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

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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.