European Journal of Inorganic Chemistry, 6 (2003) 1058-1071

Structural Investigation of the Thermal Decomposition of Ammonium Heptamolybdate by in situ XAFS and XRD

Julia Wienold, Rolf E. Jentoft, and Thorsten Ressler*

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

E-mail: Ressler@FHI-Berlin.MPG.de, Phone: (+49)-30 / 8413 3192, Fax: (+49)-30 / 8413 4405

Abstract

The decomposition of ammonium heptamolybdate (AHM, (NH4)6Mo7O24*4H2O) was studied in situ by X-ray diffraction and X-ray absorption spectroscopy as well as by thermal analysis (TG/DTA). Decomposition conditions such as reactant atmospheres, (20% oxygen, 5% propene, 5% hydrogen, pure helium, and static air), heating rates and gas flow rates are varied to reveal their influence on the decomposition. The results obtained show that the reaction pathway is influenced by the partial pressure of the decomposition products in the gas phase. The partial pressure of the decomposition products, water and ammonia, at a given temperature, is influenced mainly by the reactant gas flow rate and the heating rate. Lowering the partial pressure of ammonia and water inhibits the crystallization of the intermediate ammonium tetramolybdate (ATM) and promotes the formation of the intermediate hexagonal MoO3. The decomposition pathway under low gas phase product partial pressure is: (i) AHM; (ii) (~335 K) X-ray amorphous phase; (iii) (~520 K) hexagonal MoO3; (iv) (~ 650 K) products as a function of atmosphere are mixtures of highly disordered Mo4O11, and/or a-MoO3. Otherwise it follows: (i) AHM; (ii) (~350 K) X-ray amorphous phase; (iii) (~470 K) ATM; (iv) (~570 K) hexagonal MoO3 + a-MoO3; (~650 K) a-MoO3. The decomposition in hydrogen containing atmosphere shows a peculiar reaction scheme in which an intermediate MoO3 with unusual texture is formed prior to the reduction to MoO2 and the consecutive formation of orthorhombic Mo4O11.