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THERMAL DECOMPOSITION OF PRECIPITATES FROM AQUEOUS ALUMINIUM PHOSPHATE SOLUTION BY REACTION WITH ALKALI

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ABSTRACT

The reaction between an aqueous solution of aluminium phosphate and sodium hydroxide solution was carried out under different conditions for the pH, ageing period in the mother liquor, temperature and concentration of aqueous solutions. The resulting precipitates were examined by thermogravimetry and differential thermal analysis (TG and DTA), and the precipitates and their thermal decomposition products by X-ray diffraction study and infrared spectrophotometry. As a result, the sequence for the thermal decomposition of the precipitates is proposed in relation to their compositions.

INTRODUCTION

Although aluminium hydroxide is precipitated from aqueous aluminium salt solutions by reaction with alkali, it has been reported that aluminium hydroxide is not always precipitated from aqueous aluminium phosphate solution by the addition of alkali [1]. Therefore the thermal decomposition of the precipitates from aqueous aluminium phosphate solution by reaction with alkali has been investigated in order to clarify the composition of their precipitates in the present study.

EXPERIMENTAL

The reaction between an aqueous solution of aluminium phosphate (molar ratio [Al]/[P] = 0.5 in 0.4 mol dm^{-3} phosphoric acid) and sodium hydroxide solution in 2 mol dm^{-3} was carried out under different conditions such as the pH to prepare the precipitate, the ageing

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period of the precipitate in mother liquor, the temperatures of precipitation and ageing. The precipitates were washed with distilled water as free as possible from alkali and anions, and then dried in air, and examined by thermogravimetry and differential thermal analysis (TG and DTA) [2]. The precipitates and their thermal decomposition products were examined by X-ray diffraction study and infrared spectrophotometry [3]. The decomposition products were prepared by heating the samples at the stated temperature for 1 h after heating up to the temperature at a rate of 5°C min^{-1} under atmospheric pressure.

The aluminium concentration was determined by EDTA titration using Xylenol Orange (XO) as indicator [4]. The amount of phosphate contained in a sample was determined as follows: a sample was dissolved in nitric acid, and phosphate ion in the diluted solution was precipitated as bismuth phosphate by addition of aqueous bismuth nitrate solution ; the precipitate separated from aqueous solution was again dissolved in concentrated nitric acid, and the resulting solution, in the presence of excess EDTA, was back-titrated with bismuth nitrate solution using XO as indicator [5].

RESULTS AND DISCUSSION

Precipitates from aqueous aluminium phosphate solution by reaction with alkali

All precipitates formed at different pH are in amorphous form as illustrated in Table 1. Although the precipitate at low pH gives the molar ratio $[Al]/[P] < 1$, and at near neutral region $[Al]/[P] \approx 1$ and at higher pH $[Al]/[P] > 1$, their compositions are much influenced by the temperatures of precipitation and ageing. The molar ratio of $[Al]/[P]$ for the precipitate decreases with higher temperatures. Accordingly it seems that the composition of the precipitates are expressed as $AlPO_4 \cdot xAl(OH)_3 \cdot yH_2O$ where $x \lesssim 1$ and $y = 2 - 3$, in agreement with the infrared results. In the infrared spectra of the precipitates at 30°C (Table 1), the OH stretching band at 3300 cm^{-1}, the OH bending band at 1650 cm^{-1} and the Al-OH band at 660 cm^{-1}, which are attributed to the presence of aluminium hydroxide, appear in addition to the absorptions due to the formation of aluminium phosphate, $AlPO_4$, and the presence of its adhesive water, indicating the OH stretching band at 3400 cm^{-1}, the OH bending band at 1630 cm^{-1} and the PO_4^{3-} frequency at 1060 cm^{-1}.

Table 1 Precipitates from aqueous aluminium phosphate solution by reaction with sodium hydroxide solution at various pH values

Specimen No.	pH	Temp.,[a] °C	Molar ratio				Crystallographic composition[c]
			Al	P	H_2O	$(H_2O)^{b)}$	
1	4	30	1	1.21	5.68	3.23	A
2	5	"	1	1.10	5.32	3.03	A
3	6	"	1	1.02	4.92	2.63	A
4	7	"	1	0.94	4.32	2.60	A
5	8	"	1	0.93	4.44	2.73	A
6	9	"	1	0.93	4.14	2.61	A
7	10	"	1	0.72	4.73	2.27	A
8	11	"	1	0.62	4.78	2.41	A

a) The precipitates were aged for a day at the same temperature.

b) This value is obtained by the subtraction of the weight-loss at below 100°C from that at 1000°C.

c) A denotes amorphous type.

Thermal decomposition of precipitates

The thermal decomposition behaviour of the precipitates depends on the pH value on formation of the precipitate. The DTA curves of all specimens exhibit a broad endothermic reaction centred at about 100 °C, and the endotherm at 150°C is added as a shoulder to the samples at pH $\geq$ 8 (Fig.1). Since these reactions correspond fundamentally to the changes in shape of the TG curve (Fig.2), it is expected that the endotherm at 150°C arises from the dehydration of amorphous $Al(OH)_3$, which coexists in the precipitate, to amorphous Al_2O_3 [6]. Further, the precipitates reveal the exotherm at 650 - 850°C due to the transformation of phase in which there is no correspondence to the weight-loss in the TG curve: the temperature rises as the pH value for the formation of precipitate becomes higher, and two exothermic reactions appear in the precipitates at pH 6 - 8 and then a sharp exothermic peak is observed in the precipitate at pH $\geq$8.

On the one hand, the specimens precipitated at pH of 4, 8 and 10 at 50°C and aged for a day at the same temperature,were thermally decomposed at the different temperatures, because the precipitates at pH of 4, 8 and 10 gave the molar ratios of $[Al]/[P]/[H_2O]$ in 1:1.35 :2.79, 1:1.11:2.77 and 1:0.66:3.13, respectively. For the precipitate at pH 4, the X-ray diffraction diagram by heating shows the pattern of anhydrous amorphous aluminium phosphate at 400°C, and of

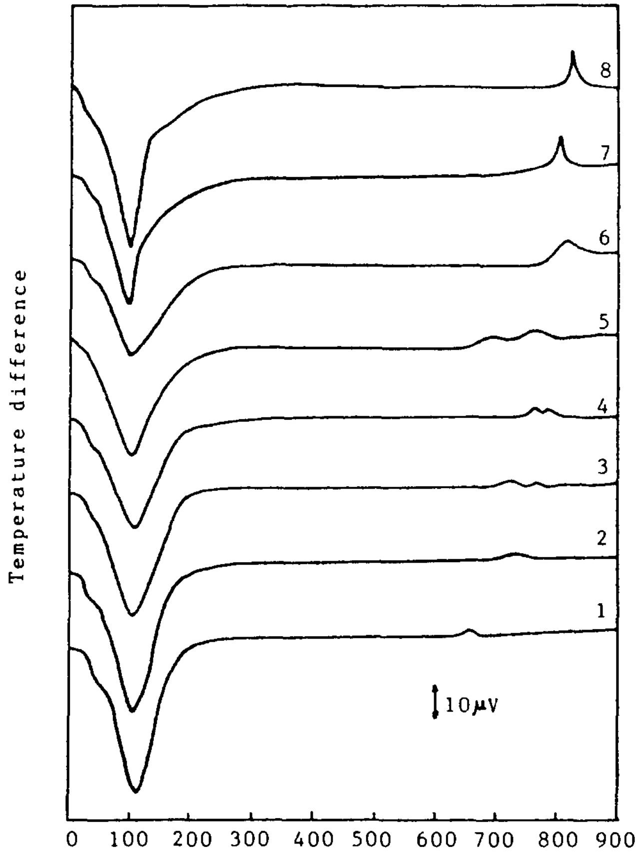

Fig. 1. DTA curves of the precipitates at different pH (numerals on curves are specimen numbers).

crystalline aluminium phosphate (orthorhombic and tridymite forms) [7] at 500°C and then of orthorhombic form at 1200°C. In this case, on heating at 500°C, the infrared spectrum gives the intense P-O stretching band at 720 cm^{-1}, attributed to crystalline aluminium phosphate. The X-ray result for the precipitate at pH 8 indicates the diffraction pattern of anhydrous amorphous aluminium phosphate at 600°C, and of the mixture of orthorhombic and tridymite forms at 700°C, and then of the both forms still remaining at 1200°C. In the infrared result, its spectrum exhibits the P-O stretching absorption at 720 cm^{-1} on heating at 700°C. The X-ray diffraction diagram of the precipitate at pH 10 reveals the pattern of anhydrous amor-

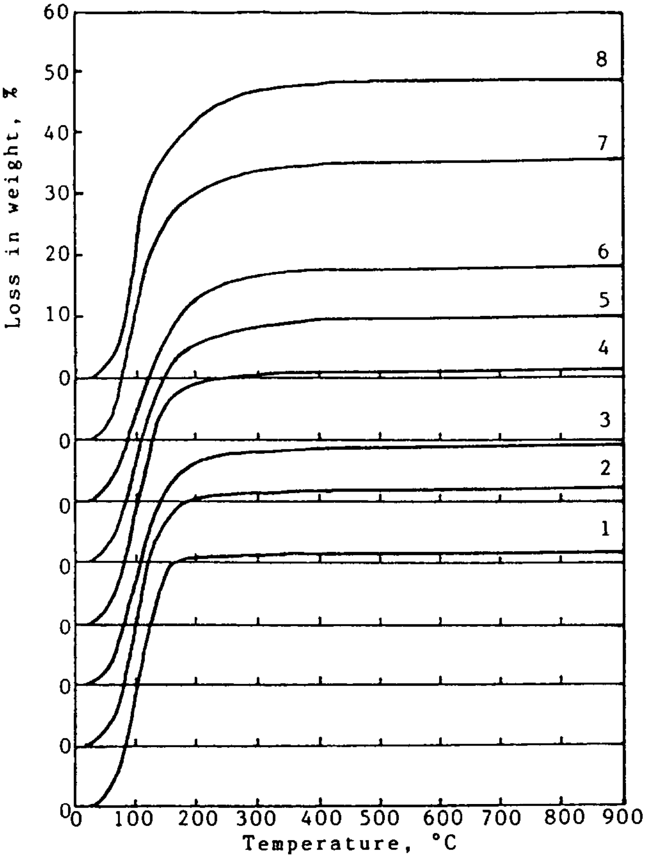

Fig. 2. TG curves of the precipitates at different pH (numerals on curves are specimen numbers).

phous aluminium phosphate at 700°C, and of the crystalline aluminium phosphate of orthorhombic and tridymite forms at 900°C, and then of α-alumina accompanied with orthorhombic form at 1200°C. The formation of α-alumina is due to the fact that the precipitate at higher pH contains excess aluminium hydroxide. Further it is found that the thermal decomposition temperature of the specimen depends on the value of pH used on forming the precipitate.

However, since the thermal decomposition process of those specimens is not so fundamentally different one from the other, the following sequence is proposed for the thermal decomposition of the precipitates from aqueous aluminium phosphate solution by the reaction with alkali:

$$\underset{\substack{\text{(amorphous)}\\(x \leq 1,\ y = 2 - 3)}}{\mathrm{ALPO_4 \cdot xAl(OH)_3 \cdot yH_2O}} \xrightarrow{100 - 110^\circ\mathrm{C}} \underset{\text{(amorphous)}}{\mathrm{AlPO_4 \cdot xAl(OH)_3}} \xrightarrow{\sim 150^\circ\mathrm{C}}$$

$$\underset{\text{(amorphous)}}{\mathrm{AlPO_4 \cdot x/2Al_2O_3}} \xrightarrow{600 - 800^\circ\mathrm{C}} \underset{\substack{\text{(orthorhombic}\\\text{and/or tridymite forms)}}}{\mathrm{AlPO_4} + \gamma\text{-}\mathrm{Al_2O_3}} \xrightarrow{\sim 1200^\circ\mathrm{C}}$$

$$\underset{\substack{\text{(orthorhombic}\\\text{and/or tridymite forms)}}}{\mathrm{AlPO_4} + \alpha\text{-}\mathrm{Al_2O_3}}$$

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