

## 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) <sup>[1]</sup>. Cesium salts of the heteropoly acid (e.g.  $\text{Cs}_x\text{H}_{3-x}[\text{PMo}_{12}\text{O}_{40}]$  ( $2 \leq x < 3$ )), 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  $\text{Cs}_2$ -salt. The implication of the structural changes observed for the activity and selectivity of heteropoly acids is discussed.

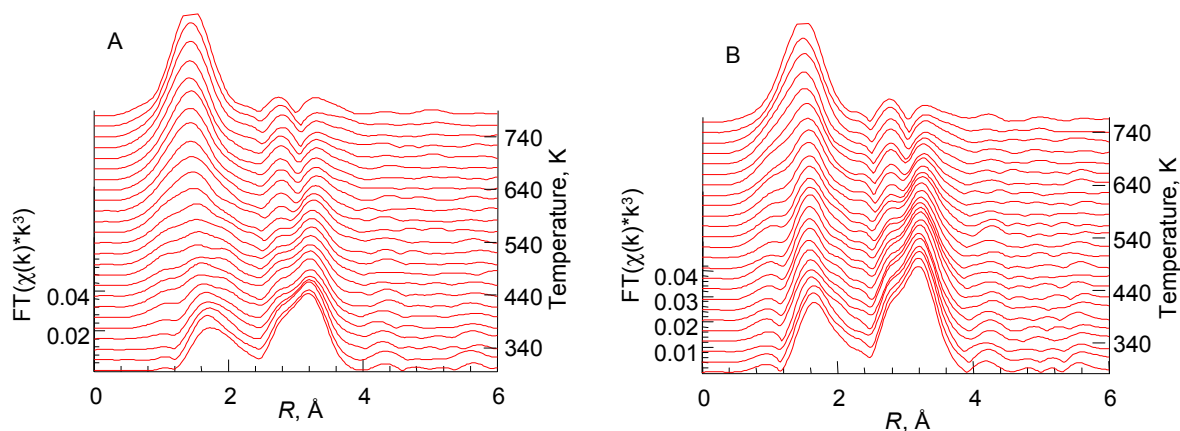
### Experimental

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.

## Results and Discussion

Heteropoly acids with a composition of  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$  and  $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$  were studied by in situ XAS and in situ XRD under mild reducing conditions ( $\text{H}_2$  or propene) and under catalytic partial oxidation reaction conditions (propene and  $\text{O}_2$ ). The in situ XAS measurements were performed at the Mo K edge in the transmission mode.



**Figure 1 A) Evolution of RDF;  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$  treated in 10% propene in Helium (RT-770K at 5 K/min) B) Evolution of RDF;  $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$  treated in 10% propene in Helium (RT-770K at 5 K/min)**

The evolution of the Fourier transformed Mo K edge  $\chi(k)$  (pseudo radial distribution function, RDF) during thermal treatment of  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 13\text{H}_2\text{O}$  and  $\text{Cs}_2\text{H}[\text{PMo}_{12}\text{O}_{40}]$  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  $\sim 400$  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. At  $\sim 600$  K formation of a molybdenum sulfated heteropoly acid (“post mortem” XRD) is observed.



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#### References:

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