

In situ bulk structural investigations of mixed molybdenum oxide catalysts

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Molybdenum containing metal oxide catalysts are widely used in industry. Their structural variety and redox properties offer a wide range of catalytic applications including partial oxidation of light alkanes and alkenes. Mixed oxide catalysts exhibiting the characteristic stoichiometry and crystal structure of $(\text{Mo}, \text{V}, \text{W})_5\text{O}_{14}$ are suitable three-dimensional model system for the more complex molybdenum based mixed oxides. Various compositions of metal cations resulting in the Mo_5O_{14} structure are described in literature[1,2,3]. However, little is known about the cooperation of the different cations and their role for the stabilization of the catalytically active phase. Here, we report in situ XAS and in situ XRD experiments to elucidate the structural evolution of a bulk Mo_5O_{14} precursor during calcinations and under propene oxidation conditions.

The starting material was prepared from aqueous solutions of ammonium heptamolybdate (AHM), ammonium metatungstate (AMT) and vanadyl oxalate. The transformation into a solid was carried out by spray drying. In situ XRD experiments were performed on a STOE STADI P powder diffractometer employing a Bühler HDK S1 chamber. The gas phase composition at the cell outlet was analyzed on line with a mass spectrometer. In situ XAS experiments were performed at beamline X1 at HASYLAB and ESRF, ID24 in transmission in a flow-reactor at atmospheric pressure in flowing reactants (~30 ml/min) combined with online gas analysis by mass spectrometry.

Activation and crystallization of the precursor were performed (i) in propene and oxygen [5] between 300 K and 773 K and (ii) according to a two-step calcination process in oxygen and helium [6]. The procedures resulted in highly crystalline Mo_5O_{14} type materials. The activation and crystallization conditions were systematically varied to reveal the dependence of the phase purity and microstructure of the catalysts formed on the preparation procedure employed. The samples studied exhibited an onset of catalytic activity at about 573 K. In situ XRD showed that the catalyst undergoes a phase transformation under reducing conditions (10% propene or 10% hydrogen). While the Mo_5O_{14} structure is stable in oxygen, it is completely reduced to a MoO_2 type material under reducing conditions at 723 K and may be re-oxidized at these temperatures in the presence of oxygen. In situ XAS experiments at the Mo-K edge and W-L_{III} edge during calcination revealed structural changes. The linkage of the building blocks of the Mo_5O_{14} structure in the precursor starts during the first treatment step in oxygen and is completed during the subsequent treatment in helium.

References

- [1] T. Ekström, M. Nygren, Acta Chem. Scand. 26, 1827 (1972)
- [2] T. Ekström, Acta Chem. Scand. 26, 1843 (1972)
- [3] L. Kihlborg, Acta Chem. Scand. 23, 1834 (1969)



NDCat-2004 French-German Summer School of Research
Saarbrücken, Sept. 28-Oct. 1st 2004



- [4] O. Ovsitser, Y. Uchida, G. Mestl, G. Weinberg, A. Blume, J. Jäger, M. Dieterle, H. Hibst, R. Schlögl, *Journal of Molecular Catalysis A* 185, 291 (2002)
- [5] Y. Uchida, G. Mestl, O. Ovsitser, J. Jäger, A. Blume, R. Schlögl, *Journal of Molecular Catalysis A: Chemical* 187, 247 (2002)
- [6] S. Knobl, G. A. Zenkovets, G. N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, G. Mestl, *Journal of Catalysis* 215, 177 (2003)