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Identification of the thermal decomposition behaviour of ammonium pentaborate

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Abstract

The thermal decomposition behaviour of ammonium pentaborate octahydrate (APB) and its conversion to boron oxide were investigated using isothermal thermogravimetry, non-isothermal thermogravimetry and differential thermal analysis.

TG and DTA curves of APB were obtained in its own decomposition atmosphere. According to these curves, the thermal decomposition of APB to boron oxide occurs in two main steps: the first step corresponds to the dehydration and the second is attributed to the deamination. It was found that the shapes of the TG curves recorded under isothermal conditions at different temperatures are strongly affected by the working temperature. Also, two endothermic peaks were observed on the DTA curve of APB, representing dehydration and deamination processes, respectively.

INTRODUCTION

Ammonium borate compounds can be readily prepared from boron-containing ores. The thermal decomposition of these compounds up to temperatures of about 873–1273 K yields boron oxide as an end product. Ammonium borate systems, $(NH_4)_2O-B_2O_3-H_2O$, have been widely studied [1, 2], although the decomposition of ammonium pentaborate, $(NH_4)_2O-5B_2O_3-8H_2O$, has not been reported in the literature.

The stoichiometric expression for the thermal decomposition of APB is

$$(NH_4)_2O \cdot 5B_2O_3 \cdot 8H_2O \xrightarrow{\text{Heat}} 5B_2O_3 + 2NH_3 + 9H_2O \quad (1)$$

APB loses approximately 75% of its water content and nearly 1% of its ammonia content as the temperature rises to 423 K. The complete conversion of APB to boron oxide requires temperatures between 873 and 1273 K, and a long heating time that depends on the deamination rate of the sample.

Experimental conditions such as temperature and heating rate have a strong influence on the dehydration and deamination steps.

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In the present work the thermal decomposition of APB to boron oxide was investigated. Different thermal analysis methods (isothermal and non-isothermal thermogravimetry, and differential thermal analysis) were employed to clarify this decomposition process.

EXPERIMENTAL

Preparation of APB sample

APB was precipitated by slow cooling of a hot solution consisting of 35.64 wt% boric acid, 49.37 wt% water and 14.99 wt% ammonia, from 363 to 298 K. Pure APB crystals were filtered and washed with acetone and then dried at room temperature. The chemical composition of the end product was determined as 63.81 wt% B_2O_3, 9.57 wt% $(NH_4)_2O$ and 26.62 wt% H_2O. Titrimetric methods were used to determine the ammonium oxide and boron oxide contents of the samples.

Thermal analysis of APB sample

DTA

Differential thermal analysis was carried out using a Shimadzu DTC 40 analyser. In the measurements, a 20 mg sample of particle size $-355 + 850$ μm was spread uniformly on the bottom of a cylindrical platinum crucible. The furnace temperature was increased from room temperature to 873 K with a constant heating rate of 5 K min^{-1}. The chart speed was selected as 2.5 mm min^{-1} and α-alumina was used as the reference material.

TG

Thermogravimetric analysis of APB was performed using the system shown in Fig. 1, which consists of a temperature-controlled furnace, a PC and a PC-compatible digital top-loading balance. The initial weight and particle size of the samples used in the isothermal and non-isothermal measurements were about 2 g and $-355 + 850$ μm, respectively. The weight losses of the sample were recorded automatically every minute by the PC which was connected to the balance. The furnace temperature was measured with a Pt–Rh thermocouple positioned near the crucible and controlled using a DTC-type temperature controller. Isothermal experiments were carried out at 423, 473, 523, 573, 623, 673, 723 and 773 K. Non-isothermal experiments were performed from room temperature to 873 K using heating rates of 0.8 and 1.0 K min^{-1}. All DTA and TG experiments were carried out in the decomposition atmosphere of the sample.

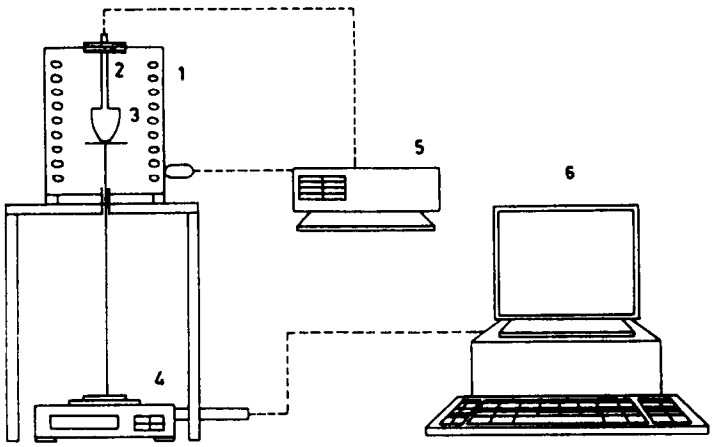

Fig. 1. Schematic diagram of the experimental set-up: 1, furnace; 2, thermocouple; 3, Pt crucible; 4, electronic balance; 5, temperature control unit; 6, computer.

RESULTS AND DISCUSSION

In general, the thermal decomposition of APB can be divided into three stages: dehydration, deamination and conversion to boron oxide. Figure 2 illustrates the isothermal dehydration curves of the samples obtained at different temperatures. Table 1 lists the ammonium oxide content of the samples taken from the furnace at different stages of the isothermal decomposition conducted at different temperatures. The boron oxide content of these samples is also presented in Fig. 3. Two main steps can be distin-

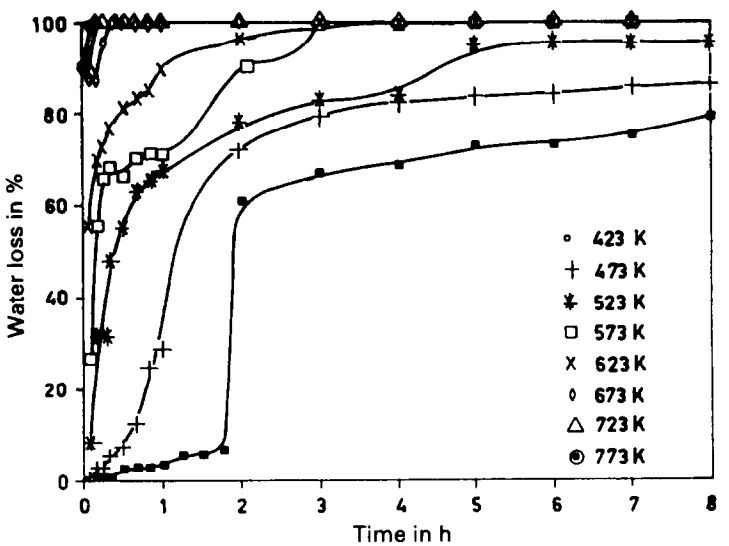

Fig. 2. Isothermal dehydration curves of APB at different temperatures.

TABLE 1

Ammonium oxide content (%) of APB samples

Time/h	Temperature/K							
	423	473	523	573	623	673	723	773
0.833	9.37	9.39	9.75	10.25	10.99	11.30	10.99	10.42
0.166	9.49	9.47	10.52	11.22	11.33	11.14	9.54	6.23
0.250	9.49	9.37	10.52	11.45	11.28	10.62	8.31	3.97
0.333	9.49	9.47	10.72	11.38	11.29	10.05	7.64	3.60
0.500	9.87	9.74	10.83	11.33	11.43	9.42	7.31	3.60
0.666	9.88	9.93	11.03	11.18	11.35	9.17	6.27	3.05
0.833	9.88	10.36	11.02	11.21	11.26	9.16	6.17	3.00
1.000	9.95	10.86	11.03	10.93	11.40		5.14	3.00
1.250	9.95							
1.500	10.03							
1.750	10.06							
2.000	11.56	12.16	11.96	10.32	9.29	6.89	1.97	
3.000	11.63	12.12	9.15	5.58	5.19			
4.000	11.74	12.16	12.07	9.05	4.99	4.16		
5.000	11.87	12.13	12.30	8.99	4.21	3.44	1.55	
6.000	11.92	12.19	12.35	8.67	4.08	3.02	1.45	
7.000	12.15	12.21	11.98	8.85	3.99	2.27	1.04	
8.000	12.69	12.24	12.00		3.88	2.17		

guished on the isothermal dehydration curves of APB up to 573 K (Fig. 2). This is due to the partial liberation of its crystal water. In the first step, APB loses nearly five moles of crystal water with formation of ammonium pentaborate trihydrate, $(NH_4)_2O \cdot 5B_2O_3 \cdot 3H_2O$. Because of the rapid dehydration these steps disappear for temperatures above 573 K and the shape of the curves becomes sharper. The second dehydration represents the release of three moles of crystal water together with a little ammonia. It is clear from the isothermal dehydration curves that dehydration can only be completed above 623 K.

The values given in Table 1 show that the ammonium oxide contents of the samples were found to be higher than the starting value of 9.57 wt% for the temperatures 423, 473 and 523 K; however, above 573 K, lower ammonium oxide contents were obtained. These results clearly suggest that the deamination step follows the dehydration of the samples.

The total boron oxide content of the samples showed an increase with increasing temperature (Fig. 3). It should be pointed out here that the time necessary for conversion of APB to boron oxide becomes shorter as the decomposition temperature increases. Boron oxide is volatile above 473 K. Therefore, the conversion percentage of boron oxide never reaches 100%, as can be seen from Fig. 3.

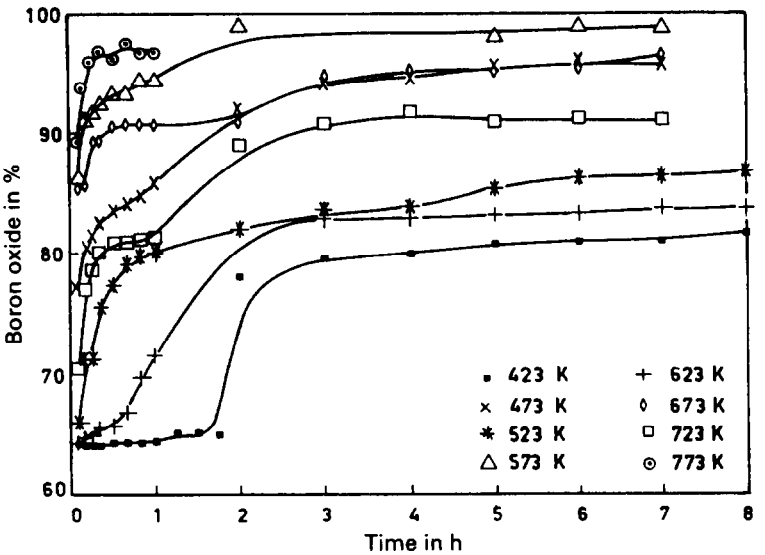

Fig. 3. Percent conversions of APB samples to boron oxide.

On the non-isothermal TG curves given in Fig. 4, two dehydration steps can also be distinguished. The first dehydration step occurs between 423 and 473 K and the second between 523 and 623 K, with weight losses of 27% and 35%, respectively. As mentioned above, the first dehydration step represents the loss of five moles of water and the second the loss of three moles of water.

The DTA curve of APB is given in Fig. 5. It contains two strong endothermic peaks. The first peak is related to the loss of five moles of crystal water in the range 443–475 K and the second to the deamination

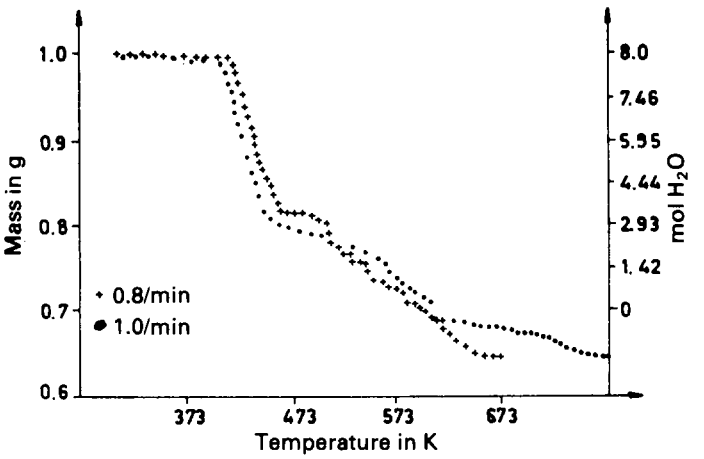

Fig. 4. Non-isothermal TG curves of APB at different heating rates.

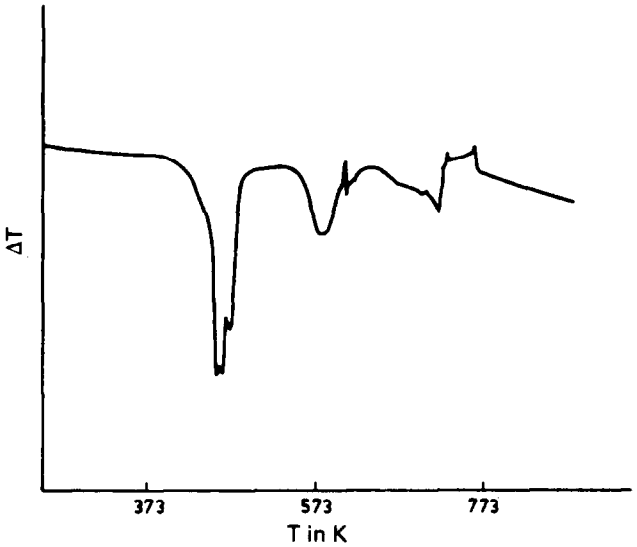

Fig. 5. DTA curve of APB.

and the dehydration of the remaining crystal water, which occur between 583 and 608 K. The results obtained from the different thermal analysis methods are in good agreement.

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