



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

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Introduction

Molybdenum oxide based catalysts promoted with other transition metals are active for the selective oxidation of propene in the presence of gas phase oxygen at temperatures above ~ 600 K. Crystalline $(\text{Mo},\text{V},\text{W})_5\text{O}_{14}$ constitutes a three-dimensional model system for the more complex molybdenum based mixed oxide catalysts that are employed industrially for various partial oxidation reactions. In the mixed oxide system little is known about the cooperation of the different metal centers and their role for the stabilization of the active phase [1,2,3]. Here we report in situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD) studies on the structural evolution of a precursor for bulk $(\text{MoVW})_5\text{O}_{14}$ during calcination and under propene oxidation conditions

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 metatungstate, and vanadyl oxalate and subsequent calcination at 623 K in air and 713 K in helium [4]. Combined in situ XRD/MS experiments were performed on a STOE Theta/theta diffractometer equipped with a XRK 900 high temperature cell and a mass spectrometer for on-line analysis. Combined transmission XAS/MS experiments were performed at the Mo K and W L_{III} edge at beamline X1 and at the V K edge at beamline E4 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

Activation and crystallization of the precursor were performed (i) in propene and oxygen between 300 K and 773 K and (ii) according to the two-step calcination process mentioned above. 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 on the preparation procedure employed. In situ XAS experiments at the Mo K edge and W L_{III} edge during calcination revealed characteristic structural changes during thermal treatment. The linkage of the building blocks of the Mo₅O₁₄ structure in the precursor starts during the first treatment step in oxygen and is completed during the subsequent treatment in helium. Under the reaction conditions employed (propene and oxygen in a ratio of 1:2), the (Mo,V,W)₅O₁₄ material prepared exhibited an onset of catalytic activity at about 570 K. In situ XRD showed that the (MoVW)₅O₁₄ catalyst undergoes a phase transformation under reducing conditions (10% propene or 10% hydrogen). While the Mo₅O₁₄ structure is stable in oxygen, it is completely reduced to a MoO₂ type material under reducing conditions at 773 K and may be re-oxidized at these temperatures in the presence of oxygen (Figure 1).

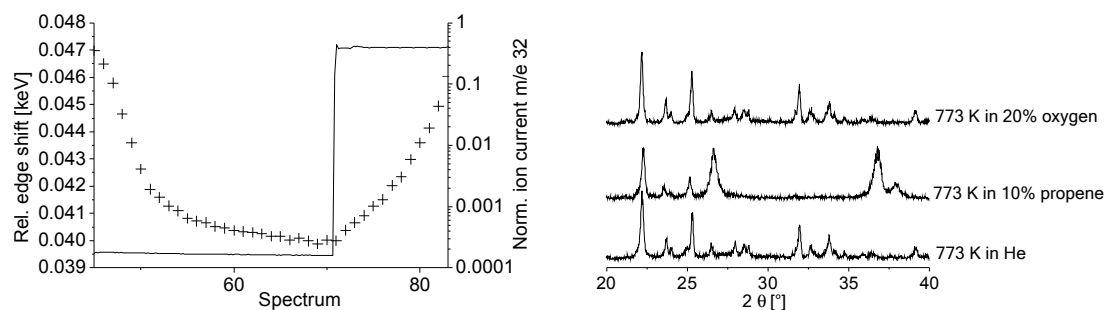


Figure 1. Redox properties of the (MoVW)₅O₁₄ structure at 773 K: reduction in 10% propene followed by reoxidation in 20% oxygen: (left) relative edge shift at the Mo K edge depending on the oxygen content of the gas atmosphere, (right) corresponding phase composition as determined by in situ XRD.

References

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