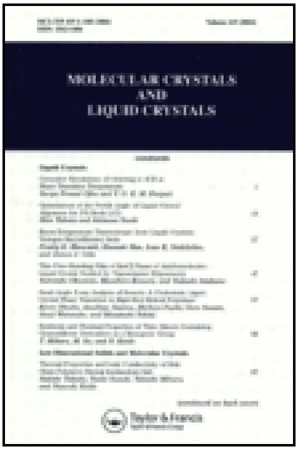

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Sol-gel synthesis of surfactant-expanded layered titanium phosphates

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Sol-gel synthesis of surfactant-expanded layered titanium phosphates.

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A new method for the direct synthesis of surfactant-expanded layered titanium phosphate has been developed by reacting cationic surfactants, orthophosphoric acid and titanium isopropoxide in alcohol solution, under hydrothermal conditions. The intercalated solids obtained have been characterized by X-ray diffraction, chemical analyses, IR spectroscopy, DTA-TGA and SEM. At low surfactant/phosphate ratio (< 0.14), the hexadecyltrimethylammonium species orientate parallel to the host layers, whereas a slanted arrangement is favoured at higher ratio. Only a single phase, with a basal spacing of 22 Å, was observed when dioctylammonium was used as surfactant.

Keywords: intercalation, cetyltrimethylammonium, layered titanium phosphate, sol-gel.

INTRODUCTION

The increasing demand of acid solids with specific and tunable characteristics, such as pore size, acidity strenght or redox properties, has led to a fast development of new inorganic solids classes which have found applications in different fields, mainly in catalysis and sorption processes. Among these new compounds, the synthesis of MCM-type mesoporous materials has recently attracted much attention[1]. These organo-inorganic precursor solids are prepared by using supramolecular long-range ordered organic species as templates for the inorganic framework, giving rise to hexagonal, lamellar and cubic structures. These studies have been preferently directed to the synthesis of tridimensional hexagonal phases, in order to create versatile porous networks upon removing the surfactant. Such porous solids have been already shown to be useful for catalysis and sorption. Recently, some efforts have been also devoted to the synthesis of lamellar phases consisting of metal oxides and phosphates, wich may open new experimental routes to intercalation chemistry[2].

We have previously reported the preparation of surfactant expanded zirconium(IV) phosphate by a sol-gel process[3]. In this paper, we apply the same methodology for the synthesis of another isostructural member of the layered metal(IV) phosphate family, such as titanium phosphate.

EXPERIMENTAL

Surfactant-expanded titanium phosphate phases were prepared by putting in contact different amounts of hexadecyltrimethylammonium (CTMA) bromide previously dissolved in 1-propanol, with orthophosphoric acid 85% solution. The resultant clear solution was aged for 30 minutes at 80°C in a thermostatized bath, and then titanium isopropoxide was added under vigorous stirring. In all cases the molar ratio P/Ti was equal to 2, whereas the ratio CTMA/P was varied between 0.14 and 2.24. The gel obtained was treated in an autoclave at 150°C during 3 days. The solids (CTMA-TiP) were recovered by centrifugation, washed with ethanol and air-dried at 60°C. The same experimental procedure, with a surfactant/phosphate ratio of 0.56, was used to synthesize dioctylammonium-expanded titanium phosphate (DOA-TiP).

Ti was analyzed by atomic absorption spectroscopy, P was determined colorimetrically and organic matter by CHN analyses. X-ray diffraction (XRD) was recorded on a Siemens D501 diffractometer using Cu K_α radiation and a graphite monochromator. TGA-DTA measurements were carried out under air using a Rigaku Thermoflex TG8110 instrument (calcined Al_2O_3 reference, 10 K min^{-1} heating rate). IR spectra were recorded with a Perkin Elmer 883 infrared spectrophotometer on KBr diluted wafers. SEM has been carried out in a JEOL SM 840 scanning electron microscope.

RESULTS AND DISCUSSION

Different CTMA intercalation compounds are obtained by varying the CTMA/P ratio in the initial solution. The chemical analysis gave in all cases P:Ti molar ratios very close to 2 and different contents of surfactant and water according to the surfactant loading (Table I).

TABLE I Chemical analyses of CTMA-TiP solids.

Sample	%H_2O	%C_{16}TMA	Empirical formula
CTMA-TiP 0.14	8.9	4.3	$Ti(CTMA_{0.02}H_{0.98}PO_4)_2.1.6H_2O$
CTMA-TiP 0.28	4.8	15.8	$Ti(CTMA_{0.09}H_{0.91}PO_4)_2.0.9H_2O$
CTMA-TiP 0.56	4.0	28.6	$Ti(CTMA_{0.21}H_{0.79}PO_4)_2.0.8H_2O$
CTMA-TiP 1.12	4.0	31.7	$Ti(CTMA_{0.22}H_{0.78}PO_4)_2.0.8H_2O$
CTMA-TiP 2.24	3.5	33.1	$Ti(CTMA_{0.24}H_{0.76}PO_4)_2.0.8H_2O$

Figure 1 shows the variation of the CTMA/P in the solids as a function of the surfactant loading. At loadings higher than 0.5 the curve reaches a plateau, with a CTMA/P ratio close to 0.25.

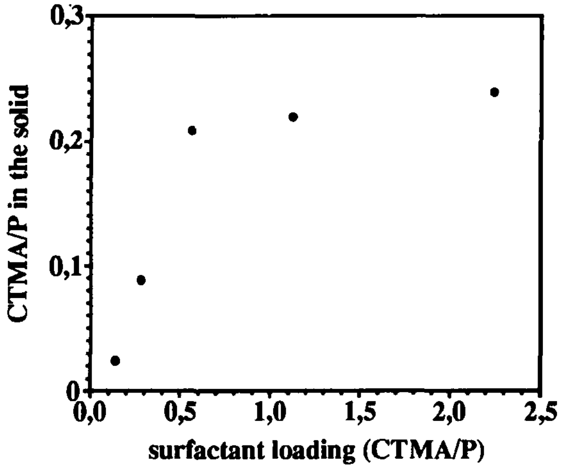
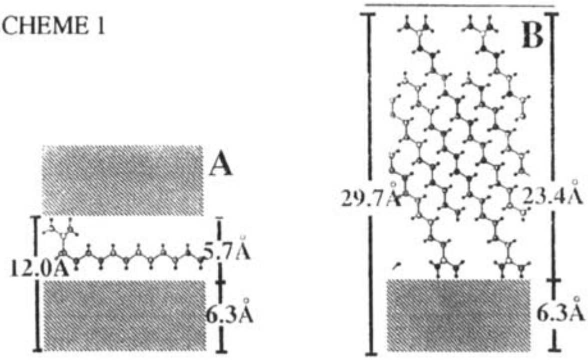


FIGURE 1 Retention diagram of CTMA into titanium phosphate as a function of the surfactant loading (CTMA/P).

SCHEME 1



The XRD patterns of the CTMA intercalates exhibit the characteristic reflections of the α-TiP structure, at 4.31 Å (d_{200}) and 2.50 Å (d_{020}), in addition to the d_{001} reflection whose position depends on the arrangement of the surfactant species (Figure 2A). These features clearly correspond to a layered solid. SEM micrographs also point to a layered structure for these solids. At low loading, the organic chain lies flat between the phosphate layers (12 Å), whereas at the highest surfactant loading, the basal spacing is 29.7 Å, which is compatible with a bilayer of CTMA orientated with an angle of 65° in respect to the layer and partially imbricated one to another (Scheme 1). The maximum retention of surfactant corresponds to a neutralisation of about 25 % of the acid groups of the phosphate framework, which might be expected considering the covering effect of the organic cations on the layer phosphate groups.

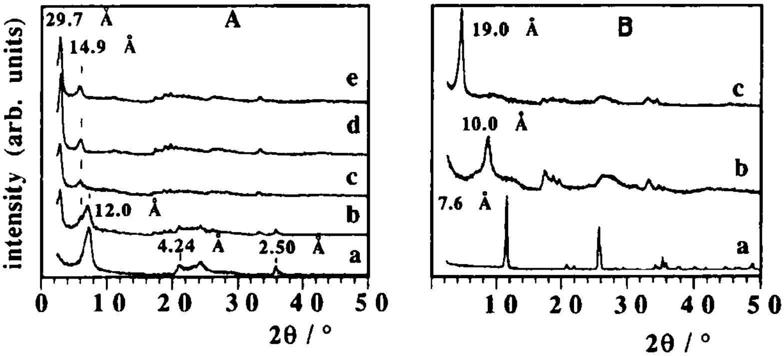


FIGURE 2 XRD patterns of **A.** CTMA-TiP intercalates with different CTMA/P molar ratio: a) 0.14, b) 0.28, c) 0.56, d) 1.12 and e) 2.24 and **B.** a) crystalline α-TiP, b) CTMA-TiP 0.56 after treatment with a HCl/ethanol solution and c) sample b) after adsorption of n-propylamine.

The surfactant can be extracted from the interlayer region upon treatment with a HCl/ethanol solution, an ethanol-expanded α-TiP phase with d_{001}= 10 Å being formed (Figure 2B). Adsorption of n-propylamine (NPA) vapours on this phase results in a solid with basal spacing of 19 Å, characteristic of the NPA-TiP intercalate[4].

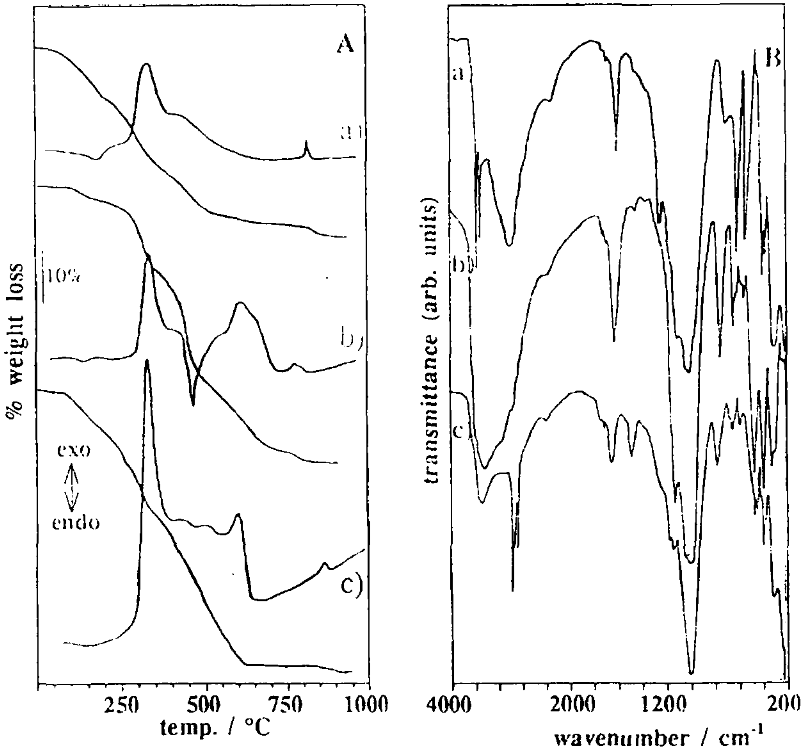


FIGURE 3 A. Thermogravimetric curves (DTA-TGA) of a) CTMA-TiP 0.14, b) CTMA-TiP 1.12 and c) DOA-TiP; B. IR spectra of a) crystalline α-TiP, b) CTMA-TiP 1.12 treated with HCl/ethanol and c) CTMA-TiP 1.12.

DTA-TGA curves corresponding to the CTMA-TiP intercalates (Figure 3A) point to the existence of a strong interaction between the closely packed surfactant alkyl chains, in the phosphate interlayer region, as revealed by exothermic effects at temperatures so high as 600 and 823 K. The high temperature exothermic effects are not observed for a surfactant flat disposition. Upon removing organic matter, the phosphate layer collapses and titanium pyrophosphate is formed, which is associated with the exothermic effect appearing at 1173 K, accompanied by a weight loss.

The IR spectra exhibit typical features of the surfactant, i.e., the vibrational modes of CH_3 and CH_2 groups (ν CH at 2928 and 1859 cm^{-1}, respectively, as well as the deformation band at 1474 cm^{-1}). The shoulder at 1227 cm^{-1} is assigned to free POH groups on the phosphate layers (Figure 3B).

The use of dialkylammonium ions (dioctylammonium) as surfactant has been investigated. The resulting expanded phase presents a basal spacing of 22 Å, which is lower than that expected for a closely packed bilayer of the organic ions in the interlayer region (26.8 Å in α-ZrP)[4]. The difficulty for generating a close packing of dialkylammonium ions may be the cause of the low crystallinity observed in these solids.

Acknowledgments

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