



In situ structural investigations of the $(\text{MoVW})_5\text{O}_{14}$ type mixed molybdenum oxide catalysts

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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 $(\text{MoVW})_5\text{O}_{14}$ 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

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 XRK900 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).

Two types of thermal treatment were applied for activation and crystallization of the precursor: (i) propene and oxygen from 300 K to 773 K and (ii) according to the two-step calcination process mentioned above. Both procedures resulted in 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 method employed. In situ XAS experiments at the Mo K edge, W L_{III} edge, and V K edge during calcination revealed characteristic structural changes during thermal treatment. 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. The



radial distribution function of the final material can be fitted with average distances from the Mo_5O_{14} structure (Figure 1). Under the reaction conditions employed (propene and oxygen in a ratio of 1:2), the $(\text{MoVW})_5\text{O}_{14}$ material prepared exhibited an onset of catalytic activity at about 570 K. In situ XRD showed that the $(\text{MoVW})_5\text{O}_{14}$ structure is stable in oxygen. Conversely the $(\text{MoVW})_5\text{O}_{14}$ catalyst undergoes reduction in 10% propene or 10% hydrogen resulting in a MoO_2 type material. Intriguingly, the MoO_2 type material can be re-oxidized at 723 K in 20 % O_2 to the Mo_5O_{14} structure (Figure 2).

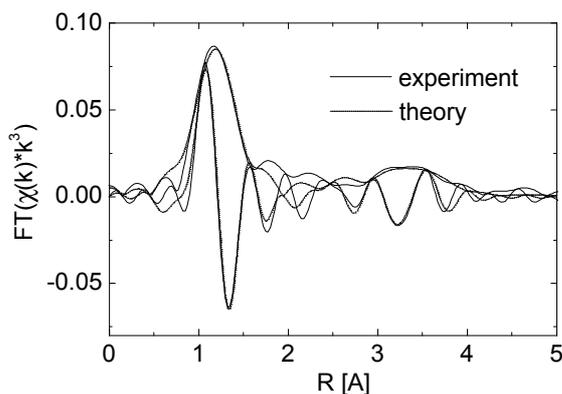


Figure 1 Radial distribution function of the $(\text{MoVW})_5\text{O}_{14}$ structure at the Mo K edge can be fitted adequately with average distances from the Mo_5O_{14} structure.

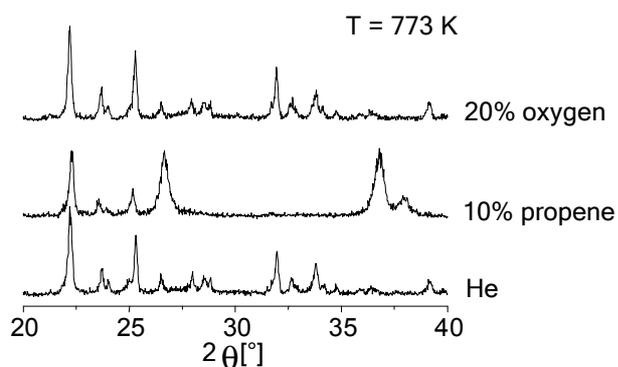


Figure 2 Redox properties of the $(\text{MoVW})_5\text{O}_{14}$ structure at 773 K as determined by in situ XRD. Reduction in 10% propene followed by reoxidation in 20% oxygen.

References

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