Tetraammineplatinum(II)-Hydrogen Ion Exchange on α-Zirconium Phosphate and the Characterization of Its Complex Cation Form[1]

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The tetraammineplatinum(II)-hydrogen-ion exchange on α-zirconium phosphate has been investigated. The ion-exchange process was examined by measuring the change in the pH values of the supernatants. α-Zirconium phosphate loaded with tetraammineplatinum(II) was characterized by means of chemical analysis, X-ray diffractometry, infrared spectroscopy, and thermal analysis. The ion-exchange reaction proceeded more easily than the hexaaminecobalt(III)-hydrogen-ion exchange, and about 50% of the hydrogen ions in α-zirconium phosphate were replaced by tetraammineplatinum(II). The interlayer distance of the exchanger expanded from 7.60 to 10.7 Å.

α-Zirconium phosphate Zr $(HPO_4)_2 \cdot H_2O$ (α-ZP) has ion-exchange properties and catalytic activities. Though the great majority of work on α-ZP has dealt with the ion exchange, some catalytic properties have been studied.[2] Also, it has been pointed out that α-ZP can be used as a catalytic support.[3] In this case, the catalyst may be prepared as follows: Metal cations are exchanged with the protons in α-ZP and then reduced to a metallic state. The resultant catalyst may have two functional components, a metal and an acidic hydrogen; that is, it may work as a bifunctional catalyst, especially when the metal is one of the platinum group.[4]

On the other hand, α-ZP has a layered structure and can form many intercalation compounds.[5] Since salt forms of α-ZP also have a layered structure, a specific reaction can be expected between those layers.

The ion-exchange properties of α-ZP are influenced by its crystallinity, which depends on the method of preparation.[6] When α-ZP is applied to a catalyst or a catalytic support, it is not necessary for α-ZP to be highly crystalline. The direct precipitation method has been employed during the course of these investigations so as to avoid differences due to the crystallinity. In the previous paper it was found that the hexaamminecobalt(III) ion, which is large, can exchange with the protons in α-ZP under suitable conditions.[7] In this work, the tetraammineplatinum(II)-hydrogen-ion exchange was studied by the batch method, and the exchanger loaded with the complex cation (ZP-Pt) was characterized by means of chemical analysis, X-ray powder diffractometry, infrared spectroscopy, and thermal analyses.

Experimental

Preparation of α-ZP and Tetraammineplatinum(II) Chloride. The α-ZP was prepared by the direct precipitation method.[8] The tetraammineplatinum(II) chloride was prepared according to the method of Kukuskine and Dkhara.[9] Identification was made by elemental analysis and X-ray powder diffraction. The residue (ash) is assumed to be platinum metal. Found: Pt, 55.45; N, 15.91; H, 3.69; Cl, 19.39%. Calcd for $[Pt(NH_3)_4]Cl_2 \cdot H_2O$: Pt, 55.45; N, 15.91; H, 3.43; Cl, 20.14%. Though the X-ray diffraction pattern of $[Pt(NH_3)_4]Cl_2 \cdot H_2O$ has been previously presented,[10] it differs from the one obtained in this work. This difference is caused by the facts that (1) only the strong reflections were recorded in the file, (2) the intensity of some diffraction peaks varied under the present experimental conditions, and (3), consequently, some peaks not listed in the file were observed as strong ones in this work. Cox analyzed the crystal structure of the complex and gave the lattice constants as $a_0=7.39\pm0.02$ and $c_0=4.21\pm0.02$ Å, and the space group as *P4/mmn*.[11] Cox and Prestone later corrected a_0 to 14.76 Å.[12] Since the diffraction peaks observed were indexed according to these constants in either case, the complex prepared was identified as $[Pt(NH_3)_4]Cl_2 \cdot H_2O$.

Ion Exchange. The ion-exchange procedures were similar to those reported previously.[7] The concentration of the complex was 0.02 mol dm^{-3}, the reaction time, 48 h, and the reaction temperature, 25 °C.

Chemical Analysis. A weighed amount of ZP-Pt was mixed with sodium peroxide powder. Twenty-five ml of water were added to the mixture in an ice bath. The slurry thus obtained was placed on a water bath and heated for several hours. Then, the precipitate was filtered off and dissolved in hydrochloric acid. Zirconium was precipitated as cupferrate from the solution and determined gravimetrically. The filtrate was neutralized with hydrochloric acid and then another 5 ml of the acid were added to it. Platinum was separated as platinum sulfide by using thioacetamide as a homogeneous precipitant. The phosphorus was determined according to the literature.[13]

Thermal Analysis. The differential scanning calorimetric (DSC) data were obtained with a Rigaku differential scanning calorimeter. Evolved gas analysis (EGA) was carried out with a Shimadzu pyrolyser-gas chromatograph.[14] The thermogravimetric (TG) curve was obtained with a Shimadzu thermal analyser DT-30 at a heating rate of 10 °C/min under a herium stream.

Structural Study. The structural change in the exchanger was measured by means of X-ray diffractometry. The powder patterns were recorded with a Rigaku Denki Geigerflex diffractometer, using Ni-filtered Cu *Kα* ($\lambda=1.542$ Å). The infrared (IR) spectra were measured on a JASCO DS-403G grating spectrophotometer.

Results and Discussion

Ion Exchange. The pH value of the supernatant solution was used as an indicator to ascertain the degree of the reaction. Figure 1 shows the pH change in the supernatant. In the first ion-exchange run, about 24% of the protons in α-ZP exchanged with the complex cation. The pH values rose, and the amount of the exchange per run decreased as the ion exchange proceeded. Then, the values reached the pH of the original solution. This ion exchange progressed more extensively than that for the hexaamminecobalt(III)-hydro-

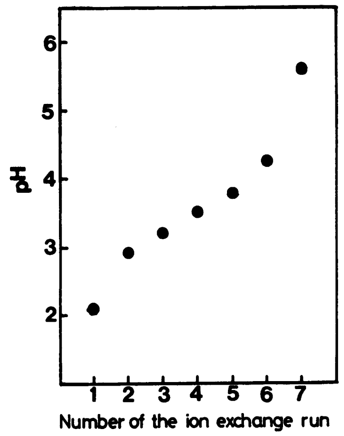

Fig. 1. pH change in the supernatant with the ion-exchange run.

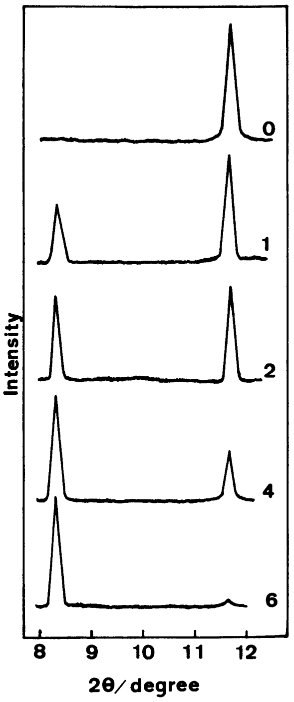

Fig. 2. Change in X-ray powder pattern of the exchanger. Numerals correspond to those of the ion-exchange runs in Fig. 1.

gen ion.[7] This difference may be explained on the basis of the size of the exchanging cation (see below).

In order to investigate the stoichiometry of the ion exchange, the composition of ZP–Pt was determined. Found: Zr, 20.2 (1.00); PO_4, 41.7 (1.96); Pt, 22.1 (0.51); N, 5.91 (1.89); H, 2.22 (9.83); weight loss by ignition, 17.9%. Calcd for $Zr[Pt(NH_3)_4]_{0.5}H(PO_4)_2\cdot1.5H_2O$: Zr, 20.7; PO_4, 43.1; Pt, 22.1; N, 6.53; H, 2.29; weight loss, 17.7%. In the parentheses are given the molar ratios of each element to zirconium. Since the ratio of nitrogen to platinum is equal to 3.7 and the hydrogen content agrees with the theoretical one, it can be said that $[Pt(NH_3)_4]^{2+}$ exchanges with two protons.

Structural Studies. Figure 2 shows the change in the X-ray diffraction patterns of the exchangers. The first peak at 8.3° (interplanar spacing of 10.7Å) appeared at the beginning of the ion exchange, and its intensity increased with the progress of the ion exchange. The intensity of the second peak decreased until it almost disappeared at the final stage of the ion exchange. The interplanar spacings of ZP–Pt are shown in Table 1.

TABLE 1. INTERPLANAR SPACINGS (*d*-VALUES) OF ZP–Pt

d/Å	I/I_0	d/Å	I/I_0
10.64	83	2.84	4
9.97	4	2.82	4
5.37	100	2.69	16
5.01	10	2.63	10
4.55	7	2.52	15
4.24	4	2.41	13
4.22	5	2.16	6
4.00	20	2.07	5
3.81	70	1.89	14
3.61	26	1.83	8
3.22	8	1.80	6
3.08	11	1.71	9
3.00	7	1.54	7

It is known that the interlayer distance of α-ZP depends on the cations present between layers. The first and the second peak correspond to the interlayer distances of ZP–Pt and α-ZP. If the ammonias coordinating to platinum are abstracted directly by α-ZP, or if they contribute to the ion exchange as ammonium ions, the ammonium form of α-ZP must be formed and the peak at 9.4° must be observed. As is shown in Fig. 2, this peak was not present in the present diffractograms.

Since the crystal structure of the salt forms of α-ZP has not been analyzed, the relationship between the interlayer distance and the counter-ion size is not clear. Generally, the interlayer distance increases with the size of the counter-ion. One of the salt forms, $ZrNaH(PO_4)_2\cdot5H_2O$ (monosodium form), has the interlayer distance of 11.8 Å[15]. The sodium ion was bonded to about four water molecules at the distance of 2.4 Å in a concentrated aqueous sodium iodide solution.[16] Assuming that the sodium ion in α-ZP retains the same structure as in the solution, the sphere with a diameter of 7.6 Å may be said to be present between the layers of the monosodium form. In hexaamminecobalt(III) ammonias coordinate octahedrally, and the complex cation can be assumed to be a sphere with a diameter of 7.6 Å.[17] The interlayer distance of ZP–Co was 11.2 Å (ZP-Co is α-ZP loaded with $[Co(NH_3)_6]^{3+}$).[7] The two interlayer distances are almost equal, in accordance with the size of the cations present. According to Cox, tetraammineplatinum(II) has a square planar structure, and the length of the side and the thickness can be estimated to be 5.7 and 2.8 Å respectively.[11] The platinum complex cation can be arranged between layers in three manners, namely, perpendicular, inclined, and parallel to the layer of α-ZP. The interlayer distance of ZP–Pt was 10.6 Å, slightly shorter than that of ZP–Co. This suggests that the plane of tetraammineplatinum(II) is not parallel to the layer of α-ZP.

The IR spectra of ZP–Pt and the ammonium form of α-ZP are shown in Fig. 3. The absorption bands whcih are

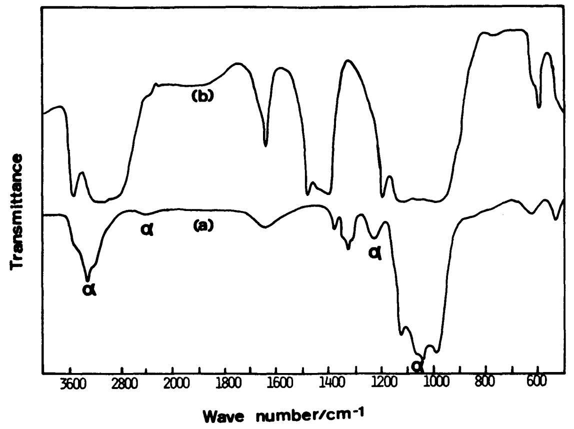

Fig. 3. IR spectrum of ZP–Pt (a) and the ammonium form of α-ZP (b).

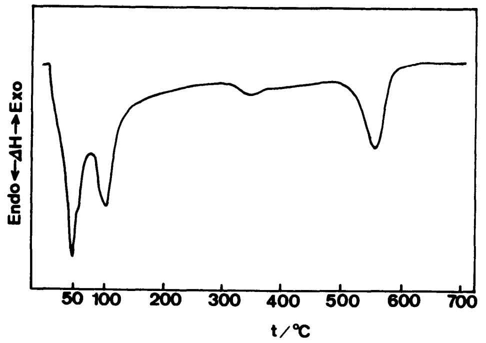

Fig. 4. DSC curve of ZP–Pt.

assigned by Horsley *et al.* are denoted by the symbol α in the figure.[18] The ammonia in tetraammineplatinum(II) ion gave absorptions at 3130, 1630, 1570, 1370, 1352, 1333, and 840 cm^{-1}.[19] The spectrum of ZP–Pt was composed of that of α-ZP and the tetraammineplatinum(II), except for the absorptions at 840 and 1570 cm^{-1}. These bands were assigned to the degenerate deformation and the rocking vibration of ammonia. According to Fujita *et al.*, the rocking vibration is sensitive to the kind of outer ion and the hydrogen bonding, and the absorption band is shifted to higher frequencies by these effects.[20] In ZP–Pt the ammonias form hydrogen bonds with the surrounding phosphate groups; consequently, the rocking vibration shifted and overlapped with the absorption bands of phosphate in the 900—1200 cm^{-1} region. It is considered that the absorption of 1570 cm^{-1} was shifted by the same cause and was observed in the 1500—1700 cm^{-1} region as a single band.

Thermal Studies. The DSC curve is shown in Fig. 4. The thermal decomposition took place in four steps, all of them endothermic. The evolution of ammonia was examined for each step. Ammonia was detected only at the third step. When ZP–Pt was decomposed in static air, the third step was observed as exothermic. This shows that the evolved ammonias were oxidized at the surface of a platinum crucible.[21] The ZP–Pt turned black after the third step, indicating that the platinum(II) ion in the solid was reduced to platinum(0) during the thermal decomposition and that nitrogen gas was evolved.

Table 2. Weight loss of ZP–Pt upon heating

t/°C	Experimental(%)	Theoretical(%)
200	8.39	6.13
420	13.4	13.6
600	17.9	17.7

In Table 2 the weight loss by heating is shown. Assuming that the possible decomposition pathways are as in the following scheme, the theoretical values are obtained. The experimental values agreed well with the theoretical ones at 420 and 600 °C, but the agreement is poor for the decomposition at 200 °C. At present it is impossible to give a proper interpretation of this disagreement.

$$\mathrm{Zr[Pt(NH_3)_4]_{0.5}H(PO_4)_2\cdot 1.5H_2O(ZP\text{-}Pt)} \xrightarrow{\approx 200\,^{\circ}\mathrm{C}}$$

$$\mathrm{Zr[Pt(NH_3)_4]_{0.5}H(PO_4)_2\ (I)} \xrightarrow{\approx 420\,^{\circ}\mathrm{C}} \mathrm{ZrPt(0)(HPO_4)_2\ (II)}$$

$$\xrightarrow{\approx 600\,^{\circ}\mathrm{C}} \mathrm{ZrPt(0)P_2O_7\ (III)}$$

Scheme 1.

Compounds (II) and (III) were amorphous. The presence of zirconium pyrophosphate could not be detected. When ZP–Pt was heated to about 900 °C in a crucible and then examined by means of X-ray diffractometry, broad peaks were present at $2\theta=39.6$ and 46.4°. These correspond to the (111) and (200) planes of platinum metal.[22]

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