



HAL
open science

Effect of sulfidation pressure on the structure and activity of Ni(CyDTA)W/ γ -Al₂O₃ hydrodesulfurization catalysts

C.E. Santolalla-Vargas, Victor Santes, V.A. Suarez-Toriello, J.A. de Los Reyes, B. Pawelec, J.L.G. Fierro, E. Dominguez Garcia, L. Oliviero, Françoise Maugé

► To cite this version:

C.E. Santolalla-Vargas, Victor Santes, V.A. Suarez-Toriello, J.A. de Los Reyes, B. Pawelec, et al.. Effect of sulfidation pressure on the structure and activity of Ni(CyDTA)W/ γ -Al₂O₃ hydrodesulfurization catalysts. *Catalysis Today*, 2021, 10.1016/j.cattod.2020.07.015 . hal-03028377

HAL Id: hal-03028377

<https://hal.science/hal-03028377v1>

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of sulfidation pressure on the structure and activity of Ni(CyDTA)W/ γ -Al₂O₃ hydrodesulfurization catalysts

C.E. Santolalla-Vargas^{1*}, Victor Santes¹, V.A. Suarez-Toriello², J.A. de los Reyes³, B. Pawelec⁴, J.L.G. Fierro⁴, E. Dominguez Garcia⁵, L. Oliviero⁵ and F. Maugé⁵

1-Departamento de Biociencias e Ingeniería, Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIEMAD), Instituto Politécnico Nacional, C.P. 07340, Ciudad de México, México

2-CONACyT-CIATEC A.C Centro de Innovacion Aplicada en Tecnologias Competitivas, Omega 201, Industrial Delta, 37545 León, Gto. México

3-Universidad A. Metropolitana-Iztapalapa, División de Ciencias Básicas e Ingeniería, Av. San Rafael Atlixco 186, Col. Vicentina, 09340, Ciudad de México, México.

4-Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, E-28049, Madrid, Spain

5- **Université de Caen Normandie**, ENSICAEN, UNICAEN, CNRS, LCS, 14000 Caen, France

*Corresponding author at:

Departamento de Biociencias e Ingeniería, Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIEMAD), Instituto Politécnico Nacional, C.P. 07340, Ciudad de México, México

Tel: +52 5557296000 ext. 52711

Email address: csantolallav@ipn.mx (C.E. Santolalla-Vargas)

Abstract

In this paper NiW/ γ -Al₂O₃ catalysts were prepared by consecutive impregnation of a W/ γ -Al₂O₃ catalyst with an aqueous solution of nickel salt. The structural control of the nickel ion precursor in the impregnation solution was achieved by the addition of 1, 2-cyclohexanediamine-N, N, N', N'-tetraacetic acid (CyDTA) as a chelating agent at different pH. The influence of the sulfidation pressure (1 bar vs 40 bar) on the activity and structure of the NiW catalysts was investigated. The catalysts performances were tested in hydrodesulfurization (HDS) of thiophene after sulfidation at atmospheric or high pressure. The catalysts were characterized by X-Ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR) and infrared spectroscopy of adsorbed CO (IR/CO) to explain the modification in surface species composition due to the chelating agent CyDTA and sulfiding conditions.

NiW catalysts prepared in presence of CyDTA and sulfided under high pressure displayed the highest HDS activity. These two factors enhanced the sulfidation degree of W-based species as characterized by XPS. A linear correlation was found between the HDS activity and the sulfidation degree. In addition, chelating agent addition induced a decrease on metal-support interaction, as pointed out by TPR, and strongly favored the creation of CUS sites on the NiWS phase as seen by IR/CO. All these features favored a high catalytic activity. In addition, high pressure sulfidation not only leads to more active NiW catalysts but improved the butene-over-butane ratio.

1. Introduction

The development of hydrotreating catalysts is of great importance for the refinery to comply with the worldwide environmental legislations [1]. The current trend of crude oil supply provides heavy crudes containing increasingly high percentages of heteroatoms (S, N, O) that are, therefore, more difficult to process. Besides, the demand for production of clean fuels is increasing. In this sense, the environmental legislations are stricter with the sulfur (S) content in road fuels i.e. diesel and gasoline. In this sense, a decrease of S content of about < 0.05 wt% has been indicated [2]. Moreover, the S content of maritime fuel are now regulated (IMO 2020).

To satisfy the environmental requirements, the development of hydrotreatment catalysts more active is necessary. Currently, industrial catalysts are sulfided CoMo, NiMo and NiW on alumina-based support. The NiW catalysts have interesting properties in HDS specifically for hydrotreatment of heavy feeds [3]. However, NiW catalysts generally exhibit low sulfidation degree due to strong metal-support interaction which limits their activity [4, 5].

To increase the activity of NiW catalyst, the preparation has been modified at different stages. For instance, modification of the conventional Al_2O_3 support [6, 7], has been considered through the pre-impregnation of additive as F and Ga [8, 9]. Among other modifications, the addition of chelating agent has been also explored [10, 11]. In this respect, the co-impregnation of chelating agent such as nitrilotriacetic acid (NTA), citric acid, ethylenediaminetetraacetic acid (EDTA) and 1,2 cyclohexanediamine- N,N,N',N' -tetraacetic acid (CyDTA) within the metal precursor impregnation solution has shown an increase of HDS activity for sulfur molecules such as 4,6 dimethyl dibenzothiophene [12, 13] and thiophene [14]. The activity increase was related to the formation of a Ni complex with the chelating agent in the impregnation solution. These complexes increase the reduction temperature for Ni, and favor the formation of NiWS species. These features can explain the increment of activity for HDS of 4,6 dimethyl dibenzothiophene of ca. three times in comparison with the counterpart prepared without chelating agent [12, 13]. As a general manner, Zuo et al. showed on a series of NiW/ Al_2O_3 with different Ni/W ratios, that increasing the WS_2 dispersion and the amount of W^{4+} species are beneficial to provide more edge sites for the formation of the NiWS phase [15]. On Mo-based systems, Chen et al. were able to show that changing the morphology, i.e. the S-/M- edge ratio, of the sulfide slab is also a way to improve the catalytic activity. In this sense, it was shown that metal amount, citric acid addition and sulfiding conditions (T, P) can modify the sulfide slab morphology [16, 17]. Indeed, high sulfidation pressure increases the S-edge/M-edge ratio leading to more truncated MoS_2 slabs. As a result, the thiophene HDS activity significantly increases after high pressure sulfidation. These data points out that CUS sites on M-edges and on S-edges do not present the same activity. As a consequence, the sulfidation parameters such as temperature [18] and pressure modified the sulfidation degree [19], but has also an important role in the formation and structure of WS_2 phase [19, 20]. Dugulan et al. have shown that sulfidation of NiW/ Al_2O_3 under high pressure increases the crystallinity of WS_2 slabs as compared with the counterpart sulfided at low pressure [19]. In addition, van Meer et al reported for NiW/ASA that high sulfidation pressure increases the average slab length [20]. These authors also showed a marked positive effect of sulfidation pressure on the thiophene HDS activity of NiW/ASA [20].

Hence, previous works have shown that chelating agent addition and high-pressure sulfidation can lead to preparation of more active catalysts. However, in-depth understanding of the impact of these parameters on the structure of active sites is lacking.

In this work, NiW/Al₂O₃ catalysts were prepared with or without CyDTA addition at different pH of impregnation, and sulfided at different pressures (1 bar or 40 bar). The thiophene HDS activity of these catalysts was studied after sulfidation at different conditions. Furthermore, these catalysts were characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy with CO adsorption (IR/CO) to account for the role of CyDTA addition, pH and sulfidation pressure on the structure of the active phase.

2. Experimental

2.1 Synthesis of the catalysts

The W/ γ -Al₂O₃ catalyst base (W nominal loading of 20 wt.%) was prepared by incipient wetness impregnation [15] of a commercial γ -Al₂O₃ (specific surface area=245m²/g, PIE=7.0, V_p=1.1 cm³/g) with aqueous solution of ammonium metatungstate (NH₄)₆H₂W₁₂O₄₀·xH₂O (Sigma–Aldrich) at pH of 4.0. After sample drying at 393 K, the Ni was incorporated onto the W/Al₂O₃ catalyst base using appropriate amount of Ni(NO₃)₂·6H₂O (98%, Sigma-Aldrich) to obtain Ni/(Ni+W)=0.4 atomic ratio. To study the effect of chelating agent and pH conditions, two NiW/Al₂O₃ samples were prepared at different pH by addition of 1,2-cyclohexanediamine-tetraacetic acid (C₁₄H₂₂N₂O₈·H₂O (99%); CyDTA) to an aqueous solutions of the nickel nitrate (CyDTA/Ni molar ratio of 1). The pH of the Ni-CyDTA solution was adjusted with the addition of ammonium hydroxide (25% vol.) to obtain pH values of 4.0 and 8.7. After impregnation, the catalysts aged for 24 h and then all solids were dried at 393 K in air. No calcination was performed before sulfidation. The W loading was 20 wt % and 4.4 wt % for Ni. The catalysts are called NiW(x), where x is the pH value of the Ni-CyDTA solution. NiW/Al₂O₃ catalyst with a similar amount of Ni and W but without CyDTA was prepared and used as a reference. Also, W/Al₂O₃ catalyst with a similar amount of W was prepared.

Table 1: Catalysts and synthesis conditions

Catalyst	Synthesis conditions
W	Without CyDTA
NiW	Without CyDTA
NiW (4.0)	Ni/CyDTA = 1, pH=4.0
NiW (8.7)	Ni/CyDTA = 1, pH=8.7

2.2 Thiophene test

Before HDS activity measurements, the oxide catalysts were sulfided *in situ* in a fixed bed stainless steel reactor at a rate of 5 K/min up to 673 K under a flow of 10 % H₂S/H₂ (30 mL/min) at 1 bar or 40 bar for 4 h. The thiophene HDS reaction was carried out in a continuous flow reactor at 623 K and atmospheric pressure with 50 mg of sulfided catalyst. Thiophene was introduced into the reactor by passing 70 mL.min⁻¹ of H₂ flow through a thiophene saturator maintained at 291 K and mixed with a flow of 20 mL.min⁻¹ 10 % H₂S/H₂. The partial pressure of thiophene, H₂ and H₂S in the mixture are 0.08

bar, 0.912 bar and 0.021 bar, respectively. After 15 h reaction, the outlet gas was analyzed by a Varian 3900 chromatograph equipped with flame ionization (FID) detector. The concentrations of butane, 1-butene, trans-2-butene, cis-2-butene, tetrahydrothiophene (THT), as well as thiophene were recorded. The reaction rate was calculated as $r_{\text{HDS}} = (F/m) \cdot X$, where F/m is the molar flow rate of thiophene per gram of catalyst and X is the thiophene HDS conversion which was near to 10 %.

2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra of the sulfided catalysts (10 % H_2S in H_2 , 673 K, 1 or 40 bar) were measured at room temperature using a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a $\text{Mg K}\alpha$ ($h\nu=1253.6$ eV) X-ray source. The freshly sulfided catalyst (ex situ sulfidation) were deposited into small glass cylinders containing isooctane in order to avoid contact with air and mounted onto a manipulator which allowed transfer from the preparation chamber into the analysis chamber of the spectrometer. The details of the XPS measurements by this spectrometer are reported elsewhere [21]. The $\text{S}/(\text{Ni}+\text{W})$ or S/W ratios were considered to determine the sulfidation degree for the NiW and W catalysts respectively.

2.4 Temperature programmed reduction

TPR experiments were carried out in a U-shape quartz reactor. After ex situ sulfidation (under flow of 10 % $\text{H}_2\text{S}/\text{H}_2$ at 673 K, 1 bar or 40 bar) about 0.1 g catalyst (precisely weighted) was placed in the reactor and purged under nitrogen flow for 1 h at room temperature (RT). Then the gas flow was switched to hydrogen and the sample was heated at a rate 5 K/min up to 1323 K. Mass spectra of released gasses were analyzed with a quadrupole Thermo ProLab mass-spectrometer. The overall accuracy on the temperature scale is about ± 5 K.

2.5 IR spectroscopy of adsorbed CO

Due to the high absorption of IR signal by the sulfided W phase, this technique is restricted to materials with loading lower than 10 wt% of W content. Thus in the present work, the NiW catalysts (4.4 wt% Ni, 20 wt% W) have to be diluted into Al_2O_3 , an inert diluent, before transmission IR experiments. Consequently, the IR spectra of the diluted samples will show the bands of CO adsorbed on the NiW/ Al_2O_3 catalyst as well as on the alumina used as support and diluent.

The (Ni)W catalysts have been diluted into pure alumina (50 % catalyst – 50 % Al_2O_3). The mixture was very carefully crushed and pressed into a self-supporting wafer (ca. 17 mg, precisely weighted, for a disc of 2 cm^2) and put into an IR quartz cell. Before the adsorption experiments, the sample was sulfided in situ in the IR cell. The catalyst was first heated to 673 K in a gas mixture containing 10 % $\text{H}_2\text{S}/\text{H}_2$ (30 mL/min) at atmospheric pressure and using heating rate of 5 K/min. The catalyst was kept at this temperature for 4 h. After sulfidation, the cell was evacuated at 673 K for 1 h and then cooled down under vacuum. CO adsorption was performed at low temperature (~ 100 K) to avoid any reaction between CO and the catalyst surface (as $\text{Ni}(\text{CO})_4$ formation), and to favor interaction with all the surface sites. Small calibrated doses of CO were introduced in the IR cell up to an equilibrium pressure of 133.3 Pa. CO was subsequently evacuated at low temperature (~ 100 K) up to a residual pressure of 10^{-3} Pa, and finally at room temperature. All the spectra presented are normalized to a disc of 10 mg and 2 cm^2 of W-based sulfided catalyst diluted into alumina.

3. Results and discussion

3.1 Thiophene HDS

The effects of preparation conditions and sulfidation pressure on the thiophene HDS reaction rate are reported in Table 2 and Table 3. The thiophene activity was measured at low conversion and pseudo-steady state (time-on-stream of 15 h).

For the catalysts sulfided at atmospheric pressure (Table 2), the NiW catalyst prepared without CyDTA exhibited a 11-fold greater thiophene HDS activity than the W catalyst. This promotion factor is in good agreement with previous papers [15, 22]. For the NiW samples prepared with chelating agent, a significant increase of activity was observed as compared with the NiW sample prepared without. Interestingly, the activity for the NiW(4.0) sample was approximately 40 % higher than that for the NiW sample prepared without chelating agent. Changing the pH of the impregnating solution can improve the preparation but in a limited manner. Indeed, the catalyst prepared at low pH (4.0) displayed a slightly greater HDS activity than that prepared at pH = 8.7 (46 vs 43 mol/h/kg).

Comparison of Table 2 and Table 3 shows that the pressure of sulfidation markedly influences the HDS activity. Indeed, after sulfidation under 40 bar, the NiW catalysts (prepared with or without CyDTA) present an HDS activity greater by about 50% compared to the corresponding catalysts sulfided under 1 bar. Note that after sulfidation under 40 bar, the catalyst prepared at high pH (8.7) displayed only a slightly greater HDS activity than that prepared at pH = 4.0 (66.9 vs 64.5 mol/h/kg)

For all the studied catalysts, the products detected in the thiophene HDS test were: tetrahydrothiophene, 1-butene, cis-2-butene, trans-2-butene and n-butane (Table 2 and Table 3). W catalyst displayed similar concentration of tetrahydrothiophene and butenes (0.4 %). For all the Ni-promoted catalysts, the main products were trans-2-butenes, cis-2-butenes, and n-butane. The detection of tetrahydrothiophene on the W catalyst was an indication of its high hydrogenation ability as compared to the C-S bond cleavage one. In contrast, promotion by Ni improved the formation of butenes. The CyDTA incorporation hardly modified the selectivity of NiW catalysts. But high pressure sulfidation slightly enhances the ratio butene/butane.

Table 2: Reaction rate^a and product yields in thiophene HDS over (Ni)W/Al₂O₃ catalysts after sulfidation at atmospheric pressure

Catalyst	Conv. (mol.%)	Butenes (mol.%)	Butane (mol. %)	Butenes/Butane Ratio	Reaction rate (RR) at steady state (mol h ⁻¹ kg ⁻¹)	Promotion effect RR _{NiW} /RR _W
W	1.0	0.4	0.2	2.0	3.0	-
NiW	9.0	6.9	2.5	2.76	34.0	11.3
NiW (4.0)	12.0	8.6	3.1	2.77	46.0	15.3
NiW (8.7)	11.0	8.1	2.9	2.79	43.0	14.3

Table 3: Reaction rate and product yields in thiophene HDS over (Ni)W/Al₂O₃ catalysts after sulfidation under high pressure (40 bar)

Catalyst	Conv. (mol.%)	Butenes (mol.%)	Butane (mol.%)	Butenes/Butane Ratio	Reaction rate (RR) at steady state (mol h ⁻¹ kg ⁻¹)	Effect of sulfidation pressure on reaction rate RR _{40bar} /RR _{1bar}
NiW	14.0	10.2	3.4	3.00	51.5	1.51
NiW (4.0)	16.0	12.1	4.0	3.02	64.5	1.40
NiW (8.7)	17.0	12.4	4.3	2.88	66.9	1.56

3.2 X-ray photoelectron spectroscopy

In order to measure the effect of sulfidation pressure and condition of preparations on the sulfidation degree, the catalysts were characterized by XPS. The amount of different W species, and atomic ratios W/Al, Ni/Al as well S/M ratio are presented in Table 4.

Table 4 shows that the W/Al and Ni/Al stayed almost constant for all the NiW catalysts. By contrast, the amount of W⁶⁺ and W⁴⁺ species is modified by the preparation procedures and composition. Thus, after sulfidation under 1 bar H₂S/H₂, the NiW catalyst exhibits greater S/W ratio (1.97) as compared to unpromoted W (1.57) indicating that Ni addition improves the sulfide amount. Nevertheless, XPS detected amount of W⁶⁺ on all the catalysts sulfided at atmospheric pressure indicating presence of oxide or oxysulfide species. Table 4 also points out that the addition of chelating agent increases the sulfidation degree of NiW phase of about 10 % - from 1.97 to 2.15. The beneficial effect of CyDTA does not change with the pH values of the impregnating solution when sulfidation is performed at 1 bar. After sulfidation under high pressure, the NiW catalysts exhibit greater amount of W sulfide phase as well as greater sulfidation degree than the catalysts treated at low sulfidation pressure. In this regard, the S/W ratio of the NiW(8.7) catalyst increases of about ~7% when sulfidation is performed at 40 bar compared to 1 bar.

Figure 1 presents the S/(Ni+W) ratios for the various NiW catalysts. These data confirm the clear beneficial effect of high pressure sulfidation, addition of chelating agent is beneficial for sulfidation degree. It shows that increasing the pH values of Ni-CyDTA is beneficial when sulfidation is performed under high pressure.

Table 4: Amount of different W forms and atomic ratios for (Ni)W/Al₂O₃ catalysts sulfided at atmospheric and high pressure, as determined by XPS

Catalyst - Sulfidation pressure	W ⁶⁺ (%)	W ⁴⁺ (%)	W/Al	Ni/Al	S/(Ni+W)	S/W
W – 1 bar	22.0	78.0	0.069	-	-	1.57
NiW – 1 bar	40.0	60.0	0.089	0.066	1.13	1.97
NiW (4.0) - 1 bar	33.0	67.0	0.082	0.062	1.21	2.13
NiW(8.7) - 1 bar	18.0	82.0	0.079	0.063	1.19	2.15

NiW - 40 bar	16.0	84.0	0.084	0.061	1.22	2.10
NiW(4.0) – 40 bar	15.0	85.0	0.087	0.059	1.28	2.14
NiW(8.7) - 40 bar	0.0	100.0	0.085	0.065	1.32	2.34

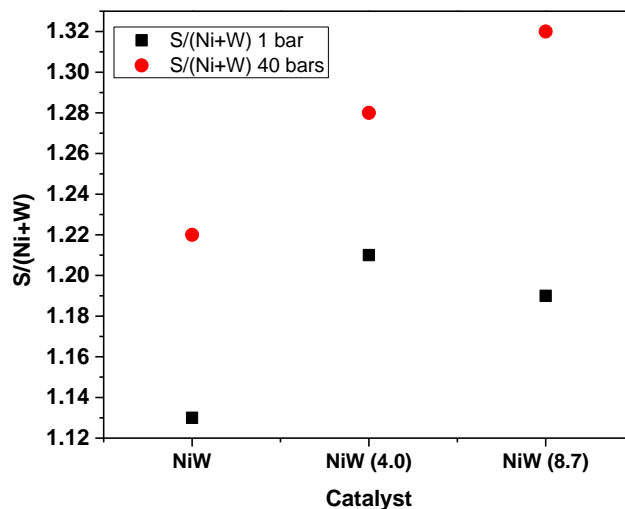


Figure 1: Effect of the sulfidation pressure on the sulfidation degree of the NiW catalysts

3.3 Temperature programmed reduction

The H_2S released during the TPR experiment on NiW and NiW(4.0) catalysts sulfided at 1 bar and 40 bar are given in Figure 2 and Figure 3. Different zones of H_2S released can be distinguished in these TPR patterns. The H_2S release at high temperature ($T > 1023$ K) corresponds to bulk WS_2 reduction. It has been used to normalize the curves and correct the temperature scale, according to ref [23]. Therefore, the area marked with a rectangle will not be discussed further. Note that the maximum intensity of this high-temperature peak does not depend on chemistry but only on the total amount of WS_2 of the studied sample [23]. Below 1000 K, three zones of H_2S release can be distinguished.

The first peak corresponds to weakly bounded sulfur. On NiW and NiW(4.0) catalysts, this H_2S release was greater and shifted towards greater temperature when sulfidation is performed under higher pressure. Indeed, on NiW sample the peak shifts from 451 K after sulfidation at 1 bar, to 481 K after sulfidation at 40 bar (Figure 2). For NiW(4.0) catalyst, the peak shifts from 497 K for low sulfidation pressure to 521 K for high sulfidation pressure (Figure 3) These two features can be related to a greater sulfur coverage of the WS_2 edges after sulfidation under high pressure as well as to better crystallized edges, i.e. more “rigid”, with more stable S-M bonds. Such phenomenon has already been reported for MoS_2 catalysts sulfided at different temperatures [24]. An increase of sulfidation pressure should lead to the same effect as an increase of temperature, since in both cases the chemical potential of sulfur is increased. The

temperatures of the 1st peak show that the CyDTA addition also leads to more rigid WS₂ edges.

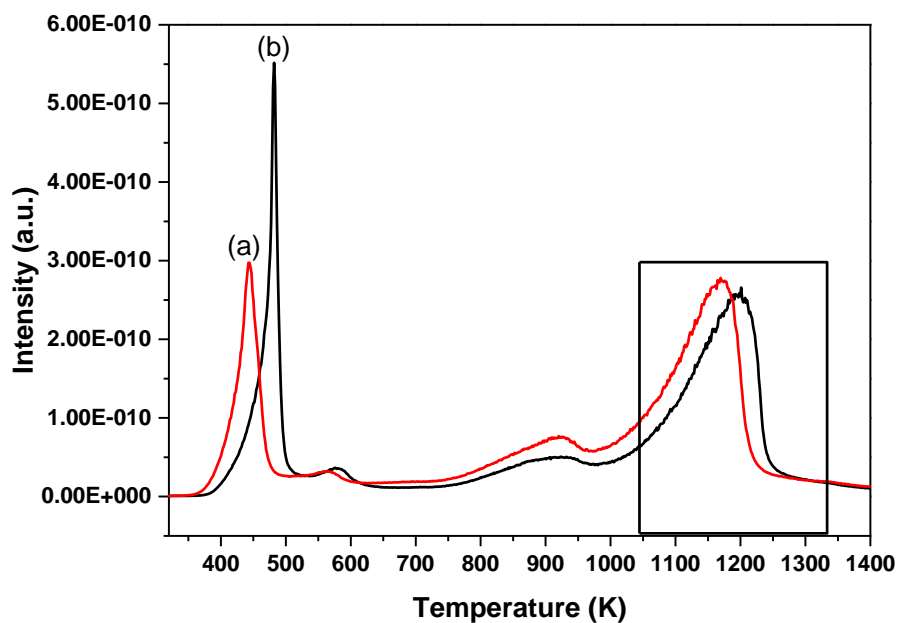


Figure 2: H₂S release during TPR experiments for NiW catalyst sulfided under 1 bar (a) and 40 bar (b)

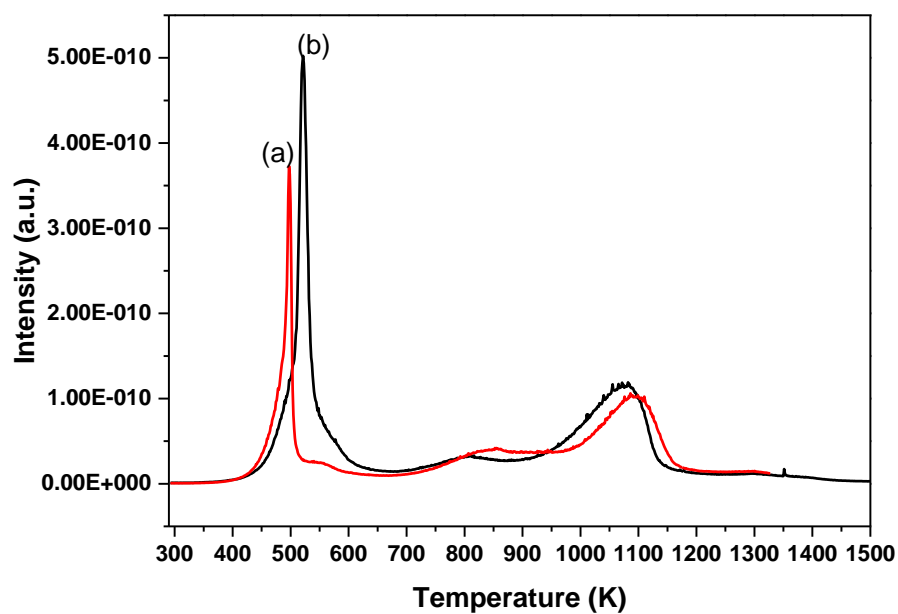


Figure 3: H₂S release during TPR experiments for NiW(4.0) catalyst sulfided under 1 bar (a) and 40 bar (b)

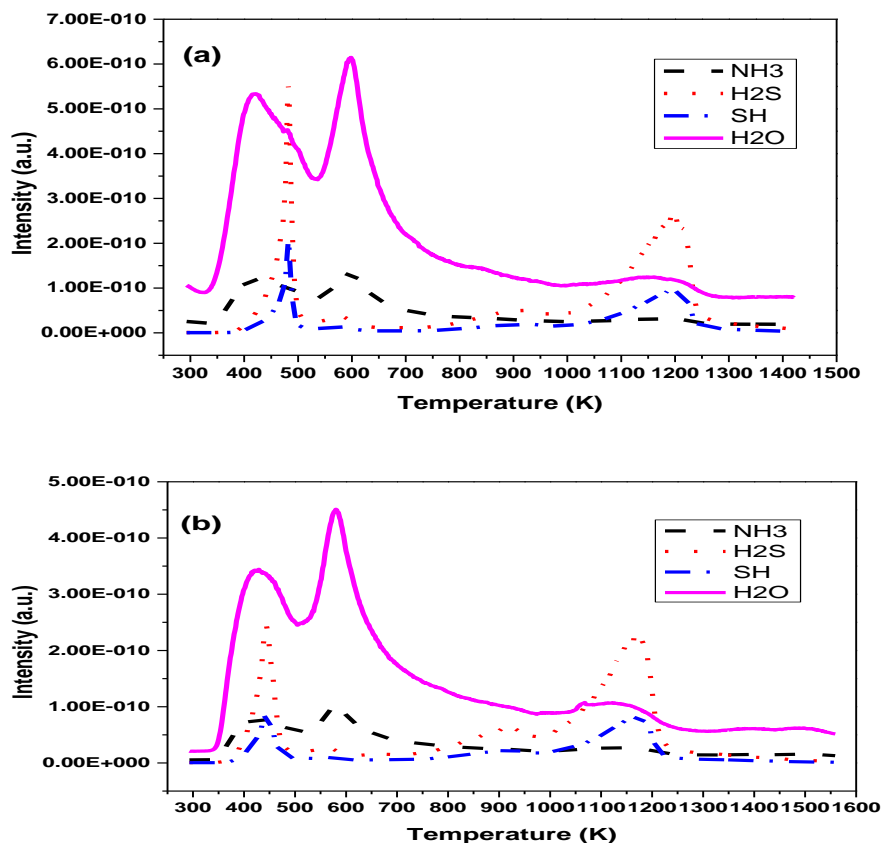


Figure 4: MS patterns of the products released during the TPR experiments for NiW catalyst sulfided: under (a) 40 bar, (b) 1 bar

On both NiW catalysts, a small peak is observed at about 580 K that is not usually encountered in the TPR patterns of sulfided catalysts. To unravel its nature, the MS patterns of all the effluents have been examined during the TPR experiments on NiW catalyst. Figure 3 shows that the position of the H₂S release peak ~578 K is close to the maximum of the second peak of water release at 593 K. The first broad water release peak (380-450 K) corresponds to the catalyst dehydration, the second water release peak (520-673 K) can be due to a reduction process. It indicates that some oxide and oxysulfide species that were present in the NiW catalysts prepared with and without chelating agent, were reduced in this temperature range. This is in agreement with the detection of oxy(sulfide) W species by XPS.

A third H₂S peak is detected between 823 K and 973 K on the NiW catalysts. Literature assigned this H₂S release to the reduction of nickel –containing sulfide species. Zuo et al. [15] suggested that this peak is directly related to the presence of NiWS species. However, this peak can also arise from a separate NiS_x phase. First, it can be noted that on both NiW and NiW(4.0) catalysts, the intensity of this peak is slightly greater when the sulfidation is performed under 1 bar than under 40 bar. Second, it appears that this peak presents a greater intensity for NiW catalyst than for the one prepared with CyDTA. Considering only these results, it cannot be decided whether the H₂S release comes from the NiS_x or NiWS phases.

In addition, TPR patterns of NiW catalyst showed a maximum of this peak at 925 K and 915 K for sulfidation at 1 bar and 40 bar, while TPR patterns of NiW with chelating

agent exhibited peaks at 850 K and 800 K for sulfidation at 1 bar and 40 bar. First, as a general manner, the high temperature of the peak 3 is related to the formation of sulfide species which are extremely difficult to reduce, indicating strong metal-support interactions [4, 5]. Second, it is shown that high pressure sulfidation decreases the strength of the metal-support interactions. This effect of high pressure sulfidation has already been reported for other sulfided systems [25]. Third, it appears that addition of CyDTA also decreases the strength of the metal-support interactions. In this regard, Scheffer et al. [26] suggested that the higher activity of CoMoS phase is attributed to the weaker active phase-support interaction. In the same way Chen et al showed that addition of chelating agent as citric acid limits the metal support interaction and leads to the formation of more active M and CoMo catalysts [17, 27]. Consequently, the catalyst NiW with chelating agent could forms NiWS species more active than NiW.

Note at last that the high-temperature reduction peak was accompanied with additional water release (Figure 3). That indicated that the sulfidation was not complete in both catalysts. This is in agreement with XPS data that pointed out some hardly reducible W oxide remaining in the NiW and NiW(4.0) catalysts.

3.4 IR spectroscopy of adsorbed CO probe

Infrared spectroscopy of adsorbed CO provides interesting information for investigation of the surface species of sulfide catalysts like the NiW ones. In particular, IR signal of CO (IR/CO) allows discriminating unpromoted W phase from NiWS one [15, 28, 29]

Figure 5 to Figure 7 show the IR spectra of CO adsorbed on sulfided W, NiW and NiW(4.0), respectively. Bands at 2197, 2188, 2160, 2119, 2064 and 2050 (sh) cm^{-1} are observed on W catalyst (Figure 5). Their intensity increases with the amount of CO introduced. From previous studies [15], these bands can be attributed to coordination of CO on Lewis acid sites of the alumina support (2197 and 2188 cm^{-1}), CO in hydrogen bonding with the support hydroxyl groups (2160 cm^{-1}) and to CO in interaction with the edges of the WS_2 crystallites (2119, 2064 and 2050(sh) cm^{-1}). Previous works already reported [15, 30, 31] these two main bands at 2119 and 2064 cm^{-1} characterized WS_2 edge sites. Note that their frequencies can be shifted according to the support nature [15, 30, 31]. Recent parallel between IR/CO spectroscopy and DFT calculations allow assigning these two bands to CO adsorbed on M- and S-edge sites of the WS_2 slab, respectively [28]. It should be mentioned that, on Mo sulfided catalysts, IR/CO spectroscopy also allows to distinguish Mo sites located on M-edge from Mo sites located on S-edge [17].

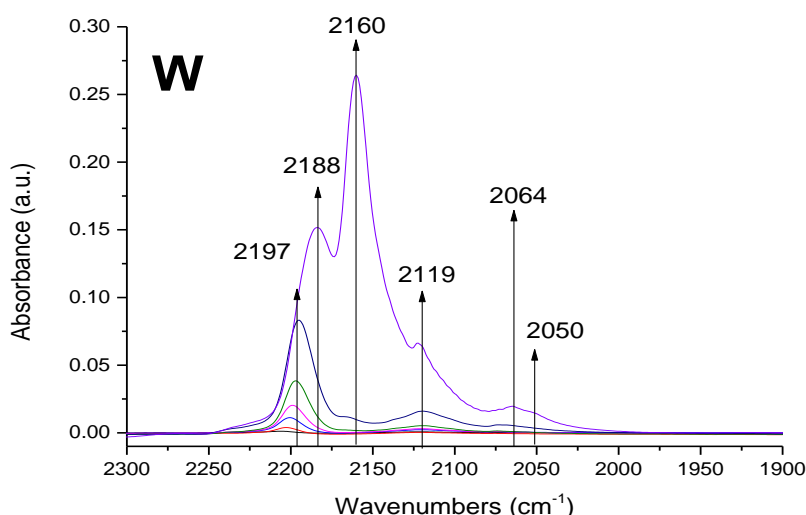


Figure 5: IR spectra of increasing doses of CO adsorbed on sulfided W catalyst ((from 5 to 129 μmol of CO per g of sulfided catalyst and further 133 Pa CO at equilibrium).

In the case of NiW catalysts, NiS_x , WS_2 and NiWS [32] phases can coexist which makes the assignment of CO adsorption bands more complicated. The IR spectra of CO adsorbed on sulfided NiW catalyst are shown in Figure 6. From these IR spectra, it is observed that the addition of Ni to W brings three new bands at 2127, 2093 and 2079 cm^{-1} . These wavenumbers are very close to those reported by Duchet et al. [31], Zuo et al. [15], Travert et al. [33] and more recently by Zavala-Sanchez[28, 29]. These authors proposed that these three bands characterize interaction between Ni and W but with different environments. Zuo et al. [15] proposed that 2127 and 2079 cm^{-1} characterized NiWS sites whereas 2094 cm^{-1} would characterize Ni particles perturbed by WS_x phase. Zavala-Sanchez et al[28, 29] + new ref refined these assignments. Hence, by considering the experimental work of Dominguez [17] on NiMo with accurate variation of the promotion degree of the catalysts as well as the DFT calculation of CO adsorbed on NiMo [33], it is proposed that 2094 and 2078 cm^{-1} characterize WS_2 edges partially promoted by Ni whereas the 2129 cm^{-1} band would characterize WS_2 edges completely promoted by Ni. It should be mentioned that the IR spectra of CO recorded on the sulfided NiW does not exhibit any clear band at 2119 cm^{-1} corresponding to unpromoted W sites on M-edge. It suggested that, on the NiW sample, the promoter Ni covers all the M-edge sites of WS_2 slabs. For the band at ~ 2060 cm^{-1} that characterizes unpromoted S-edge sites, it is difficult to draw any clear conclusion due to the broadness of the present bands.

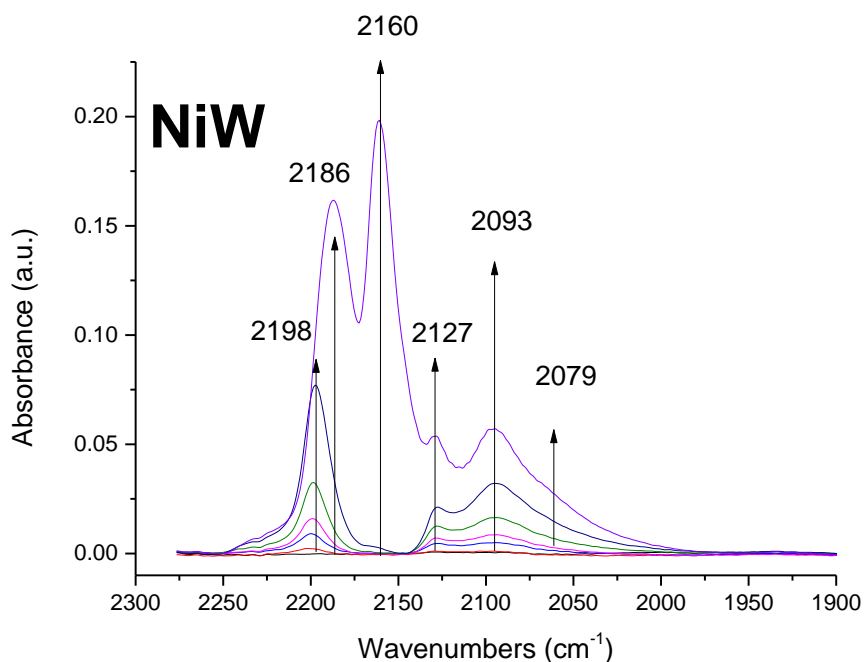


Figure 6: IR spectra of CO adsorbed at 100 K on sulfided NiW with increasing doses (from 5 to 134 μmol of CO per g of sulfided catalyst and further 133 Pa CO at equilibrium).

The IR spectra of CO adsorbed recorded on the sulfided NiW(4.0) (Figure 7) showed bands at wavenumbers close to those observed on NiW catalyst (Figure 6). Nevertheless, all the bands characterizing CO on the sulfided phase are shifted toward higher wavenumber (+3-5 cm^{-1}) on catalyst prepared with CyDTA. Note that the shoulder at about 2084 cm^{-1} , that is detected from the first doses of CO, appears much more markedly on NiW(4.0) than on NiW catalyst (Figure 7). In addition, Figure 8 shows that the intensity ratio between the bands at $\sim 2093 \text{ cm}^{-1}$ and $\sim 2127 \text{ cm}^{-1}$ is stronger on NiW(0.4) than on NiW catalysts. However the most striking feature is the greater intensity (almost 3 times) of the CO uptake on NiW(4.0) than on NiW catalyst. This points out the formation of more NiWS sites by CyDTA addition (Figure 8).

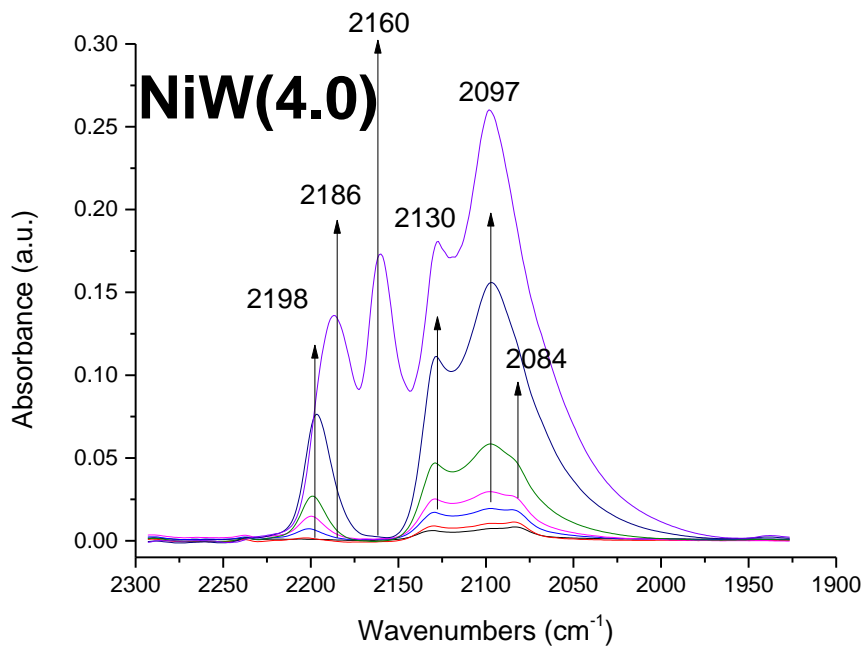


Figure 7: IR spectra of CO adsorbed on sulfided NiW(4.0) with increasing (from 5.7 to 134 μmol of CO per g of sulfided catalyst and further 133 Pa CO at equilibrium).

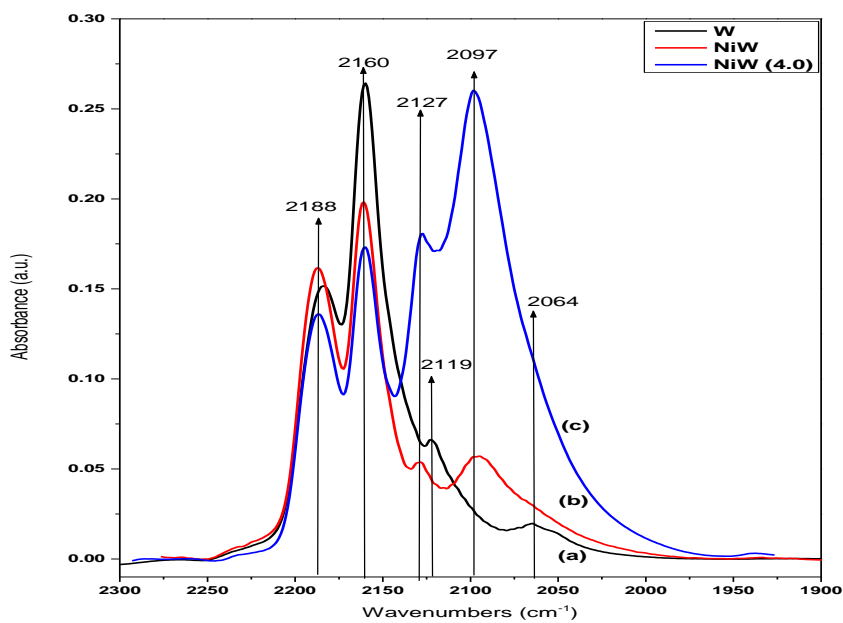


Figure 8: Comparison of IR spectra of 133 Pa of CO adsorbed on sulfided W (a), NiW (b) and NiW(4.0) (c) catalysts.

4. Discussion

The NiW catalyst prepared with chelating agent displayed higher thiophene HDS activity than the reference NiW catalyst without CyDTA. After high pressure sulfidation, the various NiW catalysts present greater activity compared to their counterparts sulfided at atmospheric pressure. These modifications in the preparation stages of NiW catalysts also induce some changes in the selectivity since some improvements of the butene-over-butane ratio can be obtained after high pressure sulfidation. Note that the Ni-promotion of the W catalyst, not only strongly increases the HDS activity but also enhances butene-to-butane ratio. In order to understand the origin of these catalytic changes, the compositions and structures of the sulfide particles were studied.

Figure 9 compares the HDS activity and the sulfiding degree, as determined by XPS, measured on the catalysts after low and high sulfidation pressure. After sulfidation under 1 bar, the most active catalyst (NiW(4.0)) shows the highest S/(Ni+W) ratio (1.21). After high sulfidation pressure, the NiW(8.7) presents the highest sulfidation degree (2.34) as well as is the greatest HDS activity. Figure 9 points out the appearance of a linear correlation between the HDS activity and the S/(Ni+W) ratio for the NiW catalyst sulfided under 1 and 40 bar. Similar trends were previously reported for dibenzothiophene HDS on CoMo/Al₂O₃ sulfided at 673 K and 4 MPa compared to the samples sulfided at 673 K and atmospheric pressure [34]. As a first conclusion, sulfidation degree is indeed a key parameter to obtain high activity of NiW-based catalyst. However, the structure of the sulfide phase has also to be considered.

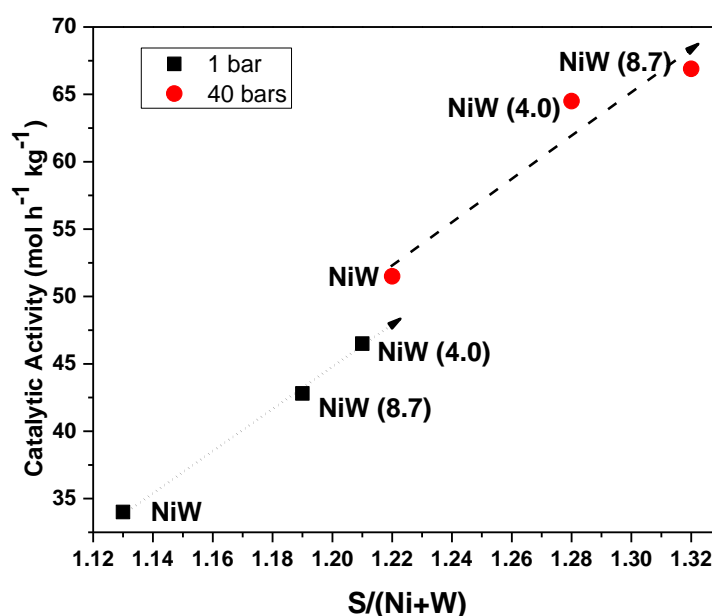


Figure 9: Relation between catalytic activity and sulfidation degree of the NiW catalysts

The activity of the HDS catalysts is generally related to the coordinatively unsaturated sites (CUS) sites formed on the edges of the promoted sulfide nanoslabs [35, 36]. In the TPR experiments, the H₂S release between 800 and 925 K (zone 3) is particularly

informative since it is related to the CUS created on Ni-based phases i.e. on NiWS phase and/or NiS_x phase. Whatever the sulfidation pressure, NiW(4.0) showed lower reduction temperature (800 K and 850 K) than NiW (915 K and 925 K). Thus, TPR patterns indicated that the creation of CUS is easier for catalysts prepared with CyDTA and when sulfidation is performed under high pressure (Figure 2, Figure 3). This is related to the strength of the metal-support interaction. These results are in agreement with the conclusions about the sulfidation pressure effect obtained on (Co)Mo catalysts. Hence, a parallel appears between the creation of CUS and the HDS performances. Indeed, NiW prepared with chelating agent or sulfided under high pressure present greater activity. Similarly, Dugulan et al. [34] showed that the high sulfidation pressure enhanced the activity as well as the Co-promotion and the formation of the mixed CoMoS phase.

Finally, on W catalysts, CO adsorption on sulfided phase showed bands at 2119 cm⁻¹ and 2064 cm⁻¹ indicating that the WS₂ slabs present both M- and S-edges. On NiW catalyst, CO spectra displayed mostly the bands at 2127 and 2093 cm⁻¹ which are ascribed to NiWS sites, completely or partially promoted by Ni, respectively [31]. On NiW(4.0), NiWS sites are also characterized by two bands 2130 and at 2097 cm⁻¹, i.e. at slightly greater wavenumbers than the counterpart without chelating agent. These $\nu(\text{CO})$ frequencies are in agreement with the change in the strength of the metal-support interaction. However, the most striking feature is the strong increment of the intensity of the NiWS bands on NiW(4.0) compared to NiW. This indicates the formation of a greater concentration of NiWS on NiW(4.0) catalyst. This is in agreement with the high catalytic activity in thiophene HDS of the catalyst prepared with CyDTA addition.

Hence, more active NiW catalysts are obtained by addition of CyDTA and sulfidation under high pressure. Furthermore, since refineries have to remove sulfur compounds selectively preventing the hydrogenation of olefins and maintaining the high octane number of gasoline [37]. This study showed that the formation of NiWS species modified the HDS thiophene products as compared to W catalysts. The NiW and NiW(4.0) displayed an increment of the ratio butenes/butanes as compared to W (Table 2), and therefore, an increase of olefins production. In this sense, NiW(4.0) displayed lower hydrogenation selectivity that would be favorable for the quality of gasoline [38].

5. Conclusions

In this work, sulfided NiW/ γ -Al₂O₃ catalysts synthesized with Ni-CyDTA solutions at two pH values were studied after sulfidation at atmospheric or high pressure (40 bar). The addition of CyDTA clearly improved the thiophene HDS activity of the NiW catalyst by a factor of 1.4. However, the influence of the pH of impregnation was limited. All catalysts sulfided under 40 bar exhibited a significantly greater HDS activity (by factor 1.5) as compared with the ones sulfided at low pressure. However, the beneficial effect of CyDTA addition measured on catalysts sulfided at 1 bar or 40 bar was similar. The CO adsorption showed the formation of NiWS phase on the catalysts prepared without and with CyDTA, although in a strongly greater amount for the catalyst prepared with the chelating agent. A correlation between catalytic activity and sulfidation degree was evidenced as well as with the intensity of the $\nu(\text{CO})$ band ascribed to NiWS sites. Finally, CyDTA and high pressure sulfidation improved the sulfidation degree of the catalysts, the amount of sulfide phase CUS sites and decrease the sulfide phase-support interactions. This leads to a strong enhancement of the hydrodesulfurization activity and slightly lowered the hydrogenation route.

Acknowledgements

In memory of Professor José Luis García Fierro. Authors thank Dr. Pavel Afanasiev for the TPR analyses. J.A. de los Reyes and V.A. Suarez Toriello acknowledge CONACYT-SENER funding for financial support. The authors thank financial support from Instituto Politécnico Nacional (Proyecto SIP 20201116 and 20201629) and the Mexican National Council for Science and Technology (CONACyT; project CB-2017-2018 # A1-S-32418).

References

- [1] D. Hughes, Chapter 12 Legislation Relating to Highway Pollution, in: S.H. Ronald, M.H. Roy (Eds.) *Studies in Environmental Science*, Elsevier 1991, pp. 453-500.
- [2] P.T. Vasudevan, J.L.G. Fierro, A Review of Deep Hydrodesulfurization Catalysis, *Catalysis Reviews*, 38 (1996) 161-188.
- [3] C. Gachet, M. Breyse, M. Cattenot, T. Decamp, R. Frety, M. Lacroix, L. de Mourgues, J.L. Portefaix, M. Vrinat, J.C. Duchet, S. Housni, M. Lakhdar, M.J. Tilliette, J. Bachelier, D. Cornet, P. Engelhard, C. Gueguen, H. Toulhoat, Optimization of the composition of Ni-W/Al₂O₃ hydrotreating catalysts using model molecules and real feedstock conversion studies, *Catalysis Today*, 4 (1988) 7-22.
- [4] B. Scheffer, P. Molhoek, J.A. Moulijn, Temperature-programmed reduction of NiOWO₃/Al₂O₃ Hydrodesulphurization catalysts, *Applied Catalysis*, 46 (1989) 11-30.
- [5] R. Yang, J. Wu, X. Li, X. Zhang, Z. Zhang, J. Guo, Hydrotreating of crude 2-ethylhexanol over Ni/Al₂O₃ catalysts: Influence of the Ni oxide dispersion on the active sites, *Applied Catalysis A: General*, 383 (2010) 112-118.
- [6] R. Palcheva, L. Dimitrov, G. Tyuliev, A. Spojakina, K. Jiratova, TiO₂ nanotubes supported NiW hydrodesulphurization catalysts: Characterization and activity, *Applied Surface Science*, 265 (2013) 309-316.
- [7] J.A. Tavizón-Pozos, V.A. Suárez-Toriello, J.A. de los Reyes, A. Guevara-Lara, B. Pawelec, J.L.G. Fierro, M. Vrinat, C. Geantet, Deep Hydrodesulfurization of Dibenzothiophenes Over NiW Sulfide Catalysts Supported on Sol-Gel Titania-Alumina, *Topics in Catalysis*, 59 (2016) 241-251.
- [8] M. Sun, D. Nicosia, R. Prins, The effects of fluorine, phosphate and chelating agents on hydrotreating catalysts and catalysis, *Catalysis Today*, 86 (2003) 173-189.
- [9] J.N. Díaz de León, M. Picquart, L. Massin, M. Vrinat, J.A. de los Reyes, Hydrodesulfurization of sulfur refractory compounds: Effect of gallium as an additive in NiWS/ γ -Al₂O₃ catalysts, *Journal of Molecular Catalysis A: Chemical*, 363-364 (2012) 311-321.
- [10] N. Koizumi, Y. Hamabe, S. Yoshida, M. Yamada, Simultaneous promotion of hydrogenation and direct desulfurization routes in hydrodesulfurization of 4,6-dimethyldibenzothiophene over NiW catalyst by use of SiO₂-Al₂O₃ support in combination with trans-1,2-diaminocyclohexane-N,N',N'-tetraacetic acid, *Applied Catalysis A: General*, 383 (2010) 79-88.
- [11] R. Palcheva, L. Kaluža, L. Dimitrov, G. Tyuliev, G. Avdeev, K. Jirátová, A. Spojakina, NiMo catalysts supported on the Nb modified mesoporous SBA-15 and HMS: Effect of thioglycolic acid addition on HDS, *Applied Catalysis A: General*, 520 (2016) 24-34.
- [12] V.A. Suárez-Toriello, C.E. Santolalla-Vargas, J.A. de los Reyes, A. Vázquez-Zavala, M. Vrinat, C. Geantet, Influence of the solution pH in impregnation with citric acid and activity of Ni/W/Al₂O₃ catalysts, *Journal of Molecular Catalysis A: Chemical*, 404-405 (2015) 36-46.
- [13] C.E. Santolalla-Vargas, V.A. Suárez Toriello, J.A. de los Reyes, D.K. Cromwell, B. Pawelec, J.L.G. Fierro, Effects of pH and chelating agent on the NiWS phase formation in NiW/ γ -Al₂O₃ HDS catalysts, *Materials Chemistry and Physics*, 166 (2015) 105-115.

- [14] G. Kishan, L. Coulier, V.H.J. de Beer, J.A.R. van Veen, J.W. Niemantsverdriet, Sulfidation and Thiophene Hydrodesulfurization Activity of Nickel Tungsten Sulfide Model Catalysts, Prepared without and with Chelating Agents, *Journal of Catalysis*, 196 (2000) 180-189.
- [15] D. Zuo, M. Vrinat, H. Nie, F. Maugé, Y. Shi, M. Lacroix, D. Li, The formation of the active phases in sulfided NiW/Al₂O₃ catalysts and their evolution during post-reduction treatment, *Catalysis Today*, 93–95 (2004) 751-760.
- [16] J. Chen, F. Maugé, J. El Fallah, L. Oliviero, IR spectroscopy evidence of MoS₂ morphology change by citric acid addition on MoS₂/Al₂O₃ catalysts – A step forward to differentiate the reactivity of M-edge and S-edge, *Journal of Catalysis*, 320 (2014) 170-179.
- [17] E. Dominguez Garcia, J. Chen, E. Oliviero, L. Oliviero, F. Maugé, New insight into the support effect on HDS catalysts: evidence for the role of Mo-support interaction on the MoS₂ slab morphology, *Applied Catalysis B: Environmental*, 260 (2020) 117975.
- [18] E.J.M. Hensen, Y. van der Meer, J.A.R. van Veen, J.W. Niemantsverdriet, Insight into the formation of the active phases in supported NiW hydrotreating catalysts, *Applied Catalysis A: General*, 322 (2007) 16-32.
- [19] A.I. Dugulan, E.J.M. Hensen, J.A.R. van Veen, Effect of pressure on the sulfidation behavior of NiW catalysts: A 182W Mössbauer spectroscopy study, *Catalysis Today*, 150 (2010) 224-230.
- [20] Y. van der Meer, E.J.M. Hensen, J.A.R. van Veen, A.M. van der Kraan, Characterization and thiophene hydrodesulfurization activity of amorphous-silica–alumina-supported NiW catalysts, *Journal of Catalysis*, 228 (2004) 433-446.
- [21] R. Navarro, B. Pawelec, J.L.G. Fierro, P.T. Vasudevan, J.F. Cambra, P.L. Arias, Deep hydrodesulfurization of DBT and diesel fuel on supported Pt and Ir catalysts, *Applied Catalysis A: General*, 137 (1996) 269-286.
- [22] Y. Villasana, F.J. Méndez, M. Luis-Luis, J.L. Brito, Pollutant reduction and catalytic upgrading of a Venezuelan extra-heavy crude oil with Al₂O₃-supported NiW catalysts: Effect of carburization, nitridation and sulfurization, *Fuel*, 235 (2019) 577-588.
- [23] P. Afanasiev, On the interpretation of temperature programmed reduction patterns of transition metals sulphides, *Applied Catalysis A: General*, 303 (2006) 110-115.
- [24] B. Baubet, E. Devers, A. Hugon, E. Leclerc, P. Afanasiev, The influence of MoS₂ slab 2D morphology and edge state on the properties of alumina-supported molybdenum sulfide catalysts, *Applied Catalysis A: General*, 487 (2014) 72-81.
- [25] T. Hattori, E. Nagata, S.i. Komai, Y. Murakami, I.r. spectra of adsorbed CO on Pt/Al₂O₃ catalysts with super-low Pt content by a diffuse reflectance fourier transform I.R. spectrometer, *Journal of the Chemical Society, Chemical Communications*, (1986) 1217-1218.
- [26] B. Scheffer, E.M. van Oers, P. Arnoldy, V.H.J. de Beer, J.A. Moulijn, Sulfidability and HDS activity of Co-Mo/Al₂O₃ catalysts, *Applied Catalysis*, 25 (1986) 303-311.
- [27] J. Chen, J. Mi, K. Li, X. Wang, E. Dominguez Garcia, Y. Cao, L. Jiang, L. Oliviero, F. Maugé, Role of Citric Acid in Preparing Highly Active CoMo/Al₂O₃ Catalyst: From Aqueous Impregnation Solution to Active Site Formation, *Industrial & Engineering Chemistry Research*, 56 (2017) 14172-14181.
- [28] L. Zavala-Sanchez, I. Khalil, L. Oliviero, J.-F. Paul, F. Maugé, Structure and Quantification of Edge Sites of WS₂/Al₂O₃ Catalysts Coupling IR/CO Spectroscopy and DFT Calculations, *ChemCatChem*, 12 (2020) 2066-2076.
- [29] L.A. Zavala-Sanchez, X. Portier, F. Maugé, L. Oliviero, Promoter Location on NiW/Al₂O₃ Sulfide Catalysts: Parallel Study by IR/CO Spectroscopy and High-Resolution STEM-HAADF Microscopy, *ACS Catalysis*, 10 (2020) 6568-6578.
- [30] G. Crepéau, University of Caen, 2002.
- [31] J.-C. Duchet, J.-C. Lavalley, S. Housni, D. Ouafi, J. Bachelier, M. Lakhdar, A. Mennour, D. Cornet, Carbon monoxide and oxygen chemisorption and functionalities of sulphided Ni-W/Al₂O₃ hydrotreating catalysts, *Catalysis Today*, 4 (1988) 71-96.
- [32] Z. Le, P. Afanasiev, D. Li, X. Long, M. Vrinat, Solution synthesis of the unsupported Ni–W sulfide hydrotreating catalysts, *Catalysis Today*, 130 (2008) 24-31.

- [33] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.F. Paul, E. Payen, CO Adsorption on CoMo and NiMo Sulfide Catalysts: A Combined IR and DFT Study, *The Journal of Physical Chemistry B*, 110 (2006) 1261-1270.
- [34] A.I. Dugulan, E.J.M. Hensen, J.A.R. van Veen, High-pressure sulfidation of a calcined CoMo/Al₂O₃ hydrodesulfurization catalyst, *Catalysis Today*, 130 (2008) 126-134.
- [35] L.S. Byskov, J.K. Nørskov, B.S. Clausen, H. Topsøe, DFT Calculations of Unpromoted and Promoted MoS₂-Based Hydrodesulfurization Catalysts, *Journal of Catalysis*, 187 (1999) 109-122.
- [36] M. Ramos, G. Berhault, D.A. Ferrer, B. Torres, R.R. Chianelli, HRTEM and molecular modeling of the MoS₂-Co₉S₈ interface: understanding the promotion effect in bulk HDS catalysts, *Catalysis Science & Technology*, 2 (2012) 164-178.
- [37] R. Palcheva, A. Spojakina, L. Dimitrov, K. Jiratova, 12-Tungstophosphoric heteropolyacid supported on modified SBA-15 as catalyst in HDS of thiophene, *Microporous and Mesoporous Materials*, 122 (2009) 128-134.
- [38] S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, On the hydrodesulfurization of FCC gasoline: a review, *Applied Catalysis A: General*, 278 (2005) 143-172.