

Structural evolution of ammonium paratungstates during thermal decomposition

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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 WO_3 and MoO_3 , respectively. The catalytic activity of these materials may depend on the treatment of the precursors. Therefore, studies of the decomposition process in order to identify and quantify tungsten oxide phases and their formation under various atmospheres, reveal correlation between catalytic activity and structural evolution of APT is very important. Here, we present results obtained from bulk structural studies on the thermal decomposition of APT in various reducing and oxidizing atmospheres. In this work the decomposition of APT is studied in situ by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Using these two complementary methods allows us to follow the evolution of the short-range and long-range structure of the phases formed during the decomposition of APT, to elucidate the evolution of the primary and secondary structure under different conditions.

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) was used as purchased. 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 W L_{III} edge (10.204 keV) (Hamburger Synchrotron Radiation Laboratory, HASYLAB, beamline X1), using a Si (311) double crystal monochromator. Temperature programmed decomposition was carried out at temperatures between 300 and 773 K 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 was mixed with boron nitride and pressed into 5 mm in diameter pellets. Analysis of the gas phase was carried out with a quadrupole mass spectrometer, QMS 200 (Pfeifer), with a time resolution of ~ 2 s. Further details about the experimental XAS set-up used can be found in [2].

Results and Discussion

The decomposition of APT proceeds via four steps (TG/DSC). The evolution of the decomposition seems to be independent of the gas phase composition up to 300°C. The sequence of phase transformations observed by in situ XRD and XAS measurements corresponds to the decomposition steps. Decomposition in flowing oxygen or static air results in WO_3 , while in propene, helium, and a mixture of propene and oxygen slight reduction to H_xWO_3 is observed; in hydrogen the reduction leads to a variety of products including W metal. Figure 1 displays the evolution of Fourier transformed W L_{III} edge $\chi(k)$ measured during the decomposition of APT in propene (Figure 1A) and in hydrogen (Figure 1B). 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. Figure 2 shows the evolution of the X-ray diffraction patterns during the decomposition of APT in hydrogen. Four distinct steps are visible in the diffraction patterns. The first and the second series of patterns up to 150°C correspond mainly to the patterns of APT with different content of crystal water. During the third step up to 300°C mainly patterns of an amorphous phase were observed, while the last step shows a variety of products including W metal. During the thermal treatment of APT the complete decomposition of the $[\text{W}_{12}\text{O}_{42}]^{12-}$ ion and formation of WO_3 was observed. This process runs through an amorphous phase. The mechanism of the structural changes of APT can



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be compared with the mechanism of the decomposition of AHM [3] and with the mechanism of the decomposition of heteropoly acids (HPA) [4].

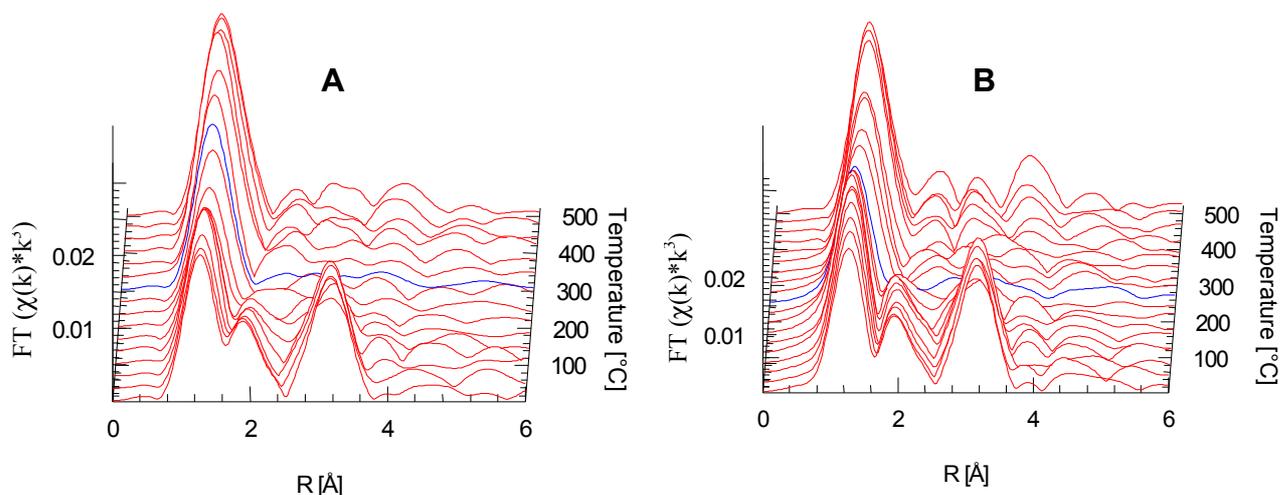


Figure 1: Fourier transformed W L_3 edge XAFS spectra of APT measured during decomposition in (A) 10 % propene in helium, (B) 5 % hydrogen in helium (temperature range from 30 to 500 °C at 6°C/min).

The heteropoly molybdates all show the Keggin structure [4]. During the decomposition of HPA the migration of the molybdenum from the Keggin anion on to cationic sites in the structure takes place. The structure of WO_3 is built of corner-sharing octahedrons. 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 no 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 [3].

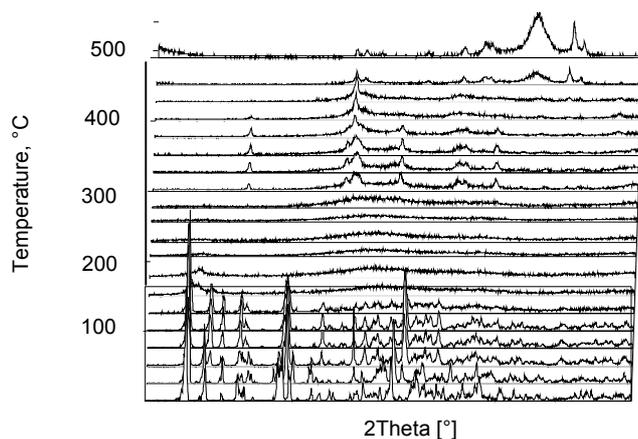


Figure 2: Evolution of X-ray diffraction patterns measured during the decomposition of APT in 5 % hydrogen in helium (RT-500°C at 6°C/min)

References

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