

## In Situ XAS Study on the Thermal Treatment of Molybdenum Heteropolyacids

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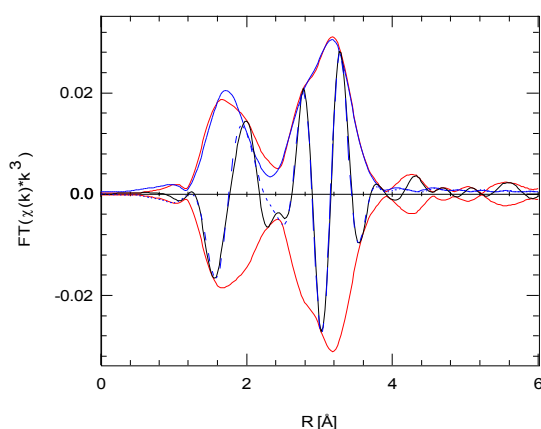
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Heteropolyacids (HPA) of the general composition  $(\text{H/Cs})_{3+x}[(\text{P/Si})\text{V}_x(\text{Mo/W})_{12-x}\text{O}_{40}]^*y\text{H}_2\text{O}$ ;  $x=0,1,2$ ;  $y=0-36$  with a Keggin structure are used as catalysts for the oxidation of methacrolein and isobutyric acid to methacrylic acid on an industrial scale [1]. In this investigation we studied the influence of different reactant atmospheres on thermal decomposition products and on the decomposition mechanism. In this connection, the stability of the 'Keggin anion', from which the structures are built, is of special interest. In addition, the role of the Vanadium atoms in the Keggin structure was examined. Former investigations have shown that in situ XAS-studies in combination with the results of in situ XRD studies are a powerful tool to elucidate the evolution of structures in long range and short range order [2].

The HPA-samples were prepared according to the literature [3]. Samples with different amount of molybdenum substituted by Vanadium ( $x = 0,1,2$ ), different number of Cesium (0,2,3) and with Silicon and Phosphorus as heteroatoms were examined. All samples were checked with XRD for impurities. It was found that the diffraction patterns of the Cs-salts fits well to simulations, calculated from single crystal data of a HPA with Potassium, which was substituted by Cesium for the calculations [ICSD 209]. The diffraction patterns of the free acids fits all well to simulations which are calculated from single crystal data of a free acid with Silicon as heteroatom [ICSD 201-009], which were modified for the HPA which contain Potassium as heteroatom respectively. For the XAS measurements the HPAs were mixed with boron nitride (10 mg HPA / 30 mg BN) and pressed into 5 mm diameter pellets. An edge jump at the Mo K edge (19.999 keV) of about 2.0 was obtained. 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 (*Bronkhorst mass flow controller*). The gas phase product composition was monitored by on-line mass spectrometry (*Pfeiffer QMS 200*).

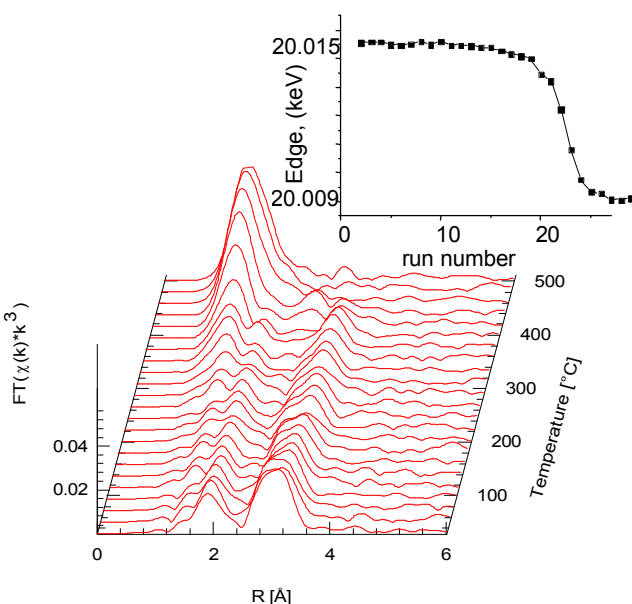
A heating rate of 5 K/min from RT to 500 °C was controlled by an Eurotherm PID temperature controller. The thermal treatment was performed in different reactant gas phases. Atmospheres with hydrogen, 20 % oxygen, propene, propene and oxygen (1:1) as well as inert atmosphere were examined. XAFS spectra at the Mo K edge in a photon energy range from 19.9 keV to 21 keV was measured with a time resolution of 4.5 min/spectra (beamline X1 at HASYLAB) and at the V K edge in a photon energy range from 5.35 keV to 6.49 keV with a time resolution of 24 min/spectra (in situ, beamline E4). At ESRF, beamline ID24, measurements at the Mo K edge were carried out under the same experimental conditions as described above but with a time resolution of about 2 sec/spectra.



**Figure 0** Experimental (solid) and theoretical (dashed) Fourier transformed  $\chi(k)$  of the Keggin anion in the free acid without Vanadium. (30 °C in 20% O<sub>2</sub>)

XAFS data reduction and analysis was performed using the software package WinXAS [4] following standard procedures. The ab-initio multiple-scattering code FEFF 7 [5] is employed to calculate theoretical XAFS phases and amplitudes for crystallographic model systems. Figure 1 shows a XAFS refinement of theoretical  $FT(\chi(k))$  of the 'Keggin anion' to an experimental  $FT(\chi(k))$  measured at 30 °C in 20% oxygen. The good agreement between theory and experiment in the range of 1.0 – 4.2 Å, Figure 1, confirms the presence of Keggin anion in the structure and allow to follow changes during thermal treatment. Furthermore it is possible to identify the onset temperature of structural collapse of the Keggin anions.

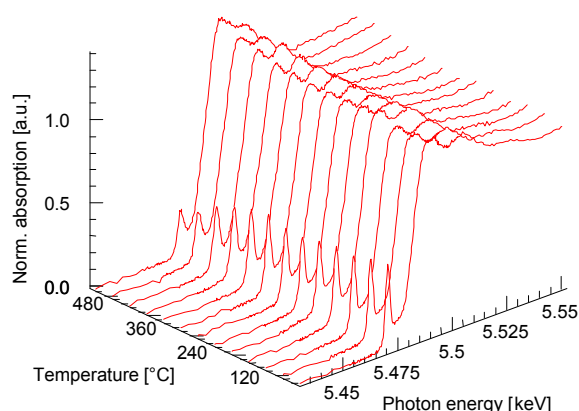
In Figure 2 the evolution of the radial distribution function (RDF) of the HPA  $H_5[PV_2Mo_{10}O_{40}] \cdot xH_2O$  with temperature in 50 % hydrogen is shown. At 300 °C, distinct changes in the RDF in the first and in the second shell are visible. At 425 °C the structure collapses. From the evolution of the edge shift it is seen that the loss of structure coincides with the reduction of molybdenum.



**Figure 2** Thermal treatment of  $H_5[PV_2Mo_{10}O_{40}] \cdot xH_2O$  in 50% H<sub>2</sub>; evolution of Mo K edge  $FT(\chi(k) \cdot k^3)$ ; Inspection: Evolution of edge position

The molybdenum is nearly completely reduced to molybdenum metal (see insertion in figure 2). For comparison, in Figure 3 the evolution of the V K edge XANES of  $H_5[PV_2Mo_{10}O_{40}] \cdot xH_2O$  is shown. Although, the resolution in temperature is less, it is visible that the reduction of vanadium takes place earliest at Temperatures above 440 °C and, thus, after that of molybdenum. Additionally it is visible, that there are no distinct changes in the V K edge XANES prior to the reduction at 480 °C. This indicates that vanadium in the structure might be not affected by the structural and electronic changes of the molybdenum.

The investigations of different heteropolyacids in different reactant atmospheres, yielded for the first time, detailed information on the stability and evolution of the Keggin anion. Furthermore, information about the state of vanadium in the HPA structure during thermal treatment is obtained and can be compared with the results of the structural evolution of molybdenum.



**Figure 3** Thermal treatment of  $H_5[PV_2Mo_{10}O_{40}] \cdot xH_2O$  in 50%  $H_2$ ; evolution of V K edge XANES

## References

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