

Synthesis and Characterization of Two Novel Fibrous Titanium Phosphates $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$

Anatoly I. Bortun,[†] Sergei A. Khainakov,[‡] Lyudmila N. Bortun,[†]
Damodara M. Poojary,[†] Julio Rodriguez,[‡] Jose R. Garcia,[‡] and
Abraham Clearfield^{*†}

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and
Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo,
33071 Oviedo, Spain

Received January 29, 1997. Revised Manuscript Received May 22, 1997[⊗]

New crystalline phases of fibrous titanium(IV) oxophosphates were prepared hydrothermally from titanium(IV) chloride in phosphoric acid solutions. The influence of several factors (concentration of reagents, molar ratio P:Ti in the reaction mixture, and reaction times) was studied. A phase diagram of the system is given. On the basis of elemental and thermal analysis, X-ray powder diffraction, ³¹P MAS NMR, and IR spectroscopy, the formula $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ was assigned to the novel compounds. The new phases (π -TiP and ρ -TiP) have different structures. The crystal structure of ρ -TiP was solved from X-ray powder data and was shown to be of the framework type with tunnels parallel to the *c*-axis direction. The absence of *n*-alkylamine intercalation processes for both compounds and other physical and behavioral similarities suggests a framework type structure for π -TiP also. The ion-exchange behavior toward alkali and alkaline earth ions was studied.

Introduction

Inorganic phosphorus-containing adsorbents have received much attention in recent years.^{1–4} This interest stems from their ability for selective uptake of specific ions,^{5,6} high thermal, radiation, and chemical stabilities,^{7,8} and resistance to oxidation.⁹ Among these materials titanium and zirconium phosphates were studied in detail.^{2,4,10}

Four different layered titanium phosphates are now known. Two of them, α - and γ -phases, containing two phosphorus atoms per one titanium atom, have been known since the 1960–70s.² The difference between them is that α -TiP has only one type of functional group, HPO_4 , and its formula can be represented as $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$,^{11,12} whereas in the corresponding γ -phase, half of the phosphorus atoms exist in the form of H_2PO_4 and the rest in the form of PO_4 groups and hence

the formula is $\text{Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$.^{11,13} These compounds closely parallel in structure and behavior the analogous zirconium phosphates.^{2,14,15} Two other layered titanium phosphate-based compounds of formula $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ¹⁶ and $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ¹⁷ with a P:Ti molar ratio 1:1 have been prepared recently, and both of them contain only dihydrogenphosphate groups. Crystalline titanium phosphates with a molar ratio P:Ti = 2:1 can be prepared by a traditional "refluxing" technique and also under hydrothermal conditions, by the reaction between a titanium-containing reagent and an excess of a sufficiently concentrated H_3PO_4 solution.^{1,2} Crystalline compounds with a low phosphorus content (P:Ti = 1:1) are formed, as a rule, when relatively dilute solutions of reagents and a small excess or deficiency of H_3PO_4 are used. The latter is in agreement with earlier data reported on studying the amorphous titanium phosphates,¹⁸ which shows that only compounds with a molar ratio P:Ti = 1:1 are formed when the concentration of titanium- and phosphorus-containing reagents and their ratio during the synthesis are low enough. The conditions necessary for the formation of α - and γ -titanium phosphates were studied in detail, but the reactions that take place with relatively low reagent concentrations and low molar ratios of P:Ti have not received sufficient attention.

[†] Texas A&M University.

[‡] Universidad de Oviedo.

[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1997.

(1) Clearfield, A.; Nancollas, G. H.; Blessing, R. H. In *Ion Exchange and Solvent Extraction*; Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1973; Vol. 5.

(2) *Inorganic Ion Exchange Materials*; Clearfield, A., Ed.; CRC Press: Boca Raton, FL, 1982.

(3) Clearfield, A. *Annu. Rev. Mater. Sci.* **1984**, *14*, 205.

(4) Alberti, G. In *Recent Developments in Ion Exchange*, Williams, P. A., Hudson, M. J., Eds.; Elsevier: London, 1987.

(5) Laskorin, B. N.; Karaseva, T. A.; Strelko, V. V. *Dokl. Akad. Nauk SSSR* **1976**, *229*, 910.

(6) Clearfield, A. *Ind. Eng. Chem. Res.* **1995**, *34*, 2865.

(7) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(8) Alberti, G.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1969**, *45*, 298.

(9) Cheng, S.; Peng, G. Z.; Clearfield, A. *I&EC Product Res. Dev.* **1984**, *23*, 219.

(10) Garcia, J. R.; Llavona, R.; Suarez, M.; Rodriguez, J. *Trends Inorg. Chem.* **1993**, *3*, 209.

(11) Christensen, A. N.; Andersen, A. G. K.; Andersen, I. G. K.; Alberti, G.; Nielsen, M.; Lehmann, S. M. *Acta Chem. Scand.* **1990**, *44*, 865.

(12) Bruque, S.; Aranda, M. A. G.; Losilla, E. R.; Olivera-Pastor, P.; Maireles-Torres, P. *Inorg. Chem.* **1995**, *34*, 893.

(13) Salvado, M. A.; Garcia-Granda, S.; Rodriguez, J. *Mater. Sci. Forum* **1994**, *166–169*, 619.

(14) (a) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117. (b) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431. (c) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(15) Clearfield, A.; Blessing, R. H.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2249.

(16) Li, Y. J.; Whittingham, M. S. *Solid State Ionics* **1993**, *63–65*, 391.

(17) Bortun, A. I.; Bortun, L. N.; Clearfield, A.; Villa-Garcia, M. A.; Garcia, J. R.; Rodriguez, J. *J. Mater. Res.* **1996**, *11*, 2490.

(18) (a) Spizyn, V. I.; Ippolitova, E. A. *Zh. Anal. Khim.* **1951**, *6*, 5. (b) Bortun, A. I.; Bortun, L. N.; Clearfield, A.; Khainakov, S. A.; Strelko, V. V.; Khryashevsky, V. N.; Kvashenko, A. P.; Voitko, I. I. *Solv. Extr. Ion Exch.* **1997**, *15*, 515.

Our main goal was the investigation of titanium phosphate synthesis in the system $\text{TiCl}_4\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$, using relatively low concentrations of phosphoric acid under hydrothermal conditions, to obtain possible new types of materials with valuable properties, and to fill in the gap in our knowledge of these materials.

Experimental Section

Reagents. All reagents were of analytical grade (Aldrich) and were used without further purification.

Synthesis of Titanium Phosphates. In all cases a 2 M aqueous solution of TiCl_4 was used as the initial source of titanium. H_3PO_4 solutions with different concentrations (1–8 M) were used as a source of phosphorus. The synthetic procedure included mixing of TiCl_4 and H_3PO_4 solutions with the desired molar ratio (P:Ti = 4–40:1) in a 100 mL stainless steel Teflon-lined vessel. Then the reaction mixture (total volume 60 mL) was sealed and heated at 190 °C for 4–10 days. The product obtained was filtered, thoroughly washed with deionized water, and dried in air at 60 °C.

Analytical Procedures. The diffractometer used was a Seifert-Scintag PAD-V with Cu K α radiation or a computer-controlled Rigaku diffractometer. In the latter case the X-ray source was a rotating anode (Cu K α) operating at 50 kV and 180 mA. The alignment of the instrument was checked using an internal standard. Thermal analysis was performed by a Mettler TA 4000 (under nitrogen, at a heating rate of 3 °C/min). The phosphorus and titanium content in the solids were determined by using a SpectraSpec DCP-AES spectrometer after dissolving a weighed amount in 0.1 M HF aqueous solution. Titanium (1000 ppm) AAS standard (Aldrich) and phosphorus (10 200 ppm) ICP/DCP standard (Aldrich) were used for the preparation of standard solutions for spectrometer calibration. IR spectra were obtained on a Perkin-Elmer 1720-X FT spectrophotometer by the KBr pellet technique. ^{31}P NMR spectra at magic angle were obtained on a Bruker MSL-300 spectrometer. Micrographs were recorded in a JEOL JSM-6100 electron microscope operating at 20 kV.

Ion-Exchange Study. Ion exchange of alkali and alkaline earth metal cations on the titanium phosphates was studied using 0.05 N $\text{MCl}_n\text{-M(OH)}_n$ (M = Li, Na, K, Cs, Ca, Sr, Ba; $n = 1, 2$) solutions with a $V:m = 200:1$ (mL:g), at room temperature. In all cases the contact time was 4 days with periodic shaking. The pH of solutions after equilibration with the adsorbent were measured using an Orion SA-720 pH meter. The final concentrations of metals of interest in solution were measured using a Varian SpectraAA-250 atomic absorption spectrometer. The rate of phosphorus hydrolysis was determined spectrophotometrically as the phosphovanadomolybdate heteropolycomplex at $\lambda = 315 \text{ nm}^{19}$ with a Perkin-Elmer model 200 instrument.

Results and Discussion

The investigation of the materials obtained under hydrothermal conditions shows the presence of three different types of titanium phosphates; α -TiP and two novel compounds, which have their most intense reflection in the XRD powder patterns at 7.34 and 7.39 Å (Figure 1). [The disparity in the intensities for ρ -TiP in the figure and table results from elimination of preferred orientation in the table data.] For convenience these novel titanium phosphates will be named π -TiP and ρ -TiP, respectively, and the positions of all their main reflections are given in Table 1. The regions of titanium phosphate formation are presented schematically in Figure 2 as a function of the H_3PO_4 concentration and the P:Ti molar ratio. The controlling factor in the synthesis is the concentration of phosphoric

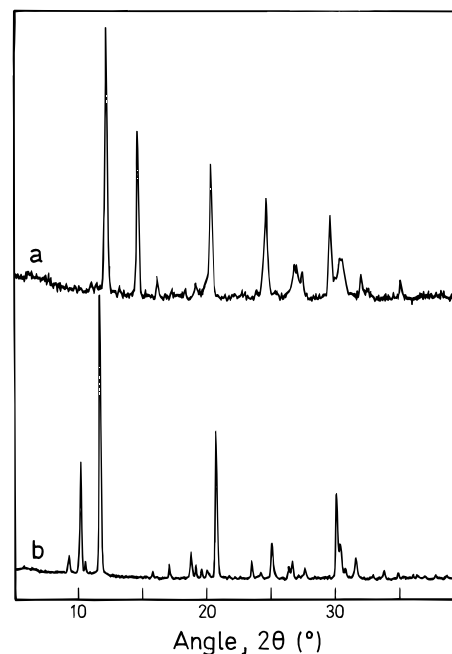


Figure 1. XRD powder patterns of (a) π -TiP and (b) ρ -TiP.

Table 1. d Spacings (in Å) and Relative Intensities (in %) of the Reflections of π -TiP and ρ -TiP

π -TiP		ρ -TiP	
d	I/I_0	d	I/I_0
7.34	100	9.29	16
6.10	51	8.49	42
5.51	7	7.39	100
5.15	5	5.52	6
4.64	9	5.11	47
4.38	52	4.66	20
3.93	3	4.64	12
3.63	49	4.57	38
3.32	19	4.47	25
3.26	13	4.40	20
3.03	43	4.23	75
2.95	23	3.75	50
2.76	16	3.65	10
2.57	12	3.52	50
2.45	5	3.49	7
2.36	7	3.35	27
2.02	8	3.31	33
1.99	9	3.20	13
		2.94	38
		2.91	39
		2.88	14
		2.81	38
		2.70	8
		2.63	15
		2.55	28
		2.42	5
		2.35	7
		2.02	18

acid in the reaction mixture, whereas the molar ratio P:Ti (or duration of hydrothermal treatment) influences mainly the product's crystallinity. α -Titanium phosphate is formed when the H_3PO_4 concentration is higher than 5 M. Decrease of phosphoric acid concentration to 4.4 M results in the formation of a mixture of α -TiP and ρ -TiP, whereas the pure ρ -TiP phase is obtained in the 3.2–4.4 M H_3PO_4 concentration range. The use of even more dilute phosphoric acid leads, initially to the formation of a mixture of π -TiP and ρ -TiP phases (2.7–3.2 M H_3PO_4) and then to the pure π -titanium phosphate (1.0–2.7 M H_3PO_4). It is worth noting that a mixture of Ti(OH)PO_4 , described previously by Cher-

(19) Michelsen, O. B. *Anal. Chem.* **1957**, *29*, 60.

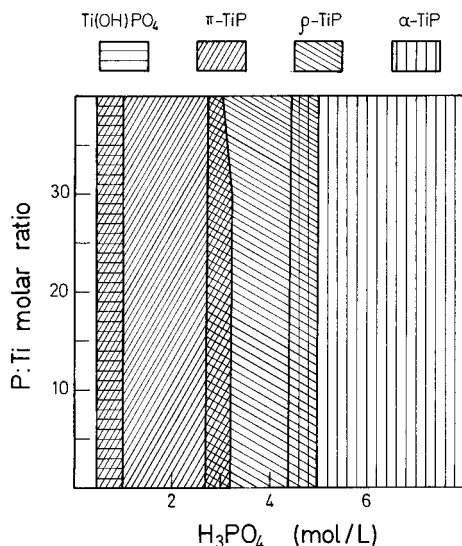


Figure 2. Phase diagram of the titanium phosphates.

Table 2. Elemental Analysis Data of π -TiP and ρ -TiP

sample	exp found, %		calcd for $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	
	Ti	P	Ti	P
π -TiP	28.90	18.70	28.40	18.34
ρ -TiP	28.33	18.25	28.40	18.34

norukov et al.,²⁰ and π -TiP is formed in a 0.3–1.0 M H_3PO_4 concentration range.

According to the elemental analysis (Table 2) the new titanium phosphates maintain the same molar ratio P:Ti = 1:1. Figure 3 shows the SEM images of these compounds. Both are fibrous materials. The fibers of π -TiP are broader and more homogeneous than those of the ρ -TiP. Conversely, the transverse section of the ρ -TiP fibers is larger than that of the π -TiP fibers.

To determine the structural formula, an additional characterization of the novel titanium phosphates has been undertaken by using X-ray diffraction, IR, and ^{31}P MAS NMR spectroscopy. Thermogravimetric (TG) analysis of the samples was also performed, and their ion-exchange behavior was studied. The crystallinity of the ρ -TiP was sufficiently developed to solve the structure of this compound from its powder diffraction data.²¹ The unit cell is triclinic, space group $P1$, with $a = 8.818(1)$, $b = 9.654(1)$, $c = 5.109(1)$, $\alpha = 93.812(2)^\circ$, $\beta = 93.665(3)^\circ$, $\gamma = 73.313(3)^\circ$, and $Z = 2$. There are two independent titanium atoms bridged by an oxygen atom. These metal atoms are octahedrally coordinated; the remaining coordination sites are completed by phosphate and water oxygen atoms. The stoichiometry requires a formula of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. Both water molecules reside on the same Ti atom and the two independent metal atoms are also bridged by a phosphate group. A polyhedral representation of the structure is shown in Figure 4. It is seen that two types of one-dimensional channels, one small and the other larger, are created by the connectivity of the octahedra and tetrahedra.

The ^{31}P MAS NMR spectra of π -TiP and ρ -TiP are presented in Figure 5. It is seen that both titanium phosphates have two peaks of equal intensity with positions at -10.8 and -24.3 ppm for π -TiP and at

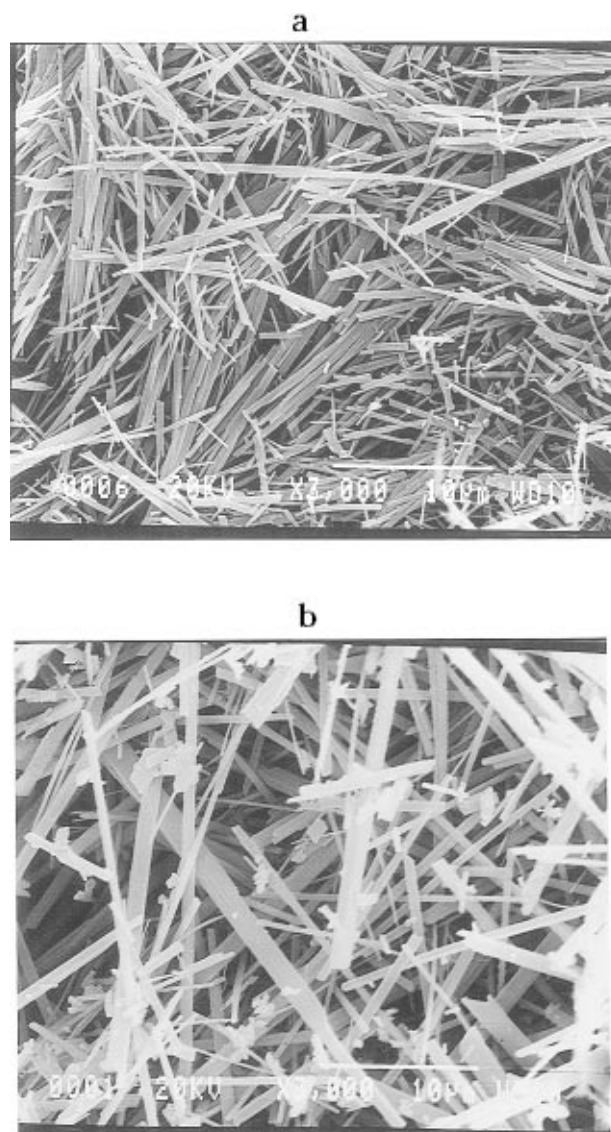


Figure 3. SEM images of (a) π -TiP (3000 \times magnification) and (b) ρ -TiP (1000 \times magnification).

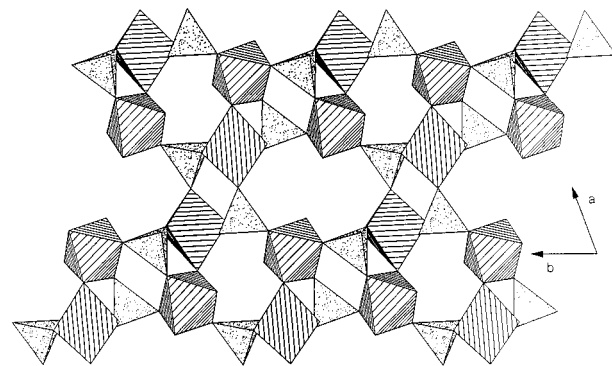


Figure 4. Section of the $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (ρ -TiP) structure.

-12.3 and -26.0 ppm for ρ -TiP. This suggests the existence of two crystallographically inequivalent or differently coordinated phosphorus atoms in the materials, which is in agreement with the crystallographic data for ρ -TiP. On the basis of the X-ray study and the data on the phosphorus shifts in layered α -TiP and γ -TiP (-10.5 ppm for H_2PO_4 group, -18.0 ppm for HPO_4 group, and -32 ppm for PO_4 group)^{16,22} and framework $\text{NaTi}_2(\text{PO}_4)_3$ (-27 ppm)²³ titanium phosphates, we as-

(20) Chernorukov, N. G.; Korschunov, I. A.; Zhuk, M. I. *Zh. Neorg. Khim.* **1982**, *27*, 3049.

(21) Poojary, D. M.; Bortun, A. I.; Bortun, L. N.; Clearfield, A. J. *Solid State Chem.*, in press.

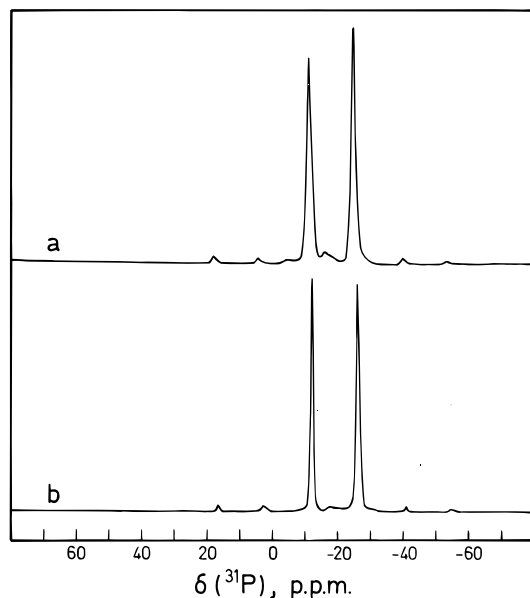


Figure 5. ^{31}P MAS NMR spectra of (a) π -TiP and (b) ρ -TiP.

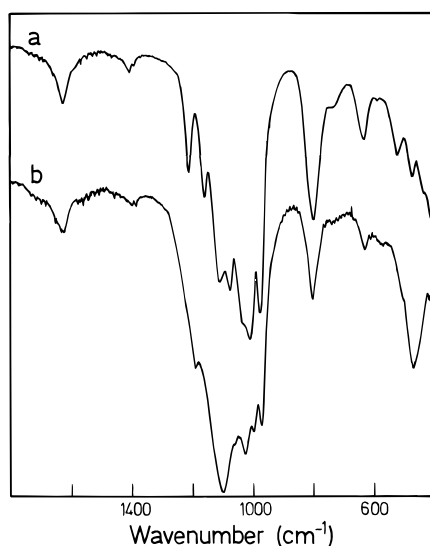


Figure 6. IR spectra of (a) π -TiP and (b) ρ -TiP.

signed the NMR peaks to crystallographically inequivalent PO_4 groups for both compounds.

As is seen in Figure 6 the stretching bands of the phosphate tetrahedron lie at 1154, 1103, 1070, 1027 (band), 1005, and 970 cm^{-1} in the IR spectrum of π -TiP, and at 1102, 1062 (band), 1029, 996, and 973 cm^{-1} in the IR spectrum of ρ -TiP.^{24,25} The bands at 627, 518, and 465 cm^{-1} in the spectra of π -TiP and 631, 565, and 472 cm^{-1} in spectra of ρ -TiP are due to mixed $\delta(\text{PO}_4)$ and $\delta(\text{Ti}-\text{O})$ vibrations.^{25,26} The bands of middle intensity at 796 and 803 cm^{-1} in the IR spectra π -TiP and ρ -TiP, respectively, cannot be assigned in a single valued manner. They can belong both to TiOH vibrations and/or to a Ti-O bond of higher order.

(22) Bortun, A. I.; Jaimez, E.; Llavona, R.; Garcia J. R.; Rodriguez, J. *Mater. Res. Bull.* **1995**, *30*, 413.

(23) Schmutz, C.; Barboux, V.; Ribot, F.; Taulelle, F.; Verdager, M.; Fernandez-Lorenzo, C. *J. Non-Cryst. Solids* **1994**, *170*, 250.

(24) Pechkovskii, V. V.; Mel'nikova, R. Ya.; Dzyuba, E. D. *Atlas Infrakrasnykh Spektrov Fosfatov. Ortofosfoty*; Nauka: Moscow, 1981.

(25) Titov, V. P.; Yakubovskaya, S. V.; Akulich, N. A.; Mel'nikova, R. Ya. *Russ. J. Inorg. Chem.* **1987**, *32*, 1711.

(26) Kochergina, L. L.; Porotnikov, N. V.; Kondratov, O. I. *Russ. J. Inorg. Chem.* **1983**, *28*, 171.

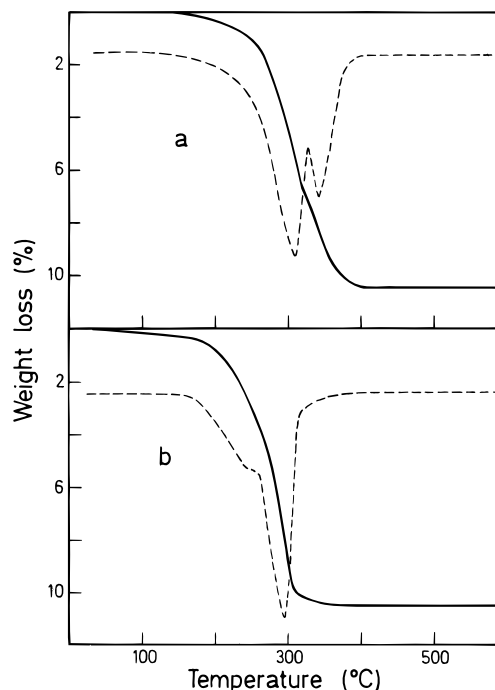
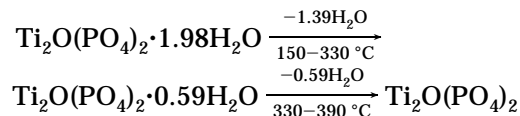


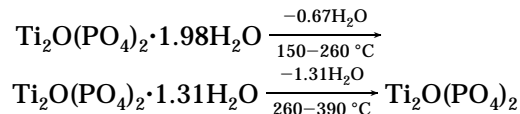
Figure 7. TG (—) and DTG (---) curves for (a) π -TiP and (b) ρ -TiP.

Examination of the TG curves (Figure 7) shows that both titanium phosphates practically do not lose weight below 150 $^{\circ}\text{C}$, which indicates that little or no physisorbed water is present in these compounds. Thermal decomposition of π -TiP and ρ -TiP occurs in two partially overlapping steps. It starts at a temperature higher than 150 $^{\circ}\text{C}$ and ends at 370–390 $^{\circ}\text{C}$, giving $\text{Ti}_2\text{O}(\text{PO}_4)_2$ as the final product in both cases. For ρ -TiP the thermal degradation takes place in the temperature ranges 150–260 $^{\circ}\text{C}$ ($\Delta M_1 = 3.58\%$) and 260–370 $^{\circ}\text{C}$ ($\Delta M_2 = 6.93\%$), whereas weight losses for π -TiP occur at 150–330 $^{\circ}\text{C}$ ($\Delta M_1 = 7.42\%$) and 330–390 $^{\circ}\text{C}$ ($\Delta M_2 = 3.12\%$). The total weight loss for both compounds is the same and equal to 10.5%. The brutto formulas of π -TiP and ρ -TiP could be represented as $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and the corresponding thermal transformations are as follows based on the change of slope in the TG curves:

π -TiP:



ρ -TiP:



The loss of zeolitic water is a reversible process. When both solids were treated at temperatures lower than 300 $^{\circ}\text{C}$ and then left in contact with humid air at room temperature, they recovered the initial water content. Thermal treatment at temperatures higher than 300 $^{\circ}\text{C}$ provokes some irreversible structural changes, probably due to condensation of functional groups. The temperature intervals at which the loss of zeolitic water takes place and the condensation processes practically overlap, especially in the case of ρ -TiP.

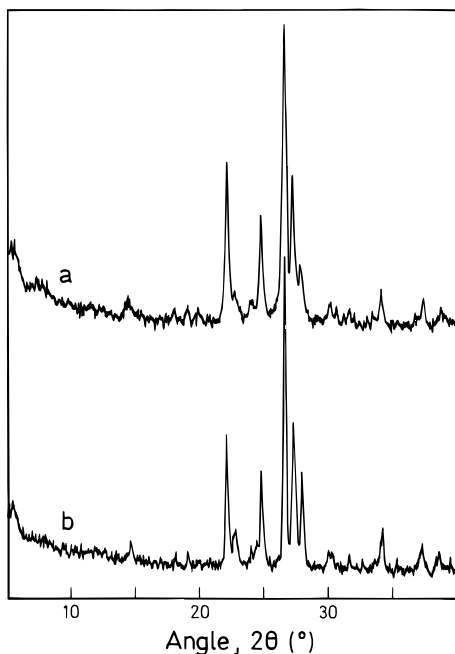


Figure 8. XRD powder patterns of (a) π -TiP and (b) ρ -TiP heated of 800 °C.

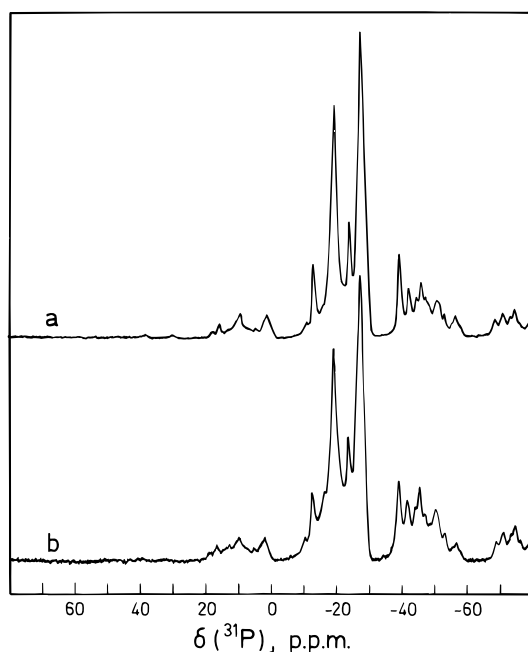


Figure 9. ^{31}P MAS NMR spectra of (a) π -TiP and (b) ρ -TiP heated of 800 °C.

Considering that both titanium phosphates have only PO_4 groups, we assume that structural changes could take place due to condensation of hydroxyl groups bonded to titanium atoms. Hydroxyl groups may arise from an equilibrium such as $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ti}_2(\text{OH})_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

Some additional information concerning the thermal decomposition of the novel titanium phosphates was obtained by X-ray, IR, and NMR spectroscopies. According to these data both π -TiP and ρ -TiP treated at 800 °C (total weight loss 10.5%) have almost identical XRD powder patterns (Figure 8), and ^{31}P NMR and IR spectra (Figures 9 and 10). The NMR spectra show four peaks: two peaks with high intensity at -19.0 and -27.0 ppm, and two peaks with low intensity at -12.5

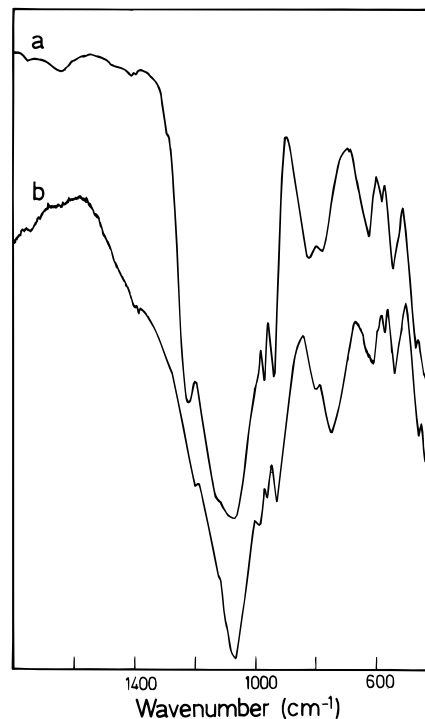


Figure 10. IR spectra of (a) π -TiP and (b) ρ -TiP heated of 800 °C.

and -23.4 ppm. It is worth noting that the positions of the main peaks do not differ considerably from the position of the peaks in the initial materials. At the same time the XRD powder patterns of the thermally treated compounds were completely changed. They are similar to those of $\text{Ti}_2\text{O}(\text{PO}_4)_2$ described by Chernorukov et al.²⁰ IR spectra of π -TiP and ρ -TiP treated at 800 °C correspond also with the IR spectrum of $\text{Ti}_2\text{O}(\text{PO}_4)_2$. This shows that both titanium phosphates undergo thermal decomposition with the formation of the same compound, namely, $\text{Ti}_2\text{O}(\text{PO}_4)_2$.

It is known that layered titanium phosphates react with alkylamines with the formation of intercalates having interlayer distances larger than those of the initial material.²⁷ By studying the reaction of *n*-alkylamines with π -TiP and ρ -TiP, in both vapor and liquid phases, no changes in the XRD powder patterns of the resulting products were found as compared with the initial materials. No changes were also detected in the TGA curves. The absence of amine adsorption indicates a rather rigid nature of their framework structures.

The possible existence in the π -TiP and ρ -TiP of Ti-OH functional groups [$\text{Ti}_2(\text{OH})_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$] suggests that these compounds may exhibit cation exchange properties in neutral and alkaline media. According to the formula $\text{Ti}_2(\text{OH})_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, their theoretical ion-exchange capacity should be 5.92 mequiv/g assuming both hydroxyl protons are exchangeable. As seen from potentiometric titration curves (Figures 11 and 12) π -TiP and ρ -TiP do adsorb alkali-metal cations. Their uptake starts at a pH higher than 3, and it is extremely low in the pH range 3–6 (0.1–0.4 mequiv/g). The increase of alkali-metal cations

(27) Alberti, G.; Costantino, U. In *Inclusion Compounds. Inorganic and Physical Aspects of Inclusion*; Atwood, J. L., Davies, J. E., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 5.

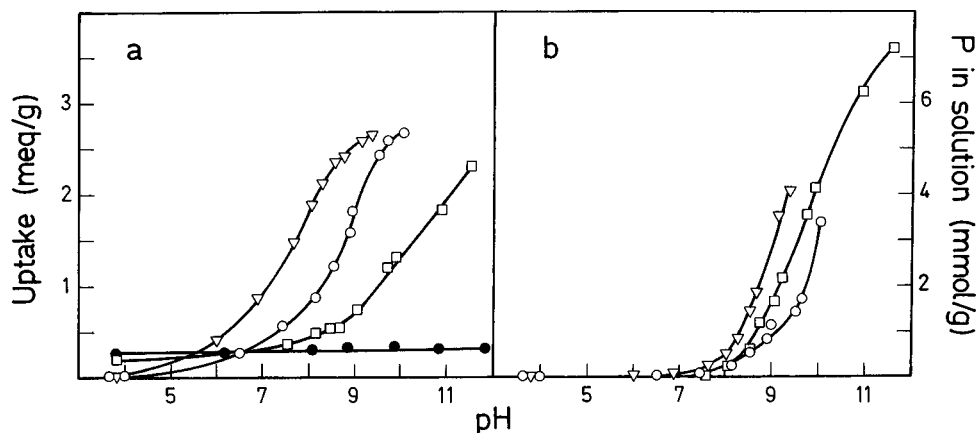


Figure 11. Li^+ (O), Na^+ (∇), K^+ (\square), and Cs^+ (\bullet) ion exchange on π -TiP: (a) adsorption and (b) hydrolysis curves as a function of the pH.

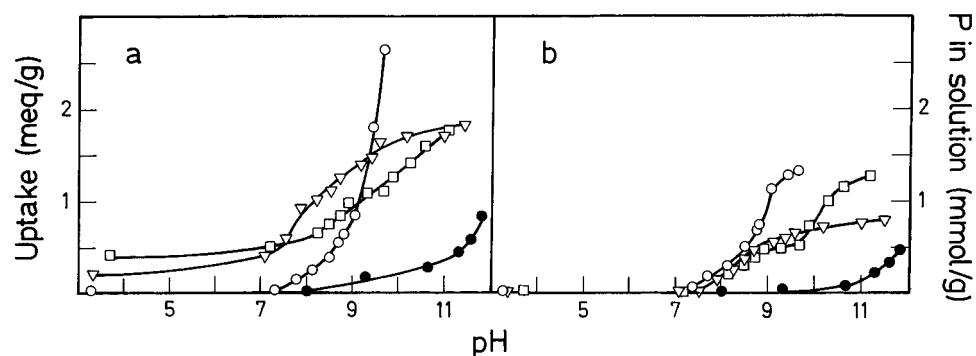
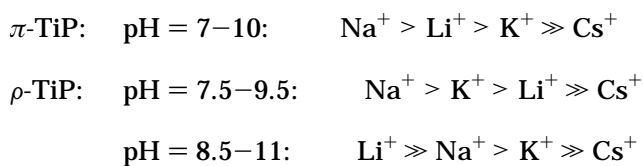


Figure 12. Li^+ (O), Na^+ (∇), K^+ (\square), and Cs^+ (\bullet) ion exchange on ρ -TiP: (a) adsorption and (b) hydrolysis curves as a function of the pH.

adsorption begins at $\text{pH} > 6-7$, and it reaches the maximum values, close to 50% of the theoretical IEC, for π -TiP 2.8 mequiv/g and for ρ -TiP 2.7 mequiv/g at $\text{pH} = 10$. This indicates that both adsorbents behave as weak acid cation exchangers. The selectivity sequences found for titanium phosphates are the following:



The data for Cs^+ show that both exchangers take up a small amount of Cs^+ ion, which is very poorly adsorbed in the entire pH range (0.1–0.5 mequiv/g). This is related to the nature of their framework structure. The π -TiP and ρ -TiP entrances to inner cavities are too small for the cesium ion, but they are large enough to accept other alkali cations.

Both novel titanium phosphates undergo hydrolytic decomposition in alkaline media, which is typical for titanium phosphate-based exchangers. It is worth noting that the chemical stability of π -TiP is much lower than that of ρ -TiP (Figures 11 and 12). π -TiP decomposes practically completely at $\text{pH} = 10-11$, whereas ρ -TiP at this pH releases about 25% of its phosphate groups.

Potentiometric titration curves of π -TiP and ρ -TiP with alkaline earth hydroxides are presented in Figure 13. It is seen that both titanium phosphates hardly exchange any of the divalent cations at $\text{pH} < 5.5-6.0$.

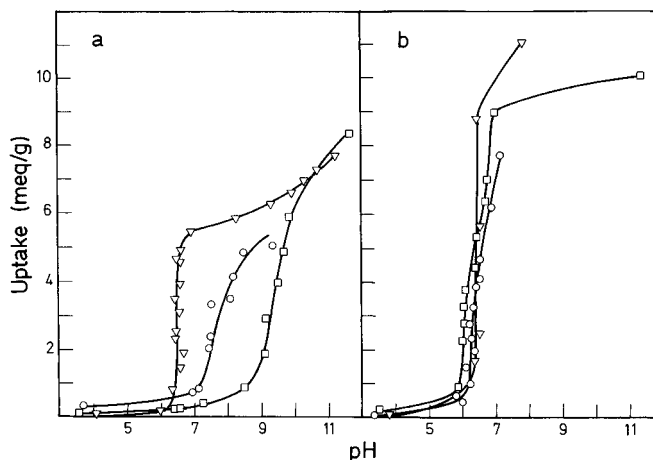


Figure 13. Ca^{2+} (O), Sr^{2+} (∇), Ba^{2+} (\square) adsorption on (a) π -TiP and (b) ρ -TiP as a function of the pH.

At higher pH an apparent dramatic increase of alkaline-earth metal cations uptake takes place. For ρ -TiP the uptake is practically independent of the type of cation. The adsorption abruptly increases as the pH increases. For π -TiP the increase of adsorption depends on the type of cation. The potentiometric titration curves for Sr are similar for both π - and ρ -TiP. There is a drastic increase of cations uptake at $\text{pH} > 6-7$, exceeding the theoretical IEC value of 5.9 mequiv/g. The uptake of Ca^{2+} and Ba^{2+} by ρ -TiP differs from that found for strontium as the uptake of these ions require higher pH values: pH 8 for Ca^{2+} , pH 9 for Ba^{2+} in comparison with pH 6.5 for Sr^{2+} . This suggests that at $\text{pH} < 6-7$ adsorption of two-charged cations takes place, whereas in alkaline media the controlling factors are the ion exchange of alkaline

earth metals in a form of monocharged cations (MOH^+) and/or the partial hydrolytic decomposition of the exchanger, which could lead to the precipitation of alkali-metal phosphates in the channels of adsorbent.²⁸ The high probability of the latter mechanism of "apparent" adsorption is confirmed by the decrease of the intensities of all reflections in the XRD powder pattern

(28) Alvarez, C.; Llavona, R.; Garcia, J. R.; Suarez, M.; Rodriguez, J. *Inorg. Chem.* **1987**, *26*, 1045.

characteristic for titanium phosphates and appearance of new reflections characteristic for titanium dioxide.

Acknowledgment. The authors gratefully acknowledge the financial support of this study by EPA Grant 094TAM0401 through the Gulf Coast Hazardous Substance Research Center (USA) and CICYT (Spain), research Project No. MAT94-0428.

CM970060C