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The Ion-exchange Properties toward Hexaamminecobalt(III) and the Characterization of the Complex Cation Form of α-Zirconium Phosphate[1)]

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The ion-exchange properties of α-zirconium phosphate have been investigated for the H^+–$[Co(NH_3)_6]^{3+}$ system. The ion-exchange process was examined by means of the variation in the pH values of the supernatant. α-Zirconium phosphate loaded with hexaamminecobalt(III) was also characterized by chemical analysis, X-ray diffractometry, infrared spectroscopy, and thermal analysis. In spite of the steric hindrance in the crystal structure of α-zirconium phosphate, the ion exchange proceeded gradually. About 30% of the hydrogen ions in α-zirconium phosphate were replaced by hexaamminecobalt(III). The interlayer distance of the exchanger expanded from 0.76 to 1.12 nm.

The ion-exchange properties of α-zirconium phosphate, $Zr(HPO_4)_2\cdot H_2O$ (α-ZP), have been studied extensively, and its crystal structure has been determined.[2)] The structure is a layered one, and zeolitic-type cavities are present between layers. The cavities are connected by openings, the largest diameter being 0.264 nm.[3)] Hence, the ions of the ionic radius smaller than 0.133 nm can be easily taken up by α-ZP. However, larger cations, such as ammonium and tetra-alkyl-ammonium ions, and cobaltocene also exchange with the proton in α-ZP.[4,5)] These facts indicate that the ion exchange on α-ZP is not necessarily restricted by the size of the exchanging cation.

It has been known that α-ZP has not only catalytic activities, but also the possibility of use as a catalyst support. For example, Nozaki *et al.* have applied α-ZP to a catalyst for the dehydration of 2-propanol,[6)] and Hattori *et al.* studied the catalytic property and the acidity of α-ZP.[7)] Alberti pointed out that α-ZP loaded with a transition metal ion was promising as a catalyst.[8)] The copper form of α-ZP, $ZrCu(PO_4)_2$ was found to be active for the oxydation of carbon monoxide.[9)]

The ion-exchange reaction has been employed to prepare a highly dispersed metal-supported catalyst, especially when the metal is a member of the platinum group.[10)] Since many metal ions are not present in neutral pH solutions, a complex cation must be used for the ion exchange. The use of the metal-ammine complex is suitable, since the ammonia molecule is small and can easily be removed by heating.

In this work, the hexaamminecobalt(III)-hydrogen ion exchange was studied, and the α-ZP loaded with the hexaamminecobalt(III) ion (ZP-Co) was characterized by chemical analysis, X-ray powder diffraction, infrared spectroscopy, and thermal analysis.

Experimental

Preparation of α-ZP and Hexaamminecobalt(III) Trichloride. By the previously reported method α-ZP was prepared.[11)] When the zirconium dichloride oxide octahydrate used as a starting material included free hydrochloric acid, the salt was washed with acetone 2—3 times. The cobalt complex was prepared according to the literature.[12)] Identification was made by means of the X-ray diffraction pattern.[13)]

Ion Exchange. The ion-exchange experiments were carried out in batches. A weighed amount of α-ZP was placed in contact with the solution of hexaamminecobalt(III) in a thermostat bath. The concentration of the solution and the reaction temperature were varied. After the mixture has been shaken continuously or left to stand with a reflux condenser for a given period of time, the solid was centrifuged from the solution. The pH value of the supernatant was measured on a pH meter. Then, the solid was again added to a new solution of the complex. The process was repeated until the pH value of the supernatant became almost equal to that of the complex solution.

Analytical Procedure. The structural change in the exchanger during the ion exchange was measured by means of X-ray diffractometry. The patterns were recorded with a Rigaku Denki Geigerflex diffractometer, using Ni-filtered Cu $K\alpha$ radiation (λ=0.1542 nm). The infrared (IR) spectra were measured on a JASCO DS-403G grating infrared spectrophotometer. The thermogravimetric (TGA) curve was obtained with a Shimadzu thermal analyser DT-30 at a heating rate of 10 °C/min in static air. The differential scanning calorimetric (DSC) data were obtained with a Rigaku differential scanning calorimeter under a helium stream to prevent the oxidation of the ammonia gas evolved at the surface of a platinum crucible.[14)]

The chemical analysis of the exchanger was carried out as follows. A weighed sample was decomposed with sodium peroxide. The precipitate was separated from the solution by filtration and then dissolved in hydrochloric acid. Zirconium was separated as cupferrate from cobalt and determined gravimetrically.[15)] Cobalt was titrated with a standardized EDTA solution, using xylenol orange as an indicator. Phosphorus was determined as magnesium pyrophosphate.[16)] Hydrogen and nitrogen were determined by elemental analysis.

Results and Discussion

Ion Exchange. To determine the optimum conditions of the ion exchange, the concentration of the complex cation and the reaction temperature were varied. The concentration range was from 0.025 to 0.2 mol dm^{-3}. The concentration of 0.025 mol dm^{-3} was equal to twice the ion-exchange capacity of the α-ZP used when the weighed amount of α-ZP was 500 mg and the volume of the solution was 100 cm^3. The concentration of 0.2 mol dm^{-3} was nearly equal to that of the saturated solution at 20 °C. Equilibrations were carried out at 25, 50, 75, and 90 °C.

In the first ion-exchange reaction at a given temperature, the equilibrium pH values of the supernatant solution were independent of the concentration of the complex cation. However, the pH values decreased at elevated temperatures. The hexaamminecobalt(III) ion is inert to the substitution of the ligand at room temperature, that is, the complex cation will persist for days. The hydrolysis of the complex cation took place at high temperatures. If the solution of the complex cation was heated at 75 or 90 °C, cobalt hydroxide was precipitated after 1.5 h or 15 min respectively. These facts indicate that, in the α-ZP–hexaamminecobalt(III) solution system, the ion exchange competes with hydrolysis at high temperatures. The change in pH values was steep at the end of ion exchange at 90 °C, and it was difficult to prevent the complex cation from hydrolyzing. The optimum experimental conditions were: concentration, 0.025 mol dm^{-3}, temperature, 75 °C, and reaction time, 1 h.

It is known that α-ZP and its salt forms have a layered structure, and that the interlayer distance depends on the size of the exchanging cation.17) The structural change in the exchanger phase is usually examined by means of X-ray diffractometry. In an X-ray powder diffractogram, the peak due to the interlayer distance appears in the lowest angle region. Two peaks were observed at $2\theta=11.7°$ and 7.9° ($d=$ 0.76 and 1.12 nm) during the ion exchange, as is shown in Fig. 1. The former originated from the interlayer distance of α-ZP. The intensity of the X-ray reflection of the latter increased, while that of the former decreased, with an increase in the uptake of the complex cation. The precise interplanar spacings (*d* values) of ZP–Co are shown in Table 1.

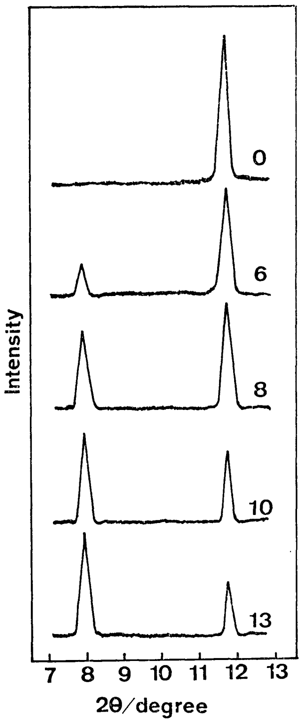

Fig. 1. Schematic diagrams of X-ray powder diffraction at the lowest angle region. Numbers in the figure represent the number of ion-exchange run.

Table 1. Interplanar spacings (*d*-values) of ZP–Co

d/nm	I/I_0
1.116	100
0.763	49
0.564	23
0.379	8
0.369	8
0.358	21
0.331	6
0.307	55
0.265	10
0.252	4
0.241	7
0.188	12

If the ammonia in the complex cation is abstracted directly by α-ZP or converted to the ammonium ion, thus contributing to the ion exchange, the ammonium form of α-ZP will be present. Since the interlayer distance of the ammonium form is 0.94 nm, the peak must be observed at $2\theta=9.4°$. This peak did not appear in powder diffractograms, however.

At the final stage of the ion exchange, the phase of α-ZP was still present (Table 1), indicating that not all the protons in α-ZP were replaced by $[Co(NH_3)_6]^{3+}$.

The IR spectra of ZP–Co and the ammonium form of α-ZP are shown in Fig. 2. The IR spectrum of α-ZP has been studied previously, and several bands have been assigned.18) The absorption bands which appear in α-ZP are denoted by the symbol α in the figure. The ammonia in hexaamminecobalt(III) ion gave absorptions in the regions of 3000—3400, 1550—1650, 1300—1400, and 800—950 cm^{-1}.19) It is clear that the spectrum of ZP–Co is composed of those of α-ZP and the hexaamminecobalt(III) ion, except for the region of 800—950 cm^{-1}, where the rocking vibrations are expected. According to Fujita *et al.*, the rocking mode is sensitive to the kinds of outer ions present and the hydrogen bonding, and the absorption band is shifted to higher frequencies by these effects.20)

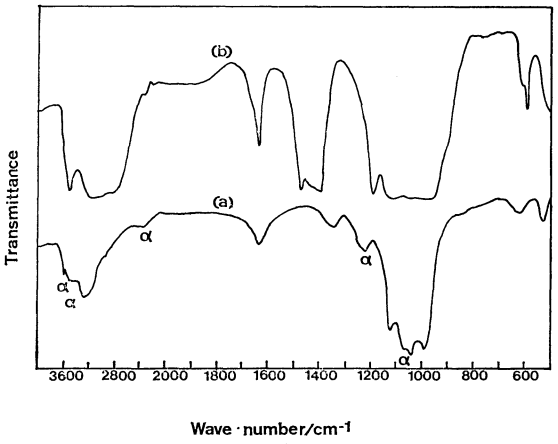

Fig. 2. IR spectra of (a) ZP–Co and (b) the ammonium form of α-ZP.

As is shown in Curve b, the ammonium ion of α-ZP gave strong and characteristic bands in the region of 1400—1500 cm^{-1}, but these bands were absent in Curve a. These facts indicate that the cobalt(III) ion was present as an ammine complex in the exchanger and that the ammonia molecules formed a hydrogen bond with the phosphate group; consequently, the rocking mode shifted to higher frequencies and overlapped with the absorption bands of phosphate.

In order to ascertain the ratio of cobalt to ammonia in ZP–Co, the composition was determined. Found: Zr, 23.8 (1.00); PO_4, 49.4 (1.99); Co, 4.53 (0.292); N, 6.40 (1.74); H, 2.68 (10.2); ignition loss, 22.6% (—). The values in parentheses are the molar ratio of each element to zirconium. It should be noted that the molar ratio of cobalt to ammonia is 1:5.96.

Figure 3 shows that ZP–Co was decomposed when heated in four steps. For each decomposition peak the presence of ammonia was examined by means of evolved gas analysis. Ammonia was detected at the third step. In static air, this decomposition was exothermic because of the oxidation of the evolved ammonia. The presence of zirconium pyrophosphate was confirmed by heating ZP–Co to about 900 °C (Fig. 4). This indicates that the unexchanged monohydrogen orthophosphate group (–HPO_4) was present in ZP–Co, was converted to pyrophosphate, and lost water at high temperatures.

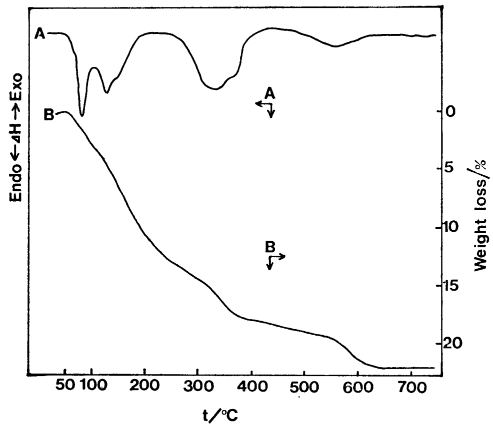

Fig. 3. DSC(A) and TGA(B) curves of ZP-Co.

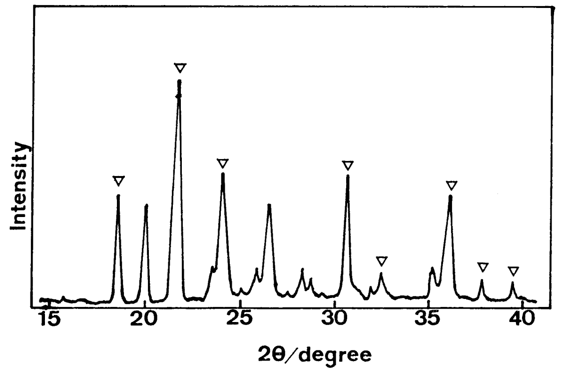

Fig. 4. Schematic diagram of X-ray powder diffraction pattern of the sample obtained by heating ZP-Co to about 900 °C. The symbol ▽ denotes the peak originating from ZrP_2O_7.

Assuming that the formula for ZP–Co is $Zr[Co(NH_3)_6]_m(H)_{2-3m}(PO_4)_2\cdot nH_2O$ (m=0—2/3) and that the reduction of Co(III) does not occur, ZP–Co decomposes according to these reactions:

$$Zr[Co(NH_3)_6]_m(H)_{2-3m}(PO_4)_2\cdot nH_2O \longrightarrow$$
$$ZrCo_m(H)_{2-3m}(PO_4)_2(s) + 6mNH_3(g) + nH_2O(g)$$
$$ZrCo_m(H)_{2-3m}(PO_4)_2 \longrightarrow (1-3m/2)ZrP_2O_7(s) +$$
$$3m/2ZrCo_{2/3}(PO_4)_2{}^*(s) + (2-3m)/2H_2O(g)$$

(The compound marked with an asterisk could not be identified by means of its X-ray diffraction pattern.) The weight loss by heating is calculated by means of the following equations:

$$100\times(17.03\times 6m+18.01\times n)/M_w = w_1(\%) \qquad (1)$$
$$100\times[17.03\times 6m+((2-3m)/2+n)\times 18.01]/M_w = w_2(\%), \qquad (2)$$

where M_w is the molecular weight of ZP–Co, and where w_1 and w_2 are the percentages of weight loss during heating to 420 and 900 °C respectively.

When the cobalt(III) ion in ZP–Co is reduced in the thermal decomposition, as in the case of $[Co(NH_3)_6]X_3$ (X=Cl, Br, I),[21] ZP–Co decomposes through these reactions:

$$Zr[Co(NH_3)_6]_m(H)_{2-3m}(PO_4)\cdot nH_2O \longrightarrow$$
$$ZrCo_m(H)_{2-2m}(PO_4)_2(s) + 17m/3\,NH_3(g) +$$
$$m/6N_2(g) + nH_2O(g)$$
$$ZrCo_mH_{2-2m}(PO_4)_2 \longrightarrow$$
$$(1-m)ZrP_2O_7(s)+mZrCo(PO_4)_2{}^*(s) + (1-m)H_2O(g)$$

Thus, Eqs. 1 and 2 become:

$$100\times(17.03\times 6m+18.01\times n-1.01\times m)/M_w$$
$$=100W/M_w=w_1\ (\%) \qquad (3)$$
$$100\times[W+(1-m)\times 18.01]/M_w=w_2\ (\%). \qquad (4)$$

The experimental values agreed approximately with those calculated according to Eqs. 3 and 4 (Table 2). These facts indicate that the reduction of the cobalt(III) ocurred during heating.

Table 2. Weight loss of ZP-Co by heating (%)

	Experimental	Calculated	
		Eqs. 1 and 2	Eqs. 3 and 4
420 °C	18.0	17.8	18.2
900 °C	22.6	20.5	21.7

In conclusion, the hexaamminecobalt(III)-hydrogen ion exchange partially proceeded in spite of the steric hindrance in the crystal structure of α-ZP. Cobalt(III) was present as a hexaammine complex cation in the exchanger.

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