Structure of Amorphous MoS₃

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The amorphous compound MoS₃ has been investigated by monochromatic X-ray photoemission (XPS) and vibrational spectroscopy, as well as by chemical extrusion aimed at identifying structural units inside MoS₃. XPS shows that all molybdenum in MoS₃ occurs in the 4+ oxidation state, while sulfur is present in at least two states, including S²⁻ and S⁴⁻ ligands in different types of coordination. This composition corresponds to a formal charge state of Mo⁴⁺(S⁴⁻)(S²⁻). The emission infrared spectrum of MoS₃ exhibits characteristic vibrations that are also encountered in the spectra of triangular Mo⁴⁺S₃ cluster compounds. Three of such cluster compounds, i.e. (NH₄)₂[Mo⁴⁺S₃H₂O, K₃[MoS₃(SCN)₃]2H₂O, and (NEt₄)₂[Mo⁴⁺S₃Cl₃] can be extruded from MoS₃ by reactions that are essentially destructive. On the basis of these results it is proposed that MoS₃ is essentially an aggregation of Mo(IV)⁵−sulfur cluster types.

Introduction

Molybdenum sulfides are widely used as catalysts for hydrotreating, where hydrosulfurization (HDS), the removal of sulfur from crude oil, is one of the most important examples.¹ HDS catalysts are prepared as highly dispersed molybdenum oxides (MoO₃ type structures) on a high surface area carrier and subsequently converted into the catalytically active molybdenum sulfides (MoS₂ type structures) via sulfidation, typically in H₂S/H₂ atmospheres at temperatures between 300 and 400 °C.² During the sulfidation, sulfur rich phases with stoichiometries of nearly 1 Mo:3 S have been observed, and consequently, MoS₃ has been assumed to be a relevant intermediate⁴⁻⁷ in sulfidation reaction:

MoO₃ → MoS₃ → MoS₂

(1)

At present, the knowledge about the reaction steps involved in the oxide−sulfide phase conversion is fragmentary, and also the structures of the oxidic precursor and the active sulfide are not precisely known.⁵ While crystalline Mo(VI) oxides⁶,¹⁰ and Mo⁴⁺S₃¹¹ provide convenient references for the determination of structural features of the oxidic and sulfided states, respectively, of the supported catalyst, a well-structured analogue for the MoS₃ intermediate is not readily available, as MoS₃ can only be prepared in the amorphous form.

MoS₃ is typically prepared from (NH₄)₂Mo⁴⁺S₄, either by acidification of an aqueous solution or by thermal decomposition in an inert gas atmosphere at temperatures between 260 and 300 °C.¹² Above 310 °C, MoS₃ decomposes to microcrystalline MoS₂,¹³ which is the thermodynamically most stable Mo(IV)−sulfur solid-state compound. The final product of the decomposition reaction

(NH₄)₂Mo⁴⁺S₄ → MoS₃ → Mo⁴⁺S₂

(2)

is essentially the same as that of the sulfidation of molybdenum oxides (reaction 1), while the reduction of Mo⁴⁺ → Mo⁴⁺ is a common feature in both reactions. The formation of amorphous MoS₃ and its further reaction to microcrystalline MoS₂ as given in (2) thus mimicks to some extent the chemistry of the sulfidation of molybdenum oxides. The well-defined structure of the (NH₄)₂MoS₄ complex and the fact that only sulfur ligands are involved lead to a reduction of complexity and make this reaction suitable for a structural chemical study.

The structure of MoS₃ has been the subject of several studies. The earliest results suggested that MoS₃ was not an individual compound but a mixture of MoS₂ and noncrystalline sulfur.¹⁴⁻¹⁶ Analysis of X-ray radial distribution functions (RDF) indicated that MoS₃ may be considered as a genuine compound and a structure with a metal−sulfur short-range order similar to the W₅S₉²− anion was proposed.¹⁷ Later, a new structural model for MoS₃ was proposed by Liang et al.,¹⁸,¹⁹ based on extended X-ray absorption fine structure (EXAFS), high-resolution RDF, X-ray photoelectron spectroscopy (XPS), vibrational spectroscopy, and magnetic susceptibility measurements. These data were interpreted in terms of the structures of the crystalline trichalcogenides of the group IVB and VB elements, and a similar structure was proposed for MoS₂ (structure 1). This model includes a chainlike arrangement of molybdenum atoms, which have a trigonal prismatic coordination of six sulfur atoms. Adjacent molybdenum atoms are bridged by three sulfur atoms along the chain. Every two metal atoms in the chain are paired up with a shorter metal−metal distance and one S−S bond in every other triangle. The proposed arrangement of MoS₃ corresponds to a formal charge state of Mo⁴⁺(S⁴⁻)(S²⁻).²⁰ Further studies from these authors appeared in agreement with this structure, in particular with the presence of two different Mo−Mo distances.²¹

Whereas diffraction and spectroscopy provide direct structural probes, important information on the nature of structural units...
can also be obtained chemically by cluster extrusion. Two of such extrusion experiments, in which MoS₃ was treated with aqueous solutions of NH₃ and KCN, yielded the (NH₄)₂-[Mo⁵V₇S₁₃]H₂O²⁻ and the K₃[Mo⁴V₇S₉(CN)₆]2H₂O²⁻ cluster compounds, respectively. As both compounds contain Mo⁴⁺ can also be obtained chemically by cluster extrusion. Two of the respective measuring cells.

Structure of Amorphous MoS₃

aqueous solutions of NH₃ and KCN, yielded the (N&)₂-

such extrusion experiments, in which MoS₃ was treated with

emission spectroscopy (IRES). We refer to the literature for further information on these methods.⁵⁻³⁵ A new extrusion experiment yields the (NE&[Mo⁵V₇S₉Cl₃]₂(Et = C₂H₅) cluster compound and gives valuable information regarding the quantification of structural units within the MoS₃ solid. This extrusion experiment, as well as the ones mentioned above, suggests a close relationship between the structure of amorphous MoS₃ and the structures of Mo(⁴V)₃-sulfur cluster compounds. Therefore, we also studied the extrusion products, in particular (NH₄)₂[Mo₃S₁₃]H₂O, as reference compounds. We propose a new structural model for MoS₃ which explains the results obtained⁵⁻¹⁹ we used this type of reaction only for the spectroscopic characterization of decomposition intermediates. This was done in situ in the respective measuring cells.

Experimental Section

Sample Preparation and Cluster Extrusion. (NH₄)₂MoS₃,²⁶ and (NH₄)₃[Mo₃S₁₃]H₂O²⁻ were prepared as described in the literature. MoS₃ was prepared according to ref 21 from a solution of 1.0 g of freshly made (NH₄)₂MoS₃ in 30 mL of degassed water, which was treated with 2 mL of concentrated HCl under stirring. The precipitated dark brown product was filtered and washed several times with H₂O, CH₃OH, CS₂, and diethyl ether, respectively, dried in an argon stream, and finally stored under argon to prevent oxidation. Since the preparation of MoS₃ by thermal decomposition of (NH₄)₂MoS₃ depends critically on the temperature and only in a narrow interval, between 280 and 300 °C, is a phase with the correct stoichiometry obtained,²⁸ we used this type of reaction only for the spectroscopic characterization of decomposition intermediates. This was done in situ in the respective measuring cells.

For the extrusion of the (NE&[Mo₃S₉Cl₃]₂ cluster compound, 0.65 g of MoS₃ was suspended in 35 mL of concentrated hydrochloric acid. The reaction mixture was boiled for 1 h under argon and filtered while hot. After adding 0.5 g of NE&-Cl, an orange solid precipitated from the yellow-green solution within 2 days with a yield of 90 mg (i.e. 9.3% related to the amount of Mo in MoS₃). Characterization was done by comparing the infrared spectrum of the extrusion product with that of (NE&)[MoS₃Cl₆]H₂O as prepared from (NH₄)₂-[Mo₃S₁₃]H₂O.²⁹

Techniques. XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with a monochromated Al Kα source (1486.3 eV) 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. The spectra of MoS₃ were measured after pressing the compound in indium foil, while (NH₄)₂-[Mo₃S₁₃]H₂O was deposited on the surface of a stainless steel sample holder from a solution in N,N-dimethylformamide (DMF) and subsequent evaporation of the solvent. All steps of the XPS sample preparation were done under inert conditions using a glovebox and a special transport vessel for introducing the samples into the UHV chamber of the spectrometer.

Raman spectra were obtained with a Spex Ramalog V (triple monochromator) and a Coherent Innova 70/4 Ar⁺ laser. The 514.5 nm line was employed at 100 mW incident power. Before measurement, (NH₄)₂MoS₃ was pressed into a wafer with a KBr back, which was mounted in the in situ cell.³⁰ The latter was purged with argon. To study the thermal decomposition product of (NH₄)₂MoS₃, the cell was heated to 260 °C for 5 min. The spectra were measured at room temperature in Ar with a spectral resolution of 8 cm⁻¹.

Infrared spectra were obtained with a Bruker IFS 113v spectrometer equipped with a pyroelectric DTGS detector, and with different beam splitters for the far and mid infrared region. Infrared spectra of (NH₄)₂MoS₃, (NH₄)₃[Mo₃S₁₃]H₂O, and of our extrusion product were measured in CsI in the absorption mode. The spectra of MoS₃ and of the thermal decomposition intermediate of (NH₄)₂MoS₃ were measured in the emission mode in a cell that is very similar to the one described by Diemann et al.,³¹ but was modified to fit in the Bruker spectrometer. Emission infrared spectroscopy was chosen because MoS₃ samples can conveniently be prepared and spectra of superior quality are obtained. MoS₃ and (NH₄)₂MoS₃ were applied as thin layers on the furnace of the cell as follows. Approximately 2 mg of the sample and 5 mL of 2-propanol were shaken in a vibrating mill. The resulting suspension was spread on the surface of the sample deposition area, and the liquid was slowly evaporated. The emission cell was purged with argon and heated up to 260 °C. The spectrum of MoS₃ and of the thermal decomposition intermediate of (NH₄)₂MoS₃ were measured with a spectral resolution of 8 cm⁻¹ after a period of 15 min to achieve thermal equilibration. Each spectrum is the sum of 500 scans, while the emission of the empty sample holder served as a background spectrum.

Results

We start with a discussion of the photoemission results. Figure 1 shows the monochromatic Mo 3d XPS spectra of (NH₄)₂[Mo₃S₁₃]H₂O (Figure 1a) and of MoS₃ (Figure 1b). The Mo 3d₅/₂ binding energy (see Table 1) of the cluster compound (229.0 eV) corresponds to the expected value for Mo(⁴V)—sulfur compounds, i.e. (NH₄)₂[Mo₃S₁₃]H₂O²⁻ and MoS₂.³² Note that the sulfur ligands in both compounds differ, but do not affect the Mo 3d₅/₂ binding energy. The Mo 3d XPS spectrum of MoS₃ (Figure 1b) shows, in principle, the same binding energy (229.1 eV). We therefore assign molybdenum in MoS₃ the same
formal oxidation state as in (NH₄)₂[Mo₃S₁₃]H₂O and MoS₂, namely, 4+. This assignment is also reasonable in view of our discussion of the extrusion experiments (vide infra). As will be discussed in detail elsewhere, the S 2p spectrum of (NH₄)₂[Mo₃S₁₃]H₂O, as shown in Figure 2a, contains three doublets corresponding to the bridging and terminal S₂⁻⁻ ligands and to the μ₃ (apical) S²⁻⁻ ligand of the cluster anion. The S 2p₂₃/₂ binding energies are given in Table 1, along with the value for MoS₂. Note that the basal plane S²⁻⁻ ligands of MoS₂ have the same binding energy as the terminal disulfide ones. The S 2p spectrum of MoS₃ (Figure 2b) consists of at least two doublets at 162.9 and 161.6 eV with an intensity ratio of 5:4. The doublet with the higher binding energy is consistent with the presence of bridging S₂⁻⁻ and/or apical S²⁻⁻ ligands and the other with either terminal S₂⁻⁻, S²⁻⁻, or both. The fact that different kinds of sulfur ligands have the same binding energy in XPS makes an accurate relative quantification impossible. We will return to this point later.

The XPS spectra of MoS₃ and (NH₄)₂[Mo₃S₁₃]H₂O strongly resemble each other and point to certain similarities in the structure of the two compounds. We conclude that MoS₃ contains molybdenum in the 4+ oxidation state, which implies that the formation of Mo⁴⁺S₃ from (NH₄)₂Mo⁵⁺S₄ is accompanied by molybdenum-sulfur redox processes, which lead to reduction of molybdenum, Mo⁴⁺ → Mo⁴⁺, and consequently to oxidation of S²⁻⁻ ligands of the MoS₃⁻⁻ anion.

The infrared spectra of (NH₄)₂[Mo₃S₁₃]H₂O and MoS₃ are shown in Figure 3. The spectrum of (NH₄)₂[Mo₃S₁₃]H₂O (Figure 3a) shows the characteristic bands of the [Mo₃S₁₃]⁻⁻ cluster anion. The bands with the highest intensity are those due to the ν(S–S) vibrations, i.e. the ν(S–S)br vibration at 544 cm⁻¹ and the ν(S–S) term vibration at 510 cm⁻¹. A characteristic

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<th>TABLE 1: XPS Data of Molybdenum Compounds</th>
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<td>(NH₄)₂[Mo₃S₁₃]</td>
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Figure 1. Mo 3d XPS spectra of (NH₄)₂[Mo₃S₁₃]H₂O (a) and MoS₃ (b).

Figure 2. S 2p XPS spectra of (NH₄)₂[Mo₃S₁₃]H₂O (a) and MoS₃ (b).

Figure 3. Absorption infrared spectrum of (NH₄)₂[Mo₃S₁₃]H₂O (a) and emission infrared spectrum of MoS₃ measured at 260 °C in argon (b).
feature of this compound is the ν(Mo=S) vibration of the apical sulfur at 459 cm⁻¹. The bands below 400 cm⁻¹ are due to coupled ν(Mo=S) vibrations.²⁵

The infrared emission spectrum of MoS₃ (Figure 3b) shows features very similar to those of the IR absorption spectrum of (NH₄)₂[MoS₁₃]H₂O, although the bands of the former are considerably broader and less well resolved. We assign the bands at 545, 520, and 470 cm⁻¹ to ν(S=S) and ν(Mo=S₉) vibrations, respectively. The band corresponding to the ν(S=S) vibration is shifted by 10 cm⁻¹ to higher wavenumbers as compared to that of (NH₄)₂[MoS₁₃]H₂O. Due to coupling of ν(Mo=S) and ν(S=S) vibrations, the actual band position of the latter depends in part on the structural environment of the disulfide ligands. A stronger coupling leads to higher values for the ν(S=S) vibrations.²⁶ The bands at 285, 330, and 380 cm⁻¹, which also have corresponding features in the spectrum of (NH₄)₂[MoS₁₃]H₂O, can be assigned to coupled ν(Mo=S) vibrations containing ν(Mo=S₉), ν(Mo=S₉), and ν(Mo=S₉) contributions. The important point to note is that virtually all the characteristic vibrational features of the [Mo₃S₁₃]²⁻ cluster anion appear to be present in the spectrum of MoS₃ as well.

The results described thus far concern MoS₃ prepared in solution. The following experiments pertain to thermally decomposed (NH₄)₂MoS₄ and serve to demonstrate that part of the terminal S²⁻ ligands as present in the MoS₃²⁻ anion indeed undergo oxidation to disulfide ligands.

Figure 4 displays the Raman spectra of (NH₄)₂MoS₄ and of a decomposition intermediate after 5 min at 260 °C. The spectrum of (NH₄)₂MoS₄ (Figure 4a) contains two sharp bands at 455 and 476 cm⁻¹ corresponding to the symmetric (ν₁(A₁)) and antisymmetric (ν₂(F₂)) ν(Mo=S) vibrations of the MoS₃²⁻ anion,²⁷ respectively. The spectrum of the decomposition intermediate (Figure 4b) also shows a band around 455 cm⁻¹, which we assign to the ν(Mo=S) vibration of Mo=Stl fragments in an environment of lower symmetry compared with the MoS₃²⁻ anion. However, two new, rather broad bands appear, one with a maximum around 350 cm⁻¹ and the other around 525 cm⁻¹. The shape of the latter one is slightly asymmetric due to a very weak shoulder around 550 cm⁻¹. The band at 525 cm⁻¹ and the shoulder at 550 cm⁻¹ are characteristic of ν(S=S) vibrations of terminal and bridging S₂²⁻ ligands, respectively, which are observed at 522 cm⁻¹ (terminal) and 553 cm⁻¹ (bridging) in the Raman spectrum of (NH₄)₂[MoS₁₃]H₂O.²⁵ The broad band with a maximum around 350 cm⁻¹ must be due to ν(Mo=S) vibrations and corresponds to the presence of bridging S₂²⁻ ligands. Although this Raman spectrum is of modest quality, it nevertheless unequivocally confirms the presence of S₂ groups in thermally decomposed (NH₄)₂MoS₄.

Figure 5 shows the infrared spectra of (NH₄)₂MoS₄ and of a thermal decomposition intermediate. The absorption IR spectrum of (NH₄)₂MoS₄ (Figure 5a) contains two sharp bands at 456 and at 478 cm⁻¹ corresponding to the symmetric and antisymmetric ν(Mo=S) vibrations of the MoS₃²⁻ anion (see above). The emission spectrum of the decomposition intermediate (Figure 5b), measured at 260 °C in argon directly after thermal equilibration (15 min), resembles that of MoS₃, as shown in Figure 5b. Its major features are broad bands around 325 and 525 cm⁻¹ and smaller but clearly visible contributions around 385 and 445 cm⁻¹. We attribute the broad band around 525 cm⁻¹ to the unresolved contributions of terminal and bridging disulfide ligands and the two bands at 325 and 385 cm⁻¹ to coupling ν(Mo=S) vibrations, as discussed above. The 445 cm⁻¹ band with shoulders at 430 and 470 cm⁻¹ is probably a superposition of ν(Mo=S) vibrations of Mo=Stl fragments (see above) and of the ν(Mo=S) vibration of apical S²⁻ ligands. The emission infrared spectrum thus indicates that the thermal decomposition product obtained after heating (NH₄)₂MoS₄ for 15 min at 260 °C possesses disulfide as well as apical sulfur ligands and is almost similar to that of amorphous MoS₃.

If MoS₃ is treated with boiling concentrated HCl, an extrusion product can be isolated from the reaction mixture by adding NEt₄Cl. The infrared spectrum of this extrusion product is shown in Figure 6. This spectrum is virtually equivalent to the one published for the (NEt₄)₂[Mo₃S₇Cl₆]H₂O cluster compound.
The following results are essential in considering a structure for amorphous MoS$_3$.

(i) The XPS Mo 3d$_{5/2}$ binding energy of 229.1 eV indicates that MoS$_3$ contains molybdenum in a formal 4+ oxidation state.

(ii) The XPS S 2p spectrum of MoS$_3$ shows the presence of different types of sulfur ligands, which may include bridging and terminal S$_2^{-}$ and bridging S$^{2-}$ ones.

(iii) The emission infrared spectrum of MoS$_3$ contains all the characteristic vibrations that are encountered in the infrared spectrum of the triangular cluster compound (NH$_4$)$_2$[Mo$_3$S$_7$]H$_2$O. The following results are essentially in agreement with the spectrum of the triangular cluster compound.

(iv) Three triangular cluster compounds, (NH$_4$)$_2$[Mo$_3$S$_7$]H$_2$O, K$_2$[Mo$_3$S$_7$(CN)$_3$]2H$_2$O, and (NEt$_3$)$_2$[Mo$_3$S$_7$Cl$_6$], can be extruded from MoS$_3$ using chemical reactions that are essentially destructive.

The thermal decomposition of (NH$_4$)$_2$MoS$_4$ according to

$$\text{(NH}_4\text{)}_2\text{Mo}^{VI}\text{S}_4 \rightarrow 2 \text{NH}_3 + \text{H}_2\text{S} + \text{Mo}^{IV}\text{S}_3$$

is accompanied by molybdenum—sulfur redox processes, namely, oxidation of $S^{2-}$ ligands of the MoS$_2^{2-}$ anion ($2S^{2-} \rightarrow S^{2-} + 2e^{-}$) and reduction of the metal (Mo$^{VI} + 2e^{-} \rightarrow$ Mo$^{IV}$). The first elementary step in (3) may be described as a proton transfer from the two NH$_3$ cations to an S$^{2-}$ ligand of the MoS$_2^{2-}$ anion, leading to NH$_3$ and a neutral [S$_2$Mo(SH$_3$)$_2$] intermediate, which immediately decomposes to gaseous H$_2$S and [MoS$_3$].

Simultaneous with the release of H$_2$S, the molybdenum—sulfur redox process takes place where the ligand oxidation reaction leads to the formation of disulfide groups and provides the electrons for the reduction of the metal. This is recognized in the Raman spectrum of Figure 4b: Treating (NH$_4$)$_2$MoS$_4$ at 260 °C for 5 min forms terminal disulfide ligands, suggesting that a resulting “mononuclear” [MoS$_3$] intermediate may formally be described as (S$^{2-}$—Mo$^{IV}$—S$^{2-}$). The latter is not expected to be stable due to the low coordination number of the metal. Stabilization is achievable by aggregation of these [S$^{-}$—Mo—S$^{-}$] fragments (indicated by the band corresponding to bridging S$^{2-}$ ligands in the Raman spectrum), where the formation of Mo$^3$—sulfur substructures is thermodynamically favored.

The aggregation of the [S$^{-}$—Mo—S$^{-}$] units is a random process. The positions of all molybdenum and sulfur atoms at the beginning of the decomposition reaction is determined by the crystal structure of (NH$_4$)$_2$MoS$_4$.

Directly after the loss of NH$_3$ and H$_2$S, the packing of the system is loose. This, in combination with the temperature of 260 °C, causes the mobility to be higher, as is usually the case within solid-state reactions, and the [S$^{-}$—Mo—S$^{-}$] fragments aggregate mainly within one plane (the ab-plane of (NH$_4$)$_2$MoS$_4$). This can be seen in the powder diffraction pattern of MoS$_3$ (cf. ref 4), which shows a reflection at $2\theta = 14.5^\circ$. This reflection corresponds to a lattice plane distance of 0.63 nm and points to a “layered structure” for MoS$_3$. During the aggregation of the [S$^{-}$—Mo—S$^{-}$] fragments different types of triangle structures (Mo—S short-range order) can be formed. There are triangles in which the three metal atoms are bonded together with only bridging S$^{2-}$ and those which also include S$_2^{-}$ ligands between two metal atoms. Both types of triangle structures can occur with and without an apical sulfur atom. These four possibilities are depicted in structures I—IV of Figure 7. Note that these structures do not represent compounds in their own right, but the building blocks within the MoS$_3$ solid, which, however, all satisfy the requirements of stoichiometry and electroneutrality.

The MoS$_3$ structure (long-range order) is essentially an interconnection of the structure types I—IV by means of sulfur ligands. There are two possibilities for interconnections. If both molybdenum atoms of two adjacent triangles have an S$^{2-}$ ligand, such as the Mo atoms at the top of structures I and II, the triangles connect via the two S$^{2-}$ ligands in an {Mo—(S)$_2$—Mo}
Figure 7. Structures of the {Mo$^{IV}$S$_2$} cluster types within MoS$_3$ and a representative part of the MoS$_3$ structure.

Treatment of MoS$_3$ with an aqueous solution of KCN produces K$_3$[Mo$_3$(CN)$_6$]2H$_2$O with a yield of ca. 35%. The reactions involved in its formation are

\[
\{ \text{Mo}^{IV}_3 \}_{\text{S}_2}^{-} + \text{CN}^{-} \rightarrow \{ \text{Mo}^{IV}_3 \text{S}_2 \}_{\text{S}_2}^{-} \text{CN}^{-} \quad (4)
\]

\[
\text{Mo}^{IV}_3 \text{S}_2^{-} + 3\text{CN}^{-} \rightarrow \text{Mo}^{IV}_3(\text{CN})_6 + \text{S}_2^{2-} \quad (5)
\]

in which the {Mo$_3$S$_2$}$^{4+}$ core is formed by subsequent sulfur redox (4) and the metal–ligand substitution (5) reactions from the {Mo$_3$S$_2$}$^{4+}$ (structure III) and the {Mo$_3$S$_2$}$^{4+}$ core (structure IV), which means that the portion of structure IV in MoS$_3$ is about 25%. The cyanolysis of MoS$_3$ is often accompanied by the formation of K$_3$[Mo$_3$(CN)$_6$]2H$_2$O in varying low percentages (<3%). Since the Mo 3d XPS spectrum of MoS$_3$ (Figure 1b) does not indicate a second molybdenum state beside Mo$^{4+}$, we argue here that the {Mo$_3$S$_2$}$^{4+}$ core is not a relevant local structure within the MoS$_3$ solid.

The remaining part of the MoS$_3$ solid (65%) can obviously not be extruded in the form of stable clusters, probably due to the absence of apical sulfur atoms (structures I and II). We therefore conclude that structures I and II together contribute to the structure of MoS$_3$ with ca. 65% and structures III and IV with ca. 25 and 10%, respectively. Such a composition favors the interconnection of triangles by Mo–S–Mo bridges over that by Mo–S–Mo ones.

EXAFS measurements by Cramer et al. have indicated that the spectrum of MoS$_3$ possesses scattering contributions from two Mo–Mo distances, 0.274 and 0.314 nm, and mainly one Mo–S distance of 0.241 nm. Metal–metal and metal–sulfur distances in our structural model can be estimated using the X-ray structure data of relevant molybdenum–sulfur cluster compounds. The Mo–Mo distance in structure III should be close to that in the [Mo$_3$S$_3$I$_2$]$^{2-}$ anion, namely, 0.272–0.275 nm, and should be slightly longer in structure I. The distance between molybdenum atoms bonded via an S$^2-$ ligand within structures II and IV is expected to be around 0.3 nm due to...
the symmetry of the triangle structure. The distances of Mo atoms of different triangles interconnected with $S^{2-}$ ligands are expected to be longer than 0.3 nm, because here an enlargement of Mo$-S$-Mo bonding angles must be involved for a minimization of the sterical interaction with the atoms of neighboring triangles (cf. also the discussion in ref 21).

Metal-sulfur distances in MoS$_2$ should fall between 0.236 and 0.248 nm according to the X-ray data of the [MoS($S$)$_3$]$^{2-}$ and the [Mo$_2$S$_2$(CN)$_3$$S_2$]$^{3-}$ cluster anions, which are $d$(Mo$-S$) = 0.236 nm, $d$(Mo$-S$) = 0.245 nm, and $d$(Mo$-S$) = 0.248 nm, while the distance between molybdenum and a bridging $S^{2-}$ ligand is expected between 0.238 and 0.240 nm. These small differences in distance would be hard to resolve in EXAFS, and an average metal-sulfur distance of 0.24 ± 0.01 nm is expected.

We thus expect two metal-metal distances in the MoS$_3$ solid, a shorter one around 0.275 nm and a longer one of about 0.31 nm, and an average metal-sulfur distance of 0.248 nm, while the distance between molybdenum and a bridging $S^{2-}$ ligand is expected between 0.236 and 0.240 nm. These small differences in distance would be hard to resolve in EXAFS, and an average metal-sulfur distance of 0.24 ± 0.01 nm is expected.

Finally, any structural model for MoS$_3$ must be able to account for its decomposition into microcrystalline MoS$_2$ at elevated temperatures:

$$\text{MoS}_3 \rightarrow \text{MoS}_2 + S^0$$

(6)

This reaction, which takes place in inert gas at temperatures above 310 °C, involves the reduction of bridging disulfide ligands due to reductive elimination of $S^{2-}$ and terminal $S_2^{2-}$ ligands$^{10,31}$ formally according to

$$\text{MoO}^{2+} \text{S} \text{S} \text{MoO}^{2+} \rightarrow \text{MoO}^{2+} \text{S} \text{MoO}^{2+} + S^0$$

(7)

During decomposition the preformed Mo$_3$ units are preserved, and after the loss of one sulfur per molybdenum center, reactive {Mo$_2$S$_8$} units may remain, similarly as has been shown for the thermal decomposition of (NH$_4$)$_2$[Mo$_6$S$_8$]H$_2$O.$^{41}$ These {Mo$_2$S$_8$} units are formed in every “layer” and aggregate to build up the MoS$_2$ lattice.

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References and Notes