

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

O. Kirilenko, F. Girgsdies, R.E. Jentoft, J. Wienold, T. Ressler

*Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG
Faradayweg 4-6, D-14195 Berlin, Germany*

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 (WO_3) and molybdenum trioxide (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 ~ 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 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).

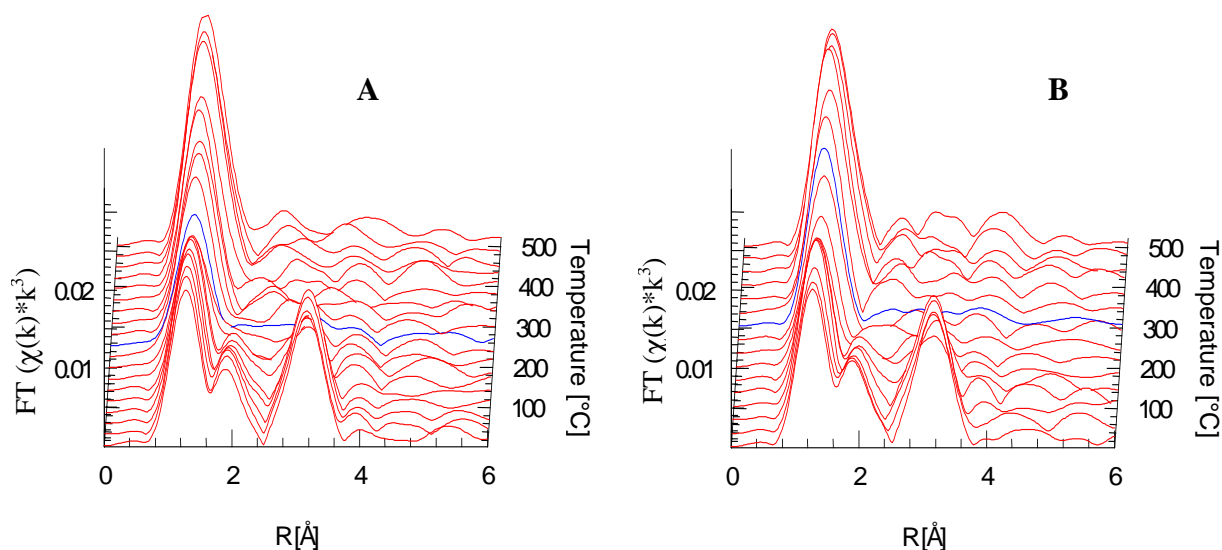


Figure 1: Fourier transformed W L_3 edge XAFS spectra of APT measured during decomposition in (A) 10 % propene + 10 % oxygen in helium, (B) in 10% propene in helium (temperature range from 30 to 500 °C at 6°C/min).

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, 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 WO_3 is detected in propene and catalytic activity in propene and oxygen. This is in contrast to the reactivity of MoO_3 in the same temperature range, where lattice oxygen can readily diffuse in the MoO_3 lattice and, thus, is available for propene oxidation. Conversely, reduction of WO_3 takes place during the decomposition of APT in hydrogen. Similar to the reduction of MoO_3 in hydrogen, this may be because of the ability of hydrogen to be incorporated in the WO_3 lattice resulting in the formation of bronzes and, subsequently, reduction of WO_3 to tungsten metal.

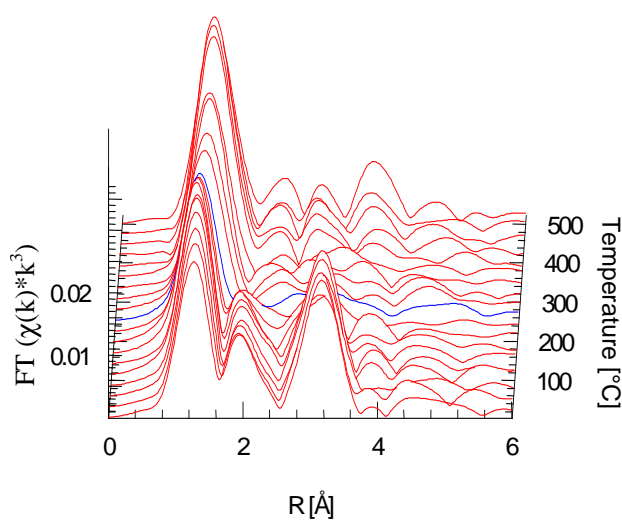


Figure 2: Fourier transformed W L_3 edge XAFS spectra of APT measured during decomposition in 5 % hydrogen in helium (temperature range from 30 to 500 °C at 6°C/min).

References

- [1] Grzybowska-Swierkosz, B., Topics in Catalysis 11/12, 23 (2000)
- [2] Wienold, J., Jentoft, R.E., Ressler T., Eur. J. Inorg. Chem., accepted.
- [3] Ressler, T., Jentoft, R.E., Wienold, J., Günter, M. M., Timpe, O., J. Phys. Chem. B 104, 6360 (2000).