ESRF	**Experiment title:** In situ investigtions of the oxidation/reduction behaviour of molybdenum oxides using time-resolved XAS	**Experiment number:** CH-960
Beamline: ID24	**Date of experiment:** from: 22.11.00 to: 28.11.00	**Date of report:** 27.02.01
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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. However, the use of these catalysts is limited by their low stability. 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. Whether or not the active catalyst consists of intact Keggin anion in a well-ordered crystalline structure is still subject to debate.

Samples with different amount 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. Phase purity was verified by XRD. 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 (4 ml total volume) under a controlled reactant atmosphere. The gas phase composition was monitored by on-line mass spectrometry. Thermal treatments were performed at a heating rate of 5 K/min from RT to 500 °C in helium, 50 % hydrogen in He, 20 % oxygen in He, 10 % propene in He, and propene and oxygen (1:1). XAFS spectra at the Mo K edge in a photon energy range from 19.9 keV to 21 keV were measured at beamline ID24 with a time resolution of about 2 sec/spectra.

From the evolution of the radial distribution function (RDF) of the HPA $H_5[PV_2Mo_{10}O_{40}]*xH_2O$ with temperature in 50 % hydrogen, a distinct changes in the RDF in the first and in the second shell at 300 °C is visible. At

425 °C the structure collapses. From the evolution of the edge shift the loss of structure can be correlated to the reduction of molybdenum. It appears that the reduction of molybdenum in HPA takes place after the collapse of the structure in agreement with in situ XRD data. In Figure 1 the evolution of the RDF together with the MS signals for water and acrolein or acrolein and acrylic acid during thermal treatment of $H_3[PMo_{12}O_{40}]$ is shown. The gases were switched from propene+oxygen (1:1) to propen. Apparently, the increase in catalytic activity and the break down of the Keggin structure are correlated. For comparison, in Figure 2, the evolution of the RDF together with the signals for H_2O and acrolein from a similar treatment of the Cesium salt $HCs_3[PVMo_{11}O_{40}]$ is shown. It seems that under the conditions employed, the structure of cesium salt remained almost unchanged. From the studies described it is evident, that the active HPA catalyst based on $H_5[PV_2Mo_{10}O_{40}]*xH_2O$ does not consist of intact Keggin anions, but of rather of rather of partially decomposed Keggin anions fragments.

Figure 1

Treatment of $H_3[PMo_{12}O_{40}]$ in propen and oxygen and propene (RT-770 K). Displayed are the contour plots of the RDF, the MS data for mass 56 and mass72 or H_2O and the temperature programm. Lines are drawn to indicate changes in the RDF.

Figure 2

Treatment of $Cs_3[PMo_{12}O_{40}]$ in propen and oxygen and propene (RT-770 K). Displayed are the contour plots of the RDF, the MS data for mass 56 and mass72 or H_2O and the temperature programm.