Thermochimica Acta, 133 (1988) 163–168
Elsevier Science Publishers B.V., Amsterdam

THE ROLE OF AMMONIUM IONS IN THE ACTIVATION OF NICKEL MOLYBDATE PRECURSORS

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ABSTRACT

The elimination of ammonium ions in the thermal activation of the nickel molybdate precursors may follow two different pathways: emission of ammonia as such and oxidative decomposition. The competition between the two mechanisms is mainly controlled by the partial pressure of oxygen but kinetic factors often play a significant role. Catalytic effect of the cell material and variations of the heating rate can modify the ratio between the two reaction rates.

INTRODUCTION

A condition which has to be fulfilled by any pH-controlling agent in the synthesis of precursors of mixed oxides to be used in catalysis is its easy elimination from the precipitate. From this point of view its volatility under heating makes of ammonia a preferred choice when compared with alkali or alkaline earth hydroxides. Nevertheless the easy oxidation of ammonia compels to check carefully the conditions of activation of the precursor, in order to avoid the occurring of hot spots inducing heterogeneity in the properties of the final oxide.

In this communication some examples of thermal decomposition of nickel molybdate precursors, containing ammonia both as crystallization space-filler and counter-cation in ammonium form,

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

are presented. Our aim is to show that the competition between the mechanisms of plain ammonia emission and oxidative decomposition is significantly affected by experimental conditions, also when the partial pressure of oxygen is not involved in an explicit way.

EXPERIMENTAL

Preparations of phase M and $NiMoO_4$ precursor have been detailed elsewhere [1, 2]. The $(NH_4)_6NiMo_9O_{32}\cdot 6H_2O$ used was a Climax product. All solids were characterized by powder X-ray diffractometry (XRD) and infrared spectroscopy (KBr pellets). Samples heated at intermediate temperatures were examined by the same techniques.

Thermal analysis experiments were carried out using a Mettler TA2000C apparatus for simultaneous TG and quantitative DTA. Samples of 30 mg were heated at a rate of 20 K min^{-1} under flowing gas in platinum cells with pierced lids, when no otherwise stated. Melting of pure indium and aluminium under nitrogen flow were used as thermometric and calorimetric standards.

RESULTS AND DISCUSSION

When the precipitation of the precursors of the system $Mo^{6+}\cdot Ni^{2+}$ is carried out in basic conditions the solid formed presents a framework known as phase M [3] Solids with the same diffraction pattern can significantly differ in stoichiometry. The general formula can be expressed as $x(NH_4)_2O\cdot yH_2O\cdot zNiO\cdot MoO_3$, with z near to 1.5. By heating this phase at temperatures of 500°C or higher biphasic systems of $NiMoO_4$ and NiO are obtained through a slow, difficult crystallization [1, 2].

The results of typical TG-DTA experiments under flowing nitrogen or oxygen are reported in figure 1. The main feature in inert atmosphere is a strong endothermic peak accompanied by loss of weight with maximum at 420°C. XRD analysis of specimens heated at intermediate temperatures show a correspondence between this phenomenon and the collapse of the structure of the precursor. In the experiment under oxygen flow a sharp hexothermic peak appears, superposed to the same endothermic phenomenon.

The influence of the amount of ammonium on the thermic phenomena is reported in table 1. The relative amount of ammonium in four

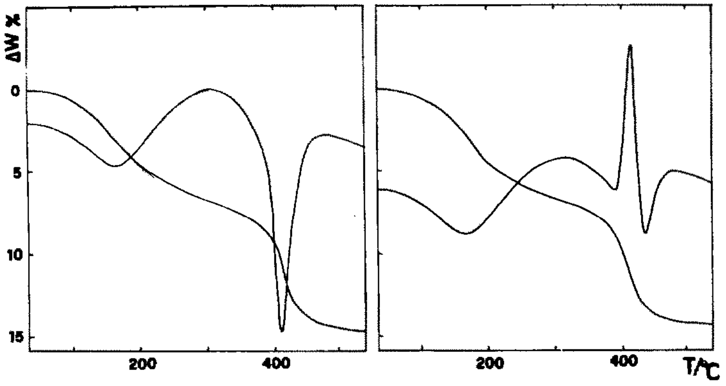

Fig. 1. DTA and TG of $x(NH_4)_2O \cdot yH_2O \cdot 1.5NiO \cdot MoO_3$ under (left) N_2 and (right) O_2 flow.

TABLE 1

Decomposition of $x(NH_4)_2O \cdot yH_2O \cdot zNiO \cdot MoO_3$. Exchanged heat and loss of weight of the peak at 420°C under nitrogen and oxygen flow as functions of the amount of ammonium.

I_{1410}/I_{920}	N_2		O_2	
	δQ (J g^{-1})	δW %	δQ (J g^{-1})	δW %
0.30	170	7.2	- 50	3.6
0.40	130	7.2	- 70	4.5
0.50	230	7.2	- 90	5.1
0.55	260	7.9	-200	6.7

different samples of phase M is indicated by the intensity ratio between the IR bands at 1410 cm^{-1} (N-H stretching) and 920 cm^{-1} (Mo-O stretching). Referring to the TG-DTA peak at 420°C the heat absorbed in the experiments in inert atmosphere and the heat released and the loss of weight in the experiments under oxygen flow appear correlated with the amount of ammonium in the precursor. The higher loss of weight in the experiments under nitrogen flow suggests that also some depletion of oxygen from the oxide can contribute to the endothermic effect. In the experiments in oxidizing conditions the degree of superposition of the hexothermic peak to the endothermic one varies with the amount of ammonium, the DTA trace in the ammonium-richer sample presenting no detectable endothermic phenomena.

The exothermic effects observed appear in agreement with the catalytic activity of mixed molybdates in the oxidation of gaseous ammonia [4]. Already at temperatures not higher than 300°C these compounds are active and selective in the mild oxidation of ammonia to nitrogen and water.

In other TG-DTA experiments the $NiMoO_4$ precursor known as phase ϕ_y [5], of stoichiometry $x(NH_4)_2O\cdot(1-x)H_2O\cdot NiMoO_4$ with very small x, was heated under oxygen or nitrogen flow. In both cases the main TG-DTA feature was a sharp hexothermic peak with maximum at about 470°C. The heat emitted was 60 J g^{-1} in nitrogen and 120 J g^{-1} in oxygen. The loss of weight corresponding with the main peak was about 0.6% of the initial weight under oxygen flow and 0.9% under nitrogen flow. XRD analysis of specimens heated to intermediate temperatures indicated that the hexothermal peak corresponded both with the collapse of the precursor framework and with the crystallization of α-$NiMoO_4$. This phenomenon allows to explain the heat released in the experiment under nitrogen flow as the difference between the heat of crystallization of the final oxide and the heat which should be absorbed by the release of ammonia.

When 9-molybdonickelate (composition $3(NH_4)_2O\cdot6H_2O\cdot NiO\cdot9MoO_3$) is heated to 500°C in oxidizing conditions a biphasic system is obtained, composed of $NiMoO_4$ and MoO_3 [6]. The TG-DTA trace of 9-molybdonickelate heated under oxygen flow is reported in figure

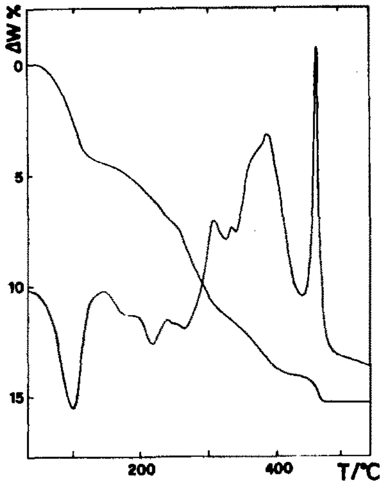

Fig. 2. DTA and TG of $3(NH_4)_2O\cdot6H_2O\cdot NiO\cdot9MoO_3$ under O_2 flow in platinum cell.

2. After the main loss of water near 100°C the loss of ammonia begins with a weak endothermic effect and continues beyond 270°C with a complex series of hexothermic peaks. XRD analysis of samples heated to intermediate temperatures show that, while the first traces of crystalline MoO_3 appear at the end of the hexothermal peak ending at 430°C, the crystallization of both oxides formed mainly corresponds with the hexothermic peak at 470°C.

Specimens heated in the same conditions (platinum cells, oxygen flow) at heating rates lower than 20 K min^{-1} show some shift towards lower temperatures of the peaks, without significant changes in the pattern of decomposition. Specimens heated under oxygen flow in α-alumina cells at different heating rates present instead different thermic phenomena. DTA traces of specimens of 15 mg of 9-molybdonickelate heated at rates of 5, 10 and 20 K min^{-1} are reported in figure 3. The specimen heated at 20 K min^{-1} (fig. 3a) by comparison with the specimen heated in platinum cell (fig. 2) presents the beginning of the hexothermic phenomena shifted to a temperature about 60°C higher. Specimens heated in alumina cells at lower heating rates (fig. 3b and 3c) present a different superposition of endothermic and hexothermic phenomena, resulting in a global endothermic effect increasing with the decrease of the

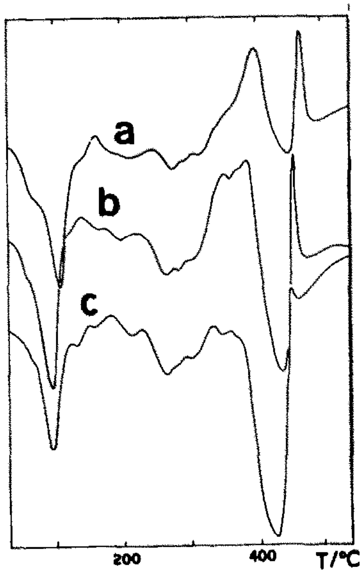

Fig. 3. DTA of $3(NH_4)_2O\cdot 6H_2O\cdot NiO\cdot 9MoO_3$ under O_2 flow in corundum cell. Heating rate: (a) 20, (b) 10, (c) 5 K min^{-1}.

heating rate.

The catalytic role played by metals in the oxidation of ammonia is well known. The decomposition of NH_4NO_3 in air has been show to be endothermic in alumina cell and hexothermic in metallic cells [7]. Moreover platinum is the more active transition metal in the catalysis of the oxidation reactions of ammonia [8], being able to decompose NH_3 to nitrogen and water starting from a temperature of 150°C. The endothermic effect observed when alumina cells were used can be partially explained by the low catalytic activity of MoO_3 in the oxidation of ammonia. Despite the activity of the mixed molybdates, MoO_3 (the main activation product of 9-molybdonickelate) is possibly the less active transition metal oxide in the oxidation reactions of ammonia [9].

The observed increase of the endothermic effect with the decrease of the heating rate deserves a tentative interpretation. The slower emission of ammonia at lower heating rate probably allows a better evacuation of the gas from the cell, decreasing the partial pressure of NH_3 over the solid. The consequently slower secondary oxidation reaction could allow a more important fraction of ammonia to be evacuated as such. Anyway a more detailed insight of the chemistry of the phenomenon is needed to support any hypothesis.

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