$[Mo_3^{IV}S_{13}]^{2\ominus}$, a Model for Crystalline MoS_2

Remarks on the Thermal Decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot n\,H_2O$ and its Catalytical Relevance**

Achim Müller* and Ekkehard Diemann

Abstract: The thermal decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot n\,H_2O$ yields microcrystalline MoS_2. The reaction has been studied by vibrational spectra and X-ray diffraction. A stepwise mechanism is proposed and discussed in terms of the structural relations between the starting material and the final product. It is shown that $[Mo_3^{IV}S_{13}]^{2\ominus}$ may be regarded as a model for crystalline molybdenum(IV) sulfide.

Hydrodesulfurization of petroleum on MoS_2/Al_2O_3 catalysts (containing promotors like Co on the edges of the MoS_2 crystallites) represents one of the most important heterogeneous catalytical reactions employed worldwide[1], as more than three billion tons of crude oil are processed per year. On the other hand, MoS_2 is an extremely versatile catalyst for rather different types of reactions, like hydrogenation, reductive etherefication, and dehydrogenation. In this communication we wish to show the structural relation between the discrete $[Mo_3S_{13}]^{2\ominus}$ ion and the crystalline molybdenum(IV) sulfide.

From many independent experiments, it turns out that MoS_2 is the most stable binary molybdenum sulfur compound in the solid state while $[Mo_3^{IV}S_{13}]^{2\ominus}$ seems to be the corresponding most stable discrete species (formed from solutions of the most higher valence state molybdenum compounds with polysulfide upon heating). Fig. 1 shows their structural relations. Removing the apical sulfur atom from $[Mo_3S_{13}]^{2\ominus}$ (*A*), the $S_2^{2\ominus}$ groups would now be ordered symmetrically around the Mo_3 triangle in structure *B*. Adjusting the bond distances d(MoMo) from 2.72 to 3.15 Å and d(SS) from about 2.0 to 3.6 Å, we see already a complete section from the MoS_2 lattice. Reversely, we can regard the $[Mo_3S_{13}]^{2\ominus}$ ion as a model for the surface of crystalline MoS_2, with $S_2^{2\ominus}$ groups at the edges and μ_3-S atoms at the basal planes of the crystallites.

The thermal decomposition illustrated schematically in Fig. 1 has also been studied experimentally (DTA/TG measurements, by IR-spectra and XRD measurements of the intermediate products)[3]. In addition we have calculated the X-ray scattered intensity for different models using *Debye*'s scattering equation[2]. Including the results from our earlier studies[3] we describe schematically the thermal decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot n\,H_2O$ as follows (cf. Fig. 1): After the loss of the water of crystallization up to 150 °C (if n was > 0) the first reaction of the anion *A* itself is the release of the apical sulfur atom as H_2S (at ca. 260 °C together with some ammonia). The bridging $S_2^{2\ominus}$ groups, which were centered below the Mo_3 plane in *A*, can now be ordered with a mirror plane through the three metal atoms. During this procedure the metal-to-metal distance keeps at about 2.7 Å. At higher temperatures from ca. 310 °C the sample loses continuously up to six equivalents of neutral sulfur (originating from the terminal $S_2^{2\ominus}$ groups in *B* as is indicated in the IR-spectra). Two electrons are left per metal center by this reductive elimination which are

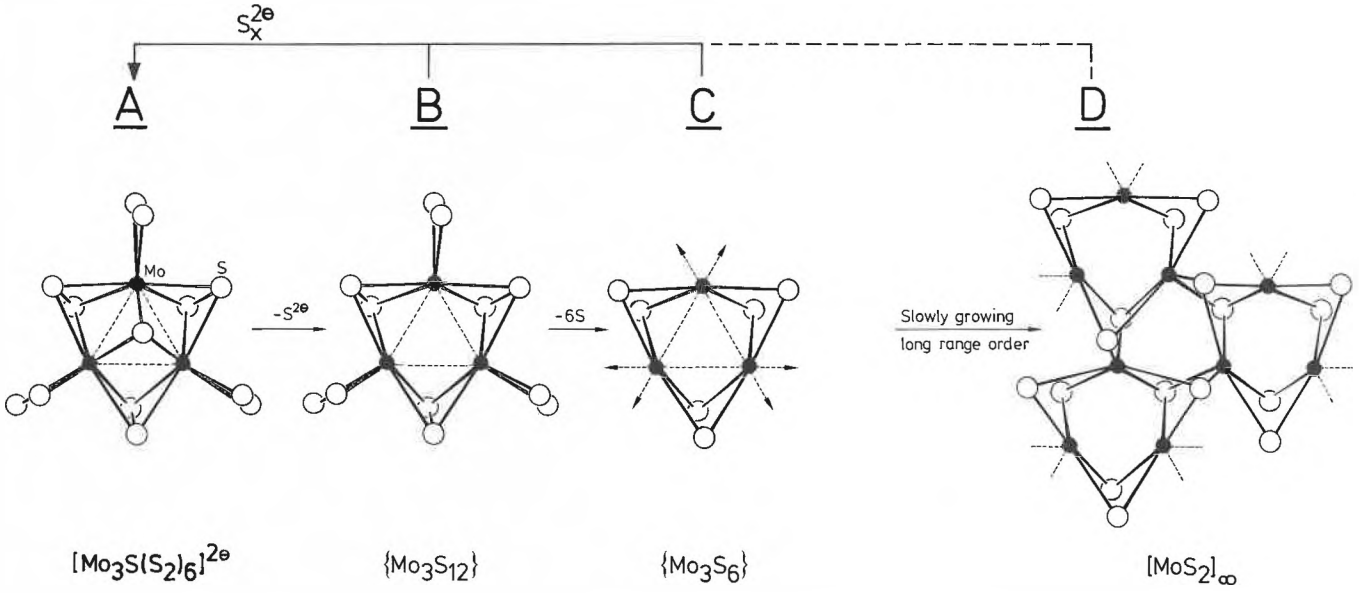

Fig. 1. Schematical presentation of the structural changes involved in the thermal decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot n\,H_2O$ (overall reaction $\rightarrow 2\,NH_3 + H_2S + 3\,MoS_2 + 6\,S^0 + n\,H_2O$); $[Mo_3S_{13}]^{2\ominus}$ can be reobtained by the reaction with $S_x^{2\ominus}$ as indicated; the hypothetical $\{Mo_3S_{12}\}$ represents a segment of crystalline MoS_2.

* *Correspondence:* Prof. Dr. A. Müller, Dr. E. Diemann
Fakultät für Chemie der Universität
Postfach 8640, Universitätsstrasse, D-4800 Bielefeld 1
(Bundesrepublik Deutschland)

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used to reduce each bridging $S_2^{2\ominus}$ group to two (bridging) $S^{2\ominus}$ ligands. The SS distance increases from 2.0 Å to 3.6 Å in the resulting fragment *C*. This unit, still with short metal-to-metal distances, will not be stable and adds immediately (bridging) $S^{2\ominus}$ ligands from neighbouring triangles to the coordinatively unsaturated Mo sites. Each

molybdenum gets now more than two metal neighbours, the MoMo distance increases to its final value (3.15 Å in the MoS_2 structure with six Mo neighbours around each metal atom).

Remarkably, during the whole reaction there is no change in the oxidation state of molybdenum as one equivalent of hydrogen sulfide and in addition only neutral sulfur is released.

Since the average number of sulfur atoms in the first coordination sphere of molybdenum does not vary strongly, the major changes in the X-ray scattered intensity of the intermediate products of the thermal decomposition should reflect the variation of the MoMo distances. We should observe two diffuse maxima in the scattering curve between 20 and 100 degree 2θ (employing $Cu_{K\alpha}$-radiation at $2\theta \approx 42$ and 86° for model structure *A*, shifting to 36 and 65°, respectively for model *D*). Although particularly at lower scattering angles the experimentally obtained curve is screened by crystalline residues of the starting material or the beginning crystallization of MoS_2, respectively, the experimental data show the behaviour as expected from the model calculations. The material with the most proceeded conversion ($T = 450\,°C$) shows two diffuse maxima between 60 and 90°, indicating the presence of both, Mo_3 triangles with short and long MoMo distances. Crystallization occurs mainly in the *ab* plane (increase of the [100] reflection and a less pronounced growing parallel to the *c* axis of MoS_2 ([002] reflection)).

Our preliminary studies regarding the catalytic activity of thermally decomposed $(NH_4)_2[Mo_3S_{13}]\cdot n\ H_2O$, e.g. for hydrodesulfurization[5], are promising as expected. We believe that reactions of (dissolved) $[Mo_3S_{13}]^{2\ominus}$ and of the small size aggregates resulting from its thermal decomposition can help to understand the reactions catalysed by MoS_2 and the corresponding promoted phases. $S_2^{2\ominus}$ surface groups have already been suspected to be involved in the reactions taking place at the catalyst[6].

Experimental

$(NH_4)_2[Mo_3S_{13}]\cdot n\ H_2O$ was prepared as described previously[4]. The thermal decomposition was done in a Linseis-L 81 thermoanalytical system at pressures of $p \approx 10^{-5}$ mbar. IR-spectra were obtained from Nujol mulls with a Beckman-IR 4250 spectrometer. $Cu_{K\alpha}$-radiation was employed for the measurement of the scattering curve with a Philips vertical powder diffractometer.

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[1] Cf. H. Topsøe, in J. P. Bonelle et al.: *Surface Properties and Catalysis by Non-Metals*, Reidel, Dordrecht (1983), p. 329f.
[2] B. E. Warren: *X-Ray Diffraction*, Addison-Wesley, Reading, MA (1968).
[3] E. Diemann, A. Müller, P. J. Aymonino, *Z. Anorg. Allg. Chem. 479* (1981) 191.
[4] A. Müller, R. G. Bhattacharyya, B. Pfefferkorn, *Chem. Ber. 112* (1979) 778.
[5] A. Müller, H. Topsøe et al., to be published.
[6] J. B. Goodenough, in H. F. Barry, P. C. H. Mitchell: *Proc. Climax 4th Int. Conf. Chem. Uses Molybdenum*, Ann Arbor (1982), p. 1.