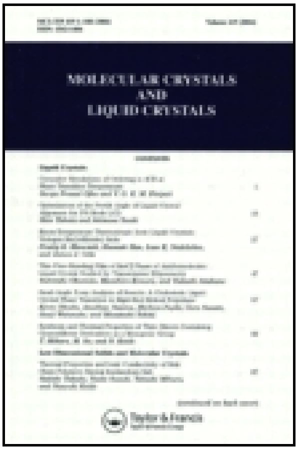

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Interlayer Reaction of Polyamine/α-Zirconium Phosphate Intercalation Compounds with Some Aldehydes

Motoki Kaneno [a] , Shunro Yamaguchi [b] , Hirokazu Nakayam [c] , Keisuke Miyakubo [a] , Takahiro Ueda [a] , Taro Eguchi [a] & Nobuo Nakamura [a]

[a] Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043

[b] Institute for Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, 567-0047

[c] Kobe Pharmaceutical University, Kobe, 658-8558, JAPAN

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Interlayer Reaction of Polyamine/α-Zirconium Phosphate Intercalation Compounds with Some Aldehydes

MOTOKI KANENO[a], SHUNRO YAMAGUCHI[b],
HIROKAZU NAKAYAMA[c], KEISUKE MIYAKUBO[a],
TAKAHIRO UEDA[a], TARO EGUCHI[a] and NOBUO NAKAMURA[a]

[a]*Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043,* [b]*Institute for Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567–0047 and* [c]*Kobe Pharmaceutical University, Kobe, 658–8558, JAPAN*

The intercalation compound between α-zirconium phosphate and *N,N'*-bis-(3-aminopropyl)-1,3-propanediamine has two different modifications with respect to the conformation of the guest amine molecules: one is "bent form" and the other "straight form." Reactivity of each phase with a series of aldehydes was examined. ^{13}C CP/MAS NMR indicated that the tetraamine reacts stereoselectively with aldehydes to form *cis*-imine in the interlayer spacing. Depending on the molecular size of aldehyde, it is found that a significant difference can be recognized in the yields of the imine products for the two phases of intercalation compounds. It is also noted that residual water molecules in the interlayer spacing play an important role in the imine formation reaction.

Keywords: intercalation; α-zirconium phosphate; *N,N'*-bis-(3-aminopropyl)-1; 3-propanediamine; stereoselective reaction; solid state NMR

INTRODUCTION

Establishment of specific and selective reaction field using organic-inorganic hybrid materials has been drawing much attention in the last few years.[1] Especially, layered phosphate family is the potential inorganic material to provide the framework for specific and selective reaction field because of its high capability to accommodate variety of basic organic compounds and to form highly stable intercalation compounds.[2]

Crystalline layered α-zirconium phosphate [α-$Zr(HPO_4)_2{\bullet}H_2O$, hereafter abbreviated as α-ZrP] is well known as one of the materials forming so-called intercalation compound.[3] α-ZrP has the interlayer distance of 0.76 nm, and each layer consists of a plane of zirconium atoms bridged by the phosphate anions, which have POH sites pointing away from the layer.[4]

Recently we have reported that *N,N'*-bis-(3-aminopropyl)-1,3-propanediamine [$H_2N\text{-}C_3H_6\text{-}NH\text{-}C_3H_6\text{-}NH\text{-}C_3H_6\text{-}NH_2$] (abbreviated as 3P4A) is intercalated into the interlayer spacing of α-ZrP and forms two different modifications depending on the temperature of sample preparation.[5] Interlayer distance of the one product prepared at $T = 283$ K (Phase 1) is $d = 1.7$ nm and the other prepared at $T = 333$ K (Phase 2) has $d = 2.0$ nm. Proposed structure of Phase 1 is "bent form" and that of Phase 2 is "straight form" (see Fig. 1). The amounts of non-protonated 3P4A molecules were approximately determined to be *ca.* 20 % of the ones intercalated in both phases by our ^{31}P NMR measurements.[5]

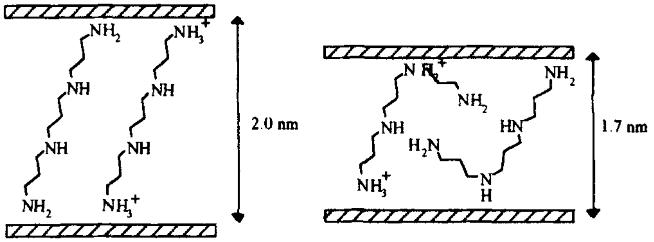
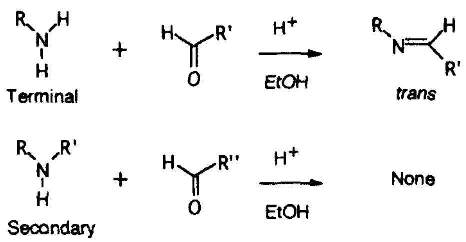


FIGURE 1. Structure of isolated 3P4A/α-ZrP intercalation compounds reacted at (a) 333 K (Phase 2) and (b) 283 K (Phase 1).

Reaction scheme of amino group with aldehyde in solution



It is known that aldehydes without α-hydrogen can react with terminal primary amino group and form imine compounds in solution as shown in the reaction scheme. Each of 3P4A/α-ZrP intercalation compounds possesses sufficient interlayer space to form reaction field for the amine molecule to undergo the reaction with guest aldehyde molecules only when the terminal amino groups are not protonated. The "bent form" which has a "free" terminal amino group is expected to react easily with aldehyde.

Present work examines possible reactions between 3P4A and various kinds of aldehydes in the interlayer spacing of 3P4A/α-ZrP system dispersed in organic solution using XRD and, ^{1}H and ^{13}C high-resolution solid-state NMR.

EXPERIMENTAL

3P4A/α-ZrP intercalation compounds were synthesized by the method reported previously.[5] All aldehydes were purchased from Wako Pure Chemical Industries Ltd. and used without further purification. Reaction of aldehyde with the intercalation compound was carried out by mixing 100 ml of 0.012 mol dm^{-3} EtOH (or other solvents) solution of aldehyde with a suspension of 0.25 g of each 3P4A intercalated α-ZrP. The suspension was filtered, washed 5 times with EtOH, and dried in vacuo.

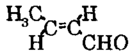
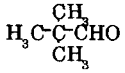
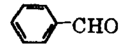
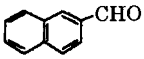
Interlayer spacings were determined by XRD. Elemental analysis was carried out by a Perkin Elmer CHN microanalyser. ^{1}H MAS and ^{13}C CP/MAS NMR spectra were measured at 4.7 T by a Bruker DSX-200 spectrometer at room temperature with a spinning rate of 5 kHz using a 7 mm ϕ MAS probe. ^{1}H MAS spectra were measured by reference to TMS. ^{13}C spectra were measured using a standard CP/MAS technique and measured by reference to TMS (glycine was used as an external standard).

RESULTS AND DISCUSSION

Reactions of various aldehydes with 3P4A in the interlayer spacing of α-ZrP were examined for both "straight form" and "bent form." Typical ^{13}C CP/MAS NMR spectra after the reaction (for 24 h) of benzaldehyde are shown in Fig. 2. In each spectrum, peaks originated from 3P4A appear in the 20 ~ 50 ppm region and aromatic peaks are at about 130 ppm. The signal at 163 ppm was assigned to the carbon of an imine product. Comparing the signal intensity at 163 ppm with those at 20 ~ 50 ppm, the yields of the imine products (*f*) were estimated. We also tried to obtain the value of *f* by the CHN chemical analyses, but found that no reliable results were obtained in the present work. Interlayer distance (*d*) in each product was determined by XRD. The values of *d* and *f* for four different aldehydes are listed in Table I, indicating that the interlayer distance after the reaction with various aldehydes remains almost unchanged in both phases.

According to these results, it follows that the protonated 3P4A works as a pillar to remain the interlayer distance unchanged. Since a 3P4A molecule has

TABLE I. Interlayer distances (*d*/nm) and yields (*f*) of imine products for various aldehydes. Reaction period is 24 h.

		bent form		straight form	
		d	*f*	*d*	*f*
(1)		1.64	0.33	1.84	0.26
(2)	 $H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CHO$	1.66	0.40	1.90	0.37
(3)		1.65	0.31	1.92	0.47
(4)		1.70	0.55	1.98	0.55

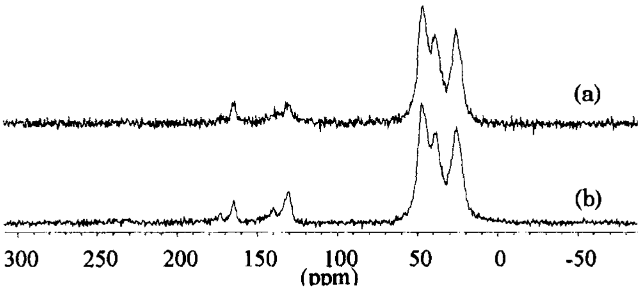


FIGURE 2. ^{13}C CP/MAS NMR spectra of benzaldehyde adsorbed in 3P4A/α-ZrP intercalation compound, (a) "straight form", and (b) "bent form". Reaction period is 24 h.

two terminal amines, the observed yields are consistent with the amount of the non-protonated 3P4A (20 %) in both phases of the intercalation compound. However, it is also noted that *f* seems to increase with the increase in the molecular size of aldehyde. These results, therefore, suggest that there may be several factors to govern this kind of interlayer reactions, *e.g.*, a sort of confinement effects on absorption,[6] conformation of 3P4A, electronic state of terminal amine, and reaction period.

To examine which of these factors is dominant on the formation of the imine compounds in the interlayer spacing, ^{13}C CP/MAS spectra of benzaldehyde (α–^{13}C is enriched by ISOTEC Co. Ltd.) absorbed in 3P4A/α-ZrP intercalation compound were recorded after the reaction for 5 h (Fig. 3). Two peaks observed distinctly at 163 ppm and 171 ppm were attributed to the imine group. It was reported that the signal of ^{13}C in C=N group with the *cis*-conformation appears at the lower filed than that with *trans*-conformation by about 4 ppm.[7] Peaks at 163 ppm and 171 ppm can therefore be assigned to the *trans*- and the *cis*-conformer of the imine product, respectively. Moreover, the large difference between the imine peak intensities implies that non-protonated "straight form" is more reactive than "bent form" to benzaldehyde. It is noted that the peak at 163 ppm is dominant in the reaction for 24 h as can be seen in Fig. 2, implying that the *trans*-conformer is the main product and no difference between the intensities of imine peaks in both phases is detectable (Fig. 2),

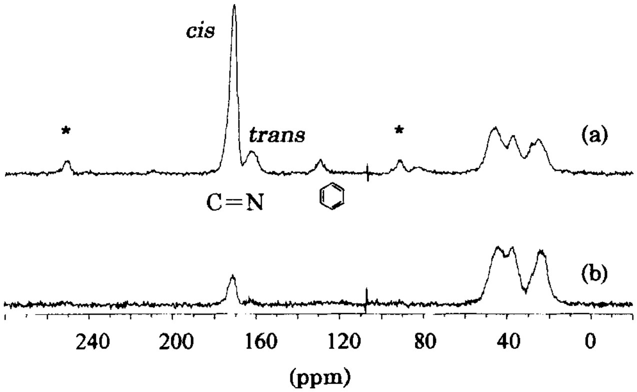


FIGURE 3. ^{13}C CP/MAS spectra of benzaldehyde-α-^{13}C absorbed in 3P4A/α-ZrP intercalation compound, (a) "straight form", and (b) "bent form". Asterisks indicate the spinning side bands. Reaction period is 5 h.

whereas a significant difference between the yields of the two forms was observed only in a few hours (5 h). We can therefore observe only in an early stage of the reaction that the reaction in "straight form" proceeds more favorably than in "bent form", indicating that the confinement effect is dominant in the early stage of the reaction.

Next, using ^{13}C CP/MAS NMR, we studied the reaction between aldehyde and "dehydrated" 3P4A/α-ZrP intercalation compound which was dehydrated for 3 days at 373 K. Any signal at *ca.* 163-171 ppm due to the imine group was not detected for each dehydrated sample. It is, therefore, suggested that the interlayer reaction of 3P4A with any aldehyde hardly takes place in the dehydrated 3P4A/α-ZrP: Similar results were obtained for both cases that pure EtOH and a mixture of EtOH : water = 1 : 1 were used as solvent for the reaction. In other words, water molecules should exist in the interlayer spacing for the aldehyde-amine reaction to occur, but water contained in the solvent does not affect the reaction rate at all. It is likely that the interlayer water works as a catalyst or as a triggering agent for the reaction.

Acknowledgment
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