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From Gas to Liquid Phase Sulfidation: An IR Spectroscopy Study

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Abstract A side by side characterization of gas and liquid phase activation of a $CoMo/Al_2O_3$ hydrodesulfurization (HDS) catalyst is reported using thiophene HDS as a test reaction and CO adsorption monitored by infrared spectroscopy. The liquid phase sulfidation (high pressure, dimethyldisulfide) leads to the formation of CoMoS sites with higher intrinsic activity compared to the gas phase (H_2S/H_2).

Keywords: Hydrotreatment · Sulfide catalyst structure · Liquid phase sulfidation · Effect of carbon · Carbon monoxide adsorption · Thiophene HDS

1 Introduction

The sulfidation of hydrotreating catalysts is a key step that strongly influences their catalytic performances. In industrial practice, this activation is performed in a liquid phase at high pressure whereas academic studies, mainly for practical reasons, often use a H_2S/H_2 gas flow at atmospheric pressure. It is well established that these two sulfidation processes lead to different active phases [1–3] and catalytic performances [4, 5]. The sulfidation stage used in academic studies should get closer to industrial conditions to obtain more relevant structure–activity relationships; a first step is to investigate the effect of the sulfidation pressure [6–10].

In liquid phase sulfidation, the sulfiding agent is not H_2S but an organosulfide molecule mixed with the feed. A wide variety of organosulfide compounds can be used, such as dimethyl(di)sulfide (DMDS, DMS) and ditertio-nonylpentasulfide (TNPS). The organosulfide can be introduced either in situ during the high pressure sulfidation [11], or ex situ as a "pre-sulfiding agent", i.e. before loading the catalyst in the reactor [1, 5]. Both procedures lead to the sulfidation of a wet catalyst either directly by the organosulfide or by the H_2S produced during its decomposition at temperature higher than 100 °C [11]. The open literature generally reports an increase in hydrodesulfurization (HDS) activity [1, 2, 4, 12] and assigns it tentatively to the presence of carbonaceous species. However, some discrepancies appear on the extent [5, 13] and the origin of this beneficial effect. The main proposals are

(i) An increased dispersion [1, 3] resulting from a blocking of the growth of MoS_2 particles by carbonaceous species, or from a more efficient heat transfer provided by the liquid phase during the oxide-sulfide transformation [14]
(ii) The formation of a new and highly active site. Chianelli et al. [3, 15] reported that carbon atoms can be introduced in the sulfide phase leading to carbide like species such as MoS_xC_y. A decrease of the metal/support interactions in the presence of carbon is also reported to form type II sites [16–18]
(iii) An improvement of the catalyst sulfidation by a better balance between sulfidation and reduction [13]

These explanations are not mutually exclusive but they remain far from the direct characterization of the active site. IR spectroscopy is a powerful technique to characterize the

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nature and number of active sites. Nitrogen monoxide, for instance is widely used as a probe to characterize hydrotreating catalyst sites, but is not completely inert since it can oxidize some sulfide phases [19]. Carbon monoxide, a more inert molecule meets better the requirements of an ideal probe molecule [20–26].

In order to gain deeper insights in the effect of liquid phase sulfidation, a commercial $CoMo/Al_2O_3$ is characterized after gas (H_2S/H_2 at atmospheric pressure) and liquid (high pressure with a mixture of DMDS, straight run gas oil and H_2) phase sulfidations. The catalytic activity is measured by the thiophene HDS test and the catalyst characterized by CO adsorption monitored by infrared spectroscopy. This combined approach will bring detailed information on the quality, quantity and on the intrinsic activity of active sites.

2 Experimental

2.1 Materials

The studied $CoMo/\gamma\text{-}Al_2O_3$ catalyst (kindly supplied by Total) contains 8.9 wt% Mo and 3.6 wt% Co.

2.2 Activation

The same sulfidation procedure is used for the thiophene HDS tests and the IR spectroscopy characterization. Identical H_2S/H_2 ratio (P_{H2S}/P_{H2}:0.05) and similar temperature profiles are applied: (i) temperature raised from room temperature to 523 K (0.5 K min^{-1}) and kept for 8 h; (ii) temperature raised from 523 to 593 K (0.3 K min^{-1}) and kept at the final temperature for 5 h.

2.2.1 Standard Gas Phase Sulfidation

The gas phase sulfidation is performed in situ in the microreactor and the IR cell at atmospheric pressure with a 30 ml min^{-1} of H_2S/H_2 (5 vol%) flowrate.

2.2.2 Standard Liquid Phase Sulfidation

The liquid phase sulfidation is conducted in a pilot plant. The sulfiding feed consists of 2.5 wt% dimethylsulfide (DMDS) diluted in straight run gas oil (300 ml h^{-1}) and H_2 (H_2/HC = 250 Nl/l). Under the sulfiding feed, the catalyst is first wet for 2 h and the temperature is subsequently increased under a pressure of 4.5 MPa. After sulfidation, the DMDS flow is stopped and the sulfided catalyst left under flowing H_2 and SRGO for 12 h. The catalyst is then unloaded at room temperature without any contact with air and kept in liquid *n*-pentane.

2.2.3 Elemental Analysis

The sulfidation degree of the catalyst after the two kinds of sulfidation method was determined by elemental analysis on a Flash2000 analyzer from Thermo Fischer. The given value is the average of three measurements.

2.3 HDS of Thiophene

2.3.1 Sulfidation Stage

The performance of the gas phase sulfided catalyst is measured immediately following its in situ sulfidation. The liquid phase sulfided catalyst is transferred to the thiophene microreactor in a glove box ($P_{O2} < 5$ ppm; $P_{H2O} < 1$ ppm) to prevent any air contact. The reactor is then connected to the test unit and purged under flowing nitrogen.

2.3.2 HDS Test

The thiophene HDS activity test is carried out in a flow microreactor at atmospheric pressure and 573 K. Thiophene is introduced by diverting a flow of hydrogen (70 ml min^{-1}) through a saturator maintained at 291 K (P_{thio}: 7.2 kPa; P_{H2}: 94.1 kPa). The reaction products are analyzed on-line using a Varian 3900 gas chromatograph equipped with a flame ionization detector (FID) and fitted with a CPSIL-5CB capillary column. Appropriate amounts of catalysts (about 30 mg) are used to keep a steady state conversion lower than 5 %. The initial reaction rates are calculated as $r_{HDS} = (F/m)X$, where F/m is the molar flow rate of reactant per gram of catalyst and X is the thiophene conversion. The uncertainty on the activity is about ±6 %.

2.4 IR Spectroscopy

2.4.1 IR Experiments

Before their introduction in the IR cell, the samples are ground and pressed to obtain a wafer (area 2 cm^2, mass about 10 mg, but precisely weighed). The spectra are recorded using a Fourier Transform IR spectrometer from Thermo-Nicolet fitted with a MCT detector. 256 scans are recorded with a resolution of 4 cm^{-1} and all the intensities are normalized to a disc of 5 mg cm^{-2} of sulfided catalyst.

2.4.2 Activation and Introduction Step

2.4.2.1 In Situ Sulfidation The gas phase sulfidation is carried out in situ on the wafer in the transmission IR cell following the standard sulfidation procedure. In some instances, the sample receives a further H_2 treatment of 2 h (30 ml min^{-1}) in order to have the same P_{H2S}/P_{H2} ratio at the end of the sulfidation for the liquid and the gas phase sulfided catalyst. After sulfidation, the temperature is kept at 593 K for 1 h under evacuation. Afterward, the sample is cooled to room temperature and then to liquid nitrogen temperature (100 K) before CO introduction. At this stage the pressure in the IR cell should be below $2.5.10^{-4}$ Pa.

2.4.2.2 Ex Situ Sulfidation Two sample are sulfided ex situ after: (i) a liquid phase sulfidation; (ii) a gas phase sulfidation performed in the microreactor and 12 h of time on stream (thiophene HDS). In order to prevent air contact, the wafer is pressed and transferred to the IR cell in a glove box ($P_{O2} < 5$ ppm; $P_{H2O} < 1$ ppm). Then, the cell is mounted on the IR setup and the gas from the glove box evacuated for 1 h at room temperature. While pumping under vacuum, the temperature is raised to 593 K (2 K min^{-1}) and kept for 1 h at this temperature. Finally the sample is cooled to liquid nitrogen temperature ($P_{cell} < 2.5.10^{-4}$ Pa). In some cases, after liquid phase sulfidation and evacuation, the sample receives a further H_2 treatment for 2 h (30 ml min^{-1}) before further evacuation.

2.4.3 *CO Adsorption Procedure*

The IR spectrum of the sulfided catalyst (called reference spectrum) is recorded at low temperature before CO introduction. Then, small calibrated (0.09 μmol) doses of CO are introduced in the IR cell and finally the sample is saturated with 133 Pa of CO. After each CO aliquots, an IR spectrum is recorded. All the CO spectra are displayed as difference spectra (i.e. spectrum after CO adsorption minus the reference spectrum). Uncertainty on bands area is about ±6 %.

2.4.4 *Spectral Analysis*

The quantification of the different sites is performed after decomposition of the spectra following the method described in Ref. [23] and using the molar absorption coefficients of $\nu_{CO/MoS2}$ and $\nu_{CO/CoMoS}$ previously reported [22].

3 Results

3.1 Sulfidation Degree

Table 1 gives the elemental analysis in sulfur of the catalyst after the two different sulfidation methods. The sulfidation state is estimated considering that sulfur is only present in the sulfide slab or as Co_9S_8.

From these results, it appears that the amount of sulfur present on the catalyst is high enough to reach almost complete sulfidation of the slabs in both cases (theoretical value S/Mo = 2). For the catalyst sulfided in gas phase, the S/Mo value is even higher than the theoretical one and can be attributed to the sulfidation of cobalt either in decoration of the slab or in Co_9S_8 (although IR study gives no evidence of Co_9S_8 formation). This result points out that at 593 K high degree of sulfidation of the catalyst is obtained in accordance with previous results [27].

3.2 Thiophene HDS Activity

Table 2 reports the thiophene HDS activity for the CoMo/Al_2O_3 catalyst sulfided in liquid and gas phase. The liquid phase sulfidation yields a higher activity (+21 %) than the gas phase.

3.3 IR Study of the Sulfided Catalysts

3.3.1 *Carbon Deposit*

The infrared spectra of the catalyst sulfided in gas and liquid phase are reported in Fig. 1. After gas sulfidation only one band is visible at 1372 cm^{-1} (Fig. 1B) attributed to the presence of a small amount of sulfate on the alumina support [28, 29]. On the contrary, after liquid phase sulfidation or gas phase sulfidation followed by thiophene exposure, no formation of sulfate species was evidenced. This is an indication that the transfer between the reactor and the IR cell is not source of oxygen contamination. Moreover, two broad bands appear at 1474 and 1554 cm^{-1} for the gas phase sulfided catalyst after thiophene reaction and at 1453 and 1578 cm^{-1} for the liquid phase sulfided catalyst (Fig. 1B). In both cases, the shape and the position of these two bands are relatively close implying that the same species are probably formed. Moreover, a post treatment with H_2 reduces their intensity in both cases. Meanwhile, for the liquid phase sulfided catalyst the bands

Table 1 Elemental analysis of CoMo catalyst after gas or liquid sulfidation

Sulfidation	wt%S	Molar ratio S/Mo	Molar ratio S/(Mo + Co)
Gas phase	7.45	2.5	1.5
Liquid phase	5.69	1.9	1.2

Table 2 Effect of sulfidation process of CoMo catalyst on thiophene HDS rate

Sulfidation	r_{thio} ($mol.h^{-1}.kg^{-1}$)
Gas phase	10.2
Liquid phase	12.3

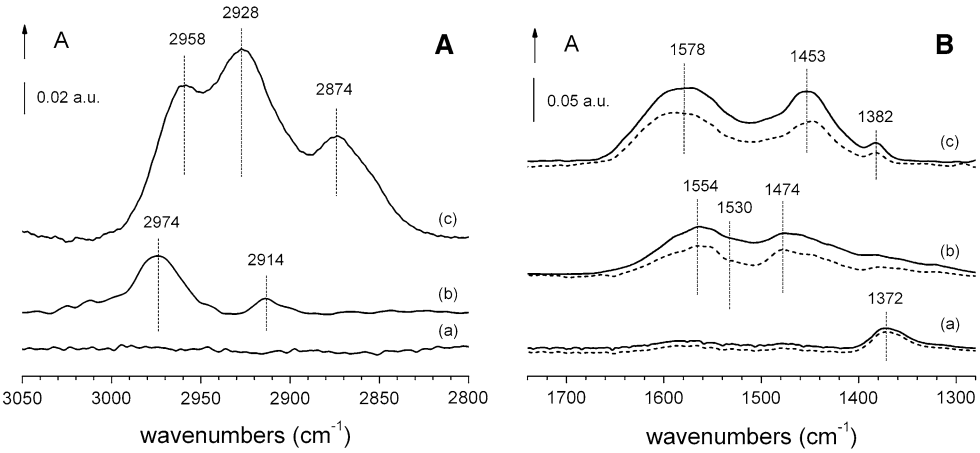


Fig. 1 IR spectra of the catalyst (*solid line*) *a* sulfided with H_2S/H_2; *b* sulfided with H_2S/H_2 and used in the thiophene reaction; *c* sulfided with a liquid phase. Addition of an H_2 post-treatment of 2 h (*dashed line*). **A** 3050–2800 cm^{-1} range; **B** 1700–1300 cm^{-1} range

shift from 1453 to 1446 cm^{-1} and from 1578 to 1592 cm^{-1}.

The presence of similar bands was already reported by Elst et al. and Vogelaar et al. and attributed to coke deposit [25, 30–32]. The decrease of the intensities upon H_2 treatment is also reported by these authors. Coke deposit has mainly been studied on zeolites and its IR signature consists of a complex group of bands between 1350 and 1650 cm^{-1} [33–37]. Among them, four bands are generally distinguished around 1370, 1490, 1540 and 1610 cm^{-1}. According to earlier investigations, the bands around 1370 and 1490 cm^{-1} are assigned to $\delta_{C\text{–}H}$ of aliphatic and olefinic species [30, 38], those around 1540 cm^{-1} to $\delta_{C\text{–}H}$ of conjugated olefinic compounds [34], whereas the band at 1610 cm^{-1} is attributed to $\nu_{C=C}$ in conjugated alkenes or aromatics. The latter shifts downward (1580–1590 cm^{-1}) with coke becoming more polyaromatic and closer to graphitic species [38]. The position of the bands reported after thiophene reaction or liquid phase sulfidation are relatively close to those reported for coke (±15 cm^{-1}). Moreover, the shift from 1578 to 1592 observed after the H_2 treatment of the catalyst sulfided in liquid phase could be explained by the partial hydrogenation of the polyaromatic species. However, their shape (FWHM and shoulders) are different. In addition, after liquid phase or gas phase sulfidation followed by thiophene exposure, the IR spectra also display groups of bands in the ν_{CH} area below 3000 cm^{-1}, an indication that carbonaceous deposits are probably not aromatic or polyaromatic species (Fig. 1A). Thus, bands in the $\delta_{C\text{–}H}$ and $\nu_{C=C}$ area cannot be attributed solely to coke.

Datka et al. [39] reported that alkenes can react with alumina to form carboxylate species identified by two bands at 1460 and 1580 cm^{-1} attributed to ν_{OCO}. A similar effect was since reported in many studies [40, 41]. The shape of the IR spectra in the 1300–1700 cm^{-1} range (Fig. 1B) is close to carboxylate species. We conclude that after liquid phase or gas phase sulfidation and subsequent thiophene exposure, a mixture of carboxylate and coke is deposited on the catalyst surface. The amount of deposit is higher for the liquid phase sulfided catalyst.

3.3.2 Sulfide Phases—CO Adsorption

3.3.2.1 Gas Phase Sulfidation The interaction of CO with the alumina support and the CoMo active sites of the catalyst sulfided in gas phase leads to four ν_{CO} bands (Fig. 2).

The interaction with Al^{3+} and AlOH sites gives bands at 2189 and 2156 cm^{-1}. Interactions with MoS_2 and CoMoS result in bands at 2111 and 2071 cm^{-1} respectively. The band at 2071 cm^{-1} result from one major contribution at 2071 cm^{-1} and a band at 2050 cm^{-1} [42].

An H_2 treatment (Fig. 3) does not modify the position and area of bands attributed to CO in interaction with Al^{3+} and AlOH sites. On the other hand, it increases from 17 and 46 % the area of the bands attributed to respectively MoS_2 and CoMoS sites and shifts downward the $\nu_{CO/MoS2}$ band

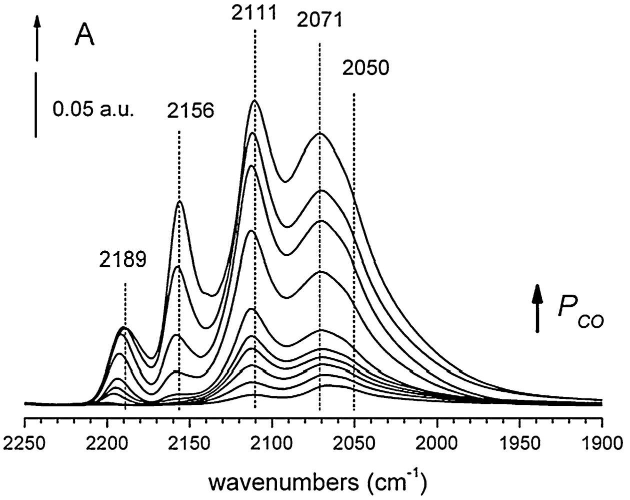


Fig. 2 IR spectra of CO adsorbed on CoMo after H_2S/H_2 sulfidation

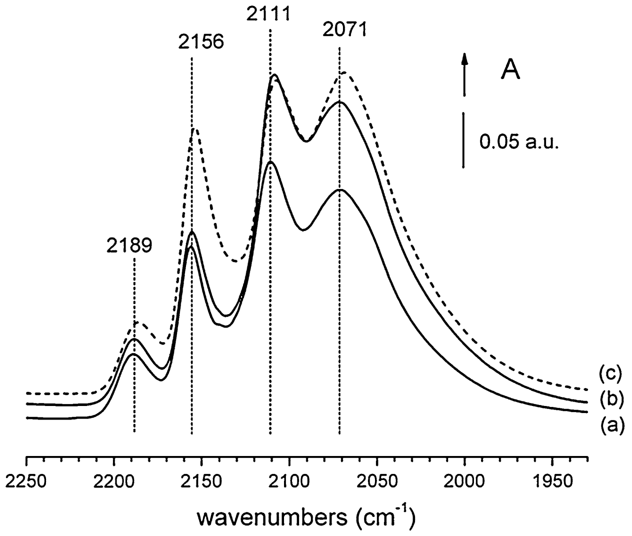


Fig. 3 IR spectra of CO adsorbed on CoMo after: (*a*) H_2S/H_2 sulfidation; (*b*) H_2S/H_2 sulfidation and H_2 treatment; (*c*) H_2S/H_2 sulfidation and HDS thiophene reaction. P_{CO}: 133 Pa

by 2 cm^{-1} (Table 3). After reaction with thiophene (Fig. 3), the four CO bands are shifted downward by 2 cm^{-1} relatively to the gas phase sulfidation, meanwhile, the $\nu_{CO/AlOH}$ band area increases by 40 %. As previously shown by Vogeelar et al. [32], the bands resulting from CO in interaction with MoS_2 and CoMoS sites have similar area after thiophene reaction and gas phase sulfidation followed by H_2 treatment. In the next paragraph, the spectra of the gas phase sulfided catalyst followed by H_2 treatment will be compared with those of the liquid phase sulfidation; this will allow to compare the surface species in the absence of H_2S since the number of CUS sites detected by CO adsorption is linked to this partial pressure [43].

3.3.2.2 Liquid Phase Sulfidation CO adsorption on the liquid phase sulfided catalyst gives also rise to four main bands albeit with different intensities and position compared to the gas phase sulfided catalyst. The CO bands at 2183, 2152, 2101 and 2054 cm^{-1}, are respectively attributed to CO in interaction with Al^{3+}, AlOH, MoS_2 and CoMoS sites. The bands of CO in interaction with CoMoS sites result from one major contribution at 2054 cm^{-1} and an additional band at 2028 cm^{-1}. The 2138 cm^{-1} band is physisorbed CO. The area of the bands associated with CO in interaction with MoS_2 and CoMoS sites decrease by 80 and 39 % in the liquid phase sulfidation compared to the gas phase (Fig. 4). The result is that the ratio A_{CoMoS}/A_{MoS2} increases from 2.5 after a gas phase sulfidation to 8.9 after a liquid phase sulfidation. An H_2 treatment after the liquid phase sulfidation increases the area of the $\nu_{CO/CoMoS}$ band by 13 % and shifts it downward by 4 cm^{-1} (Fig. 5).

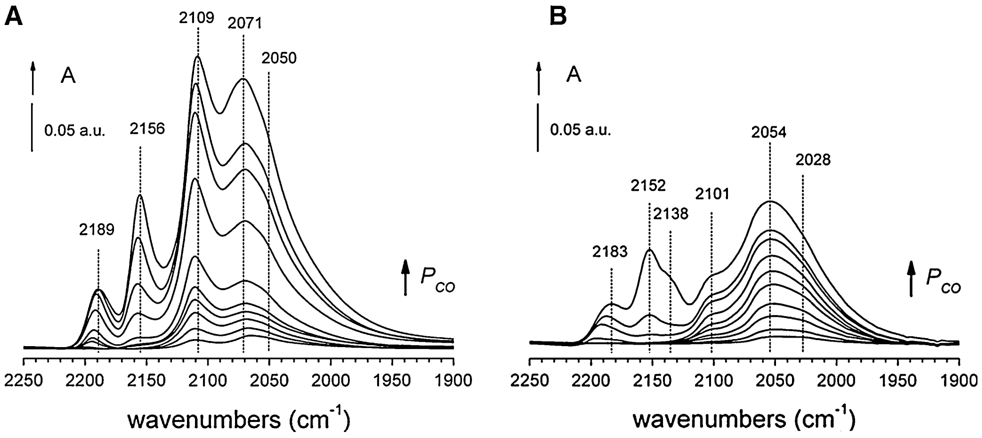
4 Discussion

4.1 Effect of Liquid Phase Sulfidation on Sulfide Sites

A liquid phase sulfidation changes drastically the IR spectrum of CO adsorbed on the CoMo catalyst: the band attributed to CO in interaction with CoMoS sites is downward shifted (−17 cm^{-1}) while its intensity is decreased. Such a strong shift of the CoMoS band has never been reported before. It points to an important modification of the nature of the sites associated with a significant increase of their electronic density [44]. The decrease of concentration could be related to a decrease of sulfidation of the metals in accordance with the lower sulfidation degree estimated from elemental analysis. The presence of carbonaceous species could also prevent the CO adsorption.

In previous studies on promoted catalysts sulfided in the gas phase, the thiophene HDS activity was reported to increase linearly with CoMoS site concentration, the latter measured by CO/IR [10, 43, 45, 46]. In the case of liquid

Fig. 4 IR spectra of increasing doses of CO adsorbed on CoMo catalyst after: **A** H_2S/H_2 sulfidation and H_2 post-treatment; **B** liquid phase sulfidation



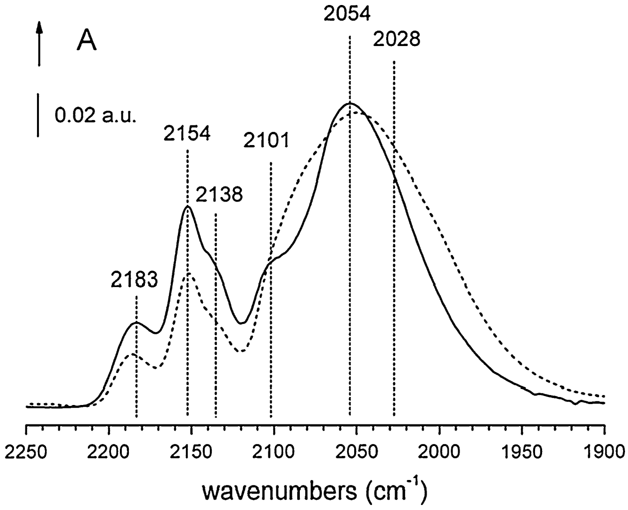


Fig. 5 IR spectra of CO adsorbed on CoMo catalyst after: liquid phase sulfidation (*solid line*), liquid phase sulfidation and H_2 treatment (*dashed line*). P_{CO}: 133 Pa

vs. gas phase sulfided catalysts, the HDS activity is not correlated anymore to the CoMoS site concentration. The activity in thiophene HDS increases (Table 2) whereas the sulfide CoMoS site concentration decreases (Table 3). Thus, upon liquid phase sulfidation, CoMoS sites with a higher intrinsic activity (Table 4) are formed and probably result from a strong increase of their electronic density.

4.2 Origins of Nature Site Modification

Several hypotheses can be proposed to explain the origin of these modifications.

4.2.1 Pressure of Sulfidation

The liquid and gas phase sulfidation methods differ by the pressure used, the former being at 4.5 MPa while the latter is performed at atmospheric pressure. However, a previous study reported the effect of gas phase sulfidation pressure[10]: CO/IR did not detect a strong shift of the $\nu_{CO/CoMoS}$ band but rather an increase of its intensity as pressure increased; no significant modification of the TOF for thiophene HDS was evidenced. Therefore, the effect of the liquid phase sulfidation on the CoMoS site nature is unlikely related to an increase of sulfidation pressure.

4.2.2 Presence of Hydrocarbon

4.2.2.1 Modification of Support Acidity The residual carboxylate/coke species observed after liquid phase sulfidation could modify the support acidity and thus the interaction slab/support. Indeed, the downward shift of the ν_{CO} band interacting with the support implies a decreased strength of the Brønsted and Lewis acidity of the alumina due to the residual hydrocarbon species. However, two points are against this hypothesis. On the one hand, such carboxylates/coke species are also observed (although in lesser quantities) after thiophene reaction on a gas phase sulfided catalyst without any parallel strong shift of the $\nu_{CO/CoMoS}$ band. On the other hand, in a previous study a correlation was observed between the position of the $\nu_{CO/CoMoS}$ and $\nu_{CO/AlOH}$ bands highlighting that modification of the Brønsted acidity of alumina shifts the $\nu_{CO/CoMoS}$ with a maximum of 5 cm^{-1} [47]. Such a value is much lower than the 17 cm^{-1} shift measured after liquid phase sulfidation. Thus the decrease of support acidity revealed by both the decrease in strength and in concentration of Lewis and Brønsted acid sites and linked to the presence of carboxylate/coke species is not the origin of the modification of the active site nature.

4.2.2.2 Formation of Carbide Like Species One other point is the formation of carbide like species such as MoS_xC_y favored by the presence of hydrocarbon during the sulfidation step and the HDS reaction [3, 15]. Carbide species provide high HDS activity but their formation is still a matter of debate since they are not stable under H_2S

Table 4 Turn over frequency of CoMoS sites estimated from HDS activityand the CoMoS site concentration of the CoMo catalyst after sulfidation and H_2 treatment

Sulfidation	Pseudo TOF (h^{-1})
Gas phase	103
Liquid phase	181

Table 3 Effect of sulfidation on the position of the ν_{CO} band and the sulfide site concentration of the CoMo catalyst

Sulfidation	ν_{CO} (cm^{-1}) of CO in interaction with		Amount of site detected (10^{-3} mol.kg^{-1})	
	MoS_2	CoMoS	MoS_2	CoMoS
Gas phase	2111	2071	80	68
Gas phase + H_2 treatment	2009	2071	93	99
Liquid phase	2101	2054	18	60
Liquid phase + H_2 treatment	–	2050	20	68

or HDS reaction conditions [48, 49]. However, the ν_{CO} fingerprint of Mo_2C is reported by Aegerter et al. [48] and Wu et al. [49] at 2054–2060 cm^{-1}; and matches the ν_{CO} attributed to CO in interaction with CoMoS sites after liquid phase sulfidation. Thus, carbide like species formation after liquid phase sulfidation can not be excluded from our results. However, if the ν_{CO} band at 2054 cm^{-1} is attributed to carbide like species, it means that CoMoS sites would not be formed, quite an unlikely scenario since cobalt is sulfided and promoted carbide sites such as Co/MoS_xC_y are not reported [50]. Therefore, it is more likely that after liquid phase sulfidation CoMoS phase presents a specific configuration that lead to electronic properties similar to Mo carbide species.

4.2.2.3 Formation of Type II or Highly Unsaturated Sites Another possibility to account for interactions between MoS_2 slabs and hydrocarbons is the intercalation of a carbon phase between the metals and the support. Vissers et al. [16–18] showed that an HDS catalyst or a cobalt catalyst prepared in a carburized alumina possess high activity. They explain this enhancement by a decrease of the metal/support interactions due to the presence of carbon and propose the formation of type II sites. Likewise, during liquid phase sulfidation, the presence of hydrocarbon on the support or in interaction with the metal while the slabs are growing could modify the slab/suppport interaction leading to sites of type II. Although such sites have not yet been detected by IR spectroscopy, the increase of the electronic density of the sulfide site is in agreement with the breaking of electronegative oxygen bridge between the sulfide phase and the support. It can also be proposed that the increase of electronic density of sulfide site is due to a lower metal-sulfur coordination [42, 51]. However, after H_2 treatment which decreases sulfur coordination only a small shift of 2 cm^{-1} is observed. Both the formation of type II or highly unsaturated sites could result from a decrease of metal/support interaction linked to specific interactions between hydrocarbon, support and metal phases during the genesis of the sulfide phases.

5 Conclusion

The effect of gas and liquid phase sulfidation was studied on a CoMo/Al_2O_3 catalyst by measuring its HDS thiophene activity and relating it to the sulfide phase properties monitored by CO adsorption followed by IR spectroscopy. The amount of accessible sulfide sites decreases upon liquid phase sulfidation but the electronic density of these sites increases significantly. This substantial modification of the nature of the site is related to an increased intrinsic activity of CoMoS sites. The modifications of the electronic properties of the sulfides sites are not related to modification of support acidity or to carbide—like species formation. It is therefore proposed that type II CoMoS or highly unsaturated sites are formed due to a decrease of the metal/support interaction linked to specific interactions between the metal and hydrocarbon during the sulfide phase genesis.

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