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Adsorption of Phenols by Alkylamine-Intercalated α-Zirconium Phosphate

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Alkylamine-intercalated α-zirconium phosphate successfully adsorbed harmful phenols, such as phenol, chlorophenol, and 2,4-dichlorophenol. The adsorption amounts of phenols are in the order; 2,4-dichlorophenol > chlorophenol > phenol. This sequence is related to the degree of hydrophobicity of these phenols. The adsorption amounts of phenols strongly depended on the content of alkylamine in the intercalation compound. In the case of butylamine, maximum adsorptions of phenols were observed when 4.4 mmol of butylamine was intercalated into α-ZrP; above this value, the adsorption amount decreased, and some butylamine was released.

α-Zirconium bis(monohydrogenphosphate) monohydrate, α-Zr(HPO$_4$)$_2$$\cdot$H$_2$O (abbreviated as α-ZrP), is known as an inorganic ion exchanger with a layer structure.[1] α-ZrP has the interlayer distance of 7.6 Å and theoretical cation exchange capacity (CEC) of 6.67 mmol g^{-1}. Each layer consists of a plane of zirconium atoms bridged by a hydrogenphosphate anion, which is an active Brönsted acid.[1,2] Therefore, *n*-alkylamines were easily intercalated into α-ZrP by the acid–base reaction.[2] MacLachlan et al.[3,4] reported the relationship between the amount of alkylamine and its arrangement in the interlayer region of α-ZrP, and clarified that an alkylamine with a short alkyl chain, such as propylamine and butylamine, has various conformations in the interlayer region, depending on the amount of alkylamine. The intercalation compound has a monolayer structure at lower loading of alkylamine and then transforms to a bilayer structure together with the increase of the interlayer distance at higher amine loading. And the alkylamine-intercalated α-ZrP with a bilayer structure has a large hydrophobic region in the interlayer space. Therefore, alkylamine-intercalated α-ZrP was utilized as host compound, the so-called pillared compound. The role of alkylamine in the interlayer region is the expansion of the interlayer distance and the induction of hydrophobicity in the interlayer region. Consequently, the introduction of alkylamine would make it possible to co-intercalate organic molecules, which were unable to be intercalated by the direct intercalation reaction. For example, propylamine-intercalated γ-Ti(PO$_4$)(H$_2$PO$_4$)$\cdot$2H$_2$O (γ-TiP) intercalated the enzyme, papain, with large molecular weight.[5] Butylamine-intercalated α-ZrP intercalated methylene blue by the exchange with butylamine molecule in the interlayer region.[6] Also, phospholipids were enable to be intercalated into γ-M(PO$_4$)(H$_2$PO$_4$)$\cdot$2H$_2$O (M = Zr, Ti) with the presence of alkylamine in aqueous solution, namely co-intercalation.[7]

Recently, various harmful environmental pollutants such as pesticides and environmental hormones are noted all over the world and many chemists have devoted their research to green chemistry. We have reported that polyamine-intercalated α-ZrP adsorbed gaseous carboxylic acid and formaldehyde, which is a compound that causes the sick-house syndrome, by the interaction of those gases with polyamine in the interlayer region.[8–11] On the other hand, aminoethanethiol-intercalated γ-TiP efficiently adsorbed toxic heavy metal ions by the function of mercapto group (–SH) in the interlayer region.[12] Montmorillonite was reported to be able to remove organophosphorus pesticides in soil.[13,14]

Very small amounts of phenols are contained in city water and their acceptable limits are strictly determined. Clays treated with organic compounds having long alkyl chains, or clays pillared by surfactant could adsorb phenols and chlorinated phenols. Their adsorption mechanism is mainly hydrophobic interaction of long alkyl chain or surfactant with phenols.[15,16] But, there was no report that alkylamine-intercalated α-ZrP had been examined as the adsorbent of harmful environment pollutants. In this work, alkylamine-intercalated α-ZrP was examined as a possible candidate to be an adsorbent for harmful phenols. The adsorption mechanism was also investigated microscopically by the measurements of XRD and solid-state NMR.

Experimental

Chemicals. α-Zirconium bis(monohydrogenphosphate) monohydrate, α-Zr(HPO$_4$)$_2$$\cdot$H$_2$O (abbreviated as α-ZrP), was prepared according to the method given in a previous paper.[17] Butylamine (CH$_3$CH$_2$CH$_2$CH$_2$NH$_2$, C$_4$N), octylamine (C$_8$N), phenol (C$_6$H$_5$OH), chlorophenol (C$_6$H$_4$(OH)Cl), and 2,4-dichlorophenol (C$_6$H$_3$(OH)Cl$_2$) of reagent grade were purchased from Wako Chemical Industries Ltd.

Intercalation of Alkylamine. α-ZrP (1.0 or 0.5 g) was suspended in 5–120 mmol dm^{-3} butylamine aqueous solution, and the suspension was stirred at room temperature for 5–24 h. For comparison, 50 mmol dm^{-3} aqueous solution of octylamine, which has twice as many carbons as butylamine, was stirred with 0.5 g of α-ZrP at room temperature for 24 h. The resultant intercalation compound was filtered, washed with distilled water, and then dried in air.

Adsorption of Phenols. A 0.1 g aliquot of each intercalation

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compound or host α-ZrP was added to 10 mL of 0.4–100 mmol dm^{-3} phenol aqueous solutions. The mixture was stirred at room temperature for 1 min–10 d. The resultant solid products were separated by centrifugation (3000 rpm), washed with distilled water, and then dried in air. The supernatants were allowed to stand and the amounts of residual phenols were determined by spectrophotometry.

Analytical Procedure. X-ray diffraction patterns were measured with a Rigaku Denki Rint 2000 diffractometer using Ni-filtered Cu Kα radiation to monitor new phases and determine their interlayer distances. The amounts of alkylamine taken up into α-ZrP were obtained by elemental analyses of C and N using a Sumigraph NC-80. ^{31}P MAS NMR spectra of the intercalation compounds were measured using a JEOL GX-270W spectrometer with a recycle delay of 20 s, accumulation of 8 FIDs, and a spinning rate of 4 kHz. ^{13}C CP/MAS NMR spectra were measured using a Varian Unity INOVA-500 spectrometer with a recycle delay of 5 s, accumulation of up to 13000 scans, and a spinning rate of 5 kHz.

The adsorption amounts of phenols were determined from the difference between the initial and final concentrations of phenols in aqueous solutions. They were measured at the wavelength (λ_{max}) of 269, 273, and 284 nm for C_6H_5OH, $C_6H_4(OH)Cl$, and $C_6H_3(OH)Cl_2$, respectively, by using a Beckman DU500 spectrophotometer. As their λ_{max} values depended on the pH values of aqueous solutions of phenols, 10 µL of 6 mol dm^{-3} hydrochloric acid was added in the supernatant in order to reduce their pH values below pK_a before the determination.

Results and Discussion

The adsorption of phenols was examined for butylamine- and octylamine-intercalated α-ZrP. Butylamine was adopted because its intercalation behavior and the structural properties of the intercalation compounds had been clarified in detail.[3] In order to investigate the effect of alkyl chain length on the adsorption ability, we selected octylamine, which has twice as many carbons as butylamine, for comparison. At first, we synthesized the intercalation compounds of both amines with the same content (6.5 mmol g^{-1} for butylamine and 6.7 mmol g^{-1} for octylamine). Their alkylamine-intercalated α-ZrPs (abbreviated as C_4N/α-ZrP and C_8N/α-ZrP) and host α-ZrP were suspended in 10 mmol dm^{-3} aqueous solutions of phenols for 1 min–10 d. The adsorption of phenols reached equilibrium at about 15 min.

Figure 1 shows the adsorption amounts (W) of phenols after 6 h. Phenols were adsorbed by alkylamine-intercalated α-ZrP, in contrast with no adsorption by the host α-ZrP. This result indicates that alkylamine in the interlayer region is indispensable for the adsorption of phenols. As α-ZrP is the solid acid with the HPO_4^{2-} group, acidic phenols (pK_a values of $C_6H_3(OH)Cl_2$, $C_6H_4(OH)Cl$, and C_6H_5OH are 7.7, 8.1, and 9.9, respectively) were not able to be adsorbed by the host α-ZrP. But, in the case of alkylamine-intercalated α-ZrP, the acidity of the host α-ZrP is regulated by the intercalation of alkylamine into the interlayer region, which makes it possible to adsorb phenols by the weak hydrophobic interaction between alkylamine and phenols. Also, for butylamine- and octylamine-intercalated α-ZrP, the adsorption amounts of phenols were in the order; $C_6H_3(OH)Cl_2 > C_6H_4(OH)Cl > C_6H_5OH$. This sequence agrees with the degree of hydrophobicity of phenols, which increases with the addition of chlorine on phenol.[15]

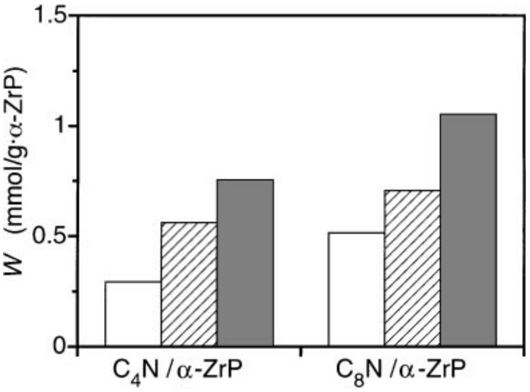

Fig. 1. Adsorption amounts (W) of phenols by alkylamine-intercalated α-ZrP. □; C_6H_5OH, ▨; $C_6H_4(OH)Cl$, ■; $C_6H_3(OH)Cl_2$.

Therefore, the adsorption mechanism is associated with the hydrophobic interaction of phenols with alkylamine in the interlayer region. This is also supported by the fact that octylamine-intercalated α-ZrP with higher hydrophobicity adsorbed more phenols than butylamine-intercalated α-ZrP.

As mentioned above, it will be essential to neutralize acidic α-ZrP to some extent to manifest weak hydrophobic interaction. Accordingly, the relationship between the adsorption amounts of phenols and the amounts of butylamine intercalated into α-ZrP was examined for butylamine-intercalated α-ZrP in detail, because the intercalation behavior of butylamine was precisely understood.[3] Figure 2 shows the relationship between the adsorption amounts (W) of phenols and the uptaken amounts (C) of butylamine in α-ZrP. The maximum adsorption amounts were different in three phenols because of their different hydrophobicity values. W of all phenols increased with the increase of C up to 4.4 mmol g^{-1}, but decreased above it. Hereafter, we indicate 4.4 mmol butylamine intercalated α-ZrP as compound I and 6.5 mmol butylamine in-

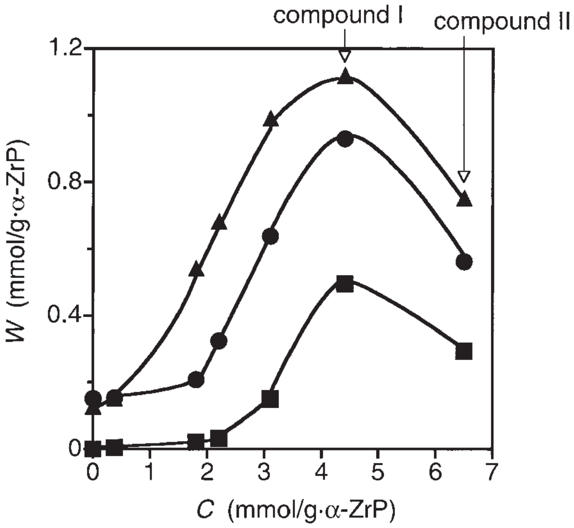

Fig. 2. The relationship between the adsorption amount (W) of phenols and the uptaked amount (C) of butylamine in α-ZrP. ■; C_6H_5OH, ●; $C_6H_4(OH)Cl$, ▲; $C_6H_3(OH)Cl_2$. Concentration of phenols; 10 mmol dm^{-3}, reaction time; 6 h.

tercalated α-ZrP as compound Ⅱ. It is known that compound Ⅰ has a bilayer structure consisting of the bent and straight conformations of butylamine and that compound Ⅱ has a bilayer structure with only straight conformation of butylamine.[3] Accordingly, the decrease of W for compound Ⅱ is curious because the $HPO_4{}^{2-}$ group of α-ZrP is completely neutralized by butylamine and the maximum hydrophobic interaction between phenols and butylamine is expected for compound Ⅱ. In order to clarify the origin of this phenomenon, we investigated the adsorption behavior of compounds Ⅰ and Ⅱ precisely.

Figures 3 and 4 show the adsorption amount of phenols (W; solid line) and the amount of deintercalated butylamine (A; dotted line) from compounds Ⅱ and Ⅰ at different initial concentrations of phenols after 6 h. The initial concentration of $C_6H_3(OH)Cl_2$ was limited to 25 mmol dm^{-3} because of its low solubility in water. In the case of compound Ⅱ (Fig. 3), W was always less than A, indicating that the adsorption of phenols by compound Ⅱ was accompanied by the release of a considerable amount of butylamine. Actually, the pH value in phenol solution rose after the adsorption of phenols due to the release of butylamine. Because compound Ⅱ is the intercalation compound with the lowest acidity due to the maximum uptaken amounts of butylamine, basic butylamine may be easily released in phenol solution with weak acidity. And then the phenol solution becomes basic, which will hamper the adsorption of phenols. On the other hand, W of compound Ⅰ increased with increasing the initial concentration of phenols, and the value was considerably larger than that of A (Fig. 4). That is, phenols were adsorbed by the compound Ⅰ with almost no release of butylamine. In compound Ⅱ, butylamine with straight conformation arranges tightly in the interlayer region and has no void space.[3] In contrast to this, butylamines with straight and bent conformation coexist in compound Ⅰ and do not arrange tightly. Therefore, compound Ⅰ has less butylamine and larger void space in the interlayer region than compound Ⅱ. The void space in the interlayer region is a necessary condition for the adsorption of phenols. Consequently, butylamine in the interlayer region of compound Ⅰ works as the pillar for the adsorption of phenols to serve the hydrophobicity of alkyl chain in butylamine, the regulation of the acidity of the host α-ZrP, and a void space in the interlayer region.

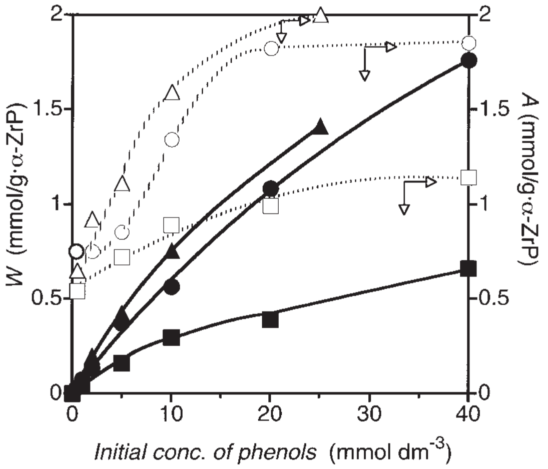

Fig. 3. Adsorption amount (W) of phenols and amount (A) of deintercalated butylamine from compound Ⅱ. ■, □; C_6H_5OH, ●, ○; $C_6H_4(OH)Cl$, ▲, △; $C_6H_3(OH)Cl_2$.

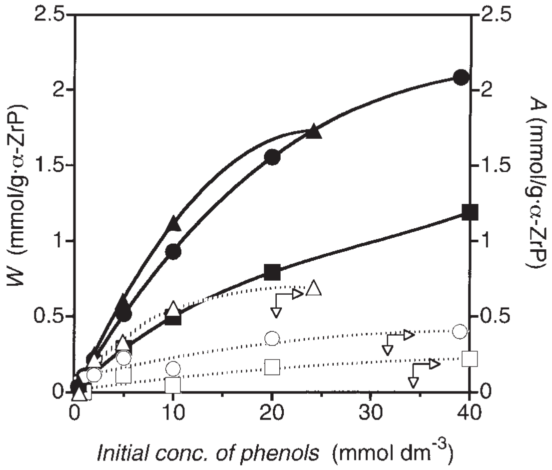

Fig. 4. Adsorption amount (W) of phenols and amount (A) of deintercalated butylamine from compound Ⅰ. ■, □; C_6H_5OH, ●, ○; $C_6H_4(OH)Cl$, ▲, △; $C_6H_3(OH)Cl_2$.

In order to clarify the adsorption mechanism of phenols microscopically, these intercalation compounds were characterized by the measurements of X-ray diffraction (XRD) and solid-state NMR. Figure 5 shows XRD patterns of compound Ⅰ before and after the reaction with various concentrations of $C_6H_3(OH)Cl_2$ aqueous solution for 6 h. Before the adsorption of $C_6H_3(OH)Cl_2$, compound Ⅰ has the interlayer distances of 16.2 and 18.0 Å. After the adsorption, their interlayer distances increased with the increase of $C_6H_3(OH)Cl_2$ concentration, and expanded up to 19.0 Å at maximum adsorption. These expansions indicate that the adsorbed $C_6H_3(OH)Cl_2$ molecule is cointercalated into interlayer region of α-ZrP but is not adsorbed on the outer surface of compounds. This fact was also confirmed by the increase of carbon contents determined by the el-

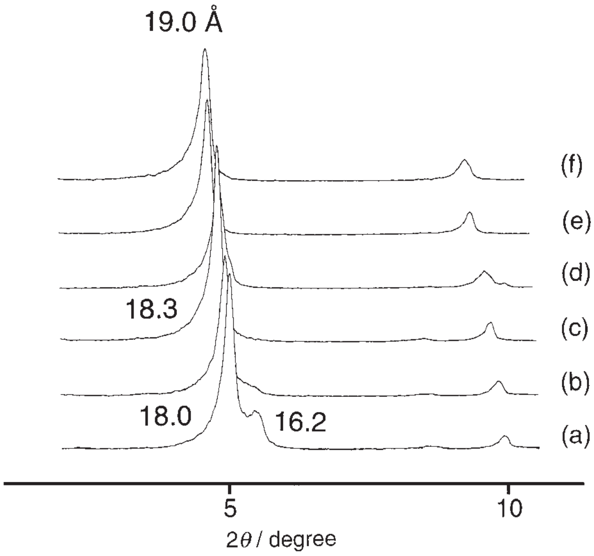

Fig. 5. XRD patterns of compound Ⅰ before and after adsorption of various concentrations of $C_6H_3(OH)Cl_2$. (a); Before, (b); 0.5 mmol dm^{-3}, (c); 2 mmol dm^{-3}, (d); 5 mmol dm^{-3}, (e); 10 mmol dm^{-3}, (f); 25 mmol dm^{-3}.

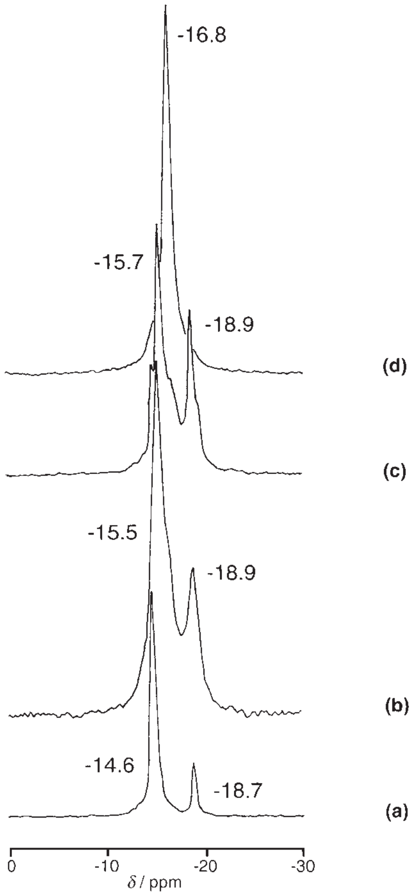

Fig. 6. ^{31}P MAS NMR spectra of compounds I and II before and after adsorption of $C_6H_3(OH)Cl_2$. (a); Compound II, (b); compound II after adsorption, (c); compound I, (d); compound I after adsorption. Concentration of phenols; 25 mmol dm^{-3}, reaction time; 6 h.

emental analysis and by the peak of $C_6H_3(OH)Cl_2$ molecule at around 120 ppm in the ^{13}C CP/MAS NMR spectrum of the intercalation compound after the adsorption of $C_6H_3(OH)Cl_2$. Figure 6 shows ^{31}P MAS NMR spectra of compounds I and II before and after the adsorption of $C_6H_3(OH)Cl_2$, which reflect the environment of phosphate group in layered phosphate.[3,4] α-ZrP shows a single peak at −18.7 ppm assigned to the $HPO_4{}^{2-}$ group. In the spectrum of compound II, the peak at −18.7 ppm of α-ZrP shifted to a low field (−14.6 ppm) due to the deprotonation of the $HPO_4{}^{2-}$ group by the reaction with butylamine (Fig. 6-a). And the peak moved to −15.5 ppm in the spectrum after the adsorption of $C_6H_3(OH)Cl_2$, which was very similar to the spectrum of compound I (Fig. 6-b, c). This indicates that butylamine in compound II changed to the conformation of compound I by the release of butylamine and that some void space was produced in the interlayer region. This result substantiates the claim that the void space is essential for the adsorption of phenols. On the other hand, the peak of compound I shifted to −16.8 ppm by the adsorption of $C_6H_3(OH)Cl_2$, in spite of no release of butylamine (Fig. 6-d). This high-field shift proves that the interaction of butylamine and phosphate group became slightly weak due to the presence of acidic phenols. Thus, $C_6H_3(OH)Cl_2$ molecule was adsorbed by the interaction with butylamine in the void space of the interlayer region. A similar tendency was observed for the other phenols, although the expansions of interlayer distance and the changes of solid-state NMR spectra were small.

Conclusion

Butylamine-intercalated α-zirconium phosphate adsorbed harmful pollutants such as phenol, chlorophenol, and 2,4-dichlorophenol. Phenols were co-intercalated into the interlayer region and the adsorption reactions of phenols reached equilibrium within 15 min. The adsorption amounts depended on the hydrophobicity of phenols; 2,4-dichlorophenol was adsorbed best in three phenols because of its higher hydrophobicity. The adsorption of phenols related to the uptaken amounts of butylamine into α-ZrP. The maximum adsorption amounts ($C_6H_3(OH)Cl_2$, $C_6H_4(OH)Cl$, and C_6H_5OH are 1.1, 0.9, and 0.5 mmol/g•α-ZrP, respectively) of phenols were reached when 4.4 mmol butylamine was uptaken into a gram of α-ZrP; above this value it decreased and some butylamine was released. For the adsorption of phenols, it was essential that the acidity and the void space in the interlayer region of the host α-ZrP were regulated by the intercalation of butylamine. Phenols were adsorbed by the hydrophobic interaction with butylamine in the interlayer region.

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