyst, while the activity of the Mo sample is not fully recovered when water is removed. The question of the origin of the water effect arises. Several hypotheses can be proposed: (i) formation of an oxidic phase, (ii) sintering or demixion of the sulfide phase, (iii) poisoning of the active sites by water and (iv) S–O exchanges of the outer layer of the sulfide slabs.

The multitechnique characterization of the catalysts of this study will allow discriminating between these proposals.

4.1. Formation of an oxidic phase

Under reaction conditions, the H₂ partial pressure is always very high (Table 2). Thus, even in the presence of added water, an oxidation of the metallic atoms of the catalyst is thermodynamically unlikely. Furthermore, IR and Raman spectroscopies of the water treated samples do not reveal the presence of any oxidic entities (MoO₃ or oxomolybdate entities), in agreement with

HRTEM analysis of the sulfide catalysts after water treatment, although the latter is not very sensitive to the presence of oxysulfide phases [48]. However, as indicated by the quasi in situ XPS analysis of the spent catalysts after testing with or without added water, no formation of a significant fraction of oxysulfide phase under the HDO conditions with added water was evidenced.

4.2. Sintering or demixion of the CoMoS phase

HRTEM observations show a decrease in the sulfide slab size after water treatment on Mo and CoMo catalyst (Table 4). Therefore, sintering of the sulfide particles cannot be considered to account for the water effect. For the CoMo catalyst, this conclusion is confirmed by the total reversibility of the water effect on the HDO activity (Table 8) as well as on the IR spectra of CO adsorbed on the CoMoS phase (Table 3). These experimental observations also prove that cobalt demixion from the CoMoS phase does not occur significantly in presence of water.

4.3. Poisoning of the active sites by water

IR monitoring of CO adsorption indicates that, at 298 K, water strongly interacts with the alumina support whereas it does not much affect the sulfide sites. On the unpromoted catalyst, DFT calculations show that H₂O is only weakly adsorbed on the preferentially exposed M-edge of MoS₂. Moreover, CO adsorption energy on this edge is much higher than that of H₂O (0.5–0.6 eV vs. 0.2 eV). Hence, molecularly adsorbed water – if any – would be displaced by CO. Although adsorption energies of H₂O and CO are similar on the S-edge (~0.7 eV), it is difficult to draw any clear conclusion from the experimental spectra because CO adsorption on S-edge sites is difficult to quantify from the IR spectra [45]. Similar conclusions can be drawn from DFT calculations of the adsorption energy of water and CO on promoted system (–0.85 eV and –1.59 eV, respectively, for the 50% promoted M-edge). These findings are in good agreement with our experimental results showing that on sulfided catalysts (Mo/Al₂O₃ and CoMo/Al₂O₃), water in the gas phase hardly competes for adsorption sites on the sulfide phase as already observed by Laurent and Delmon [25].

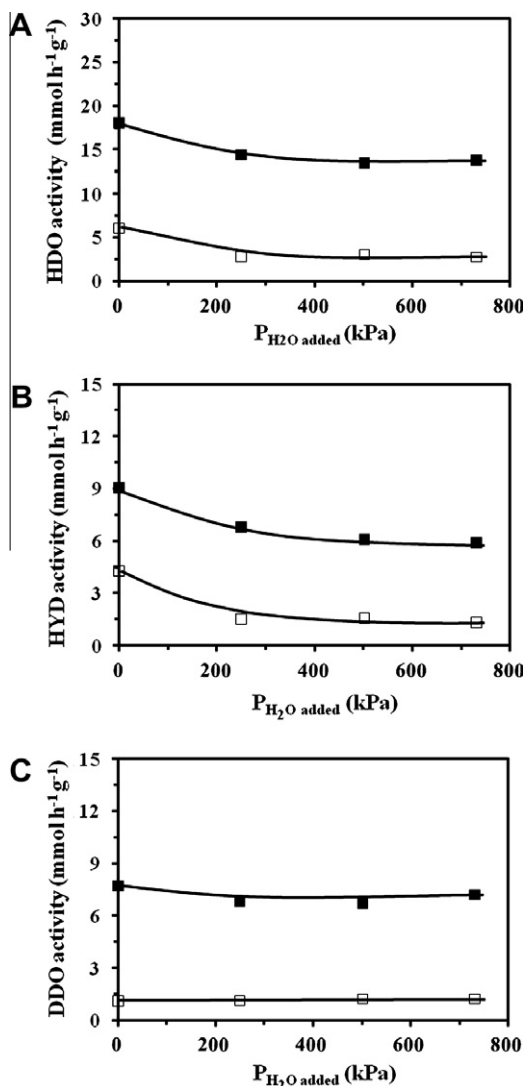


Fig. 8. Transformation of 2-ethylphenol over sulfide catalyst at 613 K less than 7 MPa of total pressure. Effect of water addition on the catalyst activity. CoMo/Al₂O₃ (solid symbols), Mo/Al₂O₃ (empty symbols). HDO activity (A); HYD activity (B), and DDO activity (C).

Table 8

Effect of water addition on the catalytic stability of sulfided (Co)Mo/Al₂O₃ for the different routes of EtPh HDO.

	A_r/A_i	
	Mo/Al ₂ O ₃	CoMo/Al ₂ O ₃
HDO	0.75 (0.96) ^a	0.91 (0.93) ^a
HYD	0.73 (0.96) ^a	0.90 (0.93) ^a
DDO	0.91 (0.96) ^a	0.92 (0.93) ^a

^a In bracket: relative activity after the same time on stream in the absence of water.

4.4. S–O exchanges of the outer layer of the sulfide slabs

DFT calculations show that a sulfur–oxygen exchange is possible on the outer layer of the sulfide slabs (Figs. 5–7). This exchange certainly modifies the electronic properties of the edge sites of the sulfide slabs and may be at the origin of the water effect experimentally observed by different techniques. Furthermore, our calculations point out that this exchange is easier on the non-promoted edges than on the promoted ones whatever the

Table 9

Surface composition of spent catalysts tested with or without added water derived from XPS spectra.

Catalyst	Condition	Mo(IV)/Al	S(-II)/Al
Mo/Al ₂ O ₃	Without H ₂ O	0.027	0.074
	With H ₂ O	0.021	0.089
CoMo/Al ₂ O ₃	Without H ₂ O	0.025	0.117
	With H ₂ O	0.027	0.095

Table 10

Evolution of the Mo–Mo computed distances (in Å) due to the S–O exchange.

	Parallel to the edge	Perpendicular to the edge
MoS ₂ without exchange	3.05 and 3.25 alternatively	3.09 ± 0.02
MoS ₂ partial exchange	Between 2.92 and 3.41	3.10 ± 0.10
MoS ₂ full exchange	Between 3.08 and 3.52	3.10 ± 0.12

degree of promotion. In the same way, the experimental data (IR, HRTEM and activity tests) demonstrate the greater water sensitivity of the unpromoted sulfided phase.

The particle size decrease after water treatment (HRTEM) is compatible with the formation of an oxy-sulfide outer layer. Indeed, the exchange of sulfur by an oxygen atom on the edges leads to a structural distortion and a crystallinity loss of the external layer of sulfide slabs. Table 10 shows the Mo–Mo distances in non-exchanged and oxygen exchanged MoS₂ model surfaces. These data clearly confirm that sulfur–oxygen exchange leads to significant changes of Mo–Mo distances. This effect can be accounted by the strong differences in Mo–O and Mo–S average bond lengths (0.19 and 0.23 nm, respectively). Such a distortion would lead to the absence of diffraction fringes from the outer Mo layer of the MoS₂ sulfide slabs. Consequently, this could explain why the sulfide particles appear smaller in HRTEM. Taking into account the Mo–Mo distance in crystalline MoS₂ (0.316 nm), the exchange of edge sulfur atoms by oxygen should lead to a decrease of ~0.6–0.7 nm of the slab length as observed by HRTEM. These values are very close to the decrease of 0.8 nm of the average slab length observed on the Mo/Al₂O₃ catalyst after water treatment. The absence of a large decrease in the slab length on CoMo/Al₂O₃ is explained by the presence of Co atoms on the MoS₂ slab edges, which (i) does not contribute to the diffraction pattern and (ii) limits the extent of S–O exchanges.

The strong decrease in CO uptake by unpromoted catalyst observed after water treatment can be explained by a decrease in the number of edge sulfide sites induced by S–O exchange. Computed adsorption energy of CO on the M-edge of MoS₂ decreases from 0.6 eV on the non-exchanged surface to 0.1 eV on the fully O-exchanged M-edge. Such a decrease can be explained by the larger electronegativity of the oxygen with respect to sulfur, which lowers the extent of back-donation of Mo d electrons in the π^* CO orbital.

5. Conclusion

Several techniques were used to understand the impact of water on the stability of Mo and CoMo sulfide catalysts supported on alumina. The main findings can be summarized as follows:

- (i) Water addition during the hydrodeoxygenation of 2-ethylphenol decreases slightly the catalyst activity. This is fully reversible on the CoMo catalyst, but partly irreversible on the unpromoted Mo catalyst.

- (ii) IR characterization highlights that a water treatment at reaction temperature leads to a strong and irreversible decrease in the number of unpromoted Mo sites, while the poisoning of the Co-promoted sites occurs to a lower extent and is fully reversible.
- (iii) HRTEM demonstrates that a water treatment at reaction temperature leads to a strong decrease in the average length of crystalline MoS₂ slabs of the unpromoted catalyst (–0.8 nm), while this length is almost unchanged on the promoted CoMo catalyst.
- (iv) DFT calculations show that incorporation of cobalt at the edge of the MoS₂ sulfide phase increases its stability toward water.

All these findings indicate that on unpromoted MoS₂ catalysts, the presence of large amounts of water at reaction temperature can lead to the exchange of a large fraction of edge sulfur atoms, hence changing the nature of MoS₂ edge sites. For Co-promoted catalyst, the extent of water poisoning is much lower and reversible because Co atoms prevent sulfur–oxygen exchanges. Hence, in H₂O, Co does not only increase the intrinsic activity of the catalyst (promotion effect) but also stabilizes active phase in the presence of water (passivation effect).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.06.006.

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FCC gasoline sulfur reduction additives: Mechanism and active sites

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Abstract

The interaction and reactivity of model sulfur compounds with gasoline sulfur reduction additives based on Zn-, Na-, and F-doped γ -Al₂O₃ have been investigated by in situ and operando infrared spectroscopy and microactivity tests. While gasoline sulfur reduction additives selectively crack tetrahydrothiophene (THT) into H₂S and butadiene they are inactive toward thiophene. When blended with a fluid catalytic cracking (FCC) catalyst, gasoline sulfur reduction additives do reduce (alkyl)thiophene contents in gasoline. There is a synergy between the FCC catalyst and the gasoline sulfur reduction additive leading to sulfur reduction. Under actual FCC conditions, Al₂O₃-based gasoline sulfur reduction additives reduce thiophenic compounds by decomposing (alkyl)THT formed via hydrogen transfer on the FCC catalyst. A balance between acid and base properties is required for an optimum activity of the additive, suggesting that THT cracking occurs on Lewis acid–base pairs through successive E2 eliminations.

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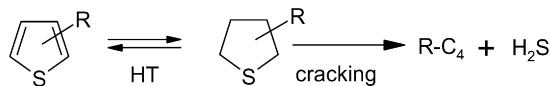
Keywords: Fluid catalytic cracking; Gasoline sulfur reduction; Tetrahydrothiophene; Thiophene; Alumina; Acid–base properties

1. Introduction

As a result of environmental legislation on motor vehicles emissions, refiners face an increasing demand for fuels containing ever lower sulfur levels [1,2]. The production of gasoline by fluid catalytic cracking (FCC) units contributes to about 33% of the gasoline pool leaving a typical refinery and is responsible for about 90% of sulfur found in gasoline. The most important class of sulfur compounds in FCC gasoline consist in thiophenic species: thiophene, alkylthiophenes, and benzothiophene [3,4]. These compounds are not present in the virgin crude and are formed in the riser either by cracking of heavier sulfur compounds [5–7] or by recombination of H₂S with olefins [8]. Thiophenic compounds are very stable in FCC conditions [7], and it is generally admitted that their conversion re-

quires previous hydrogenation by hydrogen transfer (HT) from H-donor molecules before cracking [6,9] (Scheme 1).

Although conventional hydrodesulfurization (HDS) of the FCC gasoline is an effective way to reduce the sulfur content, it decreases the octane number of the gasoline [10]. Other desulfurization processes (e.g., selective HDS, selective adsorption) minimize this octane loss, but they all require specific units (see [11–13] and references therein). Therefore, improving desulfurization within the FCC unit would be attractive, because it avoids pretreatment or post-treatment of the FCC charge or effluent in dedicated units (i.e., capital expenditure in a refinery). Modification of the FCC process parameters (e.g., riser temperature, cut points), although allowing a decrease in the sulfur content of the gasoline cut, strongly degrades yields and product quality [14,15]. For these reasons, gasoline sulfur re-



Scheme 1.

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duction catalysts in the FCC unit have been proposed by Grace Davison [16–19] and are currently implemented in some refineries. This technology uses a solid Lewis acid supported on alumina ($\text{ZnO}/\text{Al}_2\text{O}_3$) as an additive at a level of about 10 wt% of the total FCC catalyst inventory. Laboratory microactivity tests (MAT) [5,20–22] or pilot plant tests (Davison circulating riser) [16–19] have shown that these additives could decrease the sulfur content of FCC gasoline by as much as 40% without significantly affecting other yields, excepting a slight increase of coke and hydrogen production [20]. However, such a sulfur removal in the FCC gasoline mostly concerns thiophene and light alkylthiophenes contents whereas heavier sulfur species such as benzothiophene are much less affected [5,16].

The mechanism by which gasoline sulfur reduction additives reduce thiophenic compounds has not yet been fully elucidated. Considering the above mentioned mechanism (Scheme 1), Harding et al. have proposed that gasoline sulfur reduction additives primarily enhance the rate of THT cracking to H_2S , thus preventing its conversion to thiophene by dehydrogenation reactions [9]. Alternatively, Andersson et al. [20] and Myrstad et al. [23] have suggested that gasoline sulfur reduction could be due to improved hydrogen transfer to thiophenic species initiated by the increase of coke production. More recently, Shan et al. [21] and Vargas-Tah et al. [24] have proposed that sulfur reduction occurs by strong adsorption of thiophenic species on Lewis acid sites of the additive and further cracking.

The objective of the present work is to identify the active sites and the reaction mechanisms by which alumina-based gasoline sulfur reduction additives eliminate thiophenic species. Toward this objective, acid–base properties of two γ - Al_2O_3 have been modified by sodium, zinc, and fluorine incorporation, then characterized by infrared (IR) spectroscopy of adsorbed probe molecules (pyridine and CO_2) and subsequently tested for thiophene and tetrahydrothiophene decomposition. Relationships between catalytic performance and the surface properties monitored under working conditions also have been established.

2. Experimental

2.1. Al_2O_3 -based additives

Two commercial alumina samples, Catapal-C and Hi-Q, provided by Grace Davison (denoted Al_2O_3 -C and Al_2O_3 -HQ in what follows) were studied. These samples differ mainly in their Na content and their textural properties (Table 1). The surface properties of these parent aluminas were modified by doping them with sodium, zinc, and fluorine. Zinc was introduced on Al_2O_3 -HQ by impregnation with $\text{Zn}(\text{NO}_3)_2$ as described previously [16]. The impregnated powder was dried overnight at 383 K, heated at 1088 K for 4 h, and steamed for 4 h at the same temperature. X-ray diffraction (XRD) patterns revealed the presence of ZnAl_2O_4 . Sodium and fluorine were deposited on Al_2O_3 -C by dry impregnation. An aqueous solution containing the appropriate amount of Na_2CO_3 and NH_4F was contacted with alumina. After 2 h of maturation at room temperature, the catalyst was dried at 393 K for 3 h before cal-

Table 1
Surface area and composition of Al_2O_3 -based additives

Additives	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	[Na] (wt ppm)	[Zn] (wt%)	[F] (wt%)
Al_2O_3 -C	199	250	0	0
$\text{Na}_{670}/\text{Al}_2\text{O}_3$ -C	184	670	0	0
$\text{Na}_{1465}/\text{Al}_2\text{O}_3$ -C	192	1465	0	0
$\text{F}_{0.2}/\text{Al}_2\text{O}_3$ -C	188	230	0	0.2
$\text{F}_{0.4}/\text{Al}_2\text{O}_3$ -C	188	230	0	0.4
$\text{F}_{1.3}/\text{Al}_2\text{O}_3$ -C	178	220	0	1.3
Al_2O_3 -HQ	136	100	0	0
$\text{Zn}/\text{Al}_2\text{O}_3$ -HQ	110	400	10	0

ination under air (60 ml min^{-1}) up to 823 K for 3 h. XRD measurements showed that sodium and fluorine deposition did not modify the bulk structure of the alumina. The samples references and main characteristics are reported in Table 1.

2.2. Characterization by IR spectroscopy

The additives were pressed into self-supported wafers (discs of about 20 mg, 2 cm^2) and activated in situ in the IR cell by heating up to 723 K under vacuum. Pyridine was adsorbed at room temperature (133 Pa at equilibrium) and further desorbed at 423 K under vacuum (10^{-4} Pa) for 15 min to eliminate physisorbed and H-bonded pyridine from the surface. In distinct experiments, carbon dioxide was adsorbed on the activated additives at room temperature (1330 Pa at equilibrium for 15 min). Known amounts of THT were added into the cell via a calibrated volume (1.75 cm^3) and the pressure was monitored by a gauge (0–1330 Pa).

IR spectra were recorded on a Nicolet Magna 750 IR spectrometer equipped with a DTGS detector and a KBr beam splitter using a resolution of 4 cm^{-1} and 126 scans. The spectra presented in this paper were normalized to a disc of 10 mg cm^{-2} .

2.3. Catalytic tests

2.3.1. Short contact time microactivity tests

Short contact time microactivity tests (SCT-MATs) [25] were carried out in an automated fixed-bed unit at 800 K, using a commercially available FCC catalyst from Grace Davison and the $\text{Zn}/\text{Al}_2\text{O}_3$ -HQ additive blended at a level of 10 wt%. To simulate an equilibrium catalyst in a commercial unit, the catalyst and the additive were steamed separately in a fluidized bed for 4 h at 1088 K with 100% steam. After steaming, the FCC catalyst had a unit cell size 24.24 \AA , a zeolite surface area of $181 \text{ m}^2 \text{g}^{-1}$, and a matrix surface area of $31 \text{ m}^2 \text{g}^{-1}$, whereas the steamed $\text{Zn}/\text{Al}_2\text{O}_3$ -HQ additive had a surface area of $80 \text{ m}^2 \text{g}^{-1}$.

Two model feeds were used: pure hexadecane (sulfur-free feed) and a mixture of hexadecane and 3-hexylthiophene (sulfur-containing feed) with a sulfur content of 1%, similar to that of a typical FCC feed. To vary the conversion, the catalyst-to-oil ratio was adjusted in the range of 4–8 g g^{-1} at a constant feed weight of 1.5 g and a constant feed injection time of 9 s.

After the cracking experiment, the coke on FCC catalyst was determined by a carbon analyzer as described previously [25].

Gas chromatography (GC) was used to analyze the products obtained from the cracking experiments, such as hydrogen, C1–C6 gases, gasoline, LCO, and bottom fractions and gasoline composition, as described previously [25]. The yields were calculated as weight percent of reactant. The fractions of gasoline and LCO were determined at cut points of 494 and 644 K (221 and 371 °C).

The gasoline sulfur concentration was analyzed using an Agilent 6890 gas chromatograph with an atomic emission detector G2350A using techniques similar to those described previously [26]. Product yield, gasoline composition, and sulfur content at constant conversion (63%) were obtained by interpolating experimental values.

2.3.2. Continuous-flow activity tests

Continuous-flow activity tests were carried out in a quartz tubular reactor and performed at atmospheric pressure. Catalyst samples (20 mg) were introduced into the microreactor and activated under a helium flow (25 ml min⁻¹) for 1 h at 723 K. The contact time was fixed to 3.2 g h mol⁻¹ for tetrahydrothiophene and to 4.3 g h mol⁻¹ for thiophene. Reactant and reaction products were analyzed online by GC, IR spectroscopy, and mass spectrometry (MS). The gas chromatograph was a Varian Star 3400CX equipped with a 30-m CP-SIL 5CB column, maintained at 393 K, and a flame ionization detector. The IR analysis of the reaction products was performed using a tubular cell designed for gas analysis equipped with KBr windows (path length 175 mm; internal diameter 19 mm). Analysis was also performed with a quadrupole mass spectrometer (OmniStar, Pfeiffer Vacuum) to detect H₂S (*m/z* = 34).

2.3.3. IR characterization in reaction conditions (*operando* analysis)

The IR study of the catalyst in working conditions was performed using a reactor-IR cell [27,28]. This device is particularly well suited for *operando* analysis, because products of the reaction and species formed on the catalyst surface in working conditions can be analyzed simultaneously. In the reactor-IR cell, THT was sent under flow (*W/F* = 3.2 g h mol⁻¹) on the catalyst under the form of a thin disc of about 20 mg (2 cm²). In the reactor-IR cell, the reaction temperature was limited to 688 K, lower than that used in the quartz microreactor (723 K). The reactant and products were analyzed online by GC and MS. Surface species present on the catalyst were simultaneously characterized by IR spectroscopy.

3. Results

3.1. Surface properties of alumina-based additives

This section reports the effect of the dopes (Na, Zn, F) on the acid–base properties of alumina.

3.1.1. Hydroxyl groups

IR spectra of the alumina-based catalysts after activation at 723 K are presented in the region of $\nu(\text{OH})$ vibrations in Fig. 1. After activation at 723 K, the IR spectra of Al₂O₃-C and

Al₂O₃-HQ showed four main bands at about 3790, 3770, 3730, and 3685 cm⁻¹ assigned to the various OH groups of alumina [29,30]. The overall intensity of these $\nu(\text{OH})$ bands was significantly lower on Al₂O₃-HQ, due to its lower specific surface area (Table 1).

Na/Al₂O₃-C Sodium incorporation led to an overall decrease in intensity of the initial $\nu(\text{OH})$ bands (Fig. 1B). In agreement with previous studies [31,32], those with the highest frequencies (3790 and 3770 cm⁻¹) were the most affected and almost disappeared at the highest sodium loading (1465 ppm). In addition, a shoulder at 3755 cm⁻¹ (also present on Al₂O₃-C, which contains 250 ppm of Na) grew with increased sodium loading, related to the influence of Na⁺ on OH groups [32].

Zn/Al₂O₃-HQ In the presence of zinc, the bands at 3792 and 3730 cm⁻¹ decreased significantly, whereas that at 3772 cm⁻¹ increased in intensity, and a new band at 3755 cm⁻¹ appeared (Fig. 1C).

F/Al₂O₃-C Fluorine addition also significantly decreased the $\nu(\text{OH})$ bands at 3792 and 3772 cm⁻¹ (Fig. 1D). At the highest fluorine loadings, the $\nu(\text{OH})$ band at 3685 cm⁻¹ partially decreased, and a new $\nu(\text{OH})$ band at 3720 cm⁻¹ appeared.

3.1.2. Pyridine adsorption

Pyridine was adsorbed at room temperature (133 Pa at equilibrium) and further desorbed at 423 K to eliminate physisorbed and H-bonded pyridine from the surface. In such conditions, only pyridine coordinated to Lewis acid sites (LAS) was observed. Fig. 2 shows the IR spectra in the ν_{8a} range. Two ν_{8a} bands can be distinguished at 1624 and 1618 cm⁻¹, previously assigned to pyridine coordinated to tetrahedral Al³⁺ (strong LAS) and to both tetrahedral and octahedral Al³⁺ (medium to weak LAS) [33,34]. After evacuation at 523 K, only pyridine coordinated to the strongest acid sites (1624 cm⁻¹) was detected. The influence of the dopes on LAS strength was assessed using the ν_{8a} frequency, which increases with increasing acid strength, whereas quantification of the LAS was obtained from the surface area of the ν_{19b} band at about 1452 cm⁻¹ using its molar absorption coefficient (ϵ = 1.5 cm² μmol⁻¹) [35]. The total amount of LAS was determined using the surface area of this band measured after evacuation at 423 K, whereas the strongest LAS was detected considering this band after evacuation at 523 K. These data are reported in Table 2.

Na/Al₂O₃-C Sodium addition decreased the total amount of Lewis acid sites. Fig. 2A illustrates that Na incorporation decreased the concentrations of both strong and medium acid sites (bands at 1624 and 1618 cm⁻¹, respectively). Table 2 shows that addition of 420 and 1215 ppm of Na on Al₂O₃-C (Na₄₇₀/Al₂O₃ and Na₁₄₆₅/Al₂O₃, respectively) decreased the total concentration of LAS by 130 and 1360 μmol g⁻¹, respectively. This corresponds to the disappearance of ~7 and ~25 LAS per sodium atom added. These values are similar to those reported previously for various Na/Al₂O₃ samples [32]. In the case of strong LAS, Na poisoning was less effective, because the addition of 1 Na atom led to the disappearance of about 3 strong LAS for both samples.

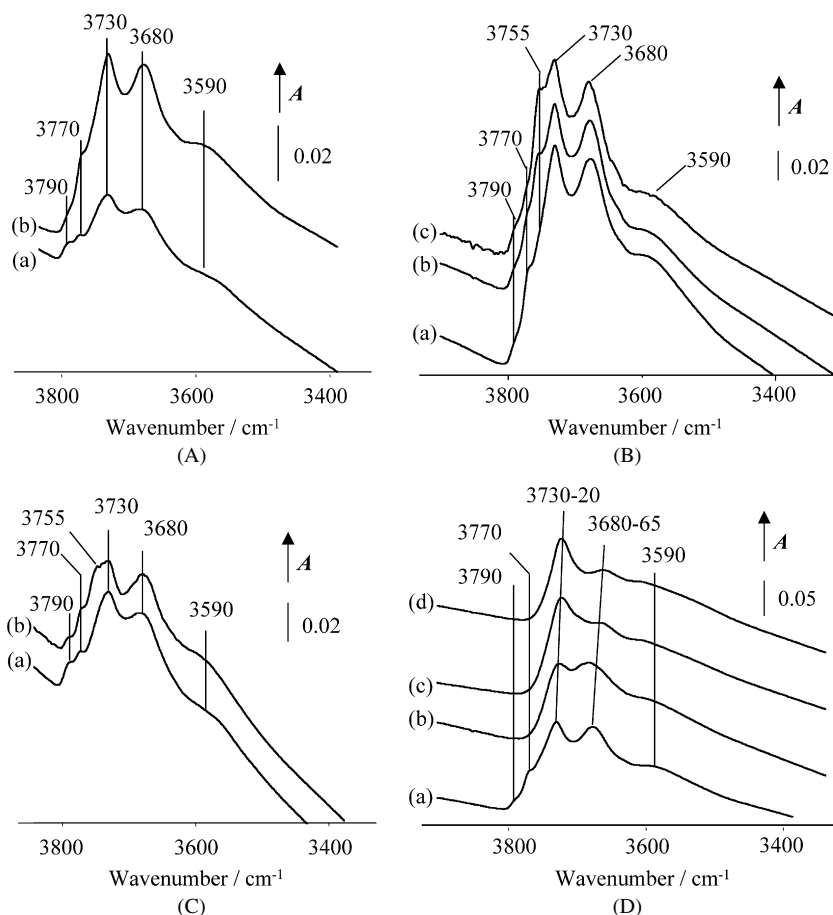


Fig. 1. IR spectra in the $\nu(\text{OH})$ region of alumina-based additives activated at 723 K. (A) Parent aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$ and (b) $\text{Al}_2\text{O}_3\text{-HQ}$; (B) Na-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$; (C) Zn-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-HQ}$, (b) $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$; (D) F-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{F}_{0.2}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{F}_{0.4}/\text{Al}_2\text{O}_3\text{-C}$, (d) $\text{F}_{1.3}/\text{Al}_2\text{O}_3\text{-C}$.

Zn/Al₂O₃-HQ Fig. 2B shows that zinc incorporation decreased the concentration of medium LAS characterized by the ν_{8a} band at 1618 cm^{-1} but increases the LAS characterized by the band at 1624 cm^{-1} (Fig. 2B). Overall, the total concentration of LAS decreased, but the amount of strongest LAS increased significantly (Table 2). The results presented in Table 2 demonstrate that the introduction of about 50 Zn atoms leads to the creation of 1 strong Lewis acid site.

F/Al₂O₃-C The addition of fluorine increased the amount of both medium and strong LAS (Table 2). The creation of 1 strong Lewis acid site requires the introduction of about 5 fluorine atoms. It should be noted that no Brønsted acid sites were detected by pyridine on fluorinated samples.

3.1.3. Carbon dioxide adsorption

Fig. 3 shows the IR spectra recorded after CO_2 adsorption at room temperature (1330 Pa at equilibrium for 15 min). On $\text{Al}_2\text{O}_3\text{-C}$ (Fig. 3A), carbon dioxide adsorption gave rise to bands at 3610 , 1648 , 1484 , and 1235 cm^{-1} , characteristic of hydrogen-carbonate species (designated HC) formed by the interaction of CO_2 with basic OH groups [36]. Additional bands in the $1700\text{--}1850\text{ cm}^{-1}$ and $1150\text{--}1250\text{ cm}^{-1}$ ranges are assigned to bridged carbonate ions (“organic-like” species, designated OC), whereas the band at 1445 cm^{-1} is assigned to

bidentate carbonate species (designated BC) [37]. A similar spectrum was obtained on $\text{Al}_2\text{O}_3\text{-HQ}$ (Fig. 3B). The integrated intensities of the carbonate and hydrogen-carbonate bands in the $1940\text{--}1120\text{ cm}^{-1}$ range are reported in Table 2.

Na/Al₂O₃-C Na addition [samples $\text{Na}_{670}/\text{Al}_2\text{O}_3$ and $\text{Na}_{1465}/\text{Al}_2\text{O}_3$ (Fig. 3A)] did not modify the nature of species formed by CO_2 adsorption but did decrease the amount of hydrogen-carbonate and carbonate species.

Zn/Al₂O₃-HQ Addition of Zn led to slight decreases in initial carbonate and hydrogen-carbonate species (Fig. 3B). In addition, two sharp bands at 1624 and 1455 cm^{-1} were detected. On pure ZnO, carbonate species also gave rise to very sharp bands, but at different wavenumbers [38]. The two bands observed on Zn/HQ at 1624 and 1455 cm^{-1} are tentatively assigned to bidentate carbonate species adsorbed on Zn^{2+} cations of the spinel structure $\text{Zn}(\text{AlO}_2)_2$.

F/Al₂O₃-C On fluorinated alumina samples, carbonate and hydrogen-carbonate species similar to those observed on the parent Al_2O_3 ($\text{Al}_2\text{O}_3\text{-C}$) were also formed by CO_2 adsorption (Fig. 3C). However, the amounts of hydrogen-carbonate, bidentate carbonate, and organic carbonate species strongly decrease in the presence of fluorine.

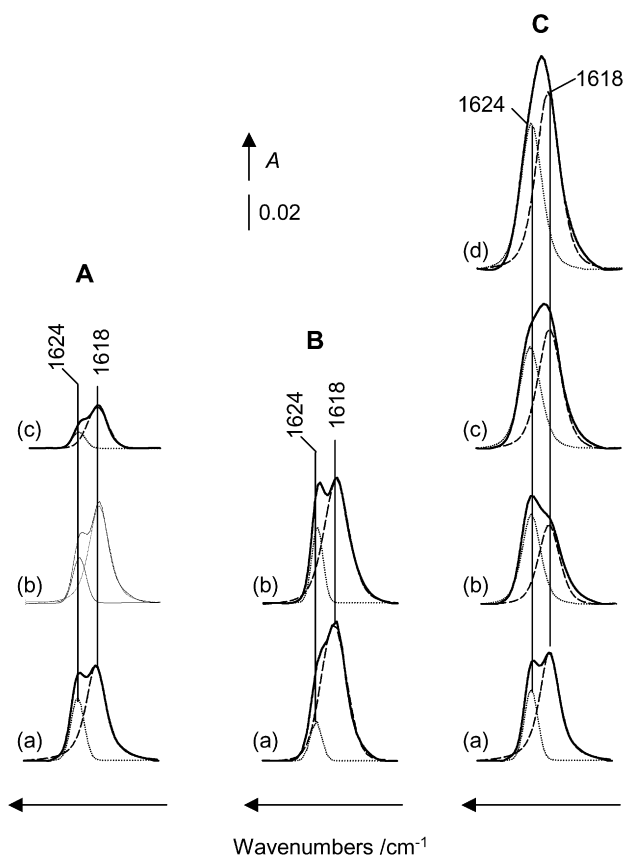


Fig. 2. ν_{8a} -spectra of pyridine adsorbed on alumina-based catalysts at room temperature (1 Torr) followed by evacuation at 423 K. (A) Na-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$; (B) Zn-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-HQ}$, (b) $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$; (C) F-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{F}_{0.2}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{F}_{0.4}/\text{Al}_2\text{O}_3\text{-C}$, (d) $\text{F}_{1.3}/\text{Al}_2\text{O}_3\text{-C}$.

Table 2
Acid–base properties of Al_2O_3 -based additives

Additives	Medium LAS ^a ($\mu\text{mol g}^{-1}$)	Strong LAS ^b ($\mu\text{mol g}^{-1}$)	Hydrogencarbonate + carbonate species ^c ($\text{au cm}^{-1} \text{mg}^{-1}$)
$\text{Al}_2\text{O}_3\text{-C}$	1620	275	3.44
$\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$	1550	220	2.50
$\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$	400	135	2.80
$\text{F}_{0.2}/\text{Al}_2\text{O}_3\text{-C}$	1650	280	1.90
$\text{F}_{0.4}/\text{Al}_2\text{O}_3\text{-C}$	1750	310	0.08
$\text{F}_{1.3}/\text{Al}_2\text{O}_3\text{-C}$	1930	440	0.04
$\text{Al}_2\text{O}_3\text{-HQ}$	1580	205	2.97
$\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$	1350	240	2.18

^a Coordinated pyridine after evacuation at 423 K.

^b Coordinated pyridine after evacuation at 623 K.

^c Specific integrated intensity of IR bands in the 1940–1120 cm^{-1} range.

3.2. THT and thiophene adsorption

The adsorption modes of THT and thiophene on Al_2O_3 -based additives were studied. Fig. 4A shows the IR spectra recorded after adsorption of increasing amounts of THT on $\text{Al}_2\text{O}_3\text{-C}$ activated at 723 K. THT adsorption led to the perturbation of the surface OH groups initially present and to the formation of a strong and broad $\nu(\text{OH})$ band centered at

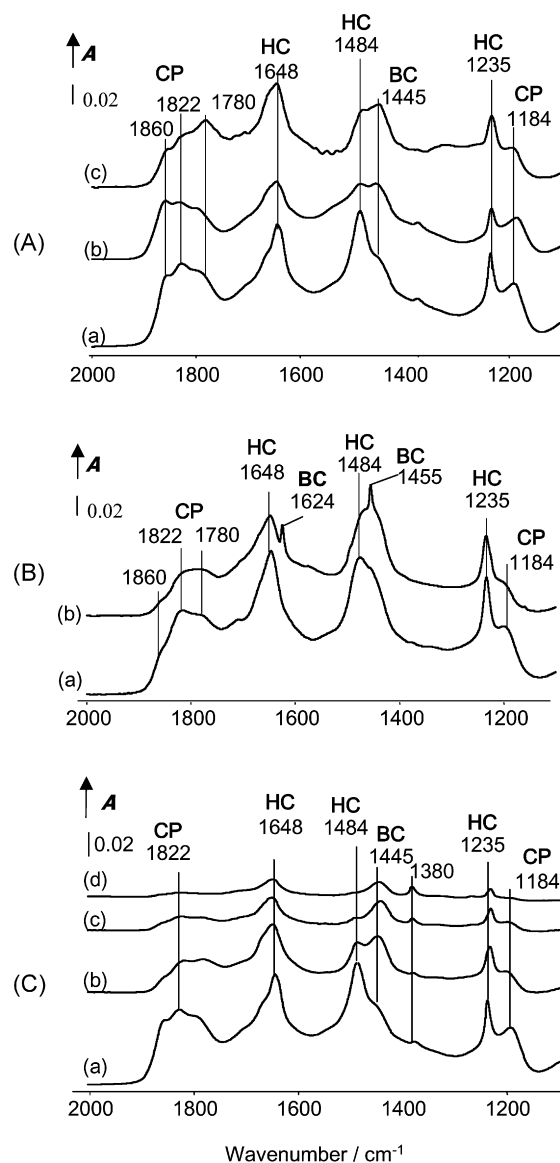


Fig. 3. IR spectra after CO_2 adsorption at room temperature on alumina-based catalysts activated at 723 K. (A) Na-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$; (B) Zn-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-HQ}$, (b) $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$; (C) F-doped aluminas: (a) $\text{Al}_2\text{O}_3\text{-C}$, (b) $\text{F}_{0.2}/\text{Al}_2\text{O}_3\text{-C}$, (c) $\text{F}_{0.4}/\text{Al}_2\text{O}_3\text{-C}$, (d) $\text{F}_{1.3}/\text{Al}_2\text{O}_3\text{-C}$. (HC: hydrogencarbonate; OC: organic carbonates; BC: bidentate carbonates.)

$\sim 3395 \text{ cm}^{-1}$ resulting from their interaction with THT by hydrogen bonding. Adsorption of thiophene in similar conditions (not shown) also led to a perturbation of initial OH groups with a $\nu(\text{OH})$ band due to hydrogen-bonded OH groups at $\sim 3605 \text{ cm}^{-1}$. This indicates that THT interacted more strongly than thiophene with the surface hydroxyl groups, due to its higher basicity (proton affinity, $\text{PA} = 849 \text{ kJ mol}^{-1}$) compared with thiophene ($\text{PA} = 815 \text{ kJ mol}^{-1}$) [39].

At low coverage, THT adsorbed on alumina $\text{Al}_2\text{O}_3\text{-C}$ gave rise to two main $\nu(\text{CH})$ bands at 2960 and 2871 cm^{-1} , shifting toward lower wavenumbers as the coverage increased (2953 and 2866 cm^{-1} at an equilibrium pressure of 133 Pa). In parallel, the $\delta(\text{CH})$ bands, observed in the 1500–1100 cm^{-1} range [40], shifted by $\sim 1\text{--}2 \text{ cm}^{-1}$ with increasing coverage.

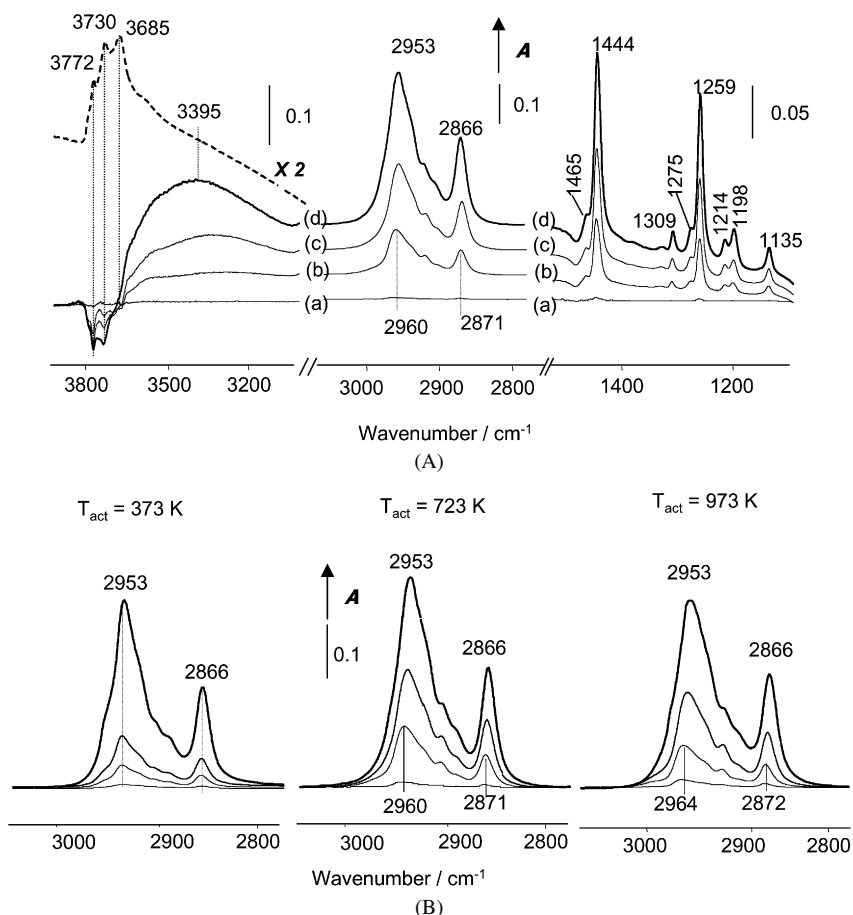


Fig. 4. (A) IR spectra after adsorption of increasing amounts of THT on $\text{Al}_2\text{O}_3\text{-C}$ activated at 723 K (from (a) $10 \mu\text{mol g}^{-1}$ to (d) 133 Pa at the equilibrium). (B) $\nu(\text{CH})$ spectra after adsorption of increasing amounts of THT on $\text{Al}_2\text{O}_3\text{-C}$ activated at 373, 723, and 973 K.

On evacuation, both the $\nu(\text{CH})$ and $\delta(\text{CH})$ bands shifted toward higher wavenumbers. Conversely, the frequencies of the $\nu(\text{C}-\text{C})$ vibrations of adsorbed THT ($1000\text{--}1100 \text{ cm}^{-1}$) remained almost constant with the coverage. The observed $\nu(\text{CH})$ and $\delta(\text{CH})$ shifts could indicate a change in adsorption modes of THT as a function of the Al_2O_3 coverage.

To discriminate the various adsorption modes of THT, similar experiments were carried out on fully hydroxylated $\text{Al}_2\text{O}_3\text{-C}$ (activated at 373 K [41]) and on $\text{Al}_2\text{O}_3\text{-C}$ dehydroxylated at 973 K. Fig. 4B shows the corresponding $\nu(\text{CH})$ spectra, the most sensitive to the THT coverage. On fully hydroxylated $\text{Al}_2\text{O}_3\text{-C}$, no shift of the $\nu(\text{CH})$ bands can be seen, and the frequencies of the most intense bands are 2953 and 2866 cm^{-1} . This allows to assign such $\nu(\text{CH})$ frequencies to hydrogen-bonded THT. Conversely, on $\text{Al}_2\text{O}_3\text{-C}$ dehydroxylated at 973 K, the $\nu(\text{CH})$ frequencies of adsorbed THT are seen at significantly higher frequencies at low coverage (2964 and 2872 cm^{-1}), shifting progressively toward 2953 and 2866 cm^{-1} with increasing coverage. It thus appears that the greater the dehydroxylation, the higher the $\nu(\text{CH})$ frequencies at low coverage. This suggests that high $\nu(\text{CH})$ frequencies observed at low coverage can be assigned to THT coordinated to Lewis acid sites of alumina. It is noteworthy that previous studies reported similar dependencies of $\nu(\text{CH})$ frequencies on the adsorption mode of alcohols [42] and pyridine [43] on Al_2O_3 . At

higher THT coverage, the decreased $\nu(\text{CH})$ frequencies can be explained by the interaction of THT with surface OH groups by hydrogen bonding. The reversibility of the $\nu(\text{CH})$ frequency shift observed on evacuation indicates that THT preferentially interacts with Lewis acid sites of $\text{Al}_2\text{O}_3\text{-C}$. Similar results are obtained when THT was adsorbed on the other Al_2O_3 -based additives used in this study.

The IR spectra recorded after thiophene adsorption on Al_2O_3 -based catalysts (not reported here) were similar to those reported in the detailed study of Quigley et al. [44]. Examination of the $\nu(\text{C}=\text{C})$ range ($1400\text{--}1450 \text{ cm}^{-1}$) shows that like THT, thiophene adsorbed on Lewis acid sites as well as on OH groups of Al_2O_3 [44].

3.3. Cracking of a model feed

The gasoline sulfur reduction activity of the $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$ additive was evaluated in a short-contact time microactivity test (SCT-MAT) fixed-bed unit at 798 K. The additive was blended with the steamed cracking catalyst (H-USY) at 10 wt%. Two model feeds were used, one sulfur-free (pure hexadecane) and the other spiked with 1% sulfur (hexadecane and 3-hexylthiophene), a level typical of FCC feeds. SCT-MAT was carried out at three different catalyst-to-oil ratios (3, 6, and 8), which led to conversions ranging from ca. 35 to ca. 70 wt%. Ta-

Table 3
Product yields and gasoline composition at constant conversion (63%)

Feed	Sulfur-free		Sulfur (1%)	
	USY	USY + Zn/Al ₂ O ₃ -HQ	USY	USY + Zn/Al ₂ O ₃ -HQ
Catalyst				
Cat/oil ratio (g/g)	7.4	8.0	6.2	6.7
Yields (wt%)				
Gas	27.6	26.8	24.9	25.4
Gasoline	35.1	34.4	35.4	35.4
LCO	36.6	36.8	35.9	35.9
Coke	0.71	1.09	0.56	0.91
Hydrogen	0.01	0.06	0.01	0.04
Gasoline composition (wt%)				
Paraffins	17.4	18.3	17.5	16.9
Isoparaffins	22.8	21.3	23.5	22.3
Aromatics	18.2	21.5	16.3	18.7
Naphthenes	3.6	3.6	3.9	3.6
Olefins	38.0	36.0	39.1	37.8

Table 4
Sulfur content and gasoline sulfur reduction at constant conversion (63 wt%)

	Sulfur content (ppm)		Sulfur reduction	
	USY	USY + Zn/Al ₂ O ₃ -C	ppm	%
Gasoline	2674	1982	692	26
LCO	6036	5698	338	6
Gasoline sulfur				
Mercaptans	18	16	2	11
THT	371	4	367	99
Thiophenol	34	26	8	23
Thiophene	408	350	58	14
Alkyl-thiophenes	1610	1339	271	17
Benzothiophene	233	242	−9	−4

Table 3 shows the product distribution at 63% conversion for both feeds, with or without the additive. In the presence of the additive, an increase in the catalyst/oil ratio by ~10% was needed to maintain conversion, indicating that the additive, blended at a level of 10%, did not significantly affect conversion. Gasoline and LCO yields were not significantly affected by the additive. Only slight increases in coke, hydrogen, and gasoline aromatics occurred for both feeds when the additive was used. Similar trends were observed over the entire range of conversions (35–70%), in agreement with previous studies using real feeds [14].

The cracking of the sulfur feed yielded about 150 different sulfur compounds, from H₂S to alkyl dibenzothiophenes. Table 4 shows the sulfur content of the gasoline and LCO fractions at 63% conversion. In the absence of additive, about 87% of the initial sulfur ended up in the gasoline range. Fig. 5 shows the sulfur content of gasoline and LCO evolution with conversion. Increasing the conversion led to decreased gasoline sulfur and increased LCO sulfur. Similar trends have been reported for real FCC feeds. On the other hand, the sulfur content of the gasoline was much higher than an FCC feed of similar sulfur content [14].

The additive led to a significant reduction in gasoline sulfur (−26%) and, to a lesser extent, in LCO sulfur (−6%, Table 3). The distribution of gasoline sulfur compounds at 63% conversion is shown in Table 4. Most of the gasoline sulfur reduction

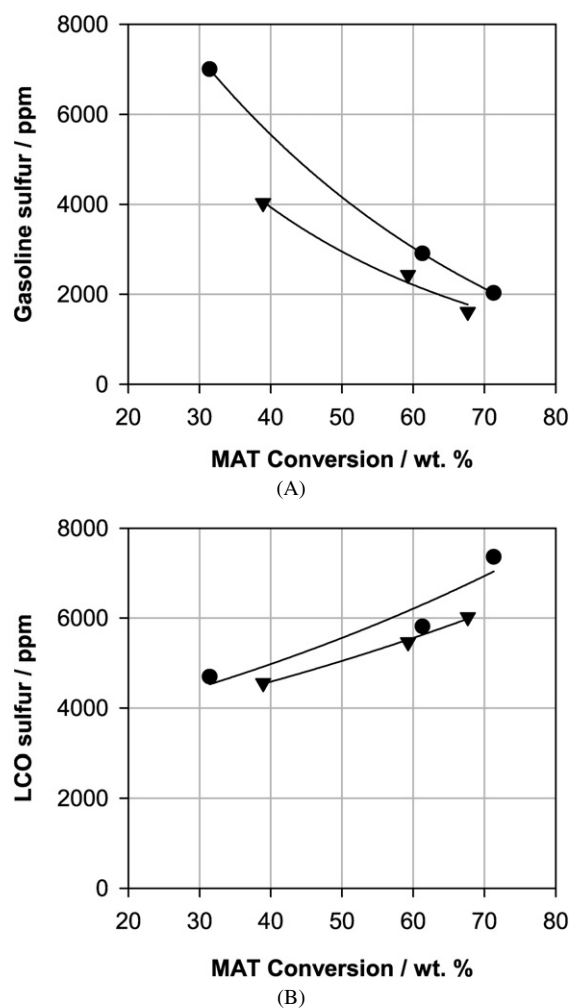


Fig. 5. Sulfur content of gasoline (A) and LCO (B) cuts versus conversion. (●) Cracking catalyst, (▼) cracking catalyst blended with Zn/Al₂O₃-C additive.

is accounted by the decreases in tetrahydrothiophene (THT), thiophene, and alkylthiophenes. In particular, the additive led to the complete elimination of THT, with much less thiophene reduction (~−15%). Conversely, benzothiophene and most LCO

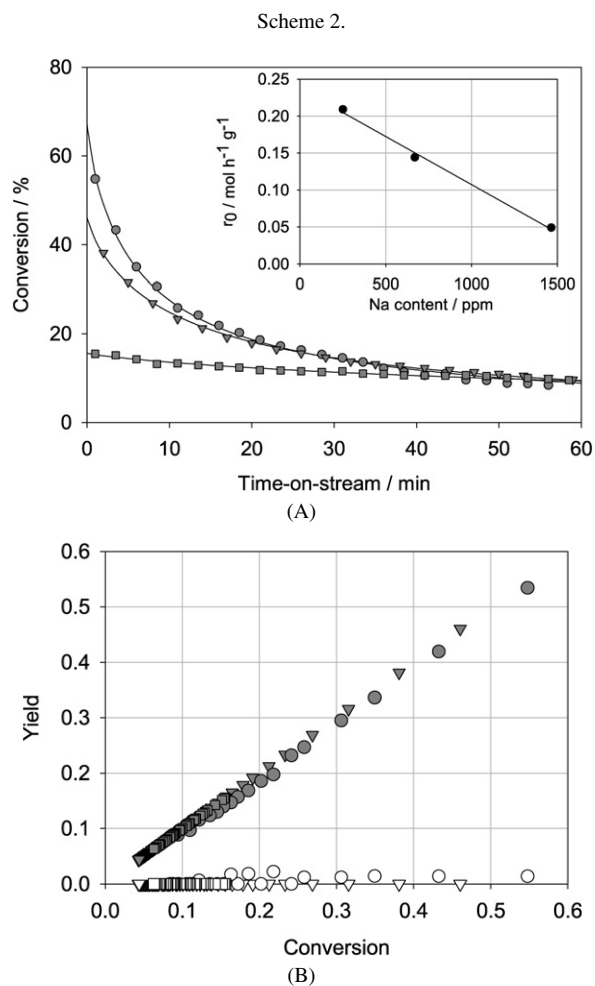
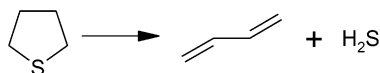


Fig. 6. Effect of Na on the conversion of THT at 723 K. (A) Conversion versus time on stream: (●) $\text{Al}_2\text{O}_3\text{-C}$, (▼) $\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$, and (■) $\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$. Inset: initial conversion rate vs Na content. (B) Selectivity plots: full symbols, cracking; open symbols, dehydrogenation.

sulfur compounds (alkylbenzothiophenes and alkylidibenzothiophenes) were hardly affected by the additive.

3.4. Thiophene and THT reactivity on alumina-based additives

The reactivity of thiophene and THT was evaluated at 723 and 823 K on pure and doped-alumina samples. The contact times (W/F) were set to 4.3 and 3.2 g h mol^{-1} for thiophene and THT, respectively. Thiophene conversions were $<1\%$. In contrast, in most of the additives, THT essentially cracked to 1,3-butadiene and H_2S according to the reaction, shown in Scheme 2.

This reaction is zero order with respect to THT. In addition, small amounts of dehydrogenation products (dihydrothiophenes and thiophene) were formed. As an example, Fig. 6A shows the evolution of the THT conversion on $\text{Al}_2\text{O}_3\text{-C}$ and $\text{Na}/\text{Al}_2\text{O}_3$ additives as a function of the time on stream

Table 5
Initial rates, conversions, cracking selectivities and deactivation constant for THT transformation

	r_0 ($\text{mol h}^{-1} \text{g}^{-1}$)	f_0 (%)	S_{crack} (%)	A ($\text{min}^{-0.85}$)
$\text{Al}_2\text{O}_3\text{-C}$	0.209	67.0	98	0.20
$\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$	0.144	46.1	100	0.12
$\text{Na}_{1465}/\text{Al}_2\text{O}_3\text{-C}$	0.049	15.6	100	0.02
$\text{F}_{0.2}/\text{Al}_2\text{O}_3\text{-C}$	0.090	28.9	94	0.21
$\text{F}_{0.4}/\text{Al}_2\text{O}_3\text{-C}$	0.059	18.9	91	0.12
$\text{F}_{1.3}/\text{Al}_2\text{O}_3\text{-C}$	0.010	3.2	100	0.01
$\text{Al}_2\text{O}_3\text{-HQ}$	0.115	36.8	96	0.16
$\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$	0.170	54.5	96	0.27
H-Y	–	50.0 ^a	35 ^a	–

^a Measured after 1 min of reaction.

at 723 K; Fig. 6B shows the corresponding selectivity plots. The other Al_2O_3 -based additives exhibited similar behaviors. As shown in Fig. 6A, the additives deactivate strongly with time on stream. To estimate the initial rates, the experimental data were fitted using the following empirical deactivation law: $r = r_0/(1 + At^{0.85})$, where A is a deactivation constant. Table 5 reports initial rates, deactivation constants, and cracking selectivities for the various additives, along with the initial rate and cracking selectivity obtained on H-Y zeolite for comparison.

As shown in Fig. 6A and Table 5, incorporation of sodium to $\text{Al}_2\text{O}_3\text{-C}$ led to a marked decrease of the initial activity, and a linear relationship existed between the initial conversion and the Na content of the three additives (inset, Fig. 6A). In any case, cracking selectivity was not affected by Na and was very high (95%) for the three additives. Similarly, the addition of fluorine to $\text{Al}_2\text{O}_3\text{-C}$ did not change the cracking selectivities but led to a very strong decrease in initial activity (Table 5), which became almost negligible for the highest fluorine content. Conversely, the addition of Zn to $\text{Al}_2\text{O}_3\text{-HQ}$ increased the initial rate by about 50%. It is noteworthy that under our conditions, Zn did not modify THT cracking selectivities, whereas a slight increase in dehydrogenation products (e.g., coke, H_2) was reported from the use of this additive in the cracking of FCC feeds [20].

To assess the affect of the degree of dehydroxylation of Al_2O_3 on catalytic activity, $\text{Al}_2\text{O}_3\text{-C}$ was activated at higher temperature (873 K vs 723 K) and then the reaction was also carried out under standard conditions (723 K). This increased activation temperature resulted in a significant increase in the initial conversion (87% vs 67%). To confirm the negative effect of hydroxylation, H_2S was added to the reactant flow (from 2 to 15 mol% H_2S). Under these conditions, added H_2S was in large excess compared with the H_2S produced by the reaction. On H_2S addition, a sharp decrease in activity occurred when up to 7 mol% of H_2S was added. The addition of more H_2S did not produce any further activity decrease.

The H-Y zeolite was also active in THT conversion, but displayed a much lower selectivity toward cracking (35%) and yielded mainly dehydrogenation products. This is in line with a previous study of THT reactivity on an equilibrium FCC catalyst [8].

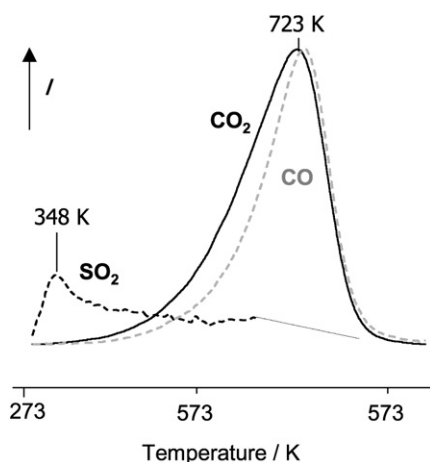


Fig. 7. Temperature-programmed oxidation of $\text{Al}_2\text{O}_3\text{-C}$ after THT decomposition at 723 K during 1 h.

Finally, examination of Table 5 shows that the deactivation constant obtained for the various Al_2O_3 -based additives increased roughly with the initial rate. This trend suggests that deactivation was due to a product. A chemical analysis of $\text{Al}_2\text{O}_3\text{-C}$ carried out after 1 h of reaction indicated a carbon content of 4.6 wt% and a much smaller amount of sulfur (<0.3 wt%).

To gain more insight into the surface species remaining after reaction (1 h time on stream), temperature-programmed oxidation (TPO) was carried out after flushing with helium at 723 K and cooling to 323 K under helium. The additives were then regenerated under a flow of pure O_2 at increasing temperatures, up to 823 K. The oxidation products were analyzed by IR spectroscopy. As shown in Fig. 7, a single peak of SO_2 occurred at low temperature (~ 348 K), whereas simultaneous production of CO and CO_2 occurred at much higher temperature (~ 723 K). This suggests that carbon and sulfur deposits belong to distinct surface species. Initial activities were fully restored after regeneration of the additives.

3.5. Operando analysis of the reaction

To gain more insight into the nature of the active sites for THT cracking, the reaction was carried out in a transmission IR-reactor cell to simultaneously obtain the IR spectra of surface species and online measurement of catalytic activity. Because of the present specifications of the IR cell, the reaction had to be carried out at lower temperature (688 K) with the same contact time of the previous section (3.2 g h mol^{-1}). Consequently, the initial conversions were significantly lower (by a factor ~ 6) than those measured in the quartz reactor. In any case, the relative activities of the additives toward THT were the same under both conditions.

3.5.1. Surface species under reaction conditions

The various additives show similar behaviors. As an example, a series of surface IR spectra recorded during the reaction of THT on $\text{Al}_2\text{O}_3\text{-C}$ is displayed in Fig. 8A, and the evolution of the conversion with the time on stream is reported in Fig. 8B. The first spectra show a perturbation of surface OH groups and

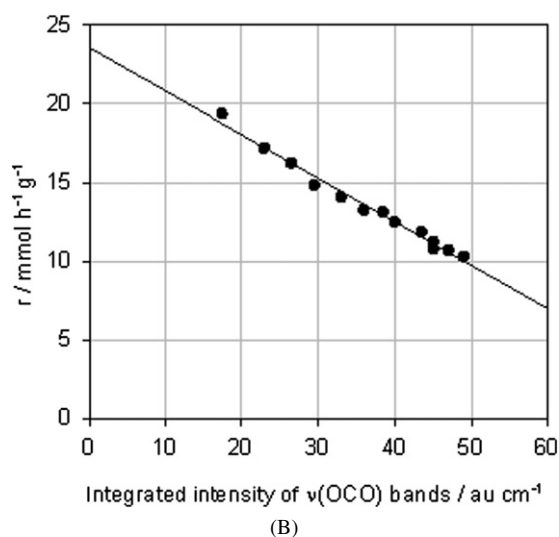
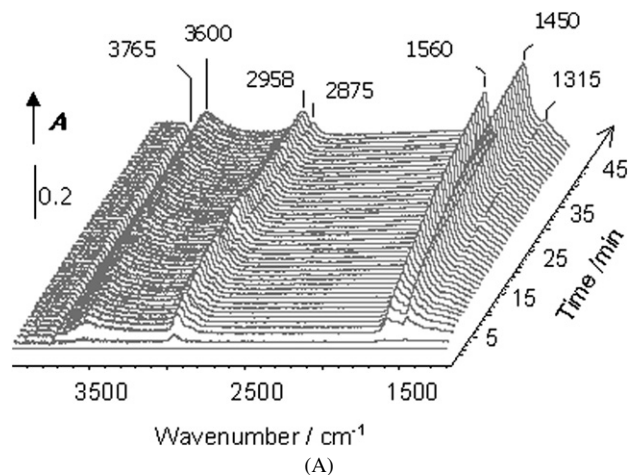


Fig. 8. (A) IR spectra recorded during THT conversion on $\text{Al}_2\text{O}_3\text{-C}$ at 688 K. (B) THT conversion versus surface area of the carboxylate $\nu(\text{OCO})$ bands.

the continuous growth of a broad $\nu(\text{OH})$ band at $\sim 3600 \text{ cm}^{-1}$. This band is located at a much higher wavenumber than the broad $\nu(\text{OH})$ band observed on THT adsorption at room temperature (3395 cm^{-1} ; Fig. 4) and assigned to the hydrogen bonding of OH groups with THT. Such a large difference indicates that under reaction conditions (688 K), H-bonding of THT with surface OH groups would be unlikely. Moreover, the continuous growth of the $\nu(\text{OH})$ band observed at 3600 cm^{-1} with the time on stream must be related to interaction of OH groups with surface species accumulating on the surface. These species gave rise to a group of $\nu(\text{CH})$ bands in the $2970\text{--}2870 \text{ cm}^{-1}$ range, two strong bands at 1565 and 1450 cm^{-1} , and a weaker band at 1315 cm^{-1} that grew continuously with the time on stream (Fig. 8A). Flushing of the catalyst with pure He at the reaction temperature decreased the $\nu(\text{CH})$ bands slightly and restored a portion of the initial OH groups. Conversely, the strong bands at 1565 and 1450 cm^{-1} (characterizing surface species in strong interaction with the catalyst) were unaffected. These bands can be assigned to either coke or carboxylate species [45]. To ascertain their assignment, similar experiments (not shown) were carried out at 873 K in static conditions on alumina and on ^{18}O -exchanged alumina. The two strong bands

were downward-shifted by 9 and 20 cm^{-1} on ^{18}O -exchanged alumina compared with on nonexchanged alumina. Such shifts allow these bands to be unambiguously assigned to asymmetric and symmetric $\nu(\text{OCO})$ stretching modes of surface carboxylate species [46].

Carboxylate species are known to be formed at high temperature on Al_2O_3 by a surface reaction involving unsaturated hydrocarbons such as ethylene [46], acetylene [45], butenes [47], or butadiene [48]. To verify whether 1,3-butadiene could be at the origin of the carboxylate species observed in the present study, the catalyst was contacted with 1,3-butadiene (150 Torr) in static conditions at high temperature (873 K) followed by evacuation at the same temperature. Similar $\nu(\text{OCO})$ bands were formed, suggesting that carboxylate species could indeed be formed by a surface reaction of 1,3-butadiene, the major product of THT cracking. This is in agreement with TPO results showing that surface carbon species contained no sulfur (Fig. 7).

Fig. 8C shows the variation of THT conversion during the reaction as a function of the surface area of the carboxylate $\nu(\text{OCO})$ bands, allowing evaluation of how carboxylate species affect catalytic activity. The linear correlation observed indicates that catalyst deactivation is likely due to the poisoning of active sites by carboxylate species.

3.5.2. Influence of Lewis acid sites

To modify the concentration of Lewis acid sites of the catalyst, various amounts of pyridine were adsorbed at 688 K before the reaction was performed. The IR spectra recorded after pyridine preadsorption (Fig. 9A) show that under such conditions, pyridine adsorbed only on the strongest LAS of alumina (ν_{8a} band at 1624 cm^{-1}). The amount of LAS poisoned by pyridine adsorption can be determined from the area of the ν_{19b} band (1452 cm^{-1}). The variation of the conversion in THT decomposition versus the amount of preadsorbed pyridine (Fig. 9B) shows that decreasing the concentration of strong LAS had a direct affect on catalytic activity.

4. Discussion

4.1. Role of gasoline sulfur reduction additives in sulfur elimination

The SCT-MATs carried out on model feeds demonstrated that the $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$ additive did not significantly affect conversion but slightly increased yields of coke, hydrogen, and aromatics (Table 3). This finding is in agreement with previous studies carried out on FCC feeds using similar gasoline sulfur reduction additives [5,14,20–22]. In the present case, however, the amount of gasoline sulfur was significantly higher than that obtained from FCC feeds of similar sulfur content. This is accounted for by the nature of the model sulfur molecule (3-hexylthiophene), converted mainly into thiophene and light alkylthiophenes belonging to the gasoline cut [8,9]. It is noteworthy that in the absence of the additive, the amount of THT formed in the gasoline cut was much higher than that usually observed for FCC feeds. In the presence of the additive,

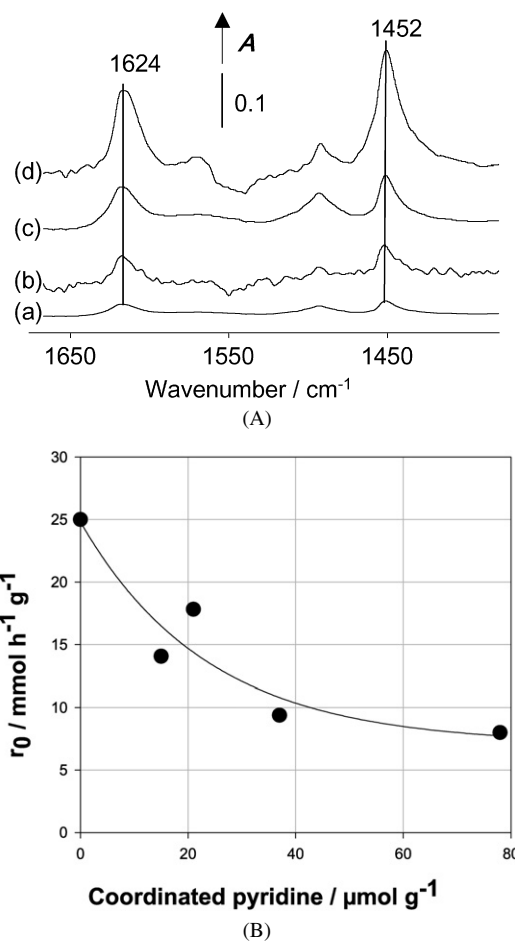


Fig. 9. Lewis acid sites poisoning by pyridine in operando condition at 688 K. (A) IR spectra recorded after pyridine preadsorption (a) 15 $\mu\text{mol/g}$, (b) 22 $\mu\text{mol/g}$, (c) 37 $\mu\text{mol/g}$, and (d) 78 $\mu\text{mol/g}$. (B) Initial conversion rate of versus the amount coordinated pyridine.

however, almost complete removal of THT occurred (Table 4). This contradicts the recent proposal of Andersson et al. [20] and Myrstad et al. [23], who linked gasoline sulfur reduction to improved hydrogen transfer to thiophenic species; in such a case, the amount of THT should be higher in the presence of the additive (Scheme 1). The relatively large amount of THT in the absence of additive demonstrates that under our conditions, the limiting factor for gasoline sulfur removal by the cracking catalyst (USY) was not the hydrogen transfer to thiophenic species, but rather the cracking of THT itself. Continuous-flow experiments showed that on H-Y zeolite, THT mainly undergoes dehydrogenation reactions leading to thiophene (65%) and, to a lesser extent, cracking reactions leading to H_2S and hydrocarbons (35%, Table 5). Similar selectivities have been reported by Leflaive et al. [8] for an equilibrium FCC catalyst. Conversely, the most active Al_2O_3 -based additives ($\text{Al}_2\text{O}_3\text{-C}$ and $\text{Zn}/\text{Al}_2\text{O}_3\text{-HQ}$) led to THT conversions of the same order of magnitude as obtained with H-Y zeolite, but were much more selective for THT cracking (>97%). Moreover, Al_2O_3 -based additives showed very low activity toward thiophene compared with THT, indicating that direct desulfurization of thiophenic species by such additives (as recently proposed by Shan et al. [21] and Vargas-Tah et al. [24]) was unlikely.

Consequently, we conclude that the key role of Al_2O_3 -based gasoline sulfur reduction additives is to selectively enhance the rate of THT cracking to butadiene and H_2S , thus preventing its conversion to thiophene by dehydrogenation reactions. Such a mechanism, initially proposed by Harding et al. [9], clearly explains the complete removal of THT as well as the significant decrease in (alkyl-)thiophene species when the gasoline sulfur reduction additive is blended to the cracking catalyst (Table 4).

In the case of real FCC feeds, the affect of process parameters on sulfur elimination has been examined previously [14]. They have been found to affect sulfur reduction as well as the main yields and product quality. Thus, improving hydrogen transfer by using RE-USY catalysts lowers the gasoline sulfur level, but also decreases olefins and the octane number [14], limiting the use of such high-hydrogen catalysts for sulfur reduction. In contrast, gasoline sulfur reduction additives do not significantly modify yields and product quality, and they improve sulfur reduction, even with RE-USY catalysts. Overall, gasoline sulfur reduction additives lead to increased hydrogen transfer to thiophenic species by preventing THT dehydrogenation. In contrast with RE-USY, this hydrogen transfer improvement is selective for thiophenic species.

4.2. Active sites for THT cracking by gasoline sulfur reduction additives

4.2.1. Acid sites

The facts that THT adsorption occurred preferentially on LAS (Fig. 4) and that selective poisoning of the strongest LAS significantly decreased the activity (Fig. 9) indicate that these sites play key roles in THT cracking. Because the doping of Al_2O_3 by sodium, zinc or fluorine changes the number and strength of Lewis acid sites, significant variations in the activities of doped Al_2O_3 can be expected. Fig. 10 shows the initial THT conversion versus the concentration of strong Lewis acid sites measured by pyridine (Table 2). The linear correlation obtained for the Na/ Al_2O_3 -C and Zn/ Al_2O_3 -HQ series of additives suggests that their activity is governed mainly by the variations in the amount of strong Lewis acid sites (Fig. 10A). No correlation between the activity of these additives and the amount of weak or (weak + strong) Lewis acid sites can be observed. The surface densities of the strong LAS of bare aluminas (Al_2O_3 -C and Al_2O_3 -HQ) are close (1.4 and $1.5 \mu\text{mol m}^{-2}$, respectively), indicating that variation in their initial activity is related mainly to the difference in their surface areas (Table 1).

Conversely, Na doping did not significantly change surface area, but did induce a significant decrease in both Lewis acidity and THT cracking activity. Sodium is a known poison of alumina for many reactions, including alcohol dehydration [32,49,50], olefin isomerization [49], cumene cracking [51], and catalytic oxidation [52]. The adverse effect of sodium on gasoline sulfur reduction additives in FCC also has been reported recently [19]. This effect is generally explained as a decrease in the number and strength of Lewis acid sites on sodium addition [32,53,54]. In agreement with the findings of Saad et al. [32], our results indicate that the amount of poisoned Lewis acid sites on alumina was significantly higher than the amount

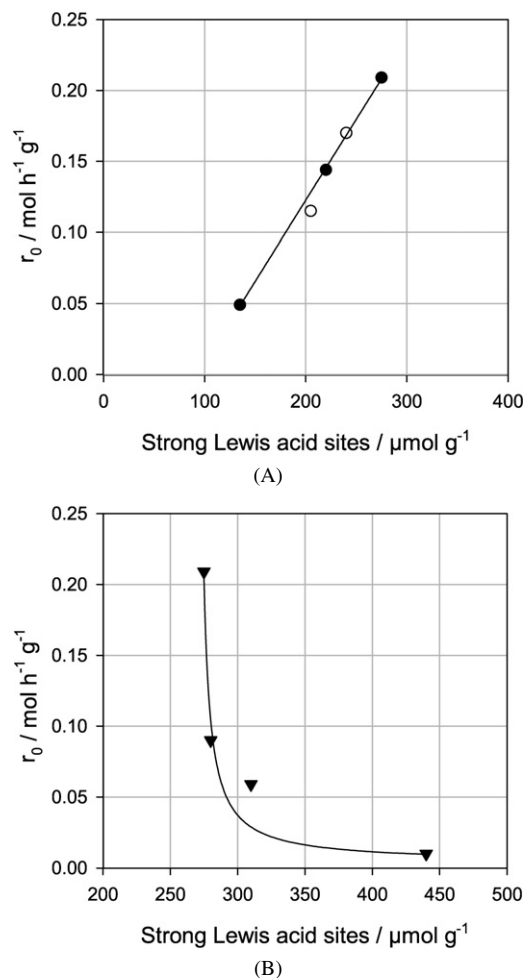


Fig. 10. Initial THT conversion rate versus the concentration of strong Lewis acid sites of alumina-based additives as measured by pyridine adsorption. (A) Na-doped (○) and Zn-doped (●) additive. (B) F-doped additives (▼).

of added Na^+ cations (Table 2). This can be explained by inductive effects from Na^+ ions localized on surface cation vacancies [32,54].

The addition of Zn to Al_2O_3 led to opposite effects, because both the amount of strong LAS and the initial activity were increased. The nature of LAS on Zn/ Al_2O_3 -HQ did not differ significantly from those of the parent alumina, because coordinated pyridine species gave rise to similar IR spectra with ν_{8a} bands at 1618 and 1624 cm^{-1} . The expected ν_{8a} frequency for pyridine coordination on Zn^{2+} was at $\sim 1605 \text{ cm}^{-1}$, as reported for pyridine adsorption on pure ZnO [36]. This indicates that the LAS of Zn/ Al_2O_3 -HQ consisted mainly of coordinatively unsaturated Al^{3+} ions, in agreement with previous studies carried out on similar materials [24,55,56]. It is noteworthy that on an atomic basis, the effect of Zn was somewhat limited, because the creation of one strong LAS required the addition of about 50 Zn^{2+} ions. This implies that an important fraction of the Zn probably was not located on the surface, but was engaged in the formation of ZnAl_2O_4 , as detected by XRD. Whereas in $\gamma\text{-Al}_2\text{O}_3$, Al^{3+} cations are distributed over both types of sites [57], in the normal spinel structure of ZnAl_2O_4 , Zn and Al occupy octahedral and tetrahedral sites, respectively [58].

This can explain why ZnAl_2O_4 formation increases the amount of strong LAS (ν_{8a} at 1624 cm^{-1} , tetrahedral Al sites [34]) at the expense of weaker LAS (ν_{8a} at 1618 cm^{-1} , involving octahedral Al sites [34]).

The behavior of F-doped additives differed from that of Na- or Zn-doped aluminas. Fluorine increased the amount of strong LAS but decreased the initial activities in THT cracking (Fig. 10B). This increased Lewis acidity on fluorine incorporation is in agreement with previous findings [59–61]. It is generally believed that at low loadings, F^- ions substitute μ_1 -OH groups, as indicated by the significant decrease in $\nu(\text{OH})$ bands at 3790 and 3770 cm^{-1} (Fig. 1C). The increase in strong Lewis acid sites is usually associated with the higher electronegativity of the F^- ion compared with the OH^- ion, leading to a strengthening of vicinal Lewis acid sites. It should be noted that increased Brønsted acidity on fluorinated aluminas has been reported previously [60,61], but was not observed in the present work; however, in those studies the fluorine content was significantly higher than that used in the present work (0.2–1.3 wt%).

In view of the correlation established between Lewis acidity and THT cracking activity for Na- and Zn-doped aluminas (Fig. 10A), the low activity of $\text{F}/\text{Al}_2\text{O}_3\text{-C}$ samples is surprising, especially because F is a known promoter of Lewis acid-catalyzed reactions [62]. This clearly indicates that Lewis acidity alone does not account for THT cracking on Al_2O_3 -based additives.

4.2.2. Basic sites

The introduction of fluorine dramatically decreases the amount of basic OH groups and basic oxygen centers, as indicated by the low amount of hydrogen carbonate and carbonate species formed on CO_2 adsorption, respectively (Fig. 3; Table 2). To the best of our knowledge, no previous study has reported the influence of fluorine on the basic properties of Al_2O_3 . The formation of hydrogen carbonate species is known to involve mainly μ_1 -OH groups [36]. The significant decrease in hydrogen carbonate species thus can be accounted for by the progressive substitution of μ_1 -OH groups by F^- ions reported above (Fig. 1C). Conversely, the decrease in carbonate species cannot be explained by a substitution of basic oxygen ions by F^- ions, which is observed only at fluorine contents greater than those used in the present work ($>3\text{ wt}\%$) [63]. On the other hand, the electron-withdrawing inductive ($-I$) effect of F^- should lead to a weakening of the basicity of vicinal surface oxygen ions, explaining the significantly decreased carbonate species formation.

Fig. 11 shows the relationship between the initial activities of $\text{F}/\text{Al}_2\text{O}_3\text{-C}$ additives in THT cracking and the amount of surface basic oxygen centers estimated from the integrated intensity of $\nu(\text{CO})$ bands of carbonate and hydrogen carbonate species formed by CO_2 adsorption (Table 2). This linear correlation is a strong indication of the involvement of basic centers (surface O^{2-} anions or μ_1 -OH groups) on $\text{F}/\text{Al}_2\text{O}_3\text{-C}$ additives in THT cracking.

On $\text{Na}/\text{Al}_2\text{O}_3\text{-C}$ additives, the amount of carbonate and hydrogen carbonate species decreased for the $\text{Na}_{670}/\text{Al}_2\text{O}_3\text{-C}$

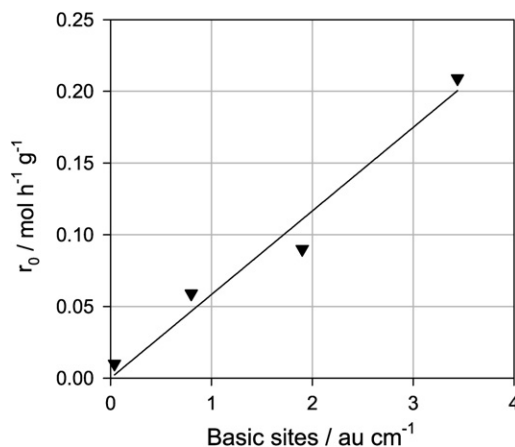


Fig. 11. Influence of the number of basic surface oxygen centers (evaluated from the total area of carbonate and hydrogen carbonate IR bands) of F-doped aluminas on initial THT conversion rate.

sample but increased for the $\text{Na}_{1650}/\text{Al}_2\text{O}_3\text{-C}$ sample (Table 2). This finding agrees with a previous study [31] and has been linked to the migration of part of Na^+ ions into the bulk of Al_2O_3 at low sodium content ($<1000\text{ ppm}$), leading to a decrease in negatively charged surface basic centers [31]. At higher sodium content, basicity increased further when Na^+ migration to the bulk no longer occurred [31].

The addition of Zn to Al_2O_3 led to the formation of peculiar bidentate carbonate species by CO_2 adsorption, characterized by two sharp $\nu(\text{CO}_2)$ bands at 1624 and 1455 cm^{-1} (Fig. 3C). Overall, however, decreased amounts of carbonate and hydrogen carbonate species formed on CO_2 adsorption were observed (Table 2). Thus, the relationship between initial activity and surface basicity observed for the $\text{F}/\text{Al}_2\text{O}_3\text{-C}$ series of additives (Fig. 11) does not hold for Na- and Zn-doped additives, and it appears that both Lewis acid and basic properties account for the THT cracking activity of Al_2O_3 -based additives.

Further insight into the nature of the active sites for THT cracking is provided by the IR spectra recorded under reaction conditions showing that catalyst deactivation is due to the formation of carboxylate species (Fig. 8). In agreement with a previous study, we found that such species can be formed by a secondary surface reaction involving 1,3-butadiene, the major product of THT cracking. These findings are consistent with the fact that faster deactivation was observed for the most active additives (Table 3). Although detailed mechanisms have been proposed for the formation of carboxylate species on Al_2O_3 from alcohols or aldehydes [64], much less is known about their formation from olefins. They could be formed by a reaction involving allylic complexes formed on (Al^{3+} , O^{2-}) pairs [47] and basic μ_1 -OH groups [45]. In any case, the formation of carboxylate species from butadiene leads to the consumption of surface oxygen centers in the form of O^{2-} ions or basic OH groups. The linear decrease in catalytic activity with the amount of carboxylate species formed during the reaction (Fig. 8) thus provides another indication of the involvement of basic centers in the cracking of THT by Al_2O_3 -based additives.

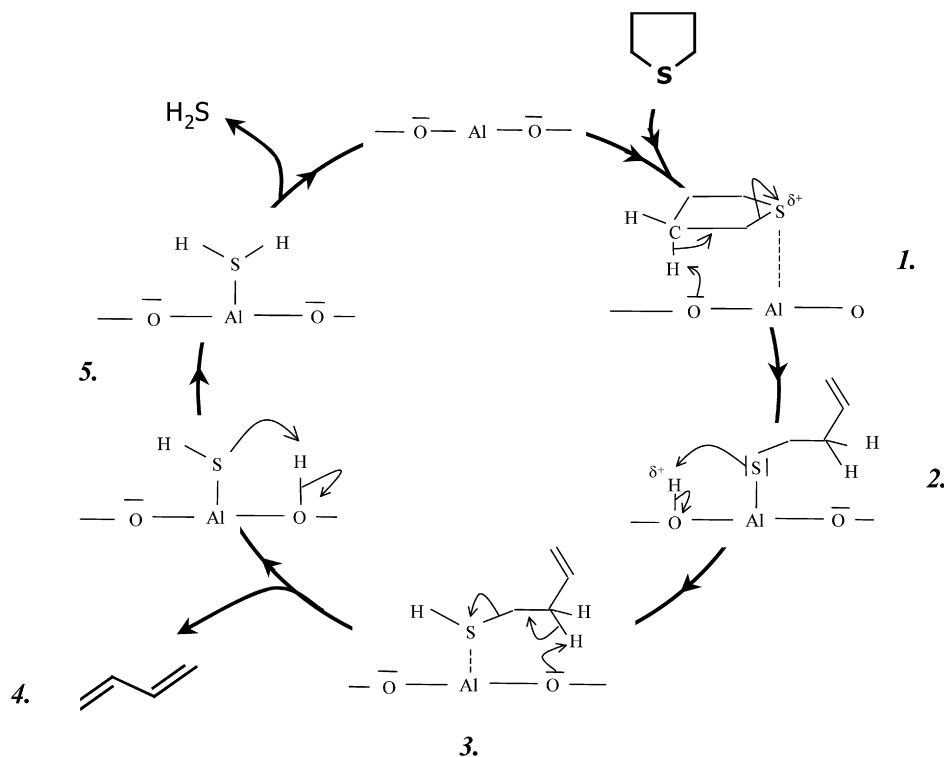


Fig. 12. Mechanism for tetrahydrothiophene decomposition on alumina-based additives.

4.2.3. Mechanism of THT cracking by Al_2O_3 -based gasoline sulfur reduction additives

THT cracking presents strong similarities with the dehydration of alcohols on alumina in olefins and water. In particular, both reactions require acid and basic centers and show comparable sensitivities toward sodium [32,49,50]. It is generally believed that alcohol dehydration on Al_2O_3 follows a E2-type elimination mechanism involving Lewis acid–base pairs [65–69]. Accordingly, we propose the reaction mechanism depicted in Fig. 12, in which the basic sites (O) may be the oxygen atoms of the μ_1 -OH group or O^{2-} anions and the acid sites (Al) are coordinatively unsaturated tetrahedral Al^{3+} sites. The coordination of THT to a strong Lewis acid site is expected to polarize the C–S bond, making possible the concerted proton abstraction in β -position by a vicinal basic site and the C–S bond cleavage, leading to a surface thiolate (step 1). The formation of butadiene requires recombination of thiolate with a proton (step 2) into a thiol, which in turn undergoes a second E2 elimination (step 3). The intermediate thiol (but-3-ene-1-thiol), which is less stable and presumably more reactive than THT, is not observed in the gas phase. Finally, H_2S is formed by recombination of the surface –SH groups with a proton (step 4). Both butadiene and H_2S may further react with the surface, leading to both carboxylate species and surface –SH groups. The formation of such surface species is fully consistent with the TPO profiles observed after the reaction (Fig. 7).

Finally, the proposed mechanism accounts for the high sensitivity of THT cracking toward modification of surface acid–base properties. In particular, it demonstrates that balanced acid–base pairs are required for optimum activity.

5. Conclusion

This contribution reports a study of acid–base properties and activities of Zn-, Na-, and F-doped Al_2O_3 on the desulfurization of model sulfur compounds. All three additives are inactive in thiophene conversion by themselves but selectively crack tetrahydrothiophene (THT) into H_2S and butadiene in the following order of activity: $\text{Zn}/\text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{Na}/\text{Al}_2\text{O}_3 > \text{F}/\text{Al}_2\text{O}_3$. In contrast, when blended with a FCC catalyst, the $\text{Zn}/\text{Al}_2\text{O}_3$ additive catalyzes a significant conversion of both THT and (alkyl)thiophene, leading to a significant decrease in their content in the gasoline fraction. This illustrates that Al_2O_3 -based gasoline sulfur reduction additives reduce thiophenic compounds by an efficient decomposition of THT produced by hydrogen transfer on an FCC catalyst.

THT cracking requires both Lewis acid and basic sites. The involvement of strong tetrahedral Al^{3+} sites has been demonstrated by specific poisoning using pyridine in operando conditions. A strong indication that basic sites are also involved in the reaction mechanism is the fact that deactivation originates from the formation of carboxylate species, leading to a blocking of surface oxygen centers.

The promoter effect of Zn on THT cracking has been assigned to formation of the spinel ZnAl_2O_4 favoring the formation of strong tetrahedral Al^{3+} acid sites at the expense of medium octahedral Al^{3+} acid sites. Conversely, Na leads to a significant decrease in the number of strong Lewis acid sites by inductive effects, thus explaining the lower activity of $\text{Na}/\text{Al}_2\text{O}_3$ additives. Fluorine enhances strong Lewis acid sites, but also strongly decreases surface basicity through substitution of μ_1 -OH groups and electron-withdrawal from surface O^{2-}

centers. In this case, Lewis basicity becomes the limiting factor for THT cracking.

Overall, our results demonstrate that a good balance of the acid–base properties is required for optimum activity, suggesting that THT cracking occurs on Lewis acid–base pairs through successive E2 elimination.

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