May, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 1535—1538 (1985)* 1535

Hexaamminecobalt(III)-Hydrogen Ion Exchange in α- and θ-Zirconium Phosphates with Various Particle-size Distribution[1)]

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(Received December 17, 1984)

The hexaamminecobalt(III)-hydrogen ion exchange in zirconium phosphates was studied by means of the batch method, mainly with regard to the particle-size distribution of zirconium phosphates. α-Zirconium phosphates were prepared by the direct-precipitation method. The degree of ion exchange increased with the fineness of the zirconium phosphates used. The ion exchange proceeded to a lesser extent in highly crystalline α-zirconium phosphate. θ-Zirconium phosphate with the interlayer distance of 10.4 Å took up the complex cation selectively and easily. Fifty percent of the protons in the θ-zirconium phosphate were thus replaced with hexaamminecobalt(III), and the interlayer distance was expanded to 11.2 Å.

An inorganic ion exchanger, α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, has been investigated by many workers. Its crystal structure is known precisely, and the ion-exchange behavior toward many cations has been discussed with regard to the structure.[2,3)] α-Zirconium phosphate acts as an ion-sieve due to its structural restriction. However, α-zirconium phosphate can also be used as an ion-exchanger with large cations, such as cobaltcene, hexaamminecobalt(III), and tetraammineplatinum(II) ions, in spite of probable steric hindrance.[4—6)]

The ion-exchange properties of α-zirconium phosphate have been influenced by the method of preparation, since the method has much effect on the crystallinity and particle-size distribution.[7)] Although the effect of crystallinity has been studied extensively, that of particle size has been investigated only for the potassium–hydrogen ion exchange by means of α-zirconium phosphate, which has the same crystallinity.[8)]

α-Zirconium phosphate also has a possibility of use as a catalyst or catalytic support.[3)] When α-zirconium phosphate is applied to a catalytic support, a complex cation which has an ionic radius larger than 1.3 Å may be used. Hexaamminecobalt(III) was selected as a model of the complex cation, and the ion exchange was studied previously. In this case, not all the protons in α-zirconium phosphate involved in the ion exchange, and the unreacted α-zirconium phosphate coexisted with the hexaamminecobalt(III) form of α-zirconium phosphate.[5)] During the course of these experiments, our attention was called to a subtle difference in the ion-exchange behavior among α-zirconium phosphates toward the complex cation.

According to Haynes, Jr., the particle-size distribution should be considered in some cases in estimating catalytic effectiveness in a heterogeneous catalyst.[9)] Synthetic zeolite catalysts are typical examples of this case. Hence, it is of interest to study the hexaamminecobalt(III)–hydrogen ion exchange with regard to the particle-size distribution of α-zirconium phosphate.

Alberti *et al.* pointed out that a highly hydrated zirconium phosphate, for example, θ-zirconium phosphate, can easily exchange several cations with large ionic radii.[10)] However, their method of preparation was complex in procedure, and severe conditions were required for the starting material. Since Kijima recently reported a simple method of preparation,[11)] the same ion exchange has now been studied with θ-zirconium phosphate.

Experimental

Preparation of α- and θ-Zirconium Phosphates and Hexaamminecobalt(III) Trichloride. α-Zirconium phosphates were prepared by two direct-precipitation methods. One of the methods was previously reported, and Samples A and B were obtained.[12)] When Sample A was prepared, the zirconium dichloride oxide octahydrate used as a starting material was purified to remove the free hydrochloric acid; Sample B was prepared without the purification. The Inoue and Yamada method was modified to prepare Sample C.[13)] The following conditions were employed: $ZrOCl_2 \cdot 8H_2O$ 0.26 mol dm^{-3}, HF 1.7 mol dm^{-3}, H_3PO_4 6.2 mol dm^{-3}; reaction temperature, 50 °C, and reaction time, 120 h. Since large crystallites were obtained, the products were sieved and the fraction under 400-mesh was used. Sample D was prepared from the large crystallites obtained in the preparation of Sample C. They were ground and sieved under a 400 mesh.

θ-Zirconium phosphate, $Zr(HPO_4)_2 \cdot 6H_2O$, was prepared according to the literature.[11)] The exchanger thus obtained will herein be referred to as Sample E. Identification was made by means of X-ray diffractometry.

Hexaamminecobalt(III) trichloride, $[Co(NH_3)_6]Cl_3$, was prepared according to the literature.[14)]

Ion Exchange. The ion exchange was carried out by the batch method. In view of the rate of the reaction and the stability of hexaamminecobalt(III) ions in the solution, the experimental conditions were determined as follows; the concentration of the complex cation, 0.02 mol dm^{-3}, reaction temperature, 90 °C, and reaction time, 30 min. After the end of the reaction, the exchanger was separated by centrifugation. The pH value of the supernatant was determined with a pH meter. The exchanger was again added to a new complex solution, and the ion exchange was carried out. This procedure was repeated until the pH value of the supernatant was over 5.

Particle-size Distribution and Structural Study. The particle-size distribution was measured with a Shimadzu centrifugal particle-size analyzer SA-CP2 for Samples A, B, and C and with a Seishin Kogyo microphotosizer SKA-5000 for Sample D. Distilled water or a sucrose solution was used as the dispersion medium.

The crystallite size of zirconium phosphates was estimated from the Scherrer equation: $D=K\lambda/\beta\cos\theta$, where K=constant(0.9), β=corrected breadth at half-height, λ=wave length(1.542 Å), and θ=Bragg angle.[15]

The change in the interlayer distance was observed by means of X-ray diffractometry. The powder patterns were recorded with a Rigaku Denki Geigerflex diffractometer, using Ni-filtered Cu $K\alpha$ radiation(λ=1.542 Å).

Results and Discussion

Particle-size Distribution. Since α-zirconium phosphate has a layered structure and has been obtained as thin hexagonal or triangular platelets,[2] the apparent Stokes radius should be considered as an approximate index. The particle-size distribution curves are shown in Fig. 1. Sample A had the *D*50 of 3 μm, where *D*50 means 50% diameter(median size); most of the fraction of the particles was present under 2 μm. The *D*50 of Sample B was 2 μm, and 32% of the particles were present between 2—1 μm. The particles of Sample C were coarse. The *D*50 was equal to 30 μm, and 50% of the sample had a diameter of 20—30 μm. Two percent of the sample were present under 5 μm. Sample D was more coarse than Sample C and had a *D*50 of 50 μm. Both Samples C and D had much the same high crystallinity.

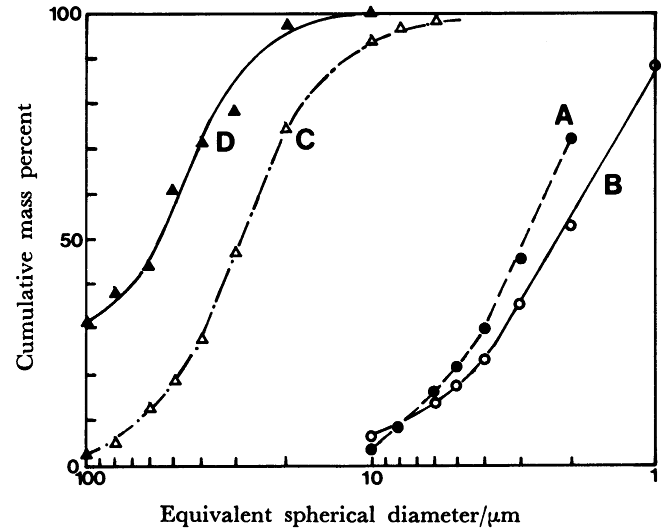

Fig. 1. Particle size distribution of Samples A,B,C, and D.

Since Sample E (θ-zirconium phosphate) was very fine, the crystallite size was measured by means of X-ray diffractometry. Sample E had an average thickness of 0.06 μm in the direction of (002). Another sample of α-zirconium phosphate (Sample F) was obtained by drying θ-zirconium phosphate in air at room temperature. The particle size of Sample F in the direction of (002) was almost equal to 0.04 μm. The estimated size is compatible with the predicted value of 0.043 μm. Since the interlayer distance of θ-zirconium phosphate decreases upon drying from 10.4 to 7.6 Å, it is possible to predict the crystallite size of Sample F. The crystallinities of Sample E and F can be considered to be much the same. The order of particle sizes was as follows: Sample F<Sample E<Sample B<Sample A<Sample C<Sample D.

Ion Exchange. The pH value of the supernatant solution was employed as an index to estimate the degree of the ion-exchange reaction.

Figure 2 shows the pH change in the supernatant. Sample A and B behaved similarly. Here, the reaction proceeded considerably at the early runs of the ion exchange. The pH change was moderate through the whole ion-exchange runs in Sample C. The degree of ion exchange per run was smaller in Sample C than in Samples A and B. In contrast to Sample C, the pH values increased rapidly in Sample D.

The above fact indicate that the particle-size distribution of the exchanger was related to the ion-exchange behavior and the degree of ion exchange. The smaller the particles were, the more easily could the reaction take place. When the pH change in Sample C is compared with that of Sample D, it can be stated that, even though the exchangers have the same crystallinity, the ion-exchange behavior differs significantly. The difference between Samples

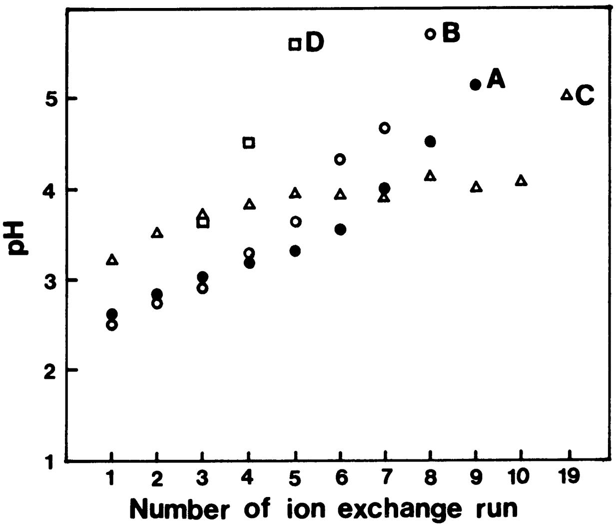

Fig. 2. pH change in the supernatant with the ion-exchange run for Samples A,B,C, and D.

In Sample C pH values of the first two runs overlapped with those of Sample A.

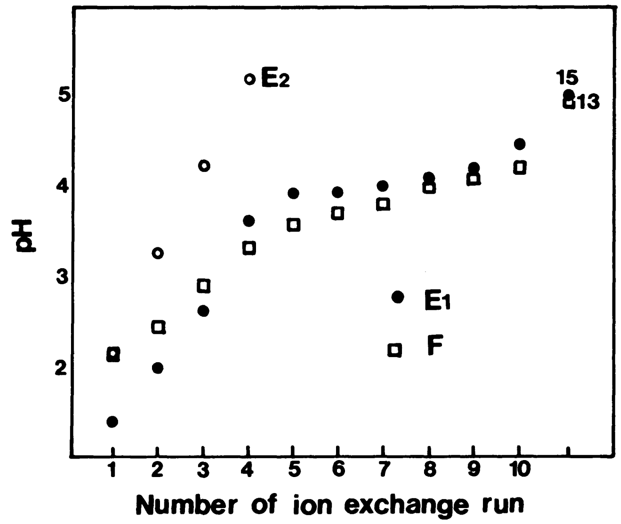

Fig. 3. pH change in the supernatant with the ion-exchange run for Samples E and F.

A and B and Sample D is probably caused by the nature of the surfaces. Since the cleavage of α-zirconium phosphate by grinding will take place mainly at the (002) plane, it is probable that the ratio of the protons on the surface to those in the crystallite increases and that the ion exchange accelerates at early runs.

The pH change in Samples E and F is shown in Fig. 3. Since θ-zirconium phosphate easily lost hydrated waters and changed to α-form in air, it must be stored in distilled water. Therefore, it is unable to weigh the exchanger to be used. In this figure, two typical pH changes are shown. The ratio of the amounts of exchanger to the volume of the complex solution was larger for E1 than for E2. The two curves appear quite different. The curves show that the pH value of the supernatant was lower for E1 than for E2 and that E1 needed more ion-exchange runs to the end of the reaction. For this difference, there are two possible explanations. One is that more complex cations must be used to replace more protons. Another is that, because the complex cation is more stable in an acidic solution than in a neutral or alkaline solution, the ion-exchange reaction proceeded more for E1.

The ion-exchange reaction proceeded extensively, especially when the ratio was high. When the complex solution was added to Sample E, the color of the exchanger surface turned orange, the same as the complex cation. These facts indicate that the ion exchange occurred fast, even at room temperature. The pH value of the supernatant for E1 was significantly low in the first run. This means that θ-zirconium phosphate took up selectively the complex cation and that the degree of the reaction was high.

In Sample F the ion exchange proceeded similarly to Samples A and B, though the pH values were lower in the first two ion-exchange runs. This is probably because the particle size of Sample F was smaller than that of Samples A and B.

Table 1. Content of nitrogen, hydrogen, and ignition loss

Sample	N(%)	H(%)	Ig. loss (%)	(H/N) molar ratio
Sample A	5.48	2.45	19.99	6.19
Sample B	6.93	2.75	21.51	5.57
Sample C	3.03	1.97	16.81	9.02
Sample D	3.02	1.95	17.14	8.98
Sample E	7.25	2.81	24.46	5.38
Sample F	4.70	2.26	19.12	6.69

Table 1 shows the contents of nitrogen and hydrogen and the ignition loss of the sample. It is possible for the molecular formula of the exchanger at the final ion-exchange run to be represented as $Zr[Co(NH_3)_6]_x(H)_{2-3x}(PO_4)_2\cdot 2H_2O(x=0—2/3)$(see below for Sample E($\theta$-zirconium phosphate)).[5,16)] The amount of nitrogen is $6x$, and that of hydrogen, $18x+(2-3x)+4=15x+6$. Thus, the following relationship is derived: molar ratio of hydrogen to nitrogen, $r=H/N=(15x+6)/6x=2.5+1/x$. When x is equal to 1/3, r becomes 5.5. This is the case for Sample E. Consequently, the larger the ratio r, the lower the degree of the ion-exchange. The degree almost corresponded to that predicted from Figs. 2 and 3 and to the order of particle size except for Sample F. For this anomalous behavior of Sample F, no adequate explanation can be given.

For θ-zirconium phosphate the compound obtained on the final ion-exchange run, referred to as θ-ZPCo, was analyzed chemically. Found; Zr, 23.9 (1.00): PO_4, 48.9 (2.02): Co, 5.15 (0.33): N, 7.25 (1.98): H, 2.81% (10.6). In parentheses are given the molar ratio of each element to zirconium. Calcd for $Zr[Co(NH_3)_6]_{0.33}H(PO_4)_2\cdot 2H_2O$; Zr, 24.5: PO_4, 51.5: Co, 5.28: N, 7.53: H, 2.99%. It should be noted that the ratio of nitrogen to cobalt was equal to 5.9. It can be stated that fifty percent of the protons in θ-zirconium phosphate were exchanged with the hexaamminecobalt(III) ion.

Structural Study. It is well known that the interlayer distance of zirconium phosphate is dependent on an existing cation between layers. In general, two peaks due to the original zirconium phosphate and its salt form appear in the lowest-angle region of an X-ray diffractogram.[5,6)] Hence, the approximate degree of the ion exchange can be estimated by comparing the intensity of the two peaks. After the final ion-exchange run, an X-ray diffractogram of each sample was recorded. As is shown in Figs. 4 and 5, the interlayer distance of α-zirconium phosphates expanded from 7.6 Å($2\theta=11.7°$) to 11.2 Å($2\theta=7.7°$).

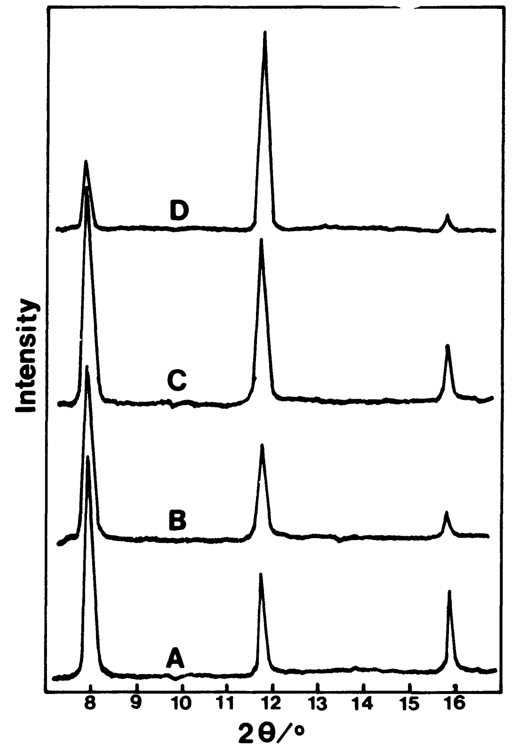

Fig. 4. Schematic diagram of X-ray powder diffraction at the lowest angle region for Samples A,B,C, and D.

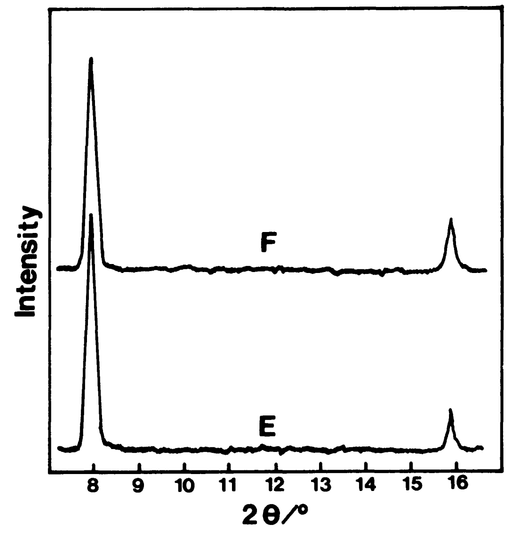

Fig. 5. Schematic diagram of X-ray powder diffraction at the lowest angle region for Samples E and F.

The X-ray diffractograms of Samples A and B were similar, but that of Sample C was different. The diffractogram of Sample D showed that most of the α-zirconium phosphates were present unreacted. These facts agreed with what would be expected from Table 1.

An interlayer distance of 11.2 Å was observed, and the peak of 10.4 Å corresponding to the interlayer distance of θ-zirconium phosphate disappeared in the first ion exchange of Sample E1. Since the difference between the two distances was small, and since θ-zirconium phosphate took up considerable amounts of the complex cation, the interlayer distance could expand easily.

In the case of Sample F, only the peak of 11.2 Å was present in the diffractogram. This differed distinctly from the cases of other α-zirconium phosphates and suggests that hydrogen–hexaamminecobalt(III) ion-exchange can be affected by factors other than those discussed in this work.

We are grateful to Mr. Seiichiro Iwafune for his measurements of the particle-size distribution.

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