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Effect of the electronic properties of Mo sulfide phase on the hydrotreating activity of catalysts supported on Al_2O_3, Nb_2O_5 and Nb_2O_5/Al_2O_3

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Activity in thiophene hydrodesulfurization (HDS) and in the three routes of 2,6-dimethylaniline (DMA) decomposition was examined on Mo sulfide catalysts supported on Al_2O_3, Nb_2O_5 and Nb_2O_5–Al_2O_3. Catalysts activity is enhanced when Mo phase is deposited on niobium-containing support. For HDS and for the hydrogenation route of DMA decomposition, the niobium-containing support strongly contributes to the catalyst activity whereas the activity of the Mo phase per Mo atom decreases with the increase of niobium amount in the support. By contrast, as for the DMA route, which leads to xylene formation (XYL), the activity of the Mo sulfide phase per Mo atom is strongly enhanced. The electronic properties of the MoS_2 phase were studied by means of IR spectroscopy of CO adsorption. Comparison of ν(CO/Mo) wavenumbers reveals an upward shift when Mo sulfide phase is deposited on Nb-containing support. The modification of the electronic properties of the sulfide phase is related to an interaction Mo–Nb either through the formation of a mixed Mo–Nb sulfide phase, or through the interaction MoS_2 slabs – support whose strength depends on the support acidity. Hence, the beneficial effect for xylene formation route is attributed to a decrease of the electron density of the Mo sulfide phase that should strengthen the DMA adsorption on the sulfide phase.

KEY WORDS: hydrotreatment; niobium; HDS; HDN; IR spectroscopy.

1. Introduction

The need for decreasing pollutant emissions as well as the necessity of refining heavier petroleum feeds have stimulated a worldwide effort for the development of catalysts with better performance in hydrotreating processes.

The conventional hydrotreating catalysts are based on pairs of metals in sulfide form, typically Co or Ni, combined with Mo or W, generally supported on alumina [1–3]. Thus, the development of new alternative catalysts can be done by changing the active sulfide phase, or by the proposition of new supports.

The development of new supports is a quite attractive option, due to the importance of the acid–base properties of the catalysts in several hydrotreating (HDT) processes, as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodearomatization (HDA) and hydrocracking (HCC) [3, 4]. Hence, the control of the support acidity should allow an adjustment of catalyst activity and selectivity.

Niobium oxide in the hydrated form, also known as niobic acid ($Nb_2O_5{\cdot}xH_2O$) stands out due to its high acidity, $H_0 \leq -5.6$. Moreover, niobium oxide either in the pure state, supported on other materials or in mixed oxides appears as a promising option for HDT reactions [5–8]. In fact, Geantet *et al.* [5] and dos Santos *et al.* [7] showed that niobia phase is sulfided during activation of the HDT catalyst, and that the extent of sulfidation of the niobium phase can be related to the catalyst activity in HCC and in HDS reactions. Thus, it appears that it is the niobium sulfide phase, which is active in HDT. It is worth noting that the intrinsic activity of unsupported or supported niobium sulfides for various HDT reactions is greater than that of conventional molybdenum sulfide [5,6,8]. Niobia was also used as a support for conventional (Ni)Mo sulfide phases. In this case, in order to overcome the problem of its low specific area, niobia was deposited on oxides, such as alumina or titania, or was used as mixed Nb–Al or Nb–Ti oxides [9,10]. On some of these preparations, activities higher than those on conventional sulfide catalysts are also reported. Finally, the use of niobium sulfide as a dopant of conventional NiMo catalysts is also a way to enhance the catalytic activity [11].

Thus, the presence of niobium is beneficial for HDT and the most promising routes appear to be the use of niobium as a dopant or as the support of a (Ni)Mo phase. In the later case, it is clear from previous work that niobium sulfide itself contributes to the HDT

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reactions. However, literature does not specify if the niobium phase plays only a direct role as active phase, or also an indirect role by modifying the activity of the (Ni)Mo sulfide phase. Moreover, the extent of the beneficial role of niobium-based catalysts depends on the reaction considered. A point to explore, is to define the role of the Nb and (Ni)Mo sulfide phases on the various functionalities of the catalysts.

The main objective of this work was to prepare Mo sulfide catalysts on niobia-modified alumina, to study their activity in HDS and HDN reactions and to compare them with similar catalysts supported on pure alumina and pure niobia. The FTIR spectroscopy of adsorbed CO was used to identify the nature of the sulfide sites.

2. Experimental

2.1. Catalysts preparation

Three supports were used, the pure oxides γ-Al_2O_3 and Nb_2O_5, and alumina-supported Nb_2O_5. The alumina was prepared by calcination of a boehmite (PURAL SB RT04/111) at 823 K for 3 h. The niobia was prepared by calcination at 773 K for 4 h of niobic acid (provided by CBMM). The Nb_2O_5/Al_2O_3 was prepared by incipient wetness impregnation of the alumina with an aqueous solution containing the appropriate amount of a niobium ammonium oxalate complex, $NH_4[NbO(C_2O_4)_2(H_2O)]\cdot(H_2O)_m$, to obtain a final support with 20 wt% of Nb_2O_5, followed by drying at 393 K for 1 h and calcination at 773 K for 4 h.

The Mo catalysts were prepared using incipient wetness impregnation to obtain catalysts with about 4.5 Mo atoms per nm^2 of support surface area. The molybdenum impregnation onto the supports was carried out using an aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and 6% of hydrogen peroxide; the latter being used to increase the heptamolybdate solubility. The pH was adjusted at 2 by adding HNO_3 in order to avoid any precipitation of molybdenum compounds. The resulting solids were dried at 393 K and calcined at 723 K. The characteristics of the catalyst are presented in Table 1.

2.2. Characterization

The supports were analyzed by X-ray diffraction on a Rigaku Miniflex diffractometer, with Cu-Kα radiation, λ = 1.5418 Å, 30 kV and 15 mA.

The surface areas and pore volumes of the supports and oxidic precursors were determined from nitrogen adsorption data at 77 K in an automated volumetric apparatus, Micromeritics ASAP 2010. Before the analyses all samples were treated *in-situ* under vacuum at 673 K.

Table 1

Composition and textural characteristics of the supports and catalysts

Material	S_{BET}[a] in $m^2\ g_{cat}^{-1}$	PV[b] in $cm^3\ g_{cat}^{-1}$	wt% Mo[c]
Al_2O_3	200	0.575	–
Mo/Al	175	0.442	12.9
Nb_2O_5/Al_2O_3	179	0.431	–
Mo/NbAl	130	0.317	11.7
Nb_2O_5	26	0.116	–
Mo/Nb	27	0.130	2.0

[a] Surface area determined by BET method.

[b] Pore volume.

[c] Introduced by impregnation.

Sulfided catalysts were characterized by FTIR spectroscopy of adsorbed CO. The oxidic catalysts were pressed into self-supported wafers (a 2 cm^2 disc of ca. 10 mg) and placed into a quartz IR cell equipped with CaF_2 windows and a cryogenic chamber. Prior to the adsorption experiments, the samples were sulfided *in situ*, according to the following procedure. The catalysts were evacuated from RT (room temperature) up to 623 K, and then contacted at 623 K for 1 h with 13.3 kPa of a gas mixture containing 10 vol% H_2S in H_2. After a rapid evacuation of the gas phase, a second dose of H_2S/H_2 mixture was put in contact with the catalyst overnight. Finally, a third dose of H_2S/H_2 mixture was contacted with the catalyst for 1 h. At last, the catalyst was evacuated at the same temperature for 45 min and cooled to 100 K. For performing CO adsorption, small calibrated doses were introduced into the IR cell up to an equilibrium pressure of 133 Pa. After each CO introduction, spectra were recorded in 256 scans using a Nicolet FTIR spectrometer. The system was subsequently evacuated at low temperature up to a residual pressure of 10^{-3} Pa. The bands of the adsorbed CO species were obtained by subtracting the spectra recorded after and before CO introduction. Band intensities were corrected for slight differences in the weight of the IR disc and normalized to a disc of 5 mg cm^{-2}.

2.3. Catalytic activity measurements

The catalysts were tested by means of two reactions: hydrodesulfurisation (HDS) of thiophene and hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA).

The thiophene HDS activity was carried out in a flow micro-reactor working at atmospheric pressure and 623 K. Appropriate amounts of catalyst were used in order to keep the conversion lower than 20%. Thiophene was introduced into the reactor by flowing hydrogen (70 mL min^{-1}) through a thiophene saturator maintained at 291 K and mixed to 20 mL min^{-1} of H_2S/H_2 (10 vol%). Products were analyzed on-line by using a Varian gas chromatograph equipped with FID detector and CPSIL-5CB capillary column. The specific rate was 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. Before the reaction, the catalysts were sulfided *in situ* with 30 mL min^{-1} of H_2S/H_2 (10 vol%) at 623 K (heating rate 3 K min^{-1}) for 1.5 h.

The 2,6-dimethylaniline HDN activity test was carried out in a stainless steel reactor at 4 MPa and 573 K. Around 0.35–0.4 g of catalyst was first sulfided *in situ* with 60 mL min^{-1} of H_2S/H_2 (10 vol%) at 4 MPa and 623 K for 2 h with a temperature ramp of 3 K min^{-1}. Thereafter, the catalyst was cooled under H_2S/H_2 to the reaction temperature and the H_2S content adjusted at 1.4% in hydrogen. The liquid feed (10 vol% 2,6-dimethylaniline, reactant; 80 vol% heptane, solvent; and 10 vol% decane, internal standard) was introduced by an HPLC pump and vaporized in the H_2S/H_2 stream. The reaction products were condensed at the reactor exit and the liquid was analyzed with a Varian gas chromatograph equipped with a CPSIL-5CB capillary column and a FID detector.

The partial pressure of 2,6-dimethylaniline was kept constant at 13 kPa for all experiments. Reaction conditions at steady state were varied by changing the contact time (55–250 h g mol^{-1}) at 56 kPa of H_2S. We determined the reaction orders for hydrogenation (HYD), xylene formation (XYL) and disproportionation (DIS) routes as zero, zero and 0.4, respectively, [12]. Activities are expressed by the rate. For the sake of uniformity of units, the activity for DIS is multiplied by $(P^0_{DMA})^{0.4}$.

3. Results

3.1. Physical characteristics

The X-ray diffractograms of the supports are shown in Figure 1. The alumina presents the typical pattern of the gamma phase, with broad peaks. On the other hand, the niobia support presents a crystalline structure characteristic to the hexagonal Nb_2O_5 phase (TT-phase), formed at mild temperature [13]. The mixed support, Nb_2O_5/Al_2O_3, presents a similar pattern to that of alumina, indicating high niobia dispersion on the alumina.

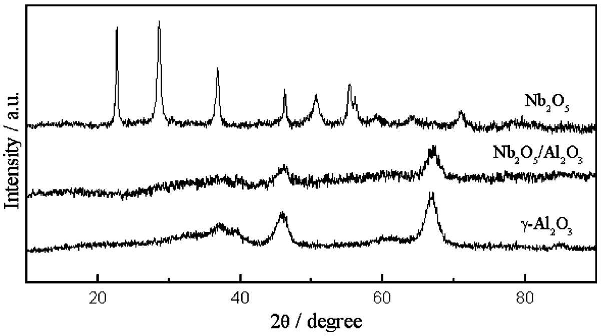


Figure 1. XRD patterns of the supports.

The surface areas and pore volumes of the supports and catalysts are presented in table 1. The high surface area of the alumina contrasts with the low one for the niobia. The niobia/alumina shows a very small decrease in surface area as compared to the pure alumina. This corroborates the XRD results that indicate preservation of the alumina structure after niobium deposition.

The Mo catalysts on γ-Al_2O_3 and Nb_2O_5/Al_2O_3 present smaller surface areas than their respective supports, but this decrease is mostly explained by the increase in catalyst density due to incorporation of ca. 10 wt% molybdenum.

3.2. FTIR spectroscopy of adsorbed CO

The sulfided Mo catalysts were characterized by FTIR spectroscopy of adsorbed CO to investigate the nature and the amount of surface sites. The CO adsorption was performed at about 100 K, in order to increase the coverage of the probe molecule on weak sites such as the OH groups of the support and the sites of the Mo phase. The sulfided niobia-supported catalysts are not transparent enough to the IR beam to allow transmittance analysis of self-supported wafers.

Figure 2 shows the spectra of adsorbed CO on the sulfided Mo catalyst supported on niobia–alumina, with increasing CO coverage. Figure 3 compares the spectra of CO adsorbed on the Mo catalysts supported on niobia–alumina and on pure alumina, for adsorption of a small CO dose that corresponds to Mo phase saturation (Figure 3A) and for adsorption of 133 Pa of CO at equilibrium (Figure 3B).

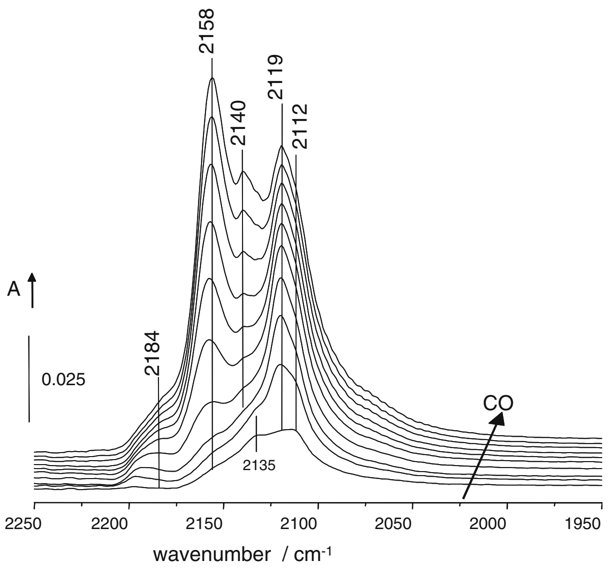


Figure 2. FTIR spectra of increasing doses of CO adsorbed at 100 K on sulfided Mo/NbAl catalyst.

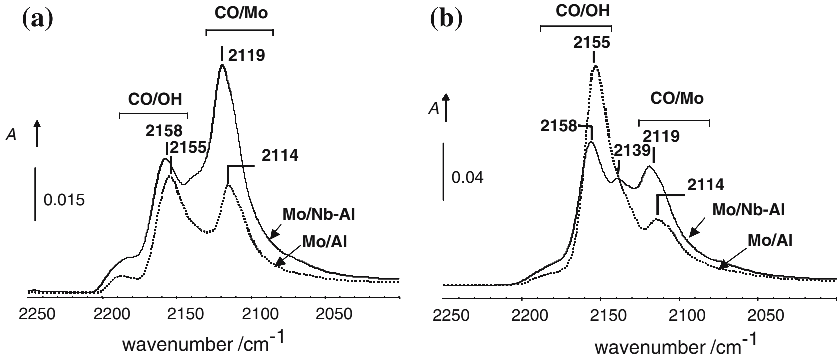


Figure 3. Comparison of FTIR spectra of CO adsorbed at 100 K on sulfided Mo/NbAl (full line) and Mo/Al (dotted line) catalysts: (a) adsorption of CO amount which correspond to Mo sulfide phase saturation (a dose of 9 μmol g^{-1}); (b) adsorption of 133 Pa of CO at equilibrium.

The bands in the region 2190–2150 cm^{-1} are characteristic of CO in interaction with the support. The band around 2180–2190 cm^{-1} is attributed to Lewis acid sites present on the alumina not covered by niobia while the band at about 2155 cm^{-1} is specific of H-bonded CO. It should be noticed that the presence of niobium in the support induces an increase of the acid strength of the OH groups, since the CO/OH band is observed at higher wavenumbers on Mo/NbAl (ν(CO) = 2158 cm^{-1}) than on Mo/Al (ν(CO) = 2155 cm^{-1}).

The bands located at lower wavenumbers characterize the interaction of CO with the sulfide phase. On Mo/Al (figure 3), the spectra show a band at 2114 cm^{-1} in agreement with previous studies [14]. On Mo/NbAl, analysis of the spectra corresponding to the first doses allows to distinguish two or even three bands. The main one is observed at 2119 cm^{-1} and shoulders appear at 2112 cm^{-1} and at ~2135 cm^{-1} (figures 2, 3). None of these bands is present in the spectrum of CO interacting with sulfided NbAl support (spectrum not shown). Regarding the shoulder at 2112 cm^{-1}, its frequency is very close to the one observed when Mo is supported on pure alumina. This can account for CO adsorption on some MoS_2 slabs without any interaction with the Nb-phase. This result, as well as the presence of Lewis sites associated with alumina, indicates also that there is not a monolayer of niobium on the surface of alumina. Figure 3 highlights that the main CO/Mo band is shifted according to the nature of the support (Mo/Al: 2114 cm^{-1}; Mo/NbAl: 2119 cm^{-1} – $\Delta\nu$(CO) = +5 cm^{-1}). This wavenumber change points out a modification of the electronic properties of the sulfided phase. Previous studies on sulfided phases (M = Mo or Ru) deposited on zeolites [15,16] and on amorphous silica alumina [17], reported an upward shift of the CO/M band when the acidity of the support increased. Since hydroxyl groups of the niobium-containing support are more acidic than on alumina (Mo/NbAl: ν(CO/OH) = 2158 cm^{-1} – Mo/Al: ν(CO/OH) = 2155 cm^{-1}), the present spectroscopic results confirm the trend. Moreover, on Mo/ASA, whose support presents some very strong acidic OH groups (although in small amount), the ν(CO/OH) signal is observed at 2175 cm^{-1} [18] while, as expected, the CO/Mo signal is shifted more upward (ν(CO/Mo) = 2128 cm^{-1} [17]) than on Mo/NbAl. Thus, the CO/Mo shift can be related to a change in the sulfide phase – support interaction. Hence, the stronger the support acidity, the lower the electron density of the sulfide phase. Similar effects were previously reported for supported metallic phases [19,20]. Nevertheless, the CO/Mo shift could also account for the genesis of a mixed Mo–Nb sulfide phase. Indeed, Gaborit *et al.* [6] showed that the formation of such a mixed phase is possible. However, in our case, one could expect that only a fraction of the MoS_2 would form a mixed phase with Nb. If the band at 2119 cm^{-1} is ascribed to a Mo–Nb mixed sulfide phase and the low intensity band at 2112 cm^{-1} is characteristic of a pure MoS_2 phase, the intensity ratio of the bands at 2119 and 2112 cm^{-1} suggests that the major fraction of the Mo sites are interacting with Nb atoms. To assess this second possibility, a series of Mo/NbAl with constant Mo loading and different Nb amount should be characterized by CO adsorption. Finally, the band at 2135 cm^{-1} is generally assigned to the formation of a pseudo-liquid phase in agreement with its development at high CO coverage. However, on Mo/NbAl catalyst, the shoulder at 2135 cm^{-1} can already be observed from the first CO doses. Hence, one cannot exclude that it characterizes CO in interaction with the sulfided NbAl support, as for example some niobium sulfide or oxysulfide phase.

The shift of the main CO/Mo band provides evidence for a change of the electronic properties of the sulfide phase in presence of niobia. The upward shift accounts for a decrease of the electron density (lowering of the back-donation from the Mo to the CO molecule) of the Mo sites of the sulfide phase when deposited on Nb-containing support. Hence, the question, which arises, is "can the modification of the electronic properties of the sulfide phase modify the activity and selectivity of the catalyst?”

3.3. Thiophene hydrodesulfurization activity

Supported molybdenum catalysts and supports alone were tested in thiophene HDS. Since the catalysts have considerably different surface areas, Table 2 presents rate constants per square meter of catalyst.

It appears that (i) the use of niobia as a support for the Mo phase is beneficial for the HDS activity; (ii) the niobium-containing supports alone present a significant HDS activity, the pure niobia support being more active. Thus, the HDS activity of the catalyst contains a contribution of both the support and the molybdenum sulfide phase. To estimate the contribution of the Mo sulfide phase to the HDS activity, we subtracted from the total catalyst activity, the activity of the support alone (Table 2 – column 3). From this value, we also deduced the Mo phase activity per Mo atom (values in parenthesis). It should be mentioned that in these calculations, we have considered that the support activities are similar on the supported molybdenum catalysts and on the pure supports.

Table 2 indicates that, when Nb amount increases, (i) the contribution of the support to the whole HDS activity strongly increases, (ii) the HDS activity of the Mo phase per Mo atom decreases.

Table 2

HDS activity of Mo catalysts and supports

Catalyst	r_{HDS} in 10^{-6} mol h^{-1} m^{-2}	Difference of activity: $r_{(catalyst)} - r_{(support)}$ in 10^{-6} mol h^{-1} m^{-2}
Al_2O_3	0	–
Mo/Al	27.0	27.0 (3.5)*
Nb_2O_5/Al_2O_3	4.4	–
Mo/NbAl	28.3	23.9 (2.4)*
Nb_2O_5	42.3	–
Mo/Nb	50.0	7.7 (1.2)*

*In parenthesis [difference of activity] per mole of Mo in mol(thiophene) mol(Mo)$^{-1}$ h^{-1}.

3.4. Dimethylaniline (DMA) hydrodenitrogenation activity

Several authors studied the HDN of alkylanilines over NiMo catalysts and they found that the denitrogenated products are formed either via direct denitrogenation (DDN) by direct ammonia elimination or via hydrogenation followed by elimination [21,22]. On the other hand, van Gestel *et al.* [12] used this model reaction over CoMo and NiMo catalysts and showed an additional pathway: the disproportionation route that forms nitrogen-containing products (scheme 1). Furthermore, these authors showed the very high activity of unpromoted Mo sites towards xylene formation via the DDN route. They marked that the activity of these unpromoted Mo sites is very sensitive to the partial pressure of H_2S.

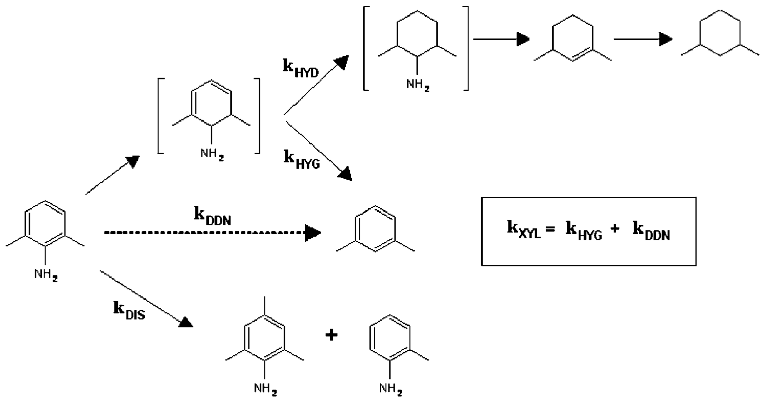
The activity for 2,6-dimethylaniline decomposition was tested on Mo sulfide catalysts, as well as on the pure supports. Table 3 reports the activity (per square meter) for the three routes.

The activity of alumina is negligible in DMA decomposition, while the sulfided niobium-containing supports present an activity, which is highest on the niobia support. These two supports are active for hydrogenation (HYD) as well as for xylene formation (XYL), their activity being more important for HYD than for XYL. The niobia support presents also a small

Table 3

Activity (per square meter) of Mo catalysts and supports in decomposition of 2,6-dimethylaniline

Catalyst	Activity in 10^{-6} mol h^{-1} m^{-2}		
	r_{HYD}	r_{XYL}	r_{DIS}
Al_2O_3	0	0	0
Mo/Al	5.62	0.76	0.02
Nb_2O_5/Al_2O_3	0.18	0.05	<0.01
Mo/NbAl	6.02	7.10	0.05
Nb_2O_5	2.02	0.59	0.03
Mo/Nb	5.04	9.59	0.08



Scheme 1. Reaction network of 2,6-dimethylaniline decomposition.

Table 4
Contribution of the Mo phase to the catalyst activity in HDN of 2,6-dimethylaniline

Catalyst	Difference of activity r(catalyst) – r (support) in 10^{-6} mol h^{-1} m^{-2}	
	r_{HYD}*	r_{XYL}*
Mo/Al	5.62 (0.73)	0.76 (0.10)
Mo/NbAl	5.84 (0.62)	7.05 (0.75)
Mo/Nb	3.02 (0.40)	9.00 (1.17)

*In parenthesis [difference of activity] per mole of Mo in mol(DMA) $mol(Mo)^{-1}$ h^{-1}.

but significant activity for the disproportionation route (DIS).

As for the Mo catalysts, the activity for the three routes depends on the nature of the support. Regarding the HYD route, the largest activity is for Mo/NbAl catalyst, while for XYL and DIS routes, it is largest with the Mo sulfide on niobia support.

Like for HDS activity, the niobium-containing supports significantly contribute to the HYD and XYL activity of the corresponding catalysts. As in the previous section, the contribution of the Mo sulfide phase was estimated (table 4) by subtracting that of the support. Fractions of activity coming from the Mo phase and from the support vary differently for HYD and XYL routes. Pure niobium support strongly contributes to HYD activity of Mo/Nb (40%), while for XYL its contribution stays moderate (6%). To compare with more accuracy the effect of the support on the activity of the sulfide phase, we calculated the intrinsic activity of the sulfide phase, taking into account the content of Mo in each catalyst (table 4 – values in parentheses). These values highlight that the HYD intrinsic activity decreases with the increase of Nb amount in the support. Conversely, XYL intrinsic activity is strongly enhanced when support acidity is increased.

DIS activity of the catalysts and of the supports alone increases in presence of niobium. This confirms the presence of acidic sites on the niobium-containing support, in agreement with the IR results presented in previous section (figure 3). Moreover, the DIS rates measured on the Mo-catalysts are always somewhat greater than on the support alone. This observation indicates the formation of acidic sites on the sulfide catalyst whatever the support nature.

4. Discussion

This work shows that modification of the support strongly affects activity and selectivity of catalysts for hydrotreatment. Comparison of HDS and HDN activities after normalization to a same surface area reveals that the largest activities are obtained on niobium-containing catalysts. This beneficial effect has several origins: (i) participation of the niobium-containing support in the catalytic activity, and (ii) change of the intrinsic activity of the Mo phase.

Results, presented in tables 2–4, point out that niobium-containing supports participate in the reaction; this contribution being particularly strong for HDS and HYD reactions. These activities could be attributed to the sulfide (or oxysulfide) niobium phase that are known to catalyze HDT reactions [5–8]. The presence of such a phase, which is shown by previous work on similar material [6], is supported by IR results (ν(CO) mode at 2135 cm^{-1}).

As indicated previously, as a first approximation, we have considered that the activities due to the support are similar in the catalysts and in the sulfided supports themselves. In this first approximation, it should be mentioned that two parameters, whose modification has a reverse effect on the support activity, are considered unchanged by the addition of the metal. First, the coverage of the support by the sulfide phase is not taken into account in this calculation. Since the coverage by the Mo sulfide phase should decrease the activity of the support, this would lead to an underestimation of the contribution of the Mo phase. The second parameter considered unchanged is the degree of sulfidation of the niobium-containing support. Indeed, in contact with either H_2S present during the activation, added to the reactants (for HDN or HDS reaction), or formed as reaction product during HDS, the niobia phase can be partially sulfided. Indeed, previous studies show that the amount of sulfided niobium in Mo (8.2 wt%)/niobia is about three times the one present in the sulfided pure niobia after sulfidation at 673 K with 10 vol% H_2S/H_2 [6]. Therefore, when Mo is added to niobium containing support, a part of the enhancement of activity for HDS and DMA decomposition can be related to the formation of a niobium sulfide (or oxy-sulfide) phase. Thus, in this case, the calculated activity per Mo atom would be overestimated.

However, even if the contribution in the activity of the support itself and of the MoS_2 phase can only be roughly calculated, a similar trend for the HDS reaction and HYD route can be observed: addition of niobium decreases the activity of the Mo sulfide phase. Several hypotheses can be proposed in order to explain the decrease in activity for HDS reaction and HYD route. First, one can exclude an effect of the sulfidation level of the Mo phase since XPS results (not presented) did not show significant variation with the nature of the support. The second point to consider is the effect of the electronic properties on the HDS and HYD activities. In fact, Gaborit *et al.* [6] demonstrated that the mixed Mo–Nb sulfide has a lower activity for HDS of dibenzothiophene than the MoS_2 phase. This could be an explanation for the decrease of the Mo activity when deposited on Nb-containing support. On the other hand, the decrease of the HYD activity appears in contradiction with the results reported by Hédoire *et al.* [16]. Indeed, these authors reported that the activity in tetralin hydrogenation of Mo sulfide was slightly enhanced by the support acidity (β-zeolites) and linked with the high-frequency shift of the ν(CO) mode of CO adsorbed on Mo supported on the more acidic support. Finally, one can also consider that the diminution of the intrinsic Mo sulfide phase activity for HDS reaction and HYD route is due to a decrease of its dispersion on niobium-containing support.

Regarding the XYL route, the present study shows a strong increase in rate of the XYL activity on Nb-containing catalysts (table 3). This makes the former proposal on the dispersion highly improbable. Note that the activity increase by a factor of 16 when Mo is added to niobia (table 3), is much larger than the increase of the amount of sulfided niobium in Mo/Nb (by a factor of 3 [7]). Thus, the contribution of the support alone cannot explain the strong increase of XYL activity observed on the Mo/Nb and Mo/NbAl catalysts. Knowing that the electronic properties of the sulfide phase are changed on niobium-containing supports, one wants to link this modification with the increase in activity for the XYL route. According to our previous work on DMA decomposition, the DDN route was claimed to involve highly-sulfur-depleted Mo sites [12]. In this way, the strong enhancement of XYL activity could be interpreted as an easier elimination, under reaction conditions, of edge sulfur atoms from the sulfided Mo phase when deposited on niobia-containing support. Comparison of the XYL activity in presence of H_2S (as in the present work) and in absence of H_2S (not presented here, [23]) supports this hypothesis. In addition, the change of the electronic properties of Mo phase depending on the support suggests a modification in the adsorptive properties of the sulfide phase towards the DMA molecule. The upward CO shift accounts for a lower electron density of the Mo sites. This should lead to a strengthening of the interaction DMA–Mo, which appears to be beneficial for the xylene route.

This electronic effect does not permit to exclude a synergy between the contribution of the Mo sulfide phase and the Nb sulfide (or oxysulfide). This synergic effect could involve the activity of NbS_x for the C–N bond cleavage. However, taking into consideration the selectivity of the bare niobium-containing supports in favor of the hydrogenation route, the high selectivity for XYL in the Mo containing catalysts should come from the Mo sulfide phase in interaction with niobium.

Therefore, this study reveals that the use of niobia-supported catalysts is a way to enhance XYL activity of the Mo sulfide phase. A similar study was performed on Ni-promoted catalysts, which confirms the very high potential for XYL route of HDN of DMA of NiMo catalysts deposited on niobium-containing support.

Hence, this study shows that niobium containing materials are very promising supports for HDT reactions, since these supports are active themselves in HDT and can also enhance intrinsic activity of the sulfide phase. Now, the key point is to develop the surface area of the niobium-containing support. Thus, an improvement of the surface area of the pure niobia or a better coverage of the alumina by the niobia phase is a way to obtain more active and selective hydrotreating catalysts.

5. Conclusions

Acidic properties of niobium-containing supports and pure alumina were compared using IR spectroscopy of adsorbed CO and activity for disproportionation route of DMA decomposition. These two methods agree to show an increase of Brønsted acidity in presence of niobium.

On the Mo sulfide catalysts, an upward shift of the wavenumber of the signal of CO in interaction with the sulfide phase is observed when the Mo phase is deposited on Nb-containing support. This reveals that the support changes the electronic properties of the sulfide phase. This electronic effect is related to a Mo–Nb interaction that can be due to the formation of a mixed Mo–Nb phase, or to a strong interaction between Mo sulfide and Nb-containing support.

The nature of the support also strongly modified the HDS and HDN properties of the Mo sulfide catalysts supported on alumina, niobia and niobia–alumina. For HDS and for HYD route of DMA decomposition, the niobium-containing support strongly contributes to the catalyst activity whereas the activity of the Mo phase per Mo atom decreases with the increase of niobium amount in the support. Conversely, regarding the XYL route of DMA decomposition, the activity of the niobium-containing support is not so marked whereas, in this case, the activity of the Mo phase per Mo atom, when deposited on niobium-containing support, is strongly enhanced. This result shows that the active sites for XYL route are very sensitive to the electronic properties of the sulfide phase. The improvement of the activity on niobium-containing catalysts is attributed to an enhancement of the strength of the interaction Mo sites – DMA. A synergetic effect between the Mo and Nb sulfide phases is also suggested.

It should be pointed out that the development of catalysts with good HDN activity and lower hydrogen consumption, as would be provided by the XYL route, is of great interest to the petroleum refining industry.

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