

## Festkörperkinetik der Reduktion und Oxidation von Molybdänoxiden

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

Abteilung Anorganische Chemie, Fritz-Haber-Institut der MPG  
Faradayweg 4-6, 14195 Berlin

Molybdenum oxide based catalysts are extensively employed for the partial oxidation of alkenes both in industrial applications and academic research ( ). Therefore, the properties of a large variety of molybdenum containing systems have been studied in detail, in particular to elucidate relationships between the structure of these systems and their catalytic behavior. The reduction of  $\text{MoO}_3$  is a crucial step in the redox mechanism of partial oxidation reactions on this material. In addition to reduction of the metal oxide catalyst, re-oxidation of the catalyst bulk is the other crucial step in the redox mechanism. The oxidation step needs to follow the reduction of the metal oxide by the alkene in order to replenish the oxygen in the bulk of the metal oxide catalyst.

Of the bulk techniques which can be employed to study a catalytically active material in situ we used X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). In addition to steady-state investigations, both techniques permit experiments with a suitable time-resolution to monitor the structural evolution of bulk phases and from that to elucidate the solid-state kinetics of the reactions involved (Figure 1) ( ). In this work we present results obtained from studies on the reduction of  $\text{MoO}_3$  in hydrogen and in propene, and on the oxidation of  $\text{MoO}_2$  in oxygen. Both isothermal and temperature-programmed experiments under various reactant concentrations are presented. A comprehensive mechanism for the reduction and the re-oxidation of  $\text{MoO}_3$  is proposed and the consequences of this mechanism for the partial oxidation of propene on  $\text{MoO}_3$  are discussed. For the reduction of  $\text{MoO}_3$  in hydrogen it was found that the reaction rate can be described by a sigmoidal rate law (nucleation-growth kinetics) with no change of the rate-determining step over a broad range of reaction conditions (623 K - 823 K, 5 vol% - 100 vol%  $\text{H}_2$ ). The formation of the suboxide  $\text{Mo}_4\text{O}_{11}$  was observed from a parallel reaction of  $\text{MoO}_3$  and  $\text{MoO}_2$ .

Furthermore, the formation of molybdenum bronzes in the early stage of the reduction was observed.

During the reduction of MoO<sub>3</sub> in propene and the oxidation of MoO<sub>2</sub>, only crystalline MoO<sub>3</sub> and MoO<sub>2</sub> were detected by in situ XRD. However, analysis of the in situ XAFS data yielded the formation of “Mo<sub>18</sub>O<sub>52</sub>” type shear-structures as intermediates of both the reduction of MoO<sub>3</sub> in propene and the oxidation of MoO<sub>2</sub> in oxygen. At temperatures below ~ 700 K oxidation of MoO<sub>2</sub> afforded a disordered MoO<sub>3</sub> with “Mo<sub>18</sub>O<sub>52</sub>” type shear-structures in the lattice. Only at temperatures above ~ 700 K complete oxidation to MoO<sub>3</sub> was observed.

The solid-state kinetics of the reduction of MoO<sub>3</sub> in propene exhibits a change in the rate-limiting step both as a function of temperature and as a function of the extent of reduction. With increasing extent of reduction at a given temperature a transition from a nuclei-growth kinetics to a three-dimensional diffusion controlled regime is observed. With decreasing temperature (< 600 K) a transition to a regime that is entirely controlled by oxygen diffusion in the MoO<sub>3</sub> lattice was found. The solid-state kinetics of the oxidation of MoO<sub>2</sub> is governed by three-dimensional diffusion.