

**In situ XAS and XRD studies on the formation of Mo suboxides during reduction of MoO<sub>3</sub>**

Ressler T., Jentoft R.E., Wienold J., Günter M.M., Timpe O.

Ressler T, Max Planck Gesellschaft, Fritz-Haber-Institut, Dept. Inorganic Chemistry, Faradayweg 4-6, D-14195 Berlin, Germany

Abstract:

Reduction of MoO<sub>3</sub> with hydrogen (5-100 vol %) in the temperature range from 573 to 833 K was studied by in situ X-ray diffraction and X-ray absorption spectroscopy. The experiments performed focused on elucidating phase composition and evolution with time under isothermal as well as temperature-programmed reduction conditions. At reaction temperatures below 698 K, the reduction of MoO<sub>3</sub> to MoO<sub>2</sub> is a one-step process without the formation of crystalline intermediates. At reduction temperatures above 723 K and H<sub>2</sub> concentrations higher than 10 vol %, Mo metal is the final product of the reduction of MoO<sub>3</sub>. In addition, at temperatures higher than 698 K, the formation of Mo<sub>4</sub>O<sub>11</sub> was observed. However, Mo<sub>4</sub>O<sub>11</sub> is not an intermediate in the reduction of MoO<sub>3</sub> but is being formed in a parallel reaction from MoO<sub>3</sub> and MoO<sub>2</sub> at temperatures above 698 K. It is shown that Mo<sub>4</sub>O<sub>11</sub> can be obtained from a reaction of MoO<sub>3</sub> and MoO<sub>2</sub> at temperatures above 773 K, affording the same phase ratio of monoclinic and orthorhombic Mo<sub>4</sub>O<sub>11</sub> as the reduction of MoO<sub>3</sub> with hydrogen. Quantitative XRD analysis reveals a sigmoidal shape of the evolution of the MoO<sub>3</sub> and MoO<sub>2</sub> phases during reduction of MoO<sub>3</sub> and an increase in the crystallite size of the phases present. This Oswald ripening indicates that a nucleation-growth kinetic mechanism governs the reduction of MoO<sub>3</sub> under the conditions studied. The results presented in this work clearly demonstrate the potential of a combined application of in situ XRD and XAFS to reveal phase composition and kinetics of solid-state reactions.