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Sulfidation Mechanism of Molybdenum Catalysts Supported on a SiO₂/Si(100) Model Support Studied by Surface Spectroscopy

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The sulfidation of disk-shaped MoO₃ particles with a thickness of 5–10 nm supported on a 5-nm-thick layer of SiO₂ on Si(100) in a mixture of 10% H₂S in H₂ at atmospheric pressure has been studied as a function of temperature. XPS and SIMS indicate the formation of Mo⁴⁺OS_x at the surface and Mo(IV) oxides (probably H_{1.6}MoO₃ or MoO₂) in the interior of the particles at temperatures between 20 and 100 °C, whereas MoS₂ forms at temperatures of 125 °C and higher. Sulfur is present in two forms, as S²⁻ and in a second form which is most probably S₂²⁻ or SH⁻, but not elemental sulfur. The additional sulfur species disappear at temperatures between 150 and 200 °C. Rutherford backscattering analysis indicates S:Mo atomic ratios of 1–1.5 at sulfidation temperatures below 100 °C and of 2–2.5 above 100 °C. It is concluded that the sulfidation of MoO₃ to MoS₂ proceeds through a Mo(IV) oxysulfide, formed initially at the outside of the particle, and Mo(IV) oxide in the interior of the particle. Sulfidic species are believed to facilitate the reduction of MoO₃ to Mo(IV) species at low temperatures.

Introduction

Sulfidation of molybdenum oxide to MoS₂ is an essential step in the activation of hydrotreating catalysts, used for the removal of sulfur and nitrogen from heavy oil fractions.¹ Although a wealth of spectroscopic information is available on the working HDS catalysts,^{1,2} much less is known about the sulfidation mechanism of the catalysts. Moulijn and co-workers^{3–6} extensively studied the sulfidation mechanism of alumina-, silica- and carbon-supported molybdenum and cobalt–molybdenum catalysts with temperature-programmed sulfidation (TPS). This technique measures the consumption and evolution of H₂S, H₂, and H₂O by a catalyst as a function of temperature and gives valuable information on sulfur content and extent of reduction. Although H₂S is consumed over almost the entire temperature range up to 700 °C where sulfidation is complete, H₂S actually evolves in a sharp peak around 250 °C, accompanied by significant hydrogen consumption. The authors attribute this to the hydrogenation of excessive sulfur, assumed to be present in elemental form. Arnoldy et al.⁴ propose the following mechanism for the sulfidation of unsupported MoO₃ under temperature-programmed conditions:

Noteworthy features of the scheme are the appearance of Mo(VI)O₂S, an oxysulfide which decomposes to MoO₂ and

elemental sulfur, as well as two alternative routes from MoO₂ to MoS₂, one proceeding through metallic molybdenum.

In this paper, we follow the sulfidation of silica-supported molybdenum oxide as a function of temperature by means of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and Rutherford backscattering spectrometry (RBS). Oxide-supported catalysts charge up during XPS and SIMS analysis, leading to peak broadening and consequent loss of resolution in XPS and to diminished intensities in SIMS. These problems can be avoided by using a conducting model support, consisting of a thin oxide layer on a conducting substrate.^{7–12} Here we use a 5-nm-thick layer of SiO₂ on a Si single crystal, onto which Mo is applied by wet chemical impregnation. Such model catalysts have the additional advantage that the direction perpendicular to the surface is defined and that depth-selective information can be obtained.^{10–12}

It is important to realize that temperature-programmed studies concern reactions in which either of the gases H₂S, H₂, and H₂O is consumed or produced under nonequilibrium conditions. The spectroscopic results presented here, on the other hand, reveal the stable Mo and S phases in the catalyst after a certain isothermal sulfidation treatment, i.e., under equilibrium conditions (at least at higher temperatures). It should be kept in mind that both approaches highlight different aspects of the sulfidation mechanism.

Experimental Section

Model Catalysts. A silicon wafer with (100) surface orientation and a diameter of 75 mm was oxidized in air at 500 °C for 24 h. Angle-dependent XPS experiments performed as explained in references 12 and 13 indicated that the SiO₂ layer is 5.1 nm thick. Molybdenum was applied from a solution of MoO₂Cl₂ (Johnson Matthey GmbH Alfa products) in ethanol (concentration 2 g/L). Ethanol was used as the solvent because it wets the silicon oxide much better than water. In order to obtain a good macroscopic spreading, the wafer was spin coated at a speed of 2800 rpm according to a procedure described by Kuipers and co-workers.¹⁴ The 75-mm wafer was cut into pieces of about 1 cm².

Sulfidation experiments were done in a quartz tube reactor, with a mixture of 10% H₂S in H₂ at a flow rate of 50 mL/min.

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MoO₃/SiO₂/Si(100)

Figure 1. AFM image of a MoO₃/SiO₂/Si(100) model catalyst prepared by spin coating a SiO₂/Si(100) model support with a solution of MoO₂Cl₂ in ethanol at 2800 rpm.

The catalyst was heated at a rate of 5 °C/min to the desired temperature and kept there for 3 h. After sulfidation, the catalyst was cooled under helium to room temperature. Next, the reactor was closed and introduced into a nitrogen-filled glovebox, where the sample was transferred to a vessel for transport under nitrogen to the XPS and SIMS spectrometers. Each sulfidation experiment was done with a fresh piece of model catalyst from the same wafer. It was checked that sulfidation of the bare SiO₂/Si wafer does not occur.

Techniques. RBS spectra were measured with an incident beam of 3.94 or 2 MeV He⁺ at the AVF-cyclotron at Eindhoven University of Technology.¹⁵ Details concerning the He beam optics and detectors have been published elsewhere.^{11,12} We adopted a scattering geometry with the incoming beam directed along the surface normal and a scattering angle of 170°. We assume that the cross sections are accurate within 5%. The resulting overall energy resolution was measured to be 18 keV.

XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with an Al K α source and a hemispherical analyzer connected to a five-channel detector. Measurements were done at 20-eV pass energy. Charging was corrected for by using the C 1s peak at 284.6 eV as a reference.

SIMS spectra were measured with a Leybold SSM 200 quadrupole mass spectrometer, using a 5-keV Ar⁺ primary beam with a current density of 0.5 μ A/cm². The total time for recording a positive and a negative spectrum was approximately 500 s, estimated to result in the removal of about one monolayer. Charge compensation was not applied.

Atomic force images were taken with a Topometrix TMX 2000 atomic force microscope (AFM), operating in constant force-contact mode, using a 1- μ m piezo electric scanner.

Results

Fresh Model Catalyst. Figure 1 shows an AFM image of a freshly prepared model catalyst made by spin coating from MoO₂Cl₂ in ethanol. The particles appear round in the plane parallel to the support with diameters in the range approximately 100–150 nm and have maximum thicknesses between 5 and 10 nm. Analysis of different parts of the spin-coated wafer reveals that the macroscopic spreading of particles on a scale of centimeters is quite satisfactory, although on the micrometer scale the local density of particles varies somewhat. The AFM picture in Figure 1 corresponds to one of the more densely populated regions.

RBS spectra taken from eight different parts of the wafer (see Figure 2 for an example) indicate that the samples contain between 1.1×10^{15} and 1.4×10^{15} Mo atoms/cm² (Table II). As the diameter of the incident ion beam is about 2 mm, the results confirm that the spin-coating procedure results in a satisfactory macroscopic spreading of the deposited particles. This means that different samples from one wafer appear homogeneous with respect to XPS, RBS, and SIMS, which probe areas in the order of several mm².

Figure 2. RBS spectra of the MoO₃/SiO₂/Si(100) model catalysts after sulfidation in 1 bar of H₂S/H₂ for 3 h at the indicated temperatures. The inset shows the scattering geometry. The S and Mo peaks are magnified by a factor 20.

The XPS spectrum of the freshly prepared sample (Figure 3) yields a binding energy of 232.2 eV for the Mo 3d_{5/2} peak, consistent with Mo⁶⁺ ions as in MoO₃ (Table I). Measurement of the Cl 2p regions showed no detectable signal due to chlorine, in agreement with the instability of MoO₂Cl₂ in air. SIMS spectra (Figure 5) reveal the characteristic positive and negative secondary ion patterns of MoO₃, as we discuss later on. The negative SIMS spectrum showed only trace amounts of Cl⁻ ions at the usual impurity levels detected in SIMS.

Thus, the freshly impregnated catalyst consists of MoO₃ particles of lateral diameter between 100 and 150 nm, thickness on the order of 5–10 nm, and a good macroscopic spreading over the model support. AFM studies show that the particles can be heated in air to approximately 325 °C without affecting their shape significantly, whereas heating at temperatures above 350 °C results in serious sintering and volatilization.²³

Sulfided Model Catalysts. RBS spectra were taken of all sulfided catalysts. Two representative spectra of catalysts sulfided at 60 and 300 °C are shown in Figure 2. The large continuum below 2.3 MeV is due to the silicon substrate. Both peaks due to Mo and S were integrated, and loadings of Mo and S atoms were calculated, see Table II. The S/Mo atomic ratio calculated from the RBS spectra (Figure 6) is between 1 and 1.5 for the catalysts sulfided at room temperature and at 60 °C, but increases to values between 2 and 2.5 when the sulfidation temperature is 100 °C or higher.

Figure 3 shows the Mo 3d and S 2p XPS spectra of the MoO₃/SiO₂/Si(100) model catalysts after sulfidation for 3 h at different temperatures. Sulfidation in H₂S/H₂ at room temperature shifts the Mo 3d spectrum from the Mo⁶⁺ position to a lower binding energy of 229.5 eV, characteristic of molybdenum in a 4+ oxidation state (Table I). This value would be consistent with MoO₂, but the presence of oxysulfide species or molybdenum bronzes is conceivable as well, as will be argued later. As Figure 3 shows, this Mo⁴⁺ state predominates in catalysts sulfided up to 100 °C. In addition to Mo, the S 2s peak is also visible at binding energies around 225–226 eV. Sulfidation at 125 °C and higher gives a Mo XPS 3d_{5/2} signal with a binding energy of 228.0–228.5 eV, characteristic of Mo⁴⁺ ions in MoS₂ (Table I). The spectra have been fitted with the VGS program fit routine. We applied a Shirley background subtraction and used Gauss–Lorentz curves for the fits. The Gauss–Lorentz ratios are between 1% and 30%. All results are given in Table III.

Figure 3 also contains the S 2p spectra of the sulfided model catalysts. The step in the background from 159 to 165 eV is an artifact of the silicon substrate. In order to facilitate the

Figure 3. XPS spectra of the $\text{MoO}_3/\text{SiO}_2$ model catalysts after sulfidation in $\text{H}_2\text{S}/\text{H}_2$ for 3 h at the indicated temperatures: (a, top) Mo 3d and S 2s region; (b, bottom) S 2p region.

interpretation, we measured the S 2p spectra of three reference compounds, $\text{MoS}_2(\text{S}^{2-})$, $\text{FeS}_2(\text{S}_2^{2-})$, and elemental sulfur, see Figure 4 and Table I. The spectra obtained after sulfidation of the model catalysts up to 150 °C appear broader than those obtained after sulfidation at 300 °C. The latter spectrum can successfully be fitted with one S 2p doublet, with a $\text{S } 2p_{3/2}$ binding energy of 161.3 eV, in agreement with the presence of S^{2-} ions (Table I). In order to fit the other spectra, a second doublet has been included, with a $\text{S } 2p_{3/2}$ binding energy of 162.0–162.4 eV. The value expected for elemental sulfur is significantly higher, 164.1 eV (Table I). Possible assignments for the intermediate sulfur species are disulfide ions, S_2^{2-} , as occur for example in FeS_2 , or sulphydryl groups, SH^- .²² At first, SH^- groups are highly unstable and not expected to survive evacuation. Second, SIMS spectra do not support the presence of SH^- . As we discuss later on, we prefer the interpretation in terms of S_2^{2-} groups. All binding energies are given in Table III.

The intensity ratio of the total S 2p and Mo 3d signals in Table III shows a maximum of about 0.4 at sulfidation temperatures of 60 and 100 °C. The maximum value is significantly higher than the S 2p/Mo 3d ratio of 0.33 measured from a completely

TABLE I: Binding Energies of Mo and S in Reference Compounds

state	compd	E_B (eV)	ref
Mo^{6+}	MoO_3	232.6	21
		232.5	16
		232.4	17, 18
		232.2	this work
Mo^{5+}		230.9–231.4	18
Mo^{4+}	MoO_2	230.8	21
		229.4	16
		229.2	17
		229.1	18, 21
	MoS_2	228.9	16
		228.8	17
		228.8	20
		228.3	this work
S^{2-}	MoS_2	162.2	16
		161.6	17
		161.9	20
		161.1	this work
S_2^{2-}	FeS_2	162.1	this work
SH^-	<i>a</i>	161.5–162.9	22
S^0	S_8, S_6	164.1	19
		164.0	this work

^a $\text{S } 2p_{3/2}$ binding energy of thiol ligands in a series of nickel complexes.

Figure 4. XPS S 2p reference spectra of $\text{MoS}_2(\text{S}^{2-})$, $\text{FeS}_2(\text{S}_2^{2-})$, and elemental sulfur (S^0).

sulfided catalyst consisting entirely of MoS_2 . In the Discussion section, we argue that sulfur is concentrated at the outside of the particles.

Static SIMS, although hindered by mass interferences of cluster ions containing O_2 and S (both 32 amu), also reflects the conversion of MoO_3 into MoS_2 . The top of Figure 5 shows positive and negative static SIMS spectra of the freshly prepared, oxidic catalyst. The most intense isotopic pattern is due to elemental Mo^+ (92–100 amu). As molecular cluster ions of oxides and sulfides are thought to result from direct emission,²⁴ the higher mass clusters of MoO^+ (108–116 amu) and MoO_2^+ (124–132 amu) give information about the coordination of molybdenum. The positive spectrum shows no indication for the presence of residual Cl from the MoO_2Cl_2 precursor. The negative SIMS spectrum of the same sample is shown in the top-right corner of Figure 5. Elemental Mo^- peaks are barely visible, but MoO^- , MoO_2^- , and MoO_3^- patterns are clearly distinguished. Although with lower intensity, even MoO_4^- peaks appear.

The SIMS spectra in Figure 5 confirm that sulfidation at relatively low temperatures, 25 and 60 °C, already results in

Figure 5. Positive (left) and negative (right) static SIMS spectra of the $\text{MoO}_3/\text{SiO}_2/\text{Si}(100)$ model catalysts, after impregnation (top) and after sulfidation at the indicated temperatures, showing the transition from MoO_3 to MoS_2 . The patterns are associated with Mo (92–100 amu), MoO (108–116), MoS + MoO_2 (124–132), MoSO + MoO_3 (140–148), and MoS_2 + MoSO_2 + MoO_4 (156–164).

TABLE II: Loadings of Mo and S and the S/Mo Atomic Ratio As Determined from the RBS Spectra of Sulfided $\text{MoO}_3/\text{SiO}_2/\text{Si}(100)$ Model Catalysts^a

T_{sulf} (°C)	Mo loading (atoms/cm ²)	S loading (atoms/cm ²)	S/Mo atomic ratio
—	1.2×10^{15}	—	—
20	1.1×10^{15}	1.6×10^{15}	1.45
60	1.3×10^{15}	1.6×10^{15}	1.23
100	1.3×10^{15}	2.7×10^{15}	2.08
125	1.2×10^{15}	3.1×10^{15}	2.58
150	1.4×10^{15}	3.0×10^{15}	2.15
200	1.3×10^{15}	2.9×10^{15}	2.23
300	1.3×10^{15}	3.2×10^{15}	2.46

^a Errors in Mo and S loading, 5%; in S/Mo, 10%.

significant uptake of sulfur by the catalyst, as evidenced by the increase in the $(\text{Mo} + 32)^+$ signal, associated with both MoO_2^+ and MoS^+ clusters, and the decrease in the $(\text{Mo} + 16)^+$ signal, which is unambiguously assigned to MoO^+ . We note however that the surface region of the catalyst contains both oxygen and sulfur after sulfidation at 25 and 60 °C.

Sulfidation at 150 °C increases the sulfur and decreases the oxygen content further, while the pattern measured after sulfidation at 300 °C resembles that of a MoS_2 reference compound, indicating that sulfidation is complete. The low

Figure 6. S/Mo atomic ratio for the $\text{MoO}_3/\text{SiO}_2$ model catalysts as a function of sulfidation temperature, determined from RBS.

TABLE III: XPS Binding Energies, Line Widths, Intensities, Assignments, and Total S/Mo XPS Intensity Ratios for the Spectra in Figure 3

T_{sulf} (°C)	state	BE (eV)	fwhm (eV)	I^a ((kcounts·eV)/s)	assignt	S/Mo XPS
—	Mo 3d	232.2	2.18	6.4	Mo^{6+} in MoO_3	—
25	Mo 3d	232.0	2.14	2.5	Mo^{6+}	0.31
		229.5	2.13	19.7	Mo^{4+}	
	S 2p	161.1	1.44	4.3	S^{2-}	
		162.3	1.40	2.6	$\text{S}_2^{2-}(\text{SH}^-)$	
60	Mo 3d	229.2	1.96	31.1	Mo^{4+}	0.44
	S 2p	161.1	1.48	7.8	S^{2-}	
		162.5	1.59	5.9	$\text{S}_2^{2-}(\text{SH}^-)$	
100	Mo 3d	229.2	2.04	31.0	Mo^{4+}	0.41
	S 2p	161.1	1.46	7.5	S^{2-}	
		162.4	1.54	5.3	$\text{S}_2^{2-}(\text{SH}^-)$	
125	Mo 3d	229.6	1.70	2.8	Mo^{4+}	0.34
		228.0	1.73	12.6	Mo^{4+}	
	S 2p	160.6	1.37	3.2	S^{2-}	
		161.8	1.44	2.1	$\text{S}_2^{2-}(\text{SH}^-)$	
150	Mo 3d	229.8	1.62	4.4	Mo^{4+}	0.34
		228.1	1.72	30.9	Mo^{4+}	
	S 2p	160.9	1.63	8.8	S^{2-}	
		162.0	1.43	3.1	$\text{S}_2^{2-}(\text{SH}^-)$	
200	Mo 3d	229.7	1.69	3.8	Mo^{4+}	0.29
		228.0	1.64	27.5	Mo^{4+}	
	S 2p	161.0	1.60	9.0	S^{2-}	
300	Mo 3d	228.5	1.46	1.5	Mo^{4+}	0.33
	S 2p	161.3	1.47	0.5	S^{2-}	

^a Error in I 1–5%.

residual MoO intensity is probably due to the intimate contact of the MoS_2 particles with the oxidic support.

The negative SIMS spectra also show the conversion of MoO_3 to MoS_2 , but in a more indirect way. Here a clear SIMS sensitivity effect is apparent: MoS_x^- clusters have much lower intensities than MoO_x^- clusters.²⁵ Nevertheless, the relative intensities of the MoO_x^- clusters decrease clearly with increasing sulfidation temperature, indicating that the original oxygen coordination of Mo is disrupted by the sulfidation. Direct evidence for Mo–S contact is given by the relative increase in the intensities of the $(\text{Mo} + 32)^-$ and $(\text{Mo} + 64)^-$ clusters.

Negative SIMS spectra of the low mass range show the sulfur isotopes at 32 and 34 amu, while peaks due to SH^- ions at 33 and 35 amu are not observed. As the work of Karolewski and Cavell²⁵ demonstrates that the SH^- ion is readily detected by SIMS, we take the absence of SH^- signals in the spectra of the sulfided model catalysts as evidence that SH groups are not present. The spectra also showed a peak at 64 amu, attributed to S_2^{2-} , with increasing intensity along with the sulfidation. However, this peak does not necessarily confirm the earlier invoked S_2^{2-} species, as the S_2^- fragment in SIMS is also obtained from MoS_2 .

Figure 7. XPS S/Mo intensity ratio divided by the RBS S/Mo atomic ratio, which is a measure of the concentration gradient between sulfur at the outside and the interior of the particles.

Discussion

The application of RBS, XPS, and SIMS gives absolute Mo and S concentrations and oxidation states of these elements, as well as information on the anions in the first coordination shell of Mo. Such data provide detailed insight into the Mo and S species present in intermediate sulfidation stages of molybdena on a flat conducting silica model support. We summarize the most important results in the following paragraph.

(1) RBS spectra show that the S:Mo atomic ratio is around 1–1.5 for sulfidation at 25 and 60 °C, while the S:Mo ratio increases to 2–2.5 for sulfidation temperatures of 100 °C and higher. (2) XPS S 2p spectra reveal the presence of at least two sulfur species, one is S^{2-} as in MoS_2 and the other has a binding energy consistent with S_2^{2-} species. The latter disappears from the spectra for sulfidation temperatures between 150 and 200 °C. Evidence for the presence of elemental sulfur has not been found. (3) Mo 3d XPS spectra show that the initially present Mo^{6+} converts largely to Mo^{4+} at room temperature. The binding energy of this Mo state that predominates in catalysts sulfided at temperatures up to 100 °C is characteristic of Mo^{4+} in an oxidic environment but is significantly higher than that of MoS_2 . Sulfidation at temperatures above 125 °C leads to formation of MoS_2 . (4) The (S 2p)/(Mo 3d) XPS intensity ratio is higher after sulfidation at 60 and 100 °C than after high-temperature sulfidation. (5) The static SIMS spectra, characteristic of the outer surface layers of the particles, show that the surface is incompletely sulfided at 25 and 60 °C and that Mo atoms can have both O and S neighbors. The spectra contain no evidence for the presence of SH^- groups at any sulfidation temperature. The Mo XPS spectra logically suggest that sulfidation should be discussed in terms of two temperature ranges: the low regime from 25 to 100 °C, where MoS_2 is absent, and the temperature regime above 100 °C, where MoS_2 dominates the XPS spectra.

Sulfidation at low temperatures results in an appreciable sulfur concentration gradient between the surface region and the interior of the particles. This is most evident if one plots the (S 2p)/(Mo 3d) XPS intensity ratio divided by the true S/Mo atomic ratio determined with RBS, as has been done in Figure 7. The thus obtained parameter has a value of about 0.15 for completely sulfided particles, i.e., where S and Mo are homogeneously mixed, but is significantly higher at low sulfidation temperatures. When a surface-sensitive technique such as XPS detects a higher S/Mo ratio than does a bulk-sensitive technique such as RBS, it implies that the sulfur concentration at the surface is higher than that in the interior toward the particle support interface.

As to the state of Mo after low-temperature sulfidation, the Mo 3d binding energy is similar to that of MoO_2 and, presumably, to that of MoO_xS_y . The presence of the latter is strongly suggested

Figure 8. Contribution of Mo^{n+} species to the XPS spectra of MoO_3/SiO_2 model catalysts as a function of sulfidation temperature.

Figure 9. Contribution of sulfur species to the XPS species of MoO_3/SiO_2 model catalysts as a function of sulfidation temperature.

by the S 2p spectra, which clearly show that sulfur is present in anionic form and not as elemental sulfur. Hence, it must be coordinated to the Mo^{4+} cation but in a form different than MoS_2 , which is absent at temperatures up to 100 °C. Because the molecular clusters in SIMS clearly show that Mo in the surface of the catalyst can be coordinated by S and by O, we propose that the surface region of catalysts sulfided at low temperatures consists of Mo(IV) oxysulfides, of the general type $Mo^{4+}O_xS_y$, where sulfur is present in two states, S^{2-} and S_2^{2-} . As to the disulfide, Polz et al.²⁶ detected S_2^{2-} in sulfided MoO_3/Al_2O_3 catalysts by means of Raman spectroscopy.

Because of the sulfur concentration gradient discussed above, we argue that the catalysts sulfided at temperatures of 100 °C and lower consist of Mo(IV) oxysulfides in the surface region. The fact that the S/Mo atomic ratio corresponds already to 1 for sulfidation at 25 and 60 °C, combined with the result that all sulfur is in anionic form and thus necessarily coordinated to molybdenum, implies that oxysulfide formation cannot be limited to the outer atomic layer but that appreciable penetration of sulfur to some depth must have occurred.

At higher temperatures, the intermediate Mo(IV) phases convert to MoS_2 . The S/Mo atomic ratio is between 2 and 2.5, i.e., somewhat higher than the expected ratio of 2. This has been noted in other studies as well.^{6,27} Evidence for the occurrence of zero-valent Mo, as invoked in the sulfidation mechanism of Arnoldy et al.⁴ discussed in the Introduction (reactions 5 and 6), has not been found, implying that Mo^0 , if involved, appears only as a transient intermediate. Figures 8 and 9 summarize the type of Mo and S species detected by XPS, as a function of sulfidation temperature.

Figure 10 gives the type of sulfur species in terms of the S^{2-}/Mo and S_2^{2-}/Mo atomic ratios. These data were calculated by combining the relative contributions of each type of sulfur from

Figure 10. Atomic ratios S^{2-}/Mo and S_2^{2-}/Mo calculated by multiplying the S/Mo atomic ratio from RBS by the fractions of S^{2-} and S_2^{2-} as determined from XPS.

XPS (Figure 9) with the total S/Mo atomic ratio from RBS (Figure 6). By doing so, we implicitly assume that both types of sulfur species are geometrically similarly distributed through the particles, which does not have to be the case. If, for example, the S_2^{2-} species were preferentially located at the outside of the particles (which is conceivable in view of the high S/Mo ratio observed in XPS at low sulfidation temperatures), then the S_2^{2-}/Mo and S^{2-}/Mo atomic ratios would be over- and underestimated, respectively. Figure 10 indicates that sulfide formation increases progressively with increasing sulfidation temperature, whereas the S_2^{2-} species appears only at intermediate sulfidation temperatures and maximizes around 100–125 °C. We suggest that this S_2^{2-} is the species that gives rise to the simultaneous H_2 consumption and H_2S evolution peaks which start around 150 °C in the TPS spectra,⁴ reflecting its removal through hydrogenation.

It is interesting that exposure of the fresh catalyst to H_2S and H_2 at room temperature is sufficient to reduce the majority of the initially Mo^{6+} ions to the Mo^{4+} state. Separate experiments on the reduction of $MoO_3/SiO_2/Si(100)$ in H_2 revealed no reduction of Mo^{6+} at temperatures below 300 °C.²⁸ We attribute the reduction of Mo^{6+} to Mo^{4+} at low temperatures to the presence of molybdenum (oxy)sulfides at the surface, which provides sites where molecular hydrogen adsorbs dissociatively. Moyes and co-workers²⁹ have shown that H–D exchange indicative of dissociative adsorption occurs on MoS_2 at a range of temperatures. According to Moyes, dissociative adsorption of hydrogen on molybdenum sulfide is likely to occur at room temperature as well.³⁰ In this respect, it is interesting that Polz et al.²⁶ suggested that S_2^{2-} in sulfided catalysts plays a role in the splitting of hydrogen. As Figure 10 shows, these S_2^{2-} species are abundant after sulfidation at low temperature. We think that hydrogen atoms thus formed diffuse into the particles and reduce Mo^{6+} to Mo^{4+} .

The phase formed at low temperature in the interior of the particles is probably a hydrogen molybdenum bronze, H_xMoO_3 , with $x \leq 2$. These phases are known to form when Pt-doped MoO_3 is exposed to H_2 , in which platinum provides sites where dissociation of H_2 occurs.^{31,32} According to Sotani and Hasegawa,³² a bronze with the nominal composition $H_{0.83}MoO_3$ is stable at temperatures up to about 120 °C, at which point it starts to decompose under evolution of water. Hence, we suggest that the $Mo(IV)$ species formed in the interior of the particles after sulfidation at temperatures between 25 and 125 °C are hydrogen molybdenum bronzes.

Summarizing, the spectroscopic results suggest the mechanism shown in Figure 11 for the sulfidation of $MoO_3/SiO_2/Si(100)$. Again, we stress that the mechanism emphasizes the stable phases

Figure 11. Schematic representation of the sulfidation mechanism of MoO_3/SiO_2 model catalysts based on surface spectroscopic data.

present under equilibrium as seen by XPS and SIMS rather than the reactions leading to their formation as detected in TPS.

For sulfidation temperatures below 100 °C, there is rapid O–S exchange in the surface region leading to $Mo(IV)$ oxysulfide formation and accompanied by bulk reduction to MoO_2 , attributed to the facilitated dissociation of molecular H_2 by the partially sulfided surface. The latter contains two sulfur species: S^{2-} and most probably S_2^{2-} , although SH^- cannot entirely be excluded. Above 125 °C, the MoO_xS_y and MoO_2 phases convert to MoS_2 , while the S_2^{2-} species disappears, most probably because of hydrogenation to H_2S .

With regard to the mechanism of Arnoldy et al.⁴ discussed in the introduction, our results support the involvement of oxysulfidic Mo species (although with Mo in the 4+ oxidation state) and $Mo(IV)$ oxides in intermediate sulfidation stages, although we think that hydrogen molybdenum bronzes are more likely to be present than MoO_2 . The presence of elemental sulfur, however, can be excluded on the basis of the S 2p XPS spectra. The S_2^{2-} species we propose instead would equally well explain the evolution of H_2S observed in the TPS spectra reported in reference 4. We have found no evidence for the occurrence of Mo metal as a stable intermediate to MoS_2 , although we can of course not exclude its involvement as a transient species.

Finally, the results are valid for rather large MoO_3 particles which have little interaction with the underlying SiO_2 support. As such, the results provide a reference with which the sulfidation of more dispersed particles can be compared. We intend to exploit the approach of using flat, thin oxide layers as model supports and surface science techniques for characterization of the model catalysts to study the sulfidation of the industrially relevant alumina-supported molybdenum and cobalt–molybdenum catalysts in the near future.

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