Synthesis of Semicrystalline Materials by Organic Compound Intercalation into Amorphous Titanium Phosphate

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It is well-known now that the intercalation of organic molecules and inorganic species into layered inorganic substances is one of the promising ways for the synthesis of new materials with finely regulated porous structure, which can be used as shape-selective catalysts, selective ion-exchangers, semiconductors, etc.[1-4] Among such layered inorganic materials are crystalline lamellar group IV element phosphates for which the intercalation mechanism and the properties of obtained pillared materials have been studied in detail.[5-10] At the same time there is no analogous information concerning the possibility of preparation of pillared materials based on amorphous group IV element phosphates, though the amorphous adsorbents possess more effective surface area and porosity in comparison with crystalline ones. An additional advantage of amorphous group IV element phosphates is that there is technology of their preparation in the form of mechanically strong spherical granules, which facilitates their large scale application.[11]

In this communication, preliminary results are presented on the reactions of spherically granular amorphous titanium phosphate with amines and phenylphosphonic acid. The intercalation leads to the ordering of the structure of the initial adsorbent with formation of *semicrystalline* phases with distinct interlayer distances the value of which depends on the type of organic compounds intercalated.

Table 1. Interlayer Distances (Å) in Titanium Phosphate Based Adsorbents

amine	TiP	α-TiP	γ-TiP	TiPPh
		7.6[a]	11.6[a]	15.2
propylamine	17.0	16.9[b]	18.4[c]	
butylamine	18.8	18.8[b]	20.0[c]	15.2, 13.2

[a] Reference 12. [b] Reference 13. [c] Reference 14.

Synthesis of titanium phosphate (Ti(OH)P) has been carried out by a gel method as described in ref 11. Before the experiments the granules of Ti(OH)P xerogel (diameter 0.25–1.00 mm) have been thoroughly washed first with 1 M solution of HCl and then with distilled water (till the pH = 3.5) and dried at 50 °C. The molar ratio P:Ti in sorbent was 0.9:1; surface area 200 $m^2\ g^{-1}$ (Ar).

The synthesis of mixed spherically granular titanium phosphate–phenylphosphonate (TiPPh) has been carried out by treatment of Ti(OH)P granules with an excess of 1 M solution of phenylphosphonic acid at 60 °C for 2 days. The granules of TiPPh have been washed with distilled water until pH = 4 and dried at 50 °C.

Intercalation compounds with amines were prepared by placing the titanium phosphate based adsorbents in an atmosphere saturated with the corresponding amine at room temperature for 3 days. The intercalated samples were dried at 50 °C.

X-ray measurements have been carried out in a Philips diffractometer, Model 1050/23 with Cu Kα radiation. TGA measurements were performed by using a Mettler Model TA 4000 (TG 50); rate of heating 10 °C min^{-1}, with an air flow of 10 mL min^{-1}. IR spectra were obtained on Perkin-Elmer infrared spectrometer 1720-X FT model by the KBr pellet technique. Microanalytical data (C and N) were obtained with a Perkin-Elmer 240B elemental analyzer.

The data of the values of interlayer distances of the synthesized pillared materials are presented in Table 1. Table 2 shows the analysis data and the total weight loss for these compounds. X-ray powder diffraction patterns of Ti(OH)P, TiPPh, and products of their reaction with butylamine are shown in Figure 1. As can be seen from these data the initial titanium phosphate is a completely amorphous material without any reflections in its X-ray diffraction pattern. At the same time its amine derivatives show distinct reflections. It means that amine intercalation into the amorphous titanium phosphate results in ordering of the polymeric (Ti–O–Ti) chains, to which functional –OH, $-H_2PO_4$, and $=HPO_4$ groups are attached, with formation of intercalated structures like that in crystalline materials. The values of interlayer distances in these compounds concur with those characteristic of the α-TiP/amine intercalation compounds,[13] though the degree of crystallinity (intensity of peaks) is considerably lower. The γ-TiP/amine intercalation compounds show larger interlayer distances.[14] This fact suggests

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Table 2. Microanalytical Data (C and N) and Experimental Weight Loss at 800 °C of the Intercalation Compounds and Those Calculated from the Formula

		experimental			theoretical		
compound	formula	% C	% N	% w.l.	% C	% N	% w.l.
Ti(OH)P−propylamine	$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(OH)_{27}(C_3H_7NH_2)_{18}$	14.95	5.72	34.64	14.83	5.77	34.19
Ti(OH)−butylamine	$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(OH)_{27}(C_4H_9NH_2)_{18}\cdot 20H_2O$	18.68	5.51	42.18	17.34	5.06	42.47
TiPPh	$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(O_3PC_6H_5)_{13.5}\cdot 36H_2O$	15.06		31.58	17.35		31.56
TiPPh−butylamine	$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(O_3PC_6H_5)_{13.5}(C_4H_9NH_2)_{18}\cdot 40H_2O$	26.13	4.15	45.06	26.27	3.60	45.13

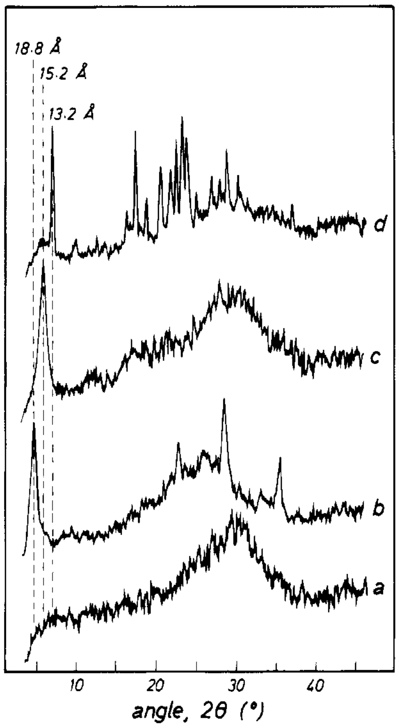

Figure 1. X-ray diffraction patterns of (a) Ti(OH)P, (b) Ti(OH)P−butylamine, (c) TiPPh, and (d) TiPPh−butylamine.

that the predominant structure of Ti(OH)P is of the α-type. Such *semicrystalline* states exist only in the presence of amine and amorphization takes place when the amine is removed from the host material (at high temperature or by treatment with solution of mineral acid).

A structural rearrangement of amorphous titanium phosphate also takes place when it is treated with a solution of phenylphosphonic acid (Figure 1c). We suppose that in this case the phenyl radicals substitute for the free hydroxyl groups of Ti(OH)P with formation of pillared, mixed, titanium phosphate−phenylphosphonate. The interlayer distance of TiPPh is 15.2 Å, which is slightly larger than that of α-titanium phenylphosphonate (α-TiPh, 15.0 Å).[15] The reaction of TiPPh with butylamine favors ordering of the material and a new basal plane spacing at 13.2 Å appears (Figure 1d), probably due to the amine intercalation as a monolayer.[16]

Acid treatment of TiPPh−butylamine gives rise to an initial *semicrystalline* TiPPh compound, which is able to react with amine again. Such operations (intercalation/desorption of amine) can be repeated many times, and in each case we have obtained essentially the same pillared compounds.

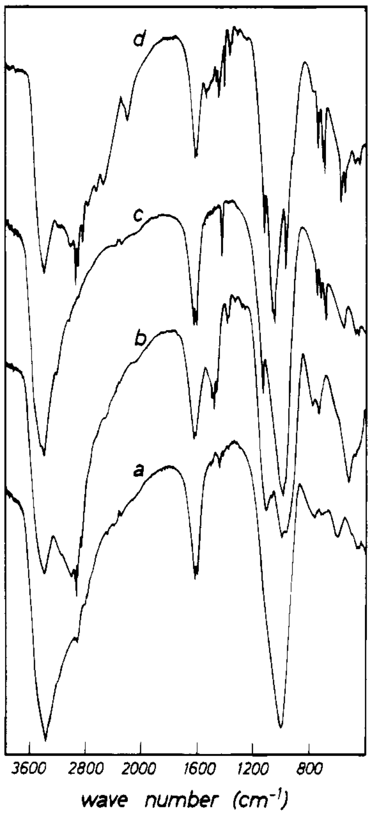

Figure 2. Infrared spectra of (a) Ti(OH)P, (b) Ti(OH)P−butylamine, (c) TiPPh, and (d) TiPPh−butylamine.

Figure 2 shows the infrared spectra of these compounds. Ti(OH)P presents the characteristic bands of the titanium phosphates; the P−OH(str) band centered at 1038 cm^{-1}, very strong, and the typical O−H(str) strong and wide band at 3400 cm^{-1}. The presence of both phosphate and phenylphosphonate groups in the TiPPh compound gives rise to two new bands at 1438 cm^{-1} (very sharp typical of phosphonic acids) and 1145 cm^{-1}. TiP−propylamine and TiPPh−butylamine compounds have the characteristic bands of the amine derivatives: 2960 cm^{-1} (strong signal typical of the N−H(str)); several peaks at 1500−1550 cm^{-1} (medium intensity, N−H(δ)); and the 1394 cm^{-1} band (low intensity, C−N(str)).

The general formulas $Ti_4O_2(HPO_4)_3(H_2PO_4)_x(OH)_{6-x}\cdot yH_2O$ is proposed for amorphous titanium phosphates.[17,18] Ti(OH)P has a P:Ti ratio of 0.9:1, a weight loss by calcination at 800 °C of 32.4% and a cationic exchange capacity of 3.5−4.0 mequiv g^{-1}, corresponding to the $Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(OH)_{27}\cdot 52.5H_2O$ formulas, derived from the earlier one for $x = {}^3/_5$.

Assuming that Ti(OH)P has a prestructure of the α-type, the intercalation of *n*-alkylamines should be

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original solids with a molecula of amine per atom of phosphorus. If we assume the earlier formula for Ti(OH)P, the saturated compounds should be composition

$$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(OH)_{27}(C_nH_{2n+1}NH_2)_{18}\cdot yH_2O$$

When Ti(OH)P is treated with phenylphosphonic acid, a product with the formula

$$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(O_3PC_6H_5)_{13.5}\cdot yH_2O$$

should be obtained if the reaction

$$Ti(OH)_4 + 2C_6H_5PO_3H_2 \rightarrow Ti(O_3PC_6H_5)_2 + 4H_2O$$

affects to all OH^- groups. The saturation of phosphate–phosphonate with butylamine should lead to the compound

$$Ti_{20}O_{10}(HPO_4)_{15}(H_2PO_4)_3(O_3PC_6H_5)_{13.5}(C_4H_9NH_2)_{18}\cdot yH_2O$$

Quantitative data derived from these hypothesis concur in good approximation with the experimental results (Table 2).

From the TGA curves (Figure 3) it is clearly seen that the thermal stability of amorphous titanium phosphate greatly increases after its modification with phenylphosphonic acid and that it is very similar to that of crystalline α-titanium phenylphosphonate. This makes it possible to use such a granular material for shape selective catalysis at appreciably high temperature.

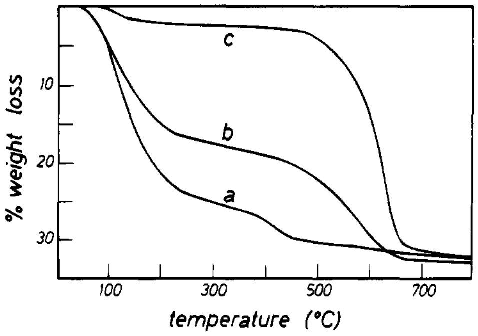

Figure 3. TGA curves for (a) Ti(OH)P, (b) TiPPh, and (c) α–TiPh.

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