



MAX-PLANCK-GESELLSCHAFT

HASYLAB Annual report, 2005



# **In situ XAS investigation of tungsten as structure directing agent during formation of $\text{Mo}_5\text{O}_{14}$ type partial oxidation catalysts**

*E. Rödel, R. Schlögl, T. Ressler*

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

## **Introduction**

Crystalline, single phase  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$  constitute three-dimensional model systems for the more complex technical catalysts for the partial oxidation of propene to acrolein and acrylic acid [1]. In the mixed oxide systems little is known about the cooperation of the different metal centers and their role for the stabilization of the active phase [2,3,4]. Here we report in situ X-ray absorption spectroscopy (XAS) and in situ X-ray diffraction (XRD) studies on the bulk structural evolution of  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$  under reducing, oxidizing, and catalytic conditions. At temperatures above  $\sim 600$  K in 5% propene and 10% oxygen the molybdenum oxide material obtained is active for the selective oxidation of propene in presence of gas phase oxygen.

## **Experimental**

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 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-through reactor at atmospheric pressure with total flow of 30 ml/min.

In isothermal redox experiments  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$  were heated in helium to 773 K. At 773 K the atmosphere was isothermally switched to 10% propene and XRD or XAS scans were measured until complete reduction of the sample. The resulting materials were re-oxidized in 20% oxygen and XRD or XAS scans were collected until no reduced phase was detectable.

## **Results and discussion**

In situ XAS and XRD confirm the structural stability of  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$  during heating in helium to 773 K. Reduction of  $(\text{MoV})_5\text{O}_{14}$  and  $(\text{MoVW})_5\text{O}_{14}$  into a  $\text{MoO}_2$  type structure occurred at 773 K in 10% propene. Re-oxidation of the reduced MoVW oxide in 20% oxygen resulted in the initial  $\text{Mo}_5\text{O}_{14}$  type phase. In case of the reduced MoV oxide re-oxidation leads to a  $\text{MoO}_3$  type structure. In situ XAS experiments at the Mo K edge, V K edge and W  $L_{III}$  edge revealed characteristic structural changes during isothermal experiments.

The XANES of a material with its characteristic edge position, pre-edge peaks, and edge features is a distinct fingerprint of an element in a characteristic structure and bonding situation. XANES spectra of initial, reduced and re-oxidized samples were compared to references of known structure and oxidation state. XANES spectra taken at the Mo K edge of the initial  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$  are compared in Figure 1. The similar XANES indicates molybdenum in the same local environment for  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$ . Therefore molybdenum can be assumed in similar coordination geometry in  $(\text{MoVW})_5\text{O}_{14}$  and  $(\text{MoV})_5\text{O}_{14}$ . In the reduced  $\text{MoO}_2$  type materials derived from the two samples the XANES is nearly identical (Figure 2). Comparison of the XANES spectrum of the reduced  $\text{MoO}_2$  type samples to a  $\text{MoO}_2$  reference reveals an edge shift of the sample to higher energy by  $\sim 2.5$  eV. The higher energy of the edge position indicates an average oxidation state of molybdenum higher than  $\text{Mo}^{4+}$ . After re-oxidation the XANES of the



MoVW oxide is the same as for the initial  $(\text{MoVW})_5\text{O}_{14}$  (Figure 3), whereas for the MoV oxide the XANES resembles a  $\text{MoO}_3$  reference (Figure 4). The slight deviations in the XANES features and edge position between  $\text{MoO}_3$  reference and the re-oxidized MoV oxide is indicative of an incorporation of vanadium in a molybdenum framework.

$(\text{MoV})_5\text{O}_{14}$  material exhibits a lower stability against gas phase oxygen compared to tungsten containing  $(\text{MoVW})_5\text{O}_{14}$ . Apparently, the presence of tungsten in the oxide systems stabilizes the  $\text{Mo}_5\text{O}_{14}$  type structure and prevents complete oxidation even under conditions of sufficient oxygen mobility and high oxidation potential of the gas phase. Furthermore, tungsten in the  $\text{MoO}_2$  type material obtained from the reduction of  $(\text{MoVW})_5\text{O}_{14}$  exerts a structure-directing effect under oxidizing conditions resulting in the re-formation of the  $\text{Mo}_5\text{O}_{14}$  type structure.

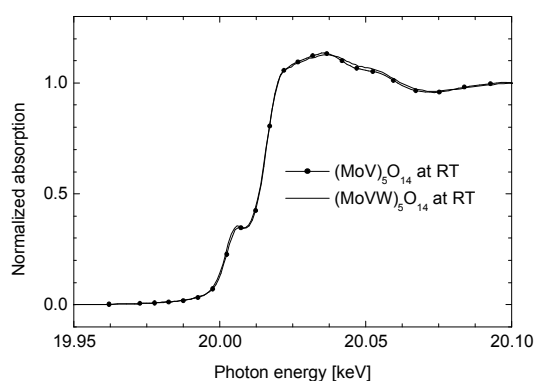


Figure 1: XANES at the Mo K edge of prepared  $\text{Mo}_5\text{O}_{14}$  structured molybdenum mixed metal oxides. In both samples molybdenum has a similar electronic structure.

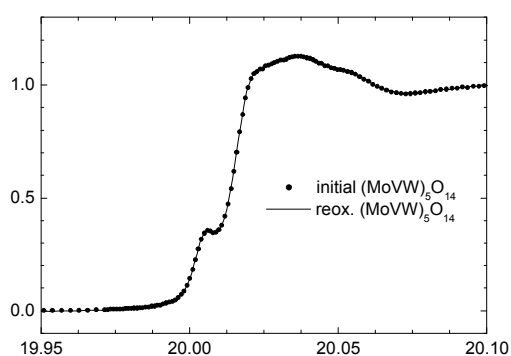


Figure 3: At the Mo K edge the electronic structure of the re-oxidized tungsten containing compound is  $\text{Mo}_5\text{O}_{14}$  type and overlays the initial XANES.

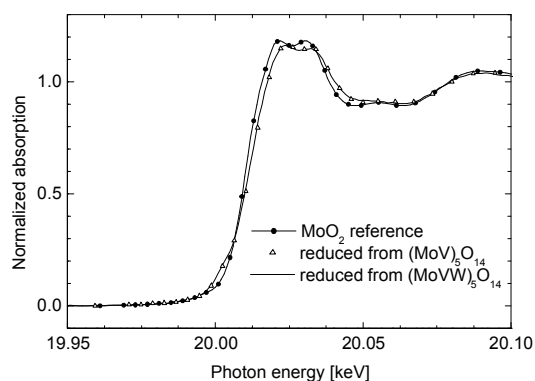


Figure 2: At the Mo K edge the edge position of the reduced molybdenum mixed metal oxide is at higher energy than for the  $\text{MoO}_2$  reference.

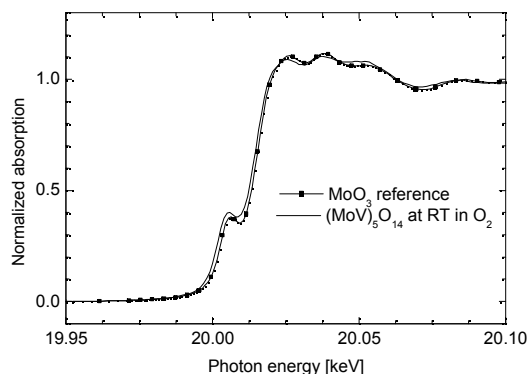


Figure 4: XANES at the Mo K edge of the re-oxidized MoV oxide is close to the  $\text{MoO}_3$  reference. The edge position of the re-oxidized sample is at lower energy than for  $\text{Mo}^{6+}$  in the reference.

## References

- [1] S. Knobl, G. A. Zenkovets, G. N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl, G. Mestl, *Journal of Catalysis* 215, 177 (2003)



MAX-PLANCK-GESELLSCHAFT

- [2] 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)
- [3] Y. Uchida, G. Mestl, O. Ovsitser, J. Jäger, A. Blume, R. Schlögl, *Journal of Molecular Catalysis A: Chemical* 187, 247 (2002)
- [4] R.K. Grasselli, *Catalysis Today* 49, 141 (1999)