ESRF	**Experiment title:** Structural In situ XAFS Studies on Molybdenum Oxide Catalysts for the Partial Oxidation of Propene	**Experiment number:** CH-1063
Beamline: ID24	**Date of experiment:** from: 10.07.01 to: 17.07.01	**Date of report:** 30.08.01
Shifts: 21	**Local contact(s):** Dr. Thomas Neisius	*Received at ESRF:*

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Report:

Heteropolyacids (HPA) with the composition $(H/Cs)_3+x[(P/Si)V_x(Mo/W)_{12}-xO_{40}]*yH_2O$; x=0,1,2; y=0-36 are used as catalysts for the partial oxidation of methacrolein and isobutyric acid to methacrylic acid on an industrial scale. In this investigation we studied the influence of different reactant atmospheres on thermal decomposition products and on the decomposition mechanism. The studies focused on the stability of the 'Keggin anion', which constitutes the building unit of the HPA structure. Samples with different amounts of molybdenum substituted by vanadium (x = 0,1,2), different number of cesium atoms (0,2,3), and with silicon and phosphorus as heteroatoms were investigated. For in situ XAS measurements the HPAs were mixed with boron nitride and pressed into 5 mm diameter pellets. Transmission X-ray absorption spectra were measured in situ with the sample pellet in a flow reactor under a controlled reactant atmosphere. The gas phase composition was monitored by on-line mass spectrometry. Thermal treatments were performed in helium, 50 % hydrogen in He, 20 % oxygen in He, 10 % propene in He, and propene and oxygen (1:1).

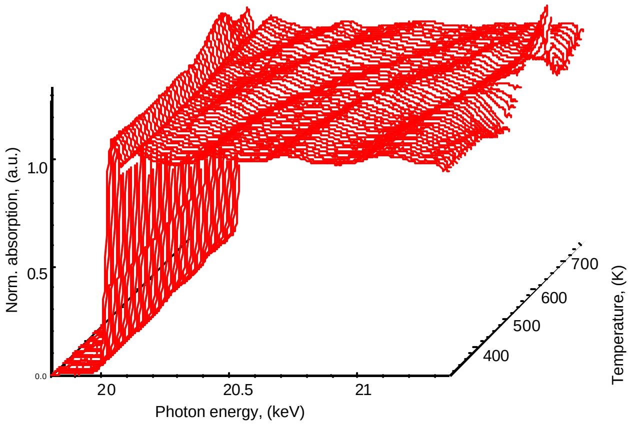

Figure 1 Evolution of X-ray absorption spectra during the thermal treatment of a mixture molybdates and vanadates.

In Figure 1, XAS data measured during thermal treatment of AHM/AMV/AMW (Mo 92 atom%, V 3.5 atom%, W 4.5 atom%) in helium (20 ml/min total flow) from 300 to 770 K with 10 K/min are shown. The data are energy calibrated, background corrected, and normalized. The experiment was carried out at the Mo K-edge, 19.999 keV, with a time resolution of 13 sec/spectra. The Figure shows pronounced *waves* in the EXAFS-region, which are not part of the absorption edge fine structure. Apparently, the *waves* are shifted in energy with increasing temperature. The origin of these *waves* is not understood yet. Unfortunately, data analysis in the XANES and in the EXAFS region is rendered difficult because of these additional structures in the EXAFS part of the spectra.

Nevertheless, several interesting experiments were performed which are less affected by the additional structure in the EXAFS. In Figure 2 the evolution of radial-distribution-function of $(Mo,V)_5O_{15}$ (7 atom% V) during thermal treatment from 300 to 773 K in 20 % oxygen is shown. The changes in the RDF indicated a complex structural evolution which is yet to be understood. A comparison of the XANES region of the $(Mo,V)_5O_{14}$ to reference spectra of $(Mo,W)_5O_{15}$ shows significant differences indicating that vanadium and tungsten are incorporated in the molybdenum oxide structure.

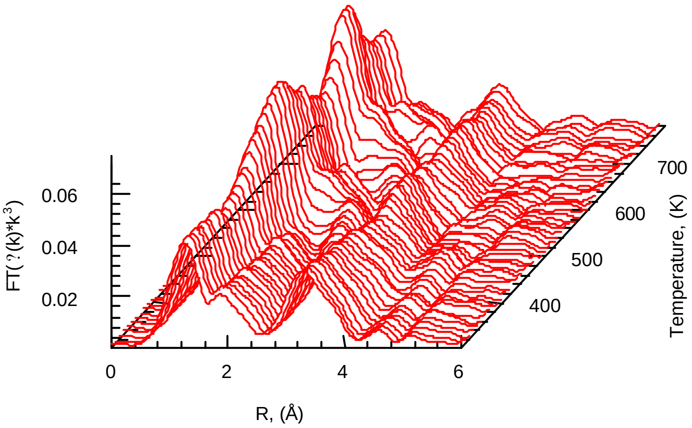

Figure 2 Evolution of radial distibution function from XAS data of the thermal treatment of $(Mo,V)_5O_{14}$

Figure 3 shows the evolution of the radial distribution function of $Cs_2H_3[PVMo_{11}O_{40}]$ during thermal treatment in propene and oxygen from 300 K to 770 K together with the MS signals of masses 18 (H_2O), 56 (acrolein) and 72 (acrylic acid). Significant correlation between the catalytic activity and the changes in the local structure of the HPA during thermal treatment can be seen. It seems that the onset of catalytic activity of the system coincides with the loss of structural integrety of the Keggin structure of the heteropoly acid.

Assistance of the ID24 staff during the experiments is gratefully acknowledged.

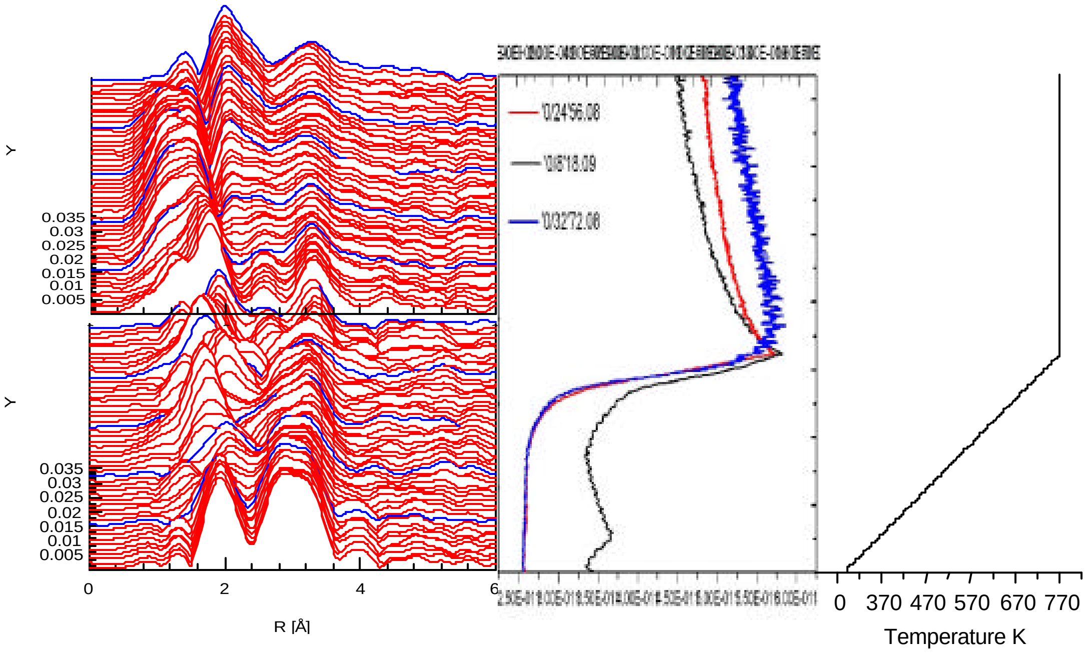

Figure 3 Evolution of RDF of $Cs_2H_3[PVMo_{11}O_{40}]$ during thermal treatment in propene and oxygen together with the MS signals of masses 18 (H_2O), 56 (acrolein) and 72 (acrylic acid).