CHEMISTRY LETTERS, pp. 241-244, 1980.

HEXAAMMINECOBALT(III)-HYDROGEN ION-EXCHANGE ON CRYSTALLINE ZIRCONIUM PHOSPHATE

Yoshitsugu HASEGAWA and Seiichi KIZAKI
Department of Industrial Chemistry, Faculty of Technology,
Tokyo University of Agriculture and Technology,
Nakamachi, Koganei, Tokyo 184

The ion-exchange reaction was studied by the batch method at 75 °C. The reaction proceeded in the pH region of 3-6. The analysis of the exchanged solid showed that $Co(NH_3)_6^{3+}$ exchanged with the protons in the exchanger, and that two phases, the cobalt complex form and α-zirconium phosphate, were present in the solid.

Many investigations have been carried out on the ion-exchange properties of crystalline zirconium phosphate $Zr(HPO_4)_2 \cdot H_2O$ (α-ZP). The application of α-ZP to a catalytic support has been also studied recently.1) Since α-ZP has a layered structure, the ion-exchange reaction is restricted by the size of exchanging cation because of steric hindrance. It will be difficult for a complex cation such as a metal ammine complex to exchange with the protons in α-ZP. The direct titration of α-ZP with MA_n + $M(OH)_m$ where M=metal cation and A=anion is often not suitable to prepare the metal cation-exchanged α-ZP, because many hydroxides are insoluble in water. In some cases an acetate of metal was used.2) However, if an acetate is also insoluble, for example platinum diacetate, the metal cation-exchanged α-ZP must be prepared by the replacement of protons in the exchanger with the metal complex cations. It is convenient to use an ammine complex cation, because the ligands are easily removed by heating. In this work hexaamminecobalt(III) ion was chosen as a model of complex cation, and the ion-exchange with the proton in α-ZP was investigated.

α-ZP was prepared by the direct precipitation method.3) Hexaamminecobalt(III) trichloride was prepared according to the literature.4) Identification was made with the X-ray powder diffraction pattern.5) The ion-exchange was carried out as follows. A weighed amount of α-ZP (500 mg) was placed in a flask and 100 cm^3 of 0.025 mol dm^{-3} hexaamminecobalt(III) trichloride solution was added. Then, the mixture was refluxed at 75°C. It took about half an hour to attain equilibrium. A reaction time of 1 h was chosen. The solid phase was centrifuged and the pH value of the supernatant was measured on a pH meter with a glass electrode. The solid was again added to 100cm^3 of the new complex salt solution. The procedure was repeated until the pH of the supernatant became 5.3-6.0. The resulting exchanger (referred to as ZP-Co) was washed with distilled water until free from chloride ion.

The X-ray diffraction pattern was obtained with a Geigerflex X-ray diffractometer with nickel filtered copper radiation. 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-gaschromatograph.[6] The composition of ZP-Co was chemically analysed.

The pH value of the supernatant was equal to about 3 at the beginning of the ion-exchange reaction and gradually increased with the process. The equilibrium pH lay between 3 to 4 and reached 6 at the end of the whole process. ZP-Co was orange in color which was the same as that of the complex salt solution.

Figure 1 shows the X-ray powder diffraction pattern of ZP-Co. The first reflection peak at 7.9° corresponding to the interplanar spacing of 11.2 Å appeared at the beginning of the ion-exchange and the intensity increased with the reaction. On the other hand, the peak of 7.6 Å (11.7°) decreased during the course of the ion-exchange. This peak represents the interlayer distance of α-ZP. Several peaks of original α-ZP were found in the diffraction pattern of ZP-Co. The presence of α-ZP was confirmed by heating the sample to about 900°C, because α-ZP was converted into zirconium pyrophosphate. The peak of 9.4 Å (9.4°) was not observed in Fig.1. This means that the ammonium form of α-ZP was not formed in the process of the ion-exchange. The X-ray diffraction pattern varied with heating of ZP-Co. The first peak shifted to 8.7 Å at 200°C and disappeared

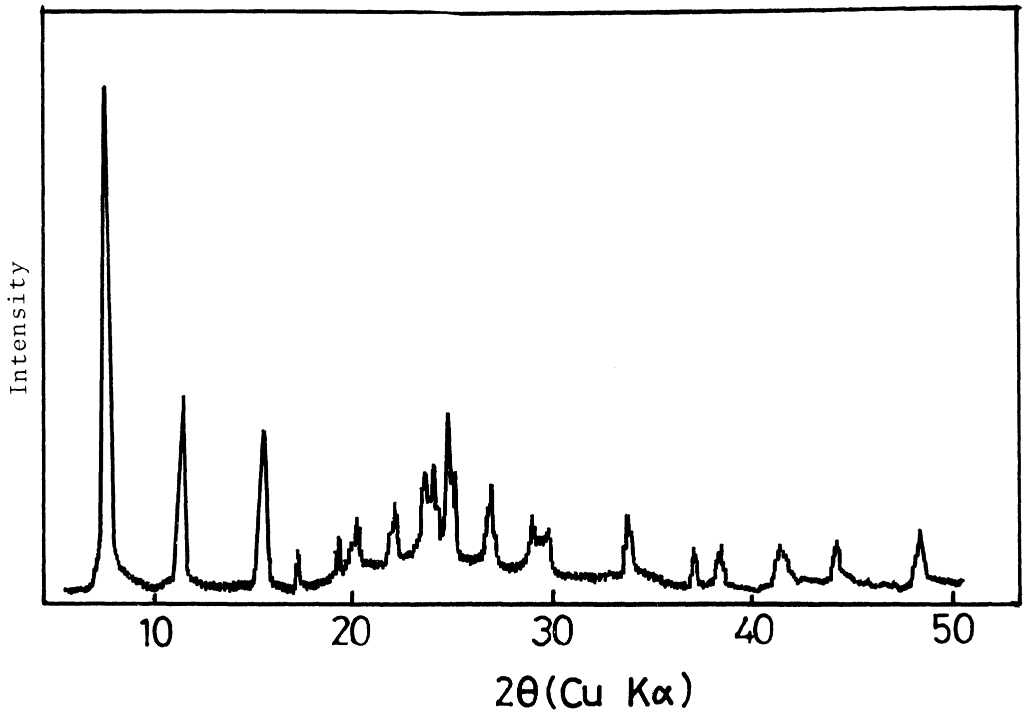

Figure 1. X-ray diffraction pattern of ZP-Co.

at 420 °C. The change in the second peak was little. This is also the case for α-ZP.3) These facts indicate that the hexaamminecobalt(III)-hydrogen ion-exchange occurred on α-ZP in spite of steric hindrance, though the exchange was not complete.

Figure 2 shows the DSC (a) and EGA (b) curve. The eluted gas was caught in 0.1 mol dm^{-3} hydrochloric acid and ammonium ion was detected with sodium tetraphenyl borate. The change in color was observed at every stage of endothermic decomposition in DSC experiment. In the temperature region of 100-120 °C dehydration occurred, because ammonia was not detected with EGA. Since the temperature is relatively low, hydrated water(s) is (are) present in ZP-Co. In consideration of the presence of α-ZP, the second peak will be due to release of a zeolitic water in α-ZP.7) The third peak overlapped the second one. The two peaks could not be isolated under the condition employed. Ammonia was evolved in the region of 120-400 °C. The last peak at 550 °C was due to the condensation of phosphate to pyrophosphate.

Weight loss of ZP-Co was measured at 450 and 900 °C as ignition loss. Each loss can be due to the water of hydration and ammonia, and all water including structural water and ammonia. Assuming that the molecular formula of ZP-Co is presented as $Zr[Co(NH_3)_6]_m(H)_{2-3m}(PO_4)_2 \cdot nH_2O$, it is possible to calculate m and n

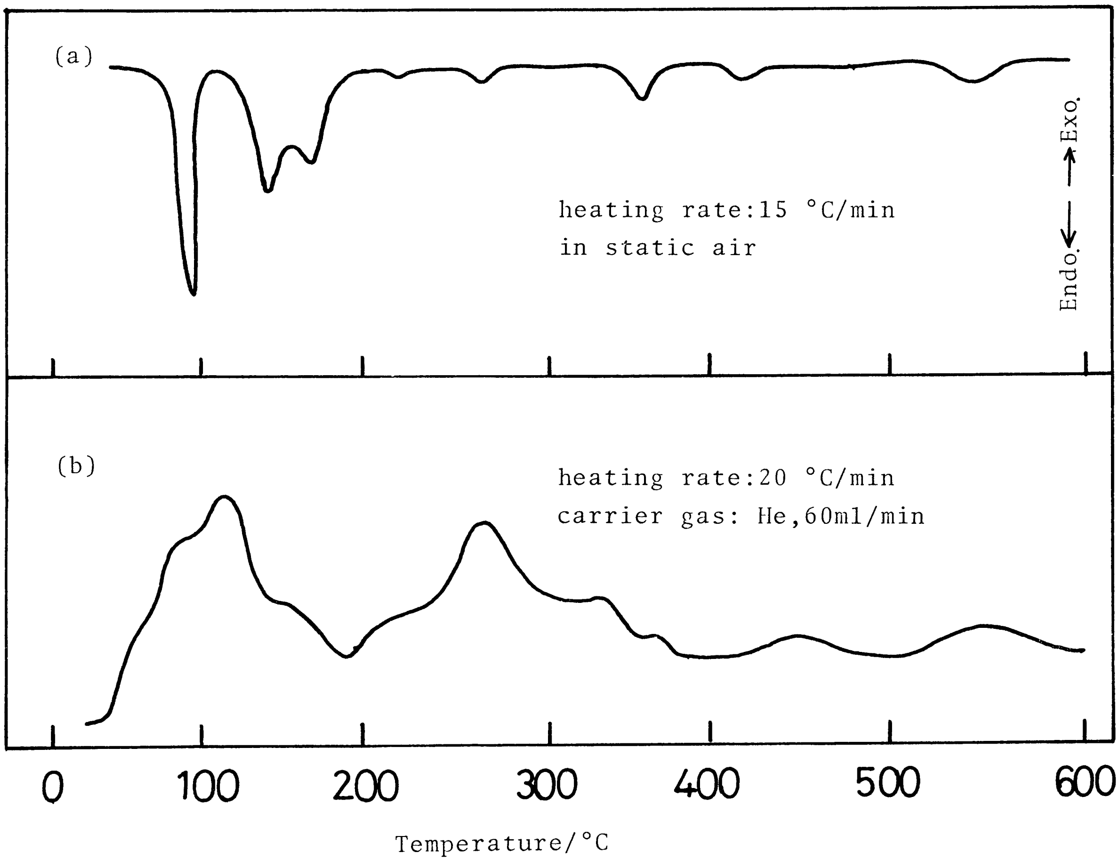

Figure 2. DSC curve (a) and EGA curve (b).

as a function of weight loss. As the value of m largely contributes to weight loss, it should be accurately determined. Weight loss was 19.7 % at 450 °C and 22.3 % at 900 °C. Consequently, the values of m and n are estimated to be 0.31 and 2.3. These agree well with those obtaind by chemical analysis.

After the first decomposition the solid remained orange in color, and then the color turned to greyish blue to blue at 450 °C. When the resulting solid was stood in air for a long time or immersed in water, the color changed to pale pink. These facts support the results of the thermal analysis and indicate that the cobalt cation-exchanged zirconium phosphate was formed by heating of ZP-Co.

Chemical composition was as follows. Found;Zr,24.81%;PO_4,51.66%;Co,4.81%;NH_3, 8.12%;ignition loss,22.27%. Calcd for $Zr[Co(NH_3)_6]_{0.30}(H)_{1.10}(PO_4)_2 \cdot 2.2H_2O$; Zr, 24.69%;$PO_4$,51.42%;Co,4.79%;$NH_3$,8.28%;ignition loss,21.49%.

These findings suggest that a large cation is able to ion-exchange with protons in α-ZP under certain conditions and that it is possible to apply α-ZP to catalytic support.

References

1) G.Alberti, Acc.Chem.Res.,11,163(1978).
2) A.Clearfield and J.M.Kalnins, J.Inorg.Nucl.Chem.,38,849(1976).
3) Y.Hasegawa and M.Kuwayama, Bull.Chem.Soc,Jpn.,51,3485(1978).
4) W.C.Fernelius ed.,"Inorganic Synthesis" Vol.II.pp.216-217, McGraw-Hill, New York (1946).
5) ASTM Powder Diffraction File 21-862.
6) Y.Hasegawa, H.Aoki, and S.Abe, Kikibunseki, 11,648(1973).
7) Y.Hasegawa, Bull.Chem.Soc.Jpn.,46,3296(1973).

(Received December 26, 1979)