Sulfidability and Hydrodesulfurization Activity of Mo Catalysts Supported on Alumina, Silica, and Carbon

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The sulfidability and hydrodesulfurization (HDS) activity of Mo catalysts supported on SiO_2, carbon and Al_2O_3 have been studied. The results are interpreted on the basis of differences in dispersion, and interaction of the Mo species with the support. Crystalline MoO_3 with a low dispersion is relatively difficult to sulfide. Large MoO_3 crystallites are found on some Mo/SiO_2 catalysts, which necessitates sulfiding above 670 K. The HDS activity of these catalysts is low because the dispersion of the sulfided species is also low. On all supports highly disperse oxidic species are readily sulfidable. On carbon microcrystalline MoS_2 is formed which is highly active for HDS. The carbon support is not gasified during sulfiding. Also on SiO_2 an easily sulfided species displays high HDS activity. Al_2O_3-supported Mo catalysts are more difficult to sulfide, because of the strong interaction with the support. It is found that two oxidic Mo species are present on Al_2O_3, but only one (a bilayer species) is a precursor to a highly active sulfided species. The monolayer species has a much smaller HDS activity when sulfided. A good correlation is found between the reducibility of oxidic species and their HDS activity with the support. A strong interaction decreases the covalent character of the Mo–S bond, resulting in a lower activity. © 1988 Academic Press, Inc.

INTRODUCTION

Mo is an essential part of commercial hydrodesulfurization (HDS) catalysts such as Ni–Mo/Al_2O_3 and Co–Mo/Al_2O_3. Furthermore, Mo without a promoter can have a high activity as well, when it is supported on a carbon carrier (1, 2). It is therefore of importance to investigate which factors determine the HDS activity of Mo catalysts.

Since the catalysts are sulfided to obtain their active form, insight into the relationships between species in the oxidic and in the sulfided catalysts can contribute to the understanding of the structure of Mo catalysts. It has been shown that temperature-programmed sulfiding (TPS) is a valuable tool in the study of the sulfiding of Mo/

Al_2O_3 (3), Co/Al_2O_3 (4), and Co–Mo/Al_2O_3 (5) catalysts. TPS is applied here to the sulfiding of Mo catalysts with different loadings and on different supports.

The catalysts used in this work have been studied previously in their oxidic form, and several Mo species have been identified. The abundance of the species depends on the Mo loading, temperature of calcination, and support used (6); the results of the investigations on the oxidic catalysts are of assistance in the interpretation of the observed rates of sulfiding, and they make it possible to deduce which species are the precursor to sulfided species with a high activity for HDS.

EXPERIMENTAL

Materials

A detailed description of the preparation of the catalysts is given elsewhere (6, 7). Mo catalysts were prepared via pore vol-

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516

Catalyst	Temperature of calcination (K)	HDS QTOF (mmol/mol · s)
Mo(2.5)/Al	675	1.1
Mo(2.5)/Al	785	1.3
Mo(2.5)/Al	895	1.1
Mo(2.5)/Al	995	0.9
Mo(0.8)/Al[a]	1125	1.8
Mo(2.5)/Al[b]	675	0.9

[a] Corrected for Mo loss during calcination.

[b] Sulfided at 875 K instead of 675 K.

ume impregnation using solutions of $(NH_4)_6$ $Mo_7O_{24} \cdot 6H_2O$. The Al_2O_3- and SiO_2-supported catalysts were calcined in air at 825 K unless otherwise indicated. The carbon-supported catalyst was only dried at 385 K (2).

Catalysts will be denoted as Mo(x)/y where x represents the Mo content expressed as the number of Mo atoms per square nanometer of support, and y represents the support used, viz., Al, Si, and C for Al_2O_3, SiO_2, and activated carbon, respectively. The catalysts are listed in Table 1.

Surface Area

Surface area and pore size distribution were determined from N_2 adsorption–desorption isotherms using a Carlo Erba 1800 Sorptomatic instrument.

Temperature-Programmed Sulfiding

More complete information on the temperature-programmed sulfiding technique is given elsewhere (3, 5). At the beginning of the TPS experiment the sulfiding mixture (3.3% H_2S, 28.1% H_2, and 68.6% Ar) is led through the reactor at ca. 295 K and the composition of the gas leaving the reactor is monitored. When no further sulfiding or adsorption takes place at 295 K the tempera-

ture of the reactor is raised continuously by 10 K/min up to ca. 1270 K.

HDS Activity

Thiophene HDS was carried out in a flow microreactor operating at 1 bar. Details of the equipment are given elsewhere (8). The catalysts were sulfided in situ in a 10 mol% H_2S/H_2 mixture (flow rate 45×10^{-6} mol/s). The temperature was raised to 675 K (or 875 K in one case) and maintained for 2 h. Subsequently a 6.2 mol% thiophene/H_2 mixture was fed into the reactor at a total rate of 37×10^{-6} mol/s at 675 K. After 2 h on stream the conversion of thiophene was determined. The activity has reached a stable level after this time (9).

The activity of an active site can be expressed by its turnover frequency (TOF). For the Mo catalysts studied the number of active sites is not known a priori, and therefore in the first instance it is assumed that all Mo ions are active so that activity is expressed as a quasi turnover frequency (QTOF), as has been done for other Mo catalysts (1, 10). The QTOF can be easily calculated from a rate constant. To obtain a meaningful rate constant the kinetic equation appropriate for the test conditions should be applied. Previously it has been assumed that under the conditions used here the reaction is first order in thiophene (10, 11), but for the present discussion it is necessary to verify the assumption. It has been noted that the HDS of thiophene over Mo/Al and of benzothiophene over Co–Mo/Al catalysts is inhibited by H_2S, and to a smaller extent by thiophene (12–14). Massoth and Chung (15) have derived an expression using Langmuir–Hinshelwood kinetics which takes into account the adsorption of H_2S. When written in another form it is also known as the Frost equation (16, 17). By extrapolation of published data for the kinetics of thiophene HDS over Co–Mo/Al catalysts (18, 19) to 675 K it is calculated that the effect of H_2S adsorption and inhibition is negligible at this temperature. Therefore under these conditions thiophene

HDS can be described as a simple first-order reaction *(20–23)*.

RESULTS

Surface Area

The surface areas of the supports were determined from BET plots and are listed in Table 2. After calcination at 825 K the surface area of Mo/Al and Mo/Si catalysts was essentially the same as the area of the supports. After calcination at 1125 K the surface area of the Mo(2.2)/Al catalysts was reduced to 44 m^2/g Al_2O_3 and the average pore radius was increased to 20 nm.

The carbon support has a large fraction of micropores. From adsorption–desorption isotherms the pore volume of the micropores are measured, and assuming the pores are cylinder-shaped, it is calculated that ca. 85% of the total surface area is located in the micropores.

Temperature-Programmed Sulfiding

The TPS patterns of Mo/C, Mo/Al, and Mo/Si catalysts are shown in Fig. 1. H_2O and H_2 partial pressures were also determined, but for clarity only the H_2S pressure is plotted. Patterns of Mo/Al catalysts with different Mo loadings have been published elsewhere *(3)*.

In general the TPS patterns of the catalysts can be divided according to the temperature at which the sulfiding processes occur:

—H_2S uptake at room temperature. The H_2S at room temperature is largely caused

TABLE 2

Surface Area and Average Pore Size of Catalyst Supports Applied

Support	BET surface area (m^2/g)	Average pore radius (nm)
Al_2O_3	213	4
SiO_2	360	5
Carbon	1350[a]	2

[a] About 85% of surface area located in micropores (radius < 1 nm).
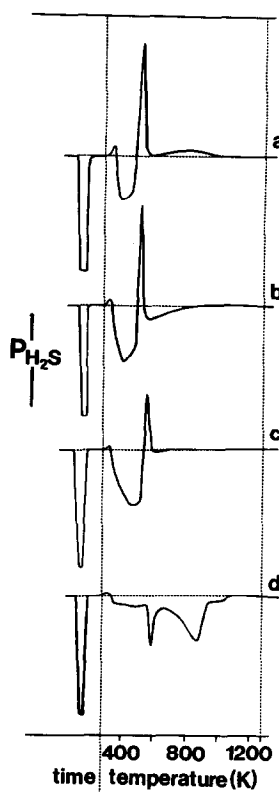

FIG. 1. TPS patterns of Mo catalysts: (a) Mo(0.8)/C, (b) Mo(2.5)/Al, (c) Mo(0.4)/Si, (d) Mo(4.1)/Si.

by physical adsorption because H_2S desorption is observed when the temperature is raised. Also, sulfiding takes place at room temperature because changes in color are seen for the Mo/Si and Mo/Al catalysts when they are exposed to the sulfiding gas.

—H_2S uptake and H_2O production up to ca. 500 K ("region 1"). In region 1 sulfiding of Mo proceeds through oxygen–sulfur exchange, i.e., no H_2 is consumed in this region, but reduction of Mo can occur by the breaking of bonds between sulfur and Mo (oxy-) sulfides, with the formation of sulfur *(3)*.

—H_2S production and H_2 consumption at ca. 500 K. At ca. 500 K, H_2S is produced by the hydrogenation of sulfur, which is formed by the reduction of Mo as described above *(3)*.

—H_2S uptake and H_2O production from 550 K up to ca. 1100 K ("region 2"). In

region 2 only a small H_2 consumption is found, which indicates that reduced Mo species are sulfided through oxygen–sulfur exchange (3).

The Mo/C catalyst is completely sulfided in region 1 (Fig. 1a), and sulfiding is followed by hydrogenation of the sulfur formed by the reduction of Mo. The carbon support is inert toward hydrogenation during TPS, also at elevated temperatures, in contrast with TPR, where gasification is observed (6).

For Mo/Al catalysts sulfiding is observed in region 1, and up to ca. 1000 K in region 2 (Fig. 1b). The H_2S production peak is superimposed on the broad H_2S consumption pattern. TPS results on Mo/Al catalysts are discussed in detail elsewhere (3).

The Mo(0.4)/Si catalyst is completely sulfided at room temperature and in region 1 (Fig. 1c), and hydrogenation of sulfur follows at 570 K. In the TPS pattern of the Mo(4.1)/Si catalyst H_2S uptake in regions 1 and 2 (Fig. 1d) is seen. About 75% of the H_2S consumption takes place in region 2. No H_2S production peak is visible but a large H_2 consumption is found at ca. 520 K which indicates that reduction takes place.

Quantitative TPS results show that Mo/C and Mo(0.4)/Si are completely sulfided at 675 K. The H_2S uptake corresponds to MoS_2 stoichiometry. For Mo/Al the S/Mo ratio is slightly below 2 even at ca. 1000 K (3).

HDS Activity

Products detected during the HDS test were 1-butene, cis- and trans-butene, butane, and H_2S, in accordance with other findings under the same conditions on Co–Mo/Al catalysts (8). HDS activities of Mo/Al catalysts are listed as a function of the temperatures of calcination and sulfiding in Table 1. The effect of Mo loading on Si- and Al-supported catalysts is shown in Fig. 2. For Mo/Al the QTOF increases up to loadings of ca. 4.5 at/nm². The same has been observed for similar catalysts elsewhere
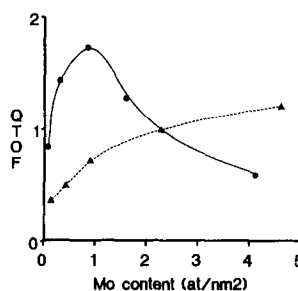

FIG. 2. HDS activity expressed as QTOF of Mo catalysts as a function of Mo loading. (▲) Mo/Al; (●) Mo/Si; (---) calculated from Eq. (1).

(24, 25). The QTOF of Mo/Al does not vary greatly with a rise in the temperature of calcination up to 995 K (Table 1). After calcination at 1125 K loss of Mo has been observed (7). When the QTOF is corrected for this loss a significantly higher QTOF value is obtained than that for the lower temperatures of calcination. At a higher temperature of sulfiding (875 K) a drop in activity of ca. 20% is observed.

For Mo/Si catalysts a maximum QTOF is observed at ca. 1 at/nm² which is higher than the corresponding QTOF of Mo/Al (Fig. 2) (10). At higher loadings the QTOF decreases, in accordance with previous results (9).

The Mo/C data are reported by Vissers et al. (2). For Mo/C the QTOF is very high at low loadings, but drops at loadings higher than ca. 0.5 at/nm² (1, 2).

DISCUSSION

TPS

The catalysts which were subjected to TPS have been studied in their oxidic form by temperature-programmed reduction (TPR) and differential scanning calorimetry (DSC) and from these techniques both qualitative and quantitative information concerning the species present has been derived (6). These results are used to clarify the effects of dispersion and interaction with the support which can be discerned in the TPS patterns (3). From TPS studies on bulk and Al_2O_3-supported MoO_3 (3) and

CoO (4, 5) it is known that sulfidability depends on dispersion, and on the interaction with the support. For samples with a low dispersion (viz., nonporous MoO_3 crystallites larger than ca. 10^{-6} m) the rate of sulfiding is determined to a large extent by mass-transfer limitations; a sulfide layer is formed around an oxidic core and the diffusion of H_2S is relatively slow (3). Obviously, in highly disperse samples this limitation is absent, and the sulfiding rate is influenced by the interaction with the support. In TPS the interaction with the Al_2O_3 support can be recognized as an H_2S consumption over a large temperature range.

Mo/Si. The Mo(0.4)/Si catalyst contains a highly disperse Mo^{6+} monolayer surface phase (6, 26). In agreement with the high dispersion found with TPR and DSC, TPS shows that sulfiding of this catalyst is rapid so that no mass transfer limitations are apparent. The shape of the TPS pattern and the absence of sulfiding in region 2 confirm that there is no strong interaction with the SiO_2 support.

The oxidic Mo(4.1)/Si catalyst contains both the highly disperse Mo species and MoO_3 crystallites (6, 27). The TPS pattern differs from the pattern of the catalyst with the lower loading in that a large H_2 consumption is seen before sulfiding in region 2 occurs. These characteristics resemble the TPS result on bulk MoO_3, which is reduced to MoO_2 before sulfiding in the TPS experiment (3). Therefore, the TPS pattern confirms that MoO_3 crystallites are present, and reduction of MoO_3 occurs prior to sulfiding because the diffusion of H_2S into the crystallite is limited by a sulfidic shell. The resulting TPS pattern is composed of the pattern of crystalline MoO_3, and of the surface phase for which the TPS pattern is known from the Mo(0.4)/Si catalyst. The amount of H_2S consumed in region 2 is in accordance with the amount of crystalline MoO_3 determined with DSC and TPR (6).

TPS shows that the oxidic Mo surface phase is readily sulfided at low temperatures, and it is likely that a disperse sulfided

monolayer phase is formed. The MoO_3 crystallites which are present in the Mo(4.1)/Si catalyst sulfide at higher temperatures, and it is possible that they are not completely sulfided after isothermal sulfiding at ca. 675 K, but only reduced to MoO_2. Since a redispersion is unlikely during sulfiding the catalysts with Mo loadings exceeding ca. 1 at/nm^2 contain crystallites of MoS_2 and possibly MoO_2. The formation of MoO_2 on Mo/Si catalysts has been indicated (28), but the present results show that a sulfided surface phase is also present.

The amount of surface phase is smaller than that in Al_2O_3 catalysts. This is an indication of the weaker interaction with the SiO_2 support, which cannot prevent the agglomeration of MoO_3 crystallites (6). Also, differences may arise during the preparation of the catalysts due to, e.g., the smaller adsorption of ions from an aqueous solution.

Mo/C. The ease of sulfiding of the Mo/C catalyst suggests that Mo is present in a highly disperse form and that the interaction with the support is negligible. This agrees well with the DSC and TPR results which pointed to the presence of highly disperse MoO_3 microcrystallites in the oxidic catalyst. The C support is not gasified during the sulfiding process, even at 1270 K, in contrast with TPR where CH_4 is formed already below 700 K (6). This is explained by the relatively high partial pressure of H_2S during TPS which blocks the active sites for gasification. Furthermore, in TPR Mo^0 is present, which is probably a better catalyst for the gasification of carbon than MoS_2.

The ease of sulfiding of the Mo/C catalysts suggests that the MoO_3 microcrystallites which are found in the Mo/C catalyst are sulfided into microcrystalline MoS_2. This view is supported by XPS measurements which show a crystallite size of 1–3 nm in both the oxidic and the sulfided catalyst (29), and also dynamic oxygen chemisorption experiments point to a very high dispersion in the sulfided catalyst (2).

Mo/Al. The width of the sulfiding pat-

tern, which extends from room temperature to ca. 1000 K, indicates that Mo is present in a disperse form and that a strong interaction with the support exists. These conclusions were also drawn on the basis of the DSC and TPR results (6). Furthermore, it has been shown that two oxidic species are present in typical Mo/Al catalysts, viz., a monolayer species with a strong interaction with the support (which will be referred to as "MoO I") and a bilayer species with a much smaller interaction with the support ("MoO II") (6). MoO I is the predominant species, especially at low loadings. The TPS patterns of Mo/Al catalysts with different loadings have been discussed elsewhere (3), and it has been found that the importance of region 2 in TPS also increases toward lower loadings. It should be kept in mind that the division in sulfiding regions is arbitrarily set at 500 K, and sulfiding occurs as a continuous process from room temperature up to ca. 1000 K. It is therefore likely that in region 2 the sulfiding of species which have started to sulfide in region 1 is completed. The sulfiding in region 2 therefore indicates that in addition to easily sulfidable species, certain Mo species are present on Al_2O_3 which are difficult to sulfide completely. On the basis of the strong interaction with the support and the abundance at low loadings it is tentatively concluded that the MoO II species and a part of the MoO I species are sulfided in region 1, and the remainder of MoO I in region 2.

From the TPS patterns of Mo/Al catalysts it can be concluded that both the MoO I and the MoO II species will be extensively sulfided after isothermal sulfiding at 675 K. The MoO II species resembles microcrystalline MoO_3 in its high dispersion and weak interaction with the support, so the sulfided form ("MoS II") will be like microcrystalline MoS_2. Indeed, EXAFS measurements (30, 31) and FTIR results (32, 33) show that very small two-dimensional slabs of MoS_2 are present in sulfided catalysts.

The MoO I species has a strong interaction with the support, which may be preserved after mild sulfiding, resulting in a (partly) sulfided monolayer species. A sulfided monolayer species has been suggested to occur in Mo/Al catalysts (2, 34), and an oxysulfide species has been found using EXAFS in mildly sulfided catalysts (30). EXAFS has not shown the presence of two sulfided forms of MoO I ("MoS I") and MoO II, respectively. This can be ascribed to the heterogeneity of this phase induced by the interaction with the support (35, 36). Furthermore, the first coordination spheres of MoS I and MoS II are similar, and differences in higher coordination spheres are difficult to detect for highly disperse species (37).

HDS Activity

For promoted Mo catalysts correlations have been found between properties of the oxidic catalyst and its HDS activity, e.g., reducibility (10, 38, 39), UV–Vis absorption (40), NO adsorption (41), and Mössbauer spectroscopy (42). These correlations suggest that, although the sulfiding of catalysts may cause structural changes, still different oxidic species will generally sulfide into different sulfidic species; i.e., no scrambling of species occurs during sulfiding. The correspondence between oxidic and sulfided species was specifically shown for Co species in Co/Al (42–44) and Co–Mo/Al (42). It has also been found that the dispersion of Mo/C (29) and Mo/Al (30, 32, 34) catalysts does not change significantly during sulfiding.

The present TPS results indicate that on the supports Mo species which are sulfidable at low temperatures are present; sulfiding already starts at room temperature. The temperature at which sulfiding occurs is too low for solid state transformations of diffusion. The ease of sulfiding of Mo species, and the sulfiding mechanism observed, make it unlikely that large structural rearrangements take place during mild sulfiding. This indicates that differences in characteristics between Mo phases (e.g.,
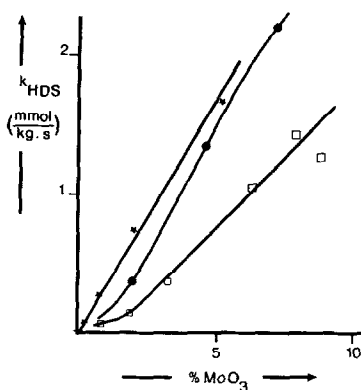
FIG. 3. HDS rate constant of Al_2O_3-, SiO_2-, and carbon-supported catalysts as a function of the amount of MoO_3 reducible at ca. 700 K. The amount of reducible MoO_3 is expressed as percentage MoO_3 (by weight) in the catalyst. TPR data taken from (6). (●) Mo/C; (★) Mo/Al; (□) Mo/Si.

dispersion and interaction with the support) may be preserved.

The purpose of the HDS test is to deduce which phases exhibit high HDS activity by combining the results obtained regarding the oxidic catalysts, the TPS results, and the HDS activities of the sulfided catalysts. A comparison of the catalysts with different temperatures of calcination and Mo loading is possible since the surface area of the catalysts studied here is relatively insensitive to these parameters. Figure 2 shows the QTOF values measured for the catalysts.

Mo/Si. The QTOF is at a maximum at a loading of ca. 1 at/nm², which is also the maximum amount of the disperse oxidic surface phase. The MoS_2 (and possibly MoO_2) crystallites which are present at higher loadings apparently do not contribute significantly to the HDS activity of the catalysts, as is indicated by the decline in QTOF toward higher loadings. It is concluded that because of the low dispersion the number of active sites in the MoS_2 crystallites is much lower than that in the sulfided surface phase.

In Fig. 3 the activity is plotted as a function of the amount of Mo which is reducible at 700 K in the oxidic catalyst. For Mo/Si samples this represents the amount of dis-

perse Mo and it is obtained by subtracting the amount of crystalline MoO_3 (as found by TPR) from the total Mo content. It can be seen that indeed the HDS activity is related to the Mo surface phase. The lower QTOF values at the lowest loadings are caused by the interaction with the support, or by compound formation (e.g., silico–molybdic acid (26, 45)).

Mo/C. The HDS activity of Mo/C catalysts is discussed in detail elsewhere (2). The QTOF values of Mo/C are very high (3.5–4.3) (2). Also, for the HDS of dibenzothiophene, Mo/C catalysts are generally more active than Mo/Al (43). However, at loadings exceeding ca. 0.5 at/nm² the HDS activity drops. This is ascribed to the loss of dispersion, as found with XPS (29) and "dynamic oxygen chemisorption" (DOC) (2). Figure 3 shows that the activity depends linearly on the Mo content, and it can be concluded that the dispersion is not adversely affected by sulfiding. The linear correlation which has been found between the O_2 chemisorption on reduced Mo/C catalysts and their HDS activity (46) also shows that the dispersion is not much influenced by sulfiding.

Mo/Al. The QTOF values depend strongly on the Mo loading and rise toward higher loadings. This suggests that the fraction of active phase increases, since it is highly unlikely that the dispersion is higher at higher loadings. The HDS activity can be correlated with the amounts of MoO I and MoO II in the oxidic catalysts. The following relationship is obtained by linear regression:

QTOF (mmol/mol · s)

$$= 3.8 \times \text{fraction MoO II}$$
$$+ 0.2 \times \text{fraction MoO I}. \quad (1)$$

When the results of Eq. (1) are plotted, the dotted line in Fig. 2 is obtained. It closely agrees with the experimentally determined QTOF values over the Mo loading range studied. The good fit between the experimental and the calculated activities shows that a QTOF of 3.8 can be assigned

to the phase to which MoO II is the precursor (MoS II), and a QTOF of 0.2 to the sulfided form of MoO I (MoS I). The HDS activity of the Mo/Al catalysts is therefore mainly due to the MoS II species. This is confirmed by plotting the HDS activity of the catalysts as a function of the amount of Mo reducible at ca. 700 K in TPR (i.e., MoO II in Mo/Al catalysts). It can be seen in Fig. 3 that the amount of MoO II in the precursor correlates well with the HDS activity. It has also been found that HDS activity of Mo/Al catalysts depends linearly on the O_2 chemisorption on catalysts which have been reduced at 773 K (46). Since DSC has shown that mainly the MoO II species is reducible at this temperature (6), the chemisorption results support the high activity attributed here to the sulfided form of MoO II. Furthermore, this is in accordance with the conclusion based on EXAFS results that the HDS activity is directly related to the edge dispersion of the MoS_2 slabs (35), since these slabs are equivalent to the phase called MoS II here.

Support for the coexistence of two sulfided Mo phases can be found in O_2 chemisorption studies on sulfided catalysts, which is a measure for the number of active sites (47, 48). These experiments show that as the Mo content is increased the amount of O_2 chemisorbed levels off, but the HDS activity still increases (2, 24). This is in agreement with a larger fraction of a MoS II species and less MoS I at higher Mo contents, analogous to MoO II and MoO I. The present results clarify the result that the QTOF of Mo/Al is lower than that of Mo/Si or Mo/C, while the EXAFS experiments show an extremely high dispersion for Mo present in the MoS_2 slabs (35), which would produce high activity; this is easily explained by the findings on the oxidic catalysts which show that only ca. 30% or less of Mo is present in the precursor to the MoS II phase, and most of Mo is present in the MoO I phase which has a much lower QTOF after sulfiding.

It appears that a variation in the temperature of calcination up to ca. 950 K (Table 1) has little influence on reducibility (7, 49), and this is reflected in the HDS activity, which is nearly constant. A temperature of calcination of ca. 800 K seems optimal, in agreement with Raman spectra and ion scattering spectroscopy (ISS) results which show a high dispersion after calcination at this temperature (50). The insensitivity of Mo/Al catalysts toward the temperature of calcination confirms that the strong interaction with the support prevents the formation of crystalline MoO_3.

An exception is formed by the Mo/Al catalyst calcined at 1125 K which has a remarkably high QTOF (Table 1). In TPR of this catalyst a large fraction of MoO II is found (7), so indeed the activity can be explained on the basis of the high QTOF of MoS II, which is formed from MoO II.

A rise in the temperature of sulfiding results in a 20% lower activity, in agreement with similar experiments (35). This is due to a loss of Mo dispersion, as was concluded from ISS and O_2 chemisorption (51), NO and O_2 chemisorption (33, 35, 51, 52), and high resolution electron microscopy (36) experiments. The MoO I species is further sulfided at higher temperatures, but this does not result in an observable rise in activity. The formation of MoS II out of the MoO I precursor does not therefore occur. Apparently the interaction with the support is still important when the MoS I phase is completely sulfided.

Effect of the Support on HDS Activity

Although the HDS activity which is plotted in Fig. 3 is normalized to the amount of active phase, differences are still seen between Mo catalysts on different supports. The reducibility of the oxidic catalysts is also strongly influenced by the support and a relationship between average reduction temperature and activity has been reported for Mo/Al and Mo/Si catalysts (10, 27). Although this correlation is generally valid the wide scatter around the observed trend makes it less useful for predicting activities.
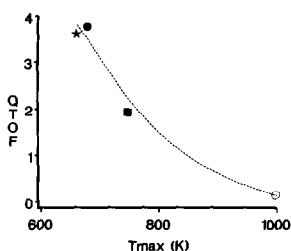
FIG. 4. HDS activity (mmol/mol · s) of the active species in Mo catalysts related to the temperature of reduction in TPR of their precursors. TPR data taken from Ref. (6). (★) Mo/C (activity data taken from (2)); (■) Mo/Si; (○) Mo/Al (MoO I); (●) Mo/Al (MoO II).

The present results show that the oxidic species which are reducible around 700 K in TPR form the most active sulfided species, so the temperature of reduction of different species should be related to HDS activity, rather than the average reduction temperature. Figure 4 shows that indeed a clear correlation exists between the temperature of the peak maximum in TPR of the oxidic species and HDS activity for the disperse species observed on C, SiO₂, and both of the two Mo species on Al₂O₃. A higher temperature of reduction of disperse species is related to a stronger interaction with the support (6, 7), so it is confirmed in Fig. 4 that a stronger interaction in the oxidic catalyst decreases HDS activity of the sulfided catalyst. Apparently the effect of the interaction persists after sulfiding. A stronger interaction is usually associated with a higher dispersion, so Fig. 3 also shows that the support not only determines the amount of active species, but also its activity, since the dispersion is not likely to be lower for the less-active species.

From Fig. 4 is appears that the activity of the MoS II species on Al₂O₃ is nearly equal to the microcrystalline MoS₂ which is present in Mo/C catalysts. Although the interaction in Mo/Si catalysts is smaller than that for the MoS I species on Al₂O₃, it still has an appreciable effect on the HDS activity. The effect of the interaction with the support is not restricted to Mo; a strong

interaction is also known to deactivate Co catalysts, because the activity of Co/C catalysts (in which the interaction is negligible) is much higher than that of Co/Al catalysts, in which a strong interaction has been demonstrated (53). Furthermore, the order of the strength of interaction with the support (Al, Si, C) is the same as that found for Re (54).

The relationship between reducibility and HDS activity suggests that both properties are controlled by a common factor, viz., the interaction with the support. The mechanism which has been proposed to explain the effect on reducibility of the interaction with the support for oxidic Mo/Al catalysts can also explain the deactivating effect on HDS in the sulfided catalysts. It is thought that in the oxidic catalyst the Mo–O–Al links polarize the Mo–O bonds, making them more difficult to reduce (3, 6). It has been found that at least some Mo–O–Al links remain in the sulfided catalyst (3, 30, 31, 34, 35, 55). Therefore, in the sulfided catalyst the Mo–S bonds of the monolayer species are similarly polarized by Mo–O–Al links. It has been argued that the important parameter for the HDS activity of a transition metal sulfide is the Mo–S bond strength, and in particular the covalent bond strength (56). The effect of the support can now be described in the same terms. The polarization of the Mo–S bonds makes them more polar, i.e., the covalency decreases, and as a result the HDS activity is lower. The activity is thus influenced by the number of Mo–O–Al links in opposite directions: on the one hand the dispersion of the oxidic and sulfided species is increased by a larger number of links with the support (57); on the other hand the activity of the species is decreased by polarization of the Mo–S bonds in the active sites, or by a decrease in the number of sites with the optimal Mo–S covalent bond strength. The active species of Fig. 4 all have high dispersions, so only the deactivating effect of the support interaction is apparent. The Mo–O–Al links are formed upon calcination of

impregnated catalysts through the condensation of MoO_4^{2-} ions with OH groups of the support (45, 58). The number of links is therefore dependent on the concentration of OH groups at the surface. It is evident that the number of Mo–O–Al links is highest for the MoS I species since Al_2O_3 contains the largest number of OH groups per unit surface area. SiO_2 contains fewer OH groups (57) and C an even smaller number (2). This is in complete agreement with the order of HDS activity.

It is remarkable in this respect that the MoS II species has an activity which is comparable with Mo/C. Apparently MoS II is not as strongly influenced by the support as MoS I. Possibly MoS II resides on top of MoS I, and then MoS I/Al can be regarded as an excellent support for other active species. Alternatively, MoS II consists of a bilayer (or multilayer) species which itself is supported by Al_2O_3. In both cases the high HDS activity originates in the top layers of a bilayer (or multilayer) structure.

For promoted catalysts the nature and the location of the promoter ions determine the HDS activity to a large extent (40, 41, 59–61). In most models such as the CoMoS model (59) and the contact-synergism model (62) the interaction of the promoter with Mo is still essential. It has been found that the structure of sulfided Mo species is hardly affected by the presence of Co (59, 63). Therefore the nature of the Mo phase can be expected to influence the HDS activity also in the promoted catalyst, and an important function of Mo could be to shield the sulfided Co species from the polarizing effect of the support. It therefore appears that the structures proposed for the unpromoted Mo catalysts are relevant to the promoted catalysts as well.

CONCLUSIONS

It is clear from the TPS results that sulfiding of disperse species is an easy process on all supports studied. Sulfiding is extensive at room temperature, and sulfiding can be completed at ca. 670 K. A strong interaction in Mo/Al catalysts causes some species to be more difficult to sulfide, but the trends in HDS activity cannot be explained by incomplete sulfiding.

The HDS activities of catalysts on different supports and with different Mo loadings can be rationalized on the basis of the nature and the amounts of species in the oxidic catalysts. This strongly suggests that during sulfiding below ca. 670 K the dispersion and (at least a part of) the interaction with the support of the oxidic species are preserved.

On all supports the HDS activity is due to disperse species, and large MoO_3 crystallites do not contribute significantly because during sulfiding they produce species with a low dispersion.

On Mo/C and Mo/Si the activity is mainly determined by the dispersion, while in Mo/Al catalysts the interaction with the support plays an important role: only the oxidic bilayer species is the precursor to an active sulfided phase. The monolayer species is inactive after sulfiding because of its strong interaction with Al_2O_3.

The deactivating effect of Al_2O_3 and, to a smaller extent, SiO_2 is caused by the polarization of the Mo–S bonds. This leads to a smaller covalency of the Mo–S bonds in the active species, and consequently to lower activity.

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