PREPARATION OF NANO-POROUS ALUMINUM PHOSPHATE USING UREA AND HEXAMETHYLENETETRAMINE

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Abstract Aluminum orthophosphate was prepared from aluminum nitrate solution and phosphoric acid solution in the molar ratio of Al/P = 1/1. Urea and hexamethylenetetramine were added in this preparation process. The thermal behavior of the obtained phosphates was analyzed by differential thermal analyses, X-ray diffraction, and Fourier transform infrared spectroscopy. Furthermore, these materials and their thermal products were estimated by scanning electron micrograph and particle size distribution. Specific surface areas 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. The acidic property was estimated from the adsorption of trimethylamine gas.

INTRODUCTION

Phosphates have been used for ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, metal surface treatment, manure, detergent, food additives, fuel cells, pigments, etc. It is well known that aluminum phosphate works in various reactions as acidic catalysts. The catalytic and adsorptive properties of materials were influenced from specific surface area¹⁻³). To improve the functional properties, nano-porous phosphate which has large specific surface area is tried to be prepared. The addition of urea and so on had some possibility to obtain large specific surface area^{4,5}).

In this work, aluminum orthophosphates containing urea and hexamethylenetetramine were prepared from aluminum nitrate solution, phosphoric

acid solution, urea and hexamethylenetetramine. The obtained precipitation was estimated by differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. Furthermore, specific surface area, pore size distribution, SEM images, particle size distribution, and adsorption of trimethylamine were measured to clarify the properties of this phosphate.

EXPERIMENTAL

0.1 mol/l of aluminum nitrate solution was mixed to 0.1 mol/l of phosphoric acid solution in the molar ratio of Al/P = 1/1. Urea and hexamethylenetetramine were added in this mixed solution to the prescribed concentration. Then, the solution was prepared to pH 7 with ammonia solution. The precipitation was filtered off and dried.

The thermal behavior of these materials was analyzed by differential thermal analyses (DTA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). DTA curves were measured with a Rigaku Denki DTA50. Thermal analyses were carried out at 10°C/min. XRD patterns were recorded on a Rigaku Denki RINT 2000M X-Ray diffractometer using monochromated CuK α radiation. The IR spectra were recorded on a Shimadzu FT-IR spectrometer FT-IR8600 with a KBr disk method.

Furthermore, these materials and their thermal products were estimated by scanning electron micrograph and particle size distribution. SEM images were observed using Hitachi F-4300. Particle size distribution was measured with laser diffraction / scattering particle size distribution HORIBA LA-910. Specific surface areas 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 Belsorp mini from BEL JAPAN, INC. The acidic property of phosphates was estimated from the adsorption of trimethylamine gas at room temperature. The 0.01 g of samples was placed in a gas bag (3000 cm³) of polyethylene, which was then filled with trimethylamine gas (16.6 ppm). The concentration of trimethylamine gas was determined with a Kitagawa gas detector after the standing for several minutes.

RESULTS AND DISCUSSION

Figure 1 shows DTA curves of samples prepared in various conditions. All samples had an endothermic peak below 100°C and samples prepared with urea indicated an endothermic peak at about 190°C in DTA curves. The broad endothermic peak at about 200°C was observed in DTA curve of sample prepared with hexamethylenetetramine (Fig. 1(e)).

All samples and their thermal products below 600°C were amorphous phase in XRD analyses. Figure 2 shows IR spectra of samples prepared in various

FIGURE 1. DTA curves of aluminum phosphates prepared in various conditions, (a) no additive, (b) urea, 0.5 mol/l, (c) urea, 1.0 mol/l, (d) urea, 1.5 mol/l, and (e) hexamethylenetetramine, 0.5 mol/l.

FIGURE 2. IR spectra of aluminum phosphates prepared in various conditions, (a) no additive, (b) urea, 0.5 mol/l, (c) urea, 1.0 mol/l, (d) urea, 1.5 mol/l, and (e) hexamethylenetetramine, 0.5 mol/l.

conditions. Samples prepared with urea had the similar IR spectrum in spite of the concentration of urea. The kind of the additives had much influence on the condition of the precipitation than the concentration of the additives. The absorption peak at about 1380 cm^{-1} in IR spectra of all samples disappeared by heating to 200°C . This peak was considered to be due to ammonia and nitrate ions. These components volatilized below 200°C . The heat treatment made the intensity of the absorption peaks at about 1670 and $3150\text{--}3600\text{ cm}^{-1}$. The materials had some condition of O-H bonding because the broad absorption peak at $3150\text{--}3600\text{ cm}^{-1}$.

The endothermic peak below 100°C was due to the volatilization of water, ammonia, and nitrogen oxide. Urea and hexamethylenetetramine were considered to be decomposed to NH_3 and CO_2 at about 190°C from DTA curves.

Table 1 indicates specific surface area of samples prepared in various conditions and their thermal products. Samples heated at 100°C had smaller specific surface area than samples heated over 200°C . The volatilization of urea, hexamethylenetetramine, a small amount of ammonium nitrate, and so on made specific surface area of materials increase. Samples prepared with urea and hexamethylenetetramine had large specific surface area than samples prepared without an additive. The concentration of urea had less influence on the specific surface area.

Table 1 Specific surface area of various aluminum phosphates

Additive	Concentration /mol·g ⁻¹	Temperature /°C			
		100	200	400	600
non	0	95.38	132.54	123.71	130.01
urea	0.5	126.23		150.42	
urea	1.0	62.40		130.47	
urea	1.5	82.84	149.85	153.18	142.21
hmt	0.5	116.74		180.69	

hmt; hexamethylenetetramine.

Figure 3 shows pore size distribution of samples heated at 100°C. Sample prepared without an additive had a large amount of pore which was a radius of about 25 nm. On the other hand, materials prepared with urea and hexamethylenetetramine had smaller pores. The pore size distribution of materials heated at 400°C is shown in Figure 4. The small pore which was below pore radius of 10 nm increased from the decomposition and volatilization of urea and hexamethylenetetramine. This increase of small pore caused the improvement of specific surface area of phosphate.

FIGURE 3. Pore size distribution of samples prepared in various conditions and heated at 100°C, (a) no additive, (b) urea, 0.5 mol/l, (c) urea, 1.0 mol/l, (d) urea, 1.5 mol/l, and (e) hexamethylenetetramine, 0.5 mol/l.

FIGURE 4. Pore size distribution of samples prepared in various conditions and heated at 400°C, (a) no additive, (b) urea, 0.5 mol/l, (c) urea, 1.0 mol/l, (d) urea, 1.5 mol/l, and (e) hexamethylenetetramine, 0.5 mol/l.

Table 2 Median and average particle sizes of various aluminum phosphates heated at 400°C

Additive	Concentration /mol•g ⁻¹	Median particle size /μm	Average particle size /μm
non	0	102.0	142.0
urea	0.5	75.1	146.1
urea	1.0	45.6	48.6
urea	1.5	135.8	211.4
hmt	0.5	50.9	58.5

hmt; hexamethylenetetramine.

From SEM images, all aluminum phosphates did not have a specified shape. Table 2 indicates the median and average particle sizes calculated from the particle size distribution of samples heated at 400°C. The average particle size of all samples was larger than the median particle size. All samples consisted of major part of small particles and minor part of much large particles. The addition of urea and hexamethylenetetramine had less influence on particle shape and size.

Figure 5 shows adsorption of trimethylamine on aluminum phosphates heated at 100°C. The adsorption ratio of all phosphates grew to 3 minutes and then kept their balance. The phosphates prepared with urea and hexamethylenetetramine indicated lower adsorption ratio than that prepared without. Urea and hexamethylenetetramine were considered to decline acidic properties of aluminum phosphate. Samples heated at 400°C had same tendency with those at 100°C. A small amount of urea and hexamethylenetetramine still remained on surface of aluminum phosphate. The longer heating time was needed to remove urea and hexamethylenetetramine.

FIGURE 5. Adsorption of trimethylamine on aluminum phosphates prepared in various conditions, (a) no additive, (b) urea, 0.5 mol/l, (c) urea, 1.0 mol/l, (d) urea, 1.5 mol/l, and (e) hexamethylenetetramine, 0.5 mol/l.

CONCLUSION

The porous aluminum phosphate was obtained by the addition of urea and hexamethylenetetramine to the preparation with water, and then heating. This materials had smaller nano-pores than pore radius of 10 nm. The addition of urea and hexamethylenetetramine had less influence on particle shape and size. The remained urea and hexamethylenetetramine in heated materials had the possibility to control the acidic properties on surface of aluminum phosphate.

REFERENCES

- 1) H. Onoda, H. Nariai, H. Maki and I. Motooka, Phosphorus Res. Bull., **12**, 139-146 (2001).
- 2) H. Onoda, H. Nariai, A. Moriwaki, H. Maki and I. Motooka, J. Mater. Chem., **12(6)**, 1754-1260 (2002).
- 3) H. Onoda, H. Nariai, H. Maki and I. Motooka, Phosphorus Res. Bull., **9**, 69-74 (1999).
- 4) K. Kandori, N. Ikegami, A. Yasukawa and T. Ishikawa, J. Coll. Interf. Sci., **182**, 425-430 (1996).
- 5) H. Onoda, H. Nariai, H. Maki and I. Motooka, J. Mater. Syn. Proc., **10(3)**, 121-126 (2002).