In situ XAS Study on the evolution of Keggin anions during thermal treatment in different atmospheres

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Polyoxometallates of the Keggin type are known for their redox properties and used for numerous applications [1]. The Keggin anion shows a particular structure, which can be ascribed as a cage of 12 distorted M-O octahedra (M = transition metal ion) and $[XO_4]^{n-}$ (X = heteroatom) subunits inside the cage, as illustrated in figure 1. The special chemical characteristics of the Keggin anions 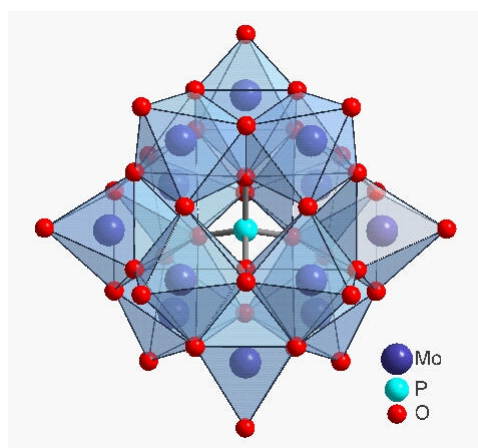are closely related to their structure. The Cs salt of the Keggin type heteropoly acids (HPA) are used as catalyst for oxidation of methacrolein and isobutyric acid to methacrylic acid on an industrial scale [2]. Nevertheless, of the numerous studies on the Keggin type HPA, the role of the Keggin anion in the named reaction is still under debate [3]. The question under debate is, if the intact Keggin unit is catalytical active or its fragment or a combination. In this study, we follow the evolution of the keggin anion during thermal treatment under catalytic conditions with in situ X-ray absorption spectroscopy (XAS). Preceeding studies have shown, that the Keggin anion can be identified by a simulation of the fourier transformed $\chi(k)$ [4]. The simulation is calculated, applying phases and amplitudes generated by the ab initio multiple scattering code FEFF7, on the base of single crystal data [ICSD 61003]. The simulation match the experimental data. According to this, changes in the

Figure 1 Presentation of the geometric arrangement in the Keggin anion $[PMo_{12}O_{40}]^{3-}$. Shown is the cage of the distorted Mo-O octahedra, with the subunit PO_4^{3-}.

Keggin anion are detectable.

Heteropoly acids with a nominal composition of $H_4[PMo_{12}O_{40}]*xH_2O$ were studied under various conditions with in situ XAS combined with simultaneous recorded mass pectroscopy. The chemical composition of the samples used is varied by partial substitution of the protons by cesium ions and substitution of one of the molybdenum atoms by vanadium. All samples were checked with XRD for impuritys. Temperature programmed decomposition was carried out in atmospheres of 20 % oxygen in helium, 10 % propene in helium and 10% propene + 10 % oxygen in helium. 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
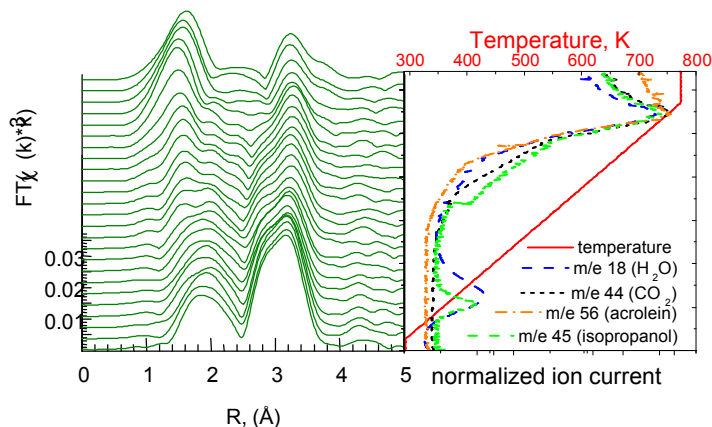

Figure 2 In situ XAS of $H_4[PVMo_{11}O_{40}]$ in propene and oxygen, 5 K/min, fourier transformed $\chi(k)$ and data from simultaneous recorded mass spectrometry

mass spectrometry (*Pfeiffer QMS 200*). A heating rate of 5 K/min from RT to 770 K was controlled by an Eurotherm PID temperature controller. Detailed XAFS data reduction and analysis is being carried out using the software package WinXAS [5] following standard procedures.
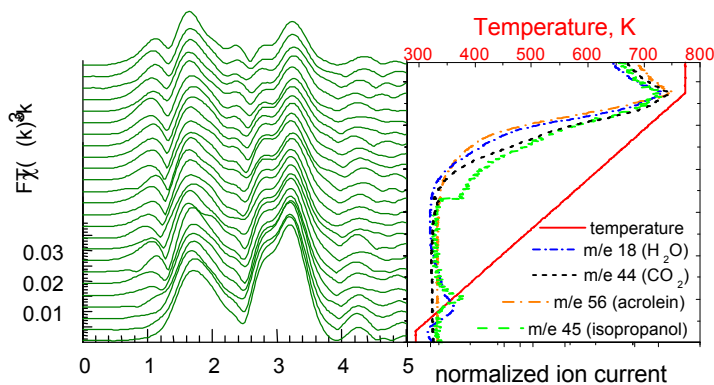

Figure 3 In situ XAS of $H_2Cs_2[PVMo_{11}O_{40}]$ in propene and oxygen, 5 K/min, fourier transformed $\chi(k)$ and data from simultaneous recorded mass spectrometry

In Figure 2 the evolution of the fourier transformed $\chi(k)$ and the corresponding MS data of the thermal treatment of $H_4[PVMo_{11}O_{40}]$ in propene and oxygen is shown. At around 340 K the loss of crystal water takes place. This occurs without a change in the initial fourier transformed $\chi(k)$ i.e. the Keggin anion is still intact. The evolution of mass 45 (isopropanol) simultaneously to the water, is due to dehydratisation of the propene. At around 570 K, the loss of structural water takes place. Simultaneously, the fourier tansformed $\chi(k)$ starts to change. At 770 K the fourier transformed $\chi(k)$ can be matched by those from MoO_3, simulated from single crystal data. In Figure 2 the evolution of the fourier transformed $\chi(k)$ and the corresponding MS data of the thermal treatment of $H_2Cs_2[PVMo_{11}O_{40}]$ in propene and oxygen is shown. Around 340 K, again, the loss of crystal water is observed, together with the corresponding evolution of isopropanol. The loss of the structural water takes place at around 600 K. Here, in contrast to the free acid, $H_4[PVMo_{11}O_{40}]$, the changes in the fourier transformed $\chi(k)$ are small. A detailed analysis of this changes is in process. The analysis of the data from mass spectroscopy shows, that there are isothermal measurements necessary at the onset of catalytic activity. This will evolve the products from the consumption of the structural water and give detailed information on the evolution of the Keggin anion corresponding to catalytic activity.

References

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