

TEM study on the single crystal Mo₁₈O₅₂ and Mo₈O₂₃

D. Wang, D. S. Su, J. Jäger, R. Schlögl

*Fritz-Haber-Institute der Max-Planck-Gesellschaft, Abteilung Anorganische Chemie,
Faradayweg 4-6, Berlin, D-14195, Germany*

Mixed molybdenum oxide catalysts are used extensively in the selective oxidation of hydrocarbons. Hence, molybdenum trioxide and molybdenum suboxides are of great interests due to their utilities as model system to elucidate the correlations between the structure and the catalytic performance [1, 2]. However, question remains whether the proposed defect structures, e.g., crystallographic shear (CS) planes [3] of these oxides play an important role in the oxygen insertion process (so called Mars-van Krevelen mechanism). As a preparation for further investigations on the structures of molybdenum oxides during reduction and oxidation, single crystal Mo₁₈O₅₂ and Mo₈O₂₃ are studied by electron diffraction and High-Resolution Transmission Electron Microscopy (HRTEM) in combination with image simulation to show the feasibility of detecting the defected structures ex-situ.

The structure of Mo₁₈O₅₂ can be regarded as derived from MoO₃ by the crystallographic shear operation along the $[1/2\mathbf{a}_M-1/6\mathbf{b}_M]$ in $(35\bar{1})_M$ plane, where subscript M denotes the vectors and planes of the MoO₃ crystal. The Mo₁₈O₅₂ formed exhibits a triclinic cell and its [100] zone corresponds to the $[\bar{1}12]$ zone of MoO₃ [4]. The structure Mo₈O₂₃ can be derived from the ReO₃ type by placing the edge-sharing MoO₆ octahedra in the (102) plane of the ReO₃ structure [5].

Diffraction patterns and high-resolution electron microscope images are taken on a Philips CM200 FEG microscope, under different focus conditions. Simulation with the Cerius package is carried out using the structure models of Mo₁₈O₅₂ and Mo₈O₂₃, along their **a**, **b** and **c** zones, with crystal thicknesses from 20 to 200 Å and focus values from -1400 to 900 Å. The [010] projected diffraction patterns of Mo₈O₂₃ show strong diffraction spots arising from the basic MoO₆ octahedra and satellite spots from the CS planes. Three of the experimental images are shown in such agreement with the simulated images that the crystallographic shear structure exhibits similar contrast for each pair. For Mo₁₈O₅₂, diffraction patterns are taken in [100] projection. The presence of the CS planes can be clearly seen due to the additional diffraction spots to those of the $[\bar{1}12]$ projected MoO₃. The [100] projected high-resolution image under appropriate thickness and focus conditions shows the CS planes directly by its contrast, with the simulated image matching its contrast. Images for MoO₃ on $[\bar{1}12]$ projection are simulated as well under the same conditions for reference.

HRTEM in combination with the image simulation techniques can be used to reveal the defected structures (e.g., CS planes) in molybdenum oxides. The coincidence of the simulation with the experiment presented confirms its reliability. Further in-situ HRTEM studies will be conducted to the molybdenum oxides to elucidate the structure evolution during the processes of reduction and oxidation.

Reference:

- [1] T. Ressler, etc., *J. Catalysis* **191** (2000) 75.
- [2] Y. Uchida, etc., to be published.
- [3] L. A. Bursill, *Proc. Roy. Soc.* **A311** (1969) 269.
- [4] L. A. Bursill, *Acta Cryst.* **A28** (1972) 187.
- [5] L. Kihlberg, *Ark. Kemi.* **21** (1963) 471.