

Intercalation of Glucosamine and Chitosan into Layered Zirconium Phosphates

Aki Hayashi, Yui Nakabayashi, Junko Yasutomi, Hirokazu Nakayama,* and Mitsutomo Tsuhako

Department of Functional Molecular Chemistry, Kobe Pharmaceutical University,
4-19-1 Motoyamakitamachi, Higashinada-ku, Kobe 658-8558

Received June 27, 2005; E-mail: hiro@kobepharma-u.ac.jp

Glucosamine was directly intercalated into γ-zirconium phosphate (γ-ZrP). The intercalation compound with a monolayer structure was obtained by the interaction between the 2-amino group of glucopyranose and the phosphate group in γ-ZrP. The uptake amount depended on the concentration of the glucosamine aqueous solution rather than reaction time, and reached 0.9 mmol per gram of γ-ZrP at the maximum. On the other hand, chitosan, polysaccharide of glucosamine, could be intercalated into alkylamine-intercalated γ-ZrP as the host compound. Chitosan-intercalated γ-ZrP showed two phases with different interlayer distances. It was confirmed from ^{13}C CP/MAS NMR spectra that chitosan exists in the interlayer region of γ-ZrP for both phases.

Layered phosphates are known as inorganic ion-exchangers and host compounds in intercalation chemistry. There are two types of layered phosphates of tetravalent metals, the α-form (α-$M(HPO_4)_2 \cdot H_2O$) and the γ-form (γ-$M(H_2PO_4)(PO_4) \cdot 2H_2O$, M = Zr, Ti, Hf, Pb, and Sn).[1,2]

The intercalation and ion-exchange properties of α-zirconium bis(monohydrogenphosphate) monohydrate, α-$Zr(HPO_4)_2 \cdot H_2O$ (abbreviated as α-ZrP), and γ-zirconium dihydrogenphosphate phosphate dihydrate, γ-$Zr(H_2PO_4)(PO_4) \cdot 2H_2O$ (abbreviated as γ-ZrP), have been examined extensively. α-ZrP has the interlayer distance, i.e., the distance between the middle of upper layer and that of lower layer, of 7.6 Å and the theoretical cation-exchange capacity (CEC) of 6.67 mmol per gram of α-ZrP. Each layer consists of a plane of zirconium atoms with octahedral ZrO_6 bridged by a tetrahedral hydrogenphosphate anion (HPO_4^{2-}), which is an active Brønsted acid (Fig. 1A).[1,2] On the other hand, the γ-layer consists of a rigid framework of octahedral ZrO_6, with the Zr atoms joined to each other with tetrahedral PO_4^{3-} and $H_2PO_4^-$ (Fig. 1B).[3] Its interlayer distance and CEC are 12.2 Å and 3.3 mmol per gram of γ-ZrP, respectively. The dihydrogenphosphate anion ($H_2PO_4^-$) has acidic protons similar to α-ZrP. Therefore, basic compounds such as *n*-alkylamine and α,ω-alkanediamine can be easily intercalated into the interlayer space of α- and γ-ZrP by the acid–base reaction.[2] MacLachlan et al. reported the relationship between the amount of alkylamine and its arrangement in the interlayer region of α-ZrP.[4,5] Alkylamine in the intercalation compound arranges as a monolayer structure at lower loading and then transforms to a bilayer structure accompanied with an increase of the interlayer distance at higher loadings of amine. Also, α,ω-alkanediamine bridges to upper and lower phosphate layers to form a monolayer structure by the interaction with two end amino groups.[6,7]

The alkylamine-intercalated layered phosphate with a bilayer structure produces hydrophobic space with a large interlayer distance. Therefore, alkylamine-intercalated layered phosphate has been utilized as the host compound for the intercalation reaction: so-called pillared compound. The role of alkylamine in

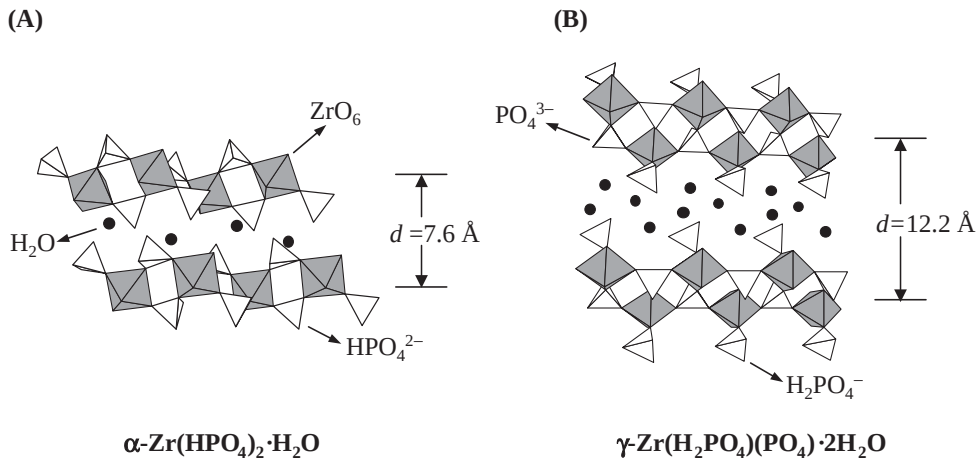

Fig. 1. Structures of (A) α-ZrP and (B) γ-ZrP.

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the interlayer space is the expansion of the interlayer distance and the induction of hydrophobicity into the interlayer region. Consequently, the presence of alkylamine in the interlayer space enables the uptake of organic molecules, which are unable to be intercalated directly. For example, the intercalation of papain, an enzyme with a high molecular weight, was possible by using propylamine-intercalated γ-$Ti(H_2PO_4)(PO_4)\cdot 2H_2O$ (γ-TiP).[8] Butylamine-intercalated α-ZrP could intercalate Methylene Blue by the exchange of butylamine with it,[9] and adsorb phenols by hydrophobic interaction with alkyl chains in the interlayer region.[10] Also, phospholipids can be co-intercalated into γ-$M(H_2PO_4)(PO_4)\cdot 2H_2O$ (M = Zr and Ti) by the presence of alkylamine in its aqueous solution.[11]

Recently, the intercalation of polymers and polymerization in the interlayer region after the intercalation of a monomer have been reported.[12,13] Kamigaito et al. synthesized a nylon 6-clay hybrid that was formed by the polymerization of ε-caprolactam into the clay organized with aminododecanoic acid.[14–16] Chitosan is classified as polyelectrolyte because the pK_a of chitosan is 6.3, and has attracted much attention as a biomass resource and new biopolymer.[17] Because chitosan is a natural macromolecule and safe for the human body, it is expected to be a new material in the medical and pharmaceutical fields such as drug delivery.[17] Furthermore, as chitosan has reactive primary amino and hydroxyl groups, and secondary hydroxy group, it is easy to modify chemically to form new functional materials. In the use of chitosan as an adsorbent, cross-linkage treatment has been essential to improve physical strength and resistance to acids and bases. In the present study, we carried out the intercalation of glucosamine and chitosan into α- and γ-ZrP to overcome these problems and open new applications of chitosan as an inorganic–organic hybrid.

Experimental

Chemicals. α- and γ-ZrP were prepared according to the method described in previous papers.[18,19] *n*-Butylamine (abbreviated as C_4N), *n*-hexylamine (C_6N), glucosamine hydrochloride (2-amino-2-deoxy-D-glucose hydrochloride), and chitosan (10) (β-(1→4)-2-amino-2-deoxy–β-D-glucose, abbreviated as chitosan (10)) of reagent grade were purchased from Wako Pure Chemical Industries Ltd.

Intercalation Procedure 1. α- or γ-ZrP (1.0 g) was suspended in 0.1 dm^3 of 0.1–0.5 mol dm^{-3} glucosamine aqueous solution, and the suspension was stirred at room temperature for 24–72 h. In the case of insoluble chitosan (10), 0.1–0.7 g of chitosan (10) was dissolved by adding hydrochloric acid, and then the solution was mixed with 1.0 g of α- or γ-ZrP. The resultant intercalation compound was filtered, washed with distilled water, and then dried in air.

Intercalation Procedure 2. α- or γ-ZrP (1.0 g) was added to 0.1 dm^3 of a 0.015–0.1 mol dm^{-3} butylamine aqueous solution, and the suspension was stirred at room temperature for 3 h. The obtained compounds (butylamine-intercalated α- or γ-ZrP) were filtrated, washed with distilled water, and then dried in air. For comparison, hexylamine-intercalated α- or γ-ZrP was synthesized by a similar method. Alkylamine-intercalated α- or γ-ZrP (0.1 g) was added to 0.1 dm^3 aqueous solutions of 0.1–0.7 g of chitosan (10). The mixture was stirred at room temperature for 1–72 h. The resultant products were separated by centrifugation (3000 rpm), washed with distilled water, and then dried in air.

Analytical Procedure. X-ray diffraction patterns were measured with a Rigaku Denki Rint 2000 diffractometer using Ni-filtered Cu Kα radiation to determine the interlayer distances. The amounts of alkylamines, glucosamine, and chitosan (10) taken up by α- and γ-ZrP were determined by elemental analyses of C and N using a Sumigraph NC-80. ^{13}C CP/MAS NMR spectra were obtained using a Varian Unity INOVA-500 spectrometer with a recycle delay of 4 s, accumulation of up to 10600 scans, and a spinning rate of 5 or 6 kHz. ATR-FTIR spectra were recorded by a Thermo Electron FT-IR 200 with the attenuated total reflectance (ATR) accessory, and with 4 cm^{-1} resolution (32 scans). Differential thermogravimetric analysis was performed with a Bruker axs TG-DTA 2000SA using a platinum–rhodium pan in an air flow at the rate of 10 °C min^{-1}.

Results and Discussion

Intercalation of Glucosamine. Glucosamine has an amino group at the 2-carbon of the glucopyranose structure. In nature, its D-form exists mainly as *N*-acetylglucosamine and is contained in chitin, mucopolysaccharide, glycoprotein, glycolipid, and lipopolysaccharide. Before performing the intercalation of chitosan, the intercalation behavior of glucosamine, which is monomer unit of chitosan, was examined first. The X-ray diffraction pattern of α-ZrP after the reaction with glucosamine was the same as that of the original α-ZrP, suggesting no intercalation. On the other hand, the interlayer distance of γ-ZrP expanded by reacting with glucosamine. Therefore, we examine only γ-ZrP hereafter.

Figure 2 shows the concentration dependence of XRD patterns for glucosamine-intercalated γ-ZrP for a 24 h reaction. The peak of the original γ-ZrP (12.2 Å) shifted to a lower angle by the reaction with glucosamine, suggesting that glucosamine was intercalated into the interlayer region of γ-ZrP. The interlayer distance was 17.0 Å for a 0.1 mol dm^{-3} glucosamine aqueous solution and expanded with increasing the concentration of glucosamine. For a 0.5 mol dm^{-3} aqueous solution, the peak of the original γ-ZrP disappeared completely

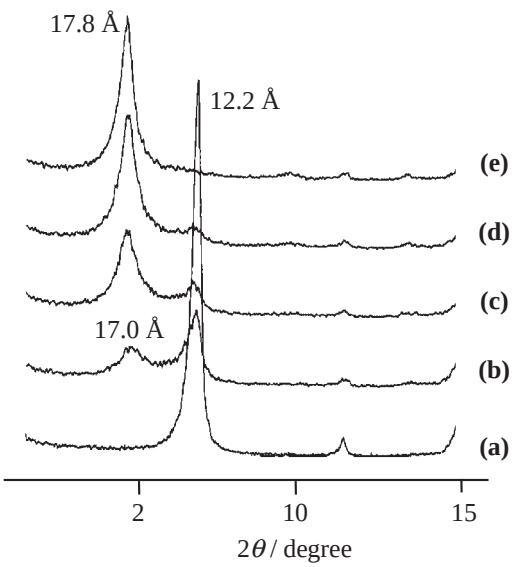

Fig. 2. XRD patterns of (a) γ-ZrP, and glucosamine-intercalated γ-ZrP reacted with (b) 0.1, (c) 0.2, (d) 0.3, and (e) 0.5 mol dm^{-3} glucosamine solution for 24 h.

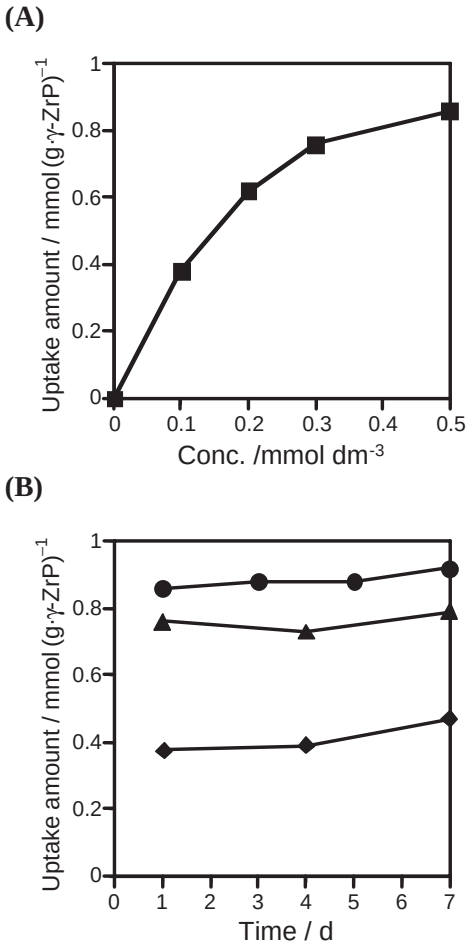

Fig. 3. (A) Concentration dependence of uptake amount of glucosamine into γ-ZrP for 24 h reaction. (B) Time dependence of uptake amount of glucosamine into γ-ZrP at the concentration of (◆) 0.1, (▲) 0.3, and (●) 0.5 mol dm^{-3} glucosamine solution.

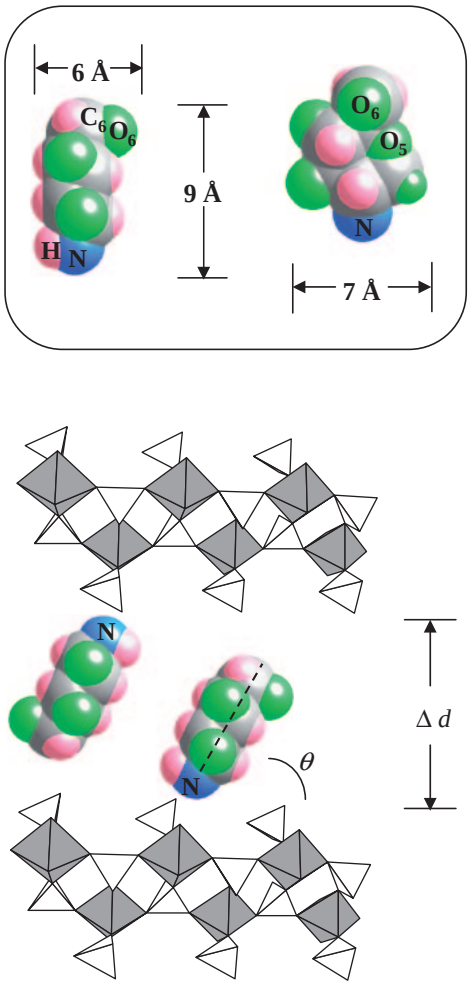

Fig. 4. Schematic model of glucosamine-intercalated γ-ZrP.

to form a single phase with the interlayer distance of 17.8 Å (Fig. 2e).

Figure 3A shows the relationship between its uptake amount and the concentration of the glucosamine aqueous solution for a 24 h reaction. The uptake amount increased with the increase of the glucosamine concentration and reached a maximum at 0.86 mmol per gram of γ-ZrP. Although there was no peak of the host γ-ZrP in the XRD pattern, the maximum uptake amount of glucosamine was not equal to the theoretical CEC (3.3 mmol per gram of γ-ZrP). The steric hindrance of the bulky glucosamine molecule would not allow the uptake of 3.3 mmol of glucosamine. Alternatively, the uptake amount increased slightly to 0.91 mmol per gram of γ-ZrP after 7 days of reaction in a 0.5 mol dm^{-3} aqueous solution as shown in Fig. 3B. Therefore, it is found that the intercalation behavior of glucosamine depended on the concentration of glucosamine rather than the reaction time.

The arrangement of glucosamine in the interlayer region can be estimated from the molecular size and the increment of the interlayer distance.[20] The increment of the interlayer distance (Δd) was calculated by subtracting the interlayer distance (9.4 Å) of anhydrous γ-ZrP from that of the intercalation compound (Fig. 4).[21] The Δd were 7.6 and 8.4 Å for the phases with the interlayer distances of 17.0 and 17.8 Å, respectively. Considering the facts that the 2-amino group interacts with the phosphate group and the distance between the 2-nitrogen and 6-carbon is 9 Å, the Δd of 7.6 and 8.4 Å means that the glucosamine molecule in the interlayer region arranges as a tilted monolayer structure as shown in Fig. 4.[22] If it arranged as a bilayer structure, the Δd should be 9–18 Å. The tilted angle (θ) relative to the phosphate layer, which is the angle between the long axis of the glucosamine molecule (dashed line in Fig. 4) and the plane of the phosphate layer, was determined to be 58° for the phase with 17.0 Å and 69° for the phase with 17.8 Å, using the equation of $\theta = \sin^{-1} \Delta d/9$ as shown in Fig. 4. The tilted angle (θ) increased with the increase of the uptake amount of glucosamine and the expansion of the interlayer distance.

Intercalation of Chitosan (10). Chitosan is an aminopolysaccharide obtained by deacetylating chitin (poly-1,4-β-*N*-acetylglucosamine), with the degree of acetylation lower than 0.40.[17] In fact, the degree of acetylation of chitosan (10) used in this work is 0.11. The molecular weight of chitosan depends on the degree of polymerization of glucosamine. Chitosan (10) used in this work has the smallest molecular weight and its vis-

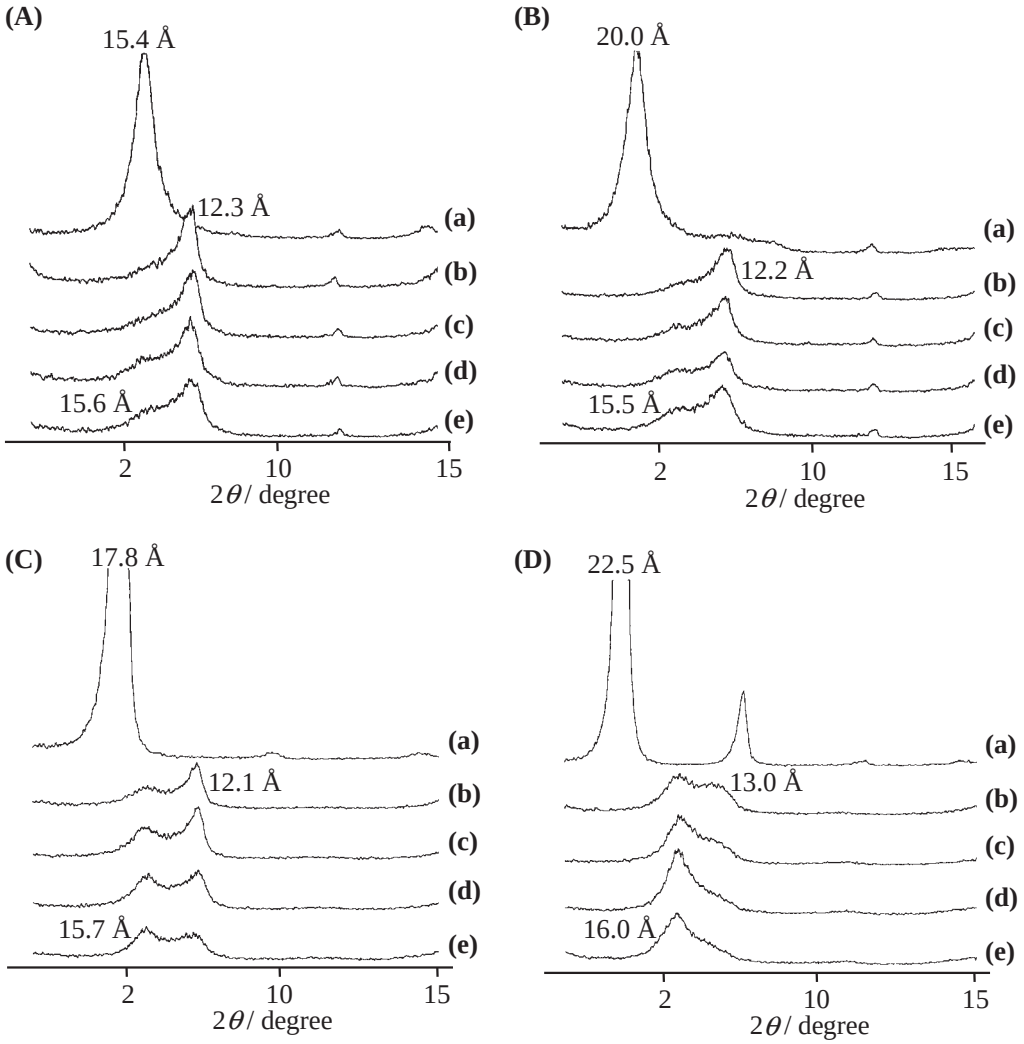

Fig. 5. XRD patterns of (A) C_4N-I, (B) C_6N-I, (C) C_4N-II, and (D) C_6N-II (a) before and after (b) 1, (c) 5, (d) 24, and (e) 72 h reaction with 0.2 g of chitosan (10).

cosity shows 8.8 cP at 20 °C. Because of the low solubility of chitosan in water, a chitosan aqueous solution was prepared by dissolving it with hydrochloric acid. Although α- or γ-ZrP was suspended in the chitosan (10) aqueous solution at various reaction conditions, the change of interlayer distance was not observed in the XRD patterns. It means that chitosan (10) could not be directly intercalated into α- or γ-ZrP, which is in marked contrast with glucosamine. It is probably due to the acidity of the reaction solution and the size of chitosan. Therefore, alkylamine-intercalated α- or γ-ZrP, that is, a pillared compound was used as the host compound. In this work, butylamine and hexylamine were used as pillar compounds to modify the interlayer space. Butylamine has been used as a pillar compound because it is able to orient in various arrangements in the interlayer region depending on the uptake amount of butylamine into α- or γ-ZrP.[4,5,23]

At first, we carried out the preliminary experiment by using butylamine-intercalated α- or γ-ZrP as the host compound. The butylamine-intercalated α- or γ-ZrP was synthesized by using a 0.1 mol dm^{-3} butylamine aqueous solution and had a maximum uptake amount of butylamine (6.5 mmol per gram of α-ZrP and 4.0 mmol per gram of γ-ZrP). After the reaction with the chitosan (10) aqueous solution, the change in the interlayer distance was observed only for butylamine-intercalated γ-ZrP, whereas there was no change for butylamine-intercalated α-ZrP. Therefore, the following experiment was performed for γ-ZrP, that is, butylamine- or hexylamine-intercalated γ-ZrP. Table 1 shows the interlayer distance (d) and uptake amount of alkylamine for the four compounds obtained by changing the reaction concentration of alkylamine at 3 h of reaction. They were abbreviated as type-I and type-II for the pillared compounds with less and more uptake amounts of

Table 1. Characteristics of Alkylamine-Intercalated γ-ZrP

	d/Å	Uptake amount /mmol (g·γ-ZrP)$^{-1}$	Reaction conc. of alkylamine /mol dm^{-3}
C_4N-I	15.4	1.5	0.015
C_4N-II	17.8	4.0	0.1
C_6N-I	20.0	1.8	0.015
C_6N-II	22.5	4.8	0.1

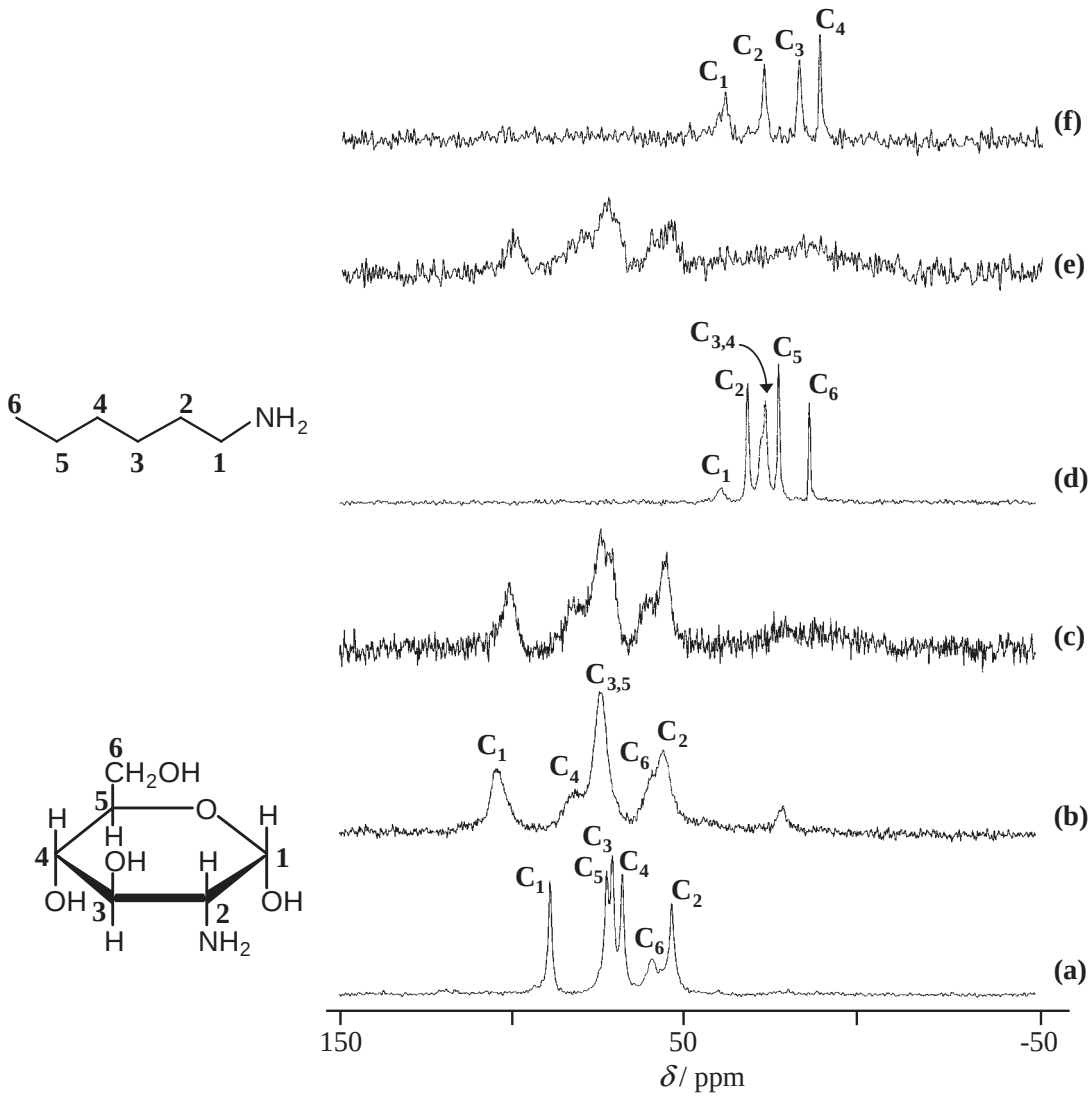

Fig. 6. ^{13}C CP/MAS NMR spectra of (a) glucosamine, (b) chitosan (10), (c) C_6N-II after the reaction with chitosan (10) (d = 16 Å), (d) C_6N-II, (e) C_4N-I after the reaction with chitosan (10) (d = 12 Å), and (f) C_4N-I.

alkylamine, respectively, as shown in Table 1.

The intercalation reaction of chitosan (10) was carried out using these pillared γ-ZrP as the host compound. Figure 5 shows XRD patterns of the products after the reaction with 0.2 g of chitosan (10) at various reaction times. It was found that the peaks due to pillared compounds (15.4 Å for C_4N-I, 20.0 Å for C_6N-I, 17.8 Å for C_4N-II, and 22.5 Å for C_6N-II) disappeared within 1 h and the interlayer distance decreased to ca. 12 and 16 Å after the reaction with chitosan (10) for any alkylamine-pillared γ-ZrP (Fig. 5A, B, C, and D-b). The same products would be obtained through the reaction with chitosan (10), even if the original interlayer distances of the four pillared compounds were different respectively. The proportion of phase with 16 Å increased with prolonged reaction time. Especially in the case of C_6N-II, the phase with 16 Å was dominant after 72 h of reaction (Fig. 5D-e). Contrary to this, the phase with 12 Å remained dominant in C_4N-I (Fig. 5A-e). Therefore, the rate of phase change from 12 to 16 Å depended on the uptake amount (type-II > type-I) of alkylamine and the interlayer distance (C_6N > C_4N) of pillared compounds.

Solid-state ^{13}C CP/MAS NMR was measured in order to examine the two phases (ca. 12 and 16 Å). Figure 6 shows ^{13}C CP/MAS NMR spectra of glucosamine, chitosan (10), and C_6N-II before and after the reaction with chitosan (10) (the reaction condition was 0.7 g of chitosan (10) and 72 h, d = 16 Å), and C_4N-I before and after the reaction with chitosan (10) (the reaction condition was 0.2 g of chitosan (10) and 1 h, d = 12 Å). The peaks of glucosamine (C_1–C_6) were attributed to 55–90 ppm as shown in Fig. 6a.[24] The broad peaks in the spectrum of chitosan (10) were assigned as shown in Fig. 6b, and a pronounced characteristic was that the peaks of C_1 and C_4 shifted to 105 and 83 ppm from 90 and 70 ppm for glucosamine by β-(1,4) linkage formation, respectively.[25] And, the peak at 30 ppm in Fig. 6b is assigned to the residual acetyl group due to the acetylation degree of 0.11. The spectrum of C_6N-II showed six peaks of the alkyl chain at 14–40 ppm (Fig. 6d). When 0.7 g of chitosan (10) was allowed to react with C_6N-II for 72 h, the product (d = 16 Å) showed sig-

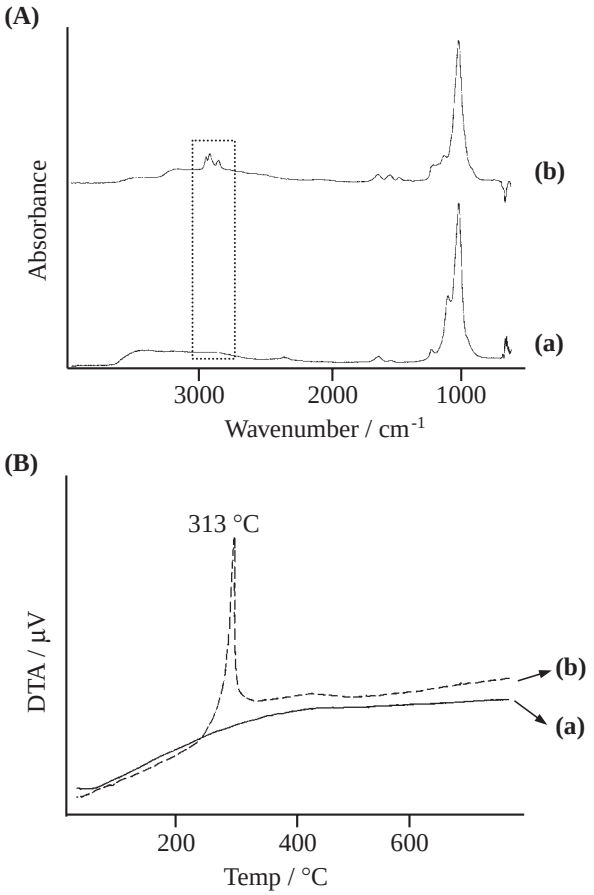

Fig. 7. (A) ATR-FTIR spectra and (B) DTA curves of C_6N-II (b) before and (a) after the reaction with chitosan (10) ($d = 16$ Å).

nals at 57–100 ppm (Fig. 6c). These chemical shifts were similar to those of chitosan (10), that is, the peaks at 100 and 82 ppm did not correspond to C_1 and C_4 of glucosamine, but those of chitosan (10). Therefore, it was proved that the phase with the interlayer distance of 16 Å was chitosan (10)-intercalated γ-ZrP without cleavage of the β-(1,4) linkage to glucosamine. The peaks of hexylamine were scarcely observed in the spectrum after the reaction with chitosan (10), suggesting that chitosan (10) was incorporated into the interlayer region by the exchange with the hexylamine molecule. Furthermore, a similar ^{13}C CP/MAS NMR spectrum was also observed in the phase with the interlayer distance of 12 Å. The peaks of butylamine at 13–40 ppm in C_4N-I disappeared and new peaks were observed at 56–100 ppm after the reaction with 0.2 g of chitosan (10) for 1 h ($d = 12$ Å) (Figs. 6e and 6f). It means that the phase with 12 Å is not the original γ-ZrP, but chitosan-intercalated γ-ZrP. Consequently, it was concluded that both phases with different interlayer distances, ca. 12 and 16 Å, were chitosan (10)-intercalated γ-ZrP. The difference of interlayer distance was caused by the different arrangement of chitosan (10) in the interlayer space.

In order to confirm the exchange of chitosan (10) with alkylamine, ATR-FTIR and DTA-TG measurements were performed as shown in Fig. 7. For the ATR-FTIR spectrum of C_6N-II, the peaks of methylene in hexylamine were observed at around 2860–2950 cm^{-1} (Fig. 7A-b). These peaks disappeared in the spectrum of C_6N-II after the reaction with chitosan (10) ($d = 16$ Å) (Fig. 7A-a). Furthermore, the DTA curve of C_6N-II showed an exothermic peak at 313 °C due to the decomposition of hexylamine as shown in Fig. 7B-b. On the other hand, there was no exothermic peak for chitosan-intercalated γ-ZrP ($d = 16$ Å) in Fig. 7B-a, suggesting no hexylamine in the interlayer region. These results revealed that chitosan (10) was incorporated into the interlayer region by the exchange with alkylamine.

The uptake amount of chitosan (10) was determined by elemental analysis (C%). Since almost all of the alkylamine was exchanged with chitosan (10), as mentioned in Figs. 6 and 7, the C% value obtained by elemental analysis was derived from the carbon of chitosan (10). However, because the number of glucosamine units was heterogeneous in chitosan (10), the uptake amount of chitosan (10) was calculated as glucosamine units. Figure 8 shows the relationship between the uptake amount as glucosamine units and the reaction time for the four pillared γ-ZrP. The uptake behavior of chitosan (10) in any alkylamine-pillared γ-ZrP was independent of the concentration of chitosan (10). The uptake amount reached equilibrium after 24 h for C_6N-II and a maximum at 0.84 mmol as glucosamine per gram of γ-ZrP (Fig. 8D), which agreed approximately with that of glucosamine into host γ-ZrP (0.91 mmol per gram of γ-ZrP). The maximum uptake amount increased in the order: C_4N-I < C_6N-I $\leqq$ C_4N-II < C_6N-II. This tendency was consistent with the behavior of phase change from 12 to 16 Å in XRD patterns (Fig. 5). This result supports that the incorporation of chitosan (10) depended on the interlayer distance and the uptake amounts of alkylamine in the pillared γ-ZrP.

Conclusion

Glucosamine could be directly intercalated into γ-ZrP. The uptake amount of glucosamine increased with its concentration and reached 0.91 mmol per gram of γ-ZrP. The arrangement in the interlayer region was a monolayer structure with the pyranose ring tilted to the phosphate layer through the interaction of the 2-amino group with the phosphate group. On the other hand, chitosan (10) could not be directly intercalated into α- and γ-ZrP, owing to the acidic solution, but the intercalation of chitosan (10) was possible by using alkylamine-intercalated γ-ZrP as the host compound. It was confirmed from the measurements by ^{13}C CP/MAS NMR and ATR-FTIR that the intercalation of chitosan (10) was achieved by the exchange with alkylamine without decomposition to glucosamine. The uptake behavior of chitosan (10) depended on the interlayer distance and the uptake amount of alkylamine in pillared γ-ZrP; the rate of uptake in C_6N-II was the fastest and in C_4N-I the slowest. Furthermore, the chitosan (10)-intercalated γ-ZrP gave two phases with different interlayer distances (ca. 12 and 16 Å) regardless of the carbon number of alkylamine in the pillared γ-ZrP, although the population of both phases was different. The arrangement of chitosan (10) in the interlayer region changed with increasing the uptake amount of chitosan (10). Thus, chitosan (10), a polymer with a high molecular weight, could be incorporated into layered phosphate by the use of pillared compounds.

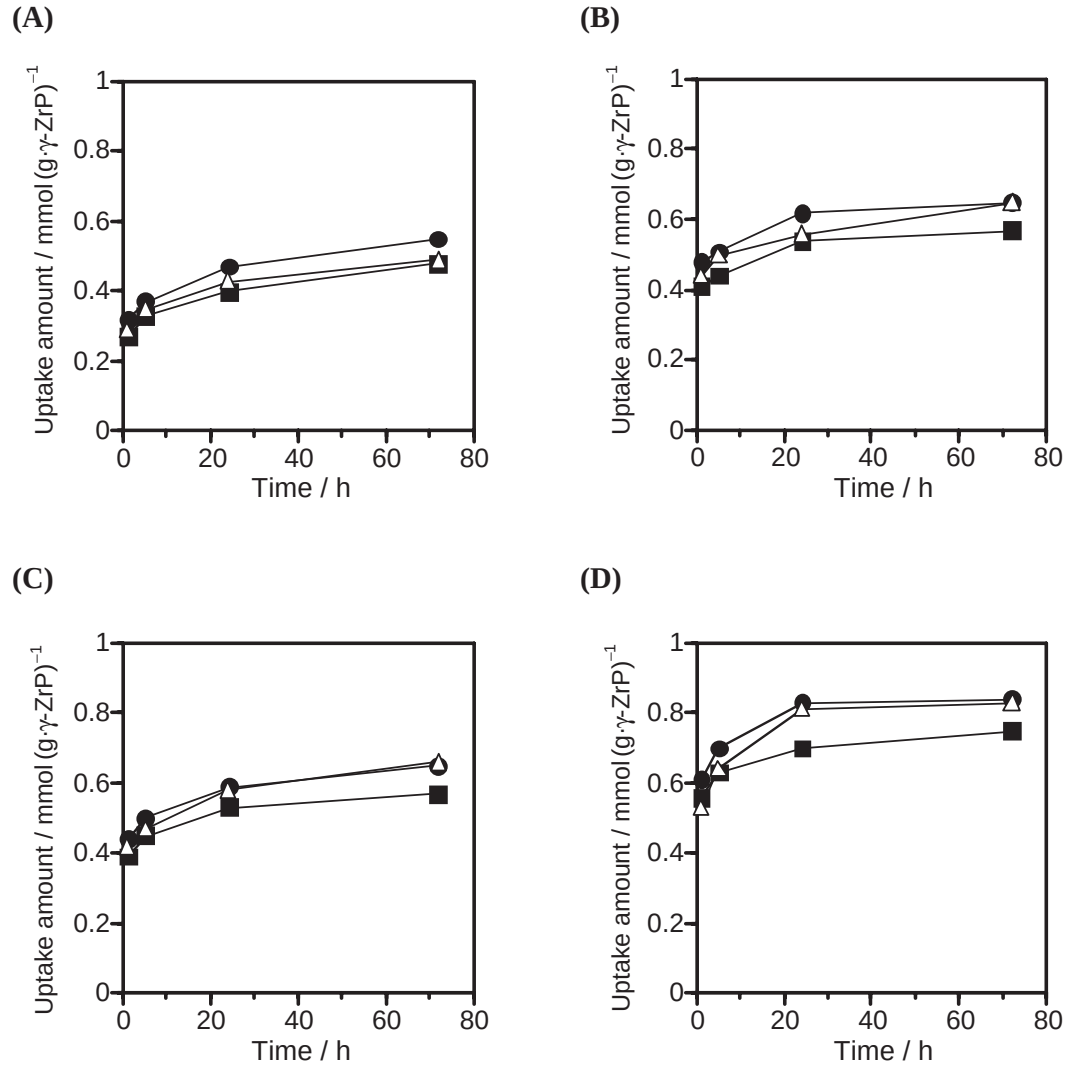

Fig. 8. Uptake amount of chitosan (10) calculated as glucosamine unit (A) C_4N-I, (B) C_6N-I, (C) C_4N-II, and (D) C_6N-II reacted with (■) 0.2, (●) 0.5, and (△) 0.7 g of chitosan (10).

References

1 A. Clearfield, *Inorganic Ion Exchange Materials*, ed. by A. Clearfield, CRC Press, Boca Raton and Florida, **1982**, pp. 1–48.

2 G. Alberti, U. Costantino, *Intercalation Chemistry*, ed. by M. S. Whittingham, A. J. Jacobson, Academic Press, Inc., New York, **1982**, pp. 147–180.

3 D. M. Poojary, B. Shpeizer, A. Clearfield, *J. Chem. Soc., Dalton Trans.* **1995**, 111.

4 D. J. MacLachlan, K. R. Morgan, *J. Phys. Chem.* **1990**, *94*, 7656.

5 D. J. MacLachlan, K. R. Morgan, *J. Phys. Chem.* **1992**, *96*, 3458.

6 M. Casciola, U. Costantino, L. D. Croce, F. Marmottini, *J. Inclusion Phenom.* **1988**, *6*, 291.

7 A. Espina, E. Jaimez, S. A. Khainakov, C. Trobajo, J. R. Garcia, J. Rodriguez, *Eur. J. Solid State Inorg. Chem.* **1997**, *34*, 959.

8 Y. Kanzaki, M. Abe, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2292.

9 M. Danjo, M. Tsuhako, H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, H. Nariai, I. Motooka, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1053.

10 A. Hayashi, H. Nakayama, M. Tsuhako, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2315.

11 Y. Kanzaki, M. Abe, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 180.

12 U. Costantino, F. Marmottini, *Mater. Chem. Phys.* **1993**, *35*, 193.

13 J. C. Amicangelo, G. L. Rosenthal, W. R. Leenstra, *Chem. Mater.* **2003**, *15*, 390.

14 A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, O. Kamigaito, *Mater. Res. Soc. Symp. Proc.* **1990**, *171*, 45.

15 A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito, *J. Mater. Res.* **1993**, *8*, 1179.

16 Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1755.

17 M. N. V. Ravi Kumar, R. A. A. Muzzarelli, C. Muzzarelli, H. Sashiwa, A. J. Domb, *Chem. Rev.* **2004**, *104*, 6017.

18 M. Tsuhako, Y. Horii, H. Nariai, I. Motooka, *Nippon Kagaku Kaishi* **1987**, 1541.

19 G. Alberti, S. Murcia-Mascaros, R. Vivani, *Mater. Sci. Forum* **1994**, *152–153*, 87.

20 M. Danjo, Y. Baba, M. Tsuhako, H. Nariai, I. Motooka, *Phosphorus Res. Bull.* **1993**, *3*, 25.
21 A. Clearfield, R. H. Blessing, J. A. Stynes, *J. Inorg. Nucl. Chem.* **1968**, *30*, 2249.
22 S. Yano, S. Inoue, Y. Yasuda, T. Tanase, Y. Mikata, T. Kakuchi, T. Tsubomura, M. Yamasaki, I. Kinoshita, M. Doe, *J. Chem. Soc., Dalton Trans.* **1999**, 1851.
23 G. Alberti, F. Marmottini, S. Cavalaglio, D. Severi, *Langmuir* **2000**, *16*, 4165.
24 K. Izumi, *Tanpakushitsu Kakusan Koso* **1984**, *29*, 282.
25 D. Capitani, V. Crescenzi, A. A. De Angelis, A. L. Segre, *Macromolecules* **2001**, *34*, 4136.