

PREPARATION OF LANTHANUM PHOSPHATE WITH *N*-BUTYLAMINE AND *N*-OCTYLAMINE

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N-butylamine and n-octylamine were added to the preparation of lanthanum phosphate from lanthanum nitrate and phosphoric acid solutions to obtain phosphate materials that had large specific surface area. The mixing solution of water and ethanol was used to solve these amines. The additional effects of amines and the mixing ratio of solvent were studied on the chemical composition, powder properties, and adsorption of basic stinking gas. Rhabdophane-type lanthanum phosphate was obtained in spite of the changes of preparation conditions. Specific surface area of lanthanum phosphate prepared in this work became over 10 times as large as that of standard phosphate.

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 [1-4]. In these applications, the catalytic and adsorptive properties of phosphates were affected from specific surface area [5-7]. To improve the functional properties, porous phosphate, which had large specific surface area, was prepared in previous reports [8,9]. The additives had some possibility to obtain large specific surface area in the fields of synthesis of inorganic materials [10-13]. Aluminum phosphates containing urea were obtained in aqueous solution [14]. By the decomposition of urea, this aluminum phosphate became porous material. The specific surface area of aluminum phosphate improved from 124 to 153 m²g⁻¹ 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 has the possibility to be used as an adsorbent for basic malodorous gases. Therefore, other additives were expected to improve the specific surface area and the removal ability of such gases [15]. Urea has basic sites at both ends. As new additives on preparation of phosphate material, malonic acid has the acidic sites at both ends and propionic acid has an acidic site at one-side. Glycine has an acidic site and a basic site at each side, and *n*-butylamine has one-sided basic site. These additives are studied to prepare porous aluminum and lanthanum phosphates [16]. Lanthanum phosphate prepared with *n*-butylamine indicated much larger

specific surface area [17]. Because *n*-butylamine was difficult to solve in water, the mixing solution of water and ethanol in the ratio of H₂O/C₂H₅OH=1/1 was used as a solvent. Therefore, it is not clear that that the addition of *n*-butylamine or the mixing solution of water and ethanol improved the specific surface area of lanthanum phosphate.

In this work, lanthanum phosphates were prepared from lanthanum nitrate and phosphoric acid solutions, with the changing the mixing ratio of water and ethanol as a solvent and the concentration of *n*-butylamine and *n*-octylamine, and their properties were studied for design of functional materials. The purpose in this work was to clear the additional effects of amines and ethanol on preparation and properties of lanthanum phosphate.

EXPERIMENTAL

0.1 mol/l of lanthanum nitrate solution was mixed with 0.1 mol/l of phosphoric acid solution in a molar ratio of La/P = 1/1. Lanthanum phosphate was expected to form in the following equation.



N-butylamine and *n*-octylamine were added in the phosphoric acid solution to 0.02, 0.1, and 0.5 mol/l before the mixing. *N*-butylamine was used as a typical amine. *N*-octyl amine was selected to estimate the influence of the amines length. The mixed solution of water/ethanol = 2/1 or 1/1 was used as a solvent to solve these amines. 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 lanthanum in the precipitates were also calculated from ICP results of these solutions, using SPS1500VR, Seiko Instruments Inc. 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 1200M X-Ray diffractometer using monochromated CuK α radiation.

Scanning electron microscopy (SEM) images of lanthanum phosphates were observed using JGM-5510LV, JEOL Ltd. The particle size distributions of these materials were measured with laser diffraction/scattering particle size distribution HORIBA LA-910. The specific surface area of phosphates was calculated from the amount of nitrogen gas adsorbed at the temperature of liquid nitrogen by BET method 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 (3000 cm³) of polyethylene, which was then filled with trimethylamine gas (15.9 ppm). The concentration of trimethylamine gas after standing for 10 minutes was determined with a Kitagawa gas detector.

RESULTS AND DISCUSSION

Preparation of lanthanum phosphate with amines

Table 1 shows La/P ratios in precipitates prepared with various additives. The increase of ethanol ratio in solvent had less influence on the La/P ratio in precipitates. By the addition of *n*-butylamine and *n*-octylamine, the La/P ratio became a little larger. It is the same phenomena that the ratio of cation/phosphorus increased by the addition of *n*-butylamine in previous papers [16,17]. A small amount of lanthanum hydroxide was considered to form in these conditions. In the conditions of 0.1 mol/l

Table 1. La/P ratio of samples from ICP results.

water/ethanol	additive	concentration	La/P
1/0	no	0 mol/l	1.014
2/1	no	0 mol/l	1.010
1/1	no	0 mol/l	1.010
1/1	<i>n</i> -butylamine	0.02 mol/l	1.046
1/1	<i>n</i> -octylamine	0.02 mol/l	1.028
1/1	<i>n</i> -butylamine	0.1 mol/l	–
1/1	<i>n</i> -octylamine	0.1 mol/l	–
1/1	<i>n</i> -butylamine	0.5 mol/l	1.151

of amines, lanthanum phosphate was not precipitated. It was considered that lanthanum cation formed the complex with amines in the ratio of La/amine = 1/1 and that this complex prevented the formation of lanthanum phosphate. Sample prepared in the condition of 0.5 mol/l of *n*-butylamine indicated higher La/P ratio. Because 0.5 mol/l of *n*-octylamine was too high concentration to solve in the solvent, sample could not be prepared.

Figure 1 shows TG curves of samples prepared in various conditions. Samples prepared with 0.5 mol/l of *n*-butylamine had much larger weight loss than others. The weight loss at 320°C was considered to be due to the volatilization and combustion of *n*-butylamine. Other samples indicated similar TG curve. Weight loss was related with the amount of amines in phosphate materials. The mixing ratio and the addition of low concentration of amines had a small change of weight loss.

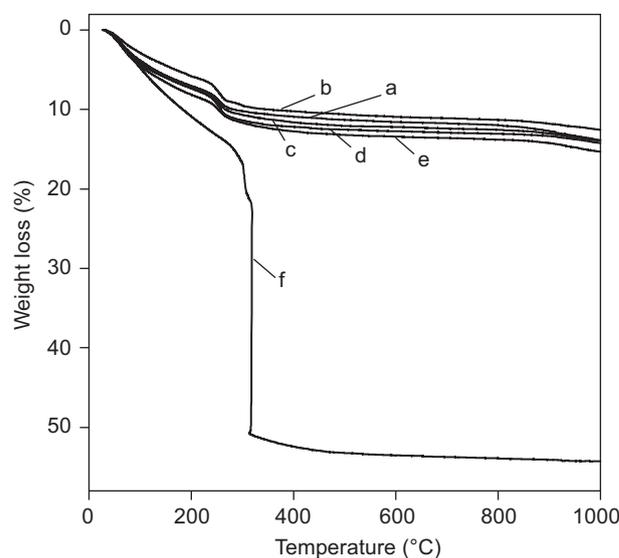


Figure 1. TG curves of lanthanum phosphates prepared in various conditions; a) no additive, H₂O/C₂H₅OH = 1/0, b) H₂O/C₂H₅OH = 2/1, c) H₂O/C₂H₅OH = 1/1, d) H₂O/C₂H₅OH = 1/1, *n*-butylamine 0.02 mol/l, e) H₂O/C₂H₅OH = 1/1, *n*-octylamine 0.02 mol/l, f) H₂O/C₂H₅OH = 1/1, *n*-butylamine 0.5 mol/l.

Figure 2 shows DTA curves of samples prepared in various conditions. Sample prepared with 0.5 mol/l of *n*-butylamine had a large exothermic peak at 320°C (Figure 2f). This peak was from the combustion of *n*-butylamine. Small endothermic peaks at 70 and 260°C were observed in DTA curves of other samples. These peaks were due to the volatilization of adsorbed and crystalline water, respectively [14,17]. The small endothermic peak at 260°C was covered by the above larger exothermic peak in DTA curve at sample prepared with 0.5 mol/l of *n*-butylamine.

Figure 3 shows XRD patterns of samples prepared in various conditions. All samples indicated the peak pattern of Rhabdophane-type lanthanum phosphate [18].

Because sample prepared with 0.5 mol/l of *n*-butylamine included a large amount of amine, the peak intensity became weak (Figure 3f). Other samples had the same

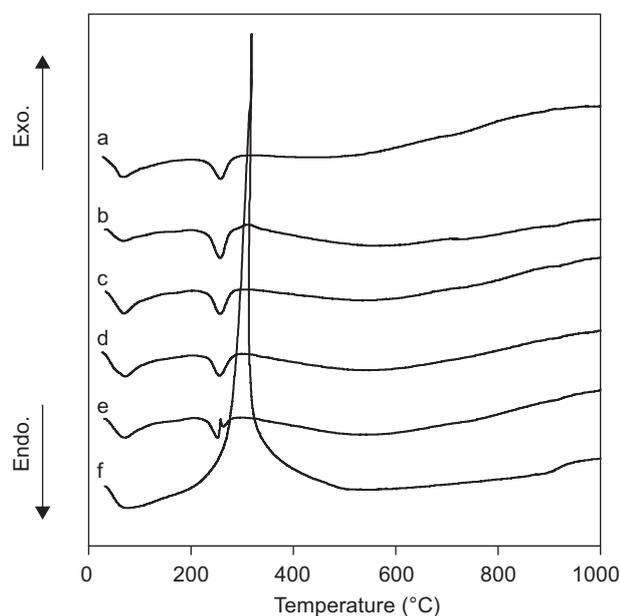


Figure 2. DTA curves of lanthanum phosphates prepared in various conditions; a) no additive, $H_2O/C_2H_5OH = 1/0$, b) $H_2O/C_2H_5OH = 2/1$, c) $H_2O/C_2H_5OH = 1/1$, d) $H_2O/C_2H_5OH = 1/1$, *n*-butylamine 0.02 mol/l, e) $H_2O/C_2H_5OH = 1/1$, *n*-octylamine 0.02 mol/l, f) $H_2O/C_2H_5OH = 1/1$, *n*-butylamine 0.5 mol/l.

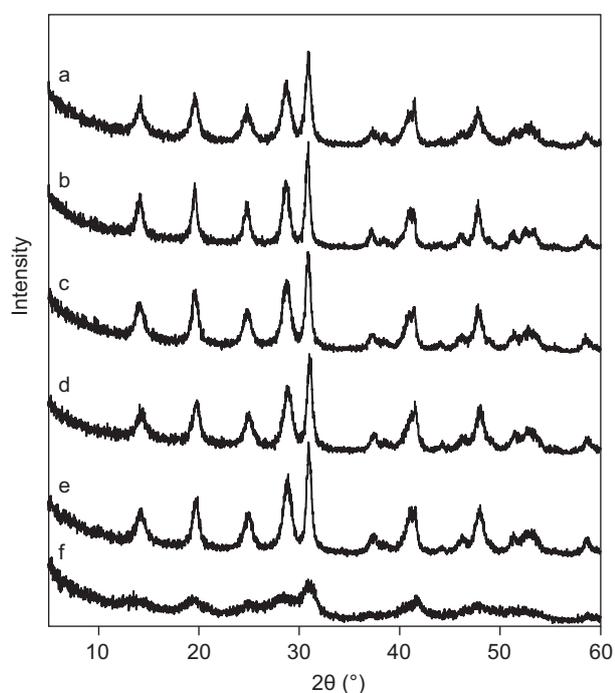


Figure 3. XRD patterns of lanthanum phosphates prepared in various conditions; a) no additive, $H_2O/C_2H_5OH = 1/0$, b) $H_2O/C_2H_5OH = 2/1$, c) $H_2O/C_2H_5OH = 1/1$, d) $H_2O/C_2H_5OH = 1/1$, *n*-butylamine 0.02 mol/l, e) $H_2O/C_2H_5OH = 1/1$, *n*-octylamine 0.02 mol/l, f) $H_2O/C_2H_5OH = 1/1$, *n*-butylamine 0.5 mol/l.

range of XRD peak intensity, because the difference of weight loss in TG curves was small (Figure 1). By heating up to 400°C, there is no change on XRD peak pattern from samples without heating. The included amines had no influence on chemical composition of phosphate materials.

Powder properties of lanthanum phosphates

Figure 4 shows SEM images of lanthanum phosphates prepared in various conditions. Samples prepared without ethanol and amines had the small homogenized particles (Figure 4a). Large particles were observed in SEM images of other samples. In particle size distribution of samples without heating, the addition of ethanol and amines made the mode of particle size larger. The mode of particle size became much larger by heating. The particle size distributions of samples heated at 400°C are shown in Figure 5. The particle size of sample prepared without ethanol and amines was ranged from 5 to 50 μm (Figure 5a). On the other hand, other samples indicated high ratio of larger particles than 100 μm. The addition of ethanol produced the aggregation of phosphate materials in this preparation.

Table 2 shows the specific surface areas of lanthanum phosphates prepared in various conditions. Because samples were heated at 100°C for 2 hours to remove the adsorbed water as a pretreatment of BET method, specific surface area of samples without heating could not be measured. In all conditions, specific surface area became larger than that of standard lanthanum phosphate. The mixing of ethanol in a solvent improved the specific surface area. The low concentration of amines suppressed this improvement. Sample prepared with 0.5 mol/l of *n*-butylamine had much larger specific surface area. It was considered from that the volatilization of amines produced the pores on phosphate particles. The addition of *n*-octylamine much improved the specific surface area of lanthanum phosphate than that of *n*-butylamine at same concentration. By heating at higher temperature, samples had larger specific surface area.

Table 2. Specific surface area of samples prepared with various additives (m^2/g).

water/ ethanol	additive	concentration (mol/l)	Temperature (°C)		
			100	200	400
1/0	–	0	7.18	13.59	12.95
2/1	–	0	23.97	47.01	48.76
1/1	–	0	56.50	69.95	71.70
1/1	<i>n</i> -butylamine	0.02	18.43	53.43	54.90
1/1	<i>n</i> -octylamine	0.02	23.26	61.93	62.35
1/1	<i>n</i> -butylamine	0.5	190.55	195.31	209.95

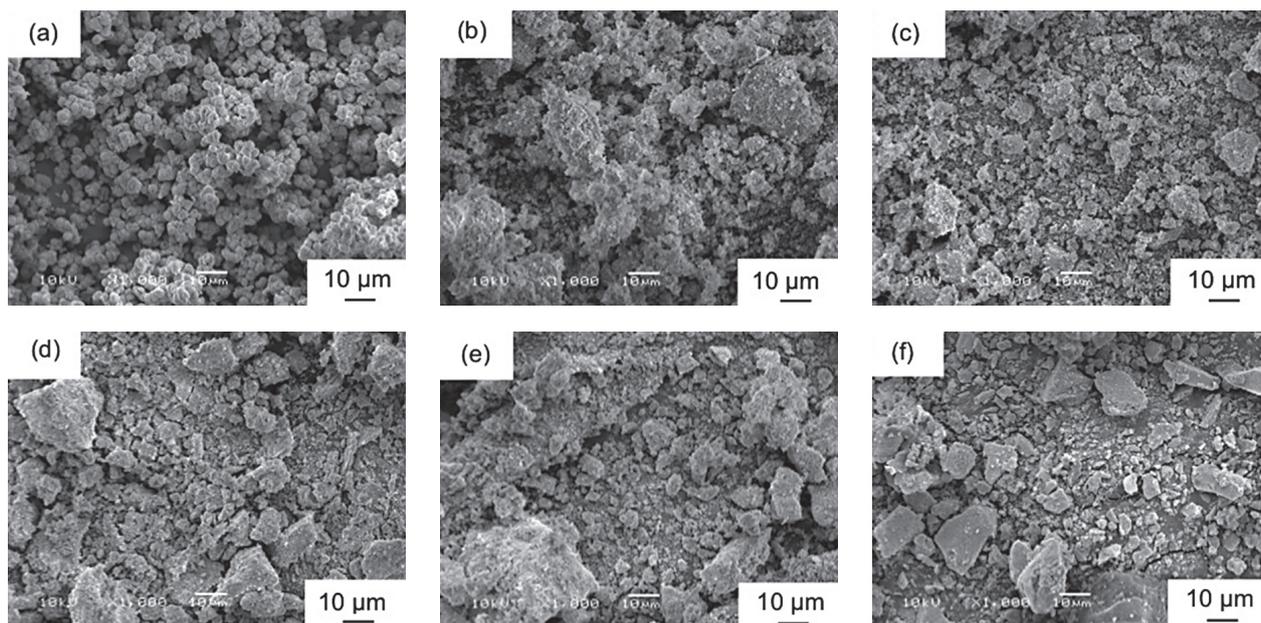


Figure 4. SEM images of lanthanum phosphates prepared in various conditions; a) no additive, $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/0$, b) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 2/1$, c) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, d) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.02 mol/l, e) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-octylamine 0.02 mol/l, f) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.5 mol/l.

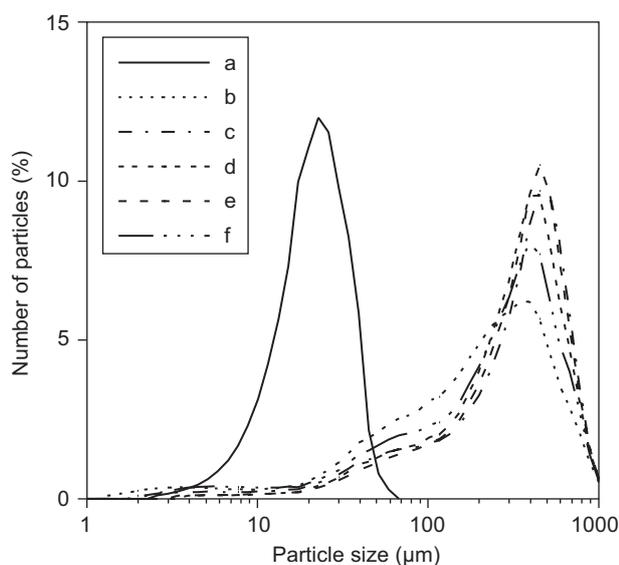


Figure 5. Particle size distribution of samples prepared in various conditions and then heated at 400 °C; a) no additive, $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/0$, b) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 2/1$, c) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, d) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.02 mol/l, e) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-octylamine 0.02 mol/l, f) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.5 mol/l.

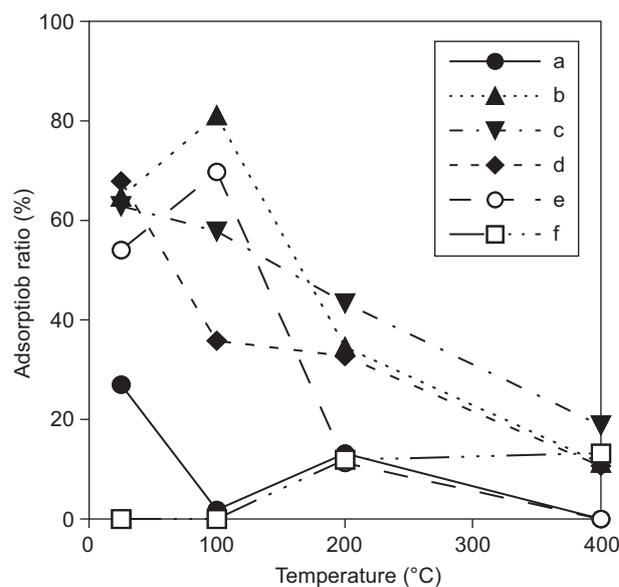


Figure 6. Adsorption of trimethylamine on lanthanum phosphate prepared in various conditions; a) no additive, $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/0$, b) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 2/1$, c) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, d) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.02 mol/l, e) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-octylamine 0.02 mol/l, f) $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 1/1$, *n*-butylamine 0.5 mol/l.

Because of the volatilization of the included ethanol and amines, phosphate materials were considered to be porous from previous papers [16,17]. It is the reason that phosphate had large specific surface area in spite of large particle size.

Adsorbent for basic stinking gas

Figure 6 shows the adsorption ratios of trimethylamine on lanthanum phosphates prepared in various conditions. Sample prepared without ethanol and amines

adsorbed 27% of trimethylamine, and this ratio became small by heating (Figure 6a). Sample prepared in H₂O/C₂H₅OH = 2/1 and 1/1 with and without 0.02 mol/l of amines indicated higher adsorption ratio than standard lanthanum phosphate (Figure 6a-e). The adsorption ratios were low in sample prepared with 0.5 mol/l of *n*-butylamine (Figure 6f). High concentration of *n*-butylamine improve specific surface area, however declined the adsorption ratio of basic stinking gas. The amount of acidic sites on surface of materials was considered to decrease with high concentration of *n*-butylamine.

CONCLUSION

By the addition of *n*-butylamine and *n*-octylamine, the ratio of La/P in precipitate became a little larger because of the formation of lanthanum hydroxide. From XRD analyses, the main composition of precipitate was Rhabdophane-type lanthanum phosphate. In the condition with 0.1 mol/l of *n*-butylamine and *n*-octylamine, lanthanum phosphate was not precipitated. The mixing of ethanol to water produced large specific surface area of this lanthanum phosphate. The addition of *n*-octylamine much improved the specific surface area of lanthanum phosphate than that of *n*-butylamine at same concentration. Especially, sample prepared with 0.5 mol/l of *n*-butylamine had much larger specific surface area. The adsorption ratio of trimethylamine was high in the case of samples prepared with the mixing solution of water and ethanol.

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