Intercalation of *n*-Alkylamines by γ-Titanium Phosphate. Synthesis of New Materials by Thermal Treatment of the Intercalation Compounds

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Received November 4, 1992. Revised Manuscript Received May 28, 1993

The mechanism of intercalation reactions between *n*-alkylamines and γ-titanium phosphate has been investigated. The composition of these intercalates reveals that only 66% of the P-OH groups present in the material may interact with amine groups of the guest molecules. The compounds with the maximum intercalation have the formula $\gamma\text{-TiH}_{0.7}(\text{PO}_4)_2\cdot1.3\text{C}_n\text{H}_{2n+1}\text{NH}_3\cdot\text{H}_2\text{O}$ (n = 1–6). Well-defined crystalline phases with lower amine content are also isolated; their general formula is $\gamma\text{-TiH}_{2-y}(\text{PO}_4)_2\cdot y\text{C}_n\text{H}_{2n+1}\text{NH}_3\cdot m\text{H}_2\text{O}$ (n = 1–6; y = 0.7, 1.0; m = 0.5, 1.0, 1.5). New materials of the $\gamma\text{-TiH}_{2-y}(\text{PO}_4)_2\cdot y\text{C}_n\text{H}_{2n+1}\text{NH}_3$ (n = 1–6; y = 0.3, 0.7, 1.0, 1.3) formula were synthesized by thermal decomposition of the intercalation compounds $\gamma\text{-TiH}_{0.7}(\text{PO}_4)_2\cdot1.3\text{C}_n\text{H}_{2n+1}\text{NH}_3\cdot\text{H}_2\text{O}$ (n = 1–6). Different routes of reactions are proposed for the intercalation and thermal decomposition processes. When y = 0.7, 1.0, 1.3 the *n*-alkylamines form a bimolecular film. When y = 0.3 the *n*-alkylamines form a monomolecular film. The inclination angle and the packing density in the interlayer space of the *n*-alkylamines were determined. The results are discussed as a function of the γ-titanium phosphate structure. The interest of these materials as molecular sieves and precursors in pillaring reactions is pointed out.

Introduction

In the past 20 years, many studies on the synthesis and characterization of a family of tetravalent metallic phosphates with lamellar structure have been made. The structural features, physicochemical properties, and applications of this rapidly growing class of compounds have been the subject of chapters in books and recent reviews.[1–8] In this way, materials with a high degree of crystallinity and stability against degradation have been obtained. These compounds behave as cationic exchangers in suspension, mainly the α and γ varieties of the Ti and Zr phosphates.[1,4,9,10] The possibility of intercalation of polar organic molecules into the interlayer spacing is well-known.[1,5,11,12]

α-Titanium phosphate, $\alpha\text{-Ti(HPO}_4)_2\cdot\text{H}_2\text{O}$ (α-TiP), is isotypic with the Zr compound, $\alpha\text{-Zr(HPO}_4)_2\cdot\text{H}_2\text{O}$ (α-ZrP). The crystal structure of this latter compound has been determined by single-crystal methods.[13] The crystal structure of α-TiP was refined by a profile least-squares analysis using X-ray powder diffraction data.[14] The basic features of the structure of γ-titanium phosphate were found by a combination of direct methods and packing considerations and show that the compound should be formulated as $\gamma\text{-Ti(H}_2\text{PO}_4)(\text{PO}_4)\cdot2\text{H}_2\text{O}$ (γ-TiP).[14] Table I shows the unit cell dimensions of the α- and γ-metal(IV) phosphates. The structural difference between α- and γ-titanium phosphate varieties is considerable.[15] In α-TiP every phosphorus atom has an acid group. In contrast, in the γ-TiP structure there are two different types of phosphorus (orthophosphate and dihydrogen phosphate). Since the acid centers are placed only in the dihydrogen phosphate groups, every phosphorus of this type has two active centers.

Table I. Unit-Cell Dimensions of Metal(IV) Phosphates

compound	*a* (Å)	*b* (Å)	*c* (Å)	β (deg)	ref
α-TiP	8.630(2)	5.006(1)	16.189(3)	110.20(1)	14
α-ZrP	9.060(2)	5.297(1)	15.414(3)	101.71(2)	13
α-HfP	9.0142(1)	5.25665(5)	15.4768(2)	101.636(1)	*a*
α-SnP	8.60	4.91	16.75	110.8	*b*
γ-TiP	5.181(1)	6.347(1)	11.881(1)	102.59(1)	14
γ-ZrP	5.376(2)	6.636(4)	24.56(1)	93.94(5)	15

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The intercalation of *n*-alkylamines in α-TiP can be represented by eq 1 (R = *n*-alkyl chain).[11] It can be observed that the topotactic acid–base reaction between the layered acid and basic guest affects all acid groups of the solid material.

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$$\alpha\text{-Ti(HPO}_4)_2\cdot\text{H}_2\text{O} + 2\text{RNH}_2 \rightarrow \text{Ti(PO}_4)_2\cdot 2\text{RNH}_3\cdot\text{H}_2\text{O} \quad (1)$$

The intercalation into γ-TiP of some alcohols and alkylamines was investigated over a decade ago,[16] in which study materials with an intercalation of lower than 54% of the acids groups were obtained. We have undertaken a systematic study of this system, and in this paper we discuss the results obtained as a function of the newly uncovered structural characteristics of γ-TiP.[14]

In addition to their possible use as molecular sieves, the metal(IV) phosphate/*n*-alkylamine intercalation materials seem to be useful as precursors in pillaring reactions[17–19] owing to their stability in aqueous medium, suitable interlayer distance, and moderate affinity of the intercalated species toward the host active centers.

To use the intercalation compounds as precursors in pillaring reactions, the value of the interlayer distance and the percentage of the interlayer volume occupied by the organic species intercalated should be considered.[20] Basal spacings and different packing indexes can be obtained by preparing compounds with different degrees of intercalation. This can be achieved by the addition of controlled amounts of the intercalating species (*n*-alkylamines) to the initial solid (γ-titanium phosphate) in acid medium[21,22] or by thermal treatment of the intercalation compounds.[23] The results obtained should be different because the preparation of intermediate phases by intercalation involves the simultaneous presence of water and *n*-alkylamine in the interlayer space of the solid. Thermal treatment at moderate temperatures gives rise to dehydration of the material followed by the desorption of the *n*-alkylamine and hence the phases obtained by this procedure will always be anhydrous.

The present paper presents a systematic study of the intercalation process of *n*-alkylamines in γ-titanium phosphate carried out in two different media, vapor and aqueous phase. The synthesis of new materials by thermal treatment is conducted by using the compounds with a greater organic content. The synthesis and characterization of a new family of 37 compounds with the general formula γ-TiH$_{2-y}$(PO$_4$)$_2$·yC$_n$H$_{2n+1}$NH$_3$·mH$_2$O (n = 1–6; y = 0.3, 0.7, 1.0, 1.3; m = 0.0, 0.5, 1.0, 1.5) is described.

Experimental Section

Materials. All chemicals used were of reagent grade. γ-TiP was obtained by the Llavona et al. procedure,[24] using 17 M H$_3$PO$_4$ and a reflux time of 10 days. The crystalline solid was washed with water until all chloride had been eliminated (test with AgNO$_3$) was dried at 50 °C and was ground to a particle size of less than 0.03 mm.

Table II. Interlayer Distance of γ-TiH$_{0.7}$(PO$_4$)$_2$·1.3RNH$_3$·H$_2$O Compounds

intercalated amine	d_{001} (Å)	intercalated amine	d_{001} (Å)
methylamine	13.5	butylamine	20.5
ethylamine	16.2	pentylamine	22.5
propylamine	18.4	hexylamine	24.6

Intercalation Procedure. Vapor phase: the γ-TiP/*n*-alkylamine intercalation compounds were obtained by γ-TiP exposure at room temperature in an atmosphere saturated with *n*-alkylamine vapor during 1–20 days and dried in air at 50 °C. Aqueous-phase γ-TiP was equilibrated with aqueous solutions of each *n*-alkylamine (0.5–10.0 mequiv of *n*-alkylamine/γ-TiP) at 25.0 ± 0.1 °C following the batch method. The solid was present in the solution in an approximate ratio of 1 g:100 mL. The solids were separated by centrifugation, washed with water, and dried in air at 50 °C.

Analytical Procedures. Analysis for phosphorus and titanium in the solid was carried out gravimetrically.[25] The pH measurements were made with an Orion SA-720 pH meter. Microanalytical data (C, H, and N) was obtained with a Perkin-Elmer 240 B elemental analyzer. Thermal analysis was performed by a Mettler TA 4000 (TG 50, DSC 30, atmosphere of nitrogen, rate of heating 5 °C/min.). The diffractometer used was a Philips 1050/23 with Cu Kα radiation.

Intercalation by *n*-Alkylamines Vapor. The *n*-alkylamine intercalation in γ-TiP may be represented by eq 2. The rate of the intercalation process decreases with increasing alkyl chain length of the amine. An equilibrium situation was reached before 6 h in the methylamine case and after 20 days when hexylamine was used. By means of C and N analysis it was proved that x is equal to 1.3 for the crystalline products of reaction 2 irrespective of the RNH$_2$ used. In the methylamine case, if the solids stay in the presence of the corresponding amine vapor atmosphere, they transform into an amorphous gel, and the percentage of amine in the solid phase increases. The treatment of the intercalated compounds in an inert atmosphere (N$_2$) at 800 °C leads to the process represented by eq 3, although it takes place in several differentiated steps (as will be discussed later). The evaluation of the total loss of weight indicates that n = 1 in every case.

$$\gamma\text{-Ti(H}_2\text{PO}_4)(\text{PO}_4)\cdot 2\text{H}_2\text{O} + x\text{RNH}_2 + (n-2)\text{H}_2\text{O} \rightarrow \gamma\text{-TiH}_{2-x}(\text{PO}_4)_2\cdot x\text{RNH}_3\cdot n\text{H}_2\text{O} \quad (2)$$

$$\gamma\text{-TiH}_{0.7}(\text{PO}_4)_2\cdot 1.3\cdot\text{RNH}_3\cdot n\text{H}_2\text{O} \rightarrow \text{TiP}_2\text{O}_7 + 1.3\text{RNH}_3 + (n+1)\text{H}_2\text{O} \quad (3)$$

X-ray diffraction (XRD) indicates that all the crystalline compounds have a lamellar nature. It can be observed that the interlayer distances of the intercalation products (Table II) increase linearly with the number of the carbon atoms of the alkyl chain (Figure 1a). The straight line follows eq 4. The intercalation compounds of amines in α-MP (M = Ti, Zr, Sn)[11,21,26] show a similar behavior:

$$d_{001} = 11.2 + 2.30n_c \quad (4)$$

Intercalation by *n*-Alkylamines in Aqueous Solution. The intercalation in aqueous solution makes possible the addition of controlled amounts of *n*-alkylamine and the attainment of crystalline phases with a composition between that of the initial material and that obtained at equilibrium when the intercalation is carried out in the vapor phase. The process may be schematized in a general way by eq 5.

$$\gamma\text{-Ti(H}_2\text{PO}_4)(\text{PO}_4)\cdot 2\text{H}_2\text{O} \rightarrow \gamma\text{-TiH}_{2-y}(\text{PO}_4)_2\cdot y\text{RNH}_3\cdot n\text{H}_2\text{O} \rightarrow \ldots \rightarrow\rightarrow \gamma\text{-TiH}_{0.7}(\text{PO}_4)_2\cdot 1.3\text{RNH}_3\cdot n\text{H}_2\text{O} \quad (5)$$

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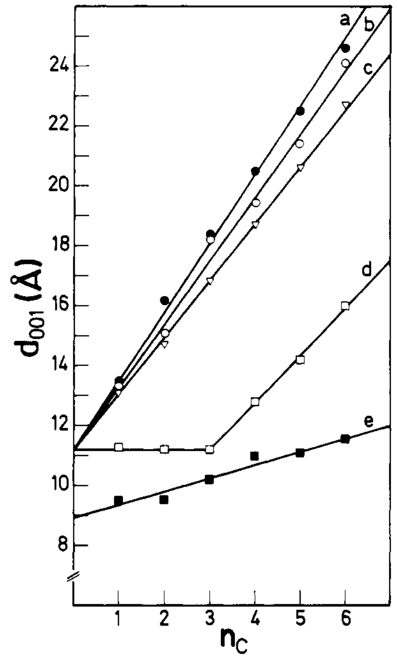

Figure 1. Interlayer distance (d_{001}) of intercalation compounds of γ-TiP with n-alkylamines as a function of the number of carbon atoms in the alkyl chain (n_c): (a) γ-$TiH_{0.7}(PO_4)_2 \cdot 1.3RNH_3 \cdot H_2O$ (●), (b) γ-$TiH_{0.7}(PO_4)_2 \cdot 1.3RNH_3$ (○), (c) γ-$TiH(PO_4)_2RNH_3$ (▽), (d) γ-$TiH_{1.3}(PO_4)_2 \cdot 0.7RNH_3$ (□), (e) γ-$TiH_{1.7}(PO_4)_2 \cdot 0.3RNH_3$ (■).

Figure 2 illustrates the titration curves of the γ-TiP with n-alkylamines (the equilibrium pH is plotted against the intercalation degree of the amine in the γ-TiP). It can be observed that the maximum number of amine moles intercalated per mol of Ti is 1.3 except in the methylamine case, which reaches higher values. All crystalline solids obtained exhibit a lamellar structure. In Figure 2, the basal spacing of the crystalline solids in the corresponding composition zone is also plotted. In the zones with only one interlayer distance, the variation of the amount of intercalated amine does not modify the basal spacing of the material. In the zones with two different interlayer distances, the intensity of the reflection at lower angle increases continuously with increasing amount of intercalated amine, being the only one present when the composition concurs with the end of the delimited zone. When the intercalation reaches the value of 1.3 mol of amine/mol of Ti, crystalline phases are always obtained whose interlayer distance concurs with that of the materials obtained in the vapor phase. When the methylamine retention exceeds the value of 1.3, the appearance of a new crystalline phase with a 15.5-Å interlayer distance is observed; it is higher than that obtained in the vapor phase (13.5 Å), and it quickly transforms into an amorphous gel similar to that obtained in the vapor phase. The solids with only one crystalline phase were submitted to thermal treatment in an inert atmosphere (N_2) from room temperature to 800 °C. The evolution of the total weight loss as well as the analysis data lead to the formula of Table III. Table IV shows the interlayer distance of the different phases obtained in the titration.

Thermal Treatment. In Figure 3 the TG and DSC curves of γ-$TiH_{0.7}(PO_4) \cdot 1.3RNH_3 \cdot H_2O$ compounds obtained by vapor intercalation are shown. The samples were treated from room temperature to 800 °C in the TG and only at 600 °C in the DSC. The process is that reported in the eq 3 when $n = 1$.

TG curves of the remaining intercalation compounds show a comparable shape. The existence of at least two well defined processes of weight loss can be observed. The first takes place at temperatures lower than 110 °C and corresponds to the loss of crystallization water. At higher temperatures the desorption of n-alkylamine and the transformation of the hydrogen phosphate groups into pyrophosphate takes place. DTG and DSC curves show that the thermal desorption process is more complicated, since 6–7 peaks are observed in every sample, indicating the presence of at least the same number of steps for the decomposition processes. The temperatures of the peaks characteristic of the DSC curves are compiled in Table V. These temperatures can be grouped into six blocks (A–F), suggesting a unique behavior in the thermal decomposition of the γ-TiP/n-alkylamine compounds.

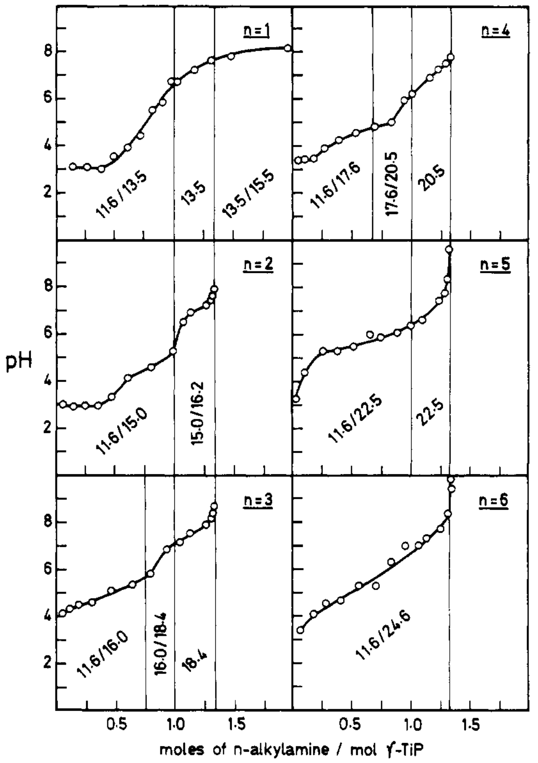

Figure 2. Titration curves of γ-TiP with aqueous solutions of $C_nH_{2n+1}NH_2$. The numbers on the figures indicate the interlayer distance (in angstroms) of the crystalline phase or phases present in every composition range.

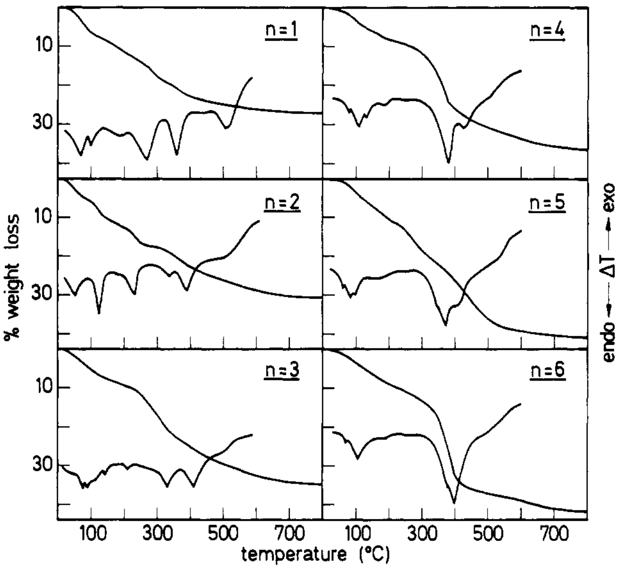

Figure 3. TG and DSC curves of the γ-$TiH_{0.7}(PO_4)_2 \cdot 1.3$-$C_nH_{2n+1}NH_3 \cdot H_2O$ compounds.

Once the thermal desorption sequence and the different step temperatures were known, we tried to isolate intermediate pure phases. In this way, masses of about 1 g of every intercalation compounds were treated at 80, 150, 250, 350, 400, 500, and 800 °C during 3 h. XRD of all the samples stabilized at the given temperatures were obtained. In all the intercalation compounds the lamellar structure is maintained until 400–500 °C. The mass changes of the samples were thermogravimetrically determined. Thus, a program was designed based upon the heating at constant rate of the γ-TiP/n-alkylamine samples from room temperature to the different temperatures chosen. Once the temperature is reached, the sample was maintained at constant temperature

Table III. Microanalytical Data (C and N) and Experimental Weight Loss at 800 °C of the Intercalation Compounds Obtained in Aqueous Solution and Those Calculated from the Formula

	experimental			calculated		
formula	% C	% N	% weight loss	% C	% N	% weight loss
γ-$\mathrm{TiH(PO_4)_2{\cdot}CH_3NH_3{\cdot}H_2O}$	5.20	4.95	23.96	4.15	4.84	23.18
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3CH_3NH_3{\cdot}1.5H_2O}$	5.75	5.69	28.62	5.06	5.90	28.00
γ-$\mathrm{TiH(PO_4)_2{\cdot}C_2H_5NH_3{\cdot}1.5H_2O}$	8.71	4.32	30.24	7.69	4.49	28.83
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_2H_5NH_3{\cdot}1.5H_2O}$	11.22	5.58	34.24	9.54	5.57	32.13
γ-$\mathrm{TiH_{1.3}(PO_4)_2{\cdot}0.7C_3H_7NH_3{\cdot}H_2O}$	8.09	3.06	27.66	8.34	3.24	26.56
γ-$\mathrm{TiH(PO_4)_2{\cdot}C_3H_7NH_3{\cdot}H_2O}$	12.22	4.47	32.95	11.36	4.42	29.97
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_3H_7NH_3{\cdot}H_2O}$	15.02	5.47	35.17	13.90	5.40	34.07
γ-$\mathrm{TiH_{1.3}(PO_4)_2{\cdot}0.7C_4H_9NH_3{\cdot}H_2O}$	11.69	2.99	31.92	10.75	3.13	29.03
γ-$\mathrm{TiH(PO_4)_2{\cdot}C_4H_9NH_3{\cdot}1.5H_2O}$	16.43	4.28	34.01	13.18	3.84	32.39
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_4H_9NH_3{\cdot}H_2O}$	19.13	5.13	39.80	15.57	5.12	37.54
γ-$\mathrm{TiH(PO_4)_2{\cdot}C_5H_{11}NH_3{\cdot}H_2O}$	18.67	4.04	36.41	17.40	4.06	35.68
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_5H_{11}NH_3{\cdot}0.5H_2O}$	21.39	4.71	38.79	21.37	4.99	39.19
γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_6H_{13}NH_3}$	24.23	5.20	39.32	24.40	4.74	39.73

Table IV. Interlayer Distances and Packing Parameters for γ-$\mathrm{TiH_{2-\mathit{y}}(PO_4)_2{\cdot}\mathit{y}RNH_3{\cdot}\mathit{n}H_2O}$ Compounds

intercalated amine	formula	d_{001} (Å)	V_p
methylamine	$y = 1.0$	13.5	0.62
	$y = 1.3$	13.5	0.81
ethylamine	$y = 1.0$	15.0	0.75
	$y = 1.3$	16.2	0.75
propylamine	$y = 0.7$	16.0	0.63
	$y = 1.0$	18.4	0.60
	$y = 1.3$	18.4	0.78
butylamine	$y = 0.7$	17.6	0.63
	$y = 1.0$	20.5	0.62
	$y = 1.3$	20.5	0.80
pentylamine	$y = 1.0$	22.5	0.63
	$y = 1.3$	22.5	0.83
hexylamine	$y = 1.3$	24.6	0.84

Table V. Temperatures (°C) Corresponding to the DSC Peaks of the γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{\cdot}H_2O}$ Intercalation Compounds

amine	A	B	C	D	E	F
methylamine	75, 105	190	270	360		510
ethylamine	60	130	230	340	385	>460
propylamine	70, 95	150	220	335	410	>500
butylamine	75, 110	130	190	375	425	>520
pentylamine	65, 90, 100	180		370	405	>500
hexylamine	70, 105	195		375	400	>500

during 3 h. The weight variation is known throughout all these processes. The results obtained are shown in Figure 4.

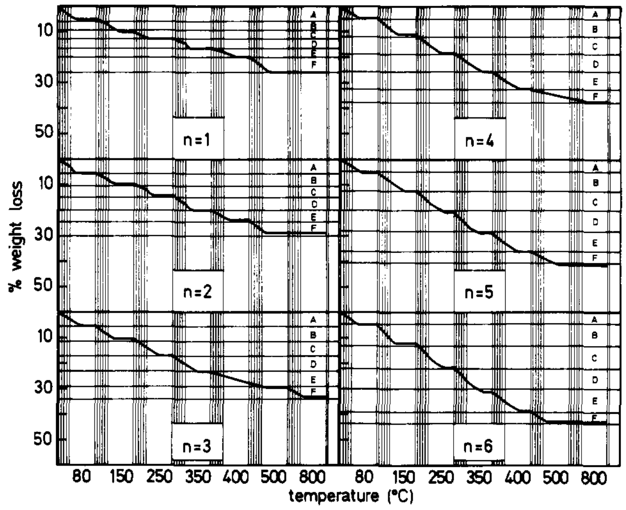

Figure 4. Dynamic-isothermal TG curves of the γ-$\mathrm{TiH_{0.7}(PO_4)_2{\cdot}1.3C_\mathit{n}H_{2\mathit{n}+1}NH_3{\cdot}H_2O}$ compounds. In the non-dashed zone, the temperature remains constant and equal to the corresponding abscissa value. In the zone between two constant temperatures (vertical lines) the rate of heating is 20 °C min^{-1}. The horizontal lines correspond to theoretical loss of weight if the process of eq 9 takes place.

Discussion

Intercalation by *n*-Alkylamine Vapor. The cross sectional area of a trans–trans alkyl chain is evaluated at 18.6 Å^2.[27] Table I shows the unit cell dimensions of some metal(IV) phosphates. If the free area for each acid center is higher than that occupied by an amine molecule, then the steric factors do not prevent the material from becoming saturated. The free area surrounding each phosphate group in α-ZrP, 24.0 Å^2, which permits the accommodation of one molecule of amine per phosphate and a monolayer is obtained only when one POH group of every two is engaged in a bond with the amino groups. The arrangement of the guests in intercalation compounds containing more than 1 mol of amine/mol of α-ZrP should lead to the formation of a bilayer since there is no room for the interpenetration of alkylchains of amines bound to phosphate groups of two facing layers. A similar behavior is observed in α-TiP[11] and α-SnP,[26] fully intercalated phases may be expected from the value of the free area per phosphate group (21.6 Å^2, α-TiP; 21.1 Å^2, α-SnP).

The free area of each POH group in γ-titanium phosphate (16.4 Å^2) is lower than the size of the cross section of the amine so that steric hindrance should be encountered for the simultaneous interaction of *n*-alkylamine with two adjacent active centers. The intercalation of 2 mol of amine/mol of γ-TiP is geometrically impossible. A similar explanation can be given for the γ-ZrP in which the free area surrounding each phosphate group is 17.8 Å^2. Costantino[16] describes that the $\mathrm{C_\mathit{n}H_{2\mathit{n}+1}NH_2}$ (n = 2–4) in the γ-TiP host forms materials with the formula γ-$\mathrm{TiH_{2-\mathit{x}}(PO_4)_2{\cdot}\mathit{x}C_\mathit{n}H_{2\mathit{n}+1}NH_3}$ (x = 1.00–1.08). Moreover a similar behavior was observed in γ-ZrP with formation of γ-$\mathrm{ZrH_{2-\mathit{x}}(PO_4)_2{\cdot}\mathit{x}C_\mathit{n}H_{2\mathit{n}+1}NH_3}$ (n = 2–4, x = 0.95–1.05) compounds. Nevertheless, he indicates that the intercalation compounds of γ-ZrP with long chain *n*-alkylamines ($n > 12$) leads to compounds γ-$\mathrm{ZrH_{0.67}(PO_4)_2{\cdot}1.33C_\mathit{n}H_{2\mathit{n}+1}NH_3}$ (n = 14, 16, 18). The differences are due to the fact that the alkylamines with a high n value (that gives rise to a higher hydrophobic effect) tend to fill all the available space and the amine content increases because of the greater strength of the van der Waals attraction forces between alkylchains. On the other hand, *Costantino indicates that the analogous intercalates of* γ-TiP contain less than 1 mol of amine/formula weight of exchanger, due to the γ-TiP dehydration, concomitant with the intercalation process. The diffusion of the guest

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[27] Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

molecules within the anhydrous portions of the crystals ($Ti(H_2PO_4)(PO_4)$, usually denoted as β-TiP[28]) seems to be very slow.

The synthesis of materials with the γ-$TiH_{0.7}(PO_4)_2 \cdot 1.3C_nH_{2n+1}NH_3 \cdot mH_2O$ (n = 1–6) formula was described in the experimental part of this paper. The intercalation degree is higher than that reached by Costantino. Probably, the discrepancy is due to the different reaction medium used (methanolic solution and aqueous or vapor media).

In the γ-$TiH_{0.7}(PO_4)_2 \cdot 1.3C_nRNH_3 \cdot H_2O$ compounds, the arrangement of the n-alkylamine in the interlayer spacing as well as the packing of the alkyl chains can be deduced.

From the change in the interlayer distance of the intercalates obtained in the vapor phase with the size of the organic molecule, it can be determined that the data are consistent with the hypothesis that the intercalation takes place with formation of a double layer of amine molecules in trans–trans conformation placed almost perpendicularly to the γ-layer. Since the length of an alkyl chain in the trans–trans conformation increases by 1.27 Å for each additional carbon atom,[27] the inclination angle should be $\alpha = \sin^{-1}(2.30/2.54) = 64.9°$.

The value obtained for the inclination angle of the alkyl chains (64.9°) does not concur with that proposed by Costantino (54.5°)[16] because he has related the interlayer distances of compounds with different alkylamine contents by adjusting the slope to the theoretical value, assuming that the N–C bonding is perpendicular to the γ-TiP layer.

Intercalation by *n*-Alkylamine in Aqueous Solution. When the intercalation process takes place in an aqueous phase, crystalline phases with a composition intermediate between that of the original γ-titanium phosphate and those of the samples synthesized in the vapor phase are obtained.

The titration curves of α-ZrP with short chain (up to C_6) alkylamines have been reported.[5,21] The intercalation reactions occur stepwise with the formation of intermediate intercalation compounds before reaching full intercalation. In many cases the first intercalate obtained has an interlayer distance of *ca.* 10.4 Å, consistent with the arrangement of amine having its alkylchain oriented mainly parallel to the layer; in this manner the increase in the interlayer distance is kept to a minimum and the amount of alkylamine intercalated obviously depends on the alkyl chain length. The other intermediate intercalation compounds are formed with a change in conformation of the alkyl chains assuming a more upright position to make room for the other incoming amines.

In this work, the results obtained indicate different reaction routes. That of the n-hexylamine is the simplest, producing the substitution phase obtained in the vapor phase in a direct way. When the intercalation reactant is methylamine or pentylamine, an intermediate phase is obtained in which the amine content is 1 mol/mol of titanium and the interlayer distances agrees with that of the solid obtained in the vapor phase, hence the n-alkylamine inclination angle in the interlayer space should be 64.9° and thus its packing density should be lower. The behavior of ethylamine is similar but the interlayer distance of the γ-$TiH(PO_4)_2 \cdot C_2H_5NH_3 \cdot H_2O$ (15.0 Å) is lower than that obtained in the vapor phase (16.2 Å); this indicates a lower inclination angle of the ethylamine molecules, estimated as 48.4°.

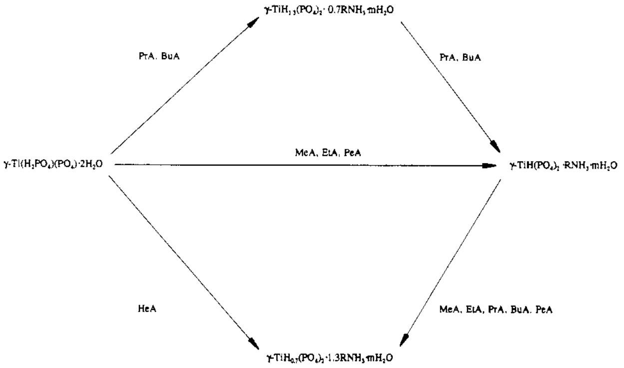

Figure 5. Reactivity of the γ-titanium phosphate in the n-alkylamine intercalation in aqueous solution.

When the intercalation reactant is n-propylamine or n-butylamine, a phase with intermediate composition is found where the degree of intercalation is 0.7 mol of amine/mol of Ti. The inclination angle of the alkyl chains, in bilamellar disposition, is only 39.0°. When the amine addition increases, these phases progress to the formation of solids where the amount of intercalated amine is 1 mol/mol of Ti, increasing the interlayer distance. Phases with interlayer distance and intercalation degree equal to that obtained in the vapor phase are obtained without increase in the interlayer distance.

The interlayer distance of the γ-$TiH_{2-y}(PO_4)_2 \cdot yC_nH_{2n+1}NH_3 \cdot mH_2O$ (n = 1, 3, 4, 5) intercalation compounds is the same when y = 1.0 or 1.3. The pH vs composition curve in Figure 2 does not show evidence of discreet phase formation. It seems likely that what is observed represents a continuous phase γ-$TiH_{2-y}(PO_4)_2 \cdot yRNH_3 \cdot mH_2O$ where y can vary smoothly from 1.0 to 1.3.

In Figure 5 are collected the reaction routes for n-alkylamine intercalation in the aqueous phase that lead to formation of crystalline phases with a γ-$TiH_{2-y}(PO_4)_2 \cdot yRNH_3 \cdot mH_2O$ composition (y = 0.7, 1.0, 1.3). In all cases, the arrangement of the n-alkylamines in the γ-TiP interlayer spacing is bilayered. These results indicate that the monolayered arrangement is not thermodynamically favored although it appears as an intermediate phase in the formation of the bilayered stable phases. Intercalation compounds with an alkyl chain arrangement parallel to the phosphate layer are not detected. This does not imply their nonexistence since their interlayer distance should be close to 11.2 Å, which is the value, obtained from eq 4 when n_c = 0, and the interlayer distance of γ-$Ti(NH_4HPO_4)(PO_4) \cdot H_2O$.[29] This means that the basal spacing would be indistinguishable in the XRD data from that of the γ-TiP.

The packing density of the n-alkylamine in the interlayer space of the γ-TiP may be expressed by the packing parameter V_p ($= V_c/V_t$), where V_c is the volume occupied by the alkyl chains and V_t is the volume available in the interlayer space excluding the presence of water.[22]

V_t can be calculated by subtracting from the interlayer distance (d_{001}) the space occupied by the γ-layers and the terminal $-NH_3^+$ groups. Referred to 1 cm² of layer, V_t will be given by the expression 6, where d_{001} and d' are expressed in cm and V_t in cm³.

$$V_t = d_{001} - d' \qquad (6)$$

Assuming that the interpenetration of the $-NH_3$ groups within the layer surface is independent of n_c, d' is equal

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[28] Clearfield, A.; Blessing, R. H.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2249.

[29] Alberti, G.; Bernasconi, M. G.; Casciola, M.; Costantino, U. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1637.

to the value of d_{001} for $n_c = 0$. Namely $d' = 11.2 \times 10^{-8}$ cm.

The volume of an alkyl chain containing n_c carbon atoms can be estimated to be $n_c(1.27 \times 10^{-8})(18.6 \times 10^{-16})$ cm^3.[27] From the data of the γ-TiP unit cell (Table I) the number of formula units per cm^2 of layer is 6.08×10^{14}. Since only some of the hydrogens participate in the intercalation process, the number of effective formula units per cm^2 of layer depends on the intercalation degree. For an intercalate with the formula γ-$TiH_{2-y}(PO_4)_2{\cdot}yRNH_3{\cdot}mH_2O$ it will be $6.08 \times 10^{14}y$. Referring to 1 cm^2 of layer, V_c will be given by the expression 7.

$$V_c = n_c\,(1.27 \times 10^{-8})(18.6 \times 10^{-16})(6.08 \times 10^{14}y)\ \text{cm}^3 \quad (7)$$

The values of the packing parameters of the isolated crystalline phases are compiled in Table IV. It is observed that the largest density of packing is obtained in the crystalline phases of higher intercalation ($y = 1.3$). In all of them the occupation of interlayer volume is between 75 and 84%. In the phases with $y = 1.0$ there are two different behaviors. When the interlayer distance concurs with that of the solids with higher intercalation (methylamine, propylamine, butylamine, and pentylamine), the packing parameter takes uniform values (0.60–0.63), lower than that obtained when $y = 1.3$. This is a logical result because the available interlayer space is the same in both types of crystalline phases, and thus, a lower intercalation will necessarily lead to a lower packing density. In the case of ethylamine the interlayer distance of the phase $y = 1.0$ is lower than that of the phase $y = 1.3$. Hence, the ratio between both packing parameters is difficult to predict a priori. The results obtained indicate that they are similar (0.75). In the phases of lower intercalation ($y = 0.7$) the arrangement of the alkyl chains is also as a bimolecular layer and the interlayer volume occupied is 63%.

Thermal Treatment. Recently,[12] it has been described that the weight loss by thermal decomposition of γ-$ZrH(PO_4)_2{\cdot}C_nH_{2n+1}NH_3{\cdot}2H_2O$ (n = 2–5) compounds consist of the following stages: (a) loss of the crystal water, (b) loss of the organic molecule, and (c) loss of the structural water originated from the decomposition of H_3PO4^- groups. Rajeh and Szirtes do not describe the existence of stable phases of composition γ-$ZrH_{2-x}(PO_4)_2{\cdot}xC_nH_{2n+1}NH_3$ ($0 < x < 1$). The data obtained in the study of the thermal behavior of the γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{\cdot}H_2O$ intercalation compounds (Table V, Figures 3 and 4) are consistent with the weight loss sequence proposed in (8).

$$\begin{aligned}&\gamma\text{-}TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{\cdot}H_2O \rightarrow\\ &\quad \gamma\text{-}TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3 \rightarrow \gamma\text{-}TiH(PO_4)_2{\cdot}RNH_3 \rightarrow\\ &\gamma\text{-}TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3 \rightarrow \gamma\text{-}TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3 \rightarrow\\ &\qquad\qquad Ti(H_2PO_4)(PO_4) \rightarrow TiP_2O_7 \quad (8)\end{aligned}$$

First the loss of the crystallization water occurs to obtain anhydrous intercalated solids of composition γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3$ at 80 °C. Later the loss of n-alkylamine takes place in steps of $^1/_3$ mol of n-alkylamine/mol of titanium. Thus, solids of γ-$TiH(PO_4)_2{\cdot}RNH_3$ (at 150 °C), γ-$TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3$ (at 250 °C) and γ-$TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3$ (at 350 °C) composition are obtained. At 400–500 °C the loss of n-alkylamine is completed obtaining $Ti(H_2PO_4)(PO_4)$. This material is amorphous when it arises from the decomposition of γ-TiP/n-hexylamine. The rest of the solids yield the reflections characteristic of the β-TiP. The XRD peaks are broad and of low intensity, indicative of a high degree of disorder. At 800 °C all materials have the TiP_2O_7 composition.

Table VI. Interlayer Distances (d_{001}, in angstroms), Monolamellar (M) or Bilamellar Disposition (B) of the Alkyl Chains, Average Inclination Angle (α, in degrees) with Respect to the Plane of the Sheet, and Packing Parameters (V_p) for the γ-Titanium Phosphate/ n-Alkylamines Intercalation Compounds Obtained by Thermal Treatment

formula	intercalated amine	d_{001} (Å)	disposition	α (deg)	V_p
$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3$	methylamine	13.3	B	56.3	0.89
	ethylamine	15.1			0.96
	propylamine	18.2			0.80
	butylamine	19.4			0.91
	pentylamine	21.4			0.91
	hexylamine	24.1			0.87
$TiH(PO_4)_2{\cdot}RNH_3$	methylamine	13.1	B	47.9	0.76
	ethylamine	14.7			0.82
	propylamine	16.8			0.77
	butylamine	18.7			0.77
	pentylamine	20.6			0.76
	hexylamine	22.7			0.75
$TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3$	methylamine	11.3	B	0	
	ethylamine	11.2			
	propylamine	11.2			
	butylamine	12.8[a]		0, 38.3[b]	0.63[b]
	pentylamine	14.2[a]			0.67[b]
	hexylamine	16.0			0.63[b]
$TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3$	methylamine	9.5[a]	M	20.5	0.89
	ethylamine	9.5			0.96
	propylamine	10.2[a]			0.80
	butylamine	11.0[a]			0.91
	pentylamine	11.1[a]			0.91
	hexylamine	11.6			0.87

[a] The peaks are broad and are of low intensity, indicate of a high degree of disorder. [b] Values obtained by assuming that the three first atoms of the alkyl chain occupy a plane parallel to the titanium phosphate layer (Figure 6).

Table VI shows the interlayer distances of the crystalline phases isolated during the thermal decomposition process of the γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{\cdot}H_2O$ compounds. The plotting of d_{001} vs n_c can be seen in Figure 1. The materials with the same amine content define straight lines as given by the expressions 9–12.

$$\gamma\text{-}TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{:}\quad d_{001} = 11.2 + 2.11n_c \quad (9)$$

$$\gamma\text{-}TiH(PO_4)_2{\cdot}RNH_3{:}\quad d_{001} = 11.2 + 1.89n_c \quad (10)$$

$$\gamma\text{-}TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3{:}\quad d_{001} = 11.2 + 1.57n_c' \quad (\text{where } n_c' = n_c - 3) \quad (11)$$

$$\gamma\text{-}TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3{:}\quad d_{001} = 8.9 + 0.44n_c \quad (12)$$

Since the increment of the alkyl chain, in the trans–trans conformation, is estimated to be 1.27 Å for each additional carbon atom, it is reasonable to assume that the amine is present in the γ-TiP as a bimolecular layer of extended molecules when the slope of the straight line defining the interlayer distances of materials with the same amine content is higher than 1.27 Å. When the value is lower than 1.27 Å, the arrangement can be monolayered.

Figure 6a shows an idealized representation of the arrangement of one n-alkylamine molecule in the interlayer spacing of the γ-TiP assuming that the N–C bonding is perpendicular to the layer. The inclination angle of the alkyl chain with respect to the plane of the sheet which predicts this representation is 53.8°.

The γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3$ and γ-$TiH(PO_4)_2{\cdot}RNH_3$ compounds have the amines present as a bimolecular layer. The inclination medium angles of the alkyl chains (Table

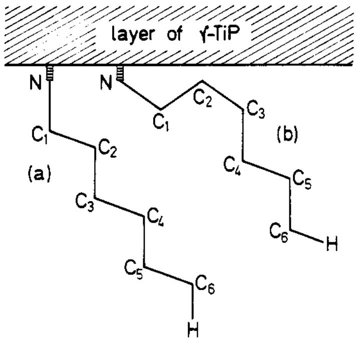

Figure 6. Idealized representation of the arrangement of n-alkylamine molecule in the interlayer spacing of the γ-TiP, assuming that (a) the N–C bonding is perpendicular to layer or (b) a part of the carbon atoms are placed parallel to the layer.

VI) decrease with the dehydration and with the decreasing of the amine content in the solid.

The data plotted in Figure 1 indicate a different behavior for the γ-$TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3$ compounds. Thus, when R = methyl, ethyl, or propyl, the interlayer distance of the intercalate compound is almost constant ($\approx$11.2 Å), and it concurs with the ordinate in the origin of the straight lines characteristic of the compounds with bilayered arrangement of the amine molecules. For higher amines the interlayer distances increase linearly with the number of the carbon atoms, the slope being higher than 1.27 Å (eq 11). This indicates a bilayered arrangement of the organic molecules. Figure 6b shows an idealized representation of the possible conformation of the amine molecules in these compounds where the three first carbon atoms are in the same plane as the nitrogen atom of the amino group.

The value of the interlayer distance of an hypothetic intercalation compound with a supposed n-alkylamine without carbon atoms (n_c = 0) might be related to the region occupied by the γ-layer and the terminal $-NH_3^+$ groups. Therefore, assuming that the interpenetration of the $-NH_3^+$ groups within the layer surface is independent of n_c and of the inclination angles of the alkyl chain, the ordinate in the origin of the d_{001} straight lines vs n_c will only depend on the mono or bilamellar arrangement of the n-alkylamines. In the γ-$TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3$ compounds, the line of the interlayer distance (Figure 1) has an ordinate in the origin (8.9 Å) different from that characteristic of the compounds with a higher intercalation degree and a bilamellar arrangement of the organic molecules (11.2 Å). Thus, the γ-$TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3$ compounds present monolamellar arrangement, in which inclination angle of the alkyl chains $\alpha = \sin^{-1}(0.44/1.27) = 20.5°$.

The values of the packing parameters of the isolated crystalline phases in the thermal treatment are compiled in Table VI. $V_p \approx 0.8$ for the γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3{\cdot}H_2O$ compounds (Table IV). In the anhydrous solids with the same intercalation degree, γ-$TiH_{0.7}(PO_4)_2{\cdot}1.3RNH_3$, the percentage of volume occupied by the n-alkylamine molecules increases ($V_p \approx 0.9$) because the space occupied by the water molecules in the hydrated compounds can be used. The inclination angle of the alkyl chains and the interlayer distance of the compounds decrease. In the γ-$TiH(PO_4)_2{\cdot}RNH_3$ intercalates, the packing parameters are high ($V_p \approx 0.8$) because the space, previously occupied by the desorbed amines, is now partially occupied by the amines which remain in the solid and the α value decreases. In the γ-$TiH_{1.3}(PO_4)_2{\cdot}0.7RNH_3$ compounds the bilamellar arrangement is maintained despite the fact that the number of active centers occupied is half of those in the initial compounds and a monolamellar arrangement would be geometrically possible. The low occupation density allows the lower amines to be placed parallel to the γ-layers. For n-butylamine this is not possible. The three carbon atoms closest to the nitrogen atom, and the nitrogen atom, occupy a plane parallel to the γ-layer, while the rest of the carbon atoms have the longitudinal axis inclined at an average of 38.3° with respect to the plane of the sheet. The γ-$TiH_{1.7}(PO_4)_2{\cdot}0.3RNH_3$ compounds have an intercalation degree too low to be a bilayered arrangement. the n-alkylamine molecules are monolayered with a low median inclination angle (20.5°), despite the fact the percentage of interlayer space occupied is relatively low ($V_p \approx 0.5$).

Conclusion

In addition to the possibility for use as molecular sieves, these intercalated materials seem to be useful as precursors in pillaring reactions owing to their stability in aqueous medium, suitable interlayer distance, moderate affinity of the intercalated species toward the host active centers and an adequate interlayer volume occupied. A good precursor in a pillaring reaction must have an interlayer distance high enough to permit the free access of the intercalation species into the interlayer spacing, and it must be similar to the interlayer distance of the pillared material. The versatility of these compounds can be seen from Tables IV and VI since they present diverse interlayer distances and packing parameters.

Acknowledgment. This work was supported by DGICYT (PB90-0792), for which grateful acknowledgement is made.