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Crystal Transition of Diammonium Hydrogen Phosphate

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Study was made to clarify the thermal properties of diammonium hydrogen phosphate by thermal gravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and X-ray powder diffraction method.

R. V. Coates and P. S. Smith already reported that the phosphate was transformed at 145°C with endothermic heat of 3.04 kJ/mol into α-form, the high temperature modification.[1] The author and J. Ando also reported that similar phase to the α-form was prepared at about 160°C in a sealed glass tube.[2]

In the present study, the phosphate sample was sealed directly with epoxy-resin or Kapton film 100 H according to the Coates and Smith's report, for TG, DTA, DSC or X-ray powder diffraction analysis, in order to prevent the decomposition reaction during measurements of its thermal properties.

Discussion was made on the economical advantage of commercial scale dry ammoniation process of fertilizer grade diammonium hydrogen phosphate for spraying wet-process phosphoric acid in the ammoniacal atmosphere at about 140°C.

Material

Diammonium hydrogen phosphate of reagent grade was pulverized to obtain powder of 150～200 mesh in size, which was dried at room temperature in the desicator containing diphosphorus pentoxide. The powderd sample was tested by chemical and X-ray powder diffraction analyses to indicate pure diammonium hydrogen phosphate.

TG, DTA and DSC Tests

TG and DTA tests were carried out at the heating rate of 2.5°C/min in the atmospheric pressure or in a sealed state with epoxy-resin. DSC test also was made at the same heating rate in the sealed state.

High temperature X-ray powder diffraction test was also made in air, in the sealed state and in the current of ammonia gas in the atmospheric pressure. Kapton film also was used to seal the sample in this case.

Temperature and Heat of Transition

Results with the TG and DTA tests are shown in Fig. 1. On heating diammonium hydrogen phosphate in air, it started to be decomposed at about 80°C. It was completely decomposed at 171°C into ammonia gas and ammonium dihydrogen phosphate (Fig. 1a). On the other hand, the sample sealed to prevent the above decompsition indicated to be transformed at about 159°C into another phase of diammonium hydrogen phosphate (Fig. 1b).

Coates and Smith had already reported that β-form, the usual phase of the phosphate was transformed at 145°C into α-form, the high temperature phase of it on heating, and the α-form was transformed at 102°C into the β-form with exothermic heat of 3.04 kJ/mol

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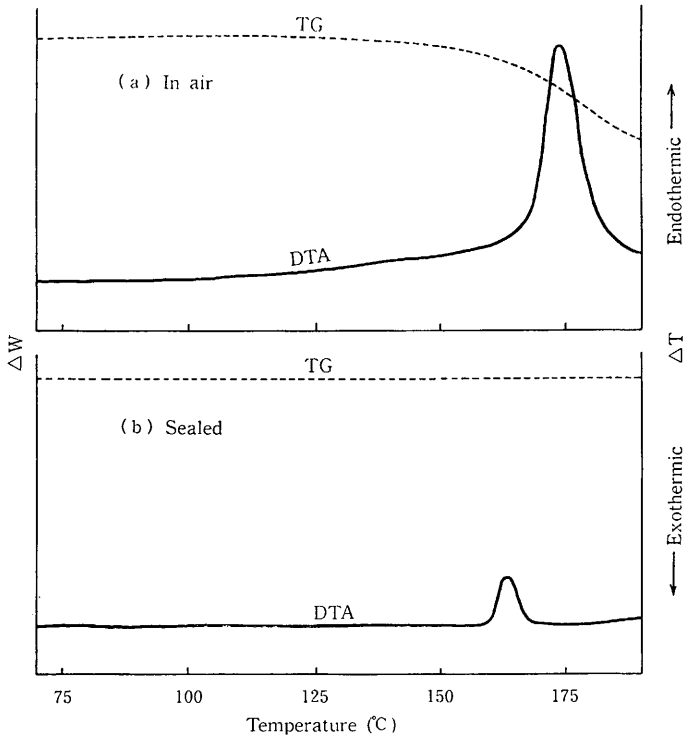

Fig. 1 TG (dotted line) and DTA (solid line) curves of $(NH_4)_2HPO_4$

Heating rate : 2.5℃/min

on cooling. In the tests, not only repetition of the heating and cooling but also the presence of a small amount of moisture (about 5%) resulted in decrease to the extent of 10℃ in the transition temperature.

DSC test indicated that β-form of the phosphate was transformed at 159℃ into the high temperature phase with endothermic heat of 3.21 kJ/mol, as was shown in Table 1. The value of the heat from DSC was calibrated by using 374807±4805 joule/mol, heat of fusion of Indium of 99.99% in purity at 156.6℃.[3] The high temprature modification of the phosphate was stable at room temperature.

Table 1 Temperature and heat of transition of $(NH_4)_2HPO_4$ mesured by DSC

Run No.	Wt. of sample (mg)	Transition temp. (℃)	Heat of transition (kJ/mol)
1	16.55	159	3.26
2	15.10	161	3.16
3	17.70	158	3.21
Ave.		159	3.21

DTA tests with samples containing a small amount of moisture indicated that the transition on heating occurred at 143℃ and 136℃ respectively with 1% and 3% in moisture content ; the transition on cooling occurred at about 90℃ with 3% of moisture content.

X-ray Powder Diffraction of the High Temperature Modification

X-ray powder diffraction pattern of the high temperature phase of diammonium hydrogen phosphate obtained in the above test was shown in Table 2. The pattern was measured at room temperature. The

Table 2 X-ray powder diffraction pattern for α'-$(NH_4)_2HPO_4$ at room temperature

$2\theta(°)$*	$d_{mess.}$(Å)	$d_{calc.}$(Å)	hkl	d_{ASTM}(Å)**
16.25	5.45	5.45	200	5.40
19.48	4.55	4.55	002	4.53
23.08	3.85	3.85	022	3.83
26.82	3.32	3.31	032	3.29
27.08	3.29	3.29	311	3.25
29.55	3.02	3.01	240	3.00
30.44	2.93	2.92	103	2.92
32.01	2.79	2.79	312	2.77
32.93	2.72	2.71	123	2.70
33.94	2.64	2.64	322	2.62
35.91	2.50	2.50	133	
36.00	2.49	2.49	223	2.48
39.70	2.27	2.28	004	
41.63	2.17	2.16	510	
43.20	2.09	2.10	204	
		$a=10.91$		$a=10.78$
	Rhombic	$b=14.46$		$b=14.46$
		$c=9.11$		$c=9.06$

* $\pm 0.01°$

** α-$(NH_4)_2HPO_4$ at 120°C[1,4]

lattice constant, a, b, c were calculated by the following equation.

$$1/d^2=h^2/a^2+k^2/b^2+1^2/c^2 \quad \text{(Rhombic)}$$

It has been assumed that the high temperature modification is slightly different from α-$(NH_4)_2HPO_4$[4] in the X-ray powder diffraction pattern, which was designated to be α'-$(NH_4)_2HPO_4$. The pattern is in a remarkable agreement with that of the high temperature phase measured at room temperature by the author and Ando.

Discussion with Fertilizer Grade Diammonium Hydrogen Phosphate

Fertilizer grade diammonium hydrogen phosphate is produced by dry neutralization process for spraying wet-process phosphoric acid in the ammoniacal atmosphere with 0.5 atm of ammonia pressure (0.5 atm of water vapour pressure) at about 140°C ; the main component of the product is α'-$(NH_4)_2HPO_4$.

It is assumed that $\beta \rightarrow \alpha'$ transition occurs even at 140°C as it is produced in the presence of water vapour in the commercial scale production plant ; the α'-phase is stable during storage at room temperature as it contains almost no moisture in the product.

It is considered that not only the heat of neutralization but also the heat of $\alpha' \rightarrow \beta$ transition is discharged when the phosphate product is granulated with a small amount of additional sulfuric acid or wet-process phosphoric acid, as the α'-phase is promptly transformed into the β-form in the presence of moisture, resulting in saving operation cost during granulation and drying.

Summary

It was found that β-diammonium hydrogen phosphate, the usual form was transformed at 159°C with endothermic heat of 3.21 kJ/mol in the ammoniacal atmosphere into the high temperature phase, which was designated to be α'-$(NH_4)_2HPO_4$. The α'-phase was stable at room temperature ; it was promptly reformed into the β-phase in the presence of moisture.

Temperature of the $\beta \rightarrow \alpha'$ transition decreased with moisture content on heating ; it was 143°C and 136°C respectively with 1% and 3% in the content. The $\alpha' \rightarrow \beta$ transition was indicated at about 90°C with the sample containing more than 3% of moisture on cooling.

It is assumed, in the commercial scale dry ammoniation process of fertilizer grade diammonium hydrogen phosphate for spraying wet-process phosphoric acid in the current of ammonia gas, that the phosphate is transformed even at about 140°C into the α'-form as it is produced in the current of water vapour, and that the high temperature modification is stable as it contains almost no moisture in the product ; the process has more economical advantage than wet-ammoniation process as the heat of $\alpha' \rightarrow \beta$ transition is discharged during granulation of the phosphate produt.

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リン酸水素二アンモニウムの構造の変化

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リン酸水素二アンモニウム（β型）の加熱変化をしらべた結果，159°C 付近で 3.21 kJ/mol の吸熱をともなって高温相に転移することが見出された．この高温相のX線回折図は α-$(NH_4)_2HPO_4$ とはやや異なるので，α′-$(NH_4)_2HPO_4$ と名づけられた，α′ 相はまたα相と異なって室温で安定であった．転移点は水分の存在によって降下し，その転移点はそれぞれ水分1％で143°C，水分3％で136°Cになった．水分3％を含む場合は，α′ 相を90°C付近に冷却するともとのβ相にもどった．