

Solid State Kinetics of the Reduction and Oxidation of Molybdenum Oxides

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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 “ $\text{Mo}_{18}\text{O}_{52}$ ” 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.

[2] T. Ressler, J. Wienold, R.E. Jentoft, T. Neisius, J. Catal. 2002, in press.



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