Insight in the thermal decomposition of Ammonium Heptamolybdate

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Ammonium heptamolybdate tetrahydrate (AHM, $(NH_4)_6Mo_7O_{24}$*4 H_2O) 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 systems ($Mo_x(V,W)_yO_3$) that find extensive industrial use for the partial oxidation of light alkenes [1]. Numerous authors have studied the decomposition of AHM [2], however no agreement regarding decomposition scheme and formation of products has been achieved yet. To reveal the influences of different atmospheres on the products and to elucidate the correlation between phase composition and catalytic activity, detailed structural studies are required.

In this work we present investigations of the decomposition of AHM by a combination of in situ XAS and in situ XRD under different decomposition atmospheres. Initially, XRD is used to identify the crystalline phases that are produced during AHM decomposition. Subsequently this information serve as a starting point for analysis of the in situ XAFS data obtained during various stages of the thermal decomposition. An overview of the long range order evolution, phase composition and crystallinity on the one hand and evolution and characteriztion of the short range on the other hand, are obtained. Additionally, the products are characterized by SEM to identify the morphology of the products. The decomposition of AHM is further studied by TG and DTA. Subsequently, the obtained informations will be correlated with catalytic activity.

For XAFS studies ammonium heptamolybdate tetrahydrate (*Aldrich*) was mixed with boron nitride (7 mg AHM / 30 mg BN) and pressed into 5 mm diameter pellets. An edge jump at the Mo K edge (19.999 keV) of about 2.0 was obtained. Transmission X-ray absorption spectra were measured in situ with the sample pellet in a flow reactor (4 ml total volume) under controlled reactant atmosphere (*Bronkhorst mass flow controller*). The gas phase composition was monitored by on-line mass spectrometry (*Pfeiffer QMS 200*). A heating rate of 5 K/min from RT to 500 °C was controlled by an *Eurotherm PID* temperature controller. The decomposition was studied in pure helium (flow of 35 ml/min), in 20% oxygen / 80% helium, in 5 % propene / 95 % helium and in 5 % H_2 / 95 % helium (total flow 44 ml/min). XAFS at the Mo K edge in a photon energy range from 19.9 keV to 21 keV was measured with a time resolution of 4.5 min/spectra under all conditions, and of 12 s/spectra for the decompositsiom in helium and oxygen. Measurements were done at HASYLAB / DESY, Beamline X1 and at ESRF, Beamline ID24.

XRD measurements were carried out on a *Stoe STADIP P* diffractometer equipped with a *Bühler HDK S1* high temperature cell (400 ml). For temperature and gase phase composition controll and gas phase analyis, the same equippment as described for the XAFS measurement is used. The same heating rates and gas phase compositions with a total flow of 100 ml/min were utilized.

Detailed XAFS data reduction and analysis was carried out using the software package WinXAS [3] following standard procedures. The ab-initio multiple-scattering code FEFF 7 [4] is employed to calculate theoretical XAFS phases and amplitudes for defined crystallographic model systems. Subsequently, a least-squares fit of a theoretical XAFS function to an experimental spectrum at a certain reaction temperature is 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 1 shows an XAFS 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.

Figure 2 shows the evolution of diffraction patterns during decomposition of AHM in 20 % oxygen. In agreement with results from thermal gravimetric analysis (TGA) at least three different stages of the decomposition can be seen in the XRD patterns. The reaction sheme for the decomposition in 20 % oxygen is as follows:

AHM $\xrightarrow{start\ @65°C}$ amorphous Phase $\xrightarrow{250°C}$ formation of the hexagonal phase with a composition of $(NH_4,H)_xMo_{6-\delta}O_{18-\delta}$*n H_2O $\xrightarrow{350°C}$ MoO_3 (orthorombic form).

For the decomposition in propene and pure helium the scheme differs only in the resulting products which are Mo_4O_{11} and a mixture of Mo_4O_{11} and MoO_3 ,respectivley. The Mo_4O_{11} is amorphous at 350 °C and crystalizes at about 450 °C. In the case of propene atmosphere the Mo_4O_{11} is reduced to MoO_2. For the decomposition in hydrogen atmosphere, the formation of MoO_3 is observed already at a temperature of 250 °C, without the formation of the hexagonal phase. Hence it is concluded that step three is the one which is most important step for tailoring the oxidation state and the composition of the product. It was found that the formation of Ammonium Octamolybdate (AOM, $(NH_4)_4Mo_8O_{26}$), which occures at 190 °C is a compeeting process to the formation of the hexagonal phase. This formation is kinetical inhibited. Sometimes small amounts of AOM are formed, however, resulting in an occurence of MoO_3 already at 300 °C, the decomposition temperature of AOM. Furthermore, at RT, the hexagonal phase transform into the AOM which is the thermodynamical stable phase at RT.

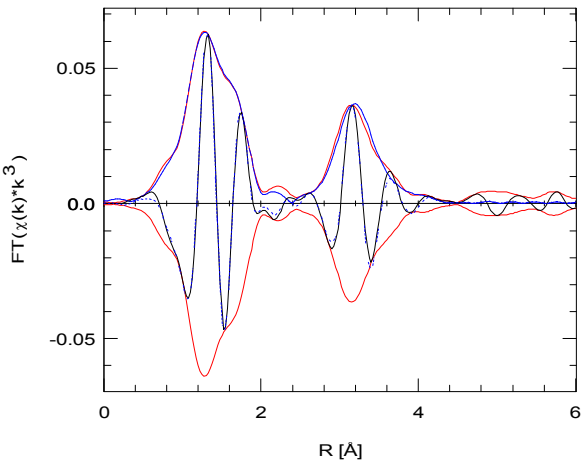

Figure 1. Experimental (solid) and theoretical (dashed) Fourier transformed χ(k) of hexagonal MoO_3. Conditions: 325 °C in 20% oxygen.

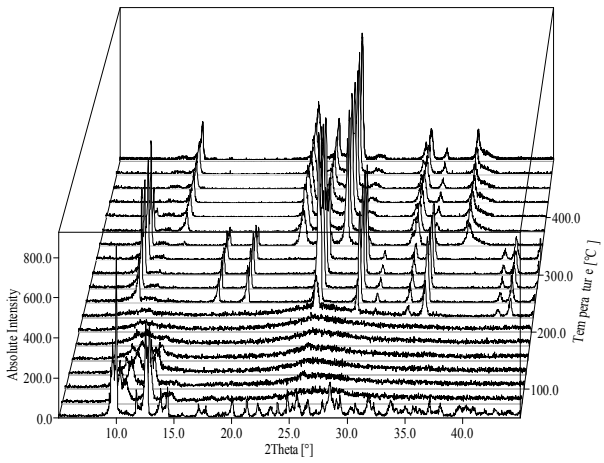

Figure 2. Evolution of X-ray patterns during thermal treatment of AHM in 20% oxygen.

References

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