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Preparation of anatase powders from fluorine-complexed titanium(IV) aqueous solution using microwave irradiation

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The microwave radiation activated precipitation of titanium dioxide from homogeneous aqueous solutions of titanium–fluoro complexes and boric acid has been carried out in batch reactors. Crystalline anatase powders with narrow monodisperse size distribution have been obtained in a short time, at low temperature and atmospheric pressure. Microwave power, irradiation time and precursor concentration determine the properties of the obtained materials, *i.e.* crystal size, powder aggregate morphology and BET surface area. The obtained materials do not show photocatalytic activity, probably due to a considerable fluoride content that is in the range of 2–5%.

Introduction

The preparation of fine anatase particles of uniform size and specific shape is an important area of research, crucial to application in fields as diverse as catalysis, wet solar cells and ceramic synthesis. Many different strategies have been essayed in order to control the growth of titania particles, using different precursors and additives. The precursor hydrolysis kinetics is the principal factor determining the growth of titania particles. As this reaction is normally very fast for the usual TiO_2 precursors, titanium alkoxides and titanium tetrachloride, the use of different precursors or the addition of ligands to retard hydrolysis and then allow controlled growth is a current topic of research. Ligands present in the reaction medium could also favour the precipitation of one of the titanium dioxide phases: either rutile or anatase.

The production of titanium dioxide through the ligand exchange (hydrolysis) reaction between ammonium hexafluoro titanate and boric acid or aluminium metal as fluoride scavengers has been widely studied.[1–3] This reaction is used to produce titania thin films onto different substrates by a liquid-phase deposition (LPD) process. In this process, some material precipitates in the bulk of the solution, thus titania powder is simultaneously obtained, which has also been characterised.[1] In a similar area of research, our group has studied a new method for the deposition of TiO_2 thin films on conducting glass by using microwave irradiation as the heating source to promote oxide formation from homogeneous aqueous solutions of different precursors.[4,5] Microwave processing offers many new possibilities that are currently being examined.[6–9] In particular, microwave assisted precipitation of particles from water solution is a recent issue in industrial crystallisation. The rationale of this technique is the use of the solvent as the coupling agent for microwaves leading to homogeneous heating of the solution. In this way, heat-enhanced processes such as hydrolysis, ligand substitution, polymerisation, *etc.*, are favoured, eventually leading to precipitation of solids such as oxides, carbonates, phosphates and many others.[10–15] The microwave irradiation of homogeneous aqueous solutions of titanium–fluoro complexes and boric acid has used in our laboratory for the preparation of TiO_2 thin films.[5] In this paper the characteristics of nanosized powders of titanium oxide produced by the same process are described.

Experimental

Experiments were carried out in a Microwave furnace Maxidigest MX 350 (Prolabo) operating at 2.45 GHz. The instrument consists of a 250 cm^3 Pyrex reactor immersed into a resonant cavity, and equipped with a condenser. A programmer allows the control of the operating power and irradiation time. The fluorine-complexed titanium(IV) solution was prepared from titanium tetraisopropoxide (TIP), HF and NH_4F. TIP (10.0 ml, 0.034 mol) was dissolved in 50 ml of ethanol to which aqueous HF (6.0 ml 40% aqueous solution, 0.136 mol) was added. A solution of NH_4F (2.52 g, 0.068 mol) in water (100 ml) was also added subsequently. In order to evaporate the alcohols, the clear solution thus obtained was heated in an open vessel until its volume was reduced to *ca.* 30 ml. The residue was diluted with water to the volume required in order to obtain the desired final concentration. The precursor aqueous solution was freshly prepared by mixing equal volumes of the former solution and boric acid solution. In each run, 80 ml of solution were exposed to microwave radiation for different times. The specific conditions for the synthesis of each sample are summarised in Table 1. At the end of the experiments, solids were centrifuged, washed three times with distilled water and dried at 60 °C. The size distribution of the freshly obtained precipitates was analysed using a Malvern Zetasizer 3. The powder was analysed by X-ray diffraction with a Rigaku Rotaflex RU-200 B instrument using Cu-Kα (1.5418 Å) radiation, and characterised by transmission electron microscopy (TEM) using a JEOL JEM 1210 microscope. Measurements of BET surface area were performed using N_2 adsorption–desorption isotherms on a Micromeritics ASAP 2000. Each sample was heated overnight at 533 K under vacuum before measurements. For UV–Vis measurements, the powder was suspended in water using an ultrasound bath and the spectrum was recorded over the wavelength range 200–800 nm using a Varian Cary UV-V spectrophotometer. TiO_2

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Table 1 Experimental conditions

Sample	[Ti] ($\times 10^{-3}$ M)	[H_3BO_3] ($\times 10^{-3}$ M)	Microwave power/W	Heating time/h
TiO_2-A	17	34	60	2.0
TiO_2-B	17	34	60	0.50
TiO_2-C	68	136	60	0.50
TiO_2-D	17	34	30	0.50
TiO_2-E	17	34	30	0.33

fluoride content was measured with an ion selective electrode after melting the sample with a CaO–NaOH mixture and dissolving the resulting mixture with dilute HCl.

The photocatalytic oxidation of phenol in aqueous suspensions of TiO_2 under UV-illumination was studied as a test experiment, in order to determine the activity of the titania powders obtained. The concentration of TiO_2 in suspension was 1.5 g L^{-1}. A 1.0×10^{-3} mol dm^{-3} phenol solution was employed as a target. Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. All experiments were carried out at 25.0 ± 0.1 °C. The pH of the phenol solution was adjusted to 3.0 with dilute $HClO_4$. The reaction mixture inside the cell was maintained in suspension by magnetic stirring and air was bubbled into the suspension throughout the experiment. A 125 W Philips HPK medium pressure mercury vapour lamp was used as a light source. The TOC (total organic carbon) of initial and irradiated samples were determined with a Shimadzu TOC 5000 total organic carbon analyser.

Results and discussion

In the titania precursor solution employed in the present work, titanium(IV) is strongly complexed by fluoride anions. However, an equilibrium exchange between water and the fluoro ligands takes place.[16] Therefore, in the presence of a fluoride scavenger like H_3BO_3, the equilibrium is displaced towards the hydrolysis reaction, leading to the formation of titanium dioxide.[3,17] The global reaction is very slow at ambient temperature. However, at higher temperatures the process is accelerated. Microwave radiation was used as the heating source in the experiments described here. The influence of microwave irradiation time and power has been investigated in four sets of experiments.

A quantitative yield of TiO_2 precipitate was observed in the preparation of TiO_2-A. For TiO_2-B the yield was 78%, only 39% for TiO_2-D and less than 20% for TiO_2-E. The yield was also quantitative for TiO_2-C, after only half an hour of irradiation. This means that increasing the precursor concentration provides a higher density of crystallisation nuclei that favours complete precipitation.

A good correlation between the size of the TiO_2 agglomerates precipitated from the most diluted precursor solutions and the time of heating was observed, the largest agglomerates corresponding to the more severe conditions (Fig. 1). TiO_2-C is not included in the figure because it is composed of larger agglomerates, which are difficult to maintain in suspension.

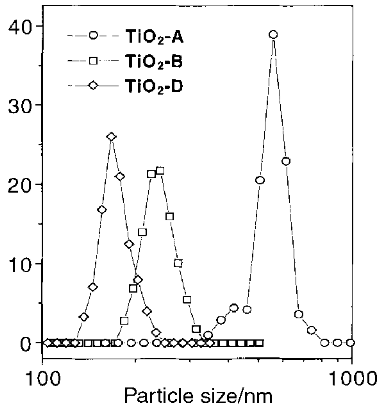

Fig. 1 Mass distribution per aggregate size of the freshly obtained precipitates for TiO_2-D (i), TiO_2-B (ii) and TiO_2-A (iii) samples.

The XRD pattern for all the samples was essentially that of anatase (see Fig. 2). Traces of rutile and $TiOF_2$ were observed for the samples obtained after the shortest irradiation time (peaks at $2\theta = 23.4°$, $TiOF_2$, and 27.4° rutile, indicated by arrows in Fig. 2). The presence of $TiOF_2$ traces in the precipitates obtained with the shortest reaction time is reasonable, since the existence of this species in titanium–fluoro complexes in aqueous solution has been described.[18] On the other hand, anatase formation is in accordance with the fact that the transformation of anatase into the thermodynamically stable rutile is inhibited by the addition of strongly titanium complexing ions, such as sulfate, phosphate or fluoride. Strongly complexing ligands hinder the condensation of TiO_6 octahedra at opposite edges to form linear chains of rutile, while growth of the spiral chains of TiO_6 octahedra constituting anatase is still possible.[19]

The peaks present different relative intensities than those of the anatase patron (which correspond to complete random order) in the XRD patterns of all samples. For example, the relative intensity of the peak corresponding to the (004) plane at 37.8° is notably increased while that of (112) plane at 38.6° is very weak (see Table 2). This fact suggests that the differential adsorption of fluoride anions on the faces of titania crystallites determines a preferential growth. It should also be noticed that the peaks are very well defined, with a small half-width, usually only attainable after annealing TiO_2 materials at temperatures well above those attained in our experimental procedure, in which the temperature increase is limited by the solution boiling point. It has been suggested that fluoride anions induce an increase in the anatase crystallinity.[20] On the other hand, peaks in the XRD pattern of the TiO_2-C sample are wider than those of the TiO_2-B sample (Fig. 3), suggesting that an increase in precursor concentration gives smaller crystallites, as we can

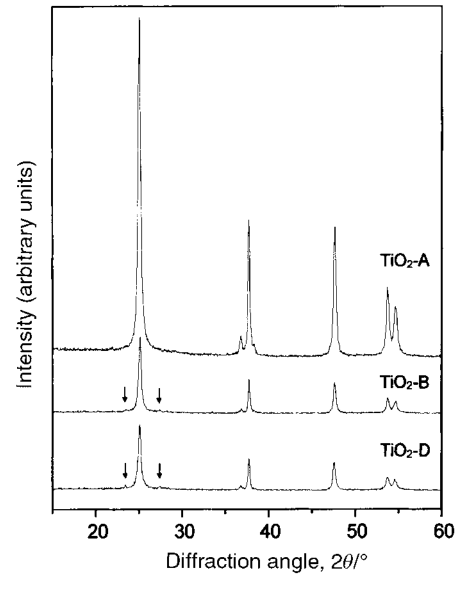

Fig. 2 XRD spectra corresponding to TiO_2 powders obtained from the same precursor solution and different microwave power and time conditions. The arrows point out minor peaks corresponding to $TiOF_2$ (left) and rutile (right) phases.

Table 2 Powder XRD data: relative peak intensity comparison between anatase patron and sample TiO_2-A

hkl	I_{rel} (patron)	I_{rel} (TiO_2-A)
101	100	100
103	10	6
004	20	42
112	10	4
200	35	42
105	20	21
211	20	16

expect considering the surely higher density of crystal growth nuclei.

TEM observations show that TiO_2-A powder consists of crystallites with elongated ellipsoid shapes mainly grouped in flower-like arrangements. Similar morphologies are observed for samples TiO_2-B and TiO_2-D (Fig. 4). A great difference is observed in the sample obtained from a higher precursor concentration, TiO_2-C. For this sample, large agglomerates are observed that seem to be made from the heavy aggregation of smaller crystallites.

BET surface area (S_{BET}) measurements give $S_{BET} = 30\ m^2\ g^{-1}$ for TiO_2-A, and $85\ m^2\ g^{-1}$ for TiO_2-B, showing that an increase in the heating time leads to a decrease in the surface area. An S_{BET} value of $140\ m^2\ g^{-1}$ was observed for sample TiO_2-C, indicating that this material is porous. Changes in sample texture observed by TEM are related to different shapes on the nitrogen adsorption–desorption isotherm (Fig. 5).

Fig. 6 shows the UV–Vis spectra obtained from the light transmitted through suspensions of TiO_2 powders with a 1 cm optical path length, prepared as in ref. 21. The concentrations of each sample are practically the same and are given in the figure caption. In ref. 21, the light scattering and light absorption spectral dependences of different TiO_2 powder suspensions are obtained from experimental transmission spectra. The $\log(1/T)$ dependence of the experimentally obtained spectra show a good correspondence in the high energy range with computed absorption spectra, due to the predominance of absorption over scattering in this range. Absorption spectra corresponding to Degussa P-25 show the best well-defined absorption edge because of the abrupt increase in the absorption. This is not so for the rest of the TiO_2 powders studied. This can be explained because the absorption edge is a consequence of the band structure and this depends on the atoms order in the solid. Therefore, Degussa P-25 shows a higher crystallinity than the rest of the powders in ref. 21. Comparing results in Fig. 6 with those of ref. 21, it can be said that the degree of crystallinity of TiO_2 obtained with microwave heating over two hours almost equals that of Degussa P-25. The absorption edge is less defined for spectra corresponding to only 30 min of microwave heating. It can be observed that in this last case, the precursor solution is still present in some amount and this causes the absorption to increase abruptly around 220 nm.

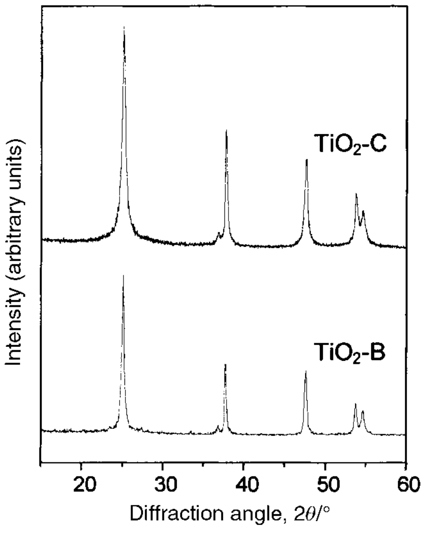

Fig. 3 XRD spectra corresponding to TiO_2 powders obtained after 30 min of 60 W microwave irradiation with the two different precursor solutions employed.

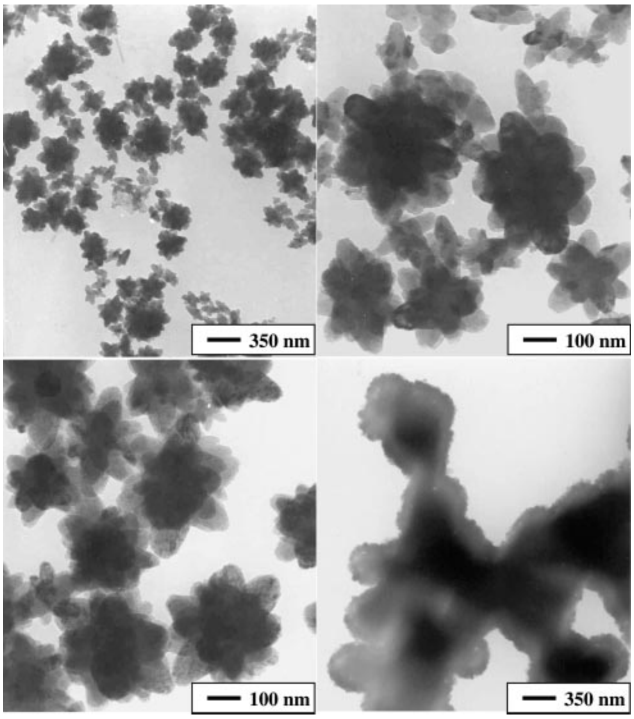

Fig. 4 TEM photographs of (top) TiO_2-A, (bottom left) TiO_2-B and (bottom right) TiO_2-C.

Elemental analysis of the different samples shows that they contain amounts of fluoride that follow particular trends. The mass percent of fluoride slightly decreases when the microwave irradiation time increases: TiO_2-B contains 3.9% F, while TiO_2-A contains 3.5% F. The most concentrated precursor solution gives the sample with more F^- content: sample TiO_2-C retains 4.4% F. Annealing reduces the fluoride content but complete removal of the halogen is never observed. For example, the sample TiO_2-A retains 2.2% F after annealing at 573 K for 2 h. This fact suggests that, although part of the fluoride anions that were adsorbed on the oxide surface could be easily removed, a significant amount must be included in the bulk of the oxide, where complete removal is difficult. Fluoride anions may substitute oxygen in the TiO_2 structure, being incorporated to some extent into the anatase lattice.[19] Nevertheless, the amounts of fluoride are lower than those reported from the same precursor in LPD experiments at lower temperature.

Deki *et al.* have reported the photocatalytic activity of anatase samples (films and powder) produced from a similar precursor.[1] Their samples are less crystalline and contain a higher amount of fluoride (7.2% fluoride in the as-synthesised sample), but despite this fact, they are photoactive in the degradation of acetaldehyde in the gas phase. We have essayed thoroughly the photocatalytic activity of our TiO_2 samples front phenol, an experiment that has been proposed as standard,[22] but no significant TOC reduction was observed. Most probably the content of fluoride is the origin of the lack of photocatalytic activity for our titania samples. Under the same experimental conditions, TiO_2 Degussa P-25 allows the complete mineralization of phenol in 6.5 h. Further informa-

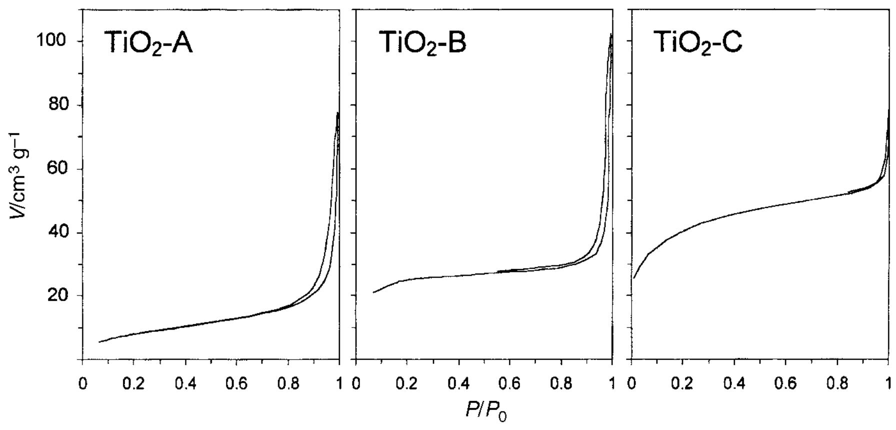

Fig. 5 N_2 gas adsorption–desorption isotherms for samples TiO_2-A, TiO_2-B and TiO_2-C. The N_2 volume is at standard temperature and pressure (STP) and P/P_o is the relative partial pressure of N_2 in equilibrium with the sample at 77 K.

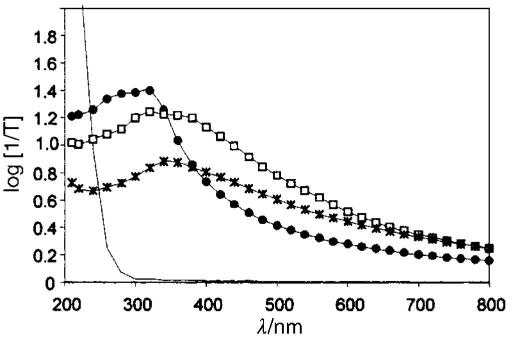

Fig. 6 Spectra obtained from the spectral measurement of light transmitted through a suspension of TiO_2 with a 1.0 cm optical path length. The concentration for both Degussa P-25 (●) and TiO_2-B (*) is 0.042 mg ml^{-1}. For TiO_2-A (□), the concentration is 0.047 mg ml^{-1}. Absorption corresponding to the precursor solution is also shown for comparison (solid line).

tion about titania doped with fluoride is given in the references. Positive effects have been found for low fluoride content. The photoactivity of TiO_2 films, obtained by a sol–gel procedure, was significantly enhanced by addition of a small amount of ammonium fluoride into the sol–gel precursor.[20] The optimum amount of F was 0.06%, a percentage far lower than those found in our samples. An improvement in the photoelectrochemical response of rutile single crystal electrodes doped with fluoride ions, in the order of 0.01%, has also been observed.[23] On the other hand, negative effects of fluoride in the photoactivity of titania have also been reported. Fluorides strongly adsorb to the TiO_2 surface and interfere with adsorption of organic substrates.[19,24] The photocatalytic activity of TiO_2 is decreased after surface fluorination with fluoromethane.[25]

Conclusions

Microwave irradiation of aqueous solutions of titanium–fluoro complexes containing boric acid as fluoride scavenger allows the synthesis of highly crystalline anatase TiO_2 powders at very low temperatures, under atmospheric pressure and in a short period of time without annealing. The crystal size and agglomeration level of the TiO_2 powders obtained can be controlled by modifying the concentration of the chemical species involved and the time of microwave irradiation. For a 0.034 M precursor concentration, the most appropriate irradiation time was two hours in order to obtain maximum yield and high crystallinity. For shorter irradiation times, yields were lower, crystallinity decreased and the fluoride content in the materials was higher, though less than previously reported.[1] Our materials did not show photocatalytic activity, contrary to previous reports.[1] We believe that this is possibly due to their contamination with fluoride anions from the precursor.

Acknowledgements

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