

**PREPARATION OF POROUS ALUMINUM  
PHOSPHATE WITH VARIOUS ACIDIC  
AND BASIC COMPOUNDS**

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Keywords and phrases: aluminum phosphate, microporous materials, chemical synthesis.

Received January 31, 2010

### Abstract

Malonic acid, propionic acid, glycine, *n*-butylamine, and urea were added to the preparation of aluminum phosphate from aluminum nitrate and phosphoric acid solutions. These additives were selected from a viewpoint of the functional groups, in short, both acidic sites, one-sided acidic site, acidic and basic sites, one-sided basic site, and both basic sites. All additives were taken into aluminum phosphate particles. Especially, glycine was easy to be included in precipitate. Specific surface area of aluminum phosphate increased by the addition of propionic acid and urea.

### 1. Introduction

Phosphates have been used for ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, metal surface treatment, fertilizer, detergents, food additives, fuel cells, pigments, and other items. The catalytic and adsorptive properties of phosphates were affected from specific surface area [6, 7, 8]. To improve the functional properties, porous phosphate, which had large specific surface area, was prepared in previous reports [1, 4]. The additives had some possibility to obtain large specific surface area in the fields of synthesis of inorganic materials [2, 3, 9, 11, 12]. Aluminum phosphates containing urea were obtained in aqueous solution [10]. By the decomposition of urea, this aluminum phosphate became porous material. The specific surface area of aluminum phosphate improved from 124 to 153m<sup>2</sup>g<sup>-1</sup> in this method.

This method indicated a weak point that, the remained urea in the phosphate particles decreased the amount of acidic sites on surface of materials. The acidic solid state materials have the possibility to be used as adsorbent for basic malodorous gases. Therefore, other additives were expected to improve the specific surface area and the removal ability of such gases [9]. Urea has basic sites at both ends. As new additives on preparation of phosphate material, malonic acid has acidic sites at both ends, and propionic acid has acidic site at one-sided acidic site. Glycine has acidic site and basic site at each side, and *n*-butylamine has one-sided basic site. These additives are studied to prepare porous lanthanum phosphate.

In this work, aluminum phosphates were prepared from aluminum nitrate and phosphoric acid solution, with the additives described above, and their properties were studied for design of functional materials.

## 2. Experimental

A total of 0.1 mol/l of aluminum nitrate solution was mixed with 0.1 mol/l of phosphoric acid solution in a molar ratio of Al/P = 1/1. Malonic acid, propionic acid, glycine, *n*-butylamine, and urea were added in the phosphoric acid solution to 0.5mol/l before the mixing. In the case of *n*-butylamine, the mixed solution of water/ethanol = 1/1 was used as a solvent. These additives were selected from a viewpoint of the functional groups, in short, both acidic sites, one-sided acidic site, acidic and basic sites, one-sided basic site, and both basic sites. The mixed solution was adjusted to pH7 with NH<sub>4</sub>OH solution. Then, the precipitates were filtered off, washed with water, and dried.

A part of the precipitates was dissolved in hydrochloric acid solution. The ratio of phosphorus and aluminum in the precipitates were also calculated from ICP results of these solutions, using Shimadzu ICPS-8000. The thermal behavior of these materials was analyzed by TG-DTA and XRD. TG and DTA curves were measured with a Shimadzu DTG-60H at a heating rate of 10°C/min under air. XRD patterns were recorded on a Rigaku Denki RINT 2000M X-Ray diffractometer by using monochromated cuK  $\alpha$  radiation.

Scanning electron microscopy (SEM) images of aluminum phosphates were observed using VE8800 from Keyence. The particle size distributions of these materials were measured with laser diffraction/scattering particle size distribution HORIBA LA-910. The specific surface area and pore size distribution of phosphates were calculated from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen by BET, and DH methods with a Belsorp mini from Bel Japan.

The adsorption of trimethylamine gas on phosphates was estimated at room temperature. A total of 0.01g of a sample was placed in a gas bag (3000cm<sup>3</sup>) of polyethylene, which was then filled with trimethylamine gas (15.9ppm). The concentration of trimethylamine gas after standing for 10 minutes was determined with a Kitagawa gas detector.

### 3. Results and Discussion

#### 3.1. Preparation of aluminum phosphate with various compounds

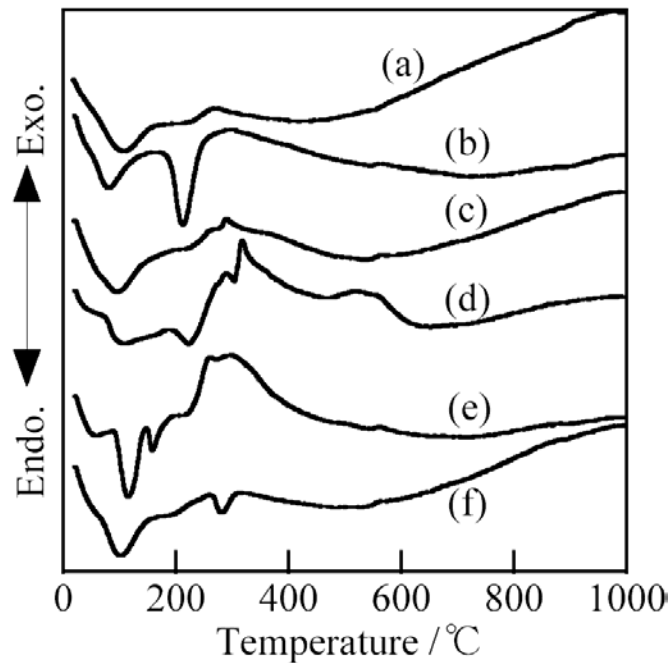
Table 1 shows Al/P ratios in precipitates prepared with various additives. The Al/P ratio was from 1.08 to 1.33. Samples were considered to contain a certain degree of aluminum hydroxide, because precipitates were filtered off at pH7. The difference between acidic and basic compounds as an additive had less influence on this Al/P ratio in precipitates.

**Table 1.** Al/P ratio of samples from ICP results

Additive		Al/P
No	-	1.166
Malonic acid	HOOC-CH <sub>2</sub> -COOH	1.331
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> -COOH	1.083
Glycine	HOOC-CH <sub>2</sub> -NH <sub>2</sub>	1.107
<i>n</i> -butylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	1.143
Urea	H <sub>2</sub> N-CO-NH <sub>2</sub>	1.090

Figure 1 shows DTA curves of samples prepared with various acidic and basic compounds. Samples prepared without additive had an endothermic peak at 110°C, and a broad endothermic peak at 150-260°C (Figure 1(a)). These peaks were considered to be due to the volatilization of adsorbed water on aluminum phosphates and included water in particles. Novel endothermic and exothermic peaks appeared by the addition of acidic and basic compounds. In general, malonic acid decomposed to acetic acid and carbon dioxide over 135°C. Because malonic acid was surrounded with aluminum phosphate, it decomposed and volatilized at 210°C (Figure 1(b)). Samples prepared with propionic

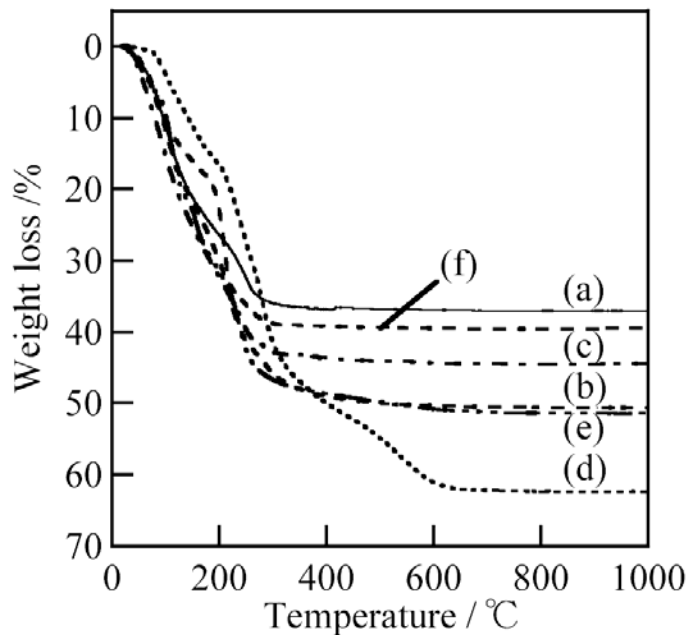
acid, glycine, and *n*-butylamine had a broad exothermic peak due to the combustion and volatilization to 600°C (Figure 1(c), (d), (e)). A small endothermic peak appeared at 280°C in DTA curve of sample prepared with urea (Figure 1(f)). This peak was own to the decomposition and volatilization of urea to ammonia and carbon dioxide [9, 10].



**Figure 1.** DTA curves of aluminum phosphates prepared with various acidic and basic compounds, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

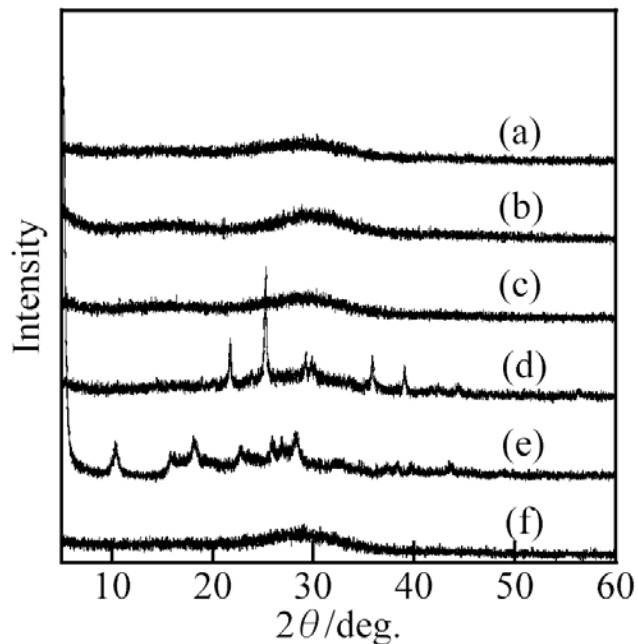
Figure 2 shows TG curves of samples prepared with various acidic and basic compounds. Sample prepared without additives had about 36% of weight loss (Figure 2(a)). The weight loss became larger by the addition of acidic and basic compounds. Each weight was about 48, 44, 62, 48, and 39 in TG curves of samples prepared with malonic acid, propionic acid, glycine, *n*-butylamine, and urea, respectively. By the calculation from the increase of weight loss, the molar ratio of additive/ $\text{AlPO}_4$  were 1/3.7, 1/4.3, 1/0.9, 1/2.6, and 1/10.0 in the precipitates prepared with malonic

acid, propionic acid, glycine, *n*-butylamine, and urea, respectively. Glycine was easy to be included in aluminum phosphate in this method.



**Figure 2.** TG curves of aluminum phosphates prepared with various acidic and basic compounds, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

Figure 3 shows XRD patterns of samples prepared with various acidic and basic compounds. Samples prepared without additives and with malonic acid, propionic acid, and urea were amorphous phase in XRD analyses. The weak peaks were observed in XRD patterns of precipitates prepared with glycine and *n*-butylamine. These peaks were not corresponding to aluminum phosphate. By heating at 400°C, these peaks disappeared. Because large amounts of glycine and *n*-butylamine were included in the precipitates, these XRD peaks were considered to be due to additives.

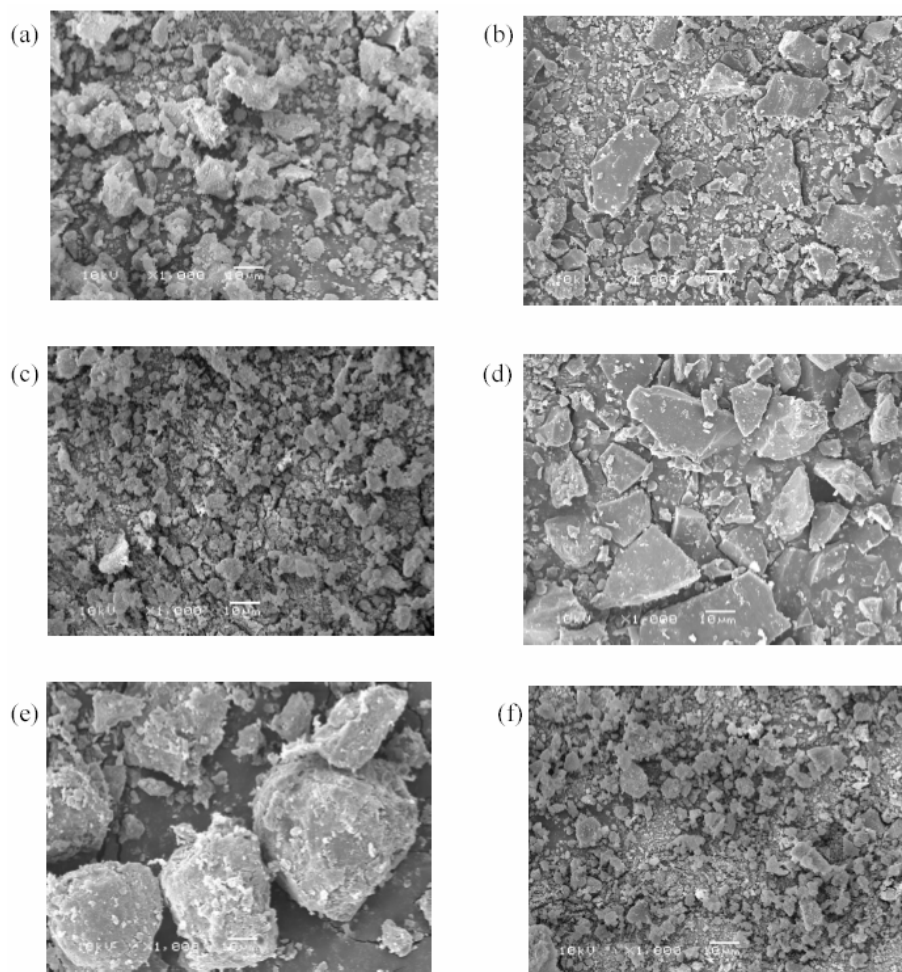


**Figure 3.** XRD patterns of aluminum phosphates prepared with various acidic and basic compounds, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

In this work, all additives were taken into aluminum phosphate particles. However, the amounts of included templates were different from their acidic and basic properties. In previous work about lanthanum phosphate [5], the compounds that have a basic site were easy to contain in precipitation, because inorganic phosphates are acidic materials. However, in aluminum phosphates, the relationship between acidic and basic properties of additives and the amounts of included additives were difficult to clear.

### 3.2. Powder properties of aluminum phosphates

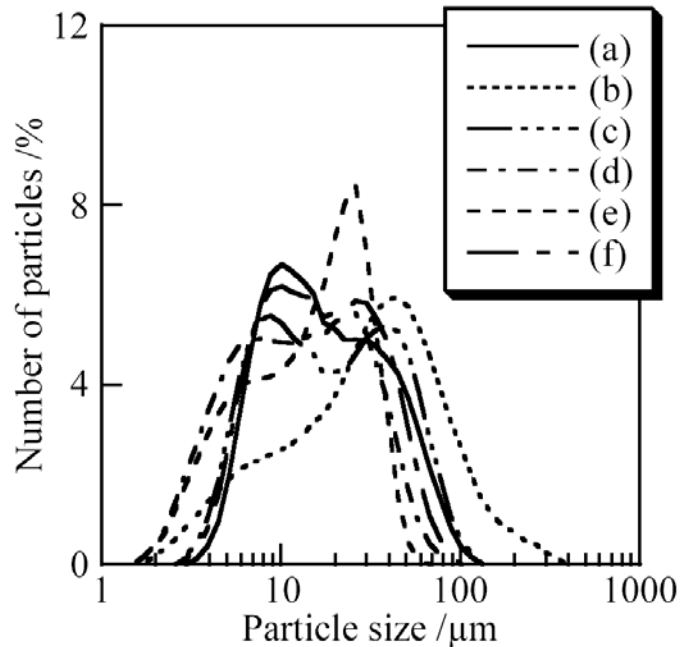
Figure 4 shows SEM images of aluminum phosphates prepared with various acidic and basic compounds. All samples prepared in this work had no specified shape. Large spherical particles were observed in sample prepared with *n*-butylamine.



**Figure 4.** SEM images of aluminum phosphates prepared with various acidic and basic compounds, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

Figure 5 shows the particle size distributions of samples prepared with various additives, and then heated at 200°C. The particle sizes of the main sample powder ranged from 2 to 200 μm.





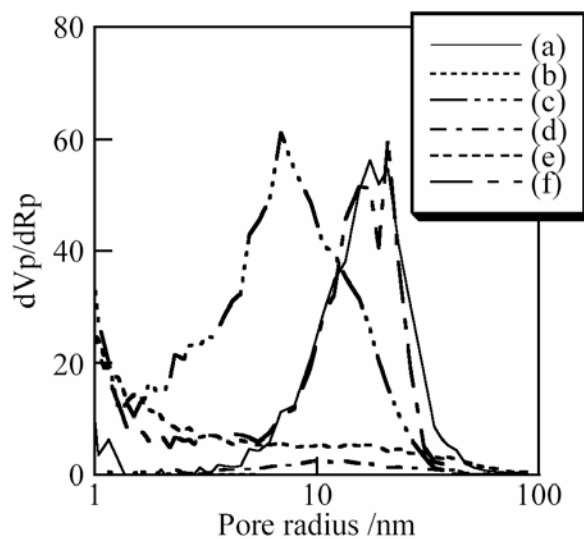
**Figure 5.** Particle size distribution of samples prepared with various compounds, and then heated at 200°C, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

Table 2 shows the specific surface areas of aluminum phosphates prepared with various acidic and basic compounds. Samples prepared with propionic acid and urea had larger specific surface area than that prepared without additives. On the other hand, samples prepared with malonic acid, glycine, and *n*-butylamine indicated smaller specific surface area. Malonic acid, glycine, and *n*-butylamine were easy to be included in aluminum phosphates from the results of TG curves. Large amount of additives covered the pores of aluminum phosphates. It is not clear that, propionic acid and urea improved the specific surface area of aluminum phosphates.

**Table 2.** Specific surface area of samples prepared with various additives /m<sup>2</sup>.g.<sup>1</sup>

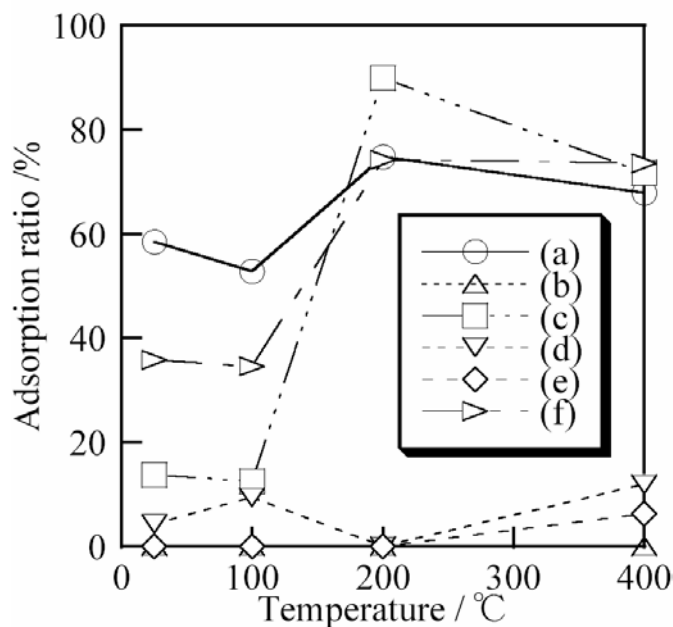
Additive		Temperature/°C		
		100	200	400
No	-	101.39	108.43	107.89
Malonic acid	HOOC-CH <sub>2</sub> -COOH	0.01	0.01	1.65
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> -COOH	150.67	160.99	135.40
Glycine	HOOC-CH <sub>2</sub> -NH <sub>2</sub>	13.50	6.86	19.35
<i>n</i> -butylamine	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	41.46	49.97	26.70
Urea	H <sub>2</sub> N-CO-NH <sub>2</sub>	98.21	122.97	108.49

Figure 6 shows the pore size distributions of aluminum phosphates prepared with various additives, and then heated at 200°C. Samples prepared without additives and with propionic acid and urea had large amount of pores. The specific surface area was related much with pore size distribution, less with particle shape and size distribution.

**Figure 6.** Pore size distribution of samples prepared with various compounds, and then heated at 200°C, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

### 3.3. Adsorbent for basic stinking gas

Figure 7 shows the adsorption ratios of trimethylamine on aluminum phosphates prepared with various acidic and basic compounds. The large parts of plots were lower than those by phosphate prepared without additive. Samples prepared without additives and with urea and propionic acid indicated higher adsorption ratio than other samples. Because the former samples had large specific surface area than the later ones, the adsorption ratio of trimethylamine was much affected by specific surface area of aluminum phosphates. These adsorption ratios of thermal products at 200°C were higher than those at 100°C. Because materials were heated for 1 hour, the decomposition and volatilization of additives took place at lower temperature than those in their TG and DTA curves.



**Figure 7.** Adsorption of trimethylamine on aluminum phosphate prepared with various compounds, (a) no addition, (b) malonic acid, (c) propionic acid, (d) glycine, (e) *n*-butylamine, and (f) urea.

#### 4. Conclusion

By the addition of acidic and basic compounds in the preparation process, aluminum phosphates containing these additives were obtained. Especially, glycine was easy to be included in precipitates. Specific surface areas of aluminum phosphates were increased by the addition of propionic acid and urea. Samples prepared without additives and with propionic acid and urea indicated high adsorption ratio of trimethylamine. Specific surface area is one of the important factors on the adsorption of basic stinking gas.

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