Sulfidation Study of Molybdenum Oxide Using MoO$_3$/SiO$_2$/Si(100) Model Catalysts and Mo$_{3}^{Δ}$—Sulfur Cluster Compounds


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Monochromatic XPS spectra of the temperature-dependent sulfidation of MoO$_3$/SiO$_2$/Si(100) model catalysts are compared with spectra of Mo–S cluster compounds in particular with those of (NH$_4$)$_2$[MoS$_4$]·H$_2$O and its thermal decomposition products. XPS is used to identify different states of sulfur and molybdenum occurring during sulfidation. The spectra show the presence of bridging disulfide ligands and of substantial amounts of Mo$^6$ in an early stage of the sulfidation. These findings suggest that the initial reaction of the MoO$_3$-type precursor with the H$_2$S/H$_2$ atmosphere consists of two elementary steps, namely an O–S exchange followed by an Mo–S redox process. © 1995 Academic Press, Inc.

1. INTRODUCTION

Hydrodesulfurization with MoS$_2$-based catalysts is a process of increasing importance and is applied in refineries all over the world. Several open questions concerning the preparation and the structure of the catalyst exist. In particular, the mechanism of the sulfidation reaction where the oxidic, MoO$_3$-type precursor is converted into the active MoS$_2$ phase is still under debate (1–4). Surface science techniques such as monochromatic X-ray photoelectron spectroscopy (XPS) can in principle reveal highly useful information on the states of both molybdenum and sulfur. However, the presence of porous, electrically insulating oxide supports generally leads to serious loss of spectral resolution, implying that a lot of potentially interesting XPS information cannot be obtained from technical HDS catalysts.

Model catalysts prepared on thin oxide films as the support offer much better opportunities for surface spectroscopies that utilize charged particles, such as XPS and SIMS (5–9). Articles from Speck and McIntyre (6), Hay-
As the precursor consists of an insulating oxidic phase, which is gradually, from the outside inward, converted to a semiconducting MoS$_2$ phase, charging becomes less with increasing degree of sulfidation. As a result the binding energies in spectra of samples in intermediate stages of sulfidation are accurate within approximately 0.4 eV only.

Samples that were treated in a reactor were always unloaded in a N$_2$-filled glove box (typically below 2 ppm H$_2$O and 1 ppm O$_2$) and transported to the XPS spectrometer in a standard transfer vessel under N$_2$, to prevent contact with air.

Two additional model catalysts, an oxidic and a fully sulfided one, were prepared under slightly different conditions for TEM analysis. A MoO$_3$/SiO$_2$/Si(100) catalyst was prepared by spincasting with a solution of MoO$_3$Cl$_2$ in ethanol (10 g/liter) whereas the MoS$_2$/SiO$_2$/Si(100) was prepared by spincasting with 10 g/liter in butanol solution and subsequent sulfiding at 400°C for 3 h. This resulted in relatively thick layers of MoO$_3$ and MoS$_2$ on thin, 2- to 3-nm-thick silicon oxide layers. TEM samples were prepared in air by the small-angle cleavage technique described in the literature (16). This relatively new technique, developed for semiconductors, allows high-resolution cross-sectional analysis of the model catalysts without the obscuring artifacts produced by ion milling, the traditional sample preparation technique. Samples prepared in this way were mounted on a copper grid, providing an electron transparent tip. Cross-sectional TEM (XTEM) micrographs were taken using a Philips CM30 ST FEG electron microscope (point resolution 0.2 nm, Fig. 3 top) or a Philips CM30T electron microscope (point resolution 0.24 nm, Fig. 3 bottom). Both microscopes were operated at 300 keV.

3. RESULTS

Molybdenum–Sulfur Compounds

Figure 1 shows the XPS spectra of the (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O compound and of its thermal decomposition products. The Mo 3d spectra of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O, of the intermediate decomposition products, and of the finally formed MoS$_2$ all contain the Mo 3d$_{5/2}$ signal at a binding energy of 229.0 eV. This value is characteristic for molybdenum sulfur compounds with the metal in a formal oxidation state of 4+ (see Ref. (5) and literature cited therein). The broad S 2s peak on the low-binding-energy side of the Mo 3d doublet, however, changes definitely during the decomposition. These changes are more clearly revealed in the S 2p spectra, which are also included in Fig. 1.

The number and nature of the sulfur ligands change during the stepwise thermal decomposition of (NH$_4$)$_2$[Mo$_3$S$_{13}$]·H$_2$O to MoS$_2$. After the loss of water of crystallization around 150°C, the NH$_4^+$ cations react with the apical S$^{2-}$ around 260°C, releasing NH$_3$ and H$_2$S.
As (NH₄)₂[Mo₅S₁₃]·H₂O contains three types of sulfur ligands, and the [Mo₅S₁₃] decomposition intermediate only two, we start by analyzing the latter. The S 2p envelope fits well using two S 2p doublets of equal intensity, with S 2p₃/₂ binding energies at 163.1 and 161.8 eV, respectively. We attribute the S 2p₃/₂ at higher binding energy to the bridging S²⁻ ligands and the one at lower binding energy to terminal S²⁻ ligands. This implies that the negative charge on the bridging S²⁻ is significantly higher than that on the bridging ones. This is in agreement with the result of an SCF-X₅-SW calculation (17) and can also be rationalized from the chemical behavior; the bridging S₂⁻ entities are selectively attacked by nucleophilic agents and correspondingly the terminal ones by electrophilic agents (18). We thus conclude that the S 2p binding energy of bridging S²⁻ equals 163.1 ± 0.2 eV, and that of terminal S²⁻ is 161.8 ± 0.2 eV.

An estimate can be made for the binding energy of the apical S²⁻ by subtracting the S 2p spectrum of the [Mo₅S₁₃] decomposition intermediate formed at 260°C from the spectrum of (NH₄)₂[Mo₅S₁₃]·H₂O. This procedure results in a third S 2p doublet with an S 2p₃/₂ binding energy of 163.0 ± 0.5 eV for the apical sulfur.

The next decomposition step takes place at about 310°C and corresponds to the release of six equivalents of neutral sulfur from the three terminal S²⁻ ligands, in a reductive elimination reaction: (MoO⁵⁻·S²⁻ → MoO⁵⁺·S²⁻ + 2e⁻). Simultaneously the bridging S²⁻ ligands are reduced to S²⁻ ligands (S²⁻ + 2e⁻ → 2S²⁻) forming an [Mo₅S₁₀] intermediate, which is coordinatively unsaturated and tends to aggregate to microcrystalline MoS₂ (10). The corresponding spectrum in Fig. 1 still shows the presence of bridging S²⁻ ligands, indicating that the conditions employed, i.e., heating to 310°C for 5 min, does not yet convert all [Mo₅S₁₂] in this state. Prolonged heating of the compound at 400°C leads to the top spectrum shown in Fig. 1. The single S 2p doublet has an S 2p₃/₂ binding energy of 161.8 eV, in agreement with the value known from literature for MoS₂ (19).

The XPS spectra of the (NEt₄)₂[Mo₅S₁₃]·HCl and K₃[Mo₅S₁₃(CN)₉]·3KCN·4H₂O cluster compounds are shown in Fig. 2. Although charging seriously degrades the quality of the (NEt₄)₂[Mo₅S₁₃]·HCl spectra, the binding energies of the Mo 3d and the S 2p doublets (229.1 and 162.8 eV, respectively) can be determined with sufficient accuracy to confirm that the bridging S²⁻ ligands of the (NH₄)₂[Mo₅S₁₃]·H₂O compound possess the higher binding energy among the two disulfide ligands. The spectrum of K₃[Mo₅S₁₃(CN)₉]·3KCN·4H₂O provides a S 2p binding energy of 161.6 eV for the µ₂-S²⁻ ligands. Apparently, these have approximately the same binding energy as the basal plane µ₂-S²⁻ ligands of MoS₂. The Mo 3d binding energy of 229.3 eV again corresponds to molybdenum in a formal 4+ state.

All S 2p₃/₂ binding energies are summarized in Table 1. Note that terminal S²⁻ ligands and the basal plane µ₂-S²⁻ in MoS₂ cannot be distinguished on the basis of their XPS spectra, which is important for the interpretation of XPS spectra of sulfided molybdenum catalysts.

**Model Catalyst**

Figure 3 shows transmission electron micrographs of two model catalysts, one oxidic and the other after sulfidation.
in H₂S/H₂ at 400°C, for 3 h. The TEM micrograph of the freshly prepared, oxidic MoO₃/SiO₂/Si(100) model catalyst in Fig. 3 (top) shows two amorphous layers on top of the silicon crystal. Note that the distinction between the outer layer, MoO₃, which is approximately 3 nm thick, and the approximately 2.5-nm SiO₂ layer is clearly visible. Although the TEM image represents only a very small portion of the model catalyst, it indicates that the MoO₃ phase forms a flat layer of homogeneous thickness on the SiO₂/Si(100) model support.

Sulfidation leads to the formation of a microcrystalline MoS₂ phase containing randomly oriented stacks of slabs (Fig. 3 (bottom)). The absence of a preferred orientation indicates that there is little or no chemical interaction with the supporting SiO₂ layer. Note that the Mo loading of this model catalyst was higher than the one used for Fig. 3 (top); the thickness of the MoS₂ layer is approximately 6 nm. The images of Fig. 3 illustrate that the small-angle cleaving technique produces samples that are well suited for TEM analysis, although we should mention that quite some experience is required to have a reasonable success rate.

The monochromatic XPS spectra of the MoO₃/SiO₂/Si(100) model catalyst in Fig. 4 show the effect of sulfidation as a function of temperature. Owing to the sufficiently conducting model support and the use of a monochromated source, the different states in the Mo 3d and the S 2p regions can well be identified and also the S 2s peak on the low-binding-energy side of the Mo 3d doublet is almost entirely resolved. Although sulfidation at room temperature already has a considerable effect, the fully sulfided state appears to be reached between 250 and 300°C. Several intermediate situations emerge as well. We first describe the spectra of the limiting cases.

The Mo 3d spectrum of the oxidic precursor consists of a single Mo 3d doublet with a Mo 3d₃/₂ binding energy of 232.6 eV. This value, although characteristic of molybdenum with a formal charge of 6+ in an oxidic surrounding, is slightly higher than that of crystalline MoO₃, 232.3 eV (20), but agrees well with the binding energy of

| TABLE 1 |

<table>
<thead>
<tr>
<th>XPS S 2p Sulfidation of Mo-S and S Reference Compounds</th>
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<table>
<thead>
<tr>
<th>Compound</th>
<th>Type of S ligand</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂[Mo₃S₄]·H₂O</td>
<td>Si terminal</td>
<td>161.8</td>
</tr>
<tr>
<td></td>
<td>Si bridging</td>
<td>163.1</td>
</tr>
<tr>
<td></td>
<td>Si⁡ apical</td>
<td>163.0 ± 0.5</td>
</tr>
<tr>
<td>MoS₂</td>
<td>μ-S⁻</td>
<td>161.8</td>
</tr>
<tr>
<td>(NEt₄)₂[Mo₂S₃Cl]·HCl</td>
<td>Si bridging</td>
<td>162.8</td>
</tr>
<tr>
<td>K₂[Mo₂S₃(CN)₆]·3KCN·4H₂O</td>
<td>μ-S⁻</td>
<td>161.6</td>
</tr>
<tr>
<td>Elemental sulfur, S₂*</td>
<td>S⁡</td>
<td>164.0</td>
</tr>
</tbody>
</table>

* Reference (5).
FIG. 3. TEM micrographs of MoO$_2$/SiO$_2$/Si(100) (top, the MoO$_2$/SiO$_2$ interface is indicated by an arrow) and MoS$_2$/SiO$_2$/Si(100) (bottom).
MoO₃·H₂O, which equals 232.6 eV (20). As the MoO₃ phase on the model support prepared by hydrolysis of MoO₂Cl₂ was not calcined, the presence of a hydrated form of MoO₃ seems plausible.

The Mo 3d doublet observed for the model catalyst sulfided at 400°C has a Mo 3d₅/₂ binding energy of 229.0 eV, which is typical for molybdenum with a formal charge state of 4+ as in MoS₂. The S 2p spectrum of the sample consists of a single doublet with a S 2p₃/₂ binding energy of 161.7 eV, consistent with the S²⁻-type ligands present in MoS₂, although terminal S²⁻ would appear at the same value. The presence of the latter can therefore not be excluded.

The Mo 3d spectra of the catalysts sulfided at intermediate temperatures can all be interpreted in terms of the Mo⁶⁺ and Mo⁴⁺ doublets described above and one additional doublet with a Mo 3d₅/₂ binding energy of 230.8 eV. This doublet, already present after sulfidation at room temperature, can be assigned to molybdenum having a formal charge of 5+, possibly in an oxysulfidic surrounding. The contribution of Mo⁶⁺ disappears from the spectra of samples sulfided at 150°C and higher, while the Mo⁴⁺ starts to form in substantial amounts at sulfidation temperatures above 75°C.

All S 2p spectra can be fitted with two S 2p doublets, having binding energy values for the S 2p₃/₂ peak at 161.7 and 162.9 eV. In the S 2p XPS spectra of the model catalyst sulfided at room temperature we find both S 2p doublets. Keeping in mind the S 2p₃/₂ values found for the different sulfur ligands in (NH₄)₆[Mo₂S₆]·H₂O, we can assign the 162.9 eV S 2p₃/₂ peak to bridging S²⁻ ligands and the 161.7 eV S 2p₃/₂ peak to terminal S²⁻ and/or S²⁻ ligands. We conclude that bridging S²⁻ species are clearly present after sulfidation at low temperatures, but disappear almost completely above 200–250°C. We cannot exclude on the basis of XPS that terminal S²⁻ ligands exist at these temperatures.

Finally, we note that the O 1s signal attributable to the molybdenum oxide and oxysulfide phases disappears from the spectra of samples sulfided at 300°C and higher. This confirms that the experimental procedure that involves the unloading of the model catalyst from the sulfidation reactor in a glove box and the subsequent transportation under nitrogen to the XPS spectrometer is a legitimate one.

4. DISCUSSION

The XPS results of Fig. 4 reveal in detail how the states of molybdenum and sulfur change during temperature-programmed sulfidation. Molybdenum is initially present in the 6+ state but converts through a Mo⁵⁺ intermediate to the eventual Mo⁴⁺ present in MoS₂. Sulfur can be present in at least two, but possibly more states. Unfortunately, the measurements on the Mo₃ cluster compounds indicate that XPS does not distinguish between terminal S²⁻ and S²⁻, and hence a more detailed identification is not possible.
Nevertheless, the S 2p spectra do indicate that bridging \( S_2^2 \) groups appear at sulfidation temperatures up to 200°C, while eventually the sulfide ligands account for most of the sulfur present in the catalyst.

We suggest the following global reaction mechanism. The first step (see reaction A in Fig. 5) is an oxygen sulfur exchange at the surface of the oxidic catalyst precursor with \( H_2S \) from the gas phase, resulting in \( S^2 \) ligands bonded to Mo\( \text{VI} \) centers. This reaction, which has been postulated by others as well (21, 22), takes place at room temperature already. If the precursor consisted of crystalline Mo\( \text{O}_2 \), the terminally bonded oxygen atoms of the octahedrally coordinated Mo centers would be the first to exchange. However, we do not expect that the catalyst precursor contains crystalline Mo\( \text{O}_2 \), in fact the TEM image of Fig. 3 indicates that the molybdenum oxide is amorphous. Due to its preparation by hydrolysis of Mo\( \text{O}_2\text{Cl}_2 \) according to

\[
\text{MoO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2(\text{OH})_2 + 2\text{HCl}
\]

\[
\text{MoO}_2(\text{OH})_2 \rightarrow \text{MoO}_3 \cdot \text{H}_2\text{O},
\]

the local structure of the freshly prepared catalyst is probably closer to that of \( \alpha\)-Mo\( \text{O}_2 \cdot \text{H}_2\text{O} \) (23) and Mo\( \text{O}_2 \cdot 2\text{H}_2\text{O} \) (24). We expect \( \text{H}_2\text{O} \) and/or \( \text{OH}^- \) ligands to be present at positions where in crystalline Mo\( \text{O}_2 \) only \( \text{O}^- \) ligands occur. This makes the structure of our catalyst precursor much less compact and as a result a reaction with \( \text{H}_2\text{S} \) is much easier such that sulfidation may take place at room temperature already. Independent of any particular structural property, the formation or the release of water provides the thermodynamic driving force. We thus propose reaction A depicted in Fig. 5.

The S 2p spectra of Fig. 4 indicate that a considerable fraction of the sulfur in the catalyst sulfided at 25°C is the bridging \( S_2^2 \) ligand. We need to explain how bridging \( S_2^- \) ligands arise on the catalyst surface if we only offer \( S^2^- \) in the form of \( \text{H}_2\text{S} \) in the gas atmosphere.

The oxidation of \( S^2^- \) to \( S_2^2^- \) can only have occurred in the coordination sphere of the molybdenum. We therefore propose that the initial O–S exchange is followed by a redox reaction between two adjacent Mo\( \text{VI} \)=\( S_2^2^- \) fragments (see reaction B in Fig. 5), resulting in the formation of a bridging \( S_2^2^- \) ligand and the reduction of molybdenum. The formation of disulfide ligands during sulfidation is also observed with Raman spectroscopy by other authors (25, 26). The Mo 3d XPS spectrum of the catalysts sulfided at room temperature indicates that Mo\( \text{VI} \) is reduced to Mo\( \text{V} \) mainly. However, the XPS spectrum also indicates small amounts of Mo\( \text{V} \). They can be formed from Mo\( \text{VI} \)(\( \equiv S_2^- \))\(_2 \) fragments by conversion in analogy to reaction B in Fig. 5, to a terminal \( S_2^- \) ligand at a Mo\( \text{V} \) center.

In a further stage of the sulfidation process reductive elimination of terminal \( S_2^- \) ligands accompanied by the reduction of bridging \( S_2^2^- \) ligands takes place in reactions that also occur during the decomposition of \( (\text{NH}_4)_2[\text{Mo}_x\text{S}_y\text{S}_z] \cdot \text{H}_2\text{O} \), as discussed in connection with Fig. 1. The released sulfur is expected to react in part with \( \text{H}_2 \) to \( \text{H}_2\text{S} \).

All reaction steps described above are in agreement with the results presented in Fig. 4 as well as with more recent results on model catalyst with lower Mo loading, which will be published elsewhere (27). Due to the abundantly present \( S_2^- \) ligands, the mechanism accounts for S/Mo ratios in excess of two as have been reported in intermediate stages of sulfidation (5, 22, 26, 28), while it also explains the evolution of \( \text{H}_2\text{S} \) observed in temperature-programmed sulfidation studies by Moulijn and co-workers (21). We repeat, however, that our results are representative of Mo\( \text{O}_2 \) catalysts on a silica model support that have not been calcined and are expected to contain Mo\( \text{O}_2 \cdot x\text{H}_2\text{O} \) phases. In a subsequent paper (27) we show that precalcined catalysts sulfide at a low rate and via a slightly different mechanism.

The XPS spectra of the inorganic cluster compounds of Figs. 1 and 2 have been essential in establishing the S 2p binding energies of various types of sulfur ligands as compiled in Table 1. Although the use of monochromatic XPS in combination with an electrically conducting thin film support allows for identification of several of these sulfur states in sulfided model catalysts, it is unfortunate that terminal \( S_2^- \) and \( S^2^- \) appear to have similar binding energies. This implies that based on XPS spectra alone the presence of terminal \( S_2^- \) ligands in a sulfided Mo\( \text{S}_2 \) catalyst cannot be excluded. Their presence, however, is unlikely because terminal \( S_2^- \) ligands, if present on edges of metal centers of Mo\( \text{S}_2 \) particles, are expected to undergo reductive elimination reactions. Formation of reduced, coordinatively unsaturated Mo centers is known to occur in hydrogen atmospheres (29, 30).

The aim of this study was to gain qualitative information on the sulfidation process. Quantification is impeded by the relatively high molybdenum loading of about \( 6 \times 10^{15} \) Mo/cm\(^2 \), which corresponds to several layers. Consequently, sulfidation, particularly at lower temperatures, resulted in concentration gradients in the molybdenum layer.
(see also Ref. (5)) that makes quantification in terms of Mo:O:S stoichiometries difficult. Experiments with angle-dependent XPS showed that after 3 h of H$_2$S/H$_2$ treatment at 100°C the sulfidation at the surface was in a significantly further stage than at deeper layers. Thus, experiments on model catalysts with lower molybdenum oxide loadings (i.e., on the order of a monolayer) allow for quantitative conclusions from the XPS spectra. Such studies, which also address the effect of calcination and water on the sulfidation of MoO$_3$, are presently in progress and will be reported soon (27, 31).

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