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Thermal Decomposition Studies of the Ammonium Forms of the Crystalline Zirconium Phosphate Ion Exchanger

Yoshitsugu Hasegawa
Department of Industrial Chemistry, Tokyo University of Agriculture and Technology, Nakamachi, Koganei, Tokyo 184

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Ammonium-ion exchange on a crystalline zirconium phosphate (c-ZrP) had been studied, and the formation of two phases, $Zr(NH_4PO_4)_{1.33}(HPO_4)_{0.67}\cdot H_2O$ (Phase I) and $Zr(NH_4PO_4)_2\cdot H_2O$ (Phase II), has been found.[1] It is known that c-ZrP has two phosphate protons and that they exist in the ratio of 1 to 1.[2] However, the results obtained earlier for the ammonium-ion exchange showed that the phosphate protons seemed to exist in the ratio of 2 to 1. This result differs from that expected from the known properties of c-ZrP. In the present study, the thermal decomposition of the ammonium forms of c-ZrP was examined by means of thermogravimetry, and the enthalpy changes in the decomposition processes were measured by differential scanning calorimetry. Moreover, the changes in the phases of the samples during heating were analysed by means of X-ray powder diffraction. On the basis of these results, the state of the ammonium ions and the waters in the exchanger were discussed.

Experimental

Preparation of the Samples. c-ZrP and Phases I and II were prepared as has been described in the previous papers.[1,3]

Apparatus and Procedure. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). The TG curves were obtained with a Rigaku TJG-DTA 8020 apparatus in static air, using a platinum crucible. The DSC curves were obtained with a Rigaku DSC 8000 apparatus in a dynamic nitrogen stream and at a flow rate of 300 ml/min. The measurement was made using samples of about 5—10 mg with a mesh size of 100—200 in an aluminum pan. In both thermal measurements, the heating rate was fixed at 5 °C/min. The standard substances used were KNO_3, $KClO_4$, and Zn.

X-Ray Study. The X-ray powder patterns were obtained with Ni filtered copper X-rays, using a Rigaku Geigerflex (Rigaku Denki Co., Ltd.).

Results and Discussion

Table 1. Weight loss on heating phases I and II

Temperautre range (°C)	Total weight loss (%) TG	DSC[a]	Theoretical
Phase I			
70—270	7.4	7.4	7.3
270—400	11.6	12.1	12.5
540—640	16.0	—	18.1
Phase II			
50—270	11.0	10.8	10.4
270—400	16.0	16.0	15.5
540—640	20.0	—	20.9

a) The samples analysed by the differential scanning calorimeter were weighed batchwise after heating.

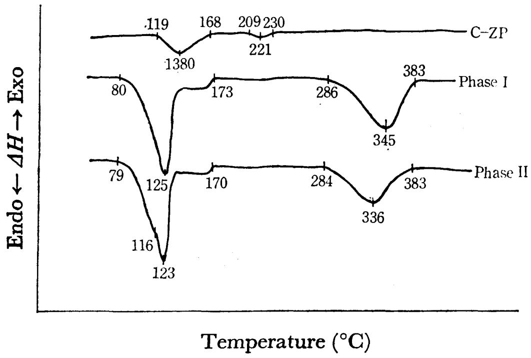

Fig. 1. The DSC curves of c-ZrP, Phases I and II.

Thermal Studies. The thermogravimetric data obtained are shown in Table 1. For each decomposition step, we attempted to detect ammonia by means of evolved gas analysis. Ammonia was found in the first and second steps. As is shown in the DSC curves (Fig. 1), the first decomposition reaction was complex. Thus, the detection of ammonia was carried out at the beginning and at the end of the reaction. Ammonia was not detected at the beginning. Hence, Phases I and II released one mole of water and almost simultaneously 0.33 or one mole of ammonia in the first step. One mole of ammonia was released in the second step. The last step corresponded to the polymerization of *ortho*-phosphate groups.

In the DSC study, the heating rate, the gas-flow rate, and the packing manner of the samples were varied in order to isolate each reaction in the first step, but the attempt was unsuccessful. The DSC curves obtained are shown in Fig. 1. The DSC curves of Phase I agreed with that of Phase II except for the details in the first step. The DSC curves in Fig. 1 showed that the enthalpy changes in the reactions were endothermic.

When the decomposition reactions of Phases I and II were compared with those of the ammonium phosphates of some metals reported by Erdey and Gal,[4] the effect of zirconium on the release of ammonia seemed to be small and the interaction between the ammonium ions and phosphate groups appeared to be dominant. The temperature range corresponding to the first decomposition is similar to that of diammonium

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1) Y. Hasegawa and H. Aoki, This Bulletin, **46**, 836 (1973).

2) A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, **26**, 117 (1964).

3) Y. Hasegawa and I. Tomita, This Bulletin, **43**, 3011 (1970).

4) L. Erdey and S. Gal, *Talanta*, **10**, 23 (1963).

monohydrogen phosphate (max., about 170 °C). The second decomposition-temperature range is similar to the decomposition temperature of ammonium chloride (max., 345 °C) or ammonium sulfate (max., 330 °C).[5] According to Erdey *et al*,[4,5] the decomposition temperature of ammonium salts is inversely proportional to the basicity of the anion bases in the salts. Hence, the ammonia released in the first and second steps will originate from the ammonium ions exchanged with the proton on c-ZrP at higher pH values, and at lower pH values, respectively (see Fig. 1 in Ref. 1). The decomposition temperature observed in the second step is higher than that expected from the basicity of the monohydrogen phosphate group. This is mainly due to the structural change in the solid phase (*cf.* X-ray study).

From the DSC curves in Fig. 1, the characteristics of the water in the ammonium-form exchanger can be deduced to be as follows. The dehydration of c-ZrP in the first step took place at a relatively higher temperature and the enthalpy change was small. This reflects the zeolitic nature of the water in c-ZrP.[6,7] In contrast to c-ZrP, the dehydration of Phases I and II shifted to a lower temperature and the DSC curves resembled that of a hydrated water. This change in the water in the exchanger is more apparent if we compare the enthalpy change, ΔH, for c-ZrP with those for Phases I and II. The ΔH's of c-ZrP and Phases I and II for the first step were equal to 5, 15, and 25 and those for the second step, to 0.6, 13, and 14 kcal/mol, respectively. It is not apparent why the second peak for c-ZrP is present. The ΔH for the dehydration of c-ZrP is about equal to that of the hydrogen bond. The ΔH's in the second step for Phases I and II showed a good agreement. In view of the structural changes in Phases I and II by heating (see X-ray study), it is assumed that the differences in the ΔH's between Phases I and II are due to the presence of 0.67 moles of ammonium in both the forms. Therefore, the enthalpy changes can be calculated to be 10 kcal/H_2O and 15 kcal/NH_3 respectively.

As the standard heat of the formation of Phases I and II and their specific heats are not known, the heat of the reaction in each step can not be calculated. However, it is interesting to compare the ΔH's obtained in this study with the heat of reaction of the ammonium phosphates. The standard heats of the formation of mono-, di-, triammonium phosphate (crystal), and ammonia (gas) are −347, −376, −402, and −11 kcal/mol respectively.[8] The specific heat of ammonia at a constant pressure as a function of the temperature has also been established.[9] Assuming that the difference in the specific heats of solid phases is negligibly small, as is assumed in the case of aquopentaammine chromium (III) complexes,[10] the heats of the reactions of, di- to mono- and of tri- to diammonium phosphate can be calculated. The resulting values are 18 kcal/mol at 500 K and 15 kcal/mol at 700 K. These values are almost equal to the ΔH's obtained for Phases I and II at the second decomposition step and to the calculated value. It may be deduced that the ammonium ions and the phosphate group in the exchanger and in the salts interact to the same extent. The deduction stated is coincident with the observation on the decomposition temperatures of Phases I and II.

Table 2. *d* Values of the compounds

Phase I		Phase II		c-ZrP 420 °C	β ZrP[a]
220 °C	420 °C	220 °C	420 °C		
7.55 vs	7.44 vs	7.50 vs	7.44 vs	7.44 vs	9.4
4.48 s	4.50 s	4.48 s	4.51 s	4.51 s	5.40
4.19 w		4.19 w			4.65
3.63 vs	3.59 s	3.63 vs	3.60 s	3.60 s	3.83
3.49 vs		3.48 vs			3.55
3.19 vw					3.30
3.08 vw		3.09 w			3.12
2.69 w	2.64 s	2.77 w	2.64 s	2.65 s	2.69
2.59 w		2.64 w			2.15
		2.58 w			

a) The values from Ref. 8.

X-Ray Study. The interplanar distances of the samples (*d* values) after heating to 220 and 420 °C in a differential scanning calorimeter are shown in Table 2. It is apparent that Phases I and II were converted to an identical phase (Phase III) by the first decomposition. After the second decomposition, both phases showed the same diffraction patterns as that of the c-ZrP heated to 420 °C. Further, the heated samples were equilibrated with vapor of ammonia and water, and then examined again. Their X-ray diffraction patterns were then identical with that of the original ones. This fact suggests that the thermal decomposition reactions are reversible. The *d* value of anhydrous zirconium bis-(monohydrogen *ortho*-phosphate) obtained above did not agree with that reported by Clearfield *et al.*[11]

It is already known that c-ZrP has a layer structure and contains a cavity with a radius of about 1.3Å and that the first reflection in the X-ray diffraction patterns represents its interlayer distance.[12] The interlayer distances accompanying the thermal decomposition differ from those with the ion exchange.[1] That is, in the ion-exchange process the interlayer distance of 9.5Å changed to 8.2Å, while in the thermal decomposition it changed to 7.5Å. These facts suggest that one water molecule contributes to the structural change in the exchanger. Moreover, the shrinkage of the interlayer distance in the thermal decomposition will cause an increase in the apparent acidity of the phosphate group and the decomposition temperature in the second step will be raised.

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