Solid State Kinetics of the Reduction and Oxidation of Molybdenum Oxides

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

Abt. Anorganische Chemie, Fritz-Haber-Institut der MPG, 14195 Berlin, Germany

Molybdenum oxide based catalysts are extensively employed for the partial oxidation of light alkenes. However, little is known about the type and density of defects in MoO_3 under reaction conditions and their implication for catalytic activity. Knowing the composition and the evolution of the bulk structure of a heterogeneous catalyst under working conditions (in situ) is a prerequisite for understanding structure-activity relationships and, eventually, for a rational catalyst design. X-ray absorption spectroscopy (XAS) can be employed to study a catalytically active material in situ. In addition to steady-state investigations, a time-resolution in the second range permits to monitor the structural evolution of bulk phases under dynamic conditions. [1] In this work we present results obtained from studies on the reduction of MoO_3 in propene and in propene and oxygen, and on the oxidation of MoO_2 in oxygen. [2] A comprehensive mechanism for the reduction and the re-oxidation of MoO_3 is proposed.

For the reduction of MoO_3 in hydrogen it was found, that the reaction rate could be described by a sigmoidal rate law (nucleation-growth kinetics). The solid-state kinetics of the reduction of MoO_3 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. Analysis of the in situ XAFS data yielded the formation of "$Mo_{18}O_{52}$" type shear-structures as intermediates of both the reduction of MoO_3 in propene and the oxidation of MoO_2 in oxygen. From in situ investigations of the evolution of the bulk structure of MoO_3 under partial oxidation reaction conditions, characteristic shear-structure defects are observed in the layer structure of MoO_3. The defects density appears to depend on both the reaction temperature and the reduction potential of

the gas phase. Apparently, a positive correlation exists between the defect density and the catalytic activity of the material.

[1] T. Ressler, J. Wienold, R.E Jentoft, T. Neisius, M.M. Günter, Topics in Catalysis 2001, 18, 45.
[