

Direct and Stepwise Intercalation of Alkylalcohols into α -Zirconium Phosphate

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Abstract. Intercalation of alkylalcohols into α -zirconium phosphate was investigated at 25°C and/or under reflux. *n*-Alcohols having two to five carbons and 2-propanol were taken up at 25°C. These alcohols, and *n*-hexanol and heptanol, also intercalated under reflux. *n*-Alcohols having eight to eighteen carbon atoms intercalated when a stepwise method was employed. 2-Butanol and tertiary amylalcohols intercalated under reflux using a butanol intercalate as a starting material. Ethanol-to-butanol intercalates were unstable at room temperature, losing alcohols and changing to α -zirconium phosphate. The particle size of the α -zirconium phosphate did not affect the intercalation of alcohols.

Key words: α -Zirconium phosphate, intercalation, *n*-alcohol, decomposition, layered compound.

1. Introduction

α -Zirconium phosphate has been investigated as a typical inorganic ion-exchanger [1]. Since this exchanger has a layered structure, many polar organic molecules can be intercalated into its interlayer region.

Costantino reported that *n*-alcohols were accommodated between the layers [2]. The disodium form of α -zirconium phosphate was used as a starting material and sophisticated experimental conditions were employed to prepare an alcohol intercalate. Szirtes *et al.* reported that γ -zirconium phosphate could act as a host for ethanol, propanol, and butanol [3]. Vanadyl alkylphosphates were also investigated as a host by Johnson *et al.* [4], who found that the phosphates were able to intercalate *n*-alcohols rapidly at room temperature. Recently, Kittaka *et al.* [5] studied intercalation from the vapor phase in vanadium pentoxide hydrate and found that the *n*-alcohols having less than seven carbon atoms could be intercalated. During the course of an intercalation study of azacompounds, we found that ethanol might be intercalated into α -zirconium phosphate at 70°C [6].

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This work describes a simple method of preparing normal and branched alkyl alcohol intercalates and the decomposition of some intercalates at room temperature.

2. Experimental

2.1. PREPARATION OF α -ZIRCONIUM PHOSPHATE

α -Zirconium phosphate was prepared according to the literature [7]. The crystallites obtained by this method are designated as ZP-1 to differentiate them from another type. If α -zirconium phosphate is used without abbreviation, it refers to ZP-1. Also, another method was employed to prepare α -zirconium phosphate having a large particle size; zirconium dichloride oxide octahydrate (16.8 g) was dissolved in water (106 mL), and hydrofluoric acid (46%, 12 mL) was added slowly, followed by orthophosphoric acid (about 85%, 83 mL) under continuous stirring. The mixture was placed in a water bath kept at 50°C and prehumidified air passed through it for 24–30 h. The precipitate was washed with distilled water. The products obtained have larger crystallite size than ZP-1 and are called ZP-2. ZP-2 was ground in an agate mortar and sieved to < 100 mesh.

α -Zirconium phosphates were identified by X-ray diffractometry, thermal analysis, and the loss on ignition. Particle size distribution was measured with a Shimadzu SA-CP3 centrifugal particle size analyser. Deionized water was used as a medium with hexametaphosphate for ZP-1. Ethylene glycol was employed for ZP-2.

2.2. PROCEDURE OF DIRECT INTERCALATION

n-Alcohols were used as purchased from Wako Pure Chemical Industries Ltd. Intercalation was carried out using a batch method. A weighed amount of α -zirconium phosphate (usually 100 mg) was added to *n*-alcohol (20 mL). The mixture was shaken continuously at 25°C for 7 days or heated with a condenser in an oil bath for a given period of time. When refluxing was chosen, a small balloon and a desiccant were attached at the top of the condenser to prevent it from retaining moisture in the air. The solid phase was then separated with centrifugation.

2.3. PROCEDURE OF STEP-WISE INTERCALATION

α -Zirconium phosphate was treated with ethanol for 3 h as described above, washed with ethanol and twice with butanol. It was then refluxed with butanol for 5 h, and allowed to stand for 12 h. A butanol intercalate prepared in advance was used as a starting material without isolation. The butanol intercalate was rinsed with pentanol, then treated with pentanol. The mixture was refluxed for 5 h and allowed to stand for 12 h at room temperature. A similar procedure was employed to prepare the hexanol intercalate using pentanol intercalate as a starting material.

The intercalation was also attempted with an increase of two carbon numbers in one procedure, for example the conversion of *n*-butanol intercalate to the *n*-hexanol one.

2.4. STRUCTURAL STUDY

Changes in the structure of the solid were measured using X-ray diffractometry. The powder patterns were recorded on a Rigaku Denki Geigerflex 2B, using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). To prevent a structural change due to the evaporation of the intercalated alcohol, a sample on a holder was covered with Mylar film.

3. Results and Discussion

The particle size distribution curves are shown in Figure 1. ZP-1 and ZP-2 had median diameters (D_{50}) of 0.3 and 33 μm , respectively. As zirconium phosphate has a layered structure, the diameter obtained is only an index which reveals the size of crystallites.

3.1. DIRECT INTERCALATION

3.1.1. *n*-Alcohols

The interlayer distance of α -zirconium phosphate depends on the size of an existing cation or molecule between the layers. Hence, an X-ray powder pattern serves as a good tool for monitoring an intercalation reaction.

Table I shows the intensity ratio of the intercalate to that of the α -phase at 25°C, and at a higher temperature. It should be noted that some alcohols were intercalated into the interlayer region of α -zirconium phosphate, even at room temperature, and that *n*-alcohols having more than six carbon atoms (*n*-hexanol) were well taken up only at higher temperature.

The solid was separated after each week, and shaken for another 7 days, followed by adding *n*-alcohols at 25°C. A reaction time of 24 days was also employed. In each case the rate of conversion was similar to that for 7 days and independent of the reaction time.

The ratio of butanol intercalate was determined as a function of reaction time in the intercalation at high temperature. Equilibrium was attained within 30 min. The α -phase was present after 48 h and 144 h for the intercalation of *n*-pentanol. The reaction time of 48 h was chosen, taking the stability of *n*-pentanol, hexanol and heptanol into account, because the liquid phase gradually became pale brown during heating.

The shorter the length of the alkyl chain the more easily the intercalation reaction took place. However, it might take a long period of time to reach equilibrium under the experimental conditions used.

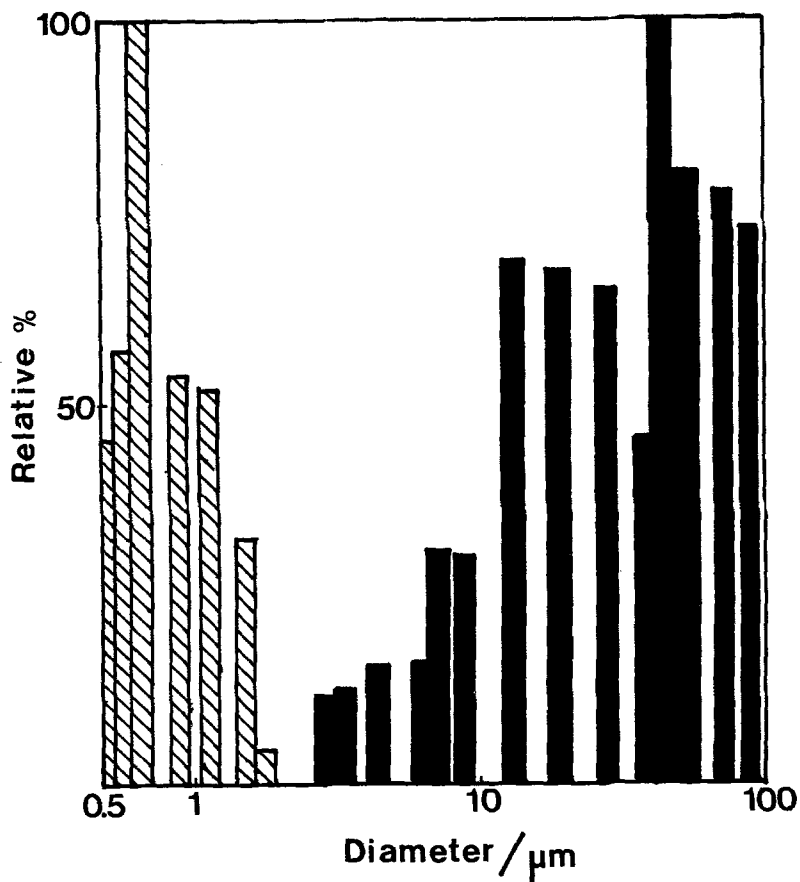


Fig. 1. Particle size distribution of ZP-1 (▨) and ZP-2 (■).

TABLE I. Intercalation of *n*-alcohols by the direct procedure.

Intensity ratio	Reaction temperature	
	25°C	Boiling point
	I_{ROH}/I_{α}	I_{ROH}/I_{α}
ethanol	21/100	100/0
<i>n</i> -propanol	100/14	100/0
<i>n</i> -butanol	100/14	100/0
<i>n</i> -pentanol	19/100	100/3
<i>n</i> -hexanol	0/100	50/100
<i>n</i> -heptanol	0/100	10/100
<i>n</i> -octanol	0/100	—

TABLE II. Intercalation of branched alcohols by the direct procedure.

Intensity ratio	Reaction temperature	
	25°C	Boiling point
	$I_{\text{ROH}}/I_{\alpha}$	$I_{\text{ROH}}/I_{\alpha}$
2-propanol	100/10	100/6
2-butanol	0/100	0/100
<i>t</i> -amylalcohol	0/100	0/100

3.1.2. Branched Alcohols

These alcohols cannot easily diffuse into the interlayer region because of steric hindrance. As Table II shows, 2-propanol was intercalated at 25°C, and the interlayer distance expanded to 15.5 Å.

3.2. STEPWISE INTERCALATION

The α -phase was sometimes observed in the intercalates of ethanol and butanol. One might guess that the ethanol intercalate was very unstable and decomposition could not be prevented (see below), or that the size of the crystallites affected the reaction. The stepwise intercalation was attempted in order to overcome these problems.

The intercalation occurred easily and rapidly, and was independent of particle size of the host materials. Table III shows the interlayer distance of the *n*-alcohol intercalates. The α -phase was not present in all intercalates. A powder diffraction pattern of butanol and *n*-tetradecanol intercalates is shown in Figure 2 as typical examples.

If the interlayer distances of the intercalates are plotted for butanol to *n*-tetradecanol as a function of the carbon number, a straight line is obtained. A *trans*-polymethylene chain is repeated by the length of 1.27 Å in an *n*-alkylalcohol. When the alkyl chain is arranged in a bilayer perpendicular to the (002) plane of α -zirconium phosphate, the gradient of the line would be expected to be 2.54 Å. As the value is 2.01 Å, the chain should be slanted at an angle of 52° ($\sin^{-1} 2.01/2.54$). This angle agrees very well with that reported by Costantino [2].

The interlayer distances of *n*-hexadecanol and *n*-octadecanol intercalates deviated from the straight line. This is caused by the fact that these two alcohols are more slanted than the others, and/or the alkyl chain is not arranged in the *trans*-conformation in the interlayer region.

Branched alcohols, 2-butanol and *t*-amylalcohol, also intercalated (see Table IV).

Since a methyl group stretches out towards the main O-C *trans*-chain in 2-propanol, the interlayer distance is slightly longer than that of the ethanol interca-

TABLE III. Intercalation of *n*-alcohols in the stepwise procedure.

	ZP-1		ZP-2	
	<i>d</i> (Å)	Δd (Å)	<i>d</i> (Å)	Δd (Å)
ethanol	14.1		14.1	
<i>n</i> -butanol	18.6		18.8	
<i>n</i> -pentanol	20.8	2.2	20.9	2.1
<i>n</i> -hexanol	23.1	2.3	23.1	2.2
<i>n</i> -heptanol	25.1	2.0	25.0	1.9
<i>n</i> -octanol	27.1	2.0	26.7	1.7
<i>n</i> -decanol	31.4	4.3	31.0	4.3
<i>n</i> -dodecanol	35.3	3.9	34.9	3.9
<i>n</i> -tetradecanol	38.6	3.3	*	
<i>n</i> -hexadecanol	41.9	3.3	*	
<i>n</i> -octadecanol	42.3	0.4	*	

* Not determined.

TABLE IV. Intercalation of branched alcohols by the stepwise procedure.

	Intensity ratio $I_{\text{ROH}}/I_{\alpha}$	Interlayer distance (Å)
2-propanol	—	15.5 ¹
2-butanol	100/15	17.0
<i>t</i> -amylalcohol	100/30	17.5

¹ The value was measured in the direct intercalation.

late. The branched methyl group did not act to expand the interlayer distance in 2-butanol, because the group is oriented downward to the main *trans*-chain. There are two branched methyl groups in *t*-amylalcohol, one of which may contribute to expanding the interlayer distance.

3.3. STRUCTURAL STABILITY

The intensity of the peak showing an interplanar spacing of the intercalate was measured (without Mylar film) as a function of time. The structural stability of intercalates (ethanol–butanol) was measured at room temperature. Figure 3 shows

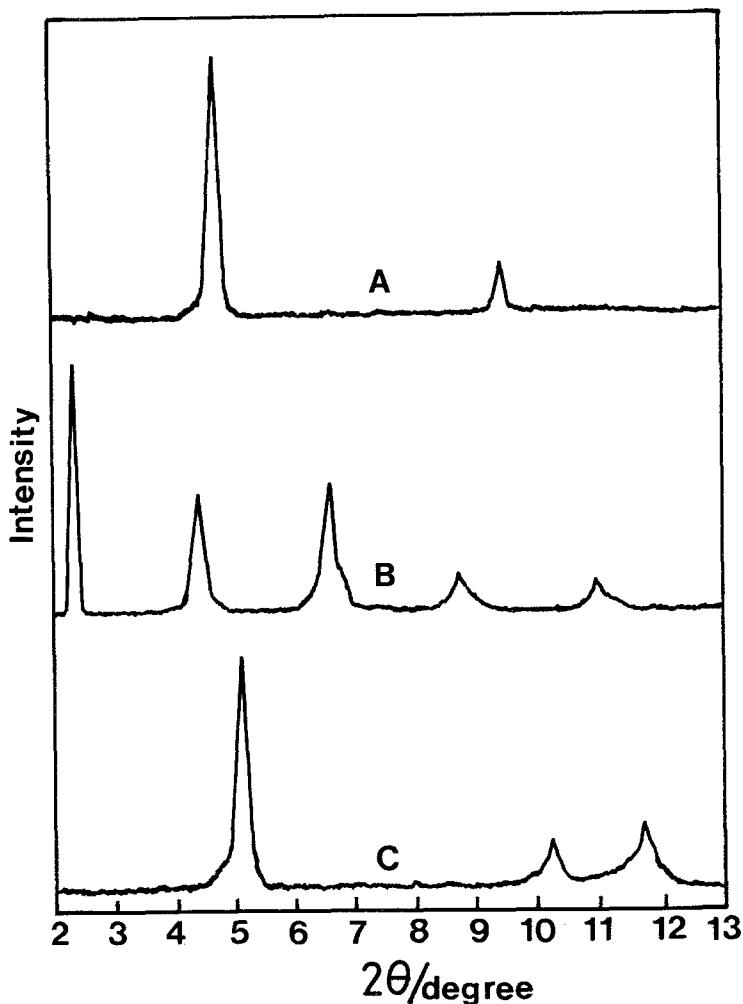


Fig. 2. X-ray diffractograms of (A) the butanol intercalate; (B) the tetradecanol intercalate; and (C) the tertiary amylalcohol intercalate. Intensity is in arbitrary units.

the kinetics of decomposition of alcohol intercalates. The initial horizontal part of the curves shows the evaporation of alcohol and the induction period of decomposition. The higher the boiling point of an alcohol the longer it took to decompose the intercalate. That is, the stability is dependent on the boiling point of the alcohol intercalated.

The ethanol intercalate was unstable. Within a few minutes three peaks were observed, showing interlayer distances of 10.1, 8.1, and 11.7 Å. After 10 min the peak showing the interlayer distance of the ethanol intercalate disappeared.

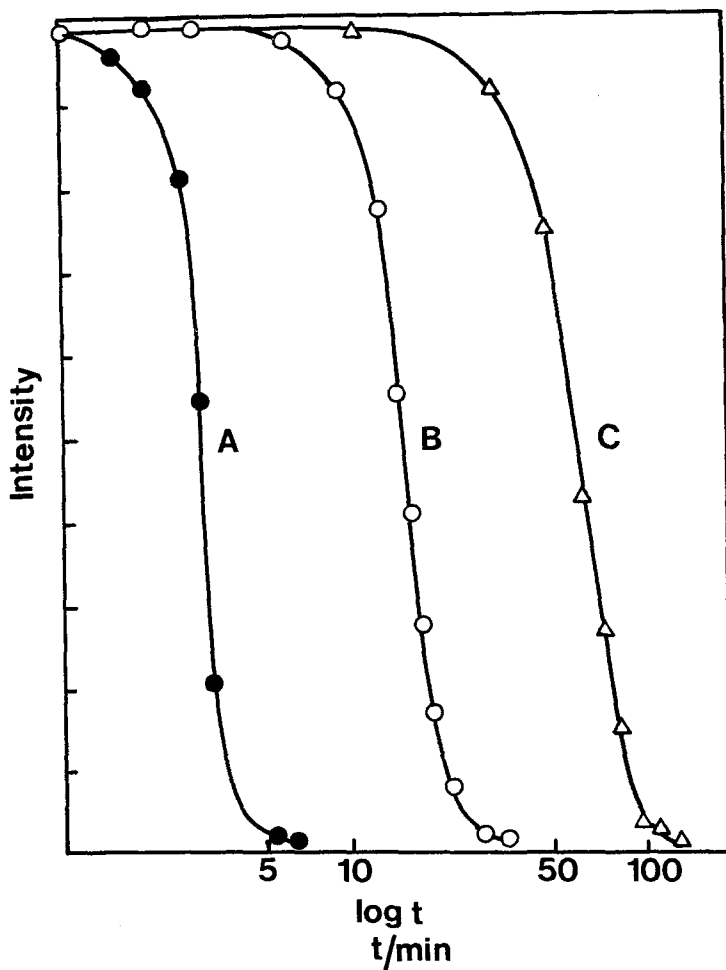


Fig. 3. Decomposition of alcohol intercalates. (A) Ethanol intercalate; (B) propanol intercalate; and (C) butanol intercalate. Intensity is in arbitrary units.

The propanol intercalate was also unstable. When the product was exposed to ambient air, a new phase ($d = 10.6 \text{ \AA}$) and the α -phase appeared. The peak at 16.5 \AA originating from the propanol intercalate diminished completely after 10 min. Only the α -phase was observed after 1 h.

The butanol intercalate was stable for about 1 h at room temperature. The intensity of the reflection at 18.5 \AA decreased with time, but no new peak was observed in the X-ray diffractogram. The peak at 10.3 \AA appeared after 1 h, and its intensity increased gradually with a decrease in that at 18.5 \AA . The butanol intercalate phase disappeared after 2 h. The intermediate phase was stable at room temperature for about 20 days.

The pentanol intercalate lost the guest slowly. The α -phase appeared after 7 h. The hexanol intercalate changed to an amorphous solid after about 5 days.

The interlayer distance of the intermediate phase was almost identical to the sum of the thickness of zirconium phosphate (6.3 Å) and an alkyl chain (4.0 Å) [8]. These facts suggest that the alkyl chain is oriented parallel to the zirconium phosphate layer in the intermediate phase.

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