

## Implications of Defects in the Bulk Structure of MoO<sub>3</sub> for the Oxidation of Propene

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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. However, little is known about the type and density of defects in MoO<sub>3</sub> under reaction conditions and their implication for catalytic activity.

In situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) are excellent bulk techniques, which permit studying the structural evolution of a catalytically active material. In addition to steady-state investigations, experiments can be performed 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. <sup>[1]</sup> In this work we present results obtained from studies on the reduction of MoO<sub>3</sub> in propene and in propene and oxygen, and on the oxidation of MoO<sub>2</sub> in oxygen. <sup>[2]</sup> A comprehensive mechanism for the reduction and the re-oxidation of MoO<sub>3</sub> is proposed and the consequences of this mechanism for the partial oxidation of propene on MoO<sub>3</sub> are discussed.

For the reduction of MoO<sub>3</sub> in hydrogen it was found that the reaction rate could be described by a sigmoidal rate law (nucleation-growth kinetics). The formation of the suboxide Mo<sub>4</sub>O<sub>11</sub> was observed from a parallel reaction of MoO<sub>3</sub> and MoO<sub>2</sub>. 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. 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. 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.

From in situ investigations of the evolution of the bulk structure of MoO<sub>3</sub> under partial oxidation reaction conditions, characteristic shear-structure defects are observed in the layer structure of MoO<sub>3</sub>. 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 - 52.

[2] T. Ressler, J. Wienold, R.E. Jentoft, T. Neisius, *J. Catal.* **2002**, accepted.