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Surface science models for CoMo hydrodesulfurization catalysts: Influence of the support on hydrodesulfurization activity

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Flat model systems of supported oxidic CoMo hydrodesulfurization (HDS) catalysts, consisting of a conducting substrate with a thin SiO_2 or Al_2O_3 layer on top of which the active catalytic phase is deposited by spin coating, were used to study the influence of the support and the use of chelating agents on the formation of the active CoMoS phase. On Co/Al_2O_3 catalysts Co can only be partially sulfided due to the strong interaction with Al_2O_3. In the mixed phase $CoMo/Al_2O_3$ system, the presence of Mo facilitates the sulfidation of Co. Due to the interaction of Mo with the support the $Co-Al_2O_3$ interaction is blocked. In these catalysts the sulfidation of Co and Mo proceed at the same rate. In the case of $CoMo/SiO_2$ catalysts the weak interaction with the SiO_2 support results in the complete sulfidation of Co at low temperatures, while Mo sulfides at a slower rate. Thiophene HDS activity measurements showed that due to the stronger interaction, Al_2O_3 is a better support for CoMoS formation. By complexing CoMo on Al_2O_3 to chelating agents, like ethylenediaminetetraacetic acid (EDTA), the sulfidation of Co is retarded while that of Mo is facilitated. Although Mo also forms complexes with EDTA, these complexes are less stable than those of Co. Hence, the sulfidation of Mo precedes that of Co. Due to the absence of interaction with the support of the same sulfidation behavior was observed for both supports. The activity tests showed that these catalysts have the highest activity, irrespective of support. © *2001 American Vacuum Society.* [DOI: 10.1116/1.1359542]

I. INTRODUCTION

Hydrodesulfurization (HDS), the removal of sulfur from fuel streams in a refinery, is one of the largest applications of heterogeneous catalysis. Future demands for low-sulfur diesel fuels places increasingly higher demands on the performance of HDS catalysts.[1,2] Most often used catalysts for HDS are molybdenum sulfide supported on alumina, to which cobalt or nickel sulfide are added as the promoter.[2,3] For these catalysts a fairly complete picture exists of the active phase, commonly referred to as the CoMoS phase: Co atoms decorate the edges of MoS_2 slabs.[2]

Model catalysts consisting of a flat conducting substrate with a thin SiO_2 or Al_2O_3 layer on top of which the active catalytic phase is deposited have been very successful in various field of catalysis.[4] The deposition of the precursor solutions by spin coating mimics the impregnation technique used for high surface area catalysts and gives full control over the loading.[5,6] The main advantage of using these model catalysts is that sample charging in electron and ion spectroscopy is largely eliminated, resulting in excellent resolution of the complex Mo $3d$ and Co $2p$ spectra.[4]

Previous studies in our laboratory on SiO_2-supported (Co)Mo model systems demonstrated that these systems show representative activity in thiophene HDS.[7,8] On these systems the sulfidation of Co precedes that of Mo, hence the chance for Co to find the edges of MoS_2 is not high. Chelating agents like nitrilotriacetic acid (NTA) form stable complexes with Co, thereby retarding the sulfidation of Co with respect to Mo.[7] This leads to highly active catalysts, irrespective of support.[7,9]

In this article, we extend our research on CoMo model catalysts to other supports, i.e., Al_2O_3. We first focus on the preparation of the model alumina support, followed by the sulfidation of Co on various Al_2O_3-supported catalysts studied with x-ray photoelectron spectroscopy (XPS). By comparing SiO_2- and Al_2O_3-supported CoMo catalysts we show that Al_2O_3 is a better support for active phase formation. However, using chelating agents like ethylenediaminetetraacetic acid (EDTA) increases the HDS activity for CoMo catalysts on both supports, thus providing highly active HDS catalysts irrespective of the support.

II. EXPERIMENT

Silica model supports were prepared by oxidizing a Si(100) wafer in air at 750 °C for 24 h. The oxidized wafer was then cleaned and rehydroxylated in H_2O_2 and NH_4OH at 60 °C for 10 min, followed by boiling in demineralized water for 30 min. The SiO_2 layer had a thickness of 90 nm, as estimated from Rutherford backscattering.

Alumina model supports were prepared by evaporating aluminum oxide on a silicon wafer. Prior to evaporation the wafer was cleaned in a HF solution to remove the native oxide layer. The thickness of the evaporated alumina layer is approximately 5 nm thick.

Cobalt and molybdenum were applied by spin coating the model supports at 2800 rpm in N_2 with aqueous solutions of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Merck) and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Merck), respectively. The mixed-phase catalysts were prepared by spin

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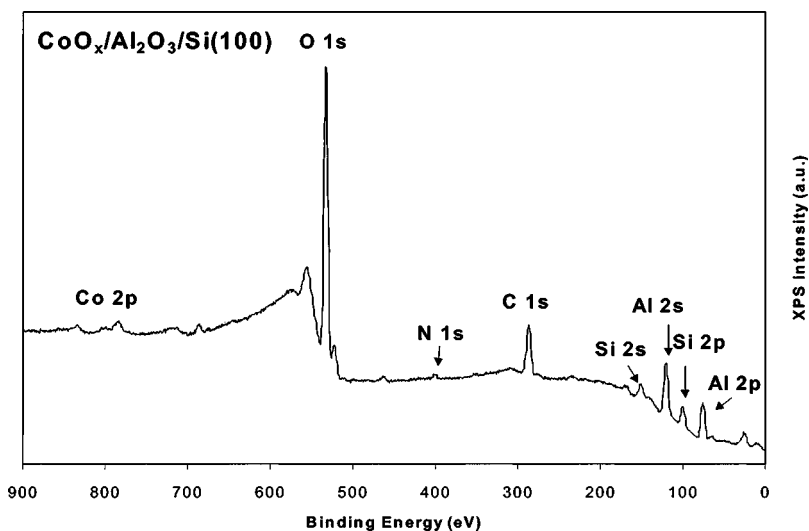
FIG. 1. XPS wide scan of an as-prepared Co/Al$_2$O$_3$/Si(100) model catalyst.

coating with aqueous solutions containing Co and Mo. The concentrations of Co and Mo in the aqueous solutions was adjusted to result in a loading of 2 Co atom/nm^2 and 6 Mo atom/nm^2 after spin coating. The dried catalysts were calcined in air at 500 °C.

The influence of a chelating agent was investigated by adding EDTA (Merck) to the aqueous solution. The EDTA solutions contained atomic Co:Mo:EDTA ratios of 2:6:5, as to complex both Co and Mo.

Sulfidation was carried out in a glass reactor under a flow of 60 ml/min of 10% H$_2$S/H$_2$ at 1 bar. The catalysts were heated at a rate of 5 °C/min (EDTA-containing samples 2 °C/min) to the desired temperature and kept there for 30 min. After sulfidation the reactor was cooled to room temperature under a helium flow and brought to a glove box, where the samples were mounted in a transfer vessel for transport to the XPS under a N$_2$ atmosphere. XPS spectra were measured on a VG Escalab 200 MK II, equipped with a standard dual source, a monochromatized Al $K\alpha$ source, and a five channeltron detector. Measurements were done at 20 eV pass energy. Charge correction was performed using the Si 2p peak of SiO$_2$ at 103.3 eV or the Al 2p peak of Al$_2$O$_3$ at 74.4 eV as a reference.

Atmospheric gas-phase thiophene HDS was used as a test reaction for the model catalysts. The measurements were carried out in a glass reactor at 400 °C and 1 bar. About 5 cm^2 of model catalyst was placed inside the reactor and was first sulfided at 400 °C for 1 h, as described above. Then a mixture of 4% thiophene/H$_2$ was passed through the reactor at a rate of 50 ml/min and at 400 °C. After 5 min the reactor was closed and operated as batch reactor. After 1 h a sample was taken with a valved syringe for gas chromatography analysis. The activity of the model catalysts is expressed as thiophene conversion (%) per 5 cm^2 of catalyst.

III. RESULTS AND DISCUSSION

A. Sulfidation of Co/Al$_2$O$_3$ and Mo/Al$_2$O$_3$

Figure 1 shows a XPS wide scan of a Co/Al$_2$O$_3$/Si(100)

model catalyst after spin coating a Co(NO$_3$)$_2$ solution. The spectrum clearly shows the presence of the expected elements. Besides the Co 2p and Al 2s and Al 2p peaks also the Si 2p and Si 2s peaks of the underlying Si substrate are present. This confirms that the alumina is a thin layer on top of the silicon substrate. The N 1s signal is due to the presence of Co(NO$_3$)$_2$ species after spin coating.

The sulfidation of calcined Co/Al$_2$O$_3$/Si(100) and Mo/Al$_2$O$_3$/Si(100) model catalysts are shown in Fig. 2. The Co 2p spectrum of unsulfided Co/Al$_2$O$_3$ in Fig. 2(A) shows the characteristics of oxidic Co species with a Co 2p binding energy of 781.5 eV and shake up features at higher binding energy. This binding energy corresponds well with that of either CoAl$_2$O$_4$ or cobalt oxide.[10] The oxidic Co species remain visible up to sulfidation temperatures of 500 °C. This supports the presence of CoAl$_2$O$_4$. It is known that these CoAl$_2$O$_4$ species are formed by diffusion of Co into the alumina support and these species are very stable against sulfidation.[11] However, Fig. 2(A) shows that a part of the Co sulfides remain at high temperatures. At 150 °C a second doublet appears at lower binding energy, i.e., 778.4 eV, which corresponds well with that of bulk cobalt sulfide.[12] This doublet remains small up to 300 °C. At higher temperatures the relative amount of the second doublet increases. Analysis of the Co 2p spectra reveals that about 50% of the cobalt is sulfided at 500 °C. The fact that Co does not sulfide completely and may diffuse into the support is also observed in high surface area alumina supported catalysts, hence this confirms that our thin film alumina supports mimics the real support quite well.

Figure 2(B) shows the stepwise sulfidation of Mo/Al$_2$O$_3$ calcined at 500 °C. The Mo 3d spectrum of the unsulfided catalyst shows a single Mo 3d doublet at 232.8 eV, corresponding to oxidic Mo^{6+}. At a sulfidation temperature of 50 °C a shoulder appears at lower binding energy and a S 2s peak can be observed around 226 eV, indicating that the sulfidation of Mo started. Around 200 °C Mo 3d features appear at 228.8 eV, corresponding to MoS$_2$. The binding en-
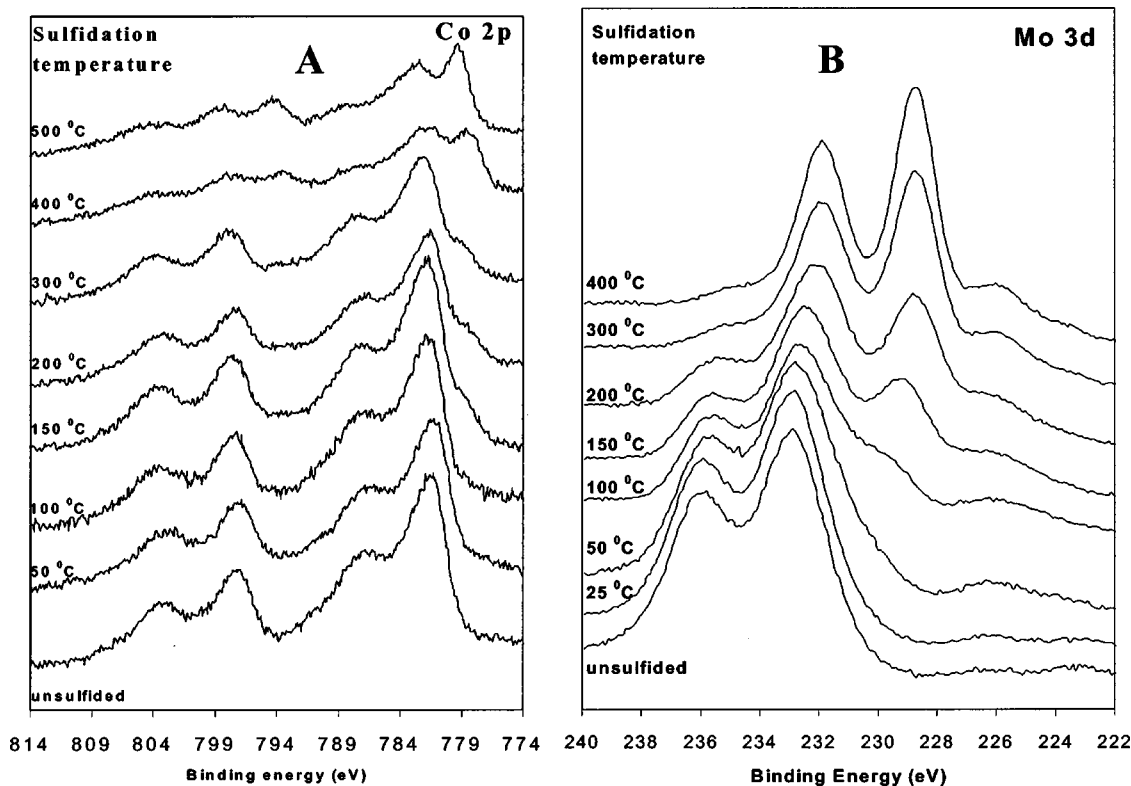
FIG. 2. XPS spectra of a calcined (A) Co/Al$_2$O$_3$/Si(100) and (B) Mo/Al$_2$O$_3$/Si(100) model catalyst sulfided at the indicated temperatures. The sulfidation of both catalysts proceeds at high temperatures due to the strong interaction with the support.

ergy of the S 2p peak at these temperatures is 161.6 eV, which is consistent with the S^{2-}-type ligands present in MoS$_2$.[13] Although the major part of Mo is sulfided to MoS$_2$ at 400 °C, the sulfidation is not complete. The Mo 3d spectra of the catalysts can all be interpreted in terms of Mo^{6+} and Mo^{4+} doublets described above and additional doublets with a binding energy of 230.5–231.5 eV. This additional doublet can be assigned to molybdenum having a formal charge of 5+, possibly in an oxysulfidic surrounding.[13]

If one compares the sulfidation of Mo/Al$_2$O$_3$ with that of Mo/SiO$_2$ published in an earlier article, it can be observed that the rate of sulfidation on Al$_2$O$_3$ is much slower than on SiO$_2$.[8] While the sulfidation of Mo/SiO$_2$ starts already at room temperature and is completed at 175 °C, on Al$_2$O$_3$ the sulfidation is retarded to higher temperatures, i.e., it starts at 50 °C and is still incomplete at 400 °C. An explanation for the difference in sulfidation behavior of Mo on Al$_2$O$_3$ and SiO$_2$ can be the difference in interaction of Mo with the supports. The interaction of Mo with Al$_2$O$_3$ is known to be strong on high surface area catalysts, while that of Mo with SiO$_2$ is rather weak. This would also confirm that both our model supports behave like their high surface area equivalents.

B. Sulfidation of CoMo/Al$_2$O$_3$

Figure 3 shows the Co 2p and Mo 3d spectra of CoMo/Al$_2$O$_3$/Si(100) calcined at 500 °C after sulfidation at various temperatures. Comparing the sulfidation of Mo in

Fig. 3(B) with that of Mo in Mo/Al$_2$O$_3$/Si(100) in Fig. 2(B), it shows that both behave quite similar. The sulfidation starts around 50 °C and is almost complete around 400 °C. If one compares the spectra after sulfidation at 300 °C, one can say that the sulfidation of Mo/Al$_2$O$_3$/Si(100) proceeds a bit faster. Overall it can be said that the presence of Co does not influence the sulfidation of Mo to a large extent.

The Co 2p spectra show a remarkable difference with that of Co/Al$_2$O$_3$/Si(100) in Fig. 2(A). Figure 3(A) shows that the sulfidation of Co starts around 50 °C and is completely sulfided around 500 °C. For Co/Al$_2$O$_3$/Si(100) it was observed that the sulfidation of Co was only 50% at 500 °C. We contributed this to diffusion of Co into the alumina support. Clearly, the presence of Mo prevents this diffusion. Craje *et al.*[11] found that Co adsorbs preferentially on Mo during preparation of CoMo/Al$_2$O$_3$ catalysts, thus Mo blocks the interaction of Co with the support. If one compares the sulfidation of Co and Mo in Fig. 3 it shows that both elements sulfide at a similar rate. Close inspection of the spectra at 300 °C shows that while Mo is almost completely sulfided, Co is largely on an oxidic state. One can imagine that these Co species are able to find the edges of the already formed MoS$_2$ slabs, thereby forming the CoMoS phase. The presence of the alumina support and its interaction with Mo prohibits the diffusion of Co into the alumina, thereby forming inactive CoAl$_2$O$_4$ species.

In an earlier article we studied the sulfidation of CoMo/SiO$_2$/Si(100) model catalysts, which showed that the
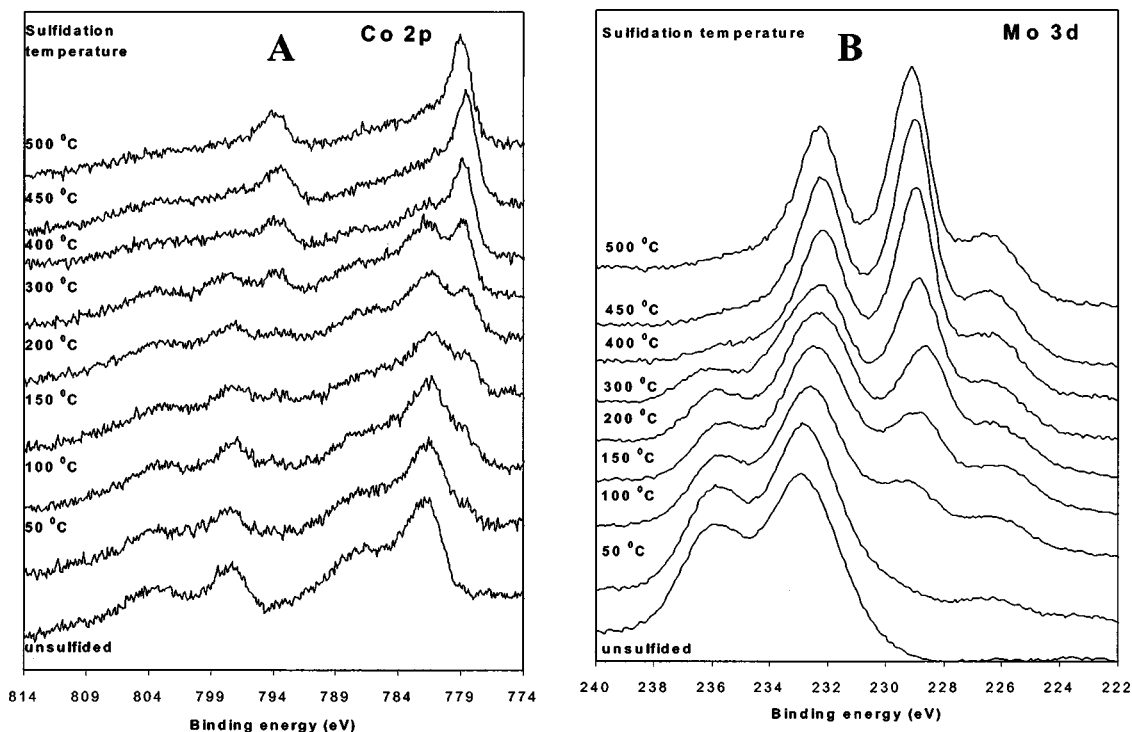
FIG. 3. Co 2*p* (A) and Mo 3*d* (B) XPS spectra of a calcined CoMo/Al$_2$O$_3$/Si(100) model catalyst during sulfidation. Due to the interaction of Mo with the support, the interaction of Co with the support is prevented and hence eases the sulfidation of Co. As a result, both sulfide at roughly the same rate.

sulfidation of Co preceded that of Mo.[8] On these catalysts the sulfidation of Co was already complete at 150 °C, while Mo sulfidation started at 50 °C and was completed around 200 °C. The chance for Co to sulfide in the presence of already formed MoS$_2$ is small, hence the formation of CoMoS is not likely. The sulfidation of both Co and Mo occurred at lower temperatures on SiO$_2$ compared to CoMo/Al$_2$O$_3$. This is caused by the stronger interaction of the alumina support, as described in the previous section.

To study the influence of chelating agents on the sulfidation of Co and Mo, a CoMoEDTA/SiO$_2$/Si(100) was sulfided at various temperatures. In these catalysts both Co and Mo are complexated to EDTA. The XPS spectra are shown in Fig. 4 and are similar to that of CoMoEDTA/Al$_2$O$_3$/Si(100) model catalysts. The Mo 3*d* spectra in Fig. 4(A) show that the sulfidation starts already at 50 °C and is complete around 200 °C. These are lower temperatures than of the conventional CoMo/Al$_2$O$_3$ catalysts in Fig. 3. The binding energy of the unsulfided catalysts is also a bit lower than that in Fig. 3, i.e., 232.0 and 232.8 eV, respectively. This indicates that Mo is indeed complexated to EDTA. Due to the complexation of Mo the interaction of Mo with the support is prevented. This explains the somewhat lower sulfidation temperatures.

The Co 2*p* spectra in Fig. 4(B) clearly show that the sulfidation of Co is retarded by the EDTA ligand. The sulfidation does not start until temperatures above 200 °C and is completed around 300 °C. At these temperatures Mo is already completely sulfided. Hence, the sulfided Co is able to migrate to the already formed MoS$_2$ edges, thereby forming CoMoS.

Another way to study the sulfidation of Co is to follow the N 1*s* XPS signal. Figure 4(C) shows the N 1*s* signal as a function of sulfidation temperature for a CoEDTA/SiO$_2$/Si(100) model catalysts. Note that the sulfidation of Co in CoEDTA/SiO$_2$ is similar to that in CoMoEDTA/SiO$_2$, however the interference of the Mo 3*p* peaks in the N 1*s* region complicates the spectrum. When the Co–EDTA complex decomposes the sulfidation is able to sulfide, thus the sulfidation of Co should cohere with a decrease of the N 1*s* signal. In Fig. 4(C) it can be seen that the N 1*s* signal decreases above 200 °C and completely disappears at 400 °C. This indeed correlates well with the sulfidation of Co in Fig. 4(B).

The observation that the Mo 3*d* and Co 2*p* spectra are similar for both SiO$_2$- and Al$_2$O$_3$-supported CoMoEDTA catalysts agrees with the observation of van Veen *et al.* who concluded that chelating agents like NTA create highly active catalysts irrespective of support.[9] De Jong *et al.*[7] observed the same for CoMoNTA model catalysts supported on either SiO$_2$ or Al$_2$O$_3$. Due to the complexation of both Co and Mo with EDTA any interaction with the support is prohibited and hence any influence of the support on, e.g., dispersion is negligible.

C. Thiophene HDS activity of CoMo model catalysts

Figure 5 shows the thiophene HDS activity results for the various catalysts, as described in Sec. II. The activity is expressed as conversion of thiophene (%) per 5 cm^2 of catalyst after 1 h of batch reaction at 400 °C in 4% thiophene/H$_2$. Recalculating our conversions into a pseudoturnover number
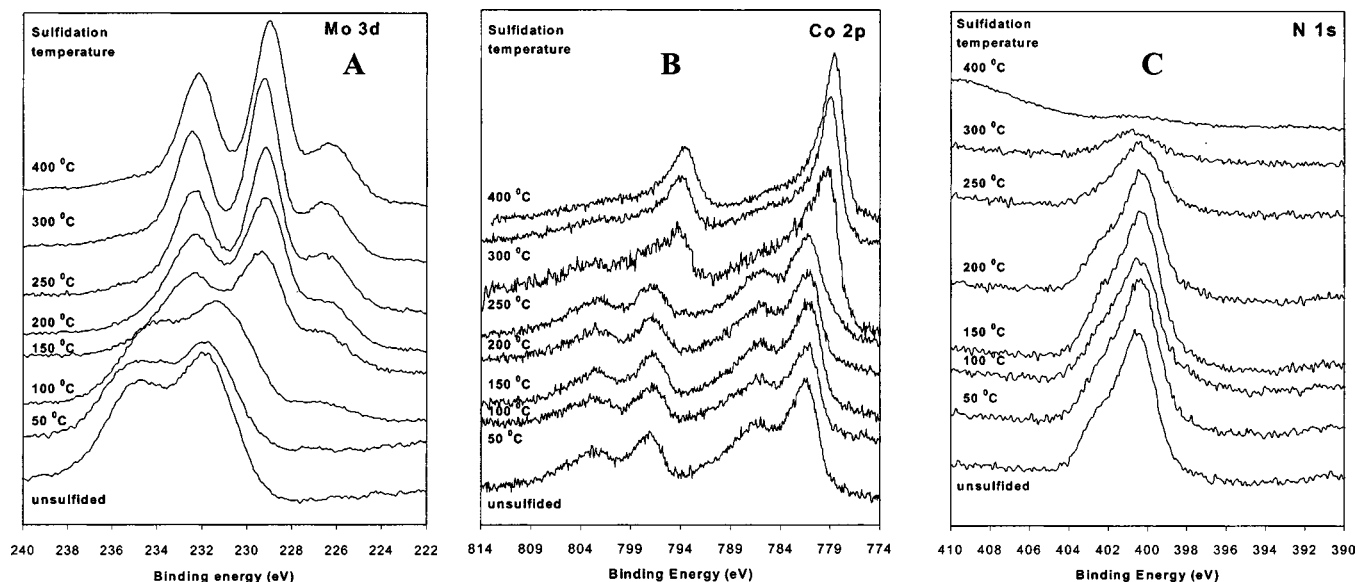
FIG. 4. XPS spectra of a uncalcined CoMoEDTA/SiO$_2$/Si(100) model catalysts in which both Co and Mo are initially forming complexes with the EDTA ligand. Due to this complexation the sulfidation of Co is retarded to temperatures where Mo is already completely sulfided. Similar spectra were observed for the Al$_2$O$_3$-supported CoMoEDTA catalyst. The decrease of the N 1s signal demonstrates the decomposition of the Co–EDTA complexes which runs parallel with the subsequent sulfidation of Co.

per Mo atom gives an activity of $\sim 10^{-2}$–10^{-1} s^{-1}, which falls in the range of high surface area CoMo catalysts.[2]

Although the activity of the Mo catalysts are low, the Mo/Al$_2$O$_3$ has a HDS activity 2–3 times higher than Mo/SiO$_2$. As explained earlier the sulfidation of both catalysts is also different. Due to the strong interaction of Mo with Al$_2$O$_3$ compared to SiO$_2$ the sulfidation occurred at higher temperature and was not complete at 400 °C. We therefore explain the difference in activity by a difference in dispersion of MoS$_2$ on the surface of the support. The uncomplete sulfidation of Mo/Al$_2$O$_3$ reveals that there are still Mo species attached to the Al$_2$O$_3$ support. These anchors to the support prevent sintering of the MoS$_2$ while on SiO$_2$ there is no anchoring and sintering is more likely.
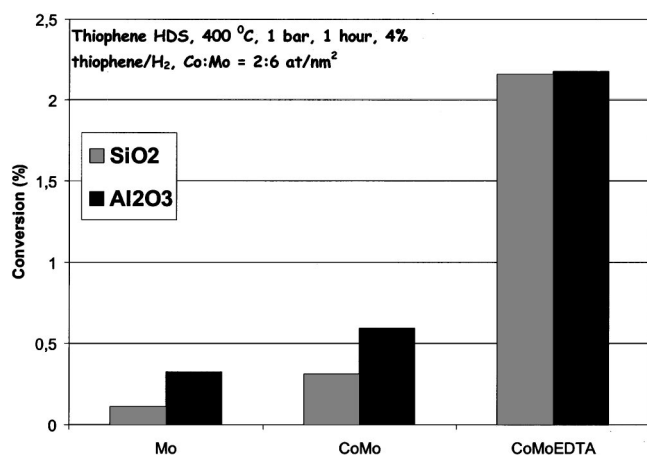

FIG. 5. Thiophene HDS activities of SiO$_2$- and Al$_2$O$_3$-supported (Co)Mo model catalysts after 1 h of batch reaction at 400 °C. The figure shows that Al$_2$O$_3$ is a better support for active phase formation. Using EDTA leads to highly active catalysts irrespective of support.

Figure 5 clearly shows the promoting effect of Co on the activity of Mo catalysts. For both supports a 2–3 times increase in activity is observed for CoMo catalysts compared to Mo catalysts. This indicates that on both supports CoMoS is present. In the case of CoMo/SiO$_2$ we stated earlier that the sulfidation of Co precedes that of Mo, hence the formation of CoMoS was not likely. However there is still a temperature regime the sulfidation of Co and Mo overlaps, i.e., where Co is not completely sulfided and Mo is partially sulfided. These nonsulfided Co species sulfide at higher temperatures in the presence of MoS$_2$ and thus can form CoMoS. This explains the promoting effect of Co in CoMo/SiO$_2$. Although on both supports the activity is increased due to the presence of Co, the Al$_2$O$_3$ supported catalyst shows higher activity. As explained in a previous section, due to the interaction of Mo with Al$_2$O$_3$ the Co sulfidation is facilitated compared to Co/Al$_2$O$_3$ although this interaction stabilizes the cobalt oxide compared to SiO$_2$-supported Co(Mo) catalysts. It was observed that on these catalysts the sulfidation of Mo and Co proceeded simultaneously, while close inspection of the XPS spectra suggested that the sulfidation of Co even lags behind that of Mo. So it is more likely for Co to form CoMoS, which explains the higher HDS activity.

The EDTA-containing CoMo catalysts show the highest activity for both supports. For Al$_2$O$_3$ and SiO$_2$ the increase in activity with a factor 4 and 9, respectively, is observed, however the difference between the two supports has disappeared. The XPS results showed that due to the complexation of EDTA with Co, the sulfidation of Co was retarded to temperatures where Mo was already completely sulfided. We concluded that on these catalysts the chance of Co to find the edges of MoS$_2$ was the highest, which is confirmed by the results in Fig. 5. In an earlier article de Jong *et al.*[7] found the

same for CoMoNTA catalysts. However, on these systems the sulfidation of Co and Mo was not completely separated and the HDS activity was lower compared to that of our CoMoEDTA catalysts. From this we conclude that the optimum activity can be found on catalysts where the sulfidation of Mo completely precedes that of Co, irrespective of support.

IV. CONCLUSIONS

We have been able to prepare realistic models of SiO_2- and Al_2O_3-supported CoMo HDS catalysts. The thin layer Al_2O_3 model supports behaved in the same way as the high surface area Al_2O_3. For example, we found evidence for the diffusion of Co into the alumina support during sulfidation. The interaction of Mo with the alumina support prevented this diffusion, although it stabilizes Co oxide with respect to SiO_2-supported catalysts. HDS activity measurements showed that Al_2O_3 is a better support for CoMoS formation than SiO_2 and hence showed a higher activity. A higher dispersion of MoS_2 due to the strong $Mo-Al_2O_3$ interaction and the retardation of Co sulfidation attributed to this higher activity. Complexation of EDTA to Co retards the sulfidation of Co to temperatures where MoS_2 already formed, thereby

creating ideal circumstance for CoMoS formation. Due to the complexation of both Co and Mo to EDTA any interaction with the support is prevented, hence highly active catalysts irrespective of support were prepared.[14]

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