O U R N A L O F

Ceramic Processing Research

Preparation of nickel phosphates with various acidic and basic compounds

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Malonic acid, propionic acid, glycine, *n*-butylamine, and urea were added to the preparation of nickel phosphate from nickel nitrate and phosphoric acid solutions. These additives were selected from the 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. Nickel phosphate was not obtained by the addition of glycine. The Ni/P ratio became larger by the addition of *n*-butylamine. The effect of the addition of acidic and basic compounds was studied on the chemical composition, powder and functional properties of nickel phosphate materials.

Key words: Nickel phosphate, Chemical synthesis, Specific surface area, Adsorbent.

Introduction

Phosphates have been used as ceramic materials, catalysts, adsorbents, fluorescent materials, dielectric substances, for metal surface treatments, as fertilizers, detergents, food additives, in fuel cells, pigments, etc. The catalytic and adsorptive properties of phosphates are affected by the specific surface area [1-3]. To improve the functional properties, a porous phosphate, which had a large specific surface area, was prepared in previous reports [4, 5]. The additives gave some possibility to obtain large specific surface area in the fields of the synthesis of inorganic materials [6-10]. Aluminum phosphates containing urea were obtained in an aqueous solution [11]. By the decomposition of urea, this aluminum phosphate became a porous material. The specific surface area of aluminum phosphate improved from 124 to $153 \text{ m}^2\text{g}^{-1}$ by this method.

This method indicated a weak point that the remaining urea in the phosphate particles decreased the amount of acidic sites on the surfaces. The acidic solid state materials have the possibility to be used as adsorbents for basic malodorous gases. Therefore, other additives were expected to improve the specific surface area and the removal ability of such gases [10]. Urea has basic sites at both ends. As new additives for the preparation of phosphate material, malonic acid has acidic sites at both ends and propionic acid has an acidic site at one-side. Glycine has acidic site and basic site at each end, and *n*-butylamine has a one-sided basic site. These additives were studied to prepare porous nickel phosphate. In this study, nickel phosphates were prepared from a nickel nitrate and phosphoric acid solution, with the additives described above, and their properties were studied for the design of functional materials.

Experimental

0.1 mol/l of nickel nitrate solution was mixed with 0.1 mol/l of phosphoric acid solution in a molar ratio of Ni/P = 1/1. Malonic acid, propionic acid, glycine, *n*-butylamine, and urea were added to the phosphoric acid solution to 0.5 mol/l before the mixing. In the case of *n*-butylamine, a mixed solution of water/ethanol = 1/1 was used as a solvent. These additives were selected from the viewpoint of the functional groups, in short, both acidic sites, one-sided acidic site, acidic and basic sites, one-sided basic sites, one-sided basic sites. The mixed solutions were adjusted to pH7 with a NH₄OH or HNO₃ solution. Then, the precipitates were filtered off, washed with water, and dried.

A portion of the precipitates was dissolved in hydrochloric acid solution. The ratio of phosphorus and nickel in the precipitates were also calculated from ICP results of these solutions, using a 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 K minute⁻¹ in 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 nickel phosphates were observed using a JGM-5510LV, JEOL Ltd. The particle size distributions of these materials were measured with a laser diffraction/scattering particle size distribution instrument, HORIBA LA-910. The specific surface area and pore size distribution of phosphates were

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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. 0.01 g 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 nickel phosphate with various compounds

Table 1 shows Ni/P ratios in precipitates prepared with various additives. With the addition of glycine, a precipitate was not obtained. The Ni/P ratio indicated near 1 in samples prepared without an additive and with malonic acid, propionic acid, and urea. The sample prepared with *n*-butylamine had a higher Ni/P ratio than the others. It is the same tendency found in a previous paper [12] that the addition of *n*-butylamine produced a high cation ratio from the formation of a hydroxide.

Fig. 1 shows XRD patterns of samples prepared with various acidic and basic compounds. The peaks of ammo-

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

additive		Ni/P
none	-	1.013
malonic acid	HOOC-CH ₂ -COOH	1.035
propionic acid	CH ₃ CH ₂ -COOH	1.027
glycine	HOOC-CH ₂ -NH ₂	-
<i>n</i> -butylamine	CH ₃ (CH ₂) ₃ -NH ₂	1.212
urea	H_2N -CO- NH_2	0.988



Fig. 1. XRD patterns of nickel phosphates prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.

nium nickel phosphate hexahydrate, NH₄NiPO₄· $6H_2O$, were observed in XRD patterns of samples prepared without an additive, with malonic acid, propionic acid, and urea (Fig. 1(a), (b), (c), (e)). On the other hand, the sample prepared with *n*-butylamine had an amorphous phase (Fig. 1(d)). The sample heated at 100 °C indicated the same peak patterns with those without heating. By heating at 200 and 400 °C, all samples changed to be an amorphous phase.

Fig. 2 shows DTA curves of samples prepared with various acidic and basic compounds. The sample prepared without an additive had endothermic peaks at 120 and 240 °C and a small exothermic peak at 750 °C (Fig. 2(a)). These endothermic peaks were due to the volatilization of crystalline water and ammonia and dehydration condensation of the phosphate, respectively [13, 14]. These phenomena are expressed in the following reactions:

 $NH_4NiPO_4 \cdot 6H_2O \rightarrow NiHPO_4 + NH_3 + 6H_2O$ (1)

$$2NiHPO_4 \rightarrow Ni_2P_2O_7 + H_2O \tag{2}$$

The small exothermic peak corresponded to the crystallization of nickel pyrophosphate, $Ni_2P_2O_7$. A novel exothermic peak appeared at the region from 270 to 330 °C by the addition of acidic and basic compounds. This peak covered the endothermic peak due to the condensation reaction (equation (2)). Because of the appearance of the novel exothermic peak, all acidic and basic compounds in this study were considered to be included in the phosphate materials.

Fig. 3 shows TG curves of samples prepared with various acidic and basic compounds. The sample prepared with *n*-butylamine had a different TG curve from the other samples. About 41 and 7% of weight losses were calculated from chemical equations (1) and (2), respectively. The



Fig. 2. DTA curves of nickel phosphates prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.



Fig. 3. TG curves of nickel phosphates prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.

total of these weight losses corresponded with the weight loss of the sample prepared without an additive. Because samples with and without additives indicated similar TG curves, a small amount of the acidic and basic compounds was included in the nickel phosphates.

By the addition of *n*-butylamine, the XRD pattern of precipitates changed from ammonium nickel phosphate hexahydrate to an amorphous phase. Other additives had less influence on the chemical composition. A small amount of acidic and basic compounds was included in phosphate materials from DTA and TG curves.

Powder properties of nickel phosphates

Fig. 4 shows SEM images of nickel phosphates prepared with various acidic and basic compounds. The sample prepared without an additive had pillar-like particles (Fig. 4(a)). By the addition of malonic acid, these pillar particles became larger (Fig. 4(b)). The sample prepared with propionic acid indicated a broken shape of particles that had small smooth faces (Fig. 4(c)). Irregular particles were observed in SEM images of the sample prepared with *n*-butylamine (Fig. 4(d)). The sample prepared with urea had a substantial disturbed pillar particles (Fig. 4(e)). The addition of acidic and basic compounds had influence on the particle shape of nickel phosphate.

Fig. 5 shows the particle size distributions of samples prepared with various additives. The major part of phosphate particles ranged from 10 to 100 μ m in samples prepared without an additive, with propionic acid, and urea (Fig. 5(a), (c), (e)). The addition of malonic acid produced a little smaller particles of nickel phosphate (Fig. 5(b)). This result appeared not to agree with the SEM images (Fig. 4), because other samples formed a mass of particles in the measurements of particle size distributions. On the other hand, a broad particle size distribution was observed in the sample prepared with *n*-butylamine (Fig. 5(d)).



Fig. 4. SEM images of nickel phosphates prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.



Fig. 5. Particle size distribution of samples prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.

Table 2 shows the specific surface areas of nickel phosphates prepared with various acidic and basic compounds. By heating, the specific surface area of nickel phosphate became smaller. The sample prepared with *n*-butylamine had a much larger specific surface area than the others [15]. By the addition of malonic acid, propionic acid, and urea, the specific surface area became smaller.

Adsorbent for basic stinking gas

Fig. 6 shows the adsorption ratios of trimethylamine

Table 2. Specific surface area of samples prepared with various additives $/m^2 \cdot g^{-1}$

additive		Temperature/°C		
		100	200	400
none	-	96.68	57.53	47.42
malonic acid	HOOC-CH ₂ -COOH	69.82	38.69	34.98
propionic acid	CH ₃ CH ₂ -COOH	79.98	40.56	36.68
glycine	HOOC-CH ₂ -NH ₂	-	-	-
<i>n</i> -butylamine	$CH_3(CH_2)_3$ - NH_2	253.35	271.15	137.15
urea	H_2N -CO- NH_2	79.36	44.70	36.98



Fig. 6. Adsorption of trimethylamine on nickel phosphate prepared with various compounds, (a) no additive, (b) malonic acid, (c) propionic acid, (d) *n*-butylamine, and (e) urea.

on nickel phosphates prepared with various acidic and basic compounds. The sample prepared with *n*-butylamine indicated a higher adsorption than the other samples. Lower adsorption ratios were observed in samples heated at 100 °C, on the other hand, samples heated at 400 °C had a higher adsorption ratio. Because the products heated at 400 °C had small specific surface area, other factors, for example the acid strength and amount of acidic sites on the surfaces of materials, were considered to have a great influence on the adsorption of the basic stinking gas.

Conclusions

With the addition of glycine, nickel phosphate was not formed in this study. The Ni/P ratio became higher in the sample prepared with *n*-butylamine. The chemical composition from XRD analyses was $NH_4NiPO_4 \cdot 6H_2O$ in samples prepared without an additive, with malonic acid, propionic acid, and urea. The sample prepared with *n*butylamine was an amorphous phase in XRD analyses. The specific surface area of phosphate materials became larger by the addition of *n*-butylamine. This addition of *n*-butylamine also improved the adsorption ratio of trimethylamine. The addition of acidic and basic compounds had an influence on the chemical composition, powder properties, and adsorption of basic stinking gas of nickel phosphates.

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