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Julien Scalbert, Frédéric Meunier, Cécile Daniel, Yves Schuurman. An operando DRIFTS investigation into the resistance against CO₂ poisoning of a Rh/alumina catalyst during toluene hydrogenation. *Physical Chemistry Chemical Physics*, 2012, 14 (7), pp.2159-2163. 10.1039/c1cp22620g . hal-00700213

HAL Id: hal-00700213

<https://hal.science/hal-00700213>

Submitted on 8 Oct 2021

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An operando DRIFTS investigation into the resistance against CO₂ poisoning of a Rh/alumina catalyst during toluene hydrogenation

Julien Scalbert,^a Frederic C. Meunier,^{*a} Cecile Daniel^b and Yves Schuurman^b

CO₂ is a major contaminant of renewable H₂ derived from biomass fermentation. The effect of the presence of CO₂ on the activity of alumina-supported Pt and Rh catalysts used for the hydrogenation of toluene at 348 K was investigated. The use of operando diffuse reflectance spectroscopy (DRIFTS) was crucial in unravelling the changes in the nature and abundance of species adsorbed at the sample surface and relating those to the changes of catalytic activity. Rhodium supported on alumina was only partly deactivated by the introduction of CO₂ during the hydrogenation of toluene, contrary to the case of Pt/alumina. Rh was only partially covered by carbonyl species derived from CO₂ and it was shown that toluene could successfully compete with some of the linearly adsorbed carbonyls for adsorption. The alumina support stored many CO₂-derived adsorbates (carbonates, hydrogenocarbonates, carboxylates) that could spill over to the metal and form carbonyl species even after the removal of CO₂ from the feed.

1. Introduction

The search for renewable alternatives to fossil fuel-derived chemicals is of ever-increasing importance. Molecular hydrogen can be produced from organic waste fermentation and carbon dioxide is formed alongside in large concentrations in some cases.^{1,2} Therefore, there is an interest in understanding any effects that CO₂ could have on a catalytic reaction in which the biomass-derived hydrogen is used, as traces of CO₂ may remain even after H₂ purification.

Some of us recently reported that an alumina-supported platinum catalyst used for toluene hydrogenation at low-temperature (*i.e.* 348 K) was readily and fully deactivated upon CO₂ introduction in a H₂/toluene feed.³ Strongly-bound carbonyl species were observed by operando diffuse reflectance FTIR spectroscopy and were shown to irreversibly poison the Pt surface sites. The use of operando DRIFTS was crucial in unravelling the origin of the deactivation because (i) no gas-phase CO could be detected in the reactor effluent and (ii) a quantitative relationship could be drawn between the concentration of Pt-CO and the deactivation extent.³

CO₂-containing H₂ feeds should therefore only be used in the cases that CO₂ activation is negligible or, at least, that any carbonyls formed by dissociation do not inhibit the catalytic activity. We suggested from a brief survey³ of the literature

dealing with the use of supercritical CO₂ as a solvent, to which this work *de facto* relates, that Ru, Ni or Rh-based formulations could be more resistant against CO₂ poisoning. These suggestions were derived from the fact that no carbonyl species or CO poisoning was noted when these metals were used for various reactions in supercritical CO₂.^{4,5}

We report here an investigation on the effect of CO₂ on an alumina-supported Rh catalyst used for toluene hydrogenation. A Pt-based material prepared from the same alumina was also tested for the sake of comparison, especially since a different reaction DRIFTS cell was used as compared to the case of the data reported in ref. 3. Spectroscopic reaction cells are by no means ideal reactors⁶⁻⁸ and therefore cross-checking some results is useful. The operando methodology, which aims to measure the catalytic activity of the sample under spectroscopic investigation, is essential to draw meaningful structure/activity relationships.⁹⁻¹⁷

Our data will show that, while Rh also led to some CO₂ dissociation and carbonyl formation, only a partial deactivation was observed and that part of the carbonyl species could be readily displaced by toluene.

2. Experimental

2.1. Materials and reagents

The two alumina-supported catalysts were supplied by Johnson Matthey Plc. and comprised 2.0 wt% Pt or 2.5 wt% Rh. Metal dispersion was measured following the method described by Binet *et al.*¹⁸ Self-supported wafers of the samples were treated in an IR quartz cell by a reducing treatment under H₂ at 673 K. Calibrated amounts of CO were then introduced into

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the cell, measuring in parallel the area of the IR bands associated with the adducts. Spectra were recorded with a Nicolet 6700 FT-IR (Fourier Transform Infrared Spectroscopy) spectrometer and treated by the Nicolet OMNIC™ software. A 1:1 ratio between CO and surface metal atoms was assumed.

The gases used were purchased from l'Air Liquide (grade Alphagaz 1). The Ar main impurities were water (<3 ppm), dioxygen (<2 ppm) and hydrocarbons (<0.5 ppm). H₂ was further filtered by a gas clean cartridge filled with (1) charcoal, which removes organic compounds down to concentrations lower than 0.1 ppm and (2) a moisture filter that removes water + oil down to below 0.1 ppm. The 10 vol.% CO₂ in a N₂ mixture was a “Melange Crystal”, the purity of which is equivalent to the grade Alphagaz 1. Toluene was purchased from Sigma Aldrich (grade Chromasol for HPLC, purity >99.9%). Because the conversion of toluene was constant under the H₂/toluene/Ar feed (*vide infra*), the concentrations of the main detrimental impurities (CO and CO₂) were not deemed significant.

2.2. Operando diffuse reflectance FTIR measurements

DRIFTS experiments were performed at ambient pressure with a high temperature DRIFT cell (from Harrick Scientific Corporation) fitted with KBr windows, using a collector assembly (Praying Mantis™). The spectrophotometer used was a Nicolet 6700 (ThermoFischer Scientific) fitted with a liquid-N₂ cooled MCT detector. The DRIFT spectra were recorded at a resolution of 4 cm⁻¹ and 32 scans accumulation.

The reaction crucible was in inox and held about 80 mg of the samples. The catalysts were pre-reduced at 623 K for 15 min in a flow of 100 STP mL min⁻¹ of 25% H₂ in Ar. The samples were then cooled to the reaction temperature of 348 K.

Gases were fed through low volume stainless-steel lines and Ar through a saturator containing liquid toluene kept at 273 K. The feed composition was: 0.17% toluene + 17% H₂ (+1.7% CO₂ if any) in N₂/Ar. The total flow rate was 150 ml min⁻¹.

The reactor effluent was analysed using a Pfeiffer quadrupolar mass spectrometer (Model Omnistar™). Several *m/z* fragments were recorded, including those at *m/z* = 91 and 98, from which the toluene and methylcyclohexane concentrations were calculated using calibration curves.

The DRIFTS spectra are reported as log (1/*R*), where *R* is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka–Munk function for strongly absorbing media such as those based on oxides.¹⁹

3. Results

3.1. Pt/alumina

The measured Pt dispersion was 63%. The results obtained on the Pt/alumina sample are only briefly discussed because an investigation obtained on a similar sample was already reported in detail elsewhere.³ Apart from using a DRIFTS reaction cell from another manufacturer, the reaction mixture was different as compared to that reported in ref. 3, *i.e.* in that case 1.6% toluene + 40% H₂ (+2 or 40% CO₂, if any). Only

a low CO₂ concentration was used in the present study so that any related deactivation could be followed more easily.

Similarly to the data reported in ref. 3, large bands that could be assigned to carbonate and hydrogenocarbonate species (*i.e.* 1660 and 1434 cm⁻¹) were immediately observed at the surface of the catalyst following the introduction of carbon dioxide in the toluene/H₂ feed (Fig. 1a). These bands, which corresponded to species formed on alumina, subsequently showed only minor variations in intensity.

A band initially observed at 1983 cm⁻¹ and gradually shifting to 2003 cm⁻¹ indicated the presence of linearly bound carbonyls forming on the platinum.^{3,20} The intensity of this band was integrated over the region 1850–2070 cm⁻¹ and its variation over time is plotted in Fig. 1b. The increase of this Pt–CO band paralleled the decay of the toluene conversion given on the same figure and rapidly fell to the level of conversion (*ca.* 12%) found in the cell loaded with KBr.

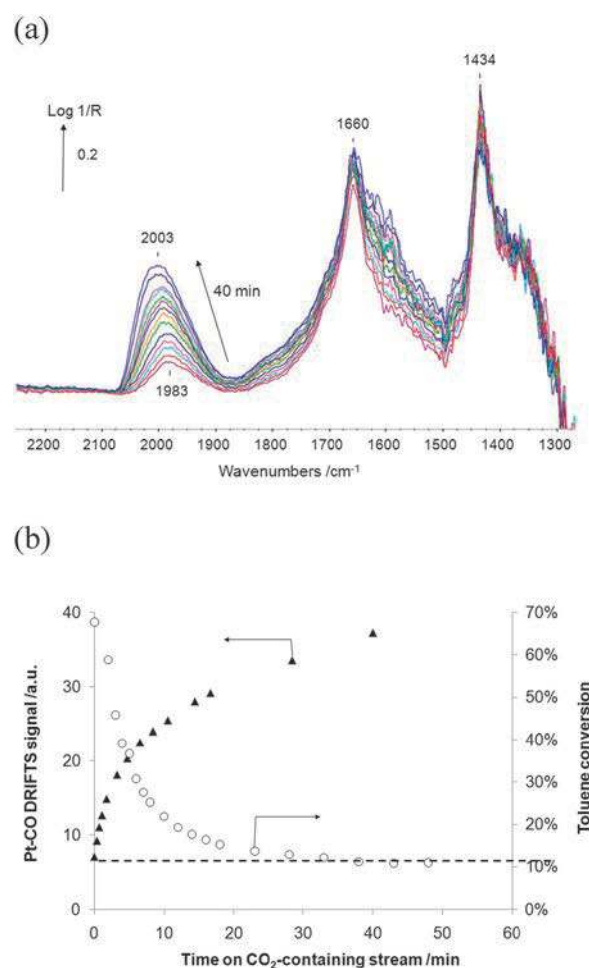


Fig. 1 (a) *In situ* DRIFTS spectra of the Pt/Al₂O₃ under a toluene + H₂ + CO₂ feed for various times on stream over a period of 40 min. The spectrum of the sample recorded at the same temperature under toluene/H₂ was used as a background. (b) Corresponding toluene conversion (○) and Pt–CO DRIFTS band intensity (▲) as a function of time. The conversion due to the DRIFTS cell reactor filled only with KBr is indicated by the dotted line. Feed: 0.17% toluene + 17% H₂ + 1.7% CO₂ in N₂/Ar. *T* = 348 K.

These data indicate that the Pt surface sites active for toluene hydrogenation were totally poisoned by adsorbed CO in about 40 min under these conditions. Neither carbonyl desorption nor any recovery of activity could be observed when CO₂ was removed from the feed (data not shown). These results are consistent with those reported earlier on a similar sample.³

3.2. Rh/alumina

The measured Rh dispersion was found to be close to 100%. The DRIFTS spectra obtained over the reduced Rh/alumina (Fig. 2a) presented several bands that can be assigned to species present on the alumina support: free and H-bonded hydroxyl groups (region 3800–2500 cm⁻¹), carboxylate (1580 and 1462 cm⁻¹) and formates (2907, 1595, 1394 and 1377 cm⁻¹).^{21,22}

In addition to the bands associated with the support, ill-defined bands were present at around 1723–1700 cm⁻¹, likely due to some residual carbonyl species that formed on the rhodium during the reduction process.

Note that similar surface species were observed in the case of the reduced Pt/alumina samples, both for the present sample (data not shown) and that reported in ref. 3.

The Rh/alumina exposed to the toluene/H₂ feed showed (Fig. 2b) new bands (*e.g.* 2926, 2854 cm⁻¹) that can all be assigned to adsorbed (and to a minor extent gas-phase) hydrocarbons, chiefly methylcyclohexane, the reaction product.³ The corresponding toluene conversion measured at the exit of the reactor was high (*ca.* 80%) and stable with time (data not shown). The DRIFTS spectrum obtained under a toluene/H₂ feed was thereafter used as a background to better monitor the changes taking place at the surface of the Rh/alumina upon the addition of CO₂.

Strong new bands associated with formates (2886, 2741, 1598, 1394 and 1377 cm⁻¹),^{21,22} hydrogenocarbonates (1637, 1431 and 1229 cm⁻¹)²³ and various ill-defined bands associated with carboxylates and carbonates could be observed in the 1700–1200 cm⁻¹ region within a few minutes following the addition of CO₂ (Fig. 3a). The toluene conversion gradually decreased, yet at a significantly slower rate than that observed in the case of Pt (see Fig. 1b and 3b). The conversion levelled off after 600 min to a value much larger than the residual conversion due to the DRIFTS cell.

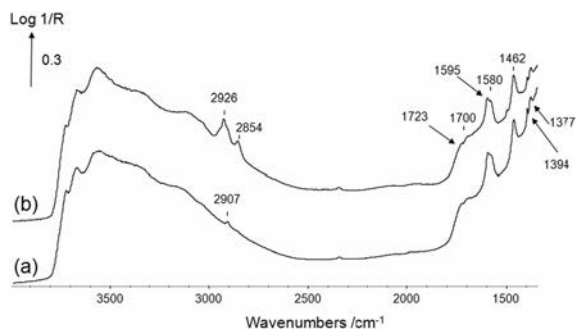


Fig. 2 *In situ* DRIFTS spectra of Rh/Al₂O₃: (a) after reduction at 623 K under 25% H₂ and (b) subsequently exposed to the toluene/H₂ feed. *T* = 348 K. The spectrum recorded over KBr was used as a background. The spectra were offset for the sake of clarity.

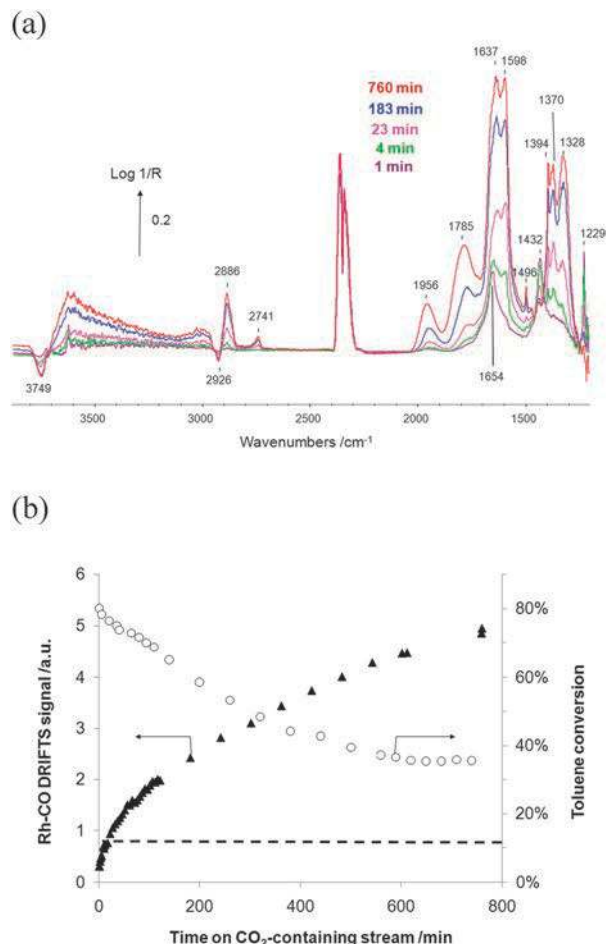


Fig. 3 (a) *In situ* DRIFTS spectra of Rh/Al₂O₃ under a toluene + H₂ + CO₂ feed for various times on stream over a period of 800 min. The spectrum of the sample recorded at the same temperature under toluene/H₂ was used as a background. (b) Corresponding toluene conversion (○) and linear Rh-CO DRIFTS band intensity (▲) as a function of time. The conversion due to the DRIFTS cell reactor filled with KBr is indicated by the dotted line. Feed: 0.17% toluene + 17% H₂ + 1.7% CO₂ in Ar. *T* = 348 K.

New bands at 1785 and 1956 cm⁻¹ were also noted. These bands were most likely due to carbonyl species adsorbed on metallic rhodium. Linearly bound Rh-CO would typically present bands in the region 2060–2000 cm⁻¹, while bridged carbonyls would absorb around 1910–1850 cm⁻¹.^{24–28}

The carbonyl wavenumbers measured under our experimental conditions were actually red-shifted, notably because of the presence of toluene at the surface of the metal. Toluene is electron-rich and leads to an increased electron-back donation from the Rh to an antibonding molecular orbital of CO, resulting in a lower carbonyl stretching vibration wavenumber, as already observed in the case of platinum.³

As a matter of fact, the carbonyl band wavenumber increased by about 80 cm⁻¹ once toluene was removed (*vide infra*). Therefore, we can confidently propose that the 1785 and 1956 cm⁻¹ bands were due, respectively, to bridged and linear carbonyls coadsorbed with toluene on metallic Rh.

All these bands continued to grow over the duration (800 min) of the experiment (Fig. 3a). The intensity of the linear

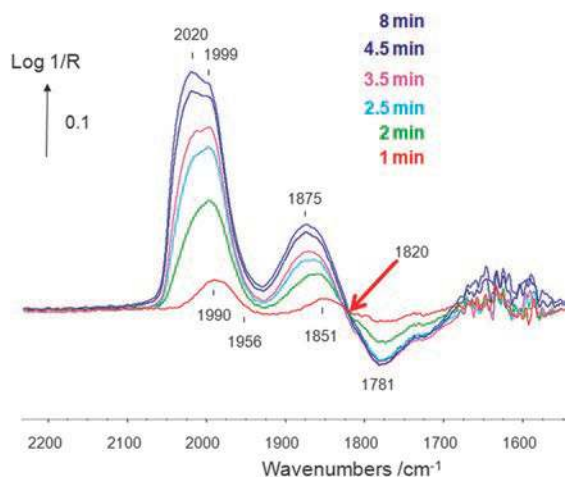


Fig. 4 DRIFTS spectra collected over the Rh/alumina after toluene was removed from the feed. The spectrum of the sample recorded at the same temperature after 800 min under toluene/H₂/CO₂ was used as a background. Feed: 17% H₂ + 1.7% CO₂ in Ar. $T = 348$ K.

carbonyl band at 1956 cm⁻¹ was integrated over the 2000–1900 cm⁻¹ region and its variation with time was compared to that of the conversion (Fig. 3b). This comparison suggests that the loss of toluene conversion was largely related to the formation of carbonyl species, although toluene conversion seemed to remain constant after 600 min, while the carbonyl band intensity still increased.

Toluene was removed from the feed after 800 min and Rh/alumina was left at the reaction temperature under the H₂/CO₂ mixture. Interestingly, new carbonyl bands appeared at around 1990 and 1851 cm⁻¹, gradually shifting to higher wavenumbers, while the band at *ca.* 1781 cm⁻¹ decreased in intensity (Fig. 4). An isobestic point (signalled by a red arrow in Fig. 4) was noted at 1820 cm⁻¹, indicating that the 1781 cm⁻¹ species was converted into that at 1875 cm⁻¹.

As anticipated in the discussion above, the results given in Fig. 4 can be rationalised by proposing the following model. The bands at *ca.* 1785 and 1956 cm⁻¹ observed in Fig. 3a corresponded to bridged and linear carbonyls coadsorbed with toluene on metallic Rh. When toluene was removed from the system, the Rh particles became less electron-rich and the wavenumbers of some of the carbonyls shifted to higher values (because of reduced back donation into the antibonding CO molecular orbital). The 1785 and 1956 cm⁻¹ bands (Fig. 3a) shifted to 1851 and 1990 cm⁻¹ (Fig. 4), respectively. The “negative” band at 1956 cm⁻¹ is actually not visible because of band overlapping and the fact that more than two carbonyl species are likely to be present, a two-band interpretation being an oversimplification.

It is yet clear that the band(s) associated with the linearly bound carbonyl (located at 1990–2020 cm⁻¹ in the absence of coadsorbed toluene) grew far beyond the expected intensity of the corresponding band observed in the presence of toluene (located at 1956 cm⁻¹). The intensity of the 2020 cm⁻¹ band was higher than 0.30 units of pseudo-absorbance after 8 min in the absence of toluene (Fig. 4), while that of the 1956 cm⁻¹ was *ca.* 0.12 after 760 min under the toluene-contained feed (Fig. 3a). This indicates that additional linear carbonyl species

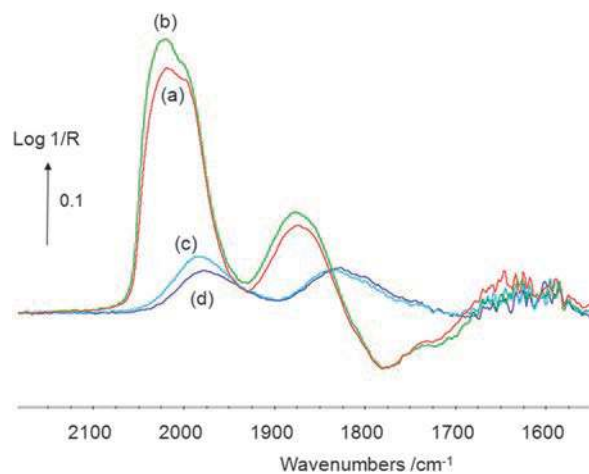


Fig. 5 DRIFTS spectra collected over the Rh/alumina: (a) with only H₂ + CO₂, 8 min after the removal of toluene, (b) with only H₂, 5 min after CO₂ was also removed, (c) toluene was back with H₂ for 1 min and (d) 10 min. $T = 348$ K.

were readily formed at the surface of the Rh once toluene was removed.

CO₂ was subsequently removed from the feed to further investigate the reactivity of the Rh-carbonyl under CO₂-free conditions. Interestingly, the intensity of the carbonyl species continued to grow (Fig. 5b), while that of carbonate/hydrogenocarbonate decreased (not shown). This suggests that these additional carbonyls arose from the reduction of adsorbates located on alumina. The fact that the linear carbonyl band intensity did not decrease also stresses that the carbonyls were strongly bound to the Rh and did not readily desorb upon CO₂ removal. When toluene was sent back into the system, the overall carbonyl intensity dramatically decreased (also taking into account the bridged carbonyl recovered at *ca.* 1781 cm⁻¹) (Fig. 5c and d). These data show that most of the linear carbonyls formed in the absence of toluene were displaced when the hydrocarbon was reintroduced.

4. Discussion

The Harrick DRIFTS reaction cell presented a non-negligible activity for the reaction considered here, similarly to the Spectra-Tech reaction chamber,³ which must be taken into account when accurate conversion and rate measurements are required.

This work shows that Rh is more resistant to CO₂ poisoning than Pt during the toluene hydrogenation at 348 K, despite the fact that Rh was also able to dissociate carbon dioxide and formed Rh–CO species. The Rh/alumina catalyst experienced a slow gradual deactivation before exhibiting a stable conversion, at least on the timescale of the experiment reported (Fig. 3b). This represents a significant improvement as compared to the case of the Pt/alumina catalyst (Fig. 1b).

The main poisoning species on the Rh were bridged carbonyls, *e.g.* bands located at 1781 and 1875 cm⁻¹ in the presence and absence of toluene, respectively (Fig. 3a and 4). The linear carbonyls, *e.g.* bands located at 1956 and 2020 cm⁻¹ in the

presence and absence of toluene, respectively, were also responsible for Rh deactivation.

However, some of the corresponding sites, mostly those associated with linearly adsorbed CO, were able to adsorb toluene even in the presence of the carbon oxides. In fact, toluene was able to displace a large fraction of linear carbonyl species when reintroduced in the feed (Fig. 5). The adsorption enthalpy of toluene must have been larger than that of CO on these specific sites and the former could successfully compete for adsorption.

Determining the true nature of the various surface Rh sites involved is beyond the scope of this work. This task is also complicated by the fact that CO adsorption can lead to dramatic dispersion/agglomeration of Rh particles *via* Rh⁺(CO)₂ species,^{25,29} (gem-dicarbonyl bands are expected around 2100 and 2035 cm⁻¹, which were yet never observed here). Rh has also been shown to reconstruct under varying reducing/oxidising conditions^{30,31} which relate to some extent to the present work where CO₂ is added/removed from the feed.

Determining an exact carbonyl concentration-deactivation pattern is also complicated by the fact that the DRIFTS beam only probed the upper layer of the sample bed, which may not have been homogeneous depending on the level of conversion, when differential conditions did not apply.

In a previous study,³ it was shown that alumina had no direct catalytic effect on toluene conversion in the case of Pt/alumina. However, the data reported here clearly showed that alumina can store carbonate/hydrogenocarbonate/carboxylate species, which then migrate and form carbonyl species on the metal.

The effect of CO₂ and the related carbonyls may affect differently Rh activity depending on the hydrocarbon being hydrogenated. In a recent contribution, Sivasankar and Frei³² showed that CO introduction totally prevented ethene hydrogenation to ethane and led to hydroformylation products.

The present work reemphasises the power of operando techniques, even when non-ideal spectroscopic reactors are used, by providing crucial clues into the origin of the deactivation of catalytic materials and the role of impurities or molecules co-fed in a reaction stream.

5. Conclusions

Rhodium supported on alumina was shown to be only partly deactivated by the introduction of CO₂ during the hydrogenation of toluene, contrary to the case of a Pt/alumina catalyst. Rh was only partially covered by carbonyl species derived from CO₂ and toluene could successfully compete with some of the linearly adsorbed CO for adsorption on the related Rh sites.

Acknowledgements

J.S. acknowledges the Région Basse-Normandie for financial support (Ph.D. grant).

Notes and references

- 1 D. Das and T. N. Veziroglu, *Int. J. Hydrogen Energy*, 2001, **26**, 13.
- 2 J. Wang and W. Wan, *Int. J. Hydrogen Energy*, 2009, **34**, 799.
- 3 A. A. Taimoor, I. Pitault and F. C. Meunier, *J. Catal.*, 2011, **278**, 153.
- 4 V. Arunajatesan, B. Subramaniam, K. W. Hutchenson and F. E. Herkes, *Chem. Eng. Sci.*, 2007, **62**, 5062.
- 5 S.-I. Fujita, T. Yamada, Y. Akiyama, H. Cheng, F. Zhao and M. Arai, *J. Supercrit. Fluids*, 2010, **54**, 190.
- 6 F. C. Meunier, *Chem. Soc. Rev.*, 2010, **39**, 4602.
- 7 B. M. Weckhuysen, A. Bensalem and R. A. Schoonheydt, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2011.
- 8 F. C. Meunier, A. Goguet, S. Shekhtman, D. Rooney and H. Daly, *Appl. Catal., A*, 2008, **340**, 196.
- 9 M. A. Bañares and S. J. Khatib, *Catal. Today*, 2004, **96**, 251.
- 10 B. M. Weckhuysen, *Chem. Commun.*, 2002, 97.
- 11 F. C. Meunier, *Catal. Today*, 2010, **155**, 164.
- 12 B. M. Weckhuysen, *Chem. Soc. Rev.*, 2010, **39**, 4557.
- 13 D. Ferri, M. S. Kumar, R. Wirz, A. Eyssler, O. Korsak, P. Hug, A. Weidenkaff and M. A. Newton, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5634.
- 14 A. Yoboué, A. Susset, A. Tougerti, D. Gallego, S. V. Ramani, M. Kalyanikar, D. S. Dolzhenkov, S. G. Wubshet, Y. Wang, S. Cristol, V. Briois, C. La Fontaine, R. M. Gauvin, J.-F. Paul and E. Berrier, *Chem. Commun.*, 2011, **47**, 4285.
- 15 P. Dhage, A. Samokhvalov, D. Repala, E. C. Duin and B. J. Tatarchuk, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2179.
- 16 S. Nassreddine, G. Bergeret, B. Jouguet, C. Geantet and L. Piccolo, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7812.
- 17 J.-F. Groust, G. Costentin, J.-M. Krafft and P. Massiani, *Phys. Chem. Chem. Phys.*, 2010, **12**, 937.
- 18 C. Binet, A. Jadi and J. C. Lavalley, *J. Chim. Phys. Phys.-Chim. Biol.*, 1989, **86**, 451.
- 19 J. Siritá, S. Phanichphant and F. C. Meunier, *Anal. Chem.*, 2007, **79**, 3912.
- 20 P. Hollins, *Surf. Sci. Rep.*, 1992, **16**, 51.
- 21 F. C. Meunier, J. P. Breen, V. Zuzaniuk, M. Olsson and J. R. H. Ross, *J. Catal.*, 1999, **187**, 493.
- 22 G. Busca, J. Lamotte, J.-C. Lavalley and V. Lorenzelli, *J. Am. Chem. Soc.*, 1987, **109**, 5197.
- 23 C. Binet, A. Jadi and J. C. Lavalley, *J. Chim. Phys. Phys.-Chim. Biol.*, 1989, **86**, 471.
- 24 Z. Zhang, A. Kladi and X. Verykios, *J. Catal.*, 1995, **156**, 37.
- 25 J. Rasko and J. Bontovics, *Catal. Lett.*, 1999, **58**, 27.
- 26 A. M. Efstathiou, T. Chafik, D. Bianchi and C. O. Bennett, *J. Catal.*, 1994, **147**, 27.
- 27 J. A. Anderson and M. M. Khader, *J. Mol. Catal. A: Chem.*, 1996, **105**, 175.
- 28 K. Hadjiivanov, E. Ivanova, L. Dimitrov and H. Knozinger, *J. Mol. Struct.*, 1995, **459**, 661–662.
- 29 F. Solymosi and H. Knozinger, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 389.
- 30 M. A. Newton, *Chem. Soc. Rev.*, 2008, **37**, 2644.
- 31 M. A. Newton, *Top. Catal.*, 2009, **52**, 1410.
- 32 N. Sivasankar and H. Frei, *J. Phys. Chem. C*, 2011, **115**, 7545.