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Structure and Organic Gas-Adsorption Properties of Some Polyamine Intercalated α-Zirconium Phosphates

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The intercalation of polyamine into α-zirconium phosphate (α-ZrP) was examined at room temperature and 80 °C. In triethylenetetramine (3E4A), tetraethylenepentamine (4E5A), and pentaethylenehexamine (5E6A) the temperature of the reactions influenced the rate of intercalation, but did not effect the structure of the intercalation compound. On the other hand, the ratios of the constituent phases in the *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine (3P4A) intercalated solid were greatly influenced by the reaction temperature, and two phases with the different interlayer distances could be formed by controlling it. In the phase with an interlayer distance of $d = 20$ Å, obtained predominantly at 80 °C, 3P4A was present as a monolayer of extended molecules in the interlayer region, in which the longitudinal axis of 3P4A was inclined at ca. 60° to the α-ZrP layers. In the phase with $d = 17$ Å, obtained at room temperature, 3P4A existed as a bent form. These polyamine intercalated solids drastically adsorbed acetic acid, formaldehyde, acetaldehyde, and cinnamaldehyde.

Layered phosphates of tetravalent metals, such as Zr(IV) and Ti(IV), are insoluble acid salts, and are known to be inorganic ion exchangers.[1,2] They can readily intercalate various organic compounds, such as amines,[3] protonated alcohols,[4] and quaternary ammonium ions.[5] Extensive studies on the intercalation of alkylamines and α,ω-alkanediamines into layered phosphates have demonstrated the formation of a bilayer and a monolayer of amine, respectively, in the interlayer region, in which the alkyl chains are inclined at roughly 60° to the zirconium or titanium phosphate layer.[6—9] Alkylamine intercalation compounds have also been used as a means for the intercalation of other guest compounds which can not be directly intercalated.[1] It has been considered to be due to an expansion of the interlayer distance of the layered phosphate by alkylamines. The detailed mechanism of this reaction was clarified by our previous study on the intercalation of methylene blue into layered phosphate.[10] Although the intercalation of methylene blue was accelerated by the presence of alkylamines, such as butylamine, it was inhibited by the presence of too much alkylamines. This was because the layered phosphate was fully intercalated by alkylamine, in which alkylamine forms a bilayer, and has no space into which other guest molecules can insert.

In order to facilitate the intercalation of the third guest molecules, polyamine was used instead of alkylamine for space-construction in the interlayer region of the layered phosphate. Recently, the intercalation of dendric polyamines into α- and γ- zirconium phosphates has been reported to verify a multi-binding mechanism between the amino groups of dendric polyamines and phosphate groups.[11] Since polyamine has different kinds of active sites, such as amino and imino groups, it is expected that intercalation compounds with various arrangements of polyamine in the interlayer region will be obtained. When polyamine is intercalated into layered phosphates, multi-binding sites exist in the interlayer region. The variation of the arrangement of polyamine and of active sites in the intercalated solids would serve as a new material with a special reaction field in the interlayer region. For example, primary or secondary amines in the interlayer region may react with aldehyde to form imine or enamine.

In the present study, polyamine intercalation compounds with various arrangements of polyamine in the interlayer region of α-zirconium phosphate (α-ZrP) were prepared by using several guest compounds having different shapes and controlling the reaction conditions. Further, the adsorption properties of acid and aldehyde gases by the polyamine intercalation compound of α-ZrP were examined in expectation of interaction with the interlayer active sites.

Experimental

Chemicals. Zirconium bis(monohydrogenphosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), was prepared according to a procedure described in a previous paper.[12] *N*-(3-Aminopropyl)-1,3-propanediamine and *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine were of reagent grade from Aldrich. The other polyamines, acetic acid, and aldehydes, were purchased from Wako Chemical Industries Ltd.

Intercalation Procedure. α-ZrP (1.0 g) was suspended in 0.1 dm^3 of a 0.1 $mol\,dm^{-3}$ aqueous polyamine solution, and the suspension was stirred at room temperature or 80 °C for 3—14 d. The resultant products were filtered, washed with distilled water, and dried in air.

Analytical Procedures. The X-ray diffraction patterns were measured with a Rigaku Denki Rint 2000 diffractometer using Ni-filtered Cu *Kα* radiation to monitor all new phases and to measure their interlayer distances. A Rigaku Denki Differential Thermogravimetric Analyzer (TG 8110) was used with a platinum rhodium pan in an air flow for DTA and TG measurements. Elemental analyses of C and N in the intercalation compound were performed with a Sumigragh NC-90-A.

Adsorption of Acid and Aldehyde Gases. The adsorption of gas was performed in a desiccator with saturated vapor of various aldehydes or acetic acid at room temperature by using 0.3 g of a polyamine intercalation compound. The amount of adsorption was measured based on the increase in weight.

Results and Discussion

Intercalation of Polyamines into *α*-ZrP. The intercalation of polyamines (1,2-diaminoethane, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, 1,3-diaminopropane, *N*-(3-aminopropyl)-1,3-propanediamine, and *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine) into *α*-ZrP was proved by the X-ray diffraction pattern, differential thermal analysis and thermogravimetry (DTA-TG), and elemental analysis. Figure 1 shows the X-ray diffraction patterns of the triethylenetetramine (3E4A), tetraethylenepentamine (4E5A), pentaethylenehexamine (5E6A), and *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine (3P4A) intercalation compounds of *α*-ZrP, obtained at 80 °C (b—e) and the 3P4A intercalation compound obtained at room temperature (f) after 7 d. In Fig. 1(b)—(f), new diffraction peaks appeared at a lower angle than that ($d = 7.6$ Å) of the host *α*-ZrP (Fig. 1(a)). Such a low angle shift in the diffraction peak clearly demonstrates that these polyamines are intercalated into *α*-ZrP along with expansion of the interlayer distances specified in Fig. 1.

Figure 2 shows DTA and TG curves for the 3E4A and 3P4A intercalation compounds of *α*-ZrP. In the DTA curve of intact *α*-ZrP (Fig. 2(a)), two endothermic peaks due to the dehydration of the water of crystallization appear at about 150 and 220 °C, and an endothermic peak by the dehydration of structural water appears at 590 °C.[1] On the contrary, the 3E4A intercalated compound (Fig. 2(b)) shows two exothermic peaks at about 360 and 510 °C with a weight loss of 13.5 and 6.5%, respectively, and the 3P4A intercalated compound (Fig. 2(c)) has three exothermic peaks at 260, 330, and 460 °C with about a 3.7, 10.4, and 10.8% weight loss, respectively. They must be ascribable to the thermal decomposition of polyamines intercalated into *α*-ZrP. The same results were obtained in the other polyamine intercalation compounds. Thus, the intercalation of polyamines into *α*-ZrP was also confirmed by DTA.

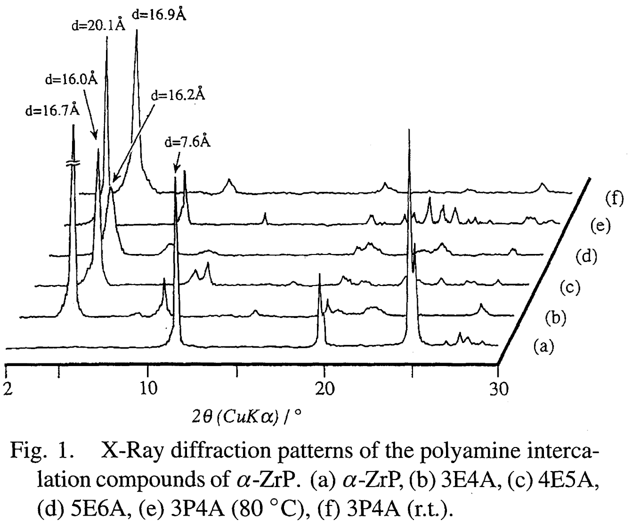

Fig. 1. X-Ray diffraction patterns of the polyamine intercalation compounds of *α*-ZrP. (a) *α*-ZrP, (b) 3E4A, (c) 4E5A, (d) 5E6A, (e) 3P4A (80 °C), (f) 3P4A (r.t.).

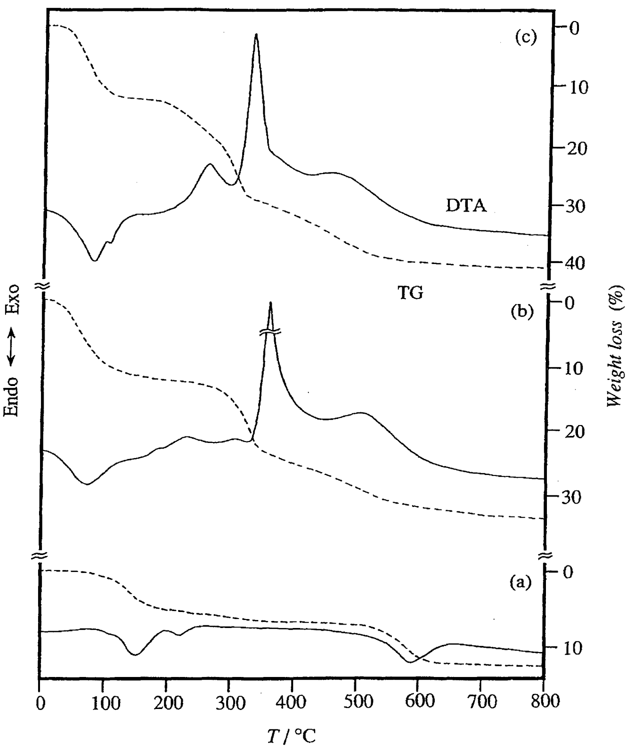

Fig. 2. DTA and TG curves of the intercalation compounds of *α*-ZrP. (a) *α*-ZrP, (b) 3E4A, (c) 3P4A (80 °C).

Effect of Reaction Temperature. The interlayer distances of the new phases and the contents of polyamine in the intercalation compounds, obtained by a reaction at room temperature or 80 °C for 7 d, are summarized in Table 1. More than two new phases with the different interlayer distances coexisted in each polyamine intercalated solid. In 3E4A, 4E5A, and 5E6A, only a slightly pronounced difference in the interlayer distance of new phases between room temperature and 80 °C was found, except for the appearance of a phase with $d = 9.4$ Å in 4E5A at 80 °C, although the contents of polyamine in the intercalation compounds obtained at room temperature were lower than those at 80 °C. The main phase (boldfaced in Table 1) did not change during a reaction of more than 7 d in each sample, indicating that the constituent phases of the polyamine (3E4A, 4E5A, 5E6A) intercalated solids were scarcely influenced by the reaction temperature, although the rates of intercalation were influenced.

Two phases with the different interlayer distances, ca. 17

Table 1. Interlayer Distances of Phases and Contents of Polyamine Intercalated Solids

Polyamine	R.T.		80 °C	
	d/Å	Content mmol g^{-1} (α-ZrP)	d/Å	Content mmol g^{-1} (α-ZrP)
3E4A	7.6 (8) 10.2 (7) **15.4** (85)	1.68	10.2 (2) **16.7** (98)	1.99
4E5A	7.6 (47) 10.2 (17) **15.8** (36)	0.90	9.4 (18) 10.2 (4) **16.0** (78)	1.28
5E6A	7.6 (53) 10.2 (22) **15.9** (25)	0.81	10.2 (12) **16.2** (88)	1.16
3P4A	**16.9** (85) 19.8 (15)	1.90	16.5 (6) **20.1** (94)	1.96

The numbers in parenthesis in table represent an estimate of the amount of each phase present.

and 20 Å, coexisted in the 3P4A intercalated solids at both room temperature and 80 °C. The main phase at room temperature was the phase with d = 17 Å, and that at 80 °C was d = 20 Å, although the contents of 3P4A were not different between the two samples.

Figure 3 shows the time course of the amounts of the two phases coexisting in the 3P4A intercalated solids at room temperature and 80 °C, as estimated from the intensities of the respective peaks in the X-ray diffraction pattern. At room temperature (Fig. 3(a)), the phase with d = 17 Å was predominantly formed with the minor formation of a phase with d = 20 Å, and the host phase (d = 7.6 Å) thoroughly disappeared after 3 d. The ratio of the two phases in the 3P4A intercalated solid remained constant since then. At 80 °C (Fig. 3(b)), the phase with d = 20 Å was mainly formed with a slight formation of the phase with d = 17 Å after 3 d. Although the ratio of the constituent phases changed slightly, an almost pure phase with d = 20 Å was obtained after 3—7 d. Thus, the ratio of the constituent phases in the 3P4A intercalated solid was largely influenced by the reaction temperature. Consequently, two phases with the different interlayer distances could be selectively formed by controlling the reaction temperature.

Arrangement of Polyamine in the Interlayer Region. Figure 4 shows the relationship between the interlayer distance of the main phase in the intercalation compounds obtained at 80 °C for 7 d, and the number of ethylene and propylene units (x and y, respectively) in the polyamine molecule. In the former, the interlayer distance increased along with increasing the number of ethylene units up to x = 3, but no further increase in the interlayer distance was observed for x = 4 and 5 (Fig. 4(a)). It will be meaningful to compare these results with the intercalation of α,ω-alkanediamines into α-ZrP. M. Casciola et al.[9] have reported that a good correlation between the interlayer distance of the fully intercalated monohydrate compounds of α,ω-alkanediamine and the number (n) of carbon atoms in the alkyl chain has been observed, and gives a straight line expressed by the equation $d = 8.93 + 1.08\ n$. Their results suggest that α,ω-alkanediamines are present as a monolayer

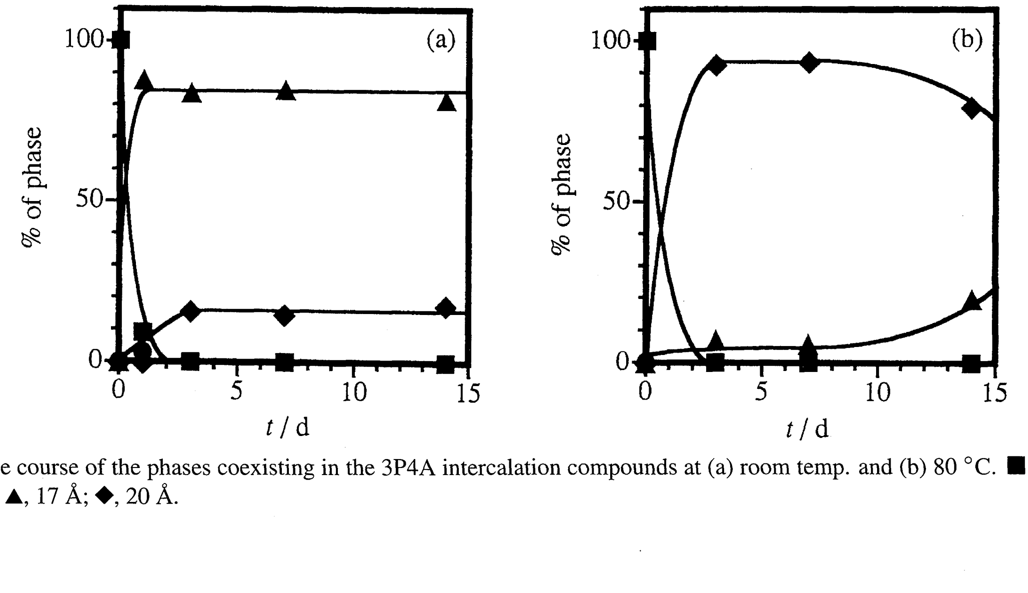

Fig. 3. Time course of the phases coexisting in the 3P4A intercalation compounds at (a) room temp. and (b) 80 °C. ■, phase with d = 7.6 Å; ▲, 17 Å; ◆, 20 Å.

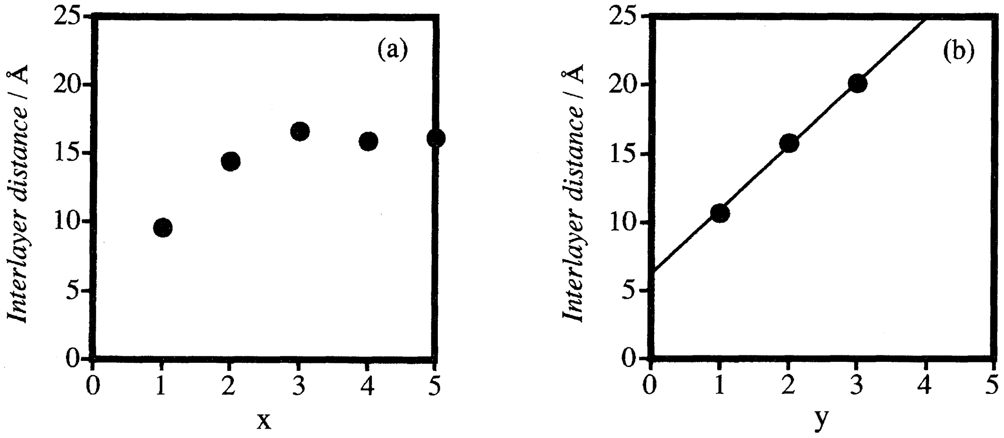

Fig. 4. Relationship between the interlayer distance of the main phase in the intercalation compounds at 80 °C and the number of ethylene and propylene units (*x* and *y*, respectively) in polyamine molecule. (a) $H_2NC_2H_4(NHC_2H_4)_{x-1}NH_2$, (b) $H_2NC_3H_6(NHC_3H_6)_{y-1}NH_2$.

of extended molecules with their alkyl chains inclined at 58° to the phosphate layers. Since the longitudinal length of diethylenetriamine (2E3A) and the 3E4A molecules with an all-*trans* conformation are nearly equal to those of diaminopentane and diaminooctane, respectively, if the polyamines are oriented in the α-ZrP layer in the same way with α,ω-alkanediamines, the interlayer distances of their intercalation compounds will be similar to those of the corresponding α,ω-alkanediamine intercalation compounds. The interlayer distances of the diaminopentane and diaminooctane intercalation compounds have been estimated to be 14.3 and 17.6 Å by the above equation, which are near to and slightly larger than the values of the interlayer distance of the 2E3A and 3E4A intercalated compounds, 14.5 and 16.7 Å, respectively. This suggests that these polyamines are present as a monolayer of extended molecules with their alkyl chains inclined at ca. 60° or a lower angle to the phosphate layers, as shown in Fig. 5(b). On the other hand, since the interlayer distances of 4E5A and 5E6A did not increase in spite of an increase in the number of ethylene units in a polyamine molecule ($x = 4$ and 5 in Fig. 4(a)), these polyamines must cause a bent form in the interlayer region, as shown in Fig. 5(a).

In the 3P4A intercalated compound, the interlayer distance increased along with increasing the number of propylene units up to $y = 3$ (Fig. 4(b)); a plot gives a straight line, suggesting that the intercalated polyamines are regularly oriented in the interlayer region of α-ZrP. The slope of the straight line was calculated to be 4.70. It is difficult to show that 3P4A forms a bilayer in the interlayer region by taking account of existence of the active sites ($-NH_2$ groups) at both the head and the tail in the 3P4A molecule. Therefore, assuming that the conformation of the C–C or C–N chain in polyamine is all-*trans* and that the length of the chain increases by 1.27 Å for each additional carbon or nitrogen atom for convenience as a alkyl chain, the angle of orientation of their longitudinal axis to the layer of α-ZrP is $\theta = \sin^{-1}(4.70/1.27\times4) = 67.7°$. In the intercalation of alkylamines and α,ω-alkanediamines into α-ZrP, it has been reported that the alkyl chains in amines incline at ca. 60° to the phosphate layers.[6—9] The value of θ for polyamines is nearly equal to those for the alkylamines and α,ω-alkanediamines. A schematic structural model of 3P4A in the phase with an interlayer distance of $d = 20.1$ Å is shown in Fig. 5(b). 3P4A forms a monolayer in the interlayer region, in which the longitudinal axis of 3P4A inclines at ca. 60° to the α-ZrP layers.

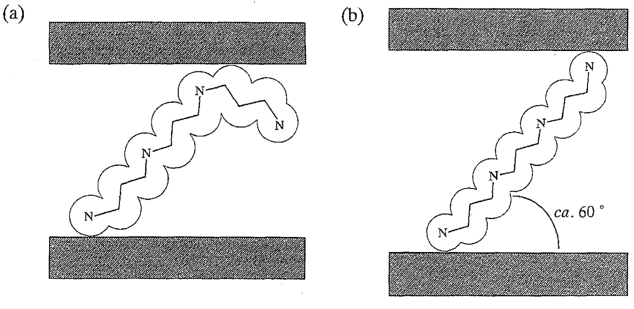

Fig. 5. Schematic structural models of polyamines intercalated into α-ZrP. (a) 3P4A (r.t.), (b) 3P4A (80 °C).

On the other hand, the interlayer distance ($d = 16.9$ Å) of the main phase in the 3P4A intercalated solid, obtained at room temperature, was similar to that ($d = 15.8$ Å) of the main phase in the *N*-(3-aminopropyl)-1,3-propanediamine (2P3A) intercalated solid at 80 °C shown in Fig. 4. In the 3P4A intercalation compound synthesized at room temperature, therefore, it is reasonable that the nitrogen atoms of one primary amine and one secondary amine in the 3P4A molecule interact with each phosphate group of the adjacent layers shown in Fig. 5(a). Thus, 3P4A intercalation compounds with the different arrangements of the guest were successfully prepared by controlling the reaction temperature.

Adsorption of Acetic Acid and Aldehyde Gases. Figure 6 shows the time dependence of the adsorption of formaldehyde by polyamine intercalation compounds of α-ZrP. In contrast with no adsorption of formaldehyde into α-ZrP itself, polyamine intercalation compounds can adsorb considerable amounts of formaldehyde. This is due to the for-

Table 2. Amount of Adsorption by Polyamine Intercalated Solids at Room Temperature and after 42 d

Intercalated solid	Adsorption amount / mmol g^{-1} (intercalated solid)			
	CH_3COOH	HCHO	CH_3CHO[b)]	Cinnamaldehyde
3E4A[a)]	119	89	24	3
4E5A[a)]	75	49	12	2
5E6A[a)]	86	54	14	2
3P4A (r.t.)	146	110	53	3
3P4A[a)]	232	125	68	6

a) synthesized at 80 °C. b) The amounts of adsorption after 2 d are listed, because the sample gradually changed to liquid like phase.

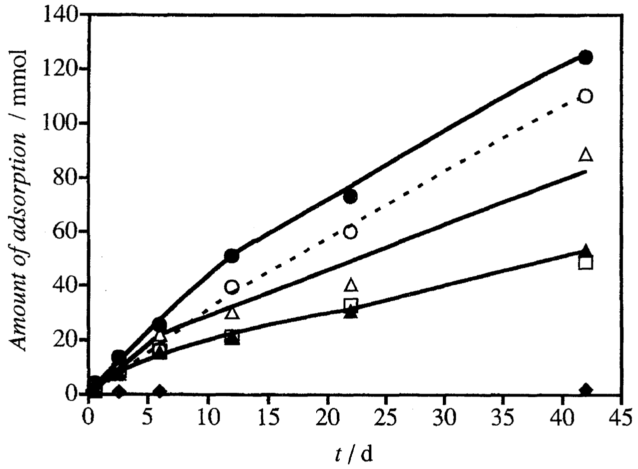

Fig. 6. Time dependence of adsorption of HCHO by polyamine intercalation compounds (1 g) of α-ZrP. △; 3E4A, □; 4E5A, ▲; 5E6A, ○; 3P4A (r.t.), ●; 3P4A (80 °C), ◆; α-ZrP.

mation of a reaction field by the intercalation of polyamine, as mentioned in the previous section. The white polyamine intercalation compounds turned to yellow upon adsorbing formaldehyde, and the color became deep along with increasing the amounts of adsorption, indicating that some kinds of reaction occured. The amounts of adsorption increased with time for all of the intercalation compounds. In the present study concerning the adsorption of aldehyde gas by polyamine intercalation compounds, it was hard to distinguish between chemical adsorption by the reaction of an amine or imine group of the polyamines and adsorption due to other mechanisms. Thus, Table 2 shows the amounts of adsorption of various gases at 42 d, except for acetaldehyde (2 d). All of the polyamine intercalation compounds adsorb considerable amounts of various aldehydes and acetic acid, although the adsorption rate depended on their vapor pressures and the polyamine intercalation compounds. As mentioned in the previous section, the polyamine intercalation compounds used in this study have different arrangements and contents of polyamines. Therefore, it is hard to directly compare the amounts of adsorption by these polyamine intercalation compounds. However, it is fruitful to compare them qualitatively. The adsorption of aldehyde and acetic acid gases must occur via the reaction of an amino or imino group with them. Therefore, the amount of adsorption will increase along with an increase in the reaction site, $-NH_2$ and $-NH-$ groups, in polyamine. However, this suggests that all aldehydes do not react directly with an amino or imino group in the intercalation compounds, because the number of formaldehyde molecules adsorbed extremely exceeds the numbers of amino and imino groups in the intercalation compound. In any case, the aldehyde adsorption capacity is closely related to the number of reaction sites of the polyamines; that is, the contents of polyamines in the intercalation compounds as listed in Table 1. Furthermore, it is meaningful to compare the amounts of adsorption of aldehydes by the 3P4A intercalation compounds synthesized at room temperature and 80 °C. The difference in the adsorption capacity by these compounds would be related to the arrangement of 3P4A in the interlayer region, because the contents of 3P4A are almost the same for both compounds. The 3P4A intercalated solid (straight, Fig. 5(b)) adsorbs more aldehydes or acetic acid than the 3P4A intercalated solid (bent, Fig. 5(a)) does. Although it is hard to figure out the adsorption mechanism microscopically at the present stage, the arrangement of polyamine in the interlayer region strongly influences the adsorption of these gases.

In conclusion, polyamine intercalation compounds were found to adsorb considerable amounts of aldehyde and acetic acid gases. By choosing polyamine and controlling the arrangement of polyamine in the interlayer region, intercalation compounds with different adsorption capacities can be obtained. These results suggest that the polyamine intercalation compounds of α-ZrP are new functional materials with a reaction field in the interlayer region. Therefore, the polyamine intercalation compounds are expected to be applied as an adsorbent of a sick-house syndrome-causing compound, aldehyde gas, released from new building materials.

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