

FORMATION OF ALUMINUM PHOSPHATES AT LOW TEMPERATURES

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In the $\text{Al}(\text{OH})_3 - \text{H}_3\text{PO}_4$ system, $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ was formed at 50 — 70°C, $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ at 70 — 110°C and the C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$ at 120 — 190°C. On the other hand, in the $\alpha\text{-Al}_2\text{O}_3 - \text{H}_3\text{PO}_4$ system no crystalline aluminum phosphate could be obtained even at 200°C.

Much interest has recently been directed to aluminum phosphates because of their industrial application as inorganic refractory coatings,¹⁾ binders,²⁾ and solid acid catalysts.³⁾ Though various kinds of aluminum phosphates are used according to each purpose in practice, reproducible methods for preparing each kind of aluminum phosphate have not been established yet.⁴⁾ The authors have reported detailed studies on the conditions of formation of various aluminum phosphates.⁵⁾ The studies carried out so far have mainly been concerned with the syntheses at temperatures higher than 300°C. In the present study, therefore, we have investigated the formation of aluminum phosphate at lower temperatures (50 — 300°C).

Aluminum hydroxide (hydrargillite type made by E. Merck Co.) and 85 % H_3PO_4 were mixed in the molar ratio $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ (R) of 1/3 in a porcelain crucible under vigorous agitation. The mixture was dehydrated by a weak flame (110°C) until the transparent liquid was obtained. Aluminum phosphate was prepared by heating this transparent liquid at 50 — 300°C for 1 — 40 days in an oven or in an electric furnace. When the heating temperature was below 100°C it took a long time before the crystallization. For example, at 50 — 80°C it took 15 to 40 days to form the aluminum phosphate crystals. No crystal formation was observed when the transparent

liquid was left in air or in a desiccator on silica gel at room temperature, even after 90 days. On the other hand, transparent liquid was not obtained in the reaction of α - Al_2O_3 (Wako Chemical Co., Ltd.) with H_3PO_4 but a semi-solid substance was formed. X-ray analysis was carried out by the method described in the previous paper.⁵⁾ The amounts of $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$,⁴⁾ the C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$, $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$, and the A and B types of $\text{Al}(\text{PO}_3)_3$ were determined from the integrated intensities of their characteristic X-ray diffraction peaks; i. e., $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ was determined by the peak at $d = 3.56 \text{ \AA}$; $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ 7.37 \AA ; the C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$ 6.86 \AA ; $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ 7.89 \AA ; the A and B types of $\text{Al}(\text{PO}_3)_3$ 4.35 and 5.47 \AA .

The amounts of various aluminum phosphates formed in the $\text{Al}(\text{OH})_3 - \text{H}_3\text{PO}_4$ system are plotted against heating temperature in Fig. 1.

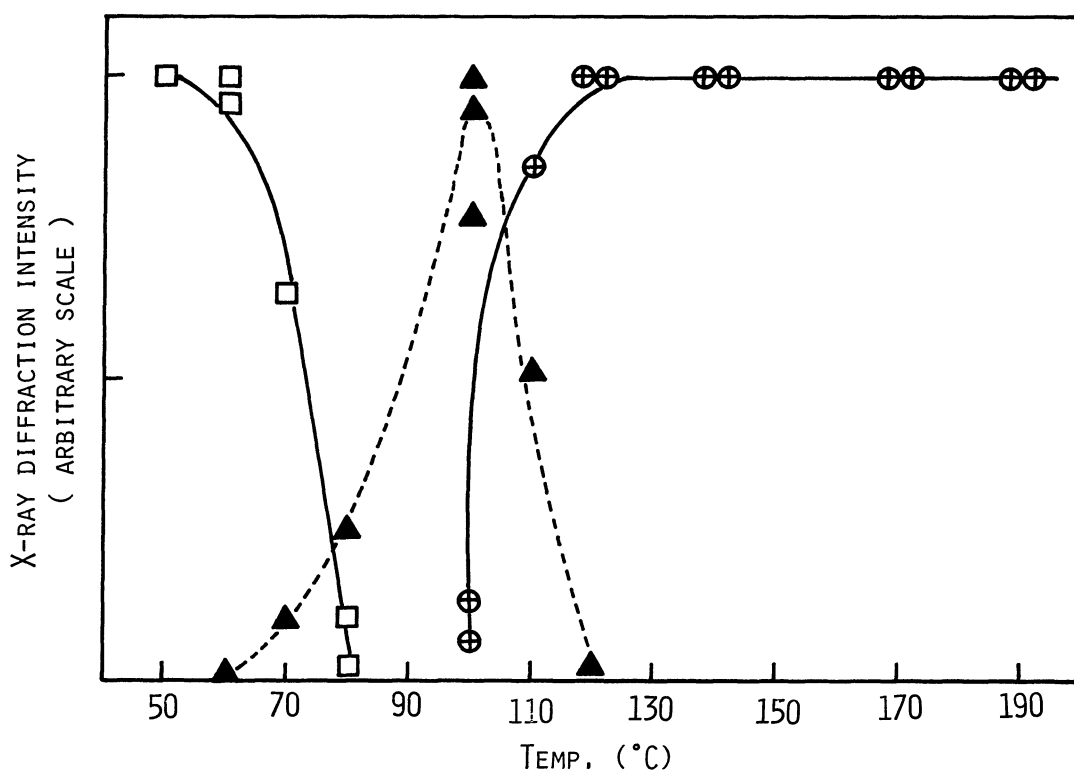


FIG. 1 RELATIONSHIP BETWEEN THE YIELDS OF ALUMINUM PHOSPHATES AND HEATING TEMPERATURE IN THE $\text{Al}(\text{OH})_3 - \text{H}_3\text{PO}_4$ SYSTEM

□ : $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, ▲ : $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
 ⊕ : $\text{Al}(\text{H}_2\text{PO}_4)_3$ C TYPE

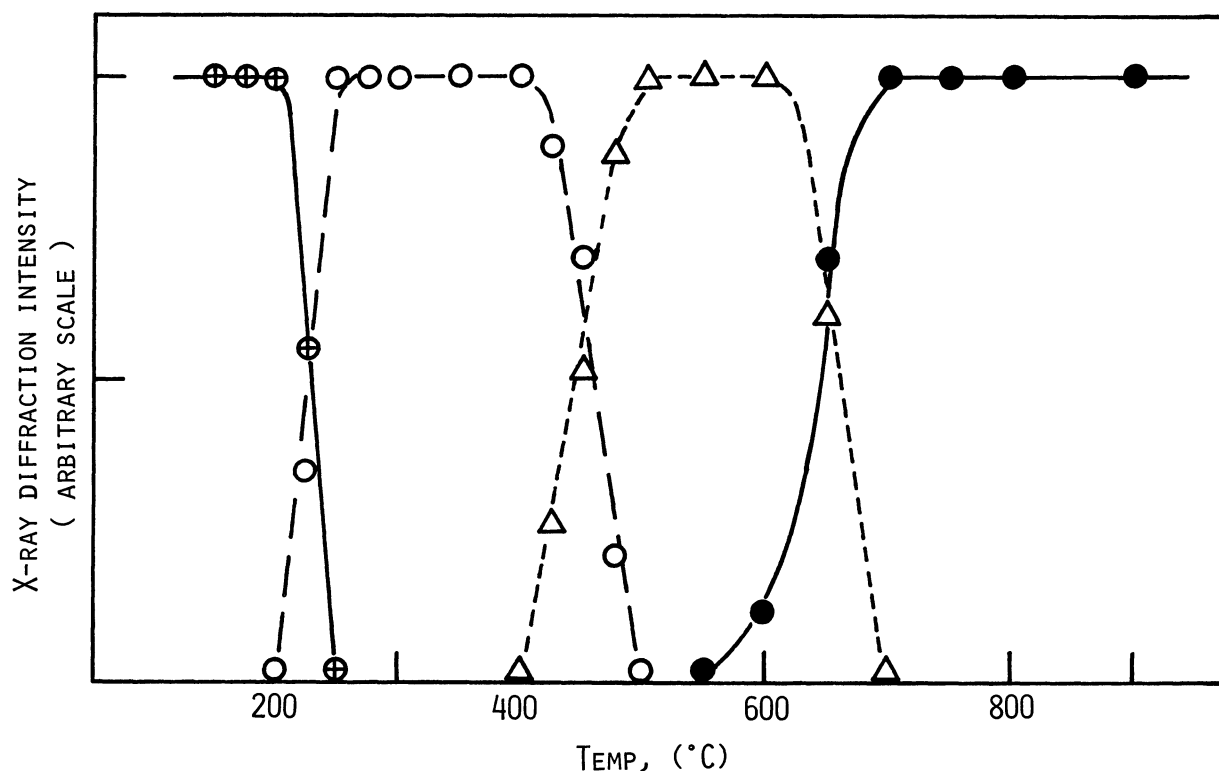
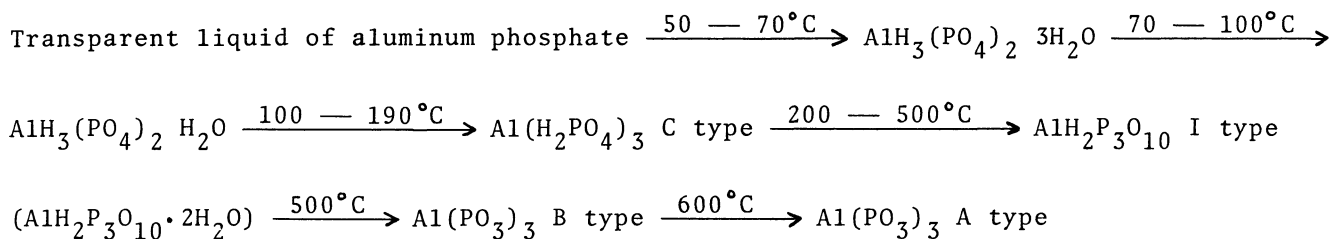


FIG. 2 RELATIONSHIP BETWEEN THE YIELDS OF ALUMINUM PHOSPHATES AND HEATING TEMPERATURE IN THE $\text{Al}(\text{OH})_3 - \text{H}_3\text{PO}_4$ SYSTEM

⊕ : $\text{Al}(\text{H}_2\text{PO}_4)_3$ C TYPE, ○ : $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$
 △ : $\text{Al}(\text{PO}_3)_3$ B TYPE, ● : $\text{Al}(\text{PO}_3)_3$ A TYPE

As a reference, the results of heating the mixture at 300 — 900°C are also shown in Fig. 2. Aluminum phosphates formed in the low temperature range 50 to 300°C are, when $R = 1/3$, $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, the C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$ and the I type of $\text{AlH}_2\text{P}_3\text{O}_{10}$ (this substance, absorbing moisture from the air, and converted immediately and completely into $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$). Thus, in this study, the amount of the I type of $\text{AlH}_2\text{P}_3\text{O}_{10}$ is represented by that of $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$. As Figs. 1 and 2 show, $\text{AlH}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ is formed at temperatures below 70°C, especially at about 50°C, but is not over 80°C. $\text{AlH}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is formed between 70 and 110°C, especially at 100°C. The C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$ is formed at 120 — 190°C. At 200 — 400°C $\text{AlH}_2\text{P}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ is well formed and $\text{Al}(\text{PO}_3)_3$ at above 500°C; while at 500 — 600°C the B type of $\text{Al}(\text{PO}_3)_3$, and above 700°C the A type are chiefly formed. Thus, the formed crystalline aluminum phosphate varies depending on the temperature of preparation written as follows:



From the results of thermal analysis the thermal transformation of the C type of $\text{Al}(\text{H}_2\text{PO}_4)_3$ into I type of $\text{AlH}_2\text{P}_3\text{O}_{10}$ is found to go through an amorphous phase.

On the other hand, the aluminum phosphate formed by the reaction of $\alpha\text{-Al}_2\text{O}_3$ with H_3PO_4 at below 200°C did not crystallize, and was shown by its X-ray diffraction patterns to be amorphous. This amorphous substance is hygroscopic and is hydrolyzed on standing in air. However, the kind of aluminum phosphate formed at temperatures above 300°C in the $\alpha\text{-Al}_2\text{O}_3 - \text{H}_3\text{PO}_4$ system is generally the same as that in the $\text{Al}(\text{OH})_3 - \text{H}_3\text{PO}_4$ system.

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