STUDY OF THE DEHYDRATION/REHYDRATION OF AMMONIUM TRIS-OXALATO ALUMINATE(III) $(NH_4)_3Al(C_2O_4)_3\cdot3H_2O$ AT CONTROLLED ATMOSPHERE

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Abstract

The study of the dehydration/rehydration of ammonium tris-oxalato aluminate(III) $(NH_4)_3Al(C_2O_4)_3\cdot3H_2O$ in flowing dinitrogen saturated with water vapor at room temperature, using thermogravimetric analysis and X-ray diffraction techniques, allowed the determination of the temperature stability domains of $(NH_4)_3Al(C_2O_4)_3\cdot3H_2O$, $(NH_4)_3Al(C_2O_4)_3\cdot2H_2O$ and the anhydrous salt. The X-ray powder diffraction profiles are reported for each of the three phases.

Keywords: ammonium tris-oxalatoaluminate(III), dehydration, rehydration, thermogravimetric analysis, X-ray powder analysis

Introduction

The oxalato-metallates have been studied for many years in our laboratory [1–5]. Their pyrolysis produces well crystallized solid oxide phases [6–8]. We have undertaken investigations on multicomponent systems including the ammonium tris-oxalato aluminate(III) with a double purpose: 1. to get a better knowledge on the precursors, particularly on their stoichiometry, the ammonium oxalato-metallates usually crystallizing at room temperature as hydrates $(NH_4)_3\mathbf{M}^{III}(C_2O_4)_3\cdot x H_2O$ ($\mathbf{M}^{III}$=Al, Fe, Cr) with x close to 3; 2. to get, after pyrolysis, a good dispersion of the metallic element at the atomic scale, which is an important step in the production of doped alumina crystallites or micronic powders. In the present paper we report the crystallization conditions of $(NH_4)_3Al(C_2O_4)_3\cdot x H_2O$ hydrates (for x=0, 2, 3) and their dehydration/rehydration in controlled atmosphere.

Experimental

Preparation and characterization of the solids

Hydrated ammonium tris-oxalato aluminate(III) has been synthesized from aqueous solutions of oxalic acid and ammonium oxalate, and from aluminum powder [9]. The reaction takes place at 80°C and is complete:

$$2Al+3H_2C_2O_4+3(NH_4)_2C_2O_4 \rightarrow 2(NH_4)_3Al(C_2O_4)_3+3H_2$$

At room temperature the salt crystallizes with 2.6 water molecules. Its structure has already been determined by single-crystal analysis [10], and the stoichiometry confirmed by manganometric titration of the oxalate ions and spectroscopic plasma emission of Al^{3+}.

Thermogravimetric analysis

The dehydration studies were performed using a Setaram G70 thermobalance equipped with a PR 540C regulating device. The heating rate was 1°C min^{-1} and the sample mass close to 100 mg. The dehydration/rehydration cycling experiments have been realized in flowing dinitrogen saturated with water vapor at room temperature.

X-ray powder analysis

X-ray powder diffraction profiles were obtained with standard Philips routine equipment (PW1720 generator, PW1050/25 goniometer, PW1965/60 detector and PW1370/01 electronic interface), which were complemented by a step-scanning device interfaced through an Apple II™ microcomputer. Time-resolved experiments [11] correspond to repetitive investigations versus time and/or temperature of selected angular diffraction domains. For atmosphere-controlled runs a special air-tight and evacuable reactor presenting Kapton™ windows has been constructed in our Laboratory and mounted on the X-ray diffraction equipment [12]. Whenever necessary, the analysed solids were pressed into the 22×11×0.5 mm depression of a heatable Au4G aluminun-alloy sample-holder [13]. Usually, the (111) and (200) diffraction-peak positions corresponding to this sample-holder were used as an internal standard for the determination of the temperature.

Results

Thermogravimetric analysis

The study of the dehydration/rehydration process of the trihydrate by thermogravimetry (Fig. 1a and b) in flowing dinitrogen saturated at room temperature with water vapor (P_{H_2O}=3333 Pa) shows that powdered crystals collected by isothermal evaporation at 25°C and dried in ambient atmosphere, have a starting water content of 2.6 molecules per formula (curve A). The first dehydration occurs in two steps corre-

sponding to the formation of the dihydrate and the anhydrous salt. On curve B (rehydration after the first dehydration) it appears that the final gain of mass is higher than the first mass-loss. Accordingly, the real trihydrate is stabilized only in the presence of an excess of water vapor ; furthermore, no observable plateau corresponding to the intermediate dihydrate is detected on this curve. Finally, after several thermal cycles, the curves are stabilized and do not highlight the formation of the dihydrate (curve C) any more.
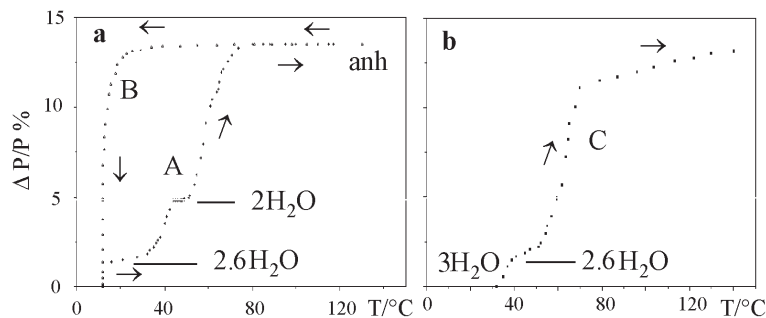

Fig. 1 Thermogravimetric analysis on the tris-oxalato trihydrate: dehydration/rehydration at P_{H_2O}=3333 Pa

X-ray diffraction analysis

In order to characterize the solids involved in the dehydration/rehydration process, we have undertaken a structural study by using X-ray powder diffraction techniques. The diffraction profile of the starting trihydrate presents an intense massif in the 11.6–13.6°2θ region. In the first step, the evolution of this selected profile *vs.* temperature has been investigated in the presence of ambient atmosphere. The results are shown in Fig. 2. By comparison with the results obtained by thermogravimetry it is possible to find three limiting profiles which are superposed in Fig. 3.
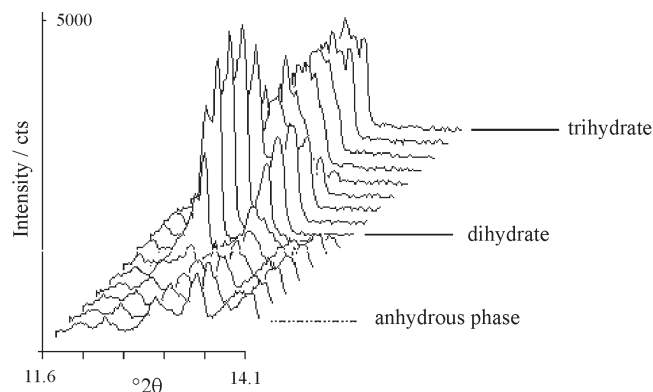

Fig. 2 Evolution of the intense X-ray profile in a selected angular domain during dehydration at P_{H_2O}=3333 Pa
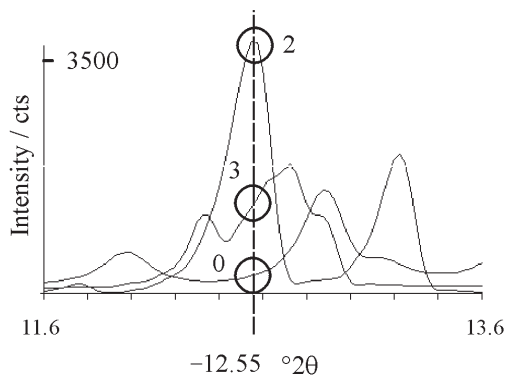
Fig. 3 The selected intense X-ray diffraction profiles corresponding to the
3 – trihydrate, 2 – dihydrate and 0 – anhydrous phase

Profiles 3, 2 and 0 correspond to the trihydrate, the dihydrate and the anhydrous phase respectively. By fixing the diffraction angle at 12.55°2θ for a constant-angle run (the observed intensity-maximum for the dihydrate), it is possible to follow precisely the structural evolution during the dehydration/rehydration reaction. The experimental curve is shown in Fig. 4. The first zone A (heating up to 100°C) corresponds to the dehydration performed at about 1°C min⁻¹, a heating rate comparable to that used for thermogravimetry (Fig. 1). The three constant-intensity levels corresponding to the trihydrate, the dihydrate and the anhydrous salt are clearly evident on this curve. After complete dehydration, the heating is switched off, and after rapid cooling (zone B), the structural evolution is explored for about 14 h (zone B′). Hence, this second zone corresponds to the rehydration at room temperature. During the rehydration, the intensity-plateau correponding to the dihydrate is never observed. This result is in complete agreement with the previous observations obtained by thermogravimetry.
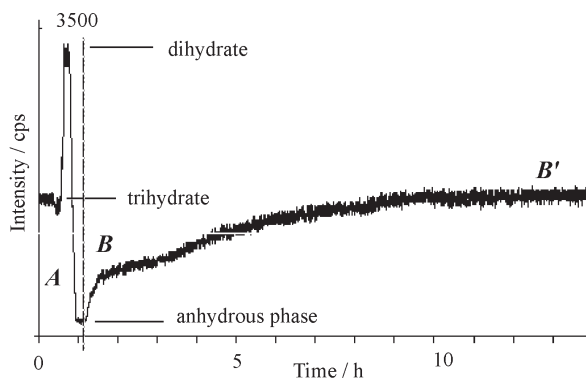

Fig. 4 Evolution of the diffraction intensity during dehydration/rehydration (fixed angle) at P_{H_2O}=3333 Pa

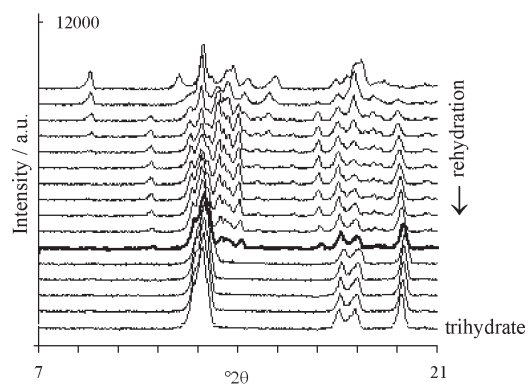**Fig. 5** Time-resolved X-ray diffraction during the rehydration of the anhydrous phase at P_{H_2O}=3333 Pa
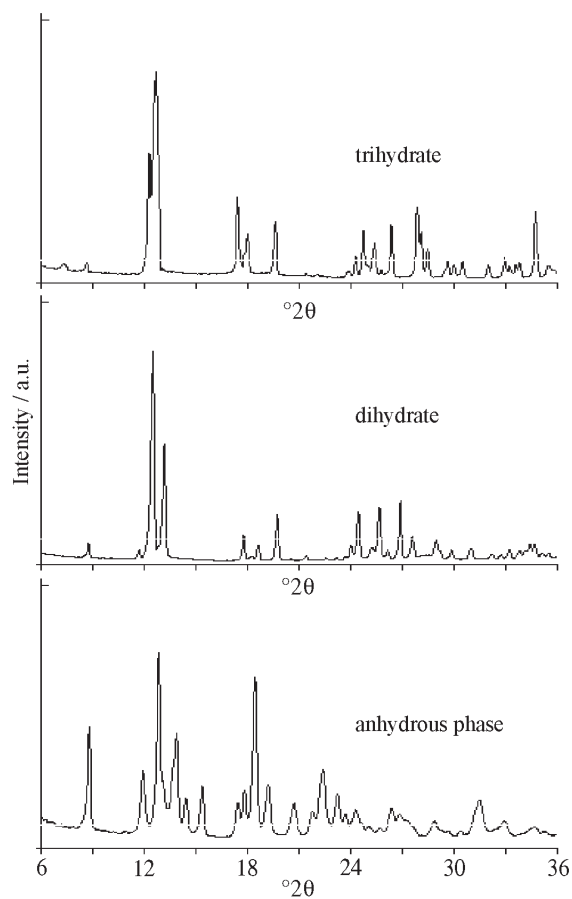

Fig. 6 X-ray powder diffraction profiles diagram

Nevertheless, one might think that observing structural evolutions at constant angular position or in a rather restrained diffraction domain (11.6–13.6°2θ) could result in the loss of very subtle information. Therefore, rehydration has also been investigated by using the time-resolved powder diffraction technique [11] in the larger 7–21°2θ domain (Fig. 5). These results confirm those reported above (Figs 1 and 4). Finally, by using the results and the temperatures detected for the existence of the three investigated phases (Fig. 4) their complete diffraction profiles could be recorded (step-scanning technique, 6–56°2θ domain, 0.025°2θ steps, 5 to 25 s counting time at each step). Since for 2θ>36° the diffracted intensities are rather low, the profiles represented in Fig. 6 have been limited at this angle.

The crystallographic data of ammonium tris-oxalatoaluminate(III) and its hydrates are presented in Table 1 [14].

Table 1 Crystallographic data for ammonium tris-oxalato aluminate(III) and its hydrates

$(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$	$(NH_4)_3Al(C_2O_4)_3 \cdot 2H_2O$	$(NH_4)_3Al(C_2O_4)_3$
Triclinique $P\bar{1}$	Monoclinique $P2_1/c$	Monoclinique $P2_1/n$
a=7.877(5) Å	a=7.791(6) Å	a=7.337(5) Å
b=10.672(7) Å	b=19.775(16) Å	b=13.365(9) Å
c=10.679(6) Å	c=10.443(8) Å	c=14.719(9) Å
α=83.31(4)°		
β=70.16(3)°	β=107.09(3)°	β=95.60(4)°
γ=69.25(3)°		
V=790(1) Å^3	V=1538(1) Å^3	V=1436(1) Å^3
Dx=1.677(7) g cm^{-3}	Dx=1.645(4) g cm^{-3}	Dx=1.595(1) g cm^{-3}
Z=2	Z=4	Z=4

Conclusions

The investigation of the dehydration/rehydration of ammonium tris-oxalato aluminate(III) $(NH_4)_3Al(C_2O_4)_3 \cdot 3H_2O$ by thermogravimetric and X-ray diffraction analysis allowed us to determine the existence and the crystallization conditions of the ammonium tris-oxalato aluminate(III) hydrates and its anhydrous salt. The crystallographic data for each of the three phases are published [14]. Complete structural investigations concerning the dihydrate and the anhydrous phase are presently in progress and will soon be published. The results reported in this paper represent the first step of the preparation and the characterization of precursors for the ultimate elaboration of mixed alumina-based oxides. A further second step concerns the determination of the ternary and quaternary systems involving water and the complex aluminum, chromium and iron oxalates.

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