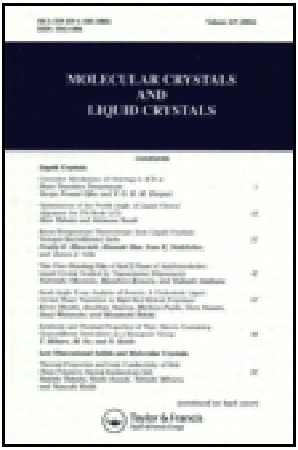

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Aki Hayashi [a] , Hirokazu Nakayama [a] , Taro Eguchi [b] , Nobuo Nakamura [b] & Mitsutomo Tsuhako [a]

[a] Kobe Pharmaceutical University, Kobe, Hyogo, 658-8558, JAPAN

[b] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, JAPAN

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Adsorption of Carboxylic Acids by Diethylenetriamine Intercalation Compound of α-$Zr(HPO_4)_2 \cdot H_2O$

AKI HAYASHI[a], HIROKAZU NAKAYAMA[a], TARO EGUCHI[b], NOBUO NAKAMURA[b] and MITSUTOMO TSUHAKO[a]

[a]*Kobe Pharmaceutical University, Kobe, Hyogo 658–8558, JAPAN and* [b]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043, JAPAN*

Two kinds of diethylenetriamine (2E3A) intercalation compounds of α-zirconium phosphate with different interlayer distances could be obtained by regulating the reaction time and temperature. Phase I (d = 10.2 Å) slowly transforms to Phase II (d = 15.8 Å) with transformation enthalpy of 30 kJ·mol^{-1} in 2E3A aqueous solution. The conformation of 2E3A in Phase I and Phase II were confirmed to be bent and all *trans* (straight) forms by ^{31}P MAS NMR and XRD measurements. Two phases have different adsorption behavior for gaseous carboxylic acids. Phase II can adsorb considerable amount of carboxylic acids whereas Phase I adsorb a little.

Keywords: α-$Zr(HPO_4)_2 \cdot H_2O$; diethylenetriamine; intercalation; adsorption; carboxylic acid

INTRODUCTION

Layered zirconium bis(monohydrogenphosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), is known as inorganic ion exchanger and host compound intercalating various organic compounds[1-5]. In the present study, diethylenetriamine (2E3A) with several active sites was investigated as guest compound. The structure and arrangement of 2E3A in the intercalation compounds were examined by using XRD and the ^{31}P MAS NMR measurements. Furthermore, it was found that they can adsorb acidic gases such as carboxylic acids.

EXPERIMENTAL

α-ZrP was prepared according to the reported procedure[6]. α-ZrP (1.0 g) was suspended in 0.1 dm^3 of 0.02 ~ 0.2 mol dm^{-3} 2E3A aqueous solution at room temperature for 30 min ~ 7 d. In order to investigate the phase transformation, the reaction of α-ZrP (1.0 g) with 0.1 dm^3 of 0.1 mol dm^{-3} 2E3A were carried out at several reaction times and temperatures (30 ~ 68 °C, 20 min ~ 69 h).

Powder X-ray diffraction patterns were measured with a Rigaku Denki Rint 2000 diffractometer using Ni-filtered Cu*K*α radiation. The amounts of 2E3A in the intercalation compounds were determined by elemental analysis using a Sumigraph NC-90A. The solid-state ^{31}P MAS NMR spectra of host α-ZrP and the intercalation compounds were obtained by a Bruker DSX-200 spectrometer operating at 81.0 MHz.

The adsorption was performed in a closed glass device with saturated vapor of various carboxylic acids at 40±0.1 ℃ (acetic acid and propionic acid) or 70±0.1 ℃ (butyric acid) by using 0.3 g of 2E3A intercalation compounds. The amount of adsorption was determined by the increase in weight.

RESULTS AND DISCUSSION

Intercalation of 2E3A

α-ZrP (1.0 g) was suspended in 0.1 dm^3 of 0.1 mol dm^{-3} 2E3A aqueous solution and the suspension was stirred at room temperature for 5 h. The intercalation compound obtained was confirmed to be a mixture of two phases with different interlayer distances (*d* = 10.2 Å and 15.8 Å). In order to obtain single phase, reaction condition was examined.

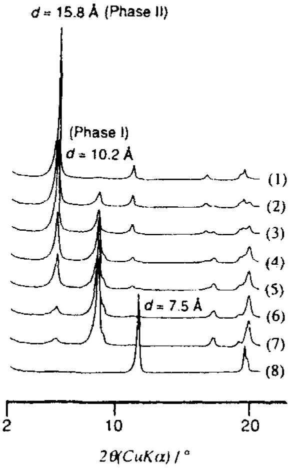

FIGURE 1 Reaction time dependence of X-ray diffraction patterns of 2E3A intercalation compounds of α-ZrP using 0.1 dm^3 of 0.1 mol dm^{-3} 2E3A. The reaction times are (1) 7d, (2) 1d, (3) 15h, (4) 5h, (5) 3h, (6) 1h, (7) 30min, and (8) 0 (α-ZrP).

Figure 1 shows the XRD patterns of 2E3A intercalation compounds of α-ZrP. On intercalating 2E3A into α-ZrP, the diffraction peak of the host α-ZrP (*d* = 7.5 Å) disappeared completely within 30 min and Phase I (*d* = 10.2 Å) was formed. Then, it transformed slowly to Phase II (*d* = 15.8 Å), and a pure Phase II was obtained after 7 d. The uptakes of 2E3A into α-ZrP were 1.5 and 2.7 mmol·g^{-1} of α-ZrP for Phase I and Phase II, respectively.

The ratio of two phases was plotted as a function of the reaction time in Figure 2. In order to elucidate the transformation rate from Phase I to Phase II quantitatively, a first-order reaction equations,

$$[\ \mathrm{I}\ ] = [\ \mathrm{I}_0\ ] \cdot \exp(\ k{\cdot}t\ ), \quad (1)$$

$$[\ \mathrm{II}\ ] = [\ \mathrm{I}_0\ ] \cdot [\ 1 - \exp(\ k{\cdot}t\ )\ ], \quad (2)$$

where [I] and [II] are the molar ratio of Phase I and Phase II, respectively, were applied. [I_0] and k is the initial molar ratio of Phase I and the transformation rate, respectively. These equations reproduce the experimental data as shown in Fig. 2.

Furthermore, in order to determine the transformation enthalpy, the intercalation compounds were systematically synthesized using 0.1 dm^3 of 0.1 mol dm^{-3} 2E3A aqueous solution at various temperature.

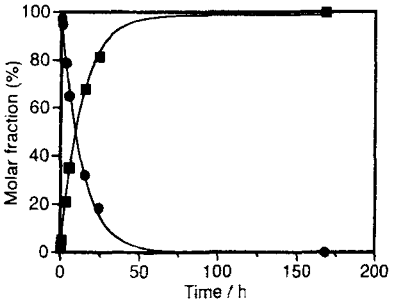

FIGURE 2 Time dependence of the mole fraction of Phase I (●) and II (■).

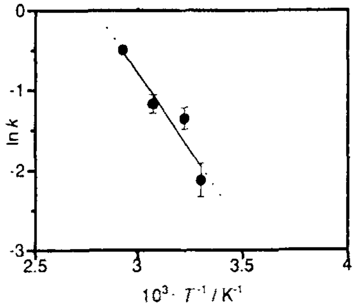

FIGURE 3 Temperature dependence of transformation rate, k, from Phase I to Phase II

From the plot of ln k vs. $1/T$ in Fig. 3 enthalpy of phase transformation is calculated to be 30 kJ·mol^{-1}.

In order to reveal the interaction between the host α-ZrP and 2E3A molecule microscopically and also to understand the origin of the transformation enthalpy, the ^{31}P MAS NMR spectra were measured for 2E3A intercalation compounds of α-ZrP (Fig.4). It is known that the host α-ZrP has only one kind of phosphate group, HPO_4, and that the signal of HPO_4 group is appeared at −18.7 ppm (Fig. 4-(8))[7]. On intercalating 2E3A into α-ZrP, this peak gradually moves to a low field. In Phase II (Fig.4-(1)) a strong peak appears at −15.7 ppm together with two weak peaks due to impurities or imperfection[8]. This main peak shifts by +2.8 ppm from that of α-ZrP because of the deprotonation of phosphate group (-P-OH → -P-O$^-$ ···H_3N^+-) as seen in the alkylamine intercalation compounds of α-ZrP[8]. It suggests that all the phosphate groups of α-ZrP interact with amino group of 2E3A in a same way. On the contrary, the peak of phosphate group in Phase I (Fig.4-(7)) shifted scarcely and was broad, because the interaction between phosphate group and 2E3A is weak and several different environments of phosphate groups exist. Therefore, the interaction between the host α-ZrP and 2E3A is considerably different for two phases.

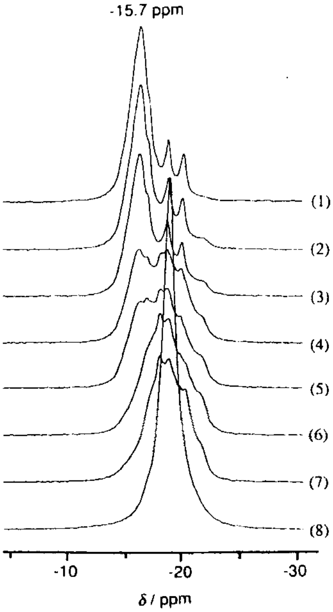

FIGURE 4 Reaction time dependence of ^{31}P MAS NMR spectra of 2E3A intercalation compounds of α-ZrP. Reaction times are (1) 7d, (2) 1d, (3) 15h, (4) 5h, (5) 3h, (6) 1h, (7) 30min, (8) 0 (α-ZrP).

Figure 5 represents the conformation of 2E3A in the interlayer region of Phase I and Phase II deduced from the above results. In Phase II the uptake of 2E3A (2.7 mmol / g) is half of maximum intercalation capacity of α-ZrP. This means that almost all HPO_4 sites interact with two terminal amino groups of 2E3A molecule in a same way (Fig. 5-(b)). This is reflected in a sharp ^{31}P signal at −15.7 ppm. As the van der Waals length along the long axis of 2E3A molecule with all *trans* form is 8.9 Å, the expansion of the interlayer distance by 8.2 Å supports above model. The transformation enthalpy from Phase I to Phase II, 30 kJ, is comparable with the barrier of internal rotation from *cis* form to *trans* form. Therefore, in Phase I, 2E3A molecules exist in bent form with 180 degree rotation against the bond between secondary amino group and its adjacent carbon atom. Therefore, the phosphate groups interacted with amino groups of 2E3A weakly and several different kinds of phosphate sites existed. This is reflected in broad ^{31}P signal. Furthermore, the expansion of the interlayer distance by 2.6 Å, is reasonable, because the size of 2E3A molecule with a bent form is 3.4 Å.

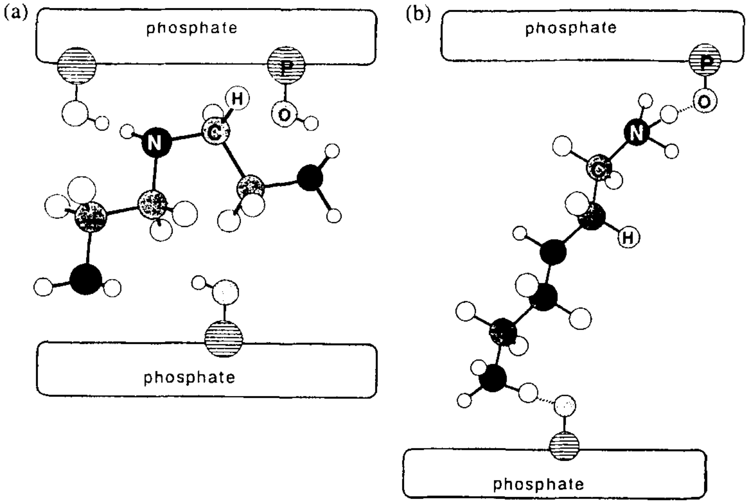

FIGURE 5 Schematic structural model of Phase I (a) and Phase II (b).

Adsorption of Carboxylic acid

Figure 6 shows time dependence of the adsorption amounts of acetic acid by Phase I and Phase II at 40 ℃. Phase II can adsorb considerable amount of acetic acid, whereas Phase I adsorb a little. The dramatic difference of adsorption capacities for these phases was also seen for other carboxylic acids (Table I).

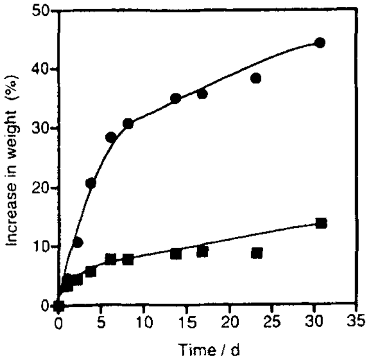

FIGURE 6 Adsorption of acetic acid by Phase I (●) and Phase II (■) at 40 ℃

TABLE I The adsorption amounts of carboxylic acid by Phase II and interlayer distances after the adsorption

Gas	CH_3COOH	CH_3CH_2COOH	$CH_3(CH_2)_2COOH$
Increase in weight (%)	44.3	32.7	34.7
Interlayer distance [a] (Å)	20.8	22.2	23.8

[a] interlayer distance of Phase II before adsorption is 15.8 Å.

In Phase II the increase of the interlayer distance by adsorption of carboxylic acid suggests that terminal protonated amino group interacts with carboxylic acid to expand the interlayer space. In contrast, terminal amino groups in Phase I can not interact with carboxylic acid probably due to smaller interlayer region and to conformation of 2E3A molecule, although it needs more experiment to establish adsorption model. Anyway, we succeeded in controlling the adsorption capacity of gaseous carboxylic acid in 2E3A intercalated α-ZrP by regulating the conformation of 2E3A in the interlayer region.

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