In Situ XAS Study on the Thermal Decomposition of Ammonium Heptamolybdate

J. Wienold, R. Jentoft, R. Schlögl, and T. Ressler

Fritz-Haber-Institut der MPG, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin,Germany

Ammonium heptamolybdate (AHM, $(NH_4)_6Mo_7O_{24}$) is a common precursor for the production of molybdenum trioxide (MoO_3) and partially reduced molybdenum oxides (MoO_{3-x}). Although these oxides exhibit only minor activity as partial oxidation catalysts, they can be viewed as model systems for much more complex mixed oxide ($Mo_x(V,W)_yO_3$) systems which find intensive industrial use in the partial oxidation of light alkenes [1]. Since the decomposition of AHM is know to proceed via a number of well-defined stages [2] which afford products of different catalytic activity, detailed structural studies are required to elucidate the short-range to long-range structure evolution of the corresponding molybdenum oxide species.

In this work we present investigations of the decomposition of AHM by a combination of in situ XAS and in situ XRD. We initially identify the crystalline phases using XRD and then use this information as a starting point for analysis of the in situ XAFS data obtained during various stages of the thermal decomposition. Later, deviations from the well-defined crystallographic structure of the decomposition products (e.g. defects such as sheer planes) will be analyzed in detail to reveal correlations between short-range structural characteristics and catalytic activity.

Ammonium heptamolybdate tetrahydrate (*Aldrich*) was mixed with boron nitride (10 mg AHM / 30 mg BN) and pressed into 5 mm in diameter pellets. The edge jump at the Mo K edge (19.999 keV) amounted to ~2.0. XAFS measurements were carried out in a flow reactor (4 ml total volume) under controlled reactant atmosphere (*Bronkhorst mass flow controller*). The gas phase product composition was continuously monitored by mass spectrometry (*Pfeiffer QMS 200*). Reaction temperature was controlled by a Eurotherm PID temperature controller and a heating rate of 5 K/min RT to 500 °C was used. Two different decomposition conditions were studied, i.e. in pure helium (flow of 35 ml/min) and in helium (80 %) and oxygen (20 %) (total flow 44 ml/min). XAFS spectra were measured at the Mo-K edge in a photon energy range from 19.9 keV to 21 keV, with a time resolution of 4.5 min/spectra.

Results of in situ XRD measurements performed either in pure helium or in 20 % oxygen and with a heating rate of 2 K/min are used as references for long-range ordered crystalline phases occurring during the decomposition of AHM. Figure 5 shows the evolution of XRD patterns during the decomposition of AHM in 20 % oxygen. At least three different stages of the decomposition can be seen in agreement with results from thermal gravimetric analysis (TGA) (Figure 4 and 5).

Figure 1 and 2 show the evolution of the Mo K edge FTχ(k) of AHM during decomposition in pure helium and in 20 % oxygen, respectively. Several stages in the decomposition can be distinguished, predominantly from their differences in their higher coordination shells. In addition, while exhibiting a similar decomposition pattern up to 350 °C, significant differences between decomposition in helium and in 20 % oxygen can be seen at higher temperatures. These differences have also been observed in XRD measurements at somewhat higher temperatures and are due to the formation of Mo_4O_{11} under pure helium.

Detailed XAFS data reduction and analysis is being carried out using the software package WinXAS [3] following standard procedures. The ab-initio multiple-scattering code FEFF 7 [4] was employed to calculate theoretical XAFS phases and amplitudes for defined crystallographic model systems. Subsequently, a least-squares fit of a theoretical EXAFS function to an experimental spectrum at a certain reaction temperature was used to confirm or reject a structure model and to refine its structural parameters (i.e. coordination numbers and distances of first neighbor shells). Figure 3 shows an EXAFS refinement of a hexagonal molybdenum trioxide structure to an experimental FTχ(k) measured at 340 °C during AHM decomposition in 20 % oxygen. The excellent agreement between theory and experiment in the range of 1.0 – 4.2 Å corroborates the XRD results for this stage of the decomposition.

From a preliminary data analysis the following decomposition steps have been identified. The first step at 75 °C results in a highly disordered phase, i.e. one without long-range order. At 200 °C the formation of a hexagonal phase, $MoO_3*(NH_3)_x*(H_2O)_y$ is observed. At a temperature of ~350 °C we found the formation of a phase which can be described as orthorhombic MoO_3. This last step is accompanied by a loss of water. Further detailed EXAFS analysis of the different AHM decomposition products is underway.

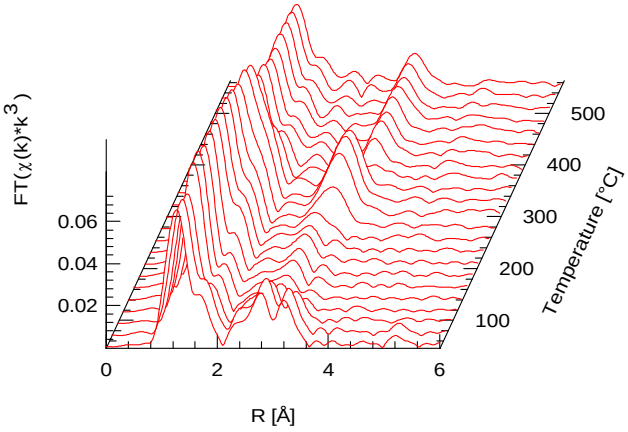

Figure 1. Thermal treatment of AHM in helium; evolution of Mo K edge FT(χ(k)*k^3)

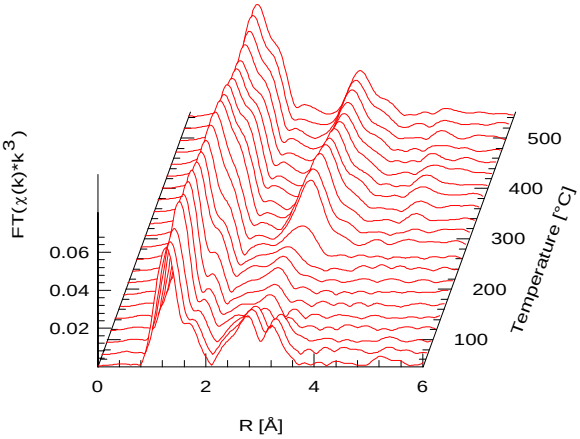

Figure 2. Thermal treatment of AHM in 20 % oxygen; evolution of Mo K edge FT(χ(k)*k^3)

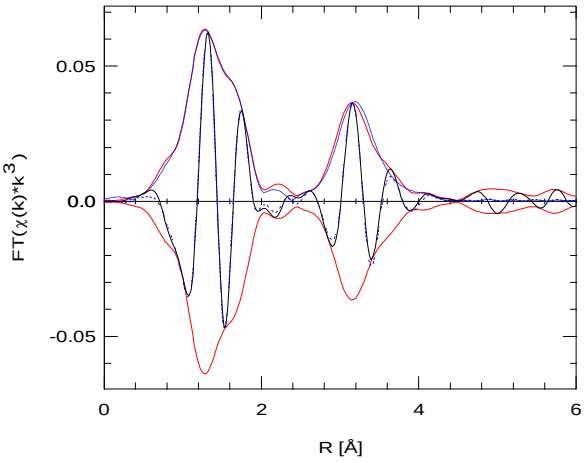

Figure 3. Experimental (325 °C, decomposition in 20 % oxygen) and theoretical Fourier-transformed (dashed) χ(k) of hexagonal MoO_3.

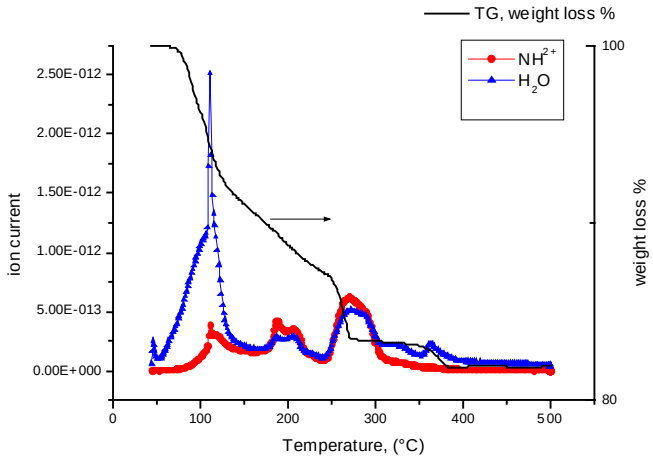

Figure 4. Evolution of MS signals of water and NH_3 during decomposition in helium plotted together with the corresponding TGA data.

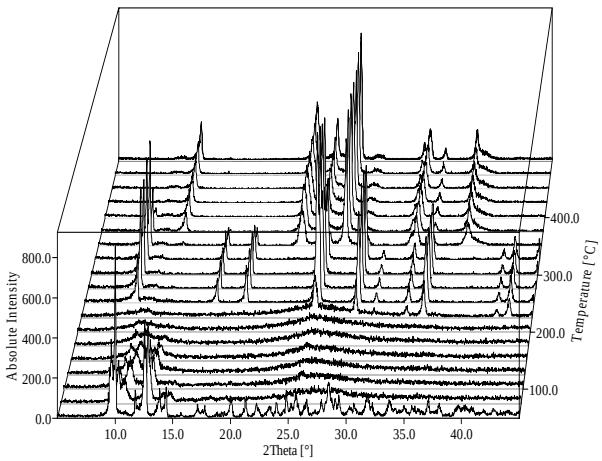

Figure 5. Thermal treatment of AHM in 20%oxygen, evolution of the X-ray diffractograms

References

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