Bulk Structural Evolution of Heteropoly Acids Under Reaction Conditions by in situ XAS and XRD

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Introduction

Heteropoly oxomolybdates (also denoted as heteropoly acids (HPA)) composed of Keggin anions constitute highly active materials for selective oxidation reactions (e.g. methacrolein to methacrylic acid)[1]. Cesium salts of the heteropoly acid (e.g. $Cs_xH_{3-x}[PMo_{12-x}V_xO_{40}]$ ($2 \leq x < 3$)), for instance, are applied on an industrial scale. It has been proposed that the active phase of the HPA under reaction conditions corresponds to the intact and undistorted Keggin structure.[2] However, other authors have suggested that the active phase rather corresponds to a modified Keggin structure.[3] This modified Keggin structure may be formed under reaction conditions by migration of molybdenum atoms from the Keggin anions onto free cationic sites in the structure. In this work, the formation of a molybdenum salified heteropoly acid as a result of autosalification under reaction conditions is described. The same structural changes due to the migration of molybdenum atoms were also found for the Cs_2-salt. The implication of the structural changes observed for the activity and selectivity of heteropoly acids is discussed.

Experimental

From in situ X-ray absorption spectroscopy (XAS) studies on the thermal treatment of HPA, information on the short-range order structure, on the average valence of the constituent metals, and on chemical speciation can be obtained. The in situ capabilities of XAS combined with mass spectrometry permit to monitor the structural evolution of heteropoly acids during thermal decomposition (activation) and to correlate the structure of the material under reaction conditions with the onset of the catalytic activity. In addition, in situ X-ray diffraction (XRD) experiments were performed to reveal the evolution of the long-range order structure of the HPA during decomposition. Eventually, a combined application of the two complementary techniques XAS and XRD enables us to describe the structural changes of HPA during different treatments both on the long-range and on the short-range order and to correlate the structural evolution observed with catalytic activity.

In situ transmission XAS experiments were performed at the Mo K edge (19.999 keV) at beamline X1 at the *Hamburg Synchrotron Radiation Laboratory*, HASYLAB, using a Si(311) double crystal monochromator (measuring time ~ 4.5 min/scan): The measurements were performed in a flow reactor (4 ml volume) in the transmission geometry. Total flow of gases was set to 40 ml/min (10% propene in helium) and a heating rate to 5 K/min was applied. Analysis of the gas phase was performed with a quadrupol mass spectrometer, *QMS 200* (*Pfeiffer*), with a time resolution of ~12 s per selected masses scan. The heteropoly acid was mixed with boron nitride (7 mg HPA, 30 mg BN) and pressed with a force of 1 ton into a 5 mm in diameter pellet resulting in an edge jump at the Mo K-edge of $\Delta\mu_x \sim 2$. Details of the experimental set up can be found in Ref. [4]. XAFS data reduction and analysis were performed using the software WinXAS 2.3. [5]

Results and Discussion

Heteropoly acids with a composition of $H_3[PMo_{12}O_{40}]*xH_2O$ and $Cs_2H[PMo_{12}O_{40}]*xH_2O$ were studied by in situ XAS and in situ XRD under mild reducing conditions (H_2 or propene) and under catalytic partial oxidation reaction conditions (propene and O_2).

The evolution of the Fourier transformed Mo K edge $\chi(k)$ (pseudo radial distribution function, RDF) during thermal treatment of $H_3[PMo_{12}O_{40}]*13H_2O$ and $Cs_2H[PMo_{12}O_{40}]$ in 10 % propene is depicted in Figure 1A and Figure 1B, respectively. The initial RDF can be very well simulated by theoretical calculations based on the structure of the undistorted Keggin

anion. In particular for the free acid, at ~ 400 K considerable changes in the first Mo – O coordination shells can be observed that indicate a distortion compared to the initial Mo – O coordination in the Keggin anion. The formation of a molybdenum salified heteropoly acid from $H_3[PMo_{12}O_{40}]*13H_2O$ was observed by "post mortem" XRD analysis.
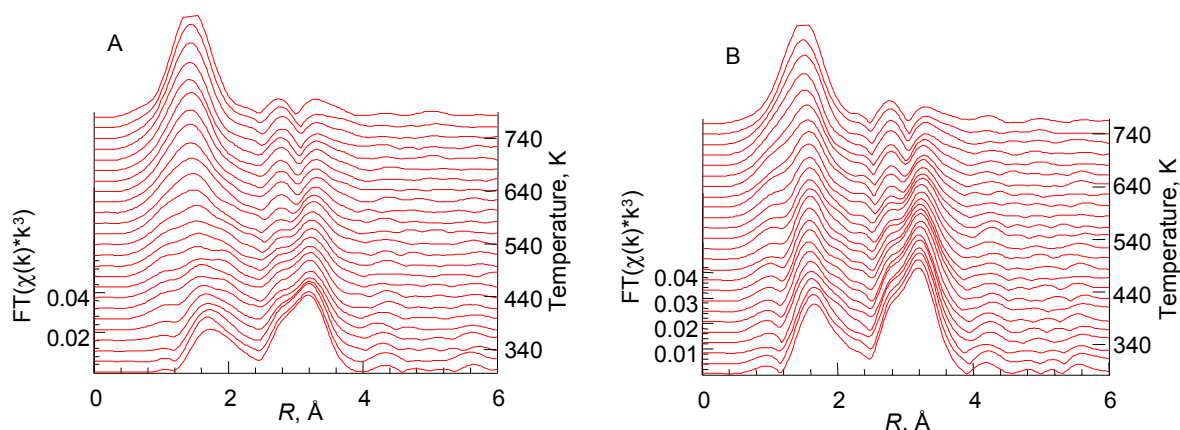
Figure 1 A) Evolution of RDF; $H_3[PMo_{12}O_{40}]*13H_2O$ treated in 10% propen in Helium (RT-770K at 5 K/min) B) Evolution of RDF; $Cs_2H[PMo_{12}O_{40}]*xH_2O$ treated in 10% propen in Helium (RT-770K at 5 K/min)

The evolution of the x-ray powder pattern during thermal treatment in 10% propene of $H_3[PMo_{12}O_{40}]*13H_2O$ and $Cs_2H[PMo_{12}O_{40}]$ is shown in figure 2A and 2B, respectively. In contrast to the comparable initial RDF and changes of the RDF during the treatment in 10% propen, the observed changes in the long range structure are different for
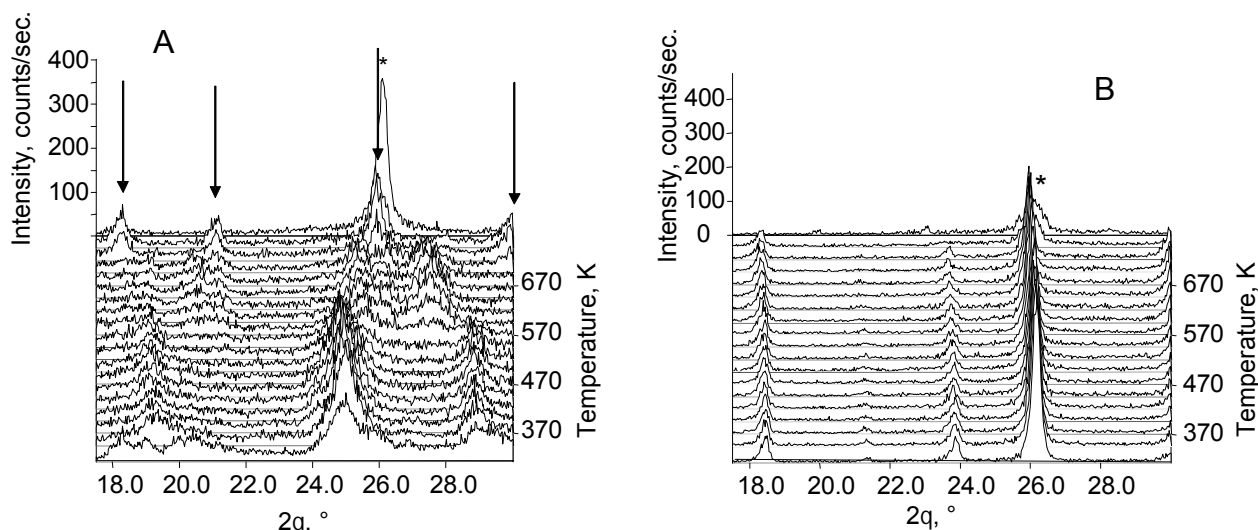
$H_3[PMo_{12}O_{40}]*13H_2O$ **Figure** 2A) Evolution of X-ray powderpattern; $H_3[PMo_{12}O_{40}]*13H_2O$ treated in 10% propen in Helium (RT-770K at 5 K/min) B) Evolution of X-ray powder pattern; $Cs_2H[PMo_{12}O_{40}]*xH_2O$ treated in 10% propen in Helium (RT-770K at 5 K/min)('↓' reflection from the molybdenumsalt, '*' reflection from MoO_2)

and $Cs_2H[PMo_{12}O_{40}]$. For $H_3[PMo_{12}O_{40}]*13H_2O$, 4 phase changes can be observed. The third at ~ 700 K leads to a phase, which can be identified as the molybdenum salified acid. At ~770 K reduction to MoO_2 occurs. In contrast, for $Cs_2H[PMo_{12}O_{40}]$ only the formation of $MoO2$ at ~755 K is observed. The observed changes in the RDF are due to the migration of molybdenum atoms from the Keggin-anion on to cationic positions in the structure. For $H_3[PMo_{12}O_{40}]*13H_2O$ this structural modifications let to the formation of a molybdenum salified heteropolyacid via two phase changes of the long range order. For the $Cs_2H[PMo_{12}O_{40}]$

no structural changes on the long range order are observed, never the less the migration of molybdenum atoms also occurs.

References

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