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Intercalation of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane by α- and γ-zirconium phosphates

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The uptake of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (tdco) by α- and γ-zirconium phosphates was studied at 25 °C. The α phosphate incompletely reacts with tdco to form an intercalated phase in which the guest molecules are arranged as a 0.68 nm thick monolayer, probably in their twisted conformation. The γ phosphate is totally converted into a single phase containing a 0.91 nm thick bilayer of tdco molecules with their molecular planes parallel to the inorganic layers.

Much attention has been paid to new families of microporous materials obtainable by the pillaring of inorganic layered compounds with polynuclear complex ions or bulky organic molecules.[1] Of particular interest to us is a new class of organic and inorganic combined host materials which would act as inclusion agents with high selectivity.[2–7] Previous studies have used mainly cyclodextrins and partially calixarenes as the organic host component to be intercalated in layered parent hosts, such as montmorillonites and zirconium phosphates.

Crown ethers are cyclic molecules in which oxygen and/or nitrogen atoms form much smaller cavities available for ionic fixing or sieving.[8] Such functions may be made more specific by the combined effects resulting from the placement of the host molecules in the interlayer space of layered crystals. Ruiz-Hitzky and Casal[9] reported the intercalation of crown ethers in montmorillonites. In these systems, however, the intercalated crown ethers could not serve as a secondary host to any other guest species because the molecular cavities were fully occupied with interlayer metal cations such as Na$^+$ and Ba^{2+}. Attempts were thus made to prepare crown ether/layered zirconium phosphate complexes in which the crown ether molecules are ionically or covalently bonded to the phosphate layers.

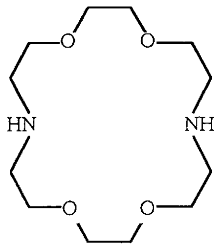
This paper describes the first attempt to examine the intercalation of cationic 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (tdco) by α- and γ-zirconium phosphates (ZrP).

Experimental

The α- and γ-ZrP samples used were the same as those used in previous work.[5] The tdco was reagent grade and used without further purification. The ZrP samples were soaked in an aqueous solution containing various amounts of tdco at 25 °C for 5 d, centrifuged, fully washed with water, and freeze-dried. The pH of the supernatants was measured with a pH meter at 25 °C. The tdco and water contents were determined by thermogravimetry (tg) at a heating rate of 10 °C min^{-1}. X-Ray diffraction measurements were made using Cu-Kα radiation. The tdco was also titrated with aqueous hydrochloric acid solution to determine its pK_a values.

Results and Discussion

Fig. 1(*a*) and 1(*b*) show the X-ray diffraction patterns of the resulting solids in the α-ZrP– and γ-ZrP–tdco systems, respectively. With increasing addition of tdco the peak at 2θ = 11.6 (d = 0.76) or 7.18° (d = 1.23 nm) attributable to the 002 reflection of the host phase in each system decreased considerably in intensity or disappeared, while a new diffraction peak appeared near 2θ = 6.22 (d = 1.42) or 4.75° (d = 1.85 nm) along with its second-order counterpart and increased in intensity, indicating that tdco is taken up by each parent host to form an intercalated phase. The interlayer spacings of the resulting intercalates were determined from the 001 reflection in the X-ray diffraction patterns and the thickness of the intercalate portion, Δ, was obtained by subtracting the thickness of the inorganic layer, 0.74 nm for α-ZrP or 0.94 nm for γ-ZrP, from the observed spacings, as previously.[5] These results are summarized in Fig. 2. The above X-ray observations indicate that an appreciable amount of α-ZrP remains unreacted even at a [tdco]/[ZrP] mixing ratio of as high as 10 : 1 while γ-ZrP is totally converted into an intercalated phase at the mixing ratio of as low as 0.5. A similar difference in reactivity was observed for the intercalation of 2-aminopropylamino-substituted β-cyclodextrin by α- and γ-ZrP.[5]



tdco

The thermogravimetric curves for the resulting solids indicated three or four steps at temperatures up to 1000 °C, as shown in Fig. 3(*a*) and 3(*b*). The first weight loss at below 100 °C is due to desorption of interlayer water and the second in the 100–300 °C temperature range is attributable to partial desorption of the organic moiety. The third and/or fourth weight loss observed at above 300 °C is primarily due to the residual organic moiety and partly to condensation of the hydrogen phosphate groups which occurs in one step near 400 °C for the α form and in two steps at 300 and 800 °C for the γ form. Combination of the thermogravimetric data for these solids and their host phosphate gave plots of tdco uptake in moles, x, per mol of α- or γ-ZrP against the amount of tdco added, Fig. 4. The uptake of tdco by γ-ZrP increases rapidly up to a constant value of x = 0.37 at its full loading. Table 1 lists the intercalation parameters for the resulting intercalates with tdco at its full loadings. The apparently low value of x = 0.11 for the α form is due to the intercalated phase coexisting with the host phase remaining. Since the X-ray observations indicate that the 002 peak of the remaining α-ZrP phase in the resulting solid is decreased in intensity down to approximately one-

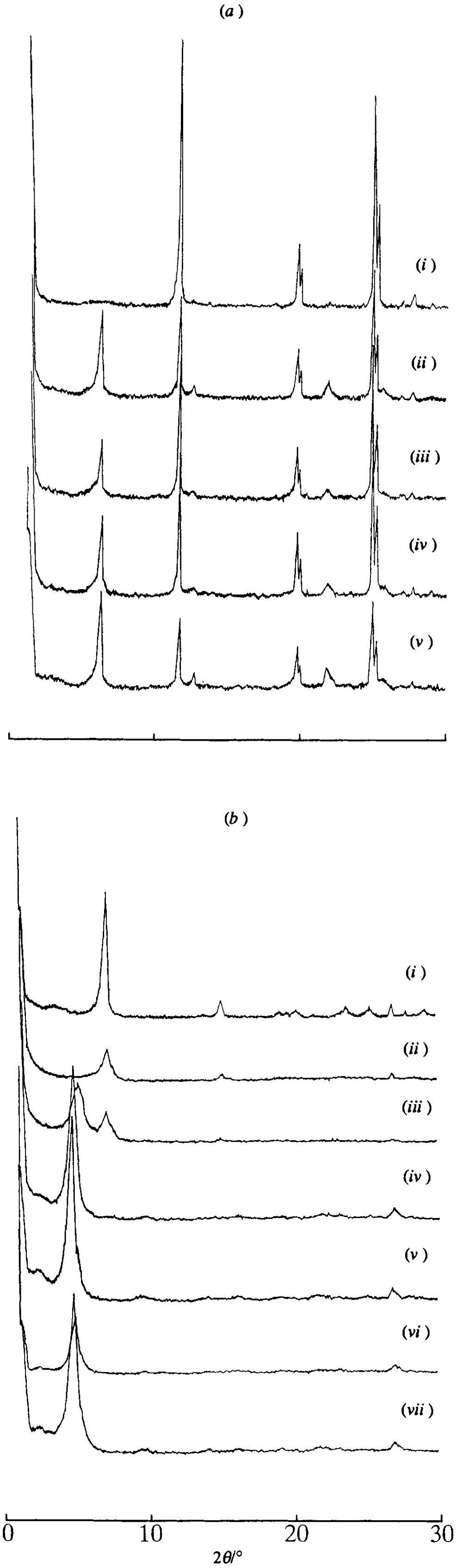


Fig. 1 X-Ray diffraction patterns of the reaction products of (*a*) α- and (*b*) γ-zirconium phosphates with tdco. Amount of tdco added (mmol per gram of host phosphate): (*a*) 0 (*i*), 1.0 (*ii*), 2.0 (*iii*), 3.0 (*iv*) and 10.0 (*v*); (*b*) 0 (*i*), 0.1 (*ii*), 0.3 (*iii*), 0.5 (*iv*), 1.0 (*v*), 1.5 (*vi*) and 2.0 (*vii*)

fourth of that of the initial state, the actual x value for the tdco intercalate of α-ZrP would be at most 0.11 times four thirds or 0.15.

The pH of the supernatants equilibrated with the resulting

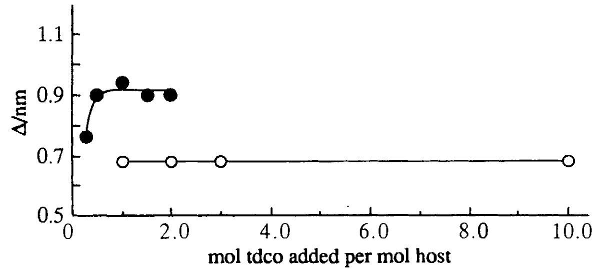


Fig. 2 Thickness of the intercalated layer, Δ (see text), as a function of tdco added for the tdco intercalates of (○) α- and (●) γ-zirconium phosphates

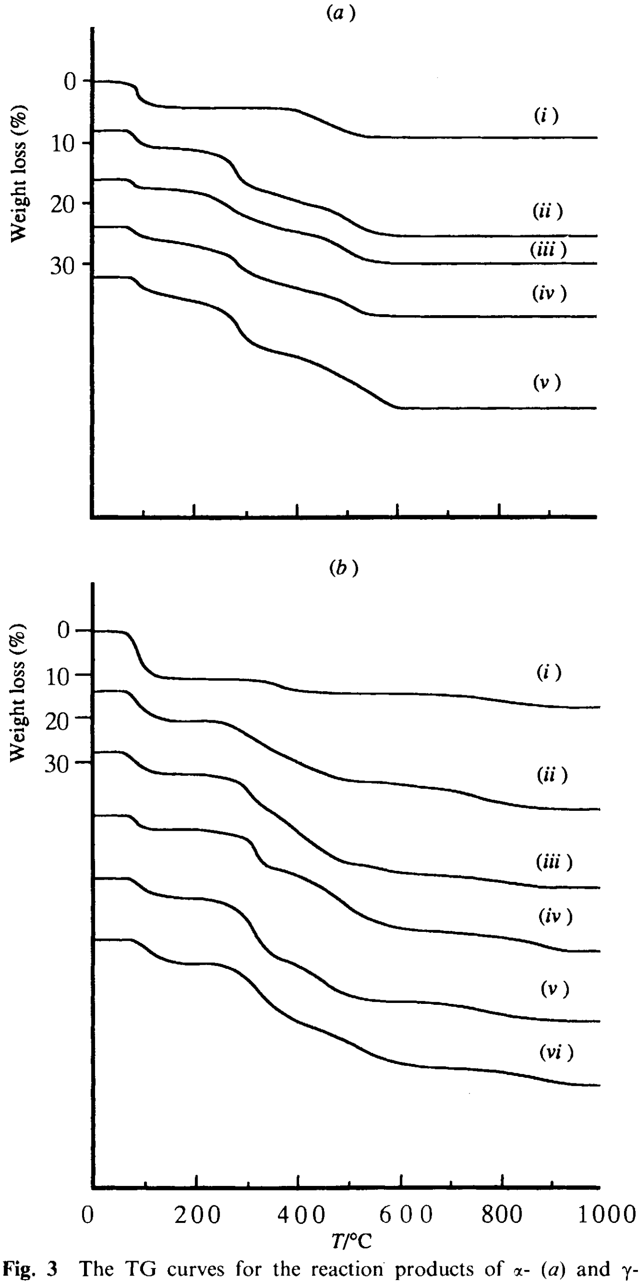


Fig. 3 The TG curves for the reaction products of α- (*a*) and γ-zirconium phosphates (*b*) with tdco. Amount of tdco added (mmol per gram of host phosphate): (*a*) 0 (*i*), 1.0 (*ii*), 2.0 (*iii*), 3.0 (*iv*) and 10.0 (*v*); (*b*) 0 (*i*), 0.3 (*ii*), 0.5 (*iii*), 1.0 (*iv*), 1.5 (*v*) and 2.0 (*vi*)

solids at high uptakes were 9.7 and 9.0 for the α and γ systems, respectively. The pK_a values of tdco were determined as *ca.* 2.8 and 8.5 from the titration of tdco with aqueous hydrochloric acid solution. These observations suggest that the intercalation of tdco molecules proceeds by replacement of one proton of each interlayer hydrogenphosphate group by the $>NH_2^+$ groups of their protonated forms to yield an ionically bonded

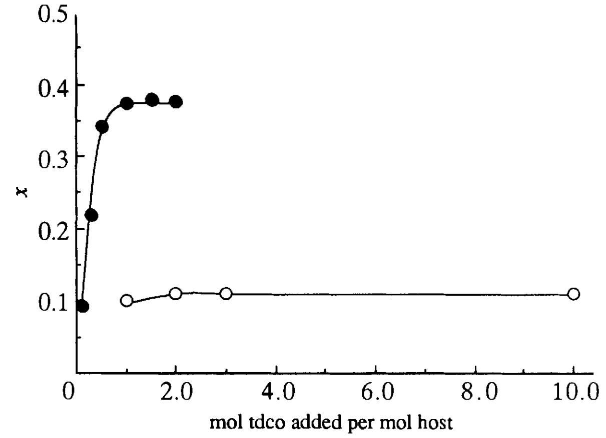


Fig. 4 Uptake of tdco by (○) α- and (●) γ-zirconium phosphates as a function of tdco added. Key as in Fig. 2

Table 1 Interlayer spacing and composition of tdco intercalates of α- and γ-zirconium phosphates

Host phase	tdco added/ mmol g^{-1}	Interlayer spacing/nm	Δ/nm	Composition*
α-ZrP	10.0	1.42	0.68	0.11
γ-ZrP	2.0	1.85	0.91	0.37

* In mol of tdco per formula weight of host phosphate, or x in $Zr(HPO_4)_2(tdco)_x{\cdot}yH_2O$ or $ZrPO_4(H_2PO_4)(tdco)_x{\cdot}yH_2O$. The x value for the α system is based on the total amount of reacted and unreacted host phase in the resulting solid.

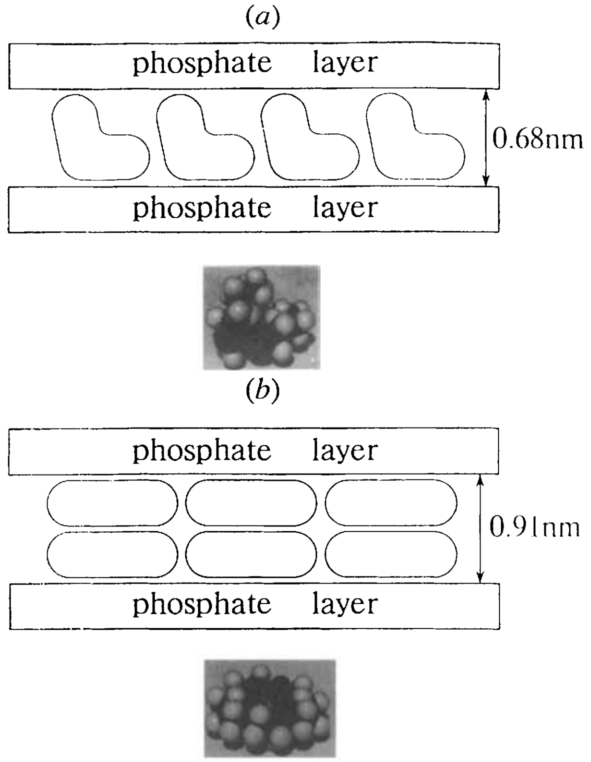


Fig. 5 Schematic representations of the probable arrangement of tdco molecules in the interlayer space of (*a*) α- and (*b*) γ-zirconium phosphates, along with CPK models for their twisted and flat conformers

$-PO^-NH_2^+<$ form. Upon intercalation the remaining $>NH$ group of each guest molecule could also capture the interlayer proton to anchor to the surface hydrogenphosphate site through a similar ionically bonded form.

α-Zirconium phosphate possesses a layer structure in which each layer consists of a plane of zirconium atoms bridged through phosphate groups located alternately above and below this plane.[10] Three oxygen atoms of the tetrahedral phosphate group are bonded to three zirconium atoms in the plane and the fourth oxygen atom bears a hydrogen and points toward an adjacent layer in the structure. The POH groups pointing up or down in each layer surface are located in a monoclinic cell with distances of 0.92 and 0.53 nm along the *a* and *b* axes, respectively. This atomic arrangement gives $0.92 \times 0.53/2$ or $0.243\ nm^2$ for the effective area per POH site. According to the Corey–Pauling–Koltun (CPK) model, the tdco molecule with its flat conformation has a van der Waals diameter of 1.05 nm and a thickness of 0.45 nm. If the tdco molecules are intercalated as a mono- or bi-layer in their flat conformation, the observed Δ value of 0.68 nm is greater than the thickness of 0.45 nm for the monolayer and less than 0.9 nm for the bilayer. The estimated x value of 0.15 is also much less than $0.243/[2\sqrt{3} \times (1.05/2)^2]$ or 0.25 evaluated for the monolayered form. On the other hand, the van der Waals thickness of the tdco molecule with its twisted conformation is *ca.* 0.7–0.75 nm, which is close to the observed Δ value of 0.68 nm. These facts suggest one possible model in which the tdco molecules intercalated in the α phase are loosely packed in their twisted conformation to form a 0.68 nm thick monolayer, as illustrated in Fig. 5(*a*). In contrast to the flat conformer, the twisted conformer would be in geometrical conformity with the staggered arrangement of the POH groups in any two adjacent layers of the α phase leading to interlayer ionic bridging through the two $>NH_2^+$ groups to the adjacent POH sites.

Recent structural studies revealed that γ-ZrP is a layered phosphate with the composition $ZrPO_4(H_2PO_4){\cdot}2H_2O$ in which two planes of zirconium atoms are linked through PO_4 groups, with $PO_2(OH)_2$ groups bonded to any two zirconium atoms in either plane.[11] The $P(OH)_2$ groups in each layer surface are located in an orthorhombic cell with distances of 0.54 and 0.66 nm along the *a* and *b* axes, respectively. The two OH groups of each $PO_2(OH)_2$ group point toward an adjacent layer in the structure. The effective area per $P(OH)_2$ site for γ-ZrP is taken as 0.54×0.66 or $0.357\ nm^2$. The observed value of 0.91 nm corresponds to twice the molecular thickness or 0.9 nm. Assuming that the tdco molecules in their flat conformation are close-packed as a bilayer with their molecular planes parallel to the inorganic layers, the maximum x value can be evaluated to be $0.357/[2\sqrt{3} \times (1.05/2)^2]$ or 0.37, in good agreement with the observation. The arrangement of the tdco molecules in the γ intercalate is strikingly different from that in the α analogue, as schematically shown in Fig. 5(*b*). This is first because the flat conformer is more advantageous under the interlayer stress due to the attractive interaction between the phosphate layers bearing the face-to-face $P(OH)_2$ groups. Secondly the flat conformer is available for bifurcated intralayer binding through the $>NH_2^+$ groups to the phosphate layer, which would be more feasibly induced by the bifunctional $P(OH)_2$ sites in the γ phase than in the α one. This bifunctional effect as well as the significant pre-expansion of interlayer space due to interlayer-bridging water molecules would be responsible for the high reactivity of γ-ZrP with tdco compared to that of α-ZrP bearing intralayer-bridging water molecules.

Acknowledgements

We thank Dr. Y. Matsushita in Miyazaki University for his helpful comments on the materials used.

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Received 14*th September* 1995; *Paper* 5/06070B