

Structure of amorphous MoS₃

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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 S₂²⁻ ligands in different types of coordination. This composition corresponds to a formal charge state of Mo^{IV}(S²⁻)(S₂²⁻). The emission infrared spectrum of MoS₃ exhibits characteristic vibrations that are also encountered in the spectra of triangular Mo^{IV}₃S₄ cluster compounds. Three of such cluster compounds, i.e. (NH₄)₂[Mo^{IV}₃S₁₃]·H₂O, K₅[Mo₃S₄(CN)₉]·2H₂O, and (NEt₄)₂[Mo^{IV}₃S₇Cl₆] 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)₃-sulfur cluster types.

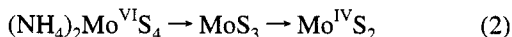
Introduction

Molybdenum sulfides are widely used as catalysts for hydrotreating, where hydrodesulfurization (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.^{2,3} 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:



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.⁸ While crystalline Mo(VI) oxides^{9,10} and Mo^{IV}S₂¹¹ 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.

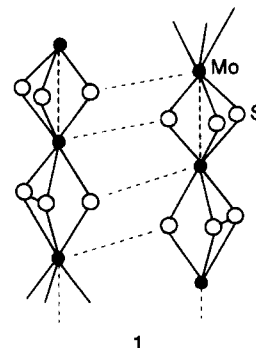
MoS₃ is typically prepared from (NH₄)₂Mo^{VI}S₄, either by acidification of an aqueous solution or by thermal decomposition in an inert gas atmosphere at temperatures between 260 and 300 °C.¹² Above 310 °C, MoS₃ decomposes to microcrystalline MoS₂,¹³ which is the thermodynamically most stable Mo(IV)-sulfur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



is essentially the same as that of the sulfidation of molybdenum oxides (reaction 1), while the reduction of Mo^{VI} → Mo^{IV} 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 W₃S₉²⁻ 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 MoS₃ (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 Mo^V(S₂²⁻)_{1/2}(S²⁻)₂. Further studies from these authors appeared in agreement with this structure, in particular with the presence of two different Mo-Mo distances.²⁰

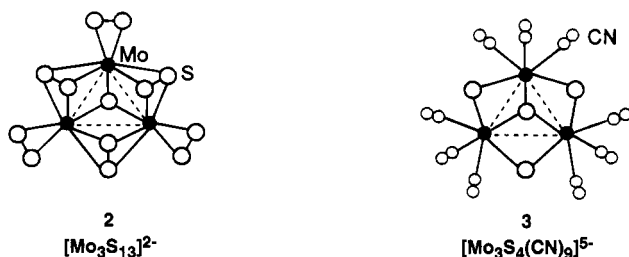


Whereas diffraction and spectroscopy provide direct structural probes, important information on the nature of structural units

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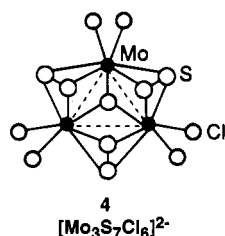
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can also be obtained chemically by cluster extrusion. Two of such extrusion experiments, in which MoS₃ was treated with aqueous solutions of NH₃ and KCN, yielded the (NH₄)₂[Mo^{IV}₃S₁₃]·H₂O²¹ and the K₅[Mo^{IV}₃S₄(CN)₉]·2H₂O²² cluster compounds, respectively. As both compounds contain Mo^{IV}



in a triangular geometry, their formation from MoS₃ under essentially destructive reaction conditions is impossible to explain on the basis of the Mo^V chainlike structure MoS₃ proposed by Liang et al.^{18,19} (structure 1). Reinvestigation of the MoS₃ structure therefore becomes necessary.

In this paper we report on the formation and the structure of amorphous MoS₃, as investigated with three spectroscopic techniques, monochromatic XPS and *in situ* Raman and infrared emission spectroscopy (IRES). We refer to the literature for further information on these methods.²³⁻²⁵ A new extrusion experiment yields the (NEt₄)₂[Mo^{IV}₃S₇Cl₆] (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(IV)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 reported here and is also compatible with spectroscopic data from the literature.

Experimental Section

Sample Preparation and Cluster Extrusion. (NH₄)₂MoS₄²⁶ and (NH₄)₂[Mo₃S₁₃]·H₂O²⁷ 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)₂MoS₄ 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)₂MoS₄ 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 (NEt₄)₂[Mo₃S₇Cl₆] 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 NEt₄Cl, 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 (NEt₄)₂[Mo₃S₇Cl₆]·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)₂MoS₄ 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)₂MoS₄, 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)₂MoS₄, (NH₄)₂[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)₂MoS₄ 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)₂MoS₄ 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)₂MoS₄ 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 3d_{5/2} binding energy (see Table 1) of the cluster compound (229.0 eV) corresponds to the expected value for Mo(IV)-sulfur compounds, i.e. (NH₄)₂[Mo₃S₁₃]·H₂O³² and MoS₂.³³ Note that the sulfur ligands in both compounds differ, but do not affect the Mo 3d_{5/2} 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

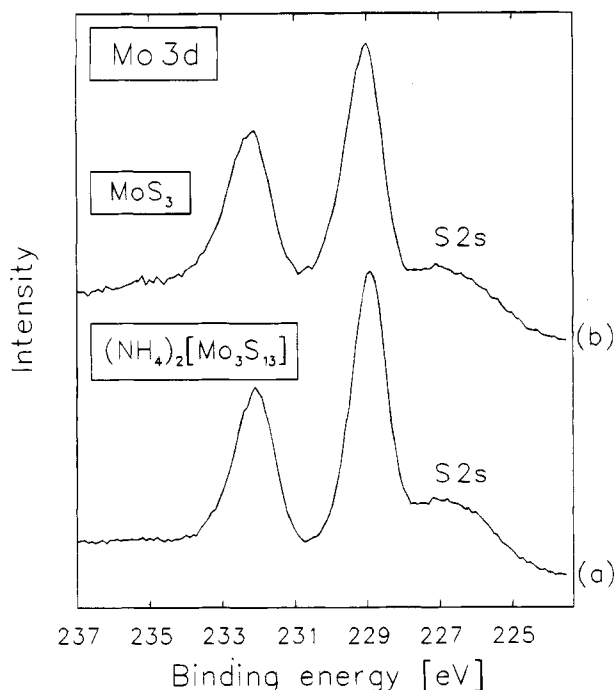


Figure 1. Mo 3d XPS spectra of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (a) and MoS_3 (b).

formal oxidation state as in $(\text{NH}_4)_2[\text{Mo}_3\text{S}]\cdot\text{H}_2\text{O}$ and MoS_2 , 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,³⁴ the S 2p spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$, as shown in Figure 2a, contains three doublets corresponding to the bridging and terminal S_2^{2-} ligands and to the μ_3 (apical) S^{2-} ligand of the cluster anion. The S 2p_{3/2} binding energies are given in Table 1, along with the value for MoS_2 . Note that the basal plane S^{2-} ligands of MoS_2 have the same binding energy as the terminal disulfide ones. The S 2p spectrum of MoS_3 (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 S_2^{2-} and/or apical S^{2-} ligands and the other with either terminal S_2^{2-} , S^{2-} , 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 MoS_3 and $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ strongly resemble each other and point to certain similarities in the structure of the two compounds. We conclude that MoS_3 contains molybdenum in the 4+ oxidation state, which implies that the formation of $\text{Mo}^{\text{IV}}\text{S}_3$ from $(\text{NH}_4)_2\text{Mo}^{\text{VI}}\text{S}_4$ is accompanied by molybdenum-sulfur redox processes, which lead to reduction of molybdenum, $\text{Mo}^{\text{VI}} \rightarrow \text{Mo}^{\text{IV}}$, and consequently to oxidation of S^{2-} ligands of the MoS_4^{2-} anion.

The infrared spectra of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ and MoS_3 are shown in Figure 3. The spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (Figure 3a) shows the characteristic bands of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster anion. The bands with the highest intensity are those

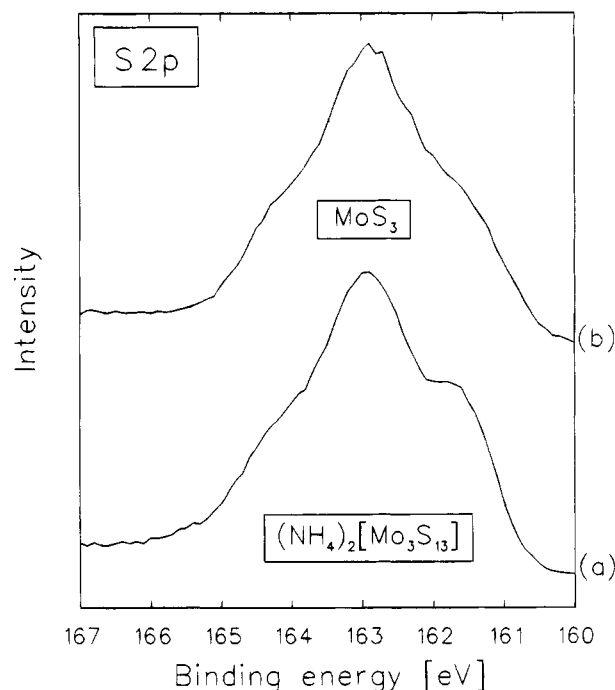


Figure 2. S 2p XPS spectra of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (a) and MoS_3 (b).

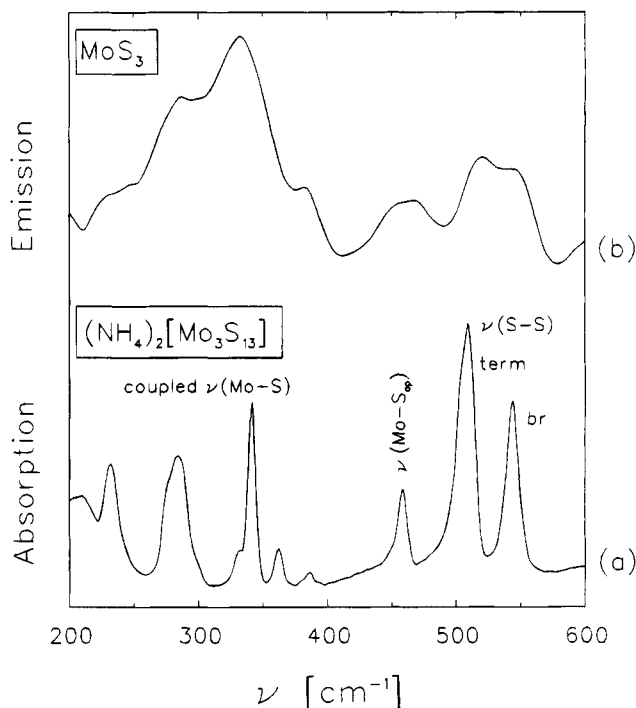


Figure 3. Absorption infrared spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (a) and emission infrared spectrum of MoS_3 measured at 260 °C in argon (b).

due to the $\nu(\text{S}-\text{S})$ vibrations, i.e. the $\nu(\text{S}-\text{S})_{\text{br}}$ vibration at 544 cm^{-1} and the $\nu(\text{S}-\text{S})_{\text{t}}$ vibration at 510 cm^{-1} . A characteristic

TABLE 1: XPS Data of Molybdenum Compounds

compound	Mo 3d _{5/2} (eV)	assignment	S 2p _{3/2} (eV)	assignment
$(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$	229.0 ± 0.2	Mo^{4+}	163.1 ± 0.2	S_2^{2-} bridging
			161.7 ± 0.2	S_2^{2-} terminal
			163.0 ± 0.5	S^{2-} apical
MoS_3	229.1 ± 0.2	Mo^{4+}	162.9 ± 0.2	S_2^{2-} bridging
			161.6 ± 0.2	S_2^{2-} terminal and/or S^{2-}
MoS_2^{33}	229.0 ± 0.2	Mo^{4+}	161.8 ± 0.2	basal plane S^{2-}

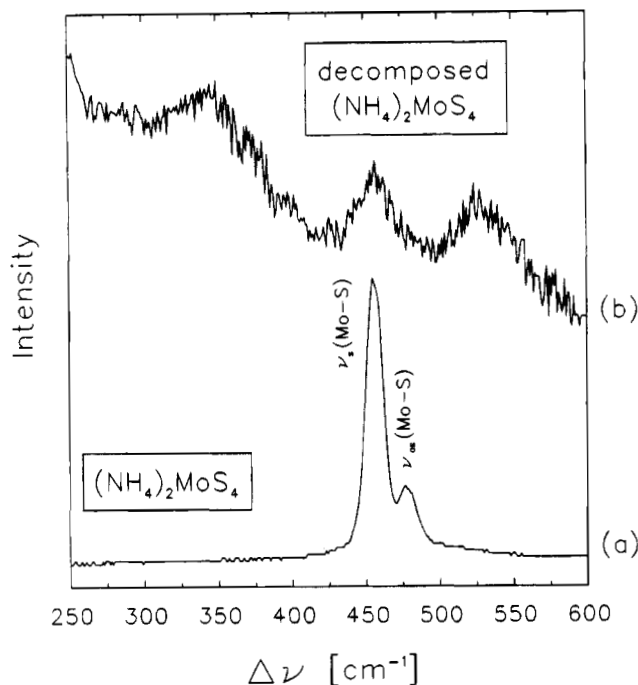


Figure 4. Raman spectra of $(\text{NH}_4)_2\text{MoS}_4$ (a) and of a decomposition intermediate after 5 min at 260 °C in argon (b).

feature of this compound is the $\nu(\text{Mo-S})$ vibration of the apical sulfur at 459 cm^{-1} . The bands below 400 cm^{-1} are due to coupled $\nu(\text{Mo-S})$ vibrations.³⁵

The infrared emission spectrum of MoS_3 (Figure 3b) shows features very similar to those of the IR absorption spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$, 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 $\nu(\text{S-S})_{\text{br}}$, $\nu(\text{S-S})_{\text{t}}$, and $\nu(\text{Mo-S}_{\text{ap}})$ vibrations, respectively. The band corresponding to the $\nu(\text{S-S})_{\text{t}}$ vibration is shifted by 10 cm^{-1} to higher wavenumbers as compared to that of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$. Due to coupling of $\nu(\text{Mo-S})$ and $\nu(\text{S-S})$ 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 $\nu(\text{S-S})$ vibrations.³⁶ The bands at 285, 330, and 380 cm^{-1} , which also have corresponding features in the spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$, can be assigned to coupled $\nu(\text{Mo-S})$ vibrations containing $\nu(\text{Mo-S}_{\text{t}})$, $\nu(\text{Mo-S}_{\text{br}})$, and $\nu(\text{Mo-S}_{\text{ap}})$ contributions. The important point to note is that virtually all the characteristic vibrational features of the $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster anion appear to be present in the spectrum of MoS_3 as well.

The results described thus far concern MoS_3 prepared in solution. The following experiments pertain to thermally decomposed $(\text{NH}_4)_2\text{MoS}_4$ and serve to demonstrate that part of the terminal S^{2-} ligands as present in the MoS_4^{2-} anion indeed undergo oxidation to disulfide ligands.

Figure 4 displays the Raman spectra of $(\text{NH}_4)_2\text{MoS}_4$ and of a decomposition intermediate after 5 min at 260 °C. The spectrum of $(\text{NH}_4)_2\text{MoS}_4$ (Figure 4a) contains two sharp bands at 455 and 476 cm^{-1} corresponding to the symmetric ($\nu_1(\text{A}_1)$) and antisymmetric ($\nu_3(\text{F}_2)$) $\nu(\text{Mo-S})$ vibrations of the MoS_4^{2-} anion,³⁷ respectively. The spectrum of the decomposition intermediate (Figure 4b) also shows a band around 455 cm^{-1} , which we assign to the $\nu(\text{Mo-S})$ vibration of $\text{Mo}=\text{S}_{\text{t}}$ fragments in an environment of lower symmetry compared with the MoS_4^{2-} 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

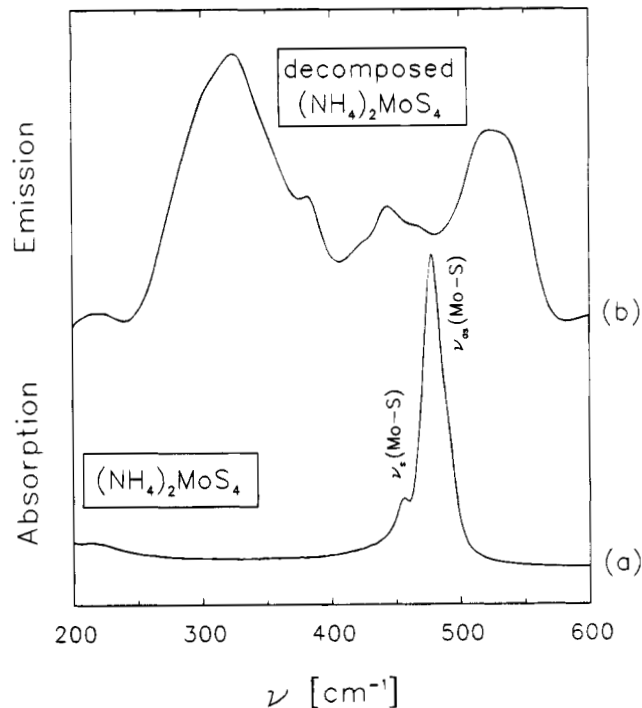


Figure 5. Absorption infrared spectrum of $(\text{NH}_4)_2\text{MoS}_4$ (a) and emission infrared spectrum of a decomposition intermediate after 15 min at 260 °C in argon (b).

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 $\nu(\text{S-S})$ vibrations of terminal and bridging S_2^{2-} ligands, respectively, which are observed at 522 cm^{-1} (terminal) and 553 cm^{-1} (bridging) in the Raman spectrum of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$.³⁵ The broad band with a maximum around 350 cm^{-1} must be due to $\nu(\text{Mo-S})$ vibrations and corresponds to the presence of bridging S_2^{2-} ligands. Although this Raman spectrum is of modest quality, it nevertheless unequivocally confirms the presence of S_2 groups in thermally decomposed $(\text{NH}_4)_2\text{MoS}_4$.

Figure 5 shows the infrared spectra of $(\text{NH}_4)_2\text{MoS}_4$ and of a thermal decomposition intermediate. The absorption IR spectrum of $(\text{NH}_4)_2\text{MoS}_4$ (Figure 5a) contains two sharp bands at 456 and at 478 cm^{-1} corresponding to the symmetric and antisymmetric $\nu(\text{Mo-S})$ vibrations of the MoS_4^{2-} 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 MoS_3 , as shown in Figure 3b. 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 coupled $\nu(\text{Mo-S})$ vibrations, as discussed above. The 445 cm^{-1} band with shoulders at 430 and 470 cm^{-1} is probably a superposition of $\nu(\text{Mo-S})$ vibrations of $\text{Mo}=\text{S}_{\text{t}}$ fragments (see above) and of the $\nu(\text{Mo-S})$ vibration of apical S^{2-} ligands. The emission infrared spectrum thus indicates that the thermal decomposition product obtained after heating $(\text{NH}_4)_2\text{MoS}_4$ for 15 min at 260 °C possesses disulfide as well as apical sulfur ligands and is almost similar to that of amorphous MoS_3 .

If MoS_3 is treated with boiling concentrated HCl, an extrusion product can be isolated from the reaction mixture by adding NET_4Cl . The infrared spectrum of this extrusion product is shown in Figure 6. This spectrum is virtually equivalent to the one published for the $(\text{NET}_4)_2[\text{Mo}_3\text{S}_7\text{Cl}_6]\cdot\text{H}_2\text{O}$ cluster compound

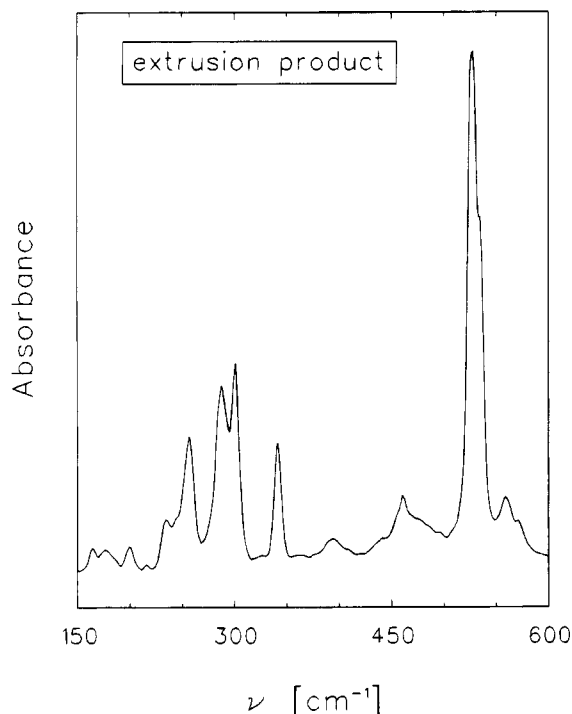


Figure 6. Absorption infrared spectrum of the extrusion product obtained by treating MoS₃ in boiling hydrochloric acid. The spectrum is virtually identical to that of the triangular (NEt₄)₂[Mo₃S₇Cl₆]·H₂O cluster compound.

as prepared from (NH₄)₂[Mo₃S₁₃]·H₂O,²⁹ where also a vibrational analysis is given. The bands at 559 and 570 cm⁻¹ are due to ν(S–S) vibrations, and the band at 461 cm⁻¹ corresponds to the ν(Mo–S) vibration of the apical sulfur. The bands between 350 and 250 cm⁻¹ are due to coupled ν(Mo–S) + ν(Mo–Cl) vibrations; those between 250 and 200 cm⁻¹ mainly correspond to deformation modes mixed with external, i.e. translational and rotational, modes. The bands at low wavenumbers, i.e. at 166 and 177 cm⁻¹, contain significant metal–metal stretching contributions. Although the band at 528 cm⁻¹ has the highest intensity, it is not discussed in ref 29; we tentatively assign this band to coupled ν(S–S) + ν(Mo–Cl) vibrations. The fact that (NEt₄)₂[Mo₃S₇Cl₆] can be prepared from both MoS₃ and (NH₄)₂[Mo₃S₁₃]·H₂O under comparable reaction conditions again points to similarities in the structures of MoS₃ and the triangular Mo₃–S_x compounds.

Discussion

The following results are essential in considering a structure for amorphous MoS₃.

(i) The XPS Mo 3d_{5/2} binding energy of 229.1 eV indicates that MoS₃ contains molybdenum in a formal 4+ oxidation state.

(ii) The XPS S 2p spectrum of MoS₃ shows the presence of different types of sulfur ligands, which may include bridging and terminal S₂²⁻ and bridging S²⁻ ones.

(iii) The emission infrared spectrum of MoS₃ contains all the characteristic vibrations that are encountered in the infrared spectrum of the triangular cluster compound (NH₄)₂[Mo₃S₁₃]·H₂O.

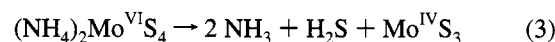
(iv) Three triangular cluster compounds, (NH₄)₂[Mo₃S₁₃]·H₂O,²¹ K₅[Mo₃S₄(CN)₉]·2H₂O,²² and (NEt₄)₂[Mo₃S₇Cl₆], can be extruded from MoS₃ using chemical reactions that are essentially destructive.

On the basis of these results, we propose that MoS₃ is essentially an aggregation of Mo(IV)₃–sulfur cluster types, from which the {Mo₃S₇}⁴⁺ and {Mo₃S₄}⁴⁺ cores—the central parts of the extrusion products—can be readily abstracted under

destructive reaction conditions. This particular interpretation of the extrusion experiments (an extrusion of preformed structures instead of a synthesis in the reaction mixture) is supported by a FAB-MS study of K₂[Mo₃S₁₃]·*n*H₂O, which has been extruded from a physical mixture of ⁹²MoS₃/¹⁰⁰MoS₃.³⁸ The mass spectrum of the extrusion product shows mainly signals due to pure ⁹²Mo₃– and ¹⁰⁰Mo₃–sulfur fragments.

The MoS₃ structure as built up from Mo₃S_x units possesses locally a relatively high degree of internal organization. How reasonable is it to assume that this kind of structure forms in a thermal decomposition of a rather simple compound as (NH₄)₂–MoS₄?

The thermal decomposition of (NH₄)₂MoS₄ according to



is accompanied by molybdenum–sulfur redox processes, namely, oxidation of S²⁻ ligands of the MoS₄²⁻ anion (2S²⁻ → S₂²⁻ + 2e) and reduction of the metal (Mo^{VI} + 2e → Mo^{IV}). The first elementary step in (3) may be described as a proton transfer from the two NH₄⁺ cations to an S²⁻ ligand of the MoS₄²⁻ anion, leading to NH₃ and a neutral {S₃Mo(SH₂)} intermediate, which immediately decomposes to gaseous H₂S and {MoS₃}. Simultaneous with the release of H₂S, 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 (NH₄)₂MoS₄ at 260 °C for 5 min forms mainly terminal disulfide ligands, suggesting that a resulting “mononuclear” {MoS₃} intermediate may formally be described as {(S²⁻)–Mo^{IV}–(S₂²⁻)}. The latter is not expected to be stable due to the low coordination number of the metal. Stabilization is achieved by aggregation of these {S–Mo–S₂} fragments (indicated by the band corresponding to bridging S₂²⁻ ligands in the Raman spectrum), where the formation of Mo₃–sulfur substructures is thermodynamically favored.

The aggregation of the {S–Mo–S₂} 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 (NH₄)₂MoS₄.³⁹ Directly after the loss of NH₃ and H₂S, 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–S₂} fragments aggregate mainly within one plane (the *ab*-plane of (NH₄)₂MoS₄).¹⁷ This can be seen in the powder diffraction pattern of MoS₃ (cf. ref 4), which shows a reflection at 2θ = 14.5°. This reflection corresponds to a lattice plane distance of 0.63 nm and points to a “layered structure” for MoS₃. During the aggregation of the {S–Mo–S₂} fragments four 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 S₂²⁻ and those which also include S²⁻ 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 MoS₃ solid, which, however, all satisfy the requirements of stoichiometry and electroneutrality.

The MoS₃ 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 S²⁻ ligand, such as the Mo atoms at the top of structures I and II, the triangles connect via the two S²⁻ ligands in an {Mo–(S)₂–Mo}

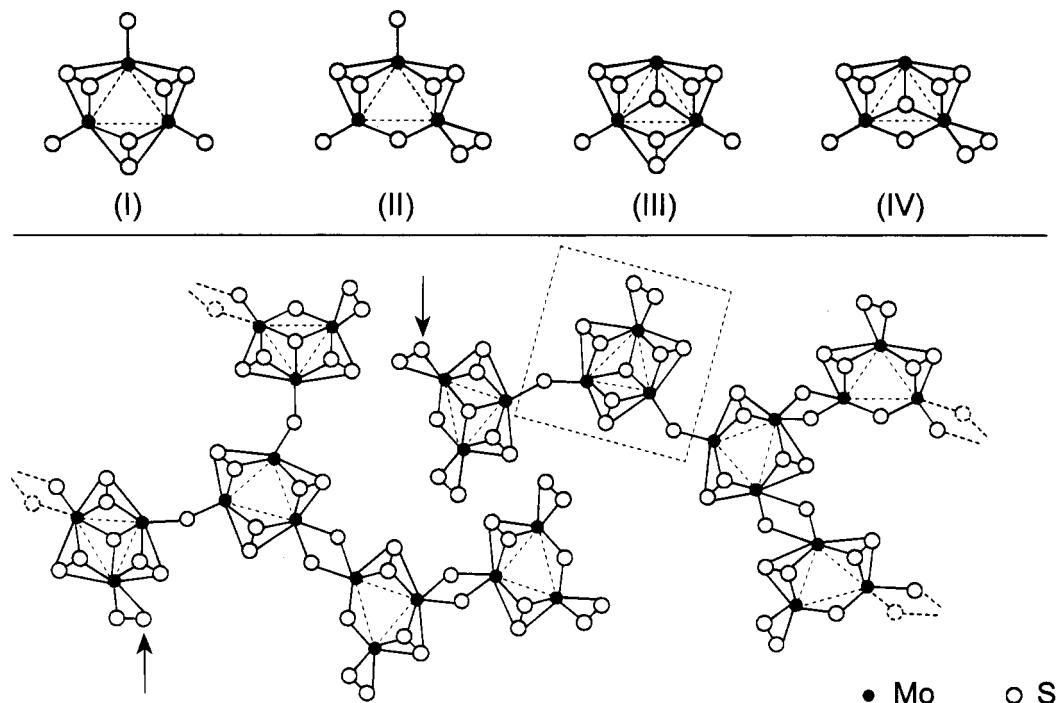


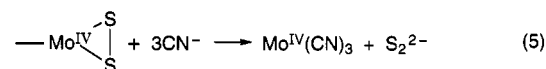
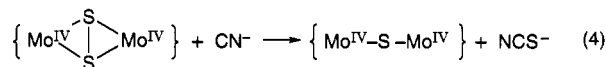
Figure 7. Structures of the $\{\text{Mo}^{\text{IV}}_3\text{-S}_9\}$ cluster types within MoS_3 and a representative part of the MoS_3 structure.

bridge. If only one S^{2-} ligand is available, as when the Mo atoms at the top of structures I and III combine, the triangles connect via an $\{\text{Mo-S-Mo}\}$ bridge. Figure 7 shows a representative part of the MoS_3 structure. Note that the interconnection of the structures I–IV preclude the presence of Mo-S_t fragments and also of coordinatively unsaturated molybdenum atoms as structures I–IV might imply. It is conceivable that Mo atoms at the boundaries of a MoS_3 particle are terminated by S_2 groups (see the arrows in Figure 7), which are required for the coordinative saturation of edge metal centers, where they impede further aggregation. This effect leads to a slightly higher stoichiometry, namely, $\text{MoS}_{3.1}\text{-MoS}_{3.2}$, which in fact was found by elemental analysis,^{13,17} in agreement with the surplus of sulfur found in the XPS spectrum. As the oxidation state of sulfur in the $\{\text{S-Mo-S}_2\}$ fragments does not change during the aggregation process, the charge state of MoS_3 can formally be written as $\text{Mo}^{\text{IV}}(\text{S}^{2-})(\text{S}_2^{2-})$. This charge stoichiometry itself cannot be obtained from the S 2p spectrum (Figure 2b) without additional structural information (vide supra). However, our structural model is in full agreement with the S 2p spectrum of MoS_3 , i.e. $(\text{S}_{2t}^{2-} + \text{S}^{2-}) : (\text{S}_{2br}^{2-} + \text{S}_{ap}^{2-}) = 4:5$.

The MoS_3 structure model (Figure 7) readily accounts for the fact that the extrusion experiments yield triangular Mo_3 cluster compounds. The $[\text{Mo}_3\text{S}_7\text{Cl}_6]^{2-}$ cluster anion forms from $\{\text{Mo}_3\text{S}_7\}^{4+}$ fragments as present in structure III (cf. dashed box) by substitution of all interconnecting sulfur ligands outside the triangle by chlorine. We correlate the yield of this reaction (ca. 10% related to the amount of Mo) with the portion of structure III in MoS_3 .

The extrusion of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ (ca. 20% on the basis of Mo) cannot straightforwardly be correlated with the portion of a substructure in MoS_3 . In this experiment MoS_3 was treated with a solution of NH_3 in H_2O for several days. From the chemistry in solution it is known that $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$ can only be synthesized in a large excess of polysulfide.^{21,27} We therefore argue that MoS_3 decomposes in the reaction mixture under formation of $(\text{NH}_4)_2\text{S}_x$. This would then enable the extrusion of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]\cdot\text{H}_2\text{O}$, in agreement with its higher relative sulfur content than MoS_3 .

Treatment of MoS_3 with an aqueous solution of KCN produces $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]\cdot 2\text{H}_2\text{O}$ with a yield of ca. 35%. The reactions involved in its formation are



in which the $\{\text{Mo}_3\text{S}_4\}^{4+}$ core is formed by subsequent sulfur redox (4) and the metal–ligand substitution (5) reactions from the $\{\text{Mo}_3\text{S}_7\}^{4+}$ (structure III) and the $\{\text{Mo}_3\text{S}_6\}^{4+}$ 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 $\text{K}_8[\text{Mo}^{\text{III}}_4\text{S}_4(\text{CN})_8]\cdot 4\text{H}_2\text{O}$ in varying low percentages (<3%).²² 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 $\{\text{Mo}^{\text{III}}_4\text{S}_4\}^{4+}$ 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 $\text{Mo-(S)}_2\text{-Mo}$ bridges over that by Mo-S-Mo ones.

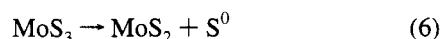
EXAFS measurements by Cramer et al.²⁰ have indicated that the spectrum of MoS_3 possesses scattering contributions from two Mo–Mo distances, 0.274 and 0.314 nm, and mainly one Mo–S distance of 0.241 nm. Metal–metal and metal–sulfur distances in our structural model can be estimated using the X-ray structure data of relevant molybdenum–sulfur cluster compounds. The Mo–Mo distance in structure III should be close to that in the $[\text{Mo}_3\text{S}_{13}]^{2-}$ anion,³² 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 nm⁴⁰ 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 neighbored triangles (cf. also the discussion in ref 21).

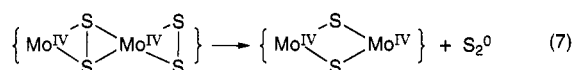
Metal–sulfur distances in MoS_3 should fall between 0.236 and 0.248 nm according to the X-ray data of the $[Mo_3S_{13}]^{2-}$ and the $[Mo_3S_4(CN)_9]^{5-}$ cluster anions,^{32,33} which are $d(Mo-S_{ap}) = 0.236$ nm, $d(Mo-S_t) = 0.245$ nm, and $d(Mo-S_{br}) = 0.248$ nm, while the distance between molybdenum 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 between 0.236 and 0.248 nm, in good agreement with the EXAFS results of Cramer et al.²⁰ Also the magnetic measurements given in ref 18 can easily be explained, as the diamagnetic properties of MoS_3 are due to the electronic structure of Mo^{IV} . The fact that two types of Mo–Mo distances are observed in MoS_3 with EXAFS has implications for the identification of intermediate phases formed during the sulfidation of molybdenum oxides. De Boer et al.⁶ encountered an MoS_3 type intermediate phase but observed only one Mo–Mo distance of 0.276 nm with EXAFS. Although this intermediate phase has the correct stoichiometry, the absence of the longer Mo–Mo distance (0.31 nm) indicates that this phase does not have the characteristic MoS_3 structure as discussed above.

Finally, any structural model for MoS_3 must be able to account for its decomposition into microcrystalline MoS_2 at elevated temperatures:



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^{30,31} formally according to



During decomposition the preformed Mo_3 units are preserved, and after the loss of one sulfur per molybdenum center, reactive $\{Mo_3S_6\}$ units may remain, similarly as has been shown for the thermal decomposition of $(NH_4)_2[Mo_3S_{13}] \cdot H_2O$.⁴¹ These $\{Mo_3S_6\}$ units are formed in every "layer" and aggregate to build up the MoS_2 lattice.

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References and Notes

- Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.
- Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 1.
- De Jong, A. M.; Borg, H. J.; van IJendoorn, L. J.; Soudant, V. G. F. M.; de Beer, V. H. J.; van Veen, J. A. R.; Niemantsverdriet, J. W. *J. Phys. Chem.* **1993**, *97*, 6477.
- Chang, C. H.; Chan, S. S. *J. Catal.* **1981**, *72*, 139.
- Payen, E.; Kasztelan, S.; Houssenbay, S.; Szymanski, R.; Grimblot, J. *J. Phys. Chem.* **1989**, *93*, 6501.
- De Boer, M.; van Dillen, A. J.; Koningsberger, D. C.; Geus, J. W. *J. Phys. Chem.* **1994**, *98*, 7862.
- Arnoldy, P.; van der Heijkant, J. A. M.; de Bok, G. D.; Moulijn, J. A. *J. Catal.* **1985**, *92*, 35.
- Knözinger, H. In *Proc. 9th Int. Congr. Catal. Calgary 1988*; Phillips, M. J., Terman, Eds.; The Chemical Institute of Canada: Ottawa, 1989; p 20.
- Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Molybdenum Supplement Vol. B1; Springer-Verlag: Berlin, 1975; p 88.
- Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Molybdenum Supplement Vol. B3a; Springer-Verlag: Berlin, 1986; p 23.
- Dickinson, R. G.; Pauling, L. *J. Am. Chem. Soc.* **1923**, *45*, 1466.
- Diemann, E.; Müller, A. *Coord. Chem. Rev.* **1973**, *10*, 79.
- Wildervanck, J. C.; Jellinek, F. Z. *Anorg. Allg. Chem.* **1964**, *328*, 309.
- Voorhoeve, R. J. H.; Wolters, H. B. M. Z. *Anorg. Allg. Chem.* **1970**, *376*, 309.
- Ratnasami, P.; Rodrigue, L.; Leonard, A. *J. Phys. Chem.* **1973**, *77*, 2242.
- Stevens, G. C.; Edmonds, T. *J. Catal.* **1975**, *37*, 544.
- Diemann, E. Z. *Anorg. Allg. Chem.* **1977**, *432*, 127.
- Liang, K. S.; DeNeufville, J. P.; Jacobson, A. J.; Chianelli, R. R. *J. Non-Cryst. Solids* **1980**, *35&36*, 1249.
- Liang, K. S.; Cramer, S. P.; Johnston, D. C.; Chang, C. H.; Jacobson, A. J.; DeNeufville, J. P.; Chianelli, R. R. *J. Non-Cryst. Solids* **1980**, *42*, 345.
- Cramer, S. P.; Liang, K. S.; Jacobson, A. J.; Chang, C. H.; Chianelli, R. R. *Inorg. Chem.* **1984**, *23*, 1215.
- Müller, A.; Diemann, E.; Krickemeyer, E.; Walberg, H.-J.; Bögge, H.; Armatage, A. *Eur. J. Solid State Inorg. Chem.* **1993**, *30*, 565.
- Müller, A.; Jostes, R.; Eltner, W.; Nie, C.-S.; Diemann, E.; Bögge, H.; Zimmermann, M.; Dartmann, M.; Reinsch-Vogell, U.; Che, S.; Cyvin, S. J.; Cyvin, B. N. *Inorg. Chem.* **1985**, *24*, 2872.
- Niemantsverdriet, J. W. *Spectroscopy in Catalysis, an Introduction*; VCH: Weinheim, 1993.
- Bates, J. B. In *Fourier Transform Infrared Spectroscopy—Application To Chemical Systems*; Ferraro, J. R., Basile, L. J., Eds.; Academic Press: New York, 1978; Vol. 1, p 99.
- Barr, J. K. *Infrared Phys.* **1969**, *9*, 97.
- McDonald, J. W.; Delbert Friesen, G.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.
- Müller, A.; Krickemeyer, E. *Inorg. Synth.* **1990**, *27*, 47.
- Prasad, T. P.; Diemann, E.; Müller, A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1895.
- Fedin, V. P.; Sokolov, M. N.; Mironov, Yu. V.; Kolesov, B. A.; Tkachev, S. V.; Fedorov, V. Ye. *Inorg. Chim. Acta* **1990**, *167*, 39.
- Müller, A.; Weber, Th. *Appl. Catal.* **1991**, *77*, 243.
- Diemann, E.; Weber, Th.; Müller, A. *J. Catal.* **1994**, *148*, 288.
- Müller, A.; Wittneben, V.; Krickemeyer, E.; Bögge, H.; Lemke, M. Z. *Anorg. Allg. Chem.* **1991**, *605*, 175.
- Patterson, T. A.; Carver, J. C.; Leyden, D. E.; Hercules, D. M. *J. Phys. Chem.* **1976**, *80*, 1702.
- Muijsers, J. C.; Weber, Th.; van Hardevelde, R. M.; Zandbergen, H. W.; Niemantsverdriet, J. W. *J. Catal.*, to be published.
- Fedin, V. P.; Kolesov, B. A.; Mironov, Yu. V.; Fedorov, V. Ye. *Polyhedron* **1989**, *8*, 2419.
- Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 142.
- Müller, A.; Fedin, V.; Hegetschweiler, K.; Amrein, W. *J. Chem. Soc., Chem. Commun.* **1992**, 1795.
- Schäfer, H.; Schäfer, G.; Weiss, A. Z. *Naturforsch.* **1969**, *B19*, 76.
- Pan, W.-H.; Leonowicz, M. E.; Siefel, E. I. *Inorg. Chem.* **1993**, *22*, 672.
- Müller, A.; Diemann, E. *Chimia* **1985**, *39*, 312.