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DSC studies on the effect of particle size on NH_4NO_3 at temperatures between 25 and 100°C

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Abstract

According to DSC measurements, NH_4NO_3 samples with particle sizes between 0.062 and 2 mm have different structural phase transition paths in the temperature range 25–100°C. Samples with particle sizes of about 2 mm underwent the transition path IV → III → II, whereas those with particle size near 0.06 mm were more likely to undergo the transition path IV → II.

INTRODUCTION

Ammonium nitrate (AN), one of the main raw materials for the fertilizer industry, has seven known solid phases in the temperature range −180–130°C [1]. The solid-state phase transformations of AN have been extensively investigated by thermal methods (DSC, DTA and dilatometry) [1–4] between 25 and 100°C. Within this range the principal solid state transitions are IV → III → II with equilibrium temperatures T_e of 32 and 84°C, respectively [5, 6]. In addition, the transition IV → II is known to occur at a T_e of 50°C [5]. The factors leading to the different transition paths are not completely understood. Moisture and other impurities [1, 4, 7], and the thermal history, including crystallization [8–12], have been claimed to have an effect.

The structure of phase IV measured at 25°C is orthorhombic, space group *Pmmn*, with cell constants $a = 5.751$ Å, $b = 5.436$ Å, $c = 4.926$ Å and $Z = 2$ [13, 14]. Phase III has an orthorhombic structure, space group *Pnma*, with cell constants $a = 7.716$ Å, $b = 5.845$ Å, $c = 7.197$ Å and $Z = 4$ [15, 16]. Choi and Prask [15] added 5 wt.% of KNO_3 to NH_4NO_3 in their measurements at 80°C. In the case of phase II, the structure is disordered, with the tetragonal space group $P\bar{4}2_1m$ or $P4/mbm$ [13, 17]. The cell

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parameters are $a = 5.7193$ (5.696) Å, $c = 4.9326$ (4.920) Å and $Z = 2$ at 70°C.

The purpose of this work was to investigate the effect of sample size and particle size (ps) (or ps distribution) on the transition path of AN in the temperature range 25°–100°C.

EXPERIMENTAL

The reagent used was p.a. NH_4NO_3, 'Baker analyzed'.

The samples are prepared in the following way. Pure AN was heated until it was completely melted (at about 170°C). The molten AN was cooled down to room temperature in a programmable warming (cooling) cupboard using a cooling rate of 2.5°C min^{-1}. The cooled sample was ground in a mortar and a part of the sample was sieved using a micro sieve set with mesh sizes 0.063, 0.088, 0.125, 0.177, 0.250, 0.354, 0.500, 0.707 and 2.000 mm. The sample sizes used for DSC measurements were 5, 10 and 15 mg.

The Perkin-Elmer PC Series DSC-7 apparatus was calibrated with indium (m.p. 156.6°C and $\Delta H = 28.47$ J g^{-1}) and benzoic acid (m.p. 123.3°C). The sample pans were aluminum, 50 μl in volume, with holes. The scanning rate was 5°C min^{-1} and the temperature range was 25–100°C. DSC measurements were made both immediately after grinding and sieving, and two weeks after sieving (samples were stored in an exsiccator). The energy of the transition III → II was measured and plotted as a function of particle size.

The moisture content of the samples was determined by Karl-Fischer titration.

Measurements were made at the University of Jyväskylä.

RESULTS AND DISCUSSION

Grinding the AN sample changed the original transiton path from IV → III → II to IV → II.

Figure 1 shows the III → II transition energies of different AN samples as a function of ps; the letters a, b, . . . , i refer to the particle size distributions indicated in Table 1. Three series of samples were measured.

The moisture content of sample a (ps 2.00–0.707 mm) in series 1 was 0.2 wt.% and it can be assumed that the moisture content was the same in all samples of series 1. The sample size for DSC measurements of series 1, which were carried out immediately after grinding, was 10 mg. As can be seen from Fig. 1 the energy of the transition III → II decreased as a function of particle size. After the samples of series 1 had been stored for two weeks in the exsiccator (no desiccant was present), the moisture content was

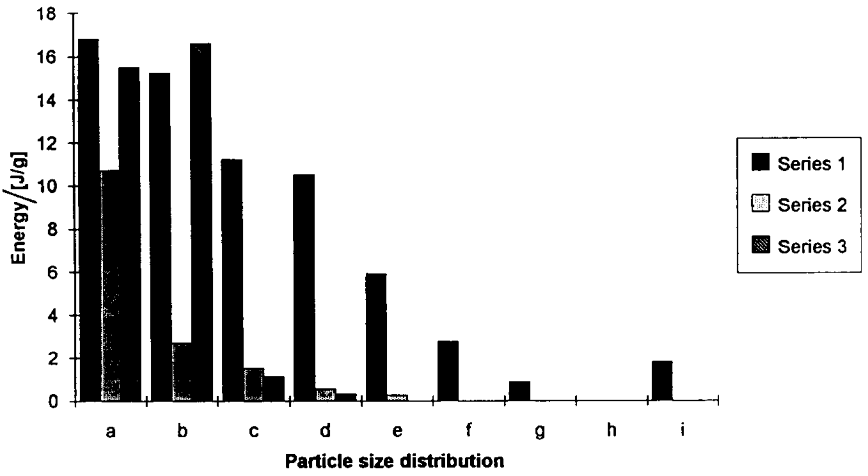

Fig. 1. Energy of transition III → II as a function of the particle size (Table 1) for three series of samples of different sample size and moisture content. Series 1, 10 mg and 0.2 wt.%; series 2, 15 mg and 0.1 wt.%; series 3, 5 mg and 0.1 wt.%.

reduced to 0.1 wt.%. New DSC measurements were then carried out using sample sizes of 15 mg (series 2) and 5 mg (series 3). In series 2, the III → II transition energy decreased logarithmically with decreasing particles size. The same trend was observed for series 3, except for sample b where ΔH was 16.3 J g^{-1}. In series 2, only sample a, and in series 3, only samples a and b, exhibited the normal or near normal III → II transition ($\Delta H = 16$ J g^{-1}) [5].

Though the size of the sample had no affect on the transition paths, the size of the particles did. The small particles acted like samples prepared by crystallization from water, in which crystals are long and needle-like and undergo transition IV → II in the temperature range 25–100°C [11]. Samples of large ps behaved like samples obtained from a melt, where no

TABLE 1

Particle sizes for the measurements reported in Fig. 1.

	Size/mm
a	2.000–0.707
b	0.707–0.500
c	0.500–0.354
d	0.354–0.250
e	0.250–0.177
f	0.177–0.125
g	0.125–0.088
h	0.088–0.063
i	<0.063

single crystals can be seen (ps 2–5 mm), and the transition IV → III → II occurs [11].

The reason for the difference between the first series and the second and third series could be the moisture content. According to our earlier work [11], it is not so much the amount of water than the location of the water in the crystals that is important. During slow crystallization from water, the water molecules have time to seek out the ideal sites, whereas during rapid crystallization from a melt the water molecules are randomly located and the structure is disordered. During the time of storage the water molecules have time to find their ideal sites, and in the temperature range 25–100°C the transition IV → II is dominant.

CONCLUSIONS

The size of the samples does not seem to affect the transition paths if the samples are dry enough, i.e. a moisture content below 0.1 wt.%, but the particle size is important. Nearly all samples with small particle size (ps <0.250 mm) underwent transition IV → II, behaving like samples crystallized from water. Those samples with ps >0.500 mm underwent the pure transition IV → III → II with no direct IV → II transition.

Our results indicate that it is not possible for fertilizer prills, ps >2.5 mm (containing pure AN), to undergo the direct transition from phase IV to phase II.

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