

In situ investigations of structure-activity correlations of mixed molybdenum oxide catalysts

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Introduction

Molybdenum containing catalysts are widely used for the selective oxidation of propene in the presence of gas phase oxygen at temperatures above ~ 600 K. Crystalline $(\text{Mo,V,W})_5\text{O}_{14}$ constitutes a three-dimensional model system for the more complex molybdenum based mixed oxide catalysts that are employed industrially for various partial oxidation reactions [1]. However, little is known about the cooperation of the different cations and their role for the stabilization of the active phase. Here we present investigations of the structural evolution of $(\text{Mo,V,W})_5\text{O}_{14}$ under propene oxidation conditions at different temperatures using in situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD).

Experimental

The $\text{Mo}_{0.68}\text{V}_{0.23}\text{W}_{0.09}$ oxide catalyst was prepared by spray-drying mixed solutions of ammonium heptamolybdate, ammonium metavanadate and vanadyl oxalate and calcined at 623 K in air and 713 K in helium [2]. Combined in situ XRD/MS 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. Measurements were conducted under atmospheric pressure in flowing reactants. Combined transmission XAS/MS experiments were performed at the Mo-K edge at beamline X1 at HASYLAB in a flow-reactor at atmospheric pressure in flowing reactants (~ 30 ml/min). Time-resolved in situ XAS experiments were carried out at the Mo-K edge utilizing an energy-dispersive spectrometer (ESRF, ID24).

Results

The $(\text{Mo,V,W})_5\text{O}_{14}$ material prepared exhibited an onset of catalytic activity at about the same temperature as MoO_3 (~ 600 K) indicating similar active sites and structure-activity correlations. Isothermal in situ XAS experiments while changing the gas atmosphere from propene to propene and oxygen revealed a decreasing average Mo oxidation state during catalysis with increasing reaction temperature. In situ XRD showed that the catalyst exhibits no phase changes during catalysis under mildly reducing conditions (10% propene, 10% oxygen). The $(\text{Mo,V,W})_5\text{O}_{14}$ employed is stable in oxygen up to 773 K, whereas it is strongly reduced in 10% propene or 10% H_2 at temperatures above 723 K.

[1] Grasselli, R.K., *Catalysis Today*, **1999**, 49, 141

[2] Knobl, S., et al., *Journal of Catalysis*, **2003**, 215, 177