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A refinement on the notion of type I and II (Co)MoS phases in hydrotreating catalysts

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The influence of Mo content on thiophene hydrodesulfurization for alumina- and carbon-supported (Co)Mo catalysts is investigated by TPR, XPS and H_2-D_2 equilibration. Activity trends for alumina-supported catalysts are explained by a gradual change of the type I MoS_2 active phase from a large to a small number of Mo-O-Al anchors. A pure type II phase without such anchors and a high HDS activity is only obtained employing chelating ligands or a carbon support. At low Mo loading a separate oxysulfidic Mo species in strong interaction with alumina exhibits an unexpectedly high HDS activity, which, however, is difficult to promote by Co.

KEY WORDS: hydrodesulfurization; thiophene; MoS_2; CoMoS; XPS; TPR; support interaction.

1. Introduction

The effect of metal loading, *i.e.*, Mo(W) and Co(Ni), on the structure and activity of hydrotreating catalysts has been the subject of numerous studies [1–12]. Alumina is the preferred support, although activated carbons also show excellent activities per gram of catalyst. The state and dispersion of the Mo sulfide phase is an important parameter. For alumina-supported Mo, it is generally found that the metal is more difficult to sulfide at the lowest loadings [1,5,6,11]. This stems from the strong interaction of Mo with the alumina basic hydroxyl groups in the oxidic precursor. After sulfidation, Mo sulfide species remain bonded to the alumina surface *via* Mo-O-Al linkages decreasing the HDS activity [13]. It is usually assumed that the MoS_2 dispersion is hardly affected when the loading is below the one corresponding to the monolayer adsorption capacity. Above this, separate MoO_3 entities are formed, resulting in bulk-like MoS_2 phases after sulfidation [14,15].

Extensive research has produced strong indications that in alumina-supported (Co)Mo sulfide there are at least two different “Co-Mo-S”-type phases: a type I phase, which is not fully sulfided, contains some Mo-O-Al linkages with the support, and a type II phase, which is fully sulfided, exhibiting only a weak Van-der-Waals interaction with the alumina. This was first noted by Candia *et al.* [16], who found a substantial higher specific (*i.e.*, per Co in “Co-Mo-S”) activity for an η-alumina-supported CoMo catalyst sulfided at 873 K (type II) than for its counterpart sulfided at 673 K (type I). Later, it was discovered that the use of the chelating ligand NTA [17] or other ligands [17–19] can induce the type I to type II transformation. Mössbauer emission spectroscopy studies indicate that the chemical state of Co remains unchanged in both phases [17,20,21]. Interestingly, HDS activities of catalysts supported by activated carbon materials are substantially higher than in the alumina case. The increased performance of the application of complexing agents has been ascribed not only to the absence of strong Mo-carbon interactions [17,20], but also to a change in the sulfidation order of Mo and the promoter elements [18,19].

Currently, there appears to be no clear definition of type I and II Mo-sulfide phases. Part of the confusion is due to the fact that one has to rely on activity comparisons, since there is no characterization technique that can unequivocally differentiate between the two types, although there have been some suggestions that EXAFS can [22]. While most authors agree that full Mo sulfidation is a necessary prerequisite for the occurrence of type II MoS_2, there is no agreement whether this should manifest itself in more extensive stacking of the MoS_2 slabs as observed by TEM. Recent results indicate that the stacking in highly-active carbon-supported MoS_2 is quite low [12,23] and there have been claims of the formation of type II “NiMoS” phases with hardly any stacking. Here, we try to obtain new insights into these matters by studying the influence of the Mo loading on the active phase development and the resulting HDS performance. TPR is used to study the oxidic precursors, while XPS gives insight in the sulfidation degree of the activated samples. Atmospheric gas-phase thiophene HDS is used as a model reaction for hydrodesulfurization and H_2-D_2 equilibration for studying hydrogen activation over the sulfided catalysts and determining the amount of exchangeable hydrogen atoms of the support [24].

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2. Experimental

2.1. Catalyst preparation

A suite of eight Mo/Al_2O_3, eight $CoMo/Al_2O_3$, six CoMo-NTA/Al_2O_3 and six CoMo-NTA/C with varying Mo loading and constant Co/Mo ratio (Co/Mo = 0.3) were prepared. Alumina (Ketjen CK-300, s.a. 263 m^2 g; p.v. 0.66 ml g) and activated carbon (Norit RX-3 Extra, s.a. 1190 m^2 g; p.v. 1.0 ml g) were employed (sieve fraction: 125–250 μm). The alumina support was calcined for 2 h at 573 K and dried overnight at 383 K before impregnation. The carbon support was only dried overnight at 383 K. Transition metals were introduced by incipient-wetness impregnation. Alumina-supported Mo was obtained by impregnation with an ammoniacal solution of ammoniumheptamolybdate (AHM, Merck, >99%) of appropriate concentration. In order to prepare alumina-supported CoMo, an aqueous impregnation solution containing 5% H_2O_2, AHM, and $Co(NO_3)_2{\cdot}6H_2O$ (Merck, >99%) of appropriate concentration was applied. After impregnation, the catalysts were dried in air for 16 h at 383 K and calcined in static air for 2 h at 723 K after heating in 1 h to this temperature. Both alumina- and carbon-supported CoMo-NTA samples were prepared by impregnation with an ammoniacal solution containing AHM, $Co(NO_3)_2{\cdot}6H_2O$ and nitrilotriacetic acid (NTA, Acros >97%, 1.2 mol NTA/mol Mo), followed by drying in air for 16 h at 383 K. Additionally, one alumina-supported Mo-NTA sample was prepared according to the same procedure. Two catalysts were prepared by sequential addition of a Co nitrate solution to Mo(1.2)/Al and Mo(10.3)/Al, followed by drying in static air for 16 h at 383 K. These catalysts are denoted as Co-Mo(1.2)/Al and Co-Mo(10.3)/Al. A special sample denoted as Mo(2.9E)/Al was prepared by extracting weakly bound Mo from 6.7 wt% Mo/Al with 100 ml 0.1 M $(NH_4)_2SO_4$ for 4 h during continuous shaking [25]. The catalyst was then dried according to the above-mentioned procedure. The amount of non-extracted Mo was determined by AAS. Also, two carbon-supported Mo catalysts were prepared, one with and one without NTA. Catalysts will be denoted as follows: [Co]Mo-[-NTA](L)/S with Co and NTA being optional, S being the support (C for carbon and Al for alumina), and L being the Mo loading in wt%. The metal contents of all catalysts was checked by AAS. In the case of NTA catalysts, the metal loading is corrected for the presence of the NTA. Here, we note that 5 wt% Mo corresponds to a surface loading of 1.19×10^{14} Mo atoms/cm^2.

The catalysts were sulfided in an H_2S/H_2 mixture (Hoekloos, 10% H_2S). The gas flow was kept at 60 N ml/min, while heating the catalyst at a rate of 6 K/min (2 K/min in the case of NTA) to 673 K. The temperature was then kept at 673 K for 2 h. After sulfidation, the catalyst was exposed to a mixture of 3.33 kPa thiophene and 1 kPa H_2S in hydrogen at a total gas flow rate of 100 N ml/min (standard conditions) at 673 K. After a stabilization period of 13 h activity measurements were started at a temperature of 623 K.

2.2. X-Ray photoelectron spectroscopy (XPS)

XP spectra were obtained with a VG Escalab 200 spectrometer equipped with an Al K_α source and a hemispherical analyzer connected to a five-channel detector. Measurements were carried out at 20 eV pass energy. Charging was corrected by using the Al 2p peak at 74.4 eV or the C 1s peak at 286.6 eV as a reference. Calcined and sulfided samples were ground and pressed in indium foil, which was placed in an iron stub in an N_2-flushed glovebox (H_2O and O_2 concentrations below 1 ppm). Subsequently, the samples were transferred to a vessel for transport under N_2 to the XPS apparatus. XP spectra were fitted with XPSPEAK (version 3.1). A Shirley background subtraction was applied and Gauss–Lorentz curves were used. S : Mo ratios were calculated using the method of Briggs and Seah [26]. The mean free path of the electrons was calculated using the formula of Tanuma [27]; MoS_2 was used as most stable phase. Cross-sections were obtained from Scofield [28].

2.3. Temperature-programmed reduction (TPR)

Catalysts were first oxidized in an O_2/He mixture (4% O_2 in He) by heating at a rate of 5 K/min to 723 K and keeping this temperature for 1 h. Subsequently, the catalysts were cooled to room temperature in flowing N_2. Temperature-programmed reduction (TPR) was performed by heating the sample at a rate of 5 K/min to 1073 K in an 8 ml/min H_2/N_2 flow (4% H_2 in N_2). The sample was then kept at this temperature for 1 h.

2.4. Reactivity evaluation

Atmospheric thiophene hydrodesulfurization was carried out in a single-pass microflow reactor that has been described in detail elsewhere [29]. In a typical experiment, an amount of catalyst was sulfided and subsequently exposed to the reactant mixture with a total flow of 100 N ml/min (composition: 3.33×10^3 Pa thiophene, 1×10^3 Pa H_2S, make-up H_2) at 673 K for 12 h. After cooling to 623 K, a steady-state activity was obtained, allowing the calculation of the intrinsic reaction rate, *i.e.*, per mol Mo. Analysis of all products is performed by gas chromatography (column: CP-SIL 5 CB).

A detailed description of the recirculation apparatus and relevant procedures for the H_2–D_2 equilibration reaction are available in ref. [24]. In short, an amount of catalyst is sulfided and after cooling to 423 K exposed to a mixture of H_2 and D_2 in Ar in recirculation mode. H_2, D_2 and HD are quantitatively analyzed by an online mass spectrometer.

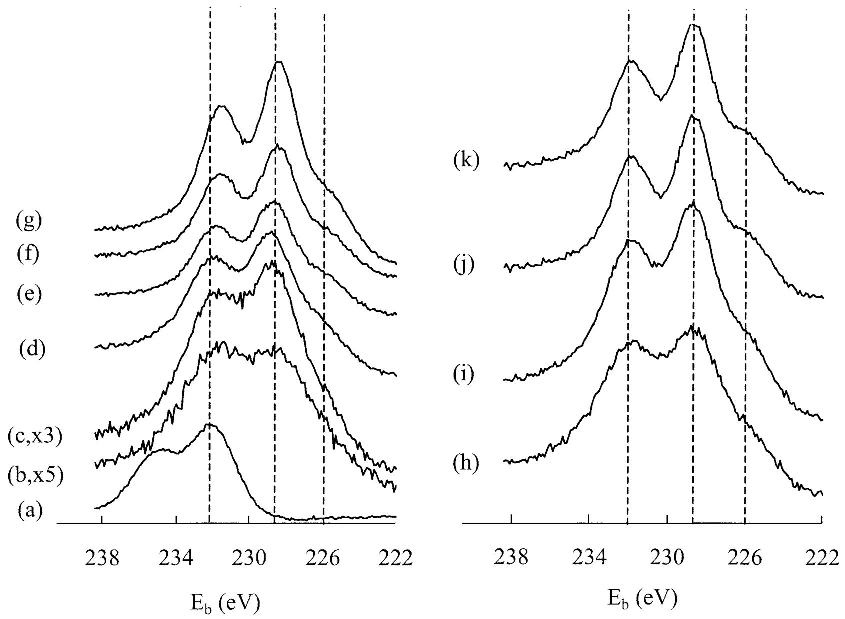

Figure 1. XP spectra of the Mo 3d envelope of Mo/Al and CoMo/Al catalysts (sulfided at 673 K unless stated otherwise): (a) calcined Mo(10.3)/Al, (b) Mo(1.2)/Al, (c) Mo(2.6)/Al, (d) Mo(4.9)/Al, (e) Mo(6.7)/Al, (f) Mo(10.3)/Al, (g) Mo(14.0)/Al, (h) CoMo(2)/Al, (i) CoMo(4.1)/Al, (j) CoMo(6.8)/Al, (k) CoMo(11.3)/Al. The Mo $3d^{5/2}$ lines at 232.0 eV (Mo^{6+}, left) and 228.7 eV (Mo^{4+}, middle) and the S 2s line at 226.0 eV (right) are indicated.

3. Results

Mo 3d XP spectra for calcined Mo(10.3)/Al and sulfided Mo/Al and CoMo/Al samples are presented in figure 1. The change in binding energy of the 3d doublet between the calcined and sulfided catalysts is associated with a change in oxidation state from Mo^{6+} to Mo^{4+} upon sulfidation [30]. This Mo^{4+} oxidation state (Mo $3d^{5/2}$: 228.8 eV) relates to MoS_2 species. The shoulder persistently present at a binding energy of 226.0 eV is the S 2s line. At Mo loadings below 6.7 wt% the spectra have to be fitted with an extra Mo 3d doublet. Sulfate S 2s lines do not have to be included because of the absence of the sulfate peak in the S 2p region [31]. The resulting binding energies (Mo $3d^{5/2}$: 230.2 eV for Mo/Al and 230.5–231.0 eV for CoMo/Al) are indicative of the presence of Mo^{5+} species [5,32]. This intermediate oxidation state reflects the presence of Mo species in an oxysulfidic environment, possibly associated with the alumina support. The width of these peaks (fwhm $\approx$ 3 eV) is larger than those of the Mo^{4+} 3d peaks (fwhm $\approx$ 2 eV), indicating that a variety of Mo^{5+} species is present. XPS fit parameters are collected in table 2. The presence of incompletely sulfided Mo species is corroborated by the plot of the S : Mo ratios as a function of the Mo loading for Mo/Al (figure 2). At low Mo loadings, the S : Mo ratio is below two. In addition, S : Mo^{4+} ratios are in excess of two in this regime, which suggests that the Mo^{5+} species are present in an oxysulfidic environment. The degree of full sulfidation,

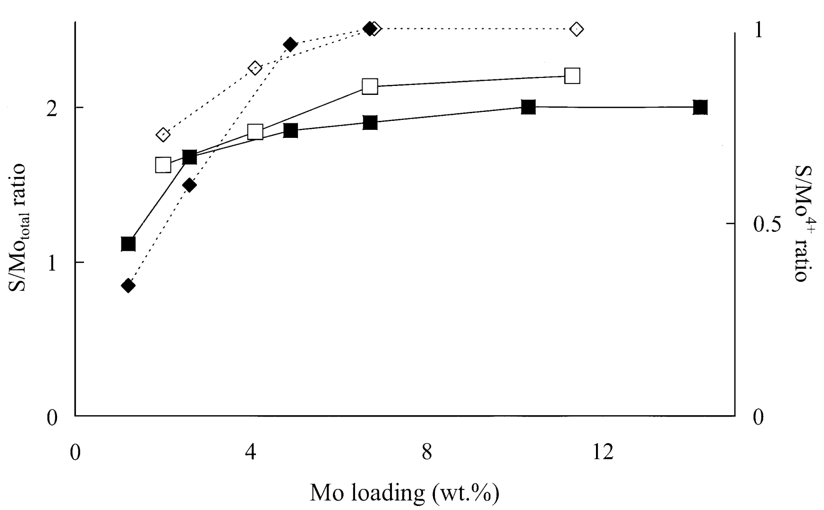

Figure 2. S : Mo (■□, left axis) and S : Mo^{4+} (◆◇, right axis) ratios for sulfided Mo/Al (■◆) and CoMo/Al (□◇).

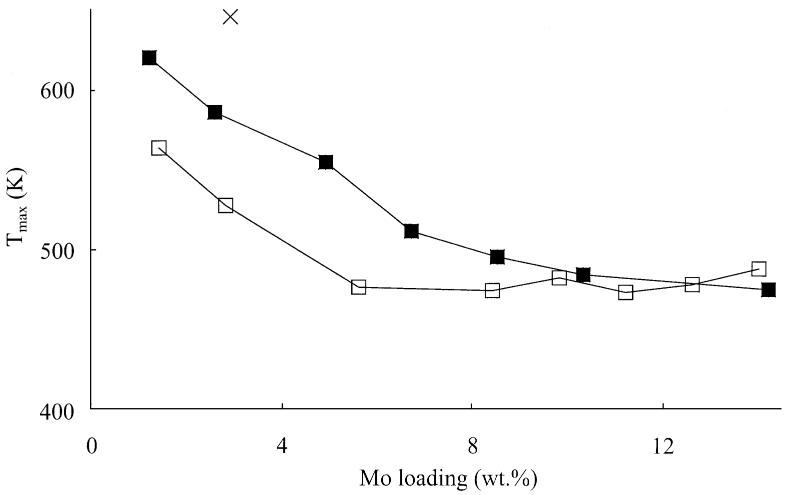

Figure 3. Temperature of the first-peak maximum of temperature-programmed reduction for calcined Mo/Al (■), Mo(2.9E)/Al (×) and CoMo/Al (□).

i.e., the fraction of Mo present in the 4+ oxidation state relative to the total amount of Mo present, is also plotted in figure 2. Clearly, the presence of Co results in a more complete sulfidation at low Mo loadings [13]. Above an Mo content of 5 wt%, sulfidation appears to be complete for (Co)Mo/Al. However, Mo^{5+} species are probably still present in low concentrations as Mo-O-Al linkages, but their relative fraction is too low to discriminate them from the prevailing MoS_2 phase by XPS. Mo 3d XP spectra were also recorded for the sulfided Mo(2.9E)/Al sample, but it proved to be impossible to separate the Mo^{5+} oxidation state from the S 2s state due to the presence of residual sulfate. XP spectra of CoMo(1.1)-NTA/Al, CoMo(2.2)-NTA/Al and CoMo(5.3)-NTA/Al only showed Mo^{4+} species, indicating full Mo sulfidation.

Figure 3 shows the temperature of the dominant peak in the TPR patterns for the (Co)Mo/Al catalysts. This feature is due to the reduction of Mo^{6+} to Mo^{4+} in Mo-oxide species [6]. The shift to lower temperatures with increasing Mo content is explained by the decreasing support interaction. The nearly constant value for T_{max} above 5 wt% Mo for Mo/Al nicely corresponds with the XPS results. This effect is less clear for the promoted catalysts, but this is probably due to the presence of Co. Although a CoO reduction peak cannot be observed at the applied Co:Mo ratios [7], the presence of metallic Co accelerates the reduction of Mo-oxide species. This effect clearly plays an important role in the easier sulfidability of the promoted catalysts. Interestingly, T_{max} for Mo(2.9E)/Al is even higher than for Mo(1.2)/Al, pointing to an Mo-oxide phase that is strongly bonded to the alumina support.

The HDS activities for various alumina-supported Mo-sulfide catalysts as a function of the Mo loading are shown in figure 4. After an initial decrease up to a loading of 5 wt%, there is an increase of the intrinsic activity that levels off. The activities of Mo-NTA(7.6)/Al and especially Mo(2.9E)/Al are substantially higher. The activities of Mo(7.6)/C and Mo-NTA(7.7)/C (not shown) are 3.5 and 3.6 mol/mol h, respectively.

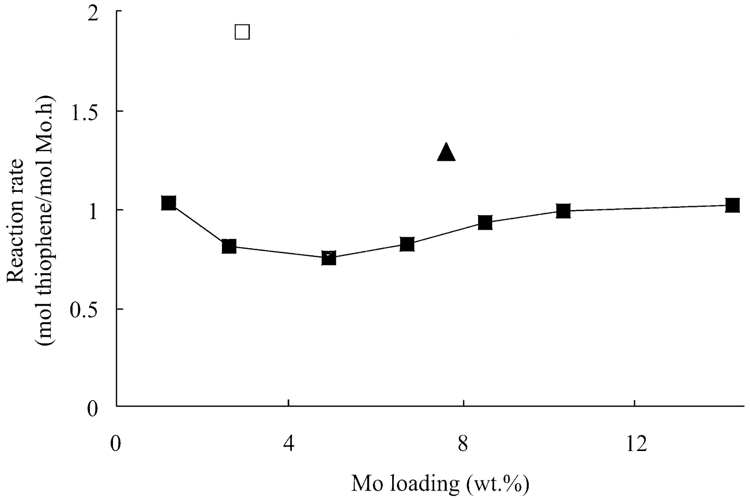

Figure 4. Intrinsic HDS activities as a function of Mo loading for sulfided Mo/Al (■), Mo(2.9E)/Al (□) and Mo-NTA(7.6)/Al (▲). Accuracies in the reaction rate (±0.02 mol/mol h).

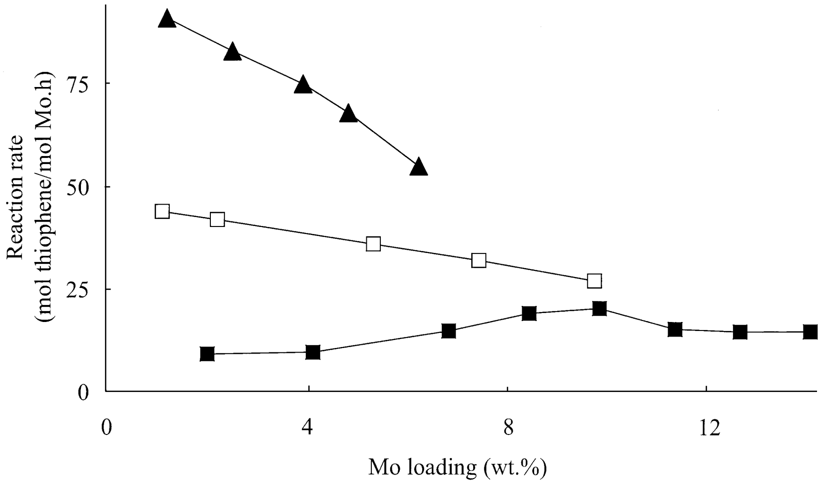

Figure 5. Intrinsic HDS activities as a function of Mo loading for sulfided CoMo/Al (■), CoMo-NTA/Al (□) and CoMo-NTA/C (▲). Accuracies in the reaction rate (±0.05 mol/mol h).

Figure 5 shows the activities for the promoted samples. Obviously, the carbon-supported catalysts are the most active followed by CoMo-NTA/Al and CoMo/Al. Notably, the activities of these catalyst series decrease with increasing Mo content except for CoMo/Al. For this series, there is an optimum at about 10 wt% Mo. Table 1 compares the activities of Mo(1.2)/Al and Mo(10.3)/Al with similar catalysts that were impregnated with cobalt nitrate. Strikingly, the promoter effect for Co-Mo(1.2)/Al is much lower than the one for Co-Mo(10.3)/Al.

Table 1
Intrinsic HDS activities for sulfided (Co-)Mo/Al catalysts.

Catalyst	Intrinsic HDS activity (mol thiophene/mol Mo h)
Mo(1.2)/Al	1.04
Co-Mo(1.2)/Al	3.42
Mo(10.3)/Al	1.02
Co-Mo(10.3)/Al	7.28

H_2–D_2 equilibration was previously used to compare reactivities of Co-sulfide and (Co)Mo-sulfide species on activated carbon [24]. It was found that the activity of Co-sulfide is two orders of magnitude lower than that of Mo-sulfide and CoMo-sulfide. Figure 6 depicts the relation between the HD formation rate and Mo content for various catalysts. These intrinsic activities decrease strongly with Mo content. The activities of CoMo-NTA/C and CoMo-NTA/Al are nearly equal. Furthermore, there is a strong promoter effect comparing Mo/Al and CoMo/Al in line with previous studies [24,32–34]. Mo(2.9E)/Al is significantly more active than Mo/Al. The amount of exchangeable hydrogen atoms initially present on the catalyst (H_0) can be calculated from such exchange experiments [24]. This almost exclusively relates to hydrogen atoms of the support,

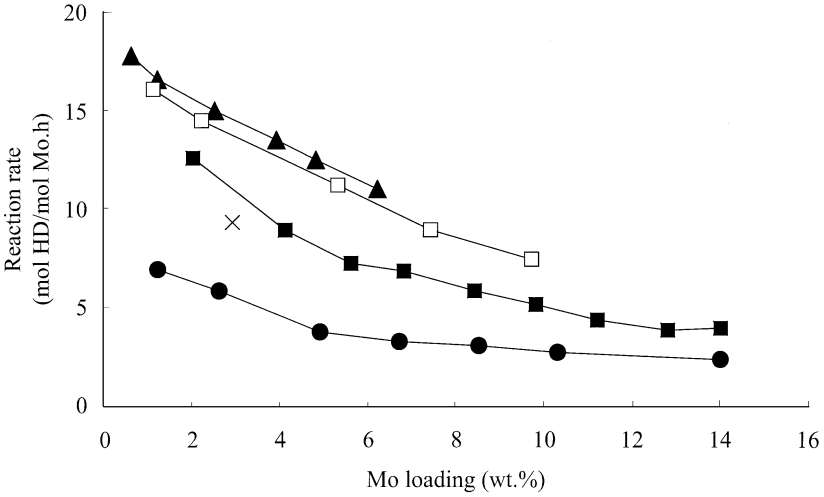

Figure 6. Intrinsic H_2–D_2 equilibration activity as a function of Mo loading for sulfided CoMo/Al (■), CoMo-NTA/Al (□), CoMo-NTA/C (▲), Mo/Al (●) and Mo(2.9E)/Al (×).

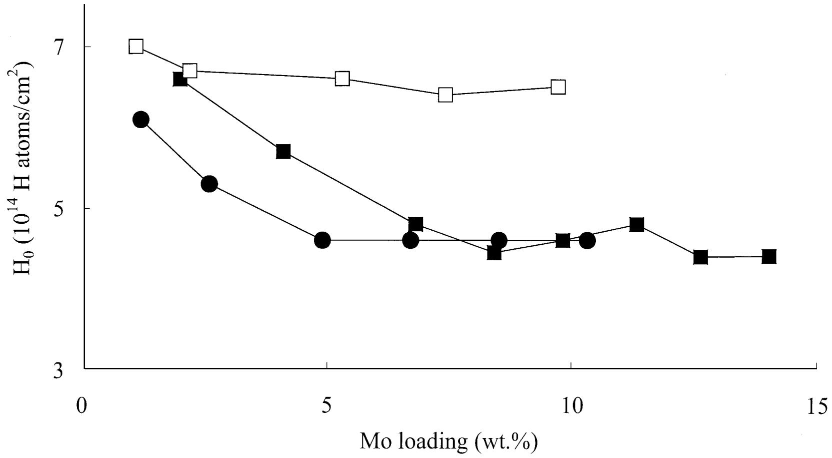

Figure 7. The amount of exchangeable hydrogen atoms (H_0) as a function of Mo loading for sulfided CoMo/Al (■), CoMo-NTA/Al (□) and Mo/Al (●).

although there is some controversy about the way hydrogen is transferred from the support to the gas phase [24,33]. Figure 7 shows the influence of Mo content on H_0 for various alumina-supported catalysts. While for (Co)Mo/Al a strong decrease in this parameter is observed, H_0 is nearly constant for their NTA counterpart.

4. Discussion

The thiophene HDS activities for Mo/Al show a peculiar trend with increasing Mo loading. There are two regimes: (i) starting from low Mo content the activity decreases up to 5 wt% Mo; and (ii) at loadings exceeding 5 wt% Mo the activity increases, levelling off at high loading. XPS indicates that a significant part of Mo is present as oxysulfidic Mo^{5+} species next to an MoS_2 phase in the first regime. Those species are increasingly difficult to sulfide toward lower loading. TPR results corroborate this by showing a strong retardation in reducibility. This derives from the strong support interaction of oxidic Mo^{6+} species in the calcined precursor, which are tetrahedrally coordinated to the alumina support [5]. They originate from the reaction between heptamolybdate and the alumina basic hydroxyl groups [35–37]. This point is underpinned by the value of exchangeable hydrogen atoms (H_0) derived from H_2–D_2 equilibration experiments (figure 7). H_0 decreases up to approximately 5 wt% Mo. The total decrease is calculated to be 2.5×10^{14} H atoms/cm^2 alumina support (after extrapolation of H_0 to zero Mo loading). This value is close to the number of basic hydroxyl groups for this particular alumina support (2.2×10^{14} per cm^2) and we conclude that these hydroxyl groups have reacted with the Mo-precursors. Sulfidation of such species leads to oxysulfidic Mo^{5+} species that remain in strong interaction with the alumina support. This contrasts with the interpretation of Li and Hercules [5] that such species remain oxidic, but we surmise this is due to the higher sulfidation temperatures applied in the present study. At higher loadings Mo-species interact mainly with coordinatively unsaturated Al^{3+} sites [35]. Such species are more easy to sulfide.

It thus appears that Mo^{5+} oxysulfidic species have a quite high intrinsic HDS activity. This is counter to the commonly held notion of lower HDS activities for sulfide species in strong interaction with the alumina support. Such strong Mo-O-Al linkages suppress the HDS activity of MoS_2-type phases. The essential difference is that in those cases these linkages are incorporated into MoS_2 structures. In this respect, it is instructive to note that Mo(2.9E)/Al has a much higher activity than conventional Mo/Al catalysts. The Na_2SO_4 treatment results in the removal of weakly bonded Mo species on coordinatively unsaturated sites [25]. We thus ascribe the high activity to the almost exclusive presence of highly active Mo^{5+} oxysulfidic species. Indeed, TPR measurements indicate that the reduction temperature for this catalyst has further increased. Unfortunately, XPS results are not conclusive due to the interference of adsorbed sulfate. On the other hand, the presence of sulfate may have induced some acidity with a possible positive influence on activity. Interestingly, Reinhoudt *et al.* [38] recently identified a type 0 "Ni-W-S" phase which is made up of small NiS_X species in close contact with an oxysulfidic W phase. We propose that the Mo oxysulfidic species can also be regarded as a separate phase. However, these species are only stable in a small Mo loading range due to more facile sulfidation for Mo relative to W. A recent detailed TEM study on Mo-based hydrotreating catalysts [39] revealed the presence of subnanometer particles with a morphology different from the well-known MoS_2 slabs. We surmise that such particles are the oxysulfidic Mo species. Despite the higher Mo loading applied by Kooyman *et al.* [39], a moderate sulfidation temperature allowed the persistence of these species.

Table 2
XP fit parameters for alumina-supported CoMo catalysts.

Catalyst		Calcined state		Sulfided state	
		E_b (eV)	A (a.u.)	E_b (eV)	A (a.u.)
Mo(1.2)/Al	Mo $3d^{5/2}$	232.7	0.054	228.8	0.040
				230.2	0.077
	S $2p^{3/2}$	–	–	161.8	0.025
Mo(2.6)/Al	Mo $3d^{5/2}$	–	–	228.8	0.133
				230.2	0.089
	S $2p^{3/2}$	–	–	162.1	0.075
Mo(4.9)/Al	Mo $3d^{5/2}$	–	–	228.8	0.389
				230.2	0.017
	S $2p^{3/2}$	–	–	162.1	0.149
Mo(6.7)/Al	Mo $3d^{5/2}$	–	–	228.7	0.560
	S $2p^{3/2}$	–	–	161.9	0.212
Mo(10.3)/Al	Mo $3d^{5/2}$	232.8	1.14	228.8	0.803
	S $2p^{3/2}$	–	–	161.7	0.311
Mo(14.2)/Al	Mo $3d^{5/2}$	232.8	1.66	228.8	1.070
	S $2p^{3/2}$	–	–	161.7	0.428
CoMo(2.0)/Al	Mo $3d^{5/2}$	232.8	0.041	228.8	0.140
				231.0	0.052
	Co $2p^{3/2}$	–	–	780.1	0.039
	S $2p^{3/2}$	–	–	162.0	0.063
CoMo(4.1)/Al	Mo $3d^{5/2}$	–	–	228.8	0.331
				230.5	0.056
	Co $2p^{3/2}$	–	–	779.3	0.132
	S $2p^{3/2}$	–	–	162.0	0.138
CoMo(6.8)/Al	Mo $3d^{5/2}$	–	–	228.7	0.702
	Co $2p^{3/2}$	–	–	780.1	0.359
	S $2p^{3/2}$	–	–	162.0	0.298
CoMo(11.3)/Al	Mo $3d^{5/2}$	232.8	1.03	228.7	1.120
	Co $2p^{3/2}$	–	–	780.0	0.649
	S $2p^{3/2}$	–	–	162.0	0.502

The intrinsic HDS activity increases again at Mo contents exceeding 4.9 wt%. Both XPS and TPR indicate easier sulfidation to be explained by more loosely bonded polymolybdate species. We envisage that the Mo^{5+} species end up in the MoS_2 structures (possibly acting as nucleation centers) and form the well-known Mo-O-Al linkages. This suppresses the activity of the resulting MoS_2 structures. With increasing Mo content, the fraction of these Mo-O-Al linkages in the MoS_2 structures will decrease, which translates to higher intrinsic HDS activities. The activities of the Mo/Al series are to be compared to that of Mo-NTA(7.6)/Al. This catalyst contains a fully sulfided MoS_2 phase and exhibits a higher activity than Mo/Al in line with the difference between CoMo-NTA/Al and CoMo/Al [17]. This strongly suggests that for Mo/Al catalysts there remains an interaction between the MoS_2 phase and the support. H_2–D_2 equilibration activities show a strong decrease up to Mo contents of 4.9 wt% followed by a smaller decrease for higher loadings. The initial strong decrease is attributed to the decreasing fraction of oxysulfidic species, which have a high exchange activity. This is underpinned by the high activities of Mo(2.9E)/Al and Mo(1.2)/Al in the oxidic state (39 mol HD/mol Mo.h). The less pronounced decrease at higher loadings most probably relates to the slight decrease in MoS_2 dispersion with increasing loading. The essential point is that the active phase in this regime is made up by MoS_2 particles.

In essence, these results indicate that type II phase MoS_2 can only be obtained by applying a chelating ligand for alumina-supported catalysts. In other cases, Mo-O-Al linkages are formed which end up in MoS_2 structures at industrially applied loadings. These structures are qualified as type I phase MoS_2. The important notion of the present study is that this latter type I phase covers a whole range of MoS_2 structures with the number of Mo-O-Al linkages as an extra parameter. In general, this number will decrease with increasing loading. However, based on activity differences between Mo/Al and Mo-NTA/Al we surmise that even at the highest loading a substantial amount of Mo-O-Al linkages exist. More severe sulfidation at elevated temperatures may also induce full Mo sulfidation and type II phases, but normally this results in a dramatic loss in dispersion [40].

XPS data on the promoted samples show a similar behavior. At low Mo content, Mo sulfidation is not complete albeit the sulfidation degree is higher in this case due to the presence of Co. Comparing the intrinsic HDS activity trends for Mo/Al and CoMo/Al, one notes that in the latter case there is no increase in activity with decreasing Mo content. There are several possible explanations. First, Co may end up in inactive Co structures [7] which will have a greater effect at low Mo content. However, Scheffer *et al.* [41] concluded that all Co atoms are sulfidable as long as calcination temperatures do not exceed 785 K, and Candia *et al.* [42] showed that less than 10% of Co ends up in inactive structures. Van Veen *et al.* [43] advanced that it is more likely that Co forms bulk sulfides than finding MoS_2 to form "Co-Mo-S" phases at low metal loading. Another explanation is that isolated tetrahedral Mo species are still present, but their activity is much lower than that of the promoted MoS_2 particles. This point is stressed by comparing Co-Mo(1.2)/Al and Co-Mo(10.3)/Al with their unpromoted counterparts. The promotion effect for Mo(10.3)/Al is much higher than for Mo(1.2)/Al, suggesting that Co is not able to promote isolated Mo^{5+} species. Similar to the Mo/Al case, the intrinsic activity for CoMo/Al increases with metal loading due to a decreasing influence of Mo-O-Al linkages. CoMo-NTA/Al catalysts show a much higher activity in line with the results for Mo/Al and the literature [17]. There is also a clear promotion effect for H_2–D_2 equilibration which was noted before [24]. Also, the decrease for CoMo/Al is qualitatively similar to the behavior of Mo/Al.

The groups of Prins [18] and Niemantsverdriet [19] have proposed an alternative explanation for the higher activity of catalysts prepared in the presence of complexing agents. Such agents retard sulfidation of the promoter element. EDTA is an even more efficient agent than NTA since it retards Co sulfidation until the moment of complete Mo sulfidation [19]. The authors suggest that the use of complexing agents is a prerequisite for the formation of highly active "Co-Mo-S" phases instead of segregated Co-sulfide strutures. The present set of data unequivocally shows that complexing agents also induce increased activities for promoter-free catalysts by decreasing metal–support interactions. We strongly believe that both processes are operative. The carbon support provides a case in which metal–support interactions are absent. Thus, we indeed found that NTA has no effect on the activity for carbon-supported Mo (comparing Mo(7.6)/C and Mo-NTA(7.7)/C) but strongly increases the performance of carbon-supported CoMo catalysts [17]. In the literature, often a twofold difference in activity is mentioned between NTA-based and conventional CoMo catalysts [17]. Our results show that this difference strongly depends on the Mo loading. The decrease in activity of CoMo-NTA/Al and CoMo-NTA/C with increasing loading must be due to a decreasing MoS_2 dispersion with increasing loading. The notion of the type I phase in hydrotreating catalysts needs to be refined in the sense that it covers a whole range of phases with the number of Mo-O-Al linkages as an extra parameter.

5. Conclusions

The presence of type I and II MoS_2 structures in hydrotreating catalysts has been investigated in more detail. Clearly, type II phases can only be obtained by suppressing Mo-support interactions, which can be efficiently achieved by using an inert support material or a complexing agent. Type I phases are defined as MoS_2 crystallites in strong contact with the alumina support through Mo-O-Al linkages. In essence, type I MoS_2 covers a wide range of phases with the number of Mo-O-Al linkages as an additional parameter. After conventional preparation, the number of such linkages decreases with increasing Mo loading, resulting in a higher HDS activity. Unexpectedly, we found that a difficult to sulfide species—most probably a strongly bonded tetrahedral Mo oxysulfidic species—exhibits a high intrinsic HDS activity, albeit Co does not promote such species.

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