Chemical modification of TiO_2 by $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ anions using the sol-gel route with controlled precipitation and hydrolysis: enhancing thermal stability

KAIS ELGHNIJI^{1*}, MOHAMED EL KHAMES SAAD¹, MANEL ARAISSI¹,
ELIMAME ELALOU¹, YOUNES MOUSSAOUI^{1,2}

¹Materials, Environment and Energy Laboratory, (06/UR/12-01) Science Faculty of Gafsa, 2112, Gafsa, University of Gafsa, Tunisia

²Laboratory of Chemistry of Natural Substances, (UR11-ES74) Science Faculty of Sfax, 3018, Sfax, University of Sfax, Tunisia

Two titanium phosphate materials ($T_p\text{P}$ and $T_h\text{P}$) have been successfully synthesized by sol-gel route with controlled precipitation and hydrolysis. The $T_p\text{P}$ material was obtained from the reaction between precipitated titania and phosphate buffer solution $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ($\text{pH} = 7.3$). The $T_h\text{P}$ material was prepared through hydrolysis of titanium in the presence of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$. The probable state of the phosphate anions in titania framework and their effect on the anatase-to-rutile transformation were characterized by ICP-AES, DTA-TG, ^{31}P NMR, FT-IR, and Raman analysis HRTEM/SEM. FT-IR and ^{31}P NMR analyses of titanium phosphate $T_p\text{P}$ calcined at low temperature showed that the phosphate species existed not only as Ti-O-P in the bulk TiO_2 but also as amorphous titanium phosphates, including bidentate $\text{Ti}(\text{HPO}_4)_2$ and monodentate $\text{Ti}(\text{H}_2\text{PO}_4)_4$. Increased calcination temperature only gave an enrichment of bidentate structure on the titania surface. For the $T_h\text{P}$ material, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ anions were introduced into the initial solution, before precipitation, what promoted their lattice localization. At high temperatures, all the phosphorus inside the bulk of TiO_2 migrated to the surface. The Raman analysis of both samples showed that the bidentate phosphates increased the temperature of the anatase-to-rutile phase transformation to more than 1000 °C with the formation of well crystalline TiP_2O_7 phase. This phenomenon was more evident for $T_p\text{P}$ sample.

Keywords: TiO_2 ; phosphorus; crystal growth; bidentate; monodentate

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1. Introduction

Preparation of anatase TiO_2 with high thermal stability is of great importance for its practical application. Various procedures and different preparation conditions were applied to improve the thermal stability of the anatase TiO_2 by constraining the growth of crystallites. The most promising methods that include surface modifications by increasing the number of adsorbed phosphates or sulfate ions, reduce the surface energy of the anatase phase. These species tend to retard the phase transition of anatase to rutile and crystallite growth. Recently, phosphate/titanium dioxides have been obtained through different preparative

routes entailing either surface modification of titanium oxide or hydroxide hydrate by anions, such as phosphates or sulfates [1–8] or hydrolysis of TiO_2 from corresponding titanium alkoxides in presence of phosphoric acid [9–12]. Ramadan et al. [13] reported a study on titanium dioxide obtained from the hydrolysis of titanium ethoxide and phosphate by impregnation with ammonium hydrogen phosphate. The authors argued that the bidentated phosphate groups HPO_4^{2-} were persistent up to 800 °C, indicating the stability of these groups within the titanium oxide structure to high temperatures. Gong [14] identified two species on the surface, namely the bridging bidentate surface complex $(\text{TiO})_2\text{PO}_2$ with C_{2v} symmetry and the electrostatically adsorbed PO_4^{3-} ion with T_d symmetry. Kazarinov et al. [15] investigated the

*E-mail: K.elghniji@yahoo.fr

adsorption of F^- , Cl^- , HSO_4^- and $H_2PO_4^-/HPO_4^{2-}$ anions on titanium dioxide by means of the radioactive tracer method. Unlike, e.g., the sulphate and chloride anions, the $H_2PO_4^-/HPO_4^{2-}$ exhibited still significant extent of adsorption on TiO_2 in neutral and alkaline solutions. However, the authors did not show the results of the effect of these anions on the anatase-to-rutile phase transformation during heat treatment. From these observations it is evident that the adsorbed phosphate ions $H_2PO_4^-/HPO_4^{2-}$ play a key role in the stabilisation of surface sites of TiO_2 .

The number of papers on phosphorus/phosphate- TiO_2 is undergoing an exponential increase. As it often occurs in case of a rapidly growing subject, a certain degree of confusion due to conflicting evidences and interpretations is present in the literature. This is probably due to the variety of synthetic methods adopted to prepare the solid. In addition, the researchers have not studied the nature and pH of phosphate species in the starting H_3PO_4 solution and the location of these species that can play different roles, depending on their nature either in the bulk, at the surface or in both.

It is well known that the high (PO_4^{3-}) or low pH (H_3PO_4) of the solution containing the titanium alkoxide dramatically affects the rate of the hydrolysis and condensation reactions in a sol-gel process. Furthermore, the use of these species as doping agents does not allow a strict control of their effect on the properties of solid. Therefore, the modification and doping of TiO_2 by $H_2PO_4^-/HPO_4^{2-}$ phosphate anions (buffer) at neutral media seems to be an advantageous method to overcome this problem.

The effect of the proportions of H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} on pH is illustrated in Fig. 1. As it can be seen, there is little H_3PO_4 in highly acidic solution and PO_4^{3-} predominates only in highly basic solutions. Within the pH range of natural water, dissolved phosphates exist as $H_2PO_4^-$ and HPO_4^{2-} with equivalent fractions.

The objective of the work reported here is to explain the role of phosphate buffer $H_2PO_4^-/HPO_4^{2-}$ located either in bulk or in both bulk and

Fig. 1. Titration of orthophosphoric acid H_3PO_4 (0.1 M) sodium hydroxide NaOH (0.1 M).

surface of TiO_2 . Two titanium phosphate materials were prepared by sol-gel route with controlled precipitation and hydrolysis. The advantage of our strategy is that it is possible to track the exact state of phosphorus in the framework of TiO_2 even at a low temperature. The first sample was obtained from the reaction between precipitated titania and phosphate anions $H_2PO_4^-/HPO_4^{2-}$. The second sample was prepared through hydrolysis and precipitation of titanium in the presence of $H_2PO_4^-/HPO_4^{2-}$. Our results showed that these phosphate species exhibited a significant extent of adsorption in neutral solution. The modification of TiO_2 by $H_2PO_4^-/HPO_4^{2-}$ phosphate anions led to two chemical states of amorphous titanium phosphate, including $Ti(HPO_4)_2$ and $Ti(H_2PO_4)_4$ after calcination in temperatures of 500 to 700 °C. More importantly, the sample obtained by precipitation retained its anatase phase even after calcination at higher temperatures (1000 to 1050 °C). Based on spectroscopic and analytical techniques, a better understanding of the thermal stability and the probable state of the phosphate species was obtained.

2. Experimental

2.1. Modification of precipitated titanium hydroxide by $H_2PO_4^-/HPO_4^{2-}$

In the preparation of precipitated titanium dioxide by the sol-gel method, titanium (IV)

isopropoxide (97 %, Aldrich) was hydrolyzed in isopropyl alcohol (99.8 %, Riedel de Haen), (molar ratio 1:5). Deionized water was added to the mixture under stirring (molar ratio between water and alcohol 1:1). The isopropanol was then evaporated in a rotary evaporator to yield concentrated white precipitate (mixture A).

The phosphate buffer solution H₂PO₄⁻/HPO₄²⁻ (pH = pK_a 7.3) was prepared by titration of 20 mL orthophosphoric acid H₃PO₄ (0.1 M) (85 %, Aldrich) with 34 mL sodium hydroxide NaOH (0.1 M) (mixture B) (Fig. 1). The resultant phosphate buffer solution (mixture B) was added under stirring to the concentrated precipitate (mixture A) to prepare titanium phosphate sample. The calculated atomic ratio of P/Ti was 0.15. For the blank TiO₂ sample, we followed the same procedure except the addition of the phosphate anions. The gel was subsequently dried at 80 °C for 6 hours. The dried materials were calcined in a muffle furnace at 500, 700, 900 and 1050 °C in air for 2 h at a heating rate of 5°/min. The prepared powders were labelled according to precipitation process (p) and calcination temperature (T): T_pP_T.

2.2. Hydrolysis and precipitation of titanium in the presence H₂PO₄⁻/HPO₄²⁻

Titanium (IV) isopropoxide was hydrolyzed in isopropanol (molar ratio 1:5) containing phosphate buffer solution H₂PO₄⁻/HPO₄²⁻ (pH = pK_a 7.3) (molar ratio between phosphate buffer solution and alcohol 1:1). The appearance of a white precipitate indicated the formation of hydrate titanium oxide. 50 mL of deionized water was added to the mixture during stirring to ensure complete precipitation. After aging at room temperature for 2 h, the sample was dried at 80 °C overnight. The calculated atomic ratio of P/Ti was 0.15. The dried materials were calcined in a muffle furnace at 500, 700, 900 and 1050 °C in air for 2 h at a heating rate of 5 °C·min⁻¹. The prepared powders were labelled according to hydrolysis process (h) and calcination temperature (T): T_hP_T.

2.3. Characterization

Differential thermal analysis-thermogravimetry (DTA-TG) experiments were carried out to monitor

crystallization behaviour using NETZSCH equipment, model STA 449, from room temperature to 1100 °C at temperature ramp rate of 5 °C·min⁻¹ in an air flow of 30 mL·min⁻¹. The bond vibrations were analyzed with a FT-IR (Shimadzu FT-IR-8400s) spectrometer by the transmission method. The ³¹P NMR/MAS spectra of the prepared TiO₂ powders were recorded on a Bruker 300 Ultra-Shield spectrometer in magnetic field of 9.4 T, corresponding to ³¹P resonance frequency of 121.5 MHz. Chemical shifts were identified using an external H₃PO₄ (85 %) reference (0 ppm). The crystalline degree of the samples was verified by Raman (LABRAM HR800) spectrometer equipped with a He-Ne ion laser emitting at a wavelength of 633 nm. The morphology and size were observed by TEM and HRTEM micrographs with a JEOL-JEM 2000EX microscope working at a 100 kV accelerating voltage. The scanning electron microscopy (SEM) and the energy dispersive X-ray spectroscopy EDX measurements were carried out on a (Philips XL 30) system operating at 20 keV.

2.4. Determination of phosphorus content

The Ti and P contents in the samples were determined by all-argon sequential (Thermo Jarrell ASH, USA) inductively coupled plasma atomic emission spectrometry (ICP-AES). Prior to the analysis, a fluorhydric acid/nitric acid mixture was prepared (in proportion of 30:70) and then 20 milligrams of each sample were transferred into a Teflon flask, and then completely dissolved in this solution using a microwave (CEM, MARS 5). The intensity of the spectral lines of 213.6 (phosphorus) and 336.1 nm (titanium) were measured.

3. Results and discussion

3.1. Thermal studies

The dried materials obtained in this study were all thermally analyzed to observe their thermal behaviour during heating. Fig. 2a and 2b give the TG and DTA curves for T, T_pP and T_hP samples. For the blank sample T, it can be observed that the total loss of weight (10 %) takes place in three

well-defined steps. The first is the main loss of weight ($\sim 6\%$) corresponding to the loss of free or adsorbed water and isopropanol, which takes place between 30 and 180 °C. This coincides with the broad endothermic peak at 126 °C. The second loss ($\sim 2\%$) and the third ($\sim 2\%$) weak loss take place between 200 to 300 °C and 300 to 400 °C, and the corresponding DTA curve shows three significant exothermic peaks at 239 °C, 297 °C, and 372 °C, respectively, which can be assigned to the superposition of the burning reaction of organic substances and crystallization process of the anatase phase (372 °C) in the xerogel. Beyond ~ 500 °C, the TG curves stabilize and a notable exothermic change appears at ~ 691 °C, what might be attributed to the anatase-to-rutile transformation. By introducing $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ anions into the reaction mixture, the position of crystallizing peak of the anatase at 372 °C shifts to 406 °C in DTA curve of T_pP , indicating that the presence of phosphate species increases the crystallization temperature of the titania powder [16]. Furthermore, there are additional weight losses of 0.7 % and 1.5 % occurring between ~ 478 °C and ~ 514 °C for T_hP and T_pP samples, respectively. These exotherms seem to correspond to the further loss of coordinated water. The DTA curve of T_pP reveals an unexpected exothermic phenomenon at ~ 1016 °C, which is not linked to any weight loss. However, we tentatively associate this peak to the anatase-to-rutile transformation. Samantaray *et al.* [17] observed a similar exothermic peak near 930 °C and its position at so high temperature agrees with the inhibiting effect of phosphate species on the transformation of anatase to rutile. Similar to the weight losses observed in TG and DTA curves, the P/Ti ratios of samples T_pP and T_hP increase with increasing temperature to reach 0.1603 and 0.157, respectively, at 500 °C. This is due to the loss of water (dehydroxylation) during heat treatment [17].

3.2. FT-IR studies

FT-IR spectra of samples calcined at increasing temperatures are shown in Fig. 3. The region of FT-IR spectra from 750 cm^{-1} to 1600 cm^{-1} , which has been assigned to phosphate groups, is of

particular interest in this work. The bands at 1384 cm^{-1} and 1470 cm^{-1} are mainly due to the decomposition of residual organic compounds in the particles (e.g. $-\text{CH}_2-$) [18], in agreement with thermal studies. The dried T_pP_{80} shows a band at 1035 cm^{-1} (Fig. 3a), which is not observed in blank TiO_2 . Meanwhile, considering the fact that no peaks corresponding to the P–O vibrations appeared in the range of 900 to 1000 cm^{-1} in H_3PO_4 aqueous solution (1000 cm^{-1}), it is reasonable to conclude that a small part of phosphorus species was introduced into the framework of TiO_2 forming Ti–O–P bond (1035 cm^{-1}) [19]. The bands at 1089, 1151, 1280, and 1115 cm^{-1} suggest that different chemical environments existed around the phosphorus after precipitation process. The three former mentioned bands can be assigned to the ν_3 and T_d vibrations of the phosphate anions H_2PO_4^- (monodentate structure) and electrostatically adsorbed PO_4^{3-} anions, respectively [20]. The later band could be assigned to ν_2 vibration of phosphate anions HPO_4^{2-} (bidentate structure) adsorbed to TiO_2 [21, 22]. These results indicate that the phosphate anions interacted strongly with the surface of TiO_2 , as reported in the introduction section. Hence, we tentatively associate these bands to the amorphous titanium phosphates $\text{Ti}(\text{HPO}_4)_2$ monodentate/ $\text{Ti}(\text{H}_2\text{PO}_4)_4$ bidentate structures. Please note, however, that in the synthesis of T_pP sample, the $\text{Ti}(\text{OC}_2\text{H}_5)_4$ are hydrolyzed rapidly and form $\text{Ti}(\text{OH})_4$. Homocondensation between Ti–OH groups leads to the formation of Ti–O–Ti bonds in precipitated TiO_2 . During the addition of phosphate buffer species, a small, but not negligible fraction of P–OH groups could be trapped into TiO_2 framework to form Ti–O–P bonds (1038 cm^{-1}). During the drying process, the great part of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ anions could only bond to the surface of precipitated TiO_2 to form a composition of amorphous titanium phosphates phases, including $\text{Ti}(\text{H}_2\text{PO}_4)_4$ and $\text{Ti}(\text{HPO}_4)_2$. Therefore, we can confirm that the phosphate may exist not only in the form Ti–O–P bond in the bulk of TiO_2 , but as amorphous phosphate anions coordinated to titania surface of TiO_2 . Calcination at 500 °C leads only to the disappearance of the 1280 cm^{-1} and 1151 cm^{-1} peaks,

Fig. 2. TG/DTA curves of prepared xerogels.

characteristic of PO₄^{3−} anions with T_d symmetry [23]. At 700 °C, the band at 1089 cm^{−1} of the monodentate phosphate disappears, whilst that of the bidentate phosphate increases in the sample, indicating the lowering of the symmetry ν₃ of phosphate anion to ν₂ (960, 980, 1045, and 1216 cm^{−1}), as revealed by ³¹P NMR. At high temperatures, several adsorption bands at 960, 980, 1045, 1105, 1184 and 1280 cm^{−1} were detected for T_pP₉₀₀ and T_pP₁₁₀₀. These bands are ascribed to the fractions of P₂O₇^{4−} on the particle surface able to form well crystallized phases of TiP₂O₇. The significant change of FT-IR trend at 1000 to 1250 cm^{−1} at 1100 °C is possibly due to the anatase-to-rutile transformation. Hence, it can be concluded that the binding of the bidentate/monodentate phosphate could retard the anatase-to-rutile phase transformation and crystallite growth.

For the sample T_hP (Fig. 3b) we detected only a single peak at 1035 cm^{−1} revealing that all phosphate species were included in the bulk titania to form Ti–O–P bonds. The intensity of this band increased with heat treatment at 500 °C, indicating the stability of this bond within the bulk of titania. After calcinations at 700 °C, the FT-IR spectrum displayed two new bands at 1105 cm^{−1} and 980 cm^{−1}, attributable to phosphate ion (bidentate structure). It is worth noting that in the synthesis of T_hP, the phosphate anions H₂PO₄[−]/HPO₄^{2−} were intimately mixed from the very beginning with the Ti(OC₂H₅)₄. During the hydrolysis reaction, the

Ti–OH aggregated with P–OH groups of phosphate anions and formed only Ti–O–P bonds in the bulk titania matrix. At high temperatures, all the phosphorus inside the bulk of titania diffused and migrated to the surface of titania [24]. Thus, at 900 °C, we can observe significant differences for the region of spectra at 1035 cm^{−1}. This band is shifted to 1056 cm^{−1} and decreases gradually with heating at 900 to 1100 °C. This indicates that the phosphorus content in the bulk TiO₂ is lowered when it is expelled to the surface of the particle, leading to the intensities enhancement of bidentate phosphate peaks (960, 980, 1105, 1184, and 1280 cm^{−1}). The intensity of these peaks is little stronger than that of T_pP_{900–1100}. Thus, at high temperatures, the bidentate phosphates on the surface are polymerized to form TiP₂O₇ with a network structure, which is found to improve the thermal stability of the anatase phase.

3.3. ³¹P MAS-NMR studies

MAS-NMR measurements were carried out to understand the behaviour of phosphate anions on the surface of T_pP sample at elevated calcination temperatures. The broadening of ³¹P NMR spectrum for T_pP₈₀ (Fig. 4a) stems from the wide distribution of phosphorus among several sites with slightly different environments, as revealed by FT-IR analysis. The phenomenon is more evident in the spectrum of T_pP₅₀₀ sample (Fig. 4b). Deconvolution of the spectrum based on Gaussian

Fig. 3. FT-IR spectra of the powders calcined at various temperatures: (a) T_pP ; (b) T_hP .

fitting resulted in the appearance of two peaks. The first one at ~ 4.49 ppm (peak 1), which is in good agreement with chemical shift values for phosphorus, coordinated via one oxygen to one titanium atom $1P-O-Ti$ bonds, forming the monodentate structure, i.e. $Ti(H_2PO_4)_4$. The second signal at ~ 10.4 ppm (peak 2), which can be assigned to phosphorus, coordinated via two oxygen to two titanium atoms $2P-O-Ti$ bonds in a bridging bidentate structure, i.e. $Ti(HPO_4)_2$ [25, 26]. The peak (1) is about 1.3-fold higher than (2). Considering the fact that no signal of electrostatically adsorbed PO_4^{3-} anions is observed, the degree of phosphorus oxidation for sample T_pP_{500} is equal to +V. The main part of the phosphorus atoms are covalently bonded to the titania surface by two $P-O-Ti$ bridges [27]. Similar results were reported by Fan *et al.* [28]. They argued that the use of H_3PO_4 as phosphorus source led to three chemical states of amorphous titanium phosphate, including $Ti_3(PO_4)_4$, $Ti(HPO_4)_2$ and $Ti(H_2PO_4)_4$ after calcination at a temperature < 600 °C. After calcination at 700 °C (Fig. 4c), the signal of amorphous titanium phosphate monodentate decreased whilst that of bidentate increased, indicating the occurrence of condensation of H-containing groups, observed also in FT-IR spectra. In this case, the peak (2) was about 2.4-fold higher than (1). For the T_pP (Fig. 4d) calcined at 900 °C, the resonance of the P_2O_7 groups at -38.6 to 52.35 ppm became predominant, while the relative intensity of the

amorphous titanium phosphate bidentate $Ti(HPO_4)_2$ appearing at low field disappeared, indicating dehydration between adjacent $P-OH$ groups of this structure. As the calcination temperature increased up to 1100 °C (Fig. 4e), the ^{31}P NMR spectrum showed a well-resolved spectrum, characteristic of a well crystalline material. The existence of lines at -38.6 , -40.5 , -42.9 , -44.5 , -46.15 , -49.48 and -52.35 ppm can be associated with the presence of several crystallographic sites for phosphorus atoms in a $3 \times 3 \times 3$ crystal structure of TiP_2O_7 [29]. A minor and narrow peak at ~ -27 ppm appeared at 900 °C. The assignment of this peak to a specific phosphate phase is not defined, but it cannot be assigned to TiP_2O_7 [30]. The peak may be related to a new titanium phosphate phase developed from TiP_2O_7 at high temperature.

3.4. Raman analysis

Fig. 5 shows Raman spectra of T_pP and T_hP samples calcined at various temperatures. Typically for T_{500} (Fig. 5a), there are three Raman active fundamental modes of the anatase phase at 399, 513 and 643 cm^{-1} [31–33]. The rutile phase (i.e. 140, 235, 445 and 609 cm^{-1}) starts to appear at 700 °C, and it becomes the only phase at 900 °C. By introducing $H_2PO_4^-/HPO_4^{2-}$ anions into the reaction mixture after precipitation process T_pP (Fig. 5b), the anatase is stabilized at higher temperatures in $T_pP_{900-1050}$. The effect of phosphate anions on

Fig. 4. ³¹P-NMR spectra of the powders calcined at (a) 80 °C; (b) 500 °C; (c) 700 °C; (d) 900 °C; (e) 1100 °C.

the thermal stability of the anatase phase is due to the following causes: (1) H₂PO₄⁻/HPO₄²⁻ anions can be strongly adsorbed on the surface sites of TiO₂ and stabilize the anatase phase structure to reduce the surface energy of anatase. (2) The growth of the anatase TiO₂ crystallites is restricted due to the phosphate anions adsorbed on the grain boundaries, inhibiting the phase transformation of anatase to rutile. Lv et al. [34] also reported that the fluoride ions F⁻ located in the titania grain boundaries, impeded direct contact of the anatase particles and prevented the phase transition of anatase to rutile. For the T_hP, the rutile phase starts to appear at 900 °C, and it becomes the only phase with traces of TiP₂O₇ phase at 1000 °C. At this temperature, T_pP and T_hP samples display new Raman peaks at 1035, 1047, and 1073 cm⁻¹, which correspond to P–O asymmetric and symmetric stretching vibrations, indicating the generation of TiP₂O₇ phase. These results are consistent with ³¹P NMR study.

Compared to T₅₀₀, there is a notable shift and broadening of the anatase main peak (146 cm⁻¹) of T_pP₅₀₀ (the peak widths of the Eg mode at 146 cm⁻¹ for samples T₅₀₀ and T_pP₅₀₀ are 12 and 20 cm⁻¹, respectively). The observed shift of the Raman peaks for T_pP₅₀₀ can be interpreted as originating from the effect of particle size in the presence of phosphate anions [35, 36]. The crystallite size of T_pP₅₀₀ (10.3 nm) is much smaller than that of T₅₀₀ (23 nm). Therefore, the Raman analysis confirms that the presence of adsorbed

H₂PO₄⁻/HPO₄²⁻ anions retards the grain growth of the titania crystallites.

HRTEM and SEM images were applied as an additional tool for determining the state and the effect of phosphate anions on TiO₂ morphology. Fig. 6a demonstrates that the T₅₀₀ sample exhibits nearly cubic particles with high anatase crystallization degree, which is confirmed by the well resolved crystal lattice of 0.32 nm in the attached HRTEM and the well defined diffraction patterns in the SAED image. However, the T_hP₅₀₀ sample (Fig. 6b) has a form of nearly shapeless and stacked particles. This confirms that the presence of phosphate at the titania grain boundaries retards the crystal growth. The particles of T_pP₅₀₀ sample (Fig. 6c) are not well dispersed having irregular morphology with poor crystallization degree. This is due to the presence of amorphous titanium phosphates (circled areas in SEM).

4. Conclusions

The control of the preparation method is very important in determining the final state of the phosphate species. The adopted procedure led to obtaining two kinds of materials, different from one another, at 500 °C.

- The T_pP₅₀₀ sample showed that the phosphate species existed not only as Ti–O–P in bulk TiO₂ but also as amorphous titanium phosphates Ti(HPO₄)₂/Ti(H₂PO₄)₄ and electrostatically adsorbed PO₄³⁻ anions on the surface of TiO₂. Upon calcination at 700 °C, the bands of H₂PO₄⁻ and PO₄³⁻ anions disappeared, whilst that of the bidentate phosphate HPO₄²⁻ increased in the sample, indicating the lowering of symmetry ν₃ and T_d of phosphate anion to ν₂.
- The T_hP₅₀₀ sample displayed only a single peak at 1038 cm⁻¹, which was ascribed to Ti–O–P bond, revealing that all phosphates species were included in the bulk titania matrix. Upon calcination at 700 °C, the enrichment of bidentated phosphate structure on the titania surface was observed.

Fig. 5. (a) Raman spectra of blank TiO_2 T, (b) T_pP and T_hP calcined at various temperatures.

Fig. 6. (a) TEM and HRTEM images of blank TiO_2 T_{500} ; (b) T_hP_{500} ; (c) T_pP_{500} . The insets to (a) and (b) show the corresponding selected area electron diffraction SAED. The insets to (a), (b), and (c) show the corresponding interplanar space. Arrows: the SEM images of T_{500} and T_pP_{500} .

- The increase in the calcination temperature up to 900 °C resulted in a clear decrease in bidentated phosphate structure of both materials. This indicated that only the bidentated phosphates HPO₄²⁻ were polymerized to form TiP₂O₇, in spite of different preparation methods.
- The FT-IR and Raman analyses showed that the surface-bound phosphate with bidentate structure delayed the formation of the anatase phase and crystallite growth and inhibited the anatase-to-rutile phase transformation.

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