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Intercalation of n-Alkylamines and n-Alkyldiamines into γ-Zirconium Phenylphosphonate Phosphate

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Abstract. Crystalline γ-zirconium phenylphosphonate phosphate was prepared according to Yamanaka's method and the intercalation behavior of n-alkylamines and n-alkyldiamines were investigated. In the case of n-alkylamines, a linear increase in interlayer distance was observed up to a carbon atom number of 12, whereas in n-alkyldiamines, only two di-amines, ethylenediamine and propylenediamine, were intercalated with respective increases in the interlayer distance. The increment of interlayer distance in both monoamines and diamines indicates the formation of a monomolecular layer in the interlayer region of the host, in contrast to the case in γ-zirconium phosphate as a host.

Key words: γ-zirconium phenylphosphonate phosphate, n-alkylamine, n-alkyldiamine, intercalation.

1. Introduction

Crystalline γ-zirconium phosphate, $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$($\gamma$-ZrP), is an inorganic ion exchanger with a layer structure [1]. Many investigations on intercalation using γ-ZrP as a host have been reported. It was reported that n-alkylamines formed a bilayer with a tilt angle of 55° against the layer when intercalated into γ-ZrP [2].

In the present study, we synthesized a γ-ZrP derivative, zirconium phenylphosphonate phosphate, $Zr(PO_4)(H_2PO_4)_{1-x}(C_6H_5PO_2OH)_x \cdot nH_2O$ (γ-ZrPP), according to Yamanaka and Hattori. Here, the interlayer —H_2PO_4 groups of γ-ZrP were replaced partially by $C_6H_5PO_2OH$ groups of phenylphosphonic acid by the topotactic reaction[3]. n-Alkylamines and n-alkyldiamines were intercalated into γ-ZrPP and compared with the behavior in γ-ZrP as a host.

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Table I. Interlayer distance and chemical composition of γ-ZrPP, $Zr(PO_4)(H_2PO_4)_{1-x}(C_6H_5PO_2OH)_x \cdot nH_2O$.

Sample No.	x	n	Interlayer distance (Å)
1	0.59	0.48	15.4
2	0.62	0.67	15.3
3	0.72	0.27	15.5

2. Experimental

2.1. Reagents and materials

The chemicals used were of reagent grade quality and were obtained from commercial sources and used without further purification. γ-Zirconium phosphate was synthesized by the reflux method according to literature [4].

One gram of γ-ZrP was dispersed into 100 mL of 1 M phenylphosphonic acid in 50% aqueous acetone and heated under reflux for 20 h. The solid was separated, washed several times with acetone and dried in air.

2.2. Intercalation of organic bases

A weighed amount(0.3 g) of γ-ZrPP was mixed with twice the equivalent of organic base to γ-ZrPP in 15 mL of ethanol.The mixture was shaken for four days. The equilibration temperature was 25 °C for alkylamines and 40 °C for alkyldiamines, respectively. The solid was collected by centrifugation and washed with ethanol and dried in air.

2.3. Instrumental data

X-ray powder diffraction(XRD) patterns were measured with a Shimadzu XD-610 diffractometer using Ni-filtered Cu$K\alpha$ radiation.

3. Results and Discussion

3.1. Preparation of γ-ZrPP

Interlayer distances and composition, which were determined by XRD and elemental analysis respectively, are reported in Table I. On the basis of the results, the average of the interlayer distance of γ-ZrPP is estimated to be 15.4 Å and about 64% of the —H_2PO_4 groups were replaced by $C_6H_5PO_2OH$ groups. Complete replacement of the —H_2PO_4 groups was not accomplished, probably because of steric hindrance of the phenyl groups in the interlayer space [5].

Table II. Interlayer distance and chemical composition of n-alkylamine intercalates of γ-ZrPP, $Zr(PO_4)(H_2PO_4)_{0.36}(C_6H_5PO_2OH)_{0.64}\cdot(RNH_2)_x \cdot nH_2O$.

Amine	x	n	Interlayer distance (Å)
Propylamine	–	–	19.03
Amylamine	0.92	0	21.75
Hexylamine	–	–	23.36
Heptylamine	1.0	0	24.25
Octylamine	–	–	27.28
Aminodecane	1.0	0	29.82
Laurylamine	0.86	0.3	32.22
Tetradecylamine	0.62	0.6	33.19

Table III. Intercalation of n-alkyldiamines into γ-ZrPP.

Diamine	Interlayer distance (Å)
Ethylenediamine	18.00
Diaminopropane	18.95
Diaminobutane	15.60
Cadaverine	15.60
Diaminohexane	15.57
Diaminooctane	15.66
Diaminononane	15.49
Diaminodecane	15.44

3.2. INTERCALATION OF n-ALKYLAMINES INTO γ-ZrPP

Table II gives interlayer distances and chemical compositions of the n-alkylamine intercalates. In Figure 1 the interlayer distances are plotted as a function of the number of carbon atoms(n) in the alkyl chain. It gives a straight line, whose slope is calculated to be 1.37. This implies that the interlayer distance increases by 1.37 Å for each additional carbon atom. Assuming that the alkyl chain of the amine has a trans, trans conformation and the guest molecules are intercalated perpendicular to the phosphate layers, the length of the alkyl chain should increase by 1.27 Å for each additional carbon atom.Therefore n-alkylamines form a bilayer when the increase in the interlayer distance is greater than 1.27 Å and a monolayer when the value is smaller than 1.27 Å.

The experimental value of 1.37 Å seems to indicate that n-alkylamines form an inclined bilayer, but this suggestion has some discrepancies. First, if the amine is intercalated with an inclination, an odd-even dependence of the carbon atoms in the alkyl chain should be found [6]. This is not the case in the present experiment.

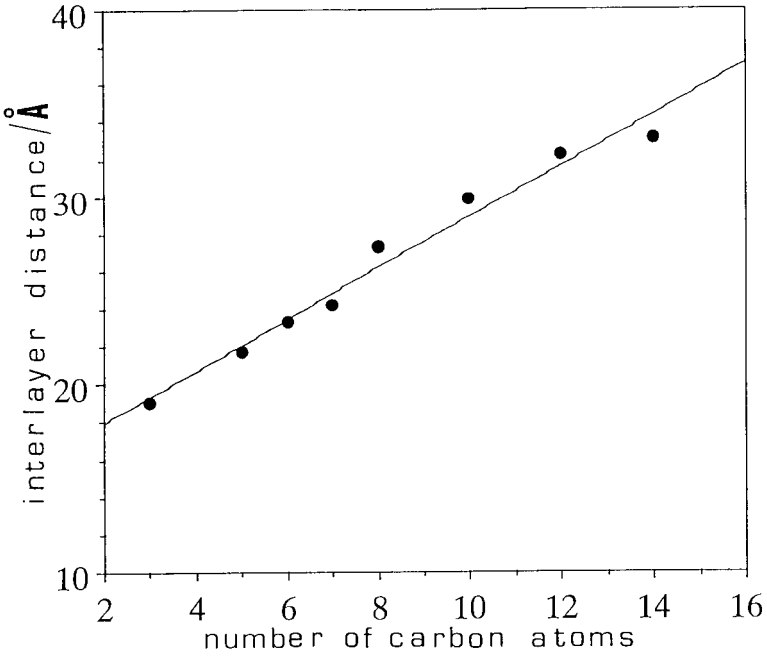

Figure 1. The interlayer distance of n-alkylamine intercalates of γ-ZrPP as a function of the number of carbon atoms in the alkyl chain.

Secondly, the increase in the interlayer distances indicates that the amines incline with the phosphate layers at an angle $\alpha = \sin^{-1}(1.37/2.54) = 30.8^\circ$ in the interlayer region. However, this is not likely because γ-ZrPP has bulky phenyl groups around the active site, the —POH group. If the amines intercalate with such a small tilt angle, steric hindrance should occur. Further, as can be seen from the chemical composition of the intercalate one mole of the amine is intercalated per formula weight of the host. Considering these points, it is probable that the amines form monolayers in the interlayer region.

Another reason for the possible formation of a monolayer may be the intercalation capacity of γ-ZrPP. The capacity of γ-ZrPP is smaller than that of γ-ZrP, because the —O_2P(OH)$_2$ groups are replaced by the —O_2P(OH) group of phenylphosphonic acid, thus reducing the protonation capability of amines. In other words, the free area around one active site may be larger and the formation of a bilayer becomes less probable.The same trend has been observed in the case of γ-zirconium phosphate phosphite [7].

3.3. INTERCALATION OF n-ALKYLDIAMINES INTO γ-ZrPP

The interlayer distance of the n-alkyldiamine intercalates are reported in Table III and in Figure 2. When ethylenediamine or diaminopropane is intercalated into

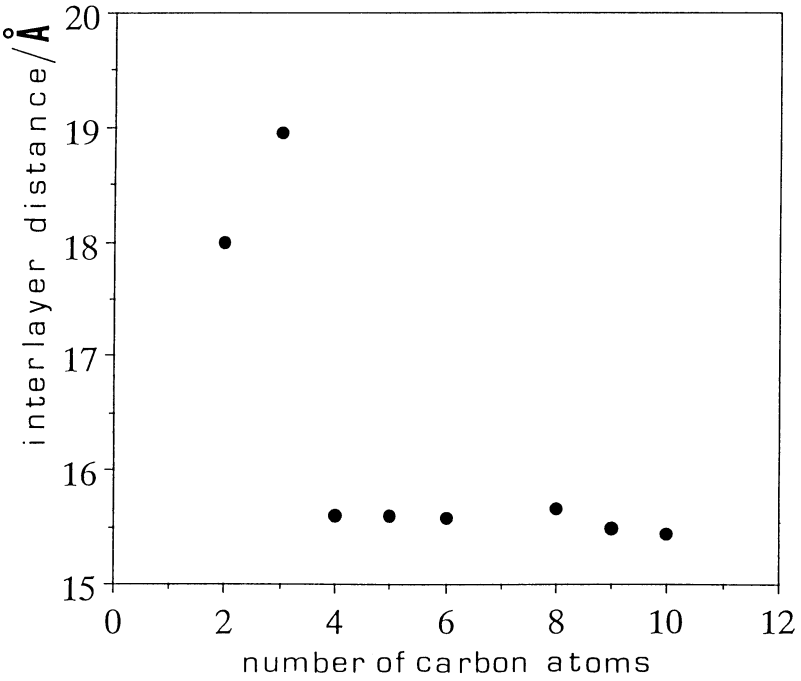

Figure 2. The interlayer distance of n-alkyldiamine intercalates of γ-ZrPP as a function of the number of carbon atoms in the alkyl chain.

γ-ZrPP, an increase in the interlayer distance is observed. However, in the case of diamines which have more than 4 carbon atoms in the alkyl chain, the interlayer distance did not increase, indicating that those diamines are excluded. The reason is not clear at present but steric hindrance owing to the phenyl group is likely. Otherwise, diamines would be intercalated, interpenetrating between adjacent layers of the host, as in the case of zirconium phosphate. The difference between the interlayer distance of the ethylenediamine- and diaminopropane intercalates is 0.95 Å. For the same reason as the intercalation of n-alkylamine, diamines may also form a monolayer.

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