

In situ XAS Study on the Decomposition of  
Ammonium Paratungstate in Various Atmospheres

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### Introduction

Mixed metal oxide systems (e.g.  $\text{Mo}_x(\text{V,W})_y\text{O}_{3-z}$ ) are employed for the partial oxidation of light alkenes [1]. Ammonium paratungstate (APT) and ammonium heptamolybdate (AHM) are used as precursors for the production of both tungsten trioxide ( $\text{WO}_3$ ) and molybdenum trioxide ( $\text{MoO}_3$ ), and in mixture for the synthesis of (Mo, W)-mixed metal oxides. The catalytic activity of these materials may depend on their structure; which in turn depends on the treatment of the precursors. Therefore, studies on the influence of different treatment parameters on the decomposition process, such as the composition of the gas phase, the heating rate, and the flow rate, combined with an analysis of the structural evolution of the precursors are required. Previously, we studied the decomposition of AHM by in situ X-ray diffraction (XRD) and in situ X-ray absorption spectroscopy (XAS) [2]. Here, we present results obtained from bulk structural studies on the thermal decomposition of APT in various reducing and oxidizing atmosphere.

### Experimental

Ammonium paratungstate (APT),  $(\text{NH}_4)_{10}\text{H}_2\text{W}_{12}\text{O}_{42} \cdot 4\text{H}_2\text{O}$  (OSRAM) and ammonium heptamolybdate (AHM),  $(\text{NH}_4)_4\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (ALDRICH) were employed as-purchased. Mechanical mixture of APT and AHM (70 wt %:30 wt%) were also investigated. Temperature programmed decomposition was carried out at temperatures between 20-500°C in atmospheres of pure helium, 5 % hydrogen in helium, 20 % oxygen in helium, 10 % propene in helium, and 10 % propene + 10 % oxygen in helium. For the in situ XAS measurements APT, AHM, and mechanical mixture of APT and AHM 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. In situ XAS experiments were performed at the Mo K edge (19.999 keV) and at the W  $L_{III}$  edge (10.204 keV) at beamline X1 at the Hamburger Synchrotron Radiation Laboratory, HASYLAB, using a Si(311) double crystal monochromator. The product composition in the gas phase was continuously monitored using a mass spectrometer in a multiple ion detection mode (QMS200 from Pfeifer) with a time resolution of  $\sim 2$  s per spectrum. Further details about the experimental XAS set-up used can be found in [3].

### Results and Discussion

Figure 1 and 2 display the evolution of Fourier transformed W  $L_3$  edge  $\chi(k)$  measured during the decomposition of APT in propene and oxygen (Figure 1A), propene (Figure 1B), and hydrogen (Figure 2). It can be seen, that in the temperature range from 30 to 300 °C the decomposition of APT proceeds independent on the gas phase composition. However, different decomposition products are obtained at 500 °C depending on the reaction atmosphere. On the one hand, the decomposition of APT in propene, and propene and oxygen results in mostly  $\text{WO}_3$  (XAS) together with minor amounts of different tungsten bronzes (XRD) (Figure 1A+B). On the other hand, the decomposition in hydrogen results in reduced tungsten oxides and eventually in the complete reduction of the intermediate reduced tungsten oxides to W metal (XRD) (Figure 2).

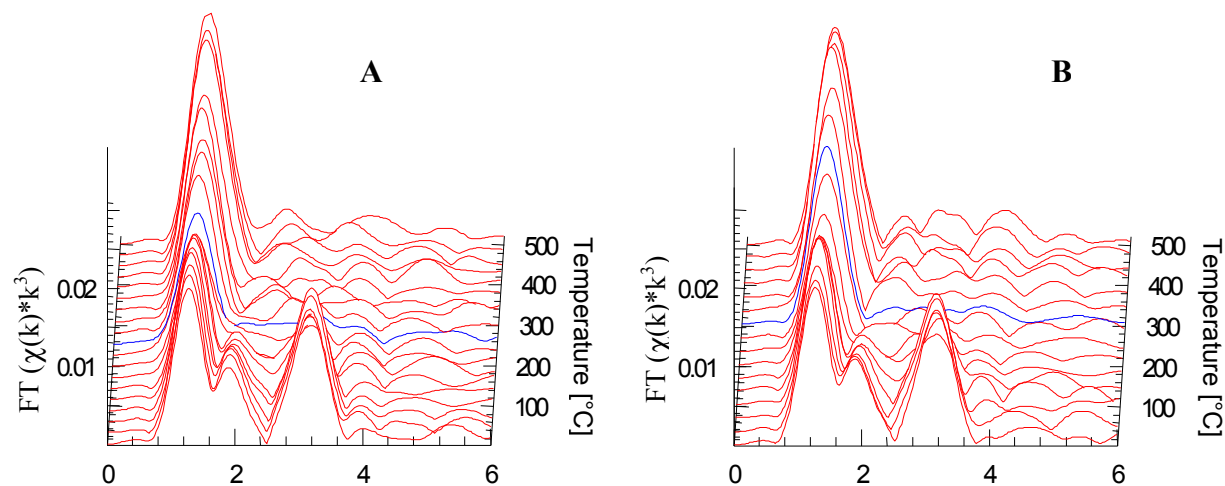


Figure 1: Fourier transformed W  $L_3$  edge XAFS spectra of APT measured during decomposition in (A) 10 % propene + 10 % oxygen in helium, (B) in 10 % propene in helium (temperature range from 30 to 500 °C at 6°C/min).

During the decomposition of APT in propene and propene and oxygen, no oxidation products of propene were detected in the gas phase. Apparently at the temperatures employed,

Figure 2: Fourier transformed W  $L_3$  edge XAFS spectra of APT measured during decomposition in 5 % hydrogen in helium (temperature range from 30 to 500 °C at 6°C/min).



the lattice oxygen is not sufficiently mobile and, hence, not available for the oxidation of propene to acrolein or carbon dioxide. Therefore, no reduction of  $\text{WO}_3$  is detected in propene and catalytic activity in propene and oxygen. This is in contrast to the reactivity of  $\text{MoO}_3$  in the same temperature range, where lattice oxygen can readily diffuse in the  $\text{MoO}_3$  lattice and, thus, is available for propene oxidation. Conversely, reduction of  $\text{WO}_3$  takes place during the decomposition of APT in hydrogen. Similar to the reduction of  $\text{MoO}_3$  in hydrogen, this may be because of the ability of hydrogen to be incorporated in the  $\text{WO}_3$  lattice resulting in the formation of bronzes and, subsequently, reduction of  $\text{WO}_3$  to tungsten metal.

#### References

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