

Effect of Calcination on Titanium Phosphate produced by H_3PO_4 Treatment of Anatase

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The effect of calcination at different temperatures on anatase treated with H_3PO_4 has been studied by several techniques, in order to understand the mechanism of the formation of stable titanium phosphates. Calcination at 573 K of the hydrated phosphate, $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, obtained by reaction of anatase with H_3PO_4 , leads to the formation of TiP_2O_7 , although its crystallinity is perturbed by the presence of an excess of phosphoric acid in the starting material. Calcination at 873 K eliminates the excess of H_3PO_4 , probably by formation of volatile P_2O_5 , and a better crystallized TiP_2O_7 is obtained. A ^{31}P magic-angle spinning nuclear magnetic resonance study of the pyrophosphate indicates that the nine lines observed in the spectrum are due to the presence of a $3 \times 3 \times 3$ cubic superlattice.

Titanium dioxide is an important component of catalysts used in some industrial processes such as selective catalytic reduction with ammonia for the removal of NO_x emissions.¹ Without additives these catalysts are soft and suffer strong abrasion at high space velocities; to be used they need to be hardened. Previous studies² have demonstrated the usefulness of phosphoric acid as an extrusion binder for improving the mechanical strength of the catalyst pellets. In spite of the beneficial mechanical properties provided by phosphoric acid the catalytic performance is somewhat degraded, owing to the important textural and chemical changes induced. Thus, it was observed that H_3PO_4 reacts with titania to form different types of titanium phosphates.^{3,4} In their precursor form, these phosphates can incorporate other cations present in the starting catalyst to produce different types of compounds.^{5,6}

In order to understand the effect of phosphoric acid on TiO_2 -based catalysts, as a first step, we have studied in some detail the transformation of TiO_2 in a stable titanium phosphate by calcination of the reaction product of anatase with an excess of H_3PO_4 at different temperatures.

Experimental

The starting sample was prepared by reaction of anatase (Degusa P-25) with H_3PO_4 in an autoclave at 473 K for 3 h. The $\text{P}_2\text{O}_5 : \text{TiO}_2$ ratio used was 1.2. The sample was dried at 400 K, without washing to eliminate the excess of H_3PO_4 .

The XRD patterns were obtained with a Philips PW 1716/30 diffractometer using graphite-monochromatized $\text{Cu-K}\alpha$ radiation. A Dupont 951 thermobalance controlled by a Dupont 990 thermal analyser was used to obtain the thermogravimetric (TG) curve, at 5°C min^{-1} , under flowing oxygen. The IR spectra were recorded with an FTIR spectrometer (Nicolet 57 DX), using the KBr pellet technique for sample preparation.

^{31}P magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded at 161.98 MHz with a Bruker MSL-400 spectrometer. The external magnetic field was 9.4 T. All measurements were carried out at 295 K and the samples were spun around the magic angle ($54^\circ 44'$ with respect to the magnetic field) in the range 4–4.5 kHz. NMR spectra were recorded after $\pi/2$ pulse excitation (3 μs) and the interval between successive accumulations (6 s) was chosen to avoid saturation effects. An 85% aqueous solution of H_3PO_4 was used as an external standard. In order to preserve quan-

titative analysis, no mathematical treatments of the NMR signal were carried out.

Results

X-Ray Diffraction (XRD)

The sample prepared by reaction of anatase with H_3PO_4 , exhibits, after heating at 400 K, the XRD pattern shown in Fig. 1(a); most of the lines correspond to the diffraction pattern of $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ($\alpha\text{-TiP}$).^{7,8} A thermal treatment of this sample at 473 K modifies the relative intensity of some

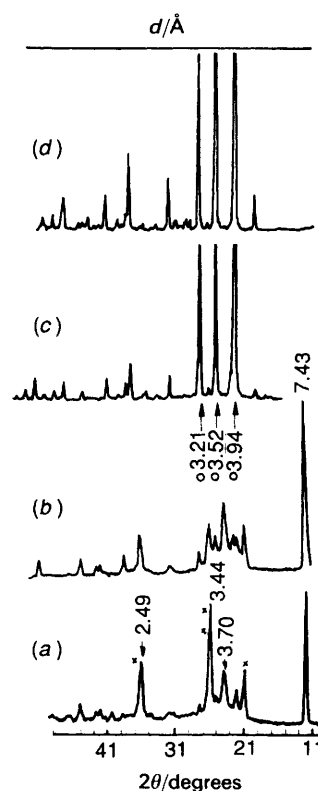


Fig. 1 XRD pattern of the titanium phosphate sample calcined at (a) 400, (b) 473, (c) 573 and (d) 973 K. (x) $\alpha\text{-TiP}$, (O) TiP_2O_7 .

lines, but does not affect other features. The first reflection (002), does not change significantly with this treatment, indicating that the interlayer distance of the layered phosphate α -TiP⁹ is not affected by the expected elimination of water molecules. Some rearrangement does however occur in the interlayer region, as evidenced mainly by the increase of the line at 3.70 Å, probably the fourth order of the main basal spacing.

When the sample is calcined at 473 K, some reflections corresponding to the main lines of TiP₂O₇¹⁰ are also observed, Fig. 1(b). After calcination at 573 K the XRD pattern consists of peaks of TiP₂O₇, with very small contributions from the α -TiP phase, Fig. 1(c). Calcination at higher temperature leads to narrowing of the TiP₂O₇ peaks and elimination of the other reflections. The pattern of pure TiP₂O₇ is observed after calcination at 973 K, Fig. 1(d).

TG Analysis

The TG curve of the starting sample is presented in Fig. 2. It shows that the weight loss takes place in three stages: 6.7% is lost during heating to 483 K, probably owing to the loss of most of the molecular water present between the α -TiP layers. The total H₂O loss corresponding to Ti(HPO₄)₂·H₂O would give a 7% loss. At temperatures close to 503 K, a sharp weight loss of 6.7% is observed, probably due to the elimination of the remaining water molecules and most of the hydroxy groups. The weight loss corresponding to OH groups of the orthophosphate would also be 7%. Between 523 and 873 K the sample continues to lose weight at a slower rate, although the loss becomes more important with increasing temperature, reaching a total loss of 16.5% in this stage. This weight loss must be due in part to the elimination of OH groups, but most of it should be assigned to the loss of unreacted phosphoric acid retained by the sample during α -TiP formation. This is eliminated, probably as volatile P₂O₅, for $T_c > 483$ K. In the 873–973 K range the sample weight is almost constant. From these data it can be concluded that the amount of free phosphoric acid in the starting sample must be close to 16 wt.%.

IR

The IR spectra of the sample calcined at different temperatures are presented in Fig. 3 and 4. The spectrum of the precursor in the 2000–4000 cm⁻¹ range, Fig. 3(a), is very similar to that observed for α -TiP.¹¹ It consists mainly of bands at 3555, 3478 and 3150 cm⁻¹, that are assigned to water molecules, and one at 3255 cm⁻¹, attributed to the (P)—O—H stretching mode;¹² the large width of this band indicates that the orthophosphate group is involved in hydrogen bonding. In the 400–2000 cm⁻¹ range, the spectrum shows a maximum at 1017 cm⁻¹ due, at least in part, to the

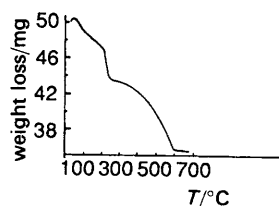


Fig. 2 Thermogravimetric curve of the starting titanium phosphate

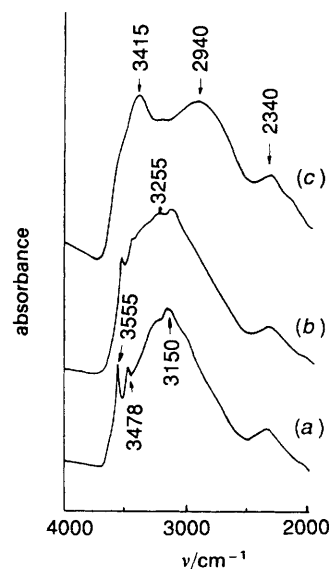


Fig. 3 IR spectrum of the titanium phosphate sample calcined at (a) 400, (b) 473 and (c) 573 K

overlapping of several $\nu_{as}(\text{PO}_3)$ and $\nu_s(\text{PO}_3)$ bands,¹³ Fig. 4(a). Pure α -TiP should exhibit a broad maximum at 1070 cm⁻¹,¹¹ the modification of this band could be due to the presence of extra H₃PO₄.

Calcination at 473 K leads to the removal of water molecules, Fig. 3(b), and the shift of the absorbance maximum to 1036 cm⁻¹, Fig. 4(b). This shift indicates a modification of (PO₃) and/or (PO₄) vibrations, due to dehydration of α -TiP and the presence of phosphoric acid in excess.

Calcination at 573 K removes the remaining water molecules and some hydroxy groups, only those OH groups with bands at 3415 and 2940 cm⁻¹ are retained, Fig. 3(c). The maximum absorbance in the 400–2000 cm⁻¹ range, corresponding to phosphate groups, is shifted to 1088 cm⁻¹, and a

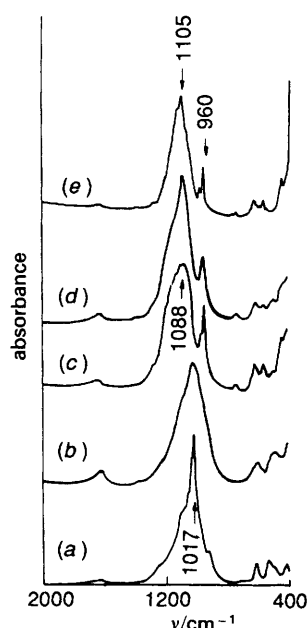


Fig. 4 IR spectrum of the titanium phosphate sample calcined at (a) 400, (b) 473, (c) 573, (d) 673 and (e) 973 K

new band at 960 cm^{-1} , due to ν_{asi} (POP) vibrations,¹⁴ indicates the formation of TiP_2O_7 , Fig. 4(c).

Calcination at 673 K leads to a decrease in the 2940 cm^{-1} band and a narrowing of the phosphate bands in the $1000\text{--}1200\text{ cm}^{-1}$ range. These effects must be related to elimination of OH groups and better crystallization of TiP_2O_7 , favoured by the removal of phosphoric acid as volatile P_2O_5 , Fig. 4(d). The absorbance maximum remains at 1088 cm^{-1} , Fig. 4(d). At $T_c = 773\text{ K}$ this maximum is shifted to 1105 cm^{-1} probably owing to the desorption of the last remaining products of the H_3PO_4 decomposition. For $T_c = 873$ and 973 K the spectrum is not substantially modified, Fig. 4(e).

NMR

The ^{31}P NMR spectrum of the starting sample heated at 473 K consists of signal A at 0 ppm and a broader signal B at -20.4 ppm , with satellite bands on both sides of the signals, Fig. 5(a). At $T_c = 573\text{ K}$ the intensity of signal A decreases and signal B disappears altogether, but some new signals are formed: C at -12 ppm , D at -34.8 ppm , E at -37.8 ppm and several broad lines of low intensity in the -35 to -50 ppm range (group of signals F), Fig. 5(b). For $T_c = 673$ the spectrum consists of signals A, now broader, C, D, E (lines D and E probably correspond to the same compound), and F, Fig. 5(c).

With increasing T_c signals A, C, D and E tend to disappear, while the components of signal F appear with larger intensities and narrower linewidth. At $T_c = 973\text{ K}$, Fig. 5(e), the components of signal F appear at -38.3 , -40.2 , -42.7 , -44.2 , -46.0 , -48.2 , -49.6 , -51.6 and -52.3 ppm , with a mean linewidth at half height of 0.6 ppm . The spectrum is formed by repetition of the same set of lines at 25 ppm intervals, with intensities that reproduce an envelope characteristic of an almost axial distortion of P tetrahedra. The large region covered by this pattern indicates that chemical shift anisotropies (CSA) are much higher than residual P–P dipolar interactions. The MAS technique used permits elimination of most dipolar interactions, but only a partial decrease in the CSA contribution. In the case of low spinning rates (important CSA), it is possible to use the moment analysis proposed by Maricq and Waugh,¹⁵ based on invari-

ance of M_2 and M_3 moments, to determine the principal values of the chemical shift tensor. From the intensities of the observed rotation side bands pattern,¹⁵ values of -80.2 , -66.9 and 17.3 ppm are obtained for the three principal components of the chemical shift tensor corresponding to the band at -44.2 ppm . From that, values of $\Delta\sigma = -36.90$ and $\eta = 0.22$ were obtained for asymmetry in the Z axis and anisotropy parameters in the XY plane. Similar values of these parameters were obtained for all components. Considering the structure of TiP_2O_7 , the axial deformation of the tetrahedra must come from P–O–P bridges formed between adjacent layers (z axis) and the orthorhombic distortion from a deformation of the phosphate groups, that will differentiate between the three P–O–Ti tetrahedral bonds.

Discussion

As shown by XRD and TG analysis, the starting sample consists mainly of $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ with an excess of H_3PO_4 . On this basis the NMR signal A has been assigned to phosphoric acid retained in the sample and signal B to titanium phosphate, in this phosphate each phosphorus tetrahedron shares three oxygens with three titanium octahedra and the fourth oxygen forms a hydroxy group perpendicular to the $\alpha\text{-TiP}$ layer. The IR spectrum shows that the sample is hydrated and that the P–O–H groups are affected by hydrogen bonding.

When the sample is calcined at 473 K, most of the interlayer water is removed, as indicated by TG and IR, and P–O–H groups form hydrogen bonds with neighbouring polyhedra, producing broadening of the 3400 cm^{-1} component in the IR spectrum. Dehydration is also responsible for the shift of the band corresponding to the PO_3 and/or PO_4 vibrations in the $400\text{--}2000\text{ cm}^{-1}$ region of the IR spectra. Partial decomposition of H_3PO_4 should account for the appearance of line C in the ^{31}P NMR spectrum.

At T_c close to 503 K an important weight loss is observed, which, as indicated by the IR spectrum obtained for $T_c = 573\text{ K}$, must be due to dehydroxylation and formation of P–O–P bridges between adjacent phosphate layers. For $T_c = 573\text{ K}$ the XRD pattern indicates that the structure is mainly that of TiP_2O_7 . At this temperature, the ^{31}P NMR spectrum shows that signal B is lost and signal C decreases, while new signals D, E and F, with larger chemical shift values are observed. These must be assigned to condensed phosphorus tetrahedra. In partially dehydroxylated samples, condensed tetrahedra in intermediate situations would be responsible for signals D and E. A possible intermediate situation could be thought of as condensed phosphorus tetrahedra affected by the presence of H_3PO_4 residues, introduced between the $\alpha\text{-TiP}$ layers prior to the phosphorus tetrahedra condensation. These effects reduce the crystallinity of the samples and explain the width of the XRD lines of the TiP_2O_7 diffractograms obtained at 573 and 673 K.

By increasing T_c to 673 K, the intensity of the NMR signal A decreases in relation to that of signal F, probably owing to the removal of part of the phosphoric acid as P_2O_5 . The increase in the linewidth of signal A could indicate the creation of different environments for the phosphoric acid, probably by interaction with TiP_2O_7 . For $T_c \geq 873\text{ K}$ most of the phosphoric acid has disappeared and the elimination of intermediate species, assigned to D and E signals, improves the crystallinity of the sample.

At $T_c = 973\text{ K}$ all techniques indicate that the only phase present is TiP_2O_7 . The existence of nine components in the NMR spectrum, each line associated with P atoms with the same chemical environment, must then indicate that the P

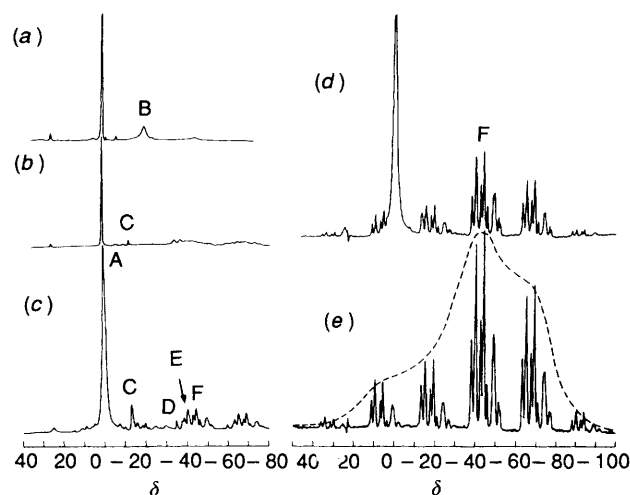


Fig. 5 NMR spectrum of the titanium phosphate sample calcined at (a) 473, (b) 573, (c) 673, (d) 773 and (e) 973 K. As the intensity of signal A decreases, the vertical display scale of the spectrum is progressively increased.

atoms are located at different crystallographic sites in the unit cell of this compound.

Many compounds $M^{IV}P_2O_7$ show a cubic phase belonging to the space group $Pa\bar{3}$ with $a_0 \approx 8 \text{ \AA}$,¹⁶ in which only one crystallographic site for P atoms is present. However, for some cations ($M^{IV} = \text{Si, Ge, Sn, Pb, Ti, Zr, Hf, Th and U}$), it has been proved that the structure is really a 27-fold superstructure having $a \approx 3a_0$, with the same space group $Pa\bar{3}$.¹⁷ The existence of a larger unit cell, having one third of the symmetry elements per unit volume, favours the occurrence of local distortions that would increase the number of crystallographic sites. In this phase, 11 different crystallographic sites for P atoms are present and, therefore, a maximum of 11 different components could be resolved in ^{31}P NMR spectra. In the case of TiP_2O_7 , if it is assumed that each of the two most intense components located at -40.2 and -44.2 ppm are the sum of two elementary components, the observed intensity pattern in the ^{31}P NMR spectrum could be interpreted on the basis of a cubic $3 \times 3 \times 3$ superlattice phase.

Although spectra of other members of the $M^{IV}P_2O_7$ family have more components than expected for the unitary cubic cell $a_0 = 8 \text{ \AA}$, the number of lines is always lower than that predicted for a $3a_0$ superstructure. From a spectroscopic point of view, slight differences in the geometry of tetrahedra could reduce the expected number of resolved components in the NMR spectra. Moreover, the existence of two monoclinic polymorphs of SiP_2O_7 ^{18,19} complicates the analysis of the NMR spectra of this member of the family.²⁰ A detailed structural study of different diphosphates is in progress, to give further insight into the interpretation of spectroscopic data.

In conclusion, the experimental results indicate that a stable titanium pyrophosphate is formed by calcination at 573 K of the precursor produced by reaction of anatase with H_3PO_4 , but its crystallinity depends on the amount of phosphoric acid retained by the sample. Moreover, considering that the α -TiP precursor has good ion-exchange properties, the crystallinity of the final TiP_2O_7 could also be affected by the presence of exchangeable cations in the interlayer space

of the precursors,^{5,6} as is the case for the samples studied previously.⁴

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Paper 2/06004C; Received 11th November, 1992