O U R N A L O F

Ceramic Processing Research

Formation of nano-pores on inorganic phosphate particles by the addition of urea

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It is important to control the powder conditions, such as porous, globular, etc., for application of such materials. In the fields of the synthesis of inorganic materials, the addition of urea etc. gave some possibility to obtain a large specific surface area, without a change of chemical composition. Materials containing urea became porous by heating because urea decomposed to ammonia and carbon dioxide. In this study, various phosphates were prepared in aqueous solutions with and without the addition of urea. The precipitation obtained was estimated by thermogravimetry-differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. The powder properties of phosphates were studied in terms of specific surface area, pore size distribution, particle size distribution, and scanning electron microscopy images. The influence of the added urea is discussed for the development of inorganic phosphate materials.

Key words: porous material, inorganic phosphate, addition of urea.

Introduction

Phosphates have been used as ceramic materials, catalysts, adsorbent, fluorescent materials, dielectric substances, for metal surface treatment, as fertilizer, detergents, food additives, fuel cells, pigments, etc. It is well known that aluminum phosphate works for various reactions as an acidic catalyst. The catalytic and adsorptive properties of materials are affected by their specific surface area [1-4]. To improve the functional properties, an attempt has been made to prepare nanoporous phosphate, which has a large specific surface area [5, 6]. The addition of urea etc. gave some possibility to obtain a large specific surface area in the fields of the synthesis of inorganic materials [7-12]. Urea was considered to decompose as follows.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$$
(1)

Phosphates are transformed to other forms of phosphates by hydrolysis and dehydration reactions at elevated temperatures. Polyphosphate, *cyclo*-phosphate, and ultraphosphate are included in a group of condensed phosphates. Polyphosphate has a chain structure in which the PO₄ unit shares two oxygen atoms; *cyclo*-phosphate has a cyclic structure; and ultraphosphate has a network structure. These condensed phosphates give the possibility of having novel functional properties. It is important that these types of phosphate materials are studied in terms of an improvement of the specific surface area for catalysts, adsorbents, etc. It is important to control the powder conditions, such as porous, globular, etc. The addition of urea gives the possibility to produce functional powder properties, without a change of chemical composition.

In this study, some types of inorganic phosphates containing urea were prepared from a target metal nitrate solution, a phosphoric acid solution, and urea. The precipitation obtained was estimated by thermogravimetry -differential thermal analysis, X-ray diffraction, and Fourier transform infrared spectroscopy. The powder properties of these phosphates were studied in terms of specific surface area, pore size distribution, particle size distribution, and scanning electron microscopy images.

Experimental

Preparation of various phosphates

0.1 mol/l of lanthanum nitrate solution was mixed with 0.1 mol/l of phosphoric acid solution in the molar ratio of La/P=1/1. Urea was added to this posphoric acid solution to a prescribed concentration before mixing (see figure captions). The precipitation, lanthanum orthophosphate, was filtered off, washed with water, and dried.

Sodium polyphosphate, NaPO₃, was synthesized by melting sodium dihydrogenphosphate and rapid cooling. 0.1 mol/l of lanthanum nitrate solution was mixed with 0.1 mol-NaPO₃/l of sodium polyphosphate solution in the molar ratio of La/P=1/3. Urea was added in this sodium polyphosphate solution to a prescribed concentration (see figure captions). The precipitation, lanthanum polyphosphate, was filtered off, washed with water, and dried.

0.1 mol/l of aluminum nitrate solution was mixed

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with 0.1 mol/l of phosphoric acid solution in the molar ratio of Al/P=1/1. Urea was added in this mixed solution to a prescribed concentration (see figure captions). Then, the solution was adjusted to pH 7 with ammonia solution. The precipitation, aluminum phosphate, was filtered off and dried.

A polyphosphoric acid solution was prepared with a cation exchange resin from sodium polyphosphate. 0.1 mol/l of aluminum nitrate solution was mixed with 0.1 mol-HPO₃/l of polyphosphoric acid solution in the molar ratio of Al/P=1/3. Urea was added in this mixed solution to the prescribed concentration (see figure captions). Then, the solution was adjusted to pH 7 with ammonia solution. The precipitation, aluminum polyphosphate, was decantated off, washed with water, and dried.

0.1 mol/l of nickel nitrate solution was mixed with 0.1 mol/l of phosphoric acid solution in the molar ratio of Ni/P=1/1. In this system, a part of the nickel nitrate was substituted for magnesium nitrate. Urea was added in this mixed solution to the prescribed concentration (see figure captions). Then, the solution was adjusted to pH 7 with ammonia solution. The precipitation, NH₄NiPO₄-NH₄MgPO₄, was filtered off and dried. Nickel-magnesium hydrogenphosphate, NiHPO₄-MgHPO₄, was obtained by heating the NH₄NiPO₄-NH₄MgPO₄ material at 200°C, and nickel-magnesium pyrophosphate, Ni₂P₂O₇-Mg₂P₂O₇, was formed at 400°C.

In this paper, the urea concentration indicated is the calculated value for the final solution, not the mixed solution, in their preparation systems.

Estimation of phosphates

The thermal behavior of these materials was analyzed by thermogravimetry-differential thermal analyses (TG-DTA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR). TG and DTA curves were measured with a Shimadzu DTA-60/60H at a heating rate of 10 K-min⁻¹ in air condition. 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, using a KBr disk method.

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, INC, respectively. Furthermore, the particle size distribution of these materials was measured with a laser diffraction/scattering particle size distribution instrument, HORIBA LA-910. Scanning electron microscopy (SEM) images were observed using a VE8800 from Keyence Co. Ltd.

Results and Discussion

Lanthanum phosphates

Figure 1 shows TG-DTA curves of lanthanum phos-



Fig. 1. TG-DTA curves of $LaPO_4$ prepared with and without urea, (a) urea 0 mol/l and (b) 0.5 mol/l.

phate prepared under various conditions. Samples showed the endothermic peaks at about 90 and 250 °C in the DTA curves. These endothermic peaks were due to the volatilization of adsorbed and crystalline water, respectively. The samples prepared with urea in the phosphoric acid solution had an endothermic peak at 200 °C (Fig. 1(b)). In the TG curves, the sample prepared with urea in the phosphoric acid solution (Fig. 1(b)) had a larger weight loss than the sample prepared without urea (Fig. 1(a)). This material was considered to contain a large amount of urea. The endothermic peak at 200 °C in the DTA curve was due to the volatilization of urea. However, there was no change in the XRD patterns by the addition of urea. IR spectra also had no notable peak, because the absorption peak from urea was small. The addition of urea had little influence on the chemical composition of the thermal products.

Lanthanum phosphate had a larger specific surface area by the addition of urea. The relationship is not clear between the preparation concentration with urea and specific surface area of lanthanum phosphate. Figure 2 shows the pore size distributions of samples prepared under various conditions and then heated at 100 °C. In the case of lanthanum phosphate, the amount of pores which radii smaller than 5 nm increased by the addition of urea without heating. The large amount of urea covered the pores on particles (Fig. 2(d)). By heating this phosphate, the amount of pores decreased in all the samples. Figure 3 shows the particle size distribution of samples heated at 100 °C. The large part of the particle distribution was in the size range from 200 to 1 micrometre. The particle size distribution of a sample prepa-



Fig. 2. Pore size distribution of $LaPO_4$ prepared in various urea concentrations and heated at 100 °C, (a) 0, (b) 0.25, (c) 0.5, and (d) 0.75 mol/l.



Fig. 3. Particle size distribution of $LaPO_4$ prepared in various urea concentrations and heated at 100 °C, (a) 0, (b) 0.25, (c) 0.5, and (d) 0.75 mol/l.

red without urea consisted of two normal distributions. The ratio of the particle size which is larger than 30 micrometre became smaller by the addition of urea. Figure 4 shows SEM images of samples heated at 100 °C. The sample prepared without urea did not have a specific shape, however materials prepared with urea were spherical. This was considered to be similar to the relationship with the preparation of spherical aluminum phosphate particles [7].

Figure 5 shows the pore size distribution of $La(PO_3)_3$ heated at 400 °C. Lanthanum polyphosphate had the pores with a size larger than 10 nm. The addition of 0.5 mol/l urea increased the large pores to about 20 nm. However, 1.5 mol/l of urea made the pores decreased in size. Because too large a volume of urea decreased the specific surface area of this phosphate, the choice of the urea concentration is important for the design of functional materials.



Fig. 4. SEM images of $LaPO_4$ prepared in various urea concentrations, (a) 0 mol/1 and (b) 0.5 mol/1.



Fig. 5. Pore size distribution of $La(PO_3)_3$ prepared in various urea concentrations and heated at 400 °C, (a) 0, (b) 0.5, and (c) 1.5 mol/l.

Aluminum phosphates

Figure 6 shows the pore size distributions of AlPO₄ prepared in various concentrations of urea. Aluminum orthophosphate prepared without urea and heated at 400 °C had a large number of 10 nm pores. By the addition of urea, pores which had radii smaller than 10 nm increased. Aluminum orthophosphates prepared with urea before heating had a small amount of pores, because the urea covered the pores of the phosphate. The formation of pores on aluminum orthophosphate was different from that on lanthanum phosphate. Lanthanum phosphate was precipitated without pH adjustment, and thus this difference was mainly caused from the preparation of urea,



Fig. 6. Pore size distribution of AIPO₄ prepared in various urea concentrations and heated at 400 °C, (a) 0, (b) 0.5, (c) 1.0, and (d) 1.5 mol/l.



Fig. 7. Pore size distribution of $Al(PO_3)_3$ prepared in various urea concentrations and heated at 400 °C, (a) 0, (b) 0.1, and (c) 0.5 mol/l.

the pH value should be considered together with the mixing procedure, etc., for the preparation of nanoporous phosphate materials.

Figure 7 shows the pore size distributions of $Al(PO_3)_3$ prepared in various urea concentrations. Because the scale of vertical axis in Figure 7 is smaller than that in Figure 6, aluminum polyphosphate had a smaller amount of pores than aluminum orthophosphate. Aluminum polyphosphate prepared without urea had pores larger than 20 nm. In the pore size distribution, the range of 2-20 nm appeared by the addition of urea.

The original aluminum phosphate had large size pores. It is possible to produce the smaller size of pores on



Fig. 8. Specific surface area of nickel-magnesium orthophosphate (NiHPO₄-MgHPO₄) in various ratios of Mg/(Mg+Ni)=x/10, (a) 0 and (b) 0.5 mol/l of urea.



Fig. 9. Specific surface area of nickel-magnesium pyrophosphate $(Ni_2P_2O_7-Mg_2P_2O_7)$ in various ratios of Mg/(Mg+Ni)=x/10, (a) 0 and (b) 0.5 mol/l of urea.

phosphate particles by the addition of urea.

Nickel and magnesium phosphates

The specific surface areas of nickel-magnesium orthophosphate are shown in Fig. 8. Nickel-magnesium hydrogenphosphate gave a small change in specific surface area as a function of the various magnesium ratios. The specific surface area of the phosphate with Mg/Ni=2/8 increased by the addition of urea.

Figure 9 shows specific surface areas of nickelmagnesium pyrophosphate. The specific surface area of nickel-magnesium pyrophosphates was from 30 to 70 $m^2 \cdot g^{-1}$. The pyrophosphate prepared at Mg/Ni=1/9 had a larger specific surface area by the addition of urea. The additional effects of urea in the preparation of nickel -magnesium phosphates are less clear than those of lanthanum and aluminum phosphates. It is considered that ammonium and hydrogen cations in NH₄MPO₄ and MHPO₄ had some influence on the change of specific surface area of these phosphates.

Conclusions

The increase of specific surface area in aluminum and lanthanum orthophosphates was larger than that in the other phosphates. A tendency was observed that an orthophosphate was more affected by the addition of urea than a condensed phosphate. Pores smaller than 10 nm in radius were increased by the addition of urea. Aluminum salts had a larger improvement of specific surface area than rare earth and transition metal salts. This was caused by their preparation system. The improvement by the addition of urea was appeared more easily in phosphates that were precipitated with pH adjustment. The concentration of urea, the pH value, and the mixing procedure are important for the preparation of nano-porous phosphate materials.

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