Syntheses of Intercalated Layered Aluminium Phosphates for Oxygen Adsorption

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Intercalated compounds from layered aluminium phosphates with such organic molecules having long methylene chains as 1,10-decanediamine and 1,10-decanediphosphonic acid were prepared in order to investigate their adsorption properties for oxygen and nitrogen gases. Though the basal spacing of the host aluminium dihydrogentriphosphate dihydrate AlH₂P₃O₁₀·2H₂O (ADHP) was 7.90 Å, the host material intercalated 1,10-decanediamine as the guest and reached 19 Å basal spacing. 1,10-decanediphosphonic acid, in which phosphorus group was directly connected to the methylene chain at the each end, was used as pillar compound instead of phosphoric acid for the synthesis of another intercalation compound. The basal spacing increased to 17 Å and the large increases in the specific surface areas and in the number of pores in every pore size were observed compared to those of the original ADHP. Excellent selective adsorption characteristics for oxygen have been obtained with the 1,10-decanediphosphonic acid intercalation compound.

Key words: intercalated aluminium phosphate, adsorption, oxygen, nitrogen

Introduction

One of the origin of the environmental problems is the combustion of fossil fuels that arises the earth-warming effect with excess of carbon dioxide and the acid-rain producing by nitrogen oxides. Oxygen combustion with pure oxygen or oxygen-concentrated air is noticeable as a solution to these problems. Then, oxygen gas for use in oxygen combustion will be required increasingly in the near future. Air separation now provides oxygen gas. Adsorption phenomenon is adopted as one of the industrial methods for the separation.

The interesting property of layered compounds is the possibility of incorporating guest such as ions and molecules into their interlayer space. They have applicability as catalyst using the micropore in the interlayer. Selection of the guest species can change the physical and chemical properties of the interlayer. Because so many pores are formed with calcinating that layered compounds are available for adsorbents.

Aluminium dihydrogentriphosphate dihydrate (ADHP) was first prepared by d'Yvoire¹⁻³⁾. Further preparations and properties were reported by Tsuhako et al⁴⁾. They also described the intercalation of alkylamines and aniline into ADHP⁵). Aluminium dihydrogentriphosphate, $AlH_2P_3O_{10}$, has two crystal structures called type I and type II. The type I is layered and absorbs moisture immediately when it is left in the air. The hydrated product is aluminium dihydrogentriphosphate dihydrate, AlH₂P₃O₁₀·2H₂O. The type II of AlH₂P₃O₁₀ is not layered compound and not hygroscopic in the air. The layered aluminium phosphates is prepared easily and have surface acidity that is effective in intercalating of basic compounds. Therefore, the layered aluminium phosphates is selected as the host compound in this study. Organic compounds were selected as the guest for their flexibility and ease to molecular design. Intercalations of the long-chain organic molecules for ADHP were attempted. Their possibility for an adsorbent was also examined.

Experimental

Preparation of host compounds

ADHP was prepared by the following way. 1 g of Al_2O_3 was added to 10 ml of 85% phosphoric acid and this mixture was stirred at room temperature for 1 h. The white gel was then transferred into a porcelain crucible and calcined in an electric furnace at 300°C for 24 h to form aluminium phosphates. Though the aluminium phosphates obtained were relatively hard, they were hygroscopic in the air and the moist products could be taken off from the crucible as thin plates. They were washed with water and dried at 40°C.

Preparation of intercalation compounds

Two intercalation compounds were synthesized. One is abbreviated to Diamine, which is synthesized following simple mixing way; 1 g of ADHP was added to 100 ml of 0.1 mol·dm⁻³ 1,10-decanediamine ethanol solution. The reactant was stirred at room temperature for 24 h. The mixture was filtered, washed with ethanol, and dried at 40°C. Another is to prepare a pillared compound of phosphonate. 1,10-decanediphosphonic acid having the same length of methylene-chain to 1,10-decanediamine was used as the pillaring compound. The methylene-chain as the guest directly connects the to host laver. 1,10-decanediphosphonic acid was prepared by the similar method to the synthesis of *n*-alkylphosphonic acids⁶⁾. To 500 ml of hexane stirred at room temperature was added 4.59 g of metallic sodium, and refluxed. To this solution was added 38.8 g of dibutylphosphite for 30 min. The refluxing was continued until the sodium metal completely dissolved. After being dissolved, 30.0 g of 1,10-dibromodecane was added and refluxed for 5 or 6 h gently. After being cooled, the precipitate was washed throughly with water. The organic layer was separated and dehydrated with sodium sulfate anhydrate. After filteration, the solution was evaporated under reduced pressure, and distilled in fruction vacuo The containing 1.10-bis(dibutylphosphite)-decane was refluxed with 300 ml of concentrated hydrochloric acid overnight. The mixture was concentrated by distilling away under reduced pressure. The product was identified by FT-IR spectroscopy (Shimadzu FTIR-8100) and NMR spectroscopy (JEOL DATUM JNM-PMX60SI). The NMR spectrum showed that the product contains 40% product. impurities except for the desired 1,10-decanediphosphonic acid. 1,10-decanediphosphonic acid was mixed instead of phosphoric acid in the synthesis stage of aluminium phosphate. 50 ml of 0.1 mol·dm⁻³ aluminium chloride aqueous solution was added to 50 ml of ethanol solution in which 7.55 g of 1,10-decanediphosphonic acid was dissolved. The mixture was transferred into a Teflon vessel and made to react at 100°C for 3 d. The precipitate was washed with ethanol and dried at 40°C. This compound is ideally aluminium 1,10-decanediphosphonate and abbreviated to Diphos.

The products were powdered and identified by X-ray diffraction analysis (Rigaku RINT2100 Ultima⁺) and FT-IR spectra. Thermogravimetric analysis and differential thermal analysis, TG-DTA, (Rigaku TAS200) was utilized. An automatic gas adsorption apparatus (Japan Bell BELSORP 28SA) was used for the specific surface area and the pore size distribution measurements. An electric balance (CAHN instrument C-2000) was used for the measurement of gas adsorption amounts.

Results and Discussion

Preparation of host compounds

X-ray diffraction patterns and FT-IR spectra of ADHP and the intercalation compounds are shown in Figs. 1 and 2. X-ray diffraction pattern of ADHP shows the prominent peak for the basal spacing of 7.90 Å. In the FT-IR spectrum, strong absorption bands for the stretching vibration of water are observed at 3580 and 3520 cm⁻¹. An absorption band for the deformation vibration is observed at 1650 cm⁻¹. Absorption bands for the stretching vibration of P-OH, PO_3^2 , PO_2 , and P-O-P are observed at 2350, 990, 1050, and 780 cm⁻¹, respectively. These diffraction pattern and IR spectrum confirm the layered aluminium dihydrogentriphosphate dihydrate was prepared.

Preparation of intercalation compounds

X-ray diffraction pattern of Diamine shows the prominent peak for the basal spacing of 19.0 Å. The basal spacing is larger by 11 Å than that of ADHP. In the FT-IR spectrum, absorption bands for the stretching vibration of $-CH_2$ are observed at 2920 and 1468 cm⁻¹. Absorption bands for N-H bond are observed at 1630 and 765 cm⁻¹. Thus, the intercalation reaction is an acid-base reaction between P-OH of ADHP and the amine. This reaction forms the amido-triphosphate with P-N bond after calcination at 200°C⁵.

X-ray diffraction pattern of Diphos shows the prominent peak for the basal spacing of 17.1 Å. The basal spacing is larger by 9 Å than that of ADHP. In the FT-IR spectrum, an absorption band for the stretching vibration of $-CH_2$ is observed at 2922 cm⁻¹, and absorption bands for the phosphonate group are observed at 850 - 1200 cm⁻¹. An absorption band for PCH₂- is observed at 1385 cm⁻¹. From these absorption bands, the decamethylenegroup is intercalated into the interlayer connected by P-C bonds. Because of the shapes of absorption bands for phosphonate group the structure of the host layer is different from that of ADHP.



Fig. 1 X-ray diffraction patterns of aluminium phosphate and intercalation compounds. ADHP is the host compound for intercalation and Diamine is the intercalate with 1,10-decanediamine. Diphos is aluminium 1,10-decanediphosphonate.



Fig. 2 FT-IR spectra of ADHP and intercalation compounds.

Thermogravimetric analysis

Figure 3 shows TG curves of ADHP and intercalation compounds. The weight of ADHP immediately decreases with starting the heat. The weight losses from 120°C to 160°C and from 400°C to 550°C are 8.1% and 5.6%, respectively. The weight loss at the lower temperature is caused by the elimination of interlayer water with endothermic reaction. Condensation dehydration of the phosphate group with endothermic reaction causes the loss at the higher temperature. The specific surface areas after calcination are shown in Table I. Large weight loss of about 30% is observed for Diamine from 350°C to 600°C.



Fig. 3 DTA and TG curves of ADHP and intercalation compounds.

Table I. Specific surface areas A_{sp} of ADHP and intercalation compounds after calcination at different temperatures.

| Calcination temp. /°C | $A_{SP}/(m^2/g)$ | | | |
|--------------------------|------------------|---------|--------|--|
| | ADHP | Diamine | Diphos | |
| 25 | 1.81 | 6.22 | 96.1 | |
| 100 | 2.49 | | 95.1 | |
| 200 | 2.38 | 6.00 | 89.6 | |
| 300 | 2.39 | | 96.3 | |
| 350 | 2.41 | 86.8 | 89.5 | |
| 400 | 2.53 | 84.7 | 82.6 | |
| 500 | 2.48 | 11.4 | 70.3 | |
| 600 | | | 54.4 | |

This loss comes from the elimination reaction by pyrolysis of the guest amine between the layers. During this temperature range, the reaction is exothermic. X-ray diffraction pattern shows the layer was contracted with the elimination after the calcinating at 350°C. The absorption band for -CH₂ markedly decreases in the FT-IR spectrum. 1,10-decanediamine is stable in the interlayer upto about 330°C though its boiling point is 278°C. Large weight loss is observed for Diphos from 50°C to 350°C, too. In the X-ray diffraction pattern, there was no change after calcination at 400°C, showing the layered structure was maintained until this temperature. The diffraction peak at 17.1 Å became weak after calcination at 500°C. Thus, the large weight loss is the elimination by pyrolysis of 1,10-decanediphosphonate intercalated with incomplete bond to the host layer. The pyrolysis of completely bound guest molecule begins at 400°C. With contracting of layer the specific surface areas decrease as shown in Table I.

Pore size distribution

Two methods were used to analyze pore size distribution. One is Micropore method⁷, that analyzes the size distribution of micropore, i.e. pore width less than 2 nm, with t-plot⁸). Another is Dollimore-Heal method⁹⁻¹⁰ on adsorption to the solids having mesopore, i.e. pore width from 2 nm to 50 nm. In mesopores capillary condensation will occur, and the pore size is calculated with Kelvin equation. Figures 4 and 5 show the pore size distributions of ADHP and intercalation compounds after calculation at different temperatures.



Fig. 4 Pore size distributions by Micropore method (left panels) and by Dollimore-Heal method (right panels) of ADHP and intercalation compounds.

Pore size distributions of Diamine in micropore region indicate some increase of pores after calcination at 350° C. In the FT-IR spectrum, the absorption band for -CH₂ was very weak after calcination at 350° C, while that for P-N bond was remained. Therefore, new pores were formed with elimination of the guest molecule. In contrast to ADHP and Diamine, Diphos shows much differences in both micropore and mesopore regions. Because the organic guest was mixed in the synthesis of Diphos, much more pillars were formed among the layer than Diamine. The calcination at 300°C gave more pores in every size than no calcined one.

Gas adsorption

The gas adsorption amounts of nitrogen and oxygen at 101.3 kPa on ADHP and intercalation compounds are listed in Table II. Large amounts of gas are adsorbed on the intercalation compound, especially for oxygen. Selective adsorption characteristics for oxygen are observed for intercalation compounds. This may be because of the lipophilic character of such organic compounds. The adsorption amount for oxygen as well as for nitrogen of Diamine after calcination at 350°C increases about four times to those for no calcination. The compound showed dark gray color after the calcination. The elimination of the amine from the interlayer causes the carbonization. The carbonized surface influences the adsorption property for oxygen. It is considered that organic molecules in the interlayer prevent from nitrogen adsorption. After calcination P-N bond was remained interlayer but the surface was carbonized. They cause the increases of the specific surface areas and the micropores and may cause the increase of adsorption amount for oxygen after calcination. The pyrolysis makes decrease of organic molecules in the interlayer and increase of adsorption amount of nitrogen. Adsorption amounts for nitrogen of Diphos are less than those for Diamine, and then the selectivity for oxygen became larger. This may be because more organic molecules were included in interlayer than Diamine. There was no change of color of Diphos with the calcination.

Materials that exhibit large adsorption amounts and selectivity for nitrogen or oxygen is desirable for adsorbents for air separation. The oxygen adsorption amounts and the selectivity for oxygen of Diphos are excellent and Diphos is promising for an oxygen separation adsorbent from air. It is now under consideration to decrease the adsorption amounts for

Table II. Adsorption characteristics of ADHP and

intercalation compounds at 101.3 kPa.

| Sample | Calcination temp. /°C | $\frac{V(O_2)}{ml(S.T.P.)g^2}$ | $\frac{V(N_2)}{ml(S.T.P.)g}$ | $V(O_2)/V(N_2)$ |
|---------|-----------------------|--------------------------------|------------------------------|-----------------|
| ADHP | 100 | 0.04 | 0.01 | 4.00 |
| Diamine | 25 | 1.56 | 0.82 | 1.90 |
| | 350 | 5.86 | 3.41 | 1.72 |
| Diphos | 25 | 1.68 | 0.58 | 2.90 |
| | 300 | 1.79 | 0.36 | 4.97 |

nitrogen of Diamine after calcination and to increase the adsorption amounts for oxygen of them.

Acknowledgment

The authers greatly appreciate helps and advices of Prof. Masato Nanasawa and Dr. Tetsuo Kuwabara from Yamanashi University in synthesizing of 1,10-decanediphosphonic acid.

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(Received December 11, 1998; accepted March 8, 1999)