

Quasi in Situ Sequential Sulfidation of CoMo/Al₂O₃ Studied Using High-Resolution Electron Microscopy

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Using a specially developed, quasi in situ vacuum-sample-transfer system, the stepwise sequential sulfidation of CoMo/ γ -Al₂O₃ was studied with transmission electron microscopy without exposing the catalyst to air. In a first step, the sulfidation was performed at 400 °C at either 1 or 10 bar pressure. In a second step, the sulfidation was performed at 600 °C and 1 bar. As the second sulfidation step was performed on the sample on the transmission electron microscopy grid, the same areas of the samples that had been studied for the first sulfidation step could be studied once more, providing detailed data on the changes in the sulfided phase. The slab length and degree of stacking have been studied in detail from the TEM/HREM images. Sulfidation at higher pressure or higher temperature results in a higher average slab size. Detailed study of the same areas of the catalysts before and after the second, more severe, sulfidation step shows that although the dispersion of the sulfided phase decreases, the total amount visible in the TEM images remains unchanged. This indicates that practically all the sulfide present is actually imaged on the micrographs. Additionally, detailed HRTEM study shows increased crystallinity of the slabs after the second sulfidation step. XPS analysis shows that after sulfidation at 400 °C and 1 bar, the degree of sulfidation is 95%, whereas after sulfidation at 600 °C and 1 bar, sulfidation is complete. The catalytic performance for thiophene hydrodesulfurization is much higher after sulfidation at 10 bar and 400 °C as compared to 1 bar and 400 °C, and decreases after the second sulfidation step (1 bar 600 °C). The latter effect is more pronounced for the sample sulfided at 10 bar in the first step, indicating that a distorted yet fully sulfided structure is the most active phase for thiophene HDS.

Introduction

Catalysts based on molybdenum sulfide are widely used in the petrochemical industry. As a result of their importance in processes such as hydrodesulfurization (HDS) of oil, a lot of research effort is spent in order to try to understand what the active sites are and how the efficiency of these catalysts can be improved. The active phase in Mo-based hydrotreating catalysts is generally considered to consist of MoS₂ slabs with the promoter (Co, Ni) atoms decorating their edges. These slabs can easily be observed using Transmission Electron Microscopy (TEM), and usually no other sulfidic phases are present (with the exception of bulk sulfides of Co or Ni in sub-optimal catalysts, where segregation of the promoter atoms from the MoS₂ has occurred).

One of the main factors governing the number of active sites is the dispersion of the slabs. The smaller the slabs, the higher

the number of edge and corner sites, which are the most active sites. However, the reliable determination of the dispersion of the slabs can be problematic and time-consuming. TEM is the most straightforward method, as the slabs can actually be visualized. Other methods used are coordination numbers obtained from EXAFS measurements, and titration methods such as dynamic oxygen chemisorption (DOC) and NO-adsorption-IR. EXAFS is not a routine method and, moreover, underestimation of the slab size frequently occurs as a result of the assumption that the sulfidic particles are ordered, while in reality they are highly disordered and distorted for active catalysts.^{1,2} Although DOC gives reliable results for unpromoted sulfided Mo catalysts,³ it is generally accepted that no simple chemisorption method has proved capable of determining the dispersion of supported metal sulfides.^{4,5} TEM analyses of MoS₂- and WS₂-containing catalysts have been performed for two decades now. A useful review of the early TEM work has been published by Delannay in 1985.⁶ The statistically valid evaluation by hand of the dispersion and the degree of stacking has been used frequently ever since the first TEM measurements for these systems became available. A decade later, Payen et al.⁶ published an extensive systematic study concerning the influence of Mo loading, support effects, and the effects of promoters (Co, Ni) and additives (P, Cs, Na, F) on the dispersion and the

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degree of stacking. These latter authors also used quantification by hand, from TEM images, of dispersion and degree of stacking, and this is still the method of choice at the moment. When care is taken to evaluate a sufficiently large number of sulfide entities (at least 250 per sample), statistically valid data are obtained.

Recently, however, some debate has been going on in the literature regarding the TEM visibility of the sulfidic phases in MoS₂- and analogous WS₂-based catalysts. Eijssbouts et al.^{8,9} presumed that very small MoS₂ particles, ~0.5 nm diameter, exist in mildly sulfided supported (Co,Ni)Mo catalysts, although they were found to be invisible in their TEM work. However, their TEM work was performed *ex situ* on microtomed samples (i.e., their thick samples were transferred through air, thus risking partial reoxidation). Using quasi *in situ* HRTEM on ground catalysts, we have shown that indeed very small Mo- and S- or W- and S-containing entities are present for catalysts obtained after certain preparation procedures.^{10,11} The probability of detecting such (sub-)nanometer particles in TEM images of realistic supported (Co, Ni)Mo catalysts is low for several reasons. First, in most studies the samples are exposed to ambient air between sulfidation and TEM analysis. The large slabs are already less stable under the electron beam in the TEM when they have been exposed to air, and the spots are much more sensitive to exposure to air.¹² Second, Mo-based catalysts are easier to sulfide than W-based catalysts, making it difficult to arrest the sulfiding process at a stage in which an intermediate Mo (oxy)sulfidic phase is dominant. Third, many TEM studies on realistic molybdenum sulfide-based catalysts use relatively thick microtomed specimens. The thickness of such specimens limits the visibility of (sub-) nanometer particles.

The existence of so-called Type I and Type II CoMoS¹³ is widely accepted. Type I CoMoS shows stronger support interaction, a lower degree of stacking of the slabs, and a lower intrinsic activity per Co atom than Type II CoMoS.¹³ Type II CoMoS is formed upon more severe sulfidation, and both Type I and Type II CoMoS can be present simultaneously.¹³

To study the mechanism of sulfidation, the most useful information on the evolution of the sulfided phase can be obtained if exactly the same areas of a sample can be studied after sequential sulfidation steps. We have used a specially developed vacuum-transfer specimen holder for TEM to transfer samples under exclusion of air and moisture from a protective atmosphere (Ar) glovebox to the microscope and vice versa.¹⁴ This was combined with the use of an airtight transportable sulfidation microreactor in which the sequential sulfidation was performed. This unique approach prevents the samples from being exposed to air or moisture between the sulfidation procedure and the TEM measurements. Simultaneously, TEM images were recorded of the thin edges of powdered catalysts to ascertain that very small entities are not masked by the support material. By using this sequential sulfidation method and studying exactly the same areas of the sample after the first and second sulfidation step, the differences in the dispersion and degree of stacking of the slabs can be followed when a catalyst is first sulfided at standard conditions and subsequently, in a second step, at more severe sulfidation conditions. Following this procedure, it will also become clear whether large variations in the number and/or size of the slabs occur in the TEM images, allowing us to draw conclusions on the "visibility" of the sulfide phase.

The TEM data were related to catalytic thiophene hydrodesulfurization (HDS) data, to determine the effect of the more severe sulfidation conditions on the catalytic performance of

the samples. For the sample sulfided at 1 bar overall pressure, the extent of sulfidation has been determined using XPS analysis.

Experimental Section

Transmission Electron Microscopy. High-resolution transmission electron microscopy (HREM) was performed using a Philips CM30ST equipped with a field emission gun operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a Au 400 mesh grid under exclusion of air in a protective atmosphere (Ar, maximum partial pressures for oxygen and water of 1 ppm) glovebox by depositing a few drops of a suspension of the ground catalyst in *n*-hexane onto the grid, followed by drying at ambient temperature. Samples were transferred to the microscope in a special vacuum-transfer sample holder under exclusion of air¹⁴ ("quasi *in situ*").

Slab length and degree of stacking distribution were determined by manually measuring at least 250 slabs per sample from the TEM images. Average slab length and fraction of Mo at the edges of the slabs (i.e., accessible for reactants) were calculated from the slab length distributions, assuming MoS₂ crystallites of hexagonal morphology.¹⁵

Stepwise Sequential Sulfidation. The oxidic CoMo/Al₂O₃ precursor, a commercially available material (Shell C444, loading 3.6 wt % Co and 9.6 wt % Mo) was sulfided in a first step at 400 °C either at 1 or 10 bar overall pressure. Samples are denoted 1b1 and 10b1, respectively. The sulfidation step at 1 bar was performed in a quartz microreactor in a gas mixture consisting of 3 vol % H₂S, 25 vol % H₂, and 72 vol % Ar. After purging the reactor with Ar for 30 min, the sample was stabilized in the sulfiding mixture at 30 °C for 30 min. Subsequently, it was heated at a rate of 600 °C h⁻¹ to 400 °C and kept at 400 °C for 1 h. The sample was cooled to room temperature in the sulfiding mixture. After the sulfidation procedure, the reactor was closed and transferred to the glovebox. The sulfidation step at 10 bar overall pressure was performed following the same temperature program, but in a steel microreactor in a gas mixture containing 10% H₂S in H₂. As the steel reactor cannot be sealed airtight before disconnecting it from the sulfidation setup, it was filled with *n*-hexane before being disconnected in order to protect the catalyst from air and moisture. After being disconnecting, the reactor was rapidly closed and transferred to the glovebox. In the glovebox, the *n*-hexane was removed by evaporation at room temperature. The samples were prepared for high-resolution transmission electron microscopy (HREM) in the glovebox on a microgrid carbon polymer film supported on a Au grid. After the sample was studied using HREM, the Au grid containing the sample was transferred to an airtight sulfidation microreactor via the glovebox and resulfided at 600 °C and 1 bar overall pressure with a mixture of 3 vol % H₂S, 25 vol % H₂, and 72 vol % Ar. The Au grid with the sample was then transferred to the microscope again via the glovebox and exactly the same areas of the sample were located once more on the Au grid and studied once again using HREM. Next to studying exactly the same areas, which is necessarily limited to small areas of the sample, the whole of the sample present on the grid was studied in order to obtain a valid general impression of slab size and degree of stacking. Sample 1b2 denotes the sample sulfided first at 400 °C and 1 bar and subsequently at 600 °C and 1 bar. Sample 10b2 denotes the sample sulfided first at 400 °C and 10 bar and subsequently at 600 °C and 1 bar.

X-ray Photoelectron Spectroscopy (XPS). XP spectra of samples 1b1 and 1b2 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. A correction for charging was made by using the Al 2p peak at 74.4 eV as a reference. Samples were ground and pressed into indium foil which was placed in a steel stub in a N₂-flushed glovebox (maximum partial pressures for oxygen and water of 1 ppm). Subsequently, the samples were transferred to a vessel for transport under N₂ 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.¹⁶ The mean free path of the electrons was calculated using the formula of Tanuma.¹⁷ MoS₂ was used as the most stable phase. Cross-sections were obtained from Scofield.¹⁸

The degree of sulfidation was determined by fitting the Mo 3d emission line. Initial fitting with one Mo 3d doublet¹⁹ yielded a well-converged fit for sample 1b2. However, the fit for sample 1b1 was not satisfactory at the high binding energy side, which points to the presence of a small fraction of oxidic Mo. Therefore, a second Mo 3d doublet with a Mo 3d^{5/2} binding energy at 232.6 eV (characteristic for MoO₃) was added to the fitting procedure for both samples. This proved indeed insignificant for sample 1b2, but resulted in a better-converged fit for sample 1b1.

Thiophene Hydrodesulfurization. The HDS of thiophene in a flow reactor was used as a catalytic test reaction. After performing one of the sulfidation procedures, the catalysts were stabilized in 16.67 vol % H₂S in hydrogen at 350 °C and atmospheric pressure for 2 h before thiophene HDS performance was tested with 6 vol % thiophene in hydrogen at 350 °C and atmospheric pressure.²⁰ We take it that such a stabilization does not change the CoMoS structure as established in the preceding sulfidation (performed at higher temperature and/or pressure).

Results and Discussion

Figure 1 shows the same area of the catalyst sulfided at 1 bar and 400 °C (1b1, top) and subsequently at 1 bar and 600 °C (1b2, bottom). Although small local changes in the slab dispersion and degree of stacking can be observed, the amount of sulfided material visible in the two images does not differ. Some slabs have grown in length, but some slabs have disappeared during the sintering process, apparently leaving constant the total amount of visible sulfided material. The average slab length over the whole sample has increased from 3.1 to 4.0 nm (Table 1). No increase in the degree of stacking is observed after the second sulfidation step. Some of the slabs seem to be more defined in the bottom image of Figure 1, indicating increased crystallinity after more severe sulfidation. Increased crystallinity is evidenced by the frequent visibility of a second direction of *d* spacings next to the slab-like structure. An example is given in Figure 2, where clearly ordered lines are visible in the slabs in a direction approximately perpendicular to the length direction of the slabs. The distortion of the MoS₂-like structure in active catalysts as described by Shido and Prins¹, seems to decrease upon more severe sulfidation. This results in a more ordered structure which shows as increased crystallinity in the TEM/HREM images. Simultaneously the catalytic activity decreases (vide infra).

Sample 1b1 is expected to contain exclusively Type I CoMoS,²¹ which is generally accepted to have strong interaction with the alumina support material. The changes in the slabs after the second sulfidation step as observed here, showing the

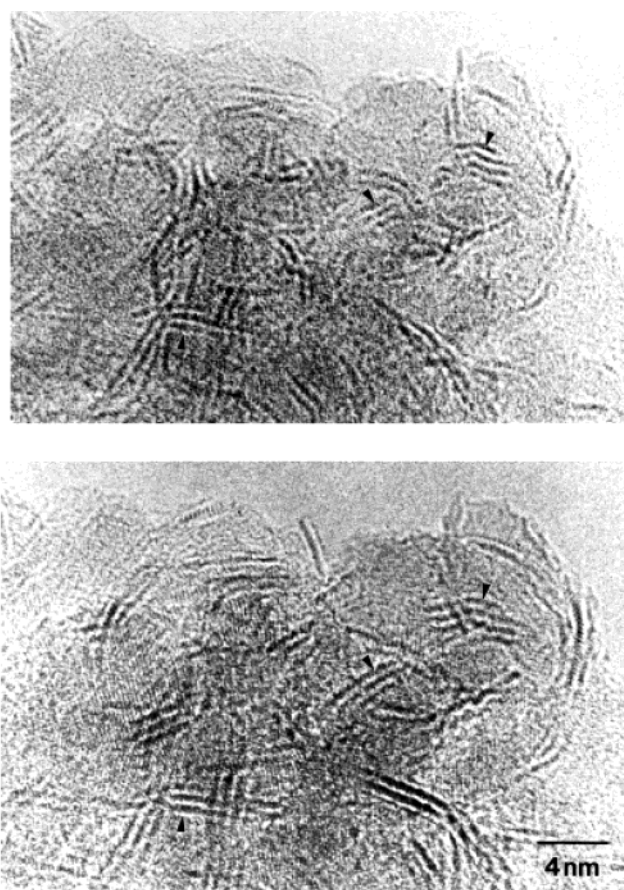


Figure 1. HREM images of sample 1b1 (top) and the same area of 1b2 (bottom).

TABLE 1: Catalyst Characterization: Activity in Thiophene Hydrodesulfurization and Dispersion Data from TEM.

catalyst	sulfidation (<i>T</i> in °C; <i>p</i> in bar)	activity ^a	average slab length ^b (nm)	fraction ^c Mo(edge)	average stacking ^b
1b1	400; 1	28.4	3.1	0.40	1.3
1b2	1b1, then 600; 1	20.5	4.1	0.28	1.3
10b1	400; 10	40.2	3.8	0.30	1.3
10b2	10b1, then 600; 1	23.7	4.4	0.25	1.5

^a % conversion of thiophene to C₄ products; selectivity is 95% for all samples. ^b From TEM images. ^c From average slab length.

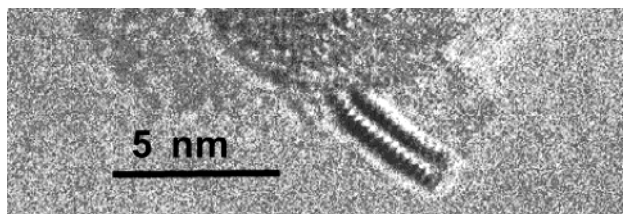


Figure 2. HREM image of a double stack of slabs clearly showing a second direction of *d* spacings.

remarkable mobility of the type I CoMoS, indicate that the processes taking place in these systems during sulfidation are perhaps more dynamic than many would expect.

As we cannot perform a second sulfidation step at pressures higher than 1 bar due to technical limitations, no data on exactly the same area are available to study the difference between samples 1b1 and 10b1. However, the data summarized in Table 1 show that the degree of stacking is the same for both 1 and 10 bar sulfidation at 400 °C, whereas the average slab length is higher for 10 bar sulfidation than for 1 bar sulfidation (3.8 nm

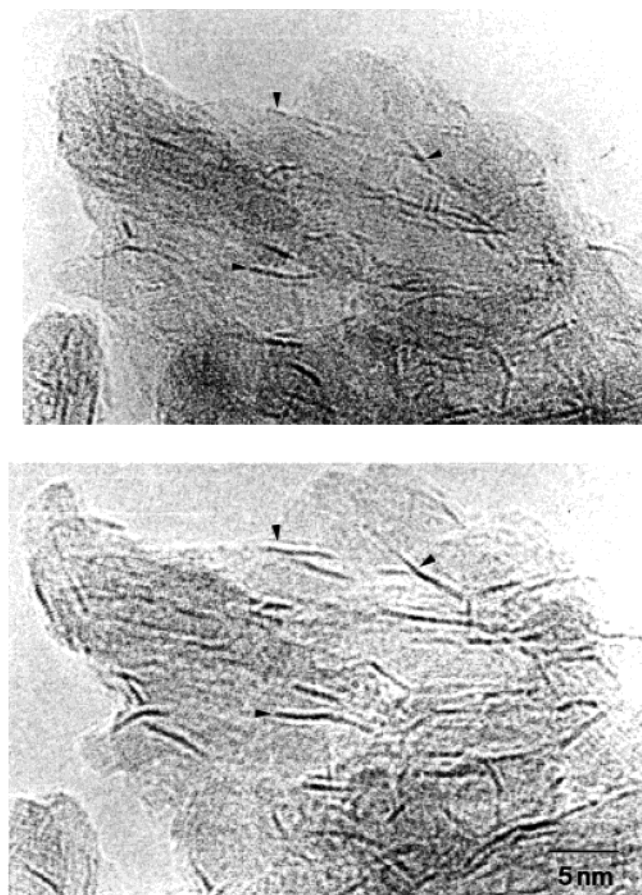


Figure 3. HREM images of sample 10b1 (top) and the same area of 10b2 (bottom).

vs 3.1 nm). XPS analysis of sample 1b1 shows that the Mo is not yet fully sulfided, as fitting with an additional Mo 3d doublet with a Mo 3d^{5/2} binding energy at 232.6 eV (characteristic for MoO₃) increased the convergence by an order of magnitude. The fraction for sample 1b1 of this additional doublet is 5%, indicating a degree of sulfidation of approximately 95%. Fitting with an additional Mo 3d^{5/2} doublet with a Mo 3d^{5/2} binding energy at 232.6 eV did not improve the convergence for sample 1b2, indicating that it is sulfided completely.

Figure 3 shows the same area of the catalyst 10b1 (top) and 10b2 (bottom). As for the data shown in Figure 1, some slabs seem to have grown in length after the second sulfidation step at 600 °C, and the average slab length over the whole sample has increased from 3.8 to 4.4 nm (Table 1). Also for this set of samples, some slabs have disappeared during the second sulfidation step, apparently leaving constant the total amount of visible sulfided material. The degree of stacking has increased slightly after the second sulfidation step. Again, for this set of samples, increased crystallinity after more severe sulfidation is indicated by better defined slabs.

The irradiation with the electron beam in the TEM prior to the second step sulfidation might, in principle, change the susceptibility of the sample to sulfidation. Thus, next to exactly the same areas (which have been exposed to the electron beam between the two sulfidation steps) also different areas (which have not been exposed to the electron beam) have been examined. The latter areas show the same general trends in slab length and degree of stacking as the areas which have been exposed to the electron beam between the two sulfidation steps. This proves that limited electron beam exposure does not influence the samples under study here.

As no additional sulfided material appears after the higher temperature sulfidation, indeed a representative part of all of the sulfided material is visible using our quasi in situ TEM/HREM method. This is in accordance with our recent finding of small, nanometer-sized, entities in mildly sulfided Mo-based catalysts.¹⁰ The latter paper clearly shows that (oxy)sulfidic material present as particles much smaller than slabs is visible using our quasi in situ TEM/HREM method, and the absence of such particles in the current study thus indicates that all sulfided material is observed. Combining these previous results with the results obtained in the current study, we can follow the evolution of the sulfided Mo-containing phase at increasing sulfidation severity. At first, very small (nanometer-sized) (oxy)sulfidic species are formed, which can be observed only on thin edges of powdered samples which have been shielded from exposure to air. After sulfidation at 400 °C, only slabs of MoS₂-like material are present. Upon more severe sulfidation at 600 °C, the slabs sinter slightly and become better defined, indicating increased crystallinity. This is in accordance with results for NiW-based catalysts as reported by van der Meer.²² Using a combination of EXAFS, XPS, Mössbauer spectroscopy, and TEM to study NiW/alumina sulfided at various temperatures, van der Meer concludes that, next to the slab length, the crystallinity also increases after sulfidation at higher temperature.

The effect of these changes in dispersion and crystallinity on the catalytic properties has been evaluated using thiophene HDS. The catalytic data are given in Table 1. For all experiments performed, the selectivity to C₄ products is practically the same at about 95%. These HDS data show that sulfidation at 400 °C and 10 bar yields by far the most active catalyst (10b1: 40.2% conversion of thiophene). Sulfidation at 400 °C and 1 bar yields a catalyst with intermediate activity (1b1: 28.4% conversion), whereas a second sulfidation step at 600 °C and 1 bar decreases the HDS activity for both samples (10b2: 23.7% conversion and 1b2: 20.5% conversion).

TEM slab length data, summarized in Table 1, show that this is not solely a dispersion effect. Regardless of the first sulfidation step, the dispersion of the slabs has decreased after the second sulfidation step. Simultaneously, the catalytic activity has decreased significantly, but the dispersion of the most active catalyst (10b1) is lower than that of the catalyst which shows intermediate activity (1b1). Furthermore, the loss in activity between samples 1b1 and 1b2 is 28%, which seems in line with a loss in fraction of Mo(edge) atoms of 30%. However, the loss in activity between samples 10b1 and 10b2 is 41%, whereas the loss in fraction of Mo(edge) atoms is only 17% between these two samples.

An obvious explanation for the difference in catalytic activity between sulfidation at 400 °C at 1 and 10 bar would be the formation of Type I CoMoS (not fully sulfided) at 1 bar and of Type II CoMoS (fully sulfided) at 10 bar. Indeed, the difference in catalytic activity, when corrected for the dispersion, is a factor 2 between samples 1b1 and 10b1, which is in agreement with data for Type I and Type II CoMoS as already described in the literature.^{13,21} Furthermore, XPS data show that sample 1b1 is not fully sulfided, indicating that improvement of catalytic activity with respect to sample 1b1 would still be possible by increasing the degree of sulfidation. It is expected that the sulfidation procedure at 400 °C and 10 bar (10b1) yields a higher degree of sulfidation than that at 400 °C and 1 bar (1b1). The TEM dispersion data point in this direction as well, with the increase in average slab length after the second sulfidation step being more pronounced for the 1b1 than for the 10b1 sample. However, apparently, in sample 1b2 the process of sulfidation

has proceeded beyond a certain optimum, as the catalytic activity has decreased even though the degree of sulfidation has increased. A simultaneous increase of crystallinity, indicating increased ordering of the structure, is observed in HREM. Furthermore, the degree of stacking hardly changes after the second sulfidation step for the 1b1 sample, which is not fully sulfided yet and thus contains a Type I CoMoS-phase which still has a strong interaction with the support material. For the 10b1 sample, the average slab length does not increase very much after the second sulfidation step, but the degree of stacking increases somewhat, indicating that the fully sulfided Type II CoMoS phase in the 10b1 sample has less interaction with the support material. Apparently the formation of either Type I or Type II CoMoS is not the only factor determining the catalytic performance. Thus, in the 10b1 catalyst the degree of sulfidation and the degree of distortion are very close to the optimal combination. The decrease in catalytic activity upon sulfidation beyond the optimum can be explained by the distortion of the sulfidic phase. Below and at the optimum, the sulfidic phase has a distorted structure with active sites. This conclusion is in agreement with the hypothesis proposed by Araki et al.²³ for the differences in activity observed for various bulk (unsupported) MoS₂ and NiMoS catalysts. It is also in line with the observations published by Shido and Prins¹, who concluded that the discrepancies in particle size determination from TEM/HREM and from EXAFS are due to distortion of the MoS₂ structure.

Upon more severe sulfidation, the distortion of the sulfidic phase decreases, as can be seen from the increased crystallinity in the TEM images of Figures 1 and 3. The well-crystallized sulfidic phase present in catalysts 1b2 and 10b2 contains less active sites than the distorted but fully sulfided phase as it is present in catalyst 10b1.

Conclusions

A higher sulfidation pressure (10 bar versus 1 bar) at 400 °C increases the degree of sulfidation and the length of the sulfide slabs in a commercial (Shell C444) CoMo/alumina catalyst. The degree of stacking of the slabs is identical for both samples. The thiophene HDS performance is much higher for the 10 bar than for the 1 bar sulfided sample.

A second sulfidation step at 1 bar and 600 °C results in a slight increase of the slab length and decreased distortion (visual as increased crystallinity in TEM/HREM images) of the slabs. The degree of stacking increases slightly for the sample sulfided at 10 bar in the first sulfidation step. This second sulfidation step decreases the thiophene HDS performance to a level independent of the pressure of the first sulfidation step.

The catalytic results cannot be explained solely based on the dispersion of the sulfide, nor on the difference between Type I and Type II CoMoS. HREM indicates increased crystallinity after the second sulfidation step. It is proposed that a distorted yet fully sulfided sulfide phase contains many active sites.

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