

Synthesis of brookite TiO₂ nanoparticles by thermolysis of TiCl₄ in strongly acidic aqueous media

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Nanometric particles of titania, brookite and rutile polymorphs were synthesised by thermolysis of TiCl₄ in concentrated HCl solutions. The Cl:Ti molar ratio seems to be the key factor in determining the crystalline phases and their relative proportions as well as the particle size and a large proportion of brookite can be obtained under specific conditions. The complex Ti(OH)₂(Cl)₂(OH)₂ seems to be the precursor of the brookite phase. The presence of chloride ions is also necessary to stabilise brookite in suspension. Depending on the acidity and the ageing conditions, different morphologies of brookite nanoparticles are obtained, namely spheroidal particles or platelets. Stable sols of pure brookite are obtained by peptization of the solid phase.

Introduction

Titanium dioxide is used largely in technological applications.^{1–6} Its current use is as a white pigment for paints or cosmetics, as a support in catalysis and as a photocatalyst. Titanium dioxide is also a common material for photovoltaic cells and appears to be interesting as a dielectric material for the next generation of ultra-thin capacitors due to its high dielectric constant.⁷ The uses and performances for a given application are, however, strongly influenced by the crystalline structure, the morphology and the size of the particles.^{8–12} Indeed, as for many other solids, nanosized TiO₂ particles are of particular interest because of their specifically size-related properties. Hence, many works have focussed on the synthesis of titanium dioxide nanoparticles.^{13–24}

Anatase and rutile are the polymorphs of TiO₂ commonly obtained by hydrolysis of titanium compounds, such as titanium tetrachloride (TiCl₄)^{13–15} or titanium alkoxides (Ti(OR)₄), in solution.^{16–19} Brookite is sometimes observed as a by-product when the precipitation is carried out in an acidic medium at low temperature.^{17,18,20,21} It is also observed after a 15 month period of ageing for a precipitate formed from TiCl₄ and ammonia.²² Classically, brookite is obtained as large crystals by hydrothermal methods at high temperature and pressure (200 ≤ *T* ≤ 400 °C, 10 ≤ *P* ≤ 400 bar) in aqueous²³ or in organic media.²⁴ In this latter case, particular amounts of sodium cations in the reaction medium seem necessary to produce pure brookite.

We report a study of the thermolysis at 100 °C of titanium tetrachloride in concentrated hydrochloric acid, showing that brookite can be obtained, under precise conditions of precipitation, quasi-quantitatively as nanoparticles. The influence of the physico-chemical conditions (acidity of the medium, nature of the anions, ageing of suspensions) on the brookite formation was investigated. The morphology and size of particles were also studied. To our knowledge, this is the first report of quasi-quantitative formation of brookite nanoparticles in an aqueous medium without strong complexing agents and in non-hydrothermal conditions.

Experimental

Synthesis

TiO₂ particles were formed by adding 1 mL of pure TiCl₄ dropwise to 50 mL (150 or 20 mL) of hydrochloric or perchloric acid, the concentration of the acid was varied between 1 and 5 mol dm⁻³. The final titanium concentration in the mixtures was 0.15 mol dm⁻³ (0.05 and 0.4 mol dm⁻³, respectively). The solutions were heated and aged at 100 °C in an oven. Some syntheses were carried out in the presence of NaCl at various concentrations.

All syntheses were performed in glass or Nalgene bottles which had been carefully cleaned with concentrated hydrochloric acid and distilled water in order to avoid the presence of sources of nucleation able to influence the crystalline structure of the precipitate.

After ageing, the solid was centrifuged, washed with distilled water and dried under a nitrogen atmosphere. In the syntheses yielding a mixture of brookite and rutile, the selective peptization of brookite in acidic media was carried out as follows. The solid collected after centrifugation was treated with a HNO₃ solution (3 mol dm⁻³) over *ca.* 20 min. The suspension was again centrifuged and the recovered solid phase was dispersed in water (the pH of the final suspension was around 1.5) and centrifuged again. After this last centrifugation, the supernatant phase contained only brookite particles while the rutile particles formed the precipitate. A portion of the sol was diluted for transmission electron microscopy and quasi-elastic light scattering measurements; another was dried at room temperature for X-ray diffraction characterization.

Techniques

X-Ray diffraction. XRD patterns were obtained using a powder diffractometer (Philips PW1830) operating in the reflection mode with CuKα radiation and equipped with a graphite back monochromator. The angular domain was between 20 and 80° (2θ). The patterns were analysed using the Philips PC APD 3.5 program package. The proportions of

the different titanium dioxide polymorphs (anatase, brookite, rutile) in the solids were evaluated from the relative areas of the 110, 121 and 101 diffraction lines of rutile, brookite and anatase phases, respectively. Calibrations were performed using particles of rutile (8 nm in mean diameter) and of anatase (10 nm mean diameter) obtained by thermolysis at 100 °C of TiCl_4 (0.15 mol dm^{-3}) in HClO_4 (5 mol dm^{-3}) and in a mixture of HCl (1 mol dm^{-3}) and Na_2SO_4 (1 mol dm^{-3}), respectively. Brookite particles are those synthesised and purified by the procedure described above.

Transmission electron microscopy (TEM). Transmission electron micrographs were obtained using a JEOL 100 CX II apparatus. Samples were prepared by evaporating very dilute suspensions onto carbon-coated grids. The *d*-spacings were calibrated using the gold pattern. Particle size distributions were determined by measuring the average diameter of *ca.* 100 particles.

High-resolution transmission electron microscopy (HR-TEM). Observations were performed with a TOPCON 002B microscope operating at 200 kV. The high-resolution (HR) images were digitized using a charge-coupled video camera device mounted above a light box. The fringe spacings were measured from the position of the Bragg peaks in the Fourier transform of the images.

Quasi-elastic light scattering (QELS). Measurements were performed on stable suspensions using an AMTEC SM 200 apparatus equipped with a He-Ne laser beam and a Brookhaven Bi2030 correlator.

Titration of titanium. Titanium concentrations were determined by colorimetry of the very stable, coloured complex formed in solution by Ti^{4+} ions with H_2O_2 .^{25,26} The Ti^{4+} solutions were diluted in hydrochloric acid (1 mol dm^{-3}) to obtain a concentration between 2×10^{-4} and $2 \times 10^{-3} \text{ mol dm}^{-3}$. A 1 mL sample of this solution was then added to 3 mL of a H_2O_2 solution (10% by volume). Measurements were performed using an Uvikon 940 spectrometer. The titration of titanium in solid samples was carried out following the same method. The solid was first isolated from the liquid by centrifugation and then dissolved in hot, concentrated sulfuric acid in the presence of ammonium sulfate.

Specific surface measurements. Specific surface areas were determined using an ASAP 2010 Micromeritics apparatus following the BET analysis. Adsorption and desorption of N_2 were performed at 77 K. Samples had been previously out-gassed by heating at 100 °C under vacuum ($3 \mu\text{m Hg}$).

Results

Thermolysis of TiCl_4 in hydrochloric acid

The XRD pattern of the solid formed after thermolysing a TiCl_4 solution ($[\text{Ti}] = 0.15 \text{ mol dm}^{-3}$, $[\text{HCl}] = 3 \text{ mol dm}^{-3}$) for 48 h [Fig. 1(a)] shows that the two polymorphs of TiO_2 , brookite and rutile, are present. TEM micrographs show particles of very distinct morphologies [Fig. 1(b)] which were identified by electron diffraction as rutile, for the elongated particles, and brookite, for the small, spheroidal aggregates. The proportion of brookite (evaluated from the XRD pattern) is *ca.* 80% of the mixture. The relative proportions of brookite and rutile do not vary beyond 48 h of ageing at 100 °C, but they are markedly dependent on the acidity of the medium and the concentration of titanium. For $[\text{Ti}] = 0.15 \text{ mol dm}^{-3}$, brookite is the main phase (*ca.* 70–80%) obtained for the acidity range of $2 \leq [\text{HCl}] \leq 4 \text{ mol dm}^{-3}$ [Fig. 2(b)]. At $[\text{Ti}] = 0.05 \text{ mol dm}^{-3}$,

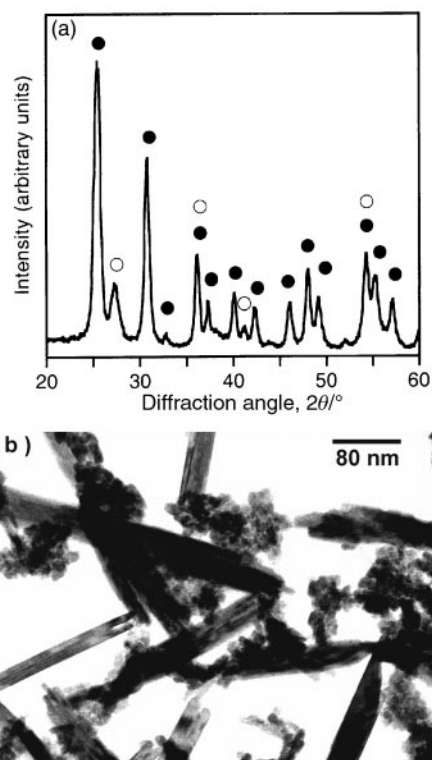


Fig. 1 XRD pattern (a) and TEM micrograph (b) of the solid obtained by thermolysing a solution of TiCl_4 (0.15 mol dm^{-3}) in HCl (3 mol dm^{-3}) at 100 °C for 48 h. The peaks are brookite (●) and rutile (○).

70% of the solid crystallises as brookite whatever the acidity, but at $[\text{Ti}] = 0.4 \text{ mol dm}^{-3}$, only rutile is obtained in 1 mol dm^{-3} HCl and 5 mol dm^{-3} HCl [Fig. 2(a), 2(c)].

The kinetics of precipitation are also very dependent on the acidity and the concentration of titanium. The rate is always slowed strongly as the acidity of the medium is increased. At $[\text{Ti}] = 0.15 \text{ mol dm}^{-3}$, no solid is recovered by centrifugation up to 5 h of thermolysis. After 24 h in 1 mol dm^{-3} HCl , no titanium is titrated in the supernatant solution indicating that the precipitation is complete, but in 5 mol dm^{-3} HCl , *ca.* 70% of titanium is still present as soluble complexes. In order to achieve the precipitation in the latter case, a 48 h thermolysis period is needed. It is also interesting to note that the third polymorph of TiO_2 , anatase, is formed in small amounts (from 10 to 20%) in the early stages of precipitation (after 5 h), as shown by XRD (Fig. 3), but disappears afterwards to yield only rutile and/or brookite (Fig. 1).

The particles of brookite have been characterised after different durations of thermolysis and separation from rutile by peptization with nitric acid (see Experimental). The difference in size of the two types of particles [Fig. 1(b)] explains their difference in peptizability. The XRD pattern of the solid recovered by drying the sol is characteristic of pure brookite (Fig. 4). After 48 h of thermolysis, TEM micrographs show primary particles of mean size 5.2 nm (standard deviation, $\sigma = 1.4 \text{ nm}$) strongly aggregated [Fig. 5(a)]. The size of the aggregates varies from 40 to 60 nm, in accordance with the results of QELS measurements [Fig. 5(b)]. After one month of thermolysis, the mean size of the aggregates does not change significantly. BET measurements also show that the specific area of brookite particles does not evolve significantly during ageing (97 and $117 \text{ m}^2 \text{ g}^{-1}$ for particles formed after 2 days and one month, respectively). However, the mean particle size within the aggregates evaluated from TEM, $D = 12.1 \text{ nm}$ ($\sigma = 2 \text{ nm}$), is notably increased, suggesting that recrystallisation of the early particles has occurred inside the aggregates during ageing [Fig. 5(c)]. HRTEM micrographs show well-

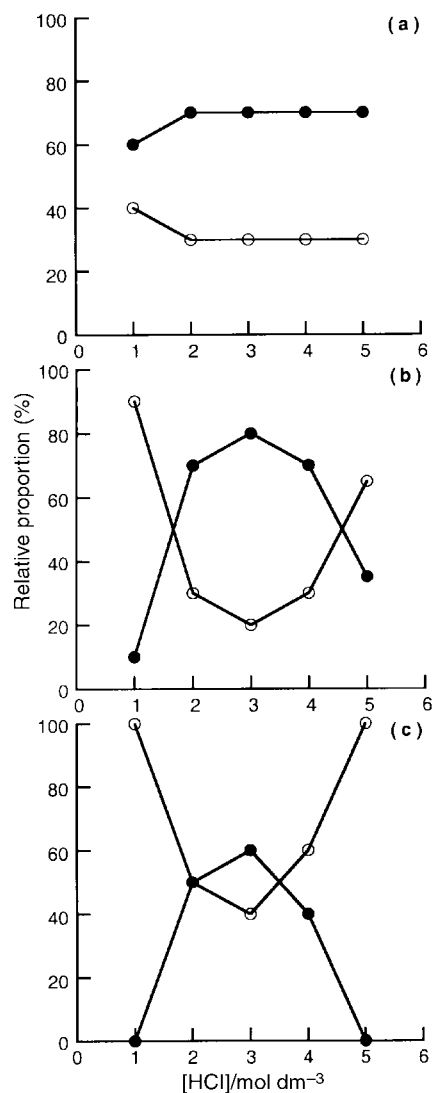


Fig. 2 Relative proportions of brookite (●) and rutile (○) formed by thermolysing a solution of TiCl_4 at 0.05 mol dm^{-3} (a), 0.15 mol dm^{-3} (b) and 0.4 mol dm^{-3} (c) in HCl medium at 100°C for 48 h.

defined, diamond-shaped platelets forming an ordered stacking as suggested by the same orientation of atomic planes within adjacent particles [Fig. 6(a), 6(b)]. The inset of Fig. 6 shows the numerical local diffraction corresponding to the amplitude of the Fourier transform of the HR image. Assignment of this electron diffraction pattern [Fig. 6(b)] indicates that these two families of planes correspond to $[1\ -1\ -1]$ and $[1\ 1\ -1]$ planes with d -spacing of 0.34 nm . These planes, forming between them an angle of 79° , are exactly parallel to the sides of particles and correspond in all likelihood to the lateral faces of the particles. As a consequence, the basal faces of the particles could correspond to the $[3\ 0\ 1]$ plane which is quasi-perpendicular (91°) to both the $[1\ -1\ -1]$ and $[1\ 1\ -1]$ planes. When the precipitation is very slow ($[\text{Ti}] = 0.05 \text{ mol dm}^{-3}$, $[\text{HCl}] = 5 \text{ mol dm}^{-3}$) similar diamond-shaped but larger platelets of brookite, mean size 40 nm , are formed after one month of thermolysis. At this stage, the precipitation is almost complete.

Thermolysis of TiCl_4 in perchloric acid

In the range of $1 \leq [\text{HClO}_4] \leq 5 \text{ mol dm}^{-3}$, the precipitation of titanium ions is complete after 24 h of thermolysis, whatever the acidity of the medium. Brookite, anatase and mainly rutile are precipitated simultaneously at the beginning of thermolysis,

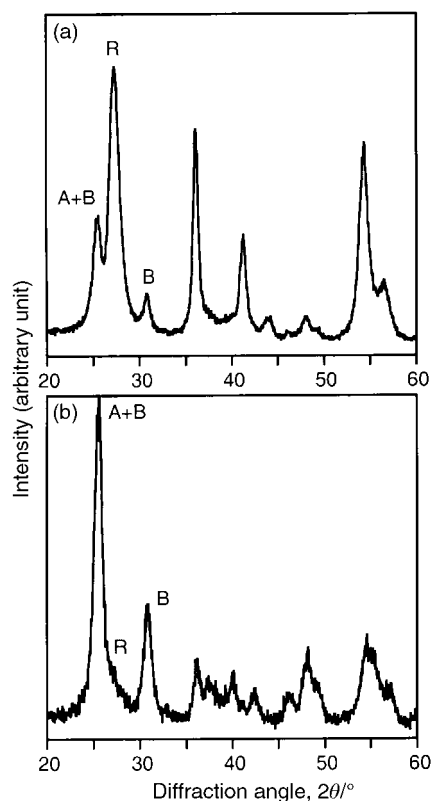


Fig. 3 XRD patterns of solids obtained by thermolysing a solution of TiCl_4 (0.15 mol dm^{-3}) (a) in $[\text{HCl}] = 1 \text{ mol dm}^{-3}$ and (b) 3 mol dm^{-3} at 100°C for 5 h; A=anatase, B=brookite, R=rutile.

but after one month of ageing at 100°C , rutile is the only solid component for the whole acidity range studied.

Influence of the chloride ions on the formation of brookite

The foregoing results show that the acidity of the medium and the nature of anions strongly influence the crystalline structure of titania particles formed upon thermolysis. In concentrated perchloric acid solutions, perchlorate ions can be coordinated to the Ti(IV) cation but the complexes are not very stable²⁷ and consequently perchlorate does not seem to have a specific role in the crystallisation of titania. On the other hand, the chloride ions seem to be essential for the formation of brookite. The influence of the chloride ion was investigated by carrying out the thermolysis of TiCl_4 in hydrochloric acid ($[\text{HCl}] = 1$ to 5 mol dm^{-3} , $[\text{Ti}] = 0.15 \text{ mol dm}^{-3}$) in the presence of various amounts of NaCl. In this manner, the Cl:Ti ratio can be varied

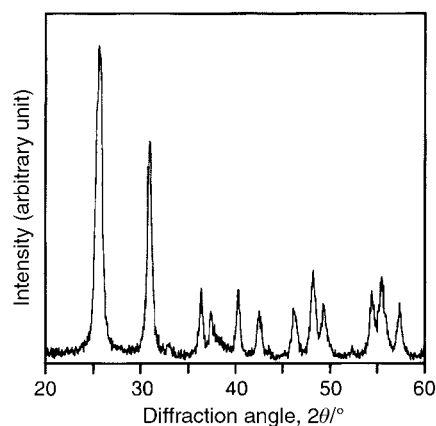


Fig. 4 XRD pattern of brookite particles resulting from the fractionation of the precipitate formed by thermolysis of a solution of TiCl_4 (0.15 mol dm^{-3}) in HCl (3 mol dm^{-3}) at 100°C for 48 h.

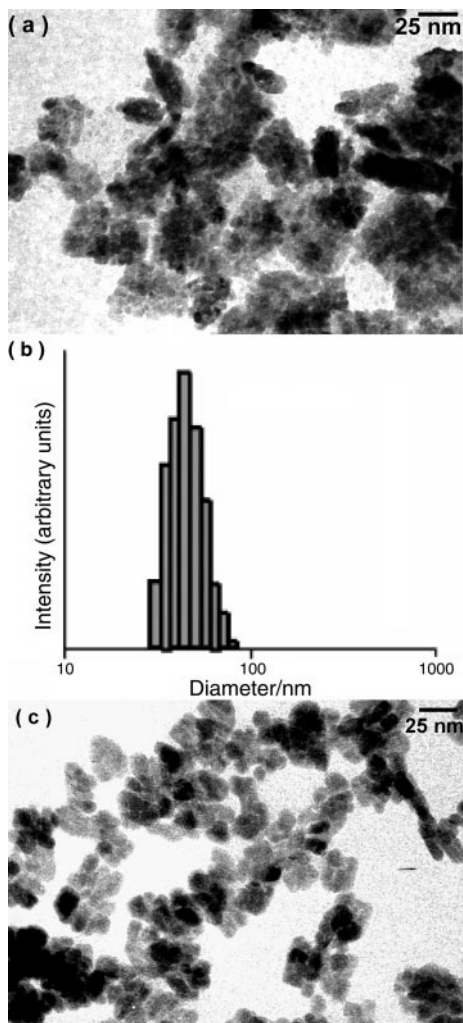


Fig. 5 Particles of brookite separated from rutile by peptization after thermolysing a solution of TiCl_4 (0.15 mol dm^{-3}) in HCl (3 mol dm^{-3}) at 100°C . TEM micrograph (a) and hydrodynamic particle size distribution (b) after 48 h of thermolysis; TEM micrograph of particles after one month of thermolysis (c).

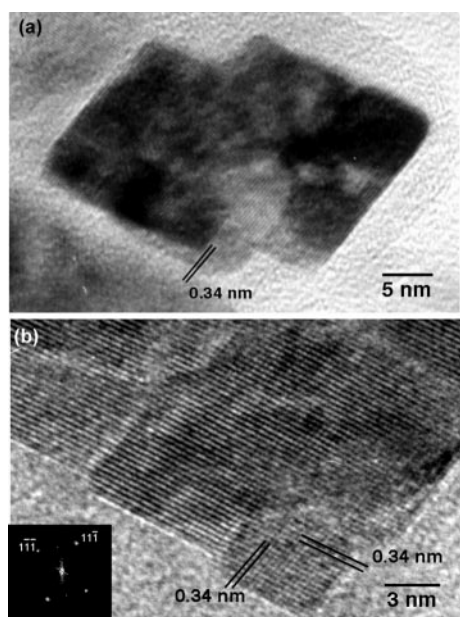


Fig. 6 HRTEM micrographs of particles of brookite separated from rutile by peptization after one month of thermolysis at 100°C (TiCl_4 0.15 mol dm^{-3} , HCl 3 mol dm^{-3}); inset, the local electron diffraction pattern.

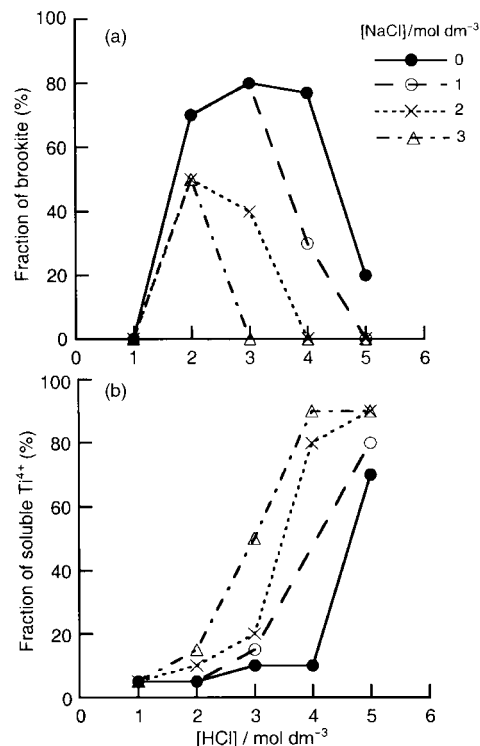


Fig. 7 Fraction of brookite in the precipitate (a) and fraction of soluble species of titanium (b) after 24 h of thermolysis for TiCl_4 (0.15 mol dm^{-3}) in HCl medium in the presence of NaCl at different concentrations.

over a large range, independently of the acidity of the medium. The results are summarised in Fig. 7. For $[\text{HCl}] > 2 \text{ mol dm}^{-3}$, the increase of Cl^- concentration strongly decreases the relative proportion of brookite in the solid phase and the amount of the solid after 24 h of thermolysis [Fig. 7(a), 7(b)]. The specific role of chloride ions is also well evidenced in Fig. 8 which represents the relative proportions of titanium (as rutile, brookite and soluble species) as a function of the $\text{Cl}_{\text{total}}:\text{Ti}$ ratio. This diagram shows that the optimal range for the formation of brookite (proportion above 50%) corresponds to a $\text{Cl}_{\text{total}}:\text{Ti}$ ratio ranging between 17 and 35. The $\text{Cl}_{\text{total}}:\text{Ti}$ ratio seems to be the pertinent parameter since the proportions reported in Fig. 8 do not depend on the various $[\text{NaCl}] + [\text{HCl}]$ combinations corresponding to the same $\text{Cl}_{\text{total}}:\text{Ti}$ ratio.

Provided that chloride ions are present in the suspension, particles of brookite are stable against recrystallisation to rutile for a long period of thermolysis. Particles of brookite formed in

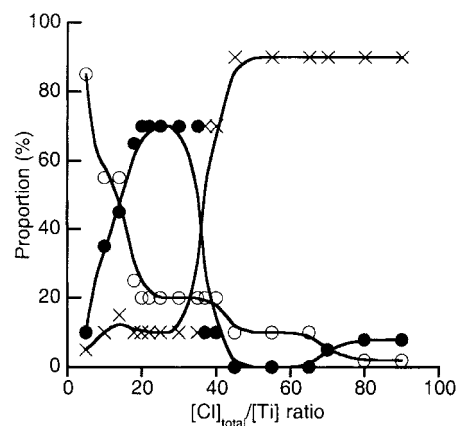


Fig. 8 Proportion of titanium as soluble complexes (\times) and as solid forms (brookite \bullet , and rutile \circ) as a function of the $\text{Cl}_{\text{total}}:\text{Ti}$ ratio after 24 h of thermolysis at 100°C for TiCl_4 .

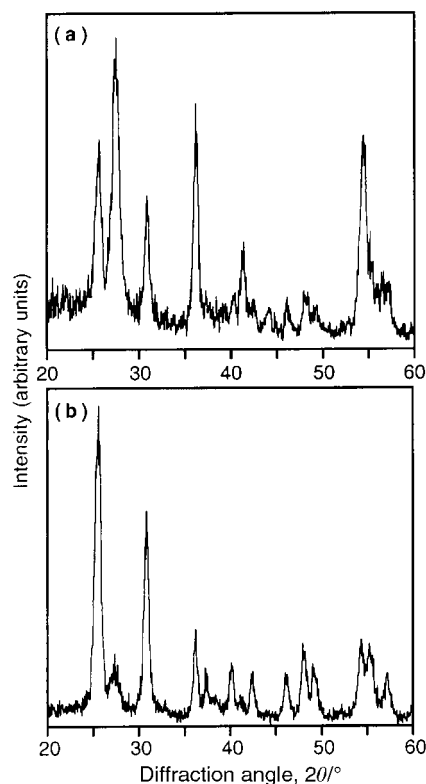


Fig. 9 XRD patterns of solids obtained after ageing brookite particles in HClO_4 (3 mol dm^{-3}) for 1 month at 100°C (a) and in the equimolar mixture of HClO_4 and NaCl (3 mol dm^{-3}) (b). [Brookite particles are initially formed by thermolysis of TiCl_4 (0.15 mol dm^{-3}) in HCl (3 mol dm^{-3}) for 24 h at 100°C .]

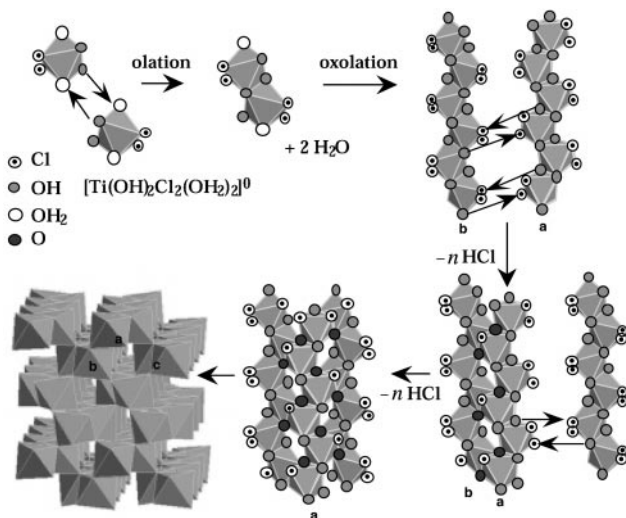


Fig. 10 Possible reaction pathway for brookite formation from the $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ complex.

3 mol dm^{-3} HCl for 0.15 mol dm^{-3} Ti , and then transferred into 1 mol dm^{-3} or 6 mol dm^{-3} HCl and aged at 100°C for one month, did not change their crystalline structure or size. On the other hand, brookite particles aged at 100°C in 3 mol dm^{-3} perchloric acid led to quasi-quantitative transformation into rutile particles [Fig. 9(a)], suggesting a dissolution–crystallisation process for the transformation. However, if the ageing was carried out in 3 mol dm^{-3} perchloric acid containing 3 mol dm^{-3} NaCl , no modification of the brookite proportion or of the particle shape occurred [Fig. 9(b)].

Discussion

A high concentration of chloride ions in the thermolysis medium of titanium appears to be necessary for the formation of brookite and also to avoid recrystallisation of brookite into rutile during ageing in suspension. As this transformation proceeds by dissolution–crystallisation because of the large changes in the size and morphology of particles, complexation of titanium ions in solution by chloride must be very likely involved.

The speciation of titanium hydroxochloro complexes at low concentration of titanium, in order to avoid precipitation, has been investigated by Nabivanets and Kudritskaya^{28–30} Upon increasing the concentration of chloride ions in strongly acidic media at elevated ionic strength, the complexes $[\text{Ti}(\text{O}-\text{H})_2(\text{OH}_2)_4]^{2+}$, $[\text{Ti}(\text{OH})_2\text{Cl}(\text{OH}_2)_3]^+$ ($\beta_1=3.55$), $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ ($\beta_2=0.40$), $[\text{Ti}(\text{OH})_2\text{Cl}_3(\text{OH}_2)]^-$ ($\beta_3=0.094$), and $[\text{Ti}(\text{OH})_2\text{Cl}_4]^{2-}$ ($\beta_4=0.083$) are successively formed. The $\text{Cl}:\text{Ti}$ ratio combined in the complexes seems to depend only upon the $\text{Cl}:\text{Ti}$ ratio in solution. Consequently, it is very likely that the thermolysis of a complex $[\text{Ti}(\text{OH})_a\text{Cl}_b(\text{OH}_2)_{6-a-b}]^{(4-a-b)+}$ leads only to the progressive increase of hydroxylation ratio $\text{HO}:\text{Ti}$, from $a=1$ up to $a=4-b$, a value corresponding to the non-electrically charged complex allowing the precipitation of solid. It is then interesting to observe that brookite is the major phase obtained in the range $17 \leq \text{Cl}:\text{Ti} \leq 35$, with $[\text{Ti}]=0.15 \text{ mol dm}^{-3}$ (Fig. 8). This range corresponds to that where the non-electrically charged complex $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ predominates in dilute titanium solution ($0.40 \leq \log[\text{Cl}^-] \leq 0.65$).³⁰ This strongly suggests that the complex $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ could be the precursor of brookite.

A schematic pathway is suggested to explain the formation of brookite from the precursor $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ (Fig. 10). The presence of aquo and hydroxo ligands in the coordination sphere of this complex allows the condensation by ololation, which involves the elimination of aquo ligands (the chloride ions being more strongly bound groups), and the formation of dimers and small chains of octahedra. When all water molecules are removed, further condensation will proceed by oxolation reaction with HCl elimination and formation of μ_3 -oxo bridges between octahedra (ab and abc structures in Fig. 10). This process allows the removal of all chloride ions from the reacting species and yields oxide. Under such conditions, chloride ions act as templates. Their presence in the coordination sphere of titanium ions orients the first steps of condensation but they are eliminated only at the end of the process.

Anionic complexes such as $[\text{Ti}(\text{OH})_2\text{Cl}_3(\text{OH}_2)]^-$ and $[\text{Ti}(\text{OH})_2\text{Cl}_4]^{2-}$ predominate for $\text{Cl}_{\text{total}}:\text{Ti} \geq 40$ (Fig. 8) ($[\text{Ti}]=0.05 \text{ mol dm}^{-3}$, $[\text{HCl}] \geq 4 \text{ mol dm}^{-3}$). The existence of these complexes may explain the high solubility of titanium and the lowering of the rate of precipitation. By thermolysis, the elimination of a chloride ligand from the $[\text{Ti}(\text{OH})_2\text{Cl}_3(\text{OH}_2)]^-$ complex forms the $[\text{Ti}(\text{OH})_2\text{Cl}_2(\text{OH}_2)_2]^0$ complex which leads to brookite as described above. Under these conditions of very slow precipitation, large platelets of brookite are formed ($\text{Cl}_{\text{total}}:\text{Ti} \geq 60$, Fig. 8). However, in very acidic media and with a high excess of chloride ions, the elimination of a hydroxo ligand with the formation of the $[\text{Ti}(\text{OH})\text{Cl}_3(\text{OH}_2)_2]^0$ complex may also occur. Dimerisation of this neutral complex likely proceeds by ololation and forms bridging OH ligands, but further condensation must proceed by substitution of chloride ions, such a process leading to rutile ($40 \leq \text{Cl}_{\text{total}}:\text{Ti} < 60$, Fig. 8). These different complexes likely coexist in equilibrium and it is difficult to be precise on the respective roles of acidity and $\text{Cl}:\text{Ti}$ ratio on the evolution of the soluble complexes during thermolysis. Experimentally, we observe that the precipitation of titanium in the presence of an excess of

NaCl leads to rutile, whereas at $[Ti]=0.05 \text{ mol dm}^{-3}$ and $[HCl] \geq 3 \text{ mol dm}^{-3}$, the formation of brookite is favoured.

Conclusion

The crystalline structure of titanium dioxide precipitated in very acidic media seems to be controlled by the nature of the anions present in the precipitation medium. While it is well known that anatase is formed in the presence of sulfate anions, we have shown that chloride ions allow the quasi-quantitative formation of brookite during thermolysis of very acidic solutions of $TiCl_4$. In the presence of non-complexing anions (*i.e.* perchlorate ions), rutile is the only isolated phase. The particles of brookite are well-defined, diamond-shaped platelets with a mean size depending on the acidity of the medium and/or the ageing time. Such nanometric particles of brookite can be easily peptized in mild acidic solution and form stable sols.

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