

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

E. Rödel, S. Knobl, R.E. Jenoft, T. Ressler

*Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG,
Faradayweg 4-6, 14195 Berlin*

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 thermal treatment 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 gas 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).

Results and discussion

Activation and crystallization of the precursor were performed according to the two-step thermal treatment mentioned above. The procedure resulted in highly crystalline Mo_5O_{14} type material. 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, V K edge and W L_{III} edge revealed characteristic structural changes during the process of thermal treatment. The building blocks of the Mo_5O_{14} structure start to link together in the precursor during the first treatment step in oxygen while the structural assembly is completed during the subsequent treatment in helium. Analysis of the XAS data measured at the three transition metal edges revealed that the characteristic features of the final material are already present after the first treatment in oxygen. During this stage, only an amorphous phase can be detected by XRD. Figure 1 shows that the pseudo radial distribution function can be fitted with average distances taken from the Mo_5O_{14} structure. Under the reaction conditions employed, the $(\text{MoVW})_5\text{O}_{14}$ material prepared exhibited an onset of catalytic activity at about 570 K. In situ



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XAS showed that the $(\text{MoVW})_5\text{O}_{14}$ 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 773 K and may be re-oxidized at these temperatures in the presence of oxygen (Figure 2). This redox behavior of the bulk material is indicative for a sufficient oxygen mobility, which is an important prerequisite for the material to function as an active partial oxidation catalyst.

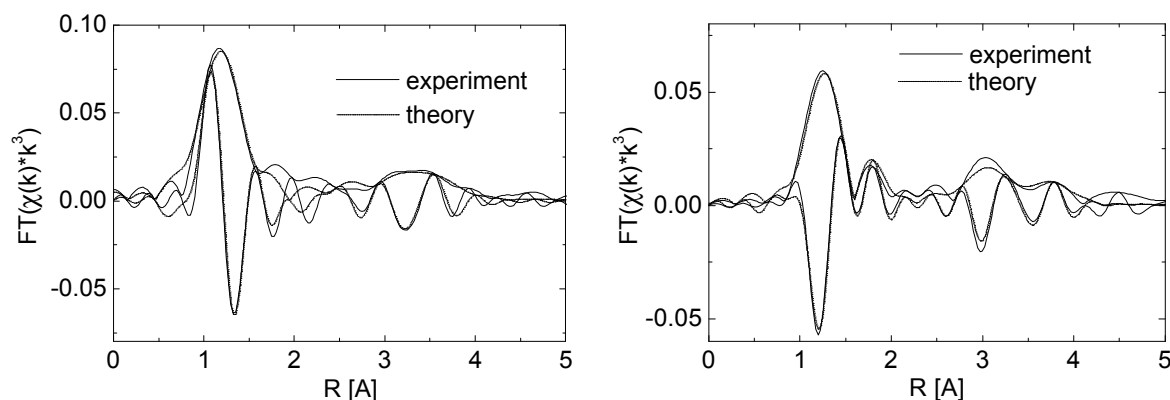


Figure 1. Radial distribution function of the $(\text{MoVW})_5\text{O}_{14}$ structure: at the Mo-K edge (left) and at the W-L_{III} edge (right) can be fitted adequately with average distances from the Mo_5O_{14} structure.

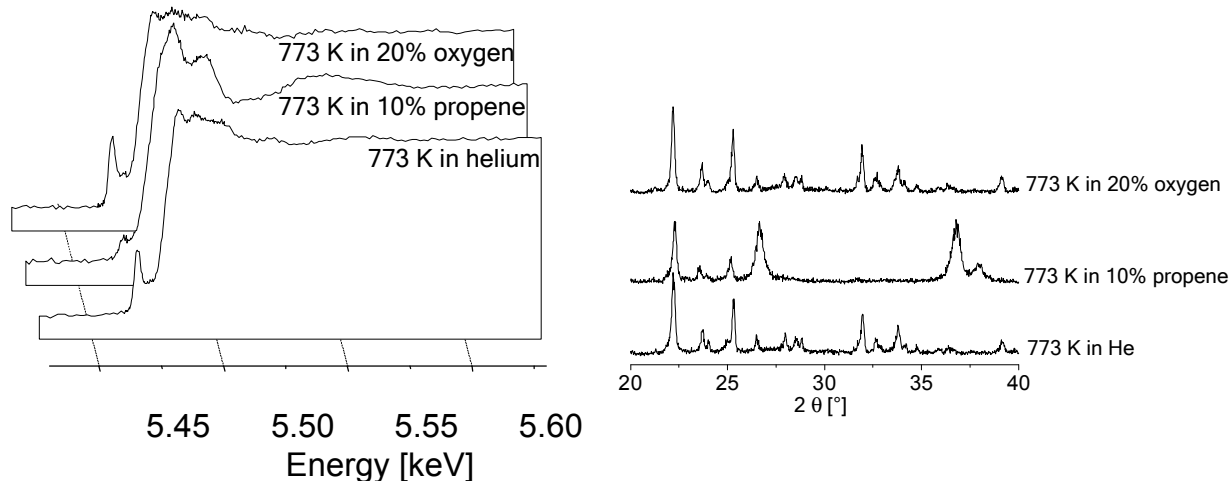


Figure 2. Left: Redox properties of the $(\text{MoVW})_5\text{O}_{14}$ structure at 773 K: reduction in 10% propene followed by reoxidation in 20% oxygen. Right: analogue in situ XRD experiment for representation of the long-range order structure

References

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