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Synthesis of the Cyclohexylammonium Form of α-Zirconium Phosphate and Its Application to Nickel(II) Ion Exchange[1)]

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The uptake of cyclohexylamine with α-zirconium phosphate was studied by means of the pH-titration method. Cyclohexylamine was loaded up to 75% of the ion-exchange capacity of α-zirconium phosphate. Chemical analysis, thermal analysis, infrared spectroscopy, and X-ray diffractometry were used to characterize the product obtained at the final step of pH titration, which was referred to as the cyclohexylammonium form. The chemical composition can be presented as $Zr(C_6H_{11}NH_3)_{1.5}(H)_{0.5}(PO_4)_2 \cdot H_2O$. The interlayer distance of the exchanger expanded to 18.4 Å upon the uptake of cyclohexylamine. The cyclohexylammonium ion was exchanged easily with the nickel(II) ion in a solution.

α-Zirconium phosphate, having a layered structure, has been investigated not only as an inorganic ion exchanger but also as the host of an intercalate.[2)] Generally, the intercalate obtained has a larger interlayer distance than that of α-zirconium phosphate, and it can be expected to show a specific reaction toward a large cation.

Primary alkylamines, such as methyl- and ethylamine, have also been studied, and the relationship between the alkyl-chain length and the interlayer distance of the product has been discussed.[3)] Clearfield and Tindwa have found that the butylamine intercalate of α-zirconium phosphate can be ion-exchanged with a large cation.[4)] Recently, the electric conductivity was measured by using the intercalation compounds of α-zirconium phosphate with propylamine.[5)] Among the compounds with a ring system, benzylamine has been studied, but the details of the work have not been published.[2)]

Since cyclohexylamine is more strongly basic in an aqueous solution than is ammonia,[6)] the ion-exchange reaction can be expected to proceed easily. In this work cyclohexylamine is selected as an intercalant (guest) and the uptake of the amine was investigated by means of the pH-titration method. The cyclohexylammonium form of α-zirconium phosphate (ZP-Cy) obtained was then used in nickel(II) ion exchange.

Experimental

Reagents. The α-zirconium phosphate was prepared according to the literature.[6)] Reagent-grade cyclohexylamine (Wako Pure Chemical Industries, Ltd.; guaranteed) was used without further purification. Reagent-grade nickel(II) dichloride hexahydrate (Koso Chemical Co., Ltd.) was also used.

pH Titration. A weighed amount of α-zirconium phosphate was equilibrated with a mixture of 0.1 mol dm^{-3} cyclohexylamine and its hydrochloride solution. The composition of the solution was adjusted so that the total amount of the cyclohexylammonium ion was always equal to 0.1 mol dm^{-3} while the ratio of cyclohexylamine to its chloride was varied in the range from 1 to 0. The mixture was shaken continuously at 25 °C for a specified period of time, and then the pH value of the supernatant was measured on a pH meter.

A slight excess of cyclohexylamine to the ion-exchange capacity of α-zirconium phosphate was added to a weighed amount of the exchanger, and the mixture was shaken at 25 °C for 48 h. Then, the solid was separated with centrifugation and dried at room temperature in air. The product thus obtained is referred to as ZP-Cy (the cyclohexylammonium form of zirconium phosphate).

Nickel(II) Ion Exchange. The ion exchange was carried out by the batch method. The nickel(II) ion was exchanged by adding a weighed amount of ZP-Cy to a solution of 0.03 mol dm^{-3} nickel chloride. The amount of nickel was equal to 150% of the total ion-exchange capacity of the α-zirconium phosphate. The mixture was shaken continuously at 25°C for 48 h. After the reaction, the solid was separated from the solution and then washed with distilled water until it was free from chloride ions. The nickel-ion content in a solution was determined by an EDTA titration using PAN (1-(2-pyridylazo)-2-naphthol) as an indicator.

Analytical Procedure. The change in the crystal structure was studied by means of X-ray diffractometry using Ni-filtered Cu $K\alpha$ radiation (λ=1.542 Å)(Rigaku Geigerflex RAD-2B). Thermogravimetric (TG) and differential thermal analysis (DTA) data were obtained on a Shimadzu thermal analyzer at the heating rate of 10 °C min^{-1} in static air. The infrared (IR) spectra were measured on a A-302 spectrophotometer (Japan Specroscopic Co., Ltd.).

The chemical composition of the nickel form was analyzed according to the method in the literature.[8)] In this work, zirconium was separated as an mandelate and then ignited to zirconium oxide and weighed. The carbon, hydrogen, and nitrogen contents of ZP-Cy and the nickel form were determined by means of elemental analysis.

Results and Discussion

To determine the equilibration time, the pH value in the solution was measured after a given period of time by adding cyclohexylamine of 4.5 meq g^{-1} α-zirconium phosphate to the samples. Since equilibrium was attained within 12 h, the reaction time of 48 h was chosen.

Figure 1 shows the titration curve of α-zirconium

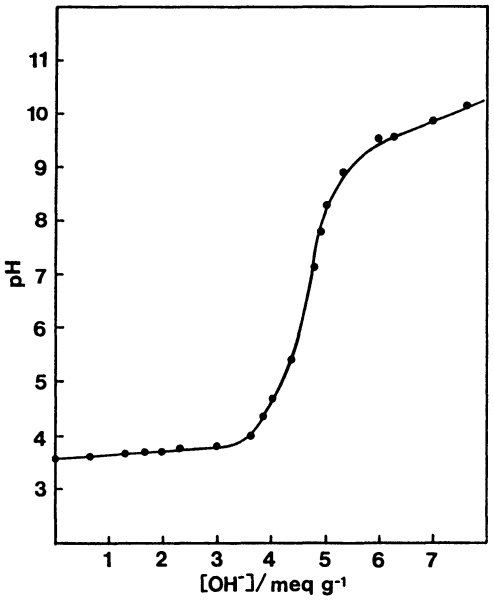

Fig. 1. pH titration curve.

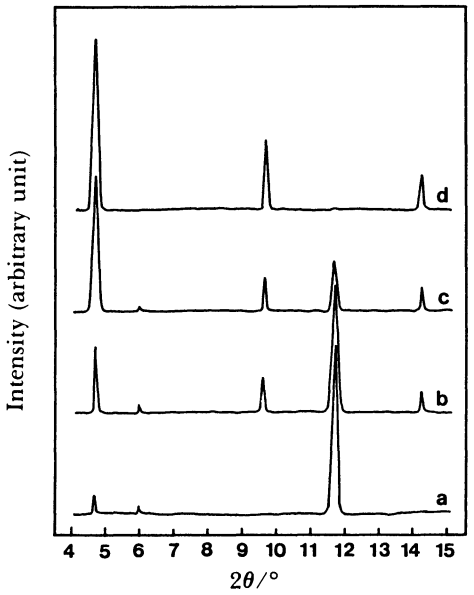

Fig. 2. Schematic diagram of X-ray powder diffraction at the lowest angle region. The percentage of ion exchange: a 15; b 30; c 45; d 60%.

phosphate with cyclohexylamine. Cyclohexylamine was taken up at a low pH value. The end point corresponded to 75% of the total ion-exchange capacity of α-zirconium phosphate.

Figure 2 shows the change in the crystal structure of the exchanger. Since α-zirconium phosphate has a layered structure, the change in the interlayer distance can be observed at the lowest angle region of the X-ray diffractogram. At the beginning of the ion-exchange reaction, only the α-zirconium phosphate phase (α-phase) was present. Between the loading from 10 to 55% of the total ion-exchange capacity of the exchanger, two phases, Phase I (interlayer distance

Table 1. The Intensity of Peaks for Dried Phases

Percentage loading/%	Interplanar spacing (d/Å)					
	18.4[a)]	17.8[b)]	14.7	9.2[a)]	8.9[b)]	7.6[c)]
			I/I_0			
15		2	53			100
30		65	100		10	67
45		100	61		13	20
55		100	32		14	1
60		100	20		17	
65	100			9	24	
70	100			15		
75	100			11		

a), b): The pair of peaks originated from one phase, as was observed in the intercalation compounds of α-$Sn(HPO_4)_2 \cdot H_2O$.[9)] c): The interlayer distance of α-zirconium phosphate.

18.4 Å) and the α-phase, were present. The ratio of Phase I to α-phase increased with an increase in the exchange process. In the region of 60—75% of the loading, however, only phase I was present.

It is possible for cyclohexylamine to form two conformations, chair and boat. Since the chair conformation is more stable than the boat one,[10)] it can be assumed that the cyclohexylamine is present as the chair conformation between the layers. While the bond length of C-C and the ∠CCC bond angle are 1.54 Å and 111° respectively in the molecule of cyclohexane, the length and the angle are 1.53 Å and 114° in the butane molecule.[11)] If the angle and the distnce of the bond between the carbon and amino groups are almost identical in the butylamine and cyclohexylamine molecules, the lengths of the two molecules can be estimeted to be equal. Since the interlayer distance is equal to 19.0 Å in the butylamine intercalate of α-zirconium phosphate[12)] and equal to 18.4 Å in the cyclohexylamine ones, the above assumption is reasonable. The estimation also suggests that the orientation of cyclohexylamine is similar to that of butylamine between the layers of zirconium phosphate. The sizes of benzylamine and cyclohexylamine can also be estimated based on the molecular sizes of cyclohexane and toluene. In consideration of the size of the amino group, the length of cyclohexylamine is calculated to be 8.7 Å, and that of benzylamine, to be 9.3 Å. Hence, the interlayer distance of the cyclohexylamine intercalates is comparable with that of the benzylamine form, having the interlayer spacing of 19.2 Å.[2)]

The solid phases formed in the exchange process tend to lose hydrated water(s). After the solid has been exposed to room air on a sample holder, the X-ray diffractogram was different from that recorded under wet conditions. For example, the solid obtained at a 45% loading showed three peaks—at 18.4 Å (2θ=4.79°), 17.8 Å (2θ=4.96°), and 14.7 Å (2θ=5.96°)— after a short exposure. Table 1 shows the intensities of the peaks obtained after drying at room temperature. The intensity of the peak at 14.7 Å reached a maximum at about

Table 2. Interplanar Spacings (d-Values) of ZP-Cy

d/Å	I/I_0	d/Å	I/I_0
18.4	100	3.68	1
9.17	11	3.54	*
6.12	6	3.38	2
5.51	*	3.25	*
4.57	1	3.12	*
4.39	*	2.98	*
4.24	2	2.87	*
4.13	1	2.75	*
3.98	1	2.65	1
3.82	3	2.61	*

"*" means that the intensity is less than unity.

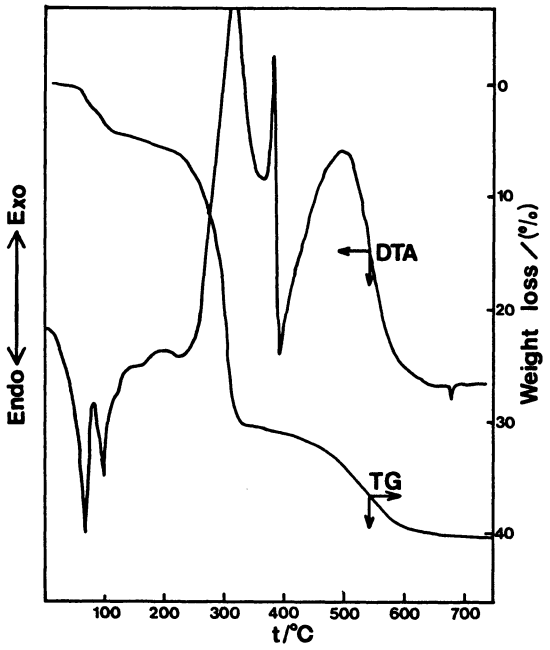

Fig. 3. Thermoanalytical curves.

a 20% loading. The intensity of the 17.8 Å peak increased up to a 60% loading. No change in the interlayer distance was observed above the 60% loading. These facts indicate that the hydrated water(s) play(s) an important role in expanding and maintaining the interlayer distance of the exchanger and that, at higher loadings, cyclohexylamine itself acts as a "pillar." Also, it is suggested that, when the intercalate compound with the amine lose hydrated water(s), the orientation of cyclohexylamine must change in the solid.

Characterization of ZP-Cy. The interplanar spacings (d-values) of ZP-Cy are shown in Table 2. The interlayer distance was comparable with those of the butylamine and benzylamine intercalate of α-zirconium phosphate described above.

Figure 3 shows the TG and DTA curves of ZP-Cy. The decomposition took place in three steps. In the first, the dehydration ocurred. In the temperature region of 200—300 °C, a weight loss and exothermic

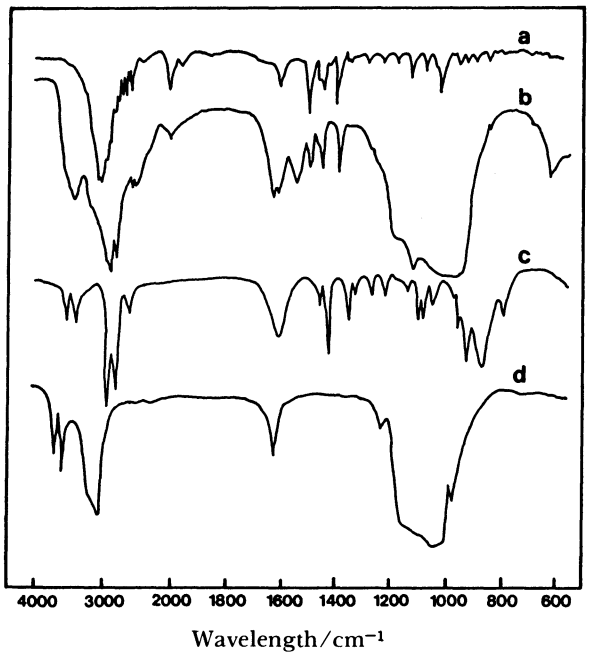

Fig. 4. Infrared spectrum of a cyclohexylamine hydrochloride, b ZP-Cy, c cyclohexylamine, and d α-zirconium phosphate.

peaks were observed. The weight loss was, however, smaller than that to be expected from the chemical formula (see below). These facts indicate that, in this step, the cyclohexylamine was evolved, decomposed, and oxidized partially on the surface of a platinum pan, and that a small amount of a residue (presumably carbon) was formed. The decomposition temperature was higher than that observed for the ammonium form, reflecting the basicity of cyclohexylamine.[13] In the temperature region of 400—500 °C, a weight loss was observed caused by the dehydration associated with the condensation of $(HPO_4)_2$ to P_2O_7. The reaction was supposed to be endothermic, but an exothermic peak appeared. This was caused by the oxidation of the residue formed at the second step, since the weight loss was larger than that to be expected from the chemical formula.

The IR spectra of ZP-Cy and related compounds are shown in Fig. 4. It is clear that the spectrum of ZP-Cy was almost identical with that of cyclohexylammonium chloride in the region of 1800—3500 cm^{-1}. Especially, the absorption was found at 2000 cm^{-1} only for the hydrochloride and ZP-Cy. This absorption is assigned to the group of NH_3^+. The absorption due to -OH stretching was present near 3500 cm^{-1} in the spectrum of ZP-Cy. These facts indicate that the cyclohexylamine was present as the cyclohexylammonium ion between the layers and that the unexchanged protons appear as $-HPO_4$, similarly to the situation in α-zirconium phosphate.

The contents of carbon, hydrogen, and nitrogen were as follows: Found: C, 24.0: H, 5.3: N, 4.3%. Calcd

for $Zr(C_6H_{11}NH_3)_{1.5}(H)_{0.5}(PO_4)_2 \cdot H_2O$: C, 24.0; H, 5.3; N, 4.3%.

It is concluded that α-zirconium phosphate uptakes cyclohexylamine up to 75% of the total ion-exchange capacity and that the cyclohexylamine is present as the cyclohexylammonium ion between the layers.

Nickel(II) Ion Exchange. The determination of nickel(II) showed that all the cyclohexylammonium ions in ZP-Cy were exchanged with Ni(II) in a solution. This also indicates that the cyclohexylamines are present as quartarnary ammonium ions between the layers of zirconium phosphate. The ion-exchange reaction did not proceed further, even if the solid phase after the first ion exchange was immersed in a nickel (II) solution. Thus, the nickel(II) in a solution can be exchanged easily only with the cyclohexylammonium ion in the solid. The product was pale green. The X-ray diffraction pattern of the product agreed well with that reported for $ZrNi(PO_4)_2 \cdot 4H_2O$. The chemical composition was as follows: Zr, 23.6; Ni, 11.6; PO_4, 47.5; H, 1.8: ignition loss, 17.4%. Calcd for $ZrNi_{0.75}H_{0.5}(PO_4)_2 \cdot 3.5H_2O$: Zr, 23.5; Ni, 11.3; PO_4, 48.9; ignition loss, 17.4%. The contents of carbon and nitrogen were within the background limit indicated by the elemental analysis.

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