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Selective synthesis of brookite, anatase and rutile nanoparticles: thermolysis of $TiCl_4$ in aqueous nitric acid

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Abstract The three polymorphs of titania (anatase, rutile and brookite) have been obtained as nanoparticles selectively and with well definite morphologies (platelets of brookite, rods of rutile) by thermohydrolysis of $TiCl_4$ in concentrated aqueous nitric acid. The selectivity of the synthesis depends strongly on the acidity of the medium. The presence of concentrated nitrate ions seems to be the determining factor for the formation of brookite and its stabilization against recrystallization.

Introduction

Titanium dioxide has found applications in many fields [1–3]. As rutile, TiO_2 is extensively used as white pigments in paint, inks and fillers [4]. Because of its harmlessness and its high UV-light absorption, rutile is also used in cosmetics, as filter in solar creams and pigment in make up. Anatase has received much more attention as semiconductor in environmental photocatalysis processes such as removal of pollutants from air and water [5–7]. It is also widely used in photovoltaic devices [8, 9]. Brookite, a less common crystalline form of titanium dioxide, has been less studied for potential applications. This probably results from the lack of synthesis methods to produce nanosized particles. Indeed, the performances for a given application are strongly influenced not only by the crystalline structure but also by the morphology and the size of the particles [10–14]. Particles with a nanometric size have a particular interest because their high surface/volume ratio induces specific properties. Consequently, controling not only the crystalline phase but also the particle size and the morphology is of major importance to study of specific properties and form the right material for the right application. Moreover, the easier the synthesis method, the cheaper the material for a given application.

Many syntheses of these TiO_2 polymorphs are described in the literature. But, on one hand, the morphology and the size of particles are not always perfectly controlled. On the other hand, the synthesis conditions result often in a production cost and ecologic consequences which are not necessarily interesting for a manufacturer (Organic solvent, titanium alkoxides as precursor, high temperature and/or pressure).

Anatase is most often synthesized by hydrothermal process [15, 16] or by precipitation from $TiCl_4$ [17–19] or $TiOSO_4$ [20] in aqueous medium. The use of sulfate ions allowing to stabilize anatase against recrystallization, widely spread in industrial synthesis [21]. Anatase is also frequently obtained by hydrolysis–condensation of metallo-organic compounds such as titanium alkoxides in ethanol or aqueous medium [22, 23]. The anatase particles obtained are generally isotropic in shape (more or less spheroidal or eventually shaped as platelets) and nanometric in size. Their size can also be adjusted by a careful control of the acidity of the precipitation medium [19]. Rutile, which is the thermodynamically stable phase of titanium oxide, is commonly obtained by thermolysis or hydrothermal treatment of acidic solutions of $TiCl_4$ [24–26]. The particles, generally rod-shaped, have their size which increase when the temperature and/or the acidity of the medium is increased. Additives (NaCl, $SnCl_4$, NH_4Cl...) are sometimes used to decrease the size of rutile particles [27]. The formation of spherical nanometric particles of rutile from the hydrolysis of titanium

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isopropoxide, in nitric acid, has also been reported [28]. Brookite is generally obtained by hydrothermal synthesis and very often as large (micrometric) particles [29–32]. Brookite have also been obtained in organic media (ethylene glycol) with $TiO(acac)_2$ as precursor and 300 °C thermal treatment [33]. Nanometric platelets of brookite ($d \approx 9$ nm) have been obtained by thermolysis of $TiCl_4$ in concentrated HCl solution ($1 < HCl < 5$ mol L^{-1}) at 95 °C 34. In this case, the Cl/Ti ratio has a strong influence on the solubility of titanium and on the orientation of the TiO_2 crystallization.

A vast majority of TiO_2 syntheses has been performed in chloride containing rich medium. Bekkerman et al. [35] reported the formation of anatase and rutile in HNO_3 and Lee et al. [36] the formation of pure brookite from concentrated $TiCl_4$ solution but there are very few studies in this medium. In this paper, we show that each polymorph can be easily obtained as nanosized particles by controlling the acidity. Selective peptization allows the isolation of pure phases. Moreover we show that brookite can be the main constituent of the solid resulting from the thermolysis of $TiCl_4$ (0.15 mol L^{-1}) in acidic nitric at 95 °C. The goal of this study is, on the one hand, to propose a really simple synthesis, and on the other hand, to better understand the formation mechanisms of the different crystalline phases of TiO_2 and to clarify the role of the medium on the nature of the zero charge precursors.

Experimental section

Synthesis

Pure $TiCl_4$ (Fluka) was slowly added to a nitric acid solution at room temperature ([Ti] = 0.15 mol L^{-1}). The acid concentration was adjusted at different values between 0.5 and 5 mol L^{-1}. These solutions were heated at 95 °C for 24 h or one week in an oven. The solid formed was centrifuged and washed with distilled water. Separation of anatase and/or brookite from rutile was achieved by selective peptization: the solid collected after washing was treated with a HNO_3 solution (3 mol L^{-1}) for ca. 20 mn. The suspension was centrifuged and the recovered solid was dispersed in water (pH around 1.5). The suspension was centrifuged again resulting in a supernatant containing only anatase or brookite (depending on the conditions), the rutile particles always remaining in the precipitate.

Techniques

Titration of titanium

Titanium concentrations were determined by colorimetry at 410 nm of the stable complex $[Ti(O_2)(OH)(H_2O)]^+$ formed when H_2O_2 is added to an acidic solution of Ti^{4+} with a concentration in the range 10^{-4}–10^{-3} mol L^{-1} [37, 38]. Measurements were performed using a Uvikon XS Bio-Tek spectrophotometer.

Determination of amorphous amount in solids

As previously [19], 40 mg of powder, dried at room temperature, were dispersed in 5 mL of HCl (6 mol L^{-1}). The mixture was sonicated for one hour. 1 mL of the suspension were then filtrated and titrated as above by UV-visible spectroscopy. It corresponds to the titanium present in the amorphous solid, which is solubilized in these conditions. We have checked that anatase, brookite or rutile nanoparticles did not dissolved in 6 mol L^{-1} hydrochloric acid.

X-Ray diffraction

XRD patterns were recorded using a powder diffractometer (Philips PW1830) operating in the reflection mode with CuK_α radiation and equipped with a graphite back monochromator. The angular domain was 20–80° (2θ). The proportions of the different titanium dioxide polymorphs in the solids were evaluated from the relative area of the 110, 121 and 101 diffraction lines of rutile, brookite and anatase phases respectively [34]. The size of particles was calculated applying the Scherrer formula [39].

Transmission electron microscopy (TEM)

Transmission electron micrographs were obtained using a JEOL 100 CX apparatus operating at 100 kV. High-resolution transmission was performed using a Philips CM20/STEM apparatus operating at 200 kV. Samples were prepared by evaporation of very dilute aqueous suspensions onto carbon-coated grids.

Results

Influence of the acidity

As deduced from XRD patterns, the solids obtained after thermolysing $TiCl_4$ were mixtures of anatase, brookite and rutile. Figure 1 represents the relative amount of the different polymorphs obtained as a function of the acid concentration, after aging the suspensions for 24 h at 95 °C. For $0.5 < [HNO_3] < 2$ mol L^{-1}, anatase was the main product while for $2 < [HNO_3] < 5$ mol L^{-1}, brookite was the major phase in the mixture.

For $0.5 < [HNO_3] < 2$ mol L^{-1}, the more metastable phase, anatase, was the preponderant phase. For example, when $[HNO_3] = 1$ mol L^{-1}, the XRD pattern shows that

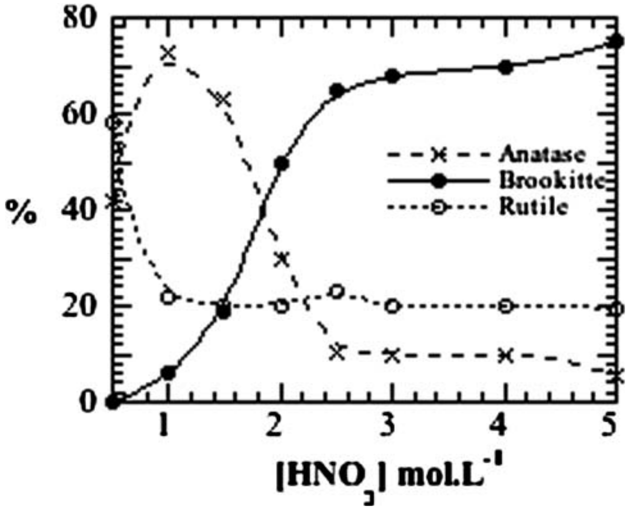

Fig. 1 Relative proportions of the different polymorphs of titanium dioxide for [Ti] = 0.15 mol L^{-1} after thermolysis for 24 h at 95 °C

the three polymorphs of TiO_2 are present (Fig. 2ai). Anatase represents 72% of the solid and there are about 22% of rutile and 6% of brookite. The amount of amorphous is negligible. After treatment of the solid and drying of the peptized fraction (see experimental part), the diffraction pattern (Fig. 2aii) is characteristic of pure anatase. TEM micrograph (Fig. 2b) shows particles about 5 nm in mean size and mostly spherical. The electron diffraction pattern (inset) confirms the anatase structure. These particles formed relatively monodispersed aggregates, 55 nm in mean size, as observed by QELS on suspensions. A strong effect of acidity on the proportions of the different phases occurred in this domain, brookite becoming strongly favored when the acidity increased.

In the range 2.5 < $[HNO_3]$ < 5 mol L^{-1} after heating at 95 °C for 24 h, brookite is the predominant phase (Fig. 1). It represented about 70% of the solid, which also contains 20% of rutile and 10% of anatase as deduced from the XRD pattern (Fig. 3ai) (the amount of amorphous is negligible). Pure brookite dispersion has been obtained by selective peptization allowing separation from the rutile particles (Fig. 3aii). TEM micrographs (Fig. 3b) show that the brookite particles formed aggregates 65 nm in mean size, as confirmed by QELS. HRTEM micrographs shows that the primary brookite particles seem to be small platelets (Fig. 3c) as it has been previously observed [19], where an ordered stacking was suggested by the observation of an identical orientation of the atomic planes within adjacent particles inside the aggregates. The lateral faces of particles were $[1\bar{1}\bar{1}]$ and $[11\bar{1}]$, both quasi-perpendicular to the basal planes [301] of the particle. The electron diffraction pattern (inset) corresponds to the brookite phase. The proportions of the different phases (Fig. 1) and the mean particle size of brookite (Table 1) did not evolve significantly with the acidity in this domain.

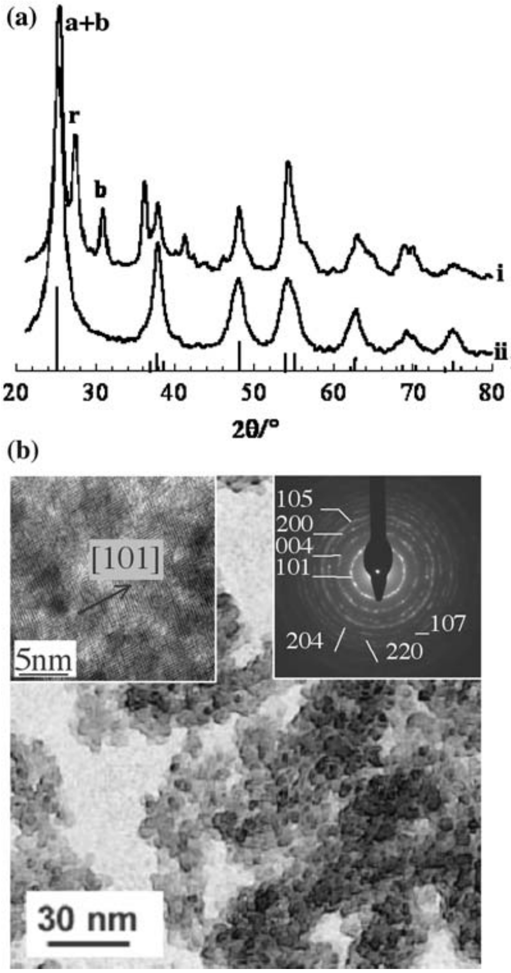

Fig. 2 (**a**) XRD patterns of (i) the initial mixture (a is for anatase, b for brookite and r for rutile), (ii) pure anatase obtained after peptization for $[HNO_3]$ = 1 mol L^{-1} and [Ti] = 0.15 mol L^{-1} after 24 h at 95 °C and (iii) JCPDS anatase reference (21–1272). (**b**) TEM micrograph of anatase particles (inset of HRTEM micrograph and electron diffraction pattern of anatase particles)

Influence of aging

The Fig. 4 presents the relative proportions of the different phases of TiO_2 after aging the aqueous suspensions at 95 °C for 7 days. A notable evolution occurred during aging. On the range 0.5 < $[HNO_3]$ < 1.5 mol L^{-1}, most of the anatase initially formed has disappeared to yield rutile and brookite. For $[HNO_3]$ = 1 mol L^{-1}, XRD pattern (Fig. 5a) shows that the composition of the solid is rutile (50%) anatase (25%) and brookite (25%) (the amount of amorphous is negligible), instead of 72% anatase, 20% rutile and 6% brookite after 24 h of thermolysis. TEM micrographs exhibit particles with very distinct morphologies

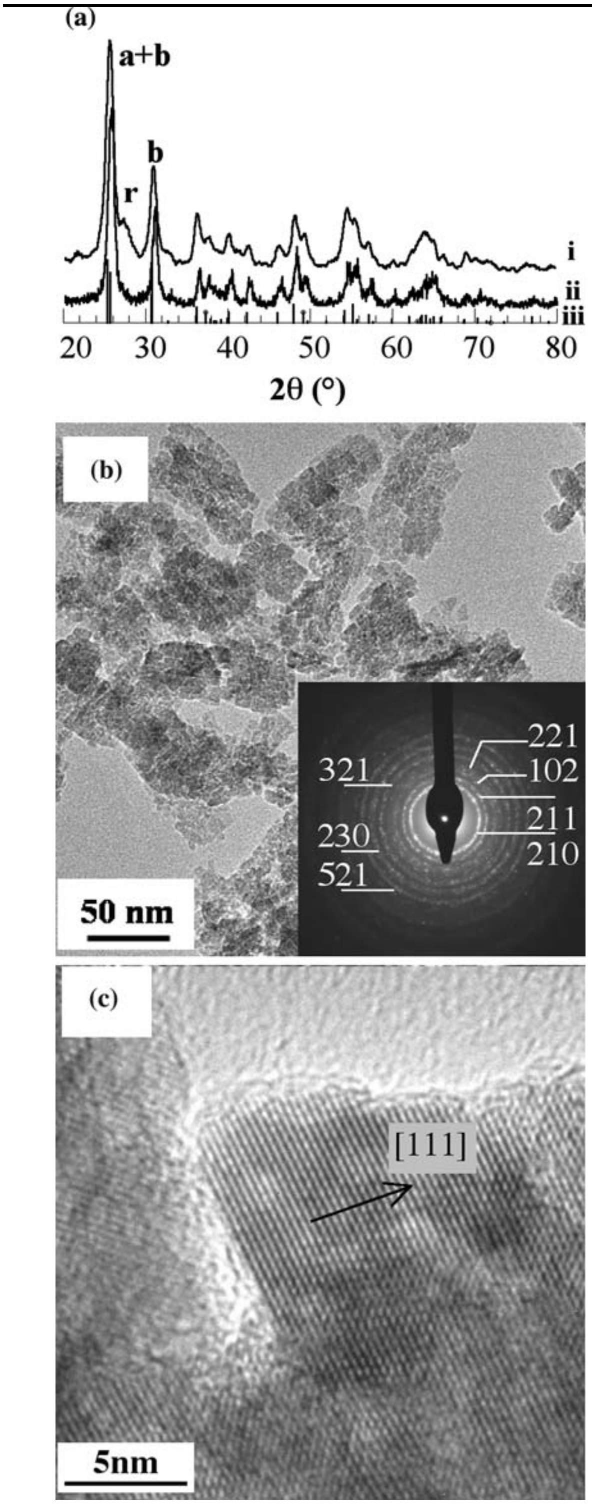

Fig. 3 (**a**) XRD patterns of (i) the initial mixture (a is for anatase, b for brookite and r for rutile), (ii) pure brookite obtained after peptization for $[HNO_3] = 3$ mol L^{-1} and $[Ti] = 0.15$ mol L^{-1} after 24 h at 95 °C and (iii) JCPDS brookite reference (76–1934). (**b**) TEM micrograph (inset of electron diffraction pattern) and (**c**) HRTEM micrograph of brookite particles

Table 1 Mean sizes by XRD of brookite nanoparticles synthesized at different acidities after 24 h or 7 days

$[HNO_3]$ mol L^{-1}	2	2.5	3	3.5	4	5
d (nm) 24 h	10.5	10.2	10.8	–	10.5	9.4
d (nm) 1 week	11.2	10.9	11.5	11.2	10.2	9.7

(Fig. 5b). The elongated ones were identified as rutile as it can be verified on the electron diffraction pattern (inset) and the small ones as a mixture of brookite and anatase. Beautiful rod-shaped particles of rutile are formed with lengths ca. 150 nm and widths ca. 15 nm. The basal face, corresponding to the $[1\bar{1}0]$ planes, is perpendicular to both [110] (*d*-spacing of 3.4 Å) (Fig. 5c) and [001] (*d*-spacing of 2.9 Å) planes (Fig. 5d). The tips of particles are pyramidal with [111] or derivative planes as faces.

In the range $1.5 < [HNO_3] < 5$ mol L^{-1}, brookite is still the main phase after 7 days of thermolysis. Anatase is no more present and seems to have been transformed into brookite because the amounts of rutile (max. 20%) have not changed during aging (the amount of amorphous is negligible). The characterization of brookite has shown that there are a weak increase in size of particles (Table 1) compared to those obtained after 24 h of thermolysis. This may be related to the disappearance of the anatase particles, which would contribute to the small increase (Oswald's ripening) of the size of brookite.

Discussion

These results show the very strong influence of the acidity on the formation of anatase, brookite and rutile varieties of

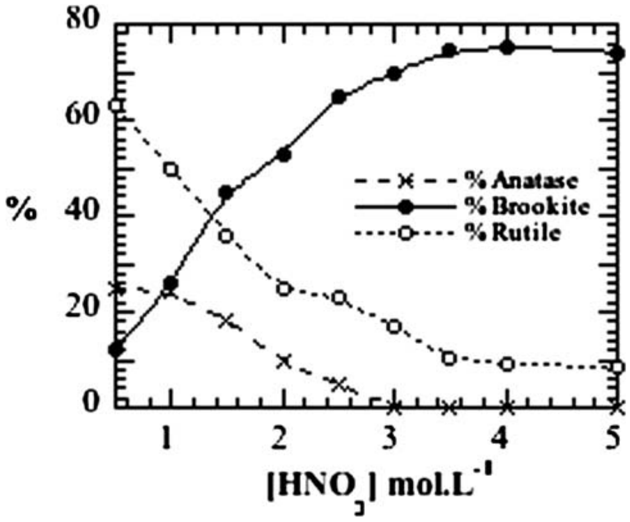

Fig. 4 Relative proportions of the titanium species for $[Ti] = 0.15$ mol L^{-1} after thermolysis of 7 days at 95 °C

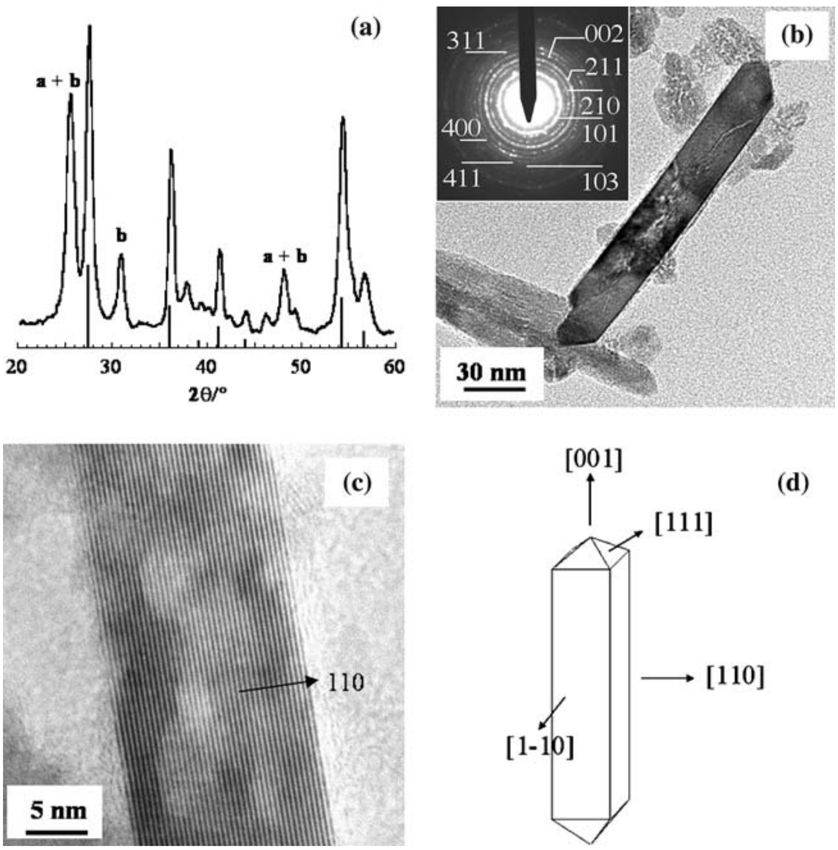

Fig. 5 (**a**) XRD pattern (i) of the particles synthesized for $[HNO_3] = 1$ mol L^{-1} after 7 days of aging at 95 °C (a is for anatase, b for brookite and r for rutile) and (ii) JCPDS rutile reference (21–1276). (**b**) TEM and (**c**) HRTEM micrographs of rutile rod (inset of electron diffraction pattern). (**d**) scheme of a rutile particle with the exposed faces

titanium oxide nanoparticles. The nature of the acid plays also a major role on the distribution of the different phases. At low acidity ($[HNO_3] \approx 1$ mol L^{-1}), anatase is the main phase after 24 h of thermolysis but rutile becomes the predominant phase after a week of thermolysis. For a weak acidity, the precipitation is fast (a white turbidity appeared in the early time of the reaction) and the solid formed is quasi-amorphous. By aging the suspension for few hours, anatase and a small amount of brookite crystallized [19]. Anatase, the least stable phase, is mainly obtained. Statistically, this phase is much easier to form than the rutile. Indeed, if we consider the formation of the dimer $[Ti_2(OH)_8(OH_2)_2]^0$ (2 octahedra sharing an edge) from the initial zero charge precursor $[Ti(OH)_4(OH_2)_2]^0$, the probability to grow a trimer with bent links (anatase structure) is higher than the one for linear links (rutile structure). During aging, under these conditions of low acidity and thus of low solubility, the phenomenon of dissolution-crystallization is slow and thus the rutile (the thermodynamically stable phase) is formed in small quantity after 12 h; the anatase phase is a transient stage which is stabilized under these conditions. Precipitation of the still soluble titanium occurs progressively during thermolysis and leads to rutile, while dissolution–crystallization process induces partial transformation of anatase into rutile with an increase of particles size. In comparison, anatase totally disappears after 48 h of thermolysis in hydrochloric acid, whatever the HCl concentration. At strong acidities ($[HNO_3] \geq 3$ mol L^{-1}), brookite remains the main phase even after a week, what confirms that brookite is well stabilized and no recrystallization into rutile is involved.

These results highlight the role of anions on the crystallization of TiO_2, in conjunction with acidity. In similar conditions (concentration of titanium and acid), aging of suspensions in the presence of perchloric acid leads exclusively to rutile [34]. With hydrochloric acid, the formation of brookite or rutile is strongly dependent on the Cl/Ti ratio. brookite was obtained when $2 < [HCl] < 4$ mol L^{-1}($17 < Cl/Ti < 34$) and rutile is the main phase when $[HCl] > 4$ mol L^{-1}. The high solubility of titanium in hydrochloric acid is also an important point [34]. The proportion of brookite with acidity do not vary significantly between 2 and 5 mol L^{-1} in nitric acid. This specificity of the nitric medium to stabilize the brookite likely results from a low solubility of TiO_2 (at the difference of chloride medium) (Fig. 6) and an ability to complex the Ti(IV) cation. Nitrate ions are obviously much less complexing than chloride and there are only scarce data on the role of nitrate as ligand and thus its possible role in the formation of brookite. Nabivanets [40] showed the existence of cationic complexes of titanium, without identifying them, for an

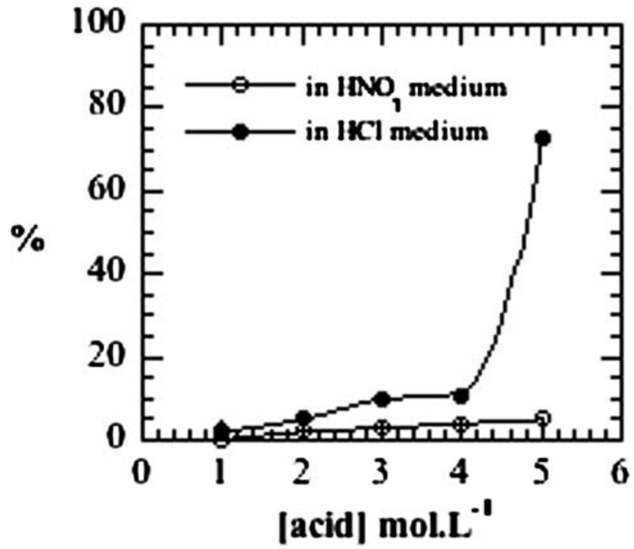

Fig. 6 Fraction of titanium soluble species after 24 h of thermolysis of $TiCl_4$ in HNO_3 and HCl

acidity going up to $[HNO_3] = 11$ mol L^{-1}. However, the compound $TiO(NO_3)_2$ has been isolated in the study of the solubility of titanium hydroxide in HNO_3 [41]. One may assume that in concentrated nitric acid medium, complexes such as $[Ti(OH)_a(NO_3)_b(OH_2)_{6-a-b}]^{(4-a-b)+}$ gives the non charged species $[Ti(OH)_2(NO_3)_2(OH_2)_2]^0$ during thermolysis. This last species could act as precursor for brookite, according to the reaction pathway previously proposed in chloride medium involving the $[Ti(OH)_2Cl_2(OH_2)_2]^0$ complex [34]. The very low solubility of TiO_2 in nitric acid (Fig. 6) avoids dissolution–crystallization phenomena very often involved in crystalline transformation and growth of particles by Ostwald's ripening [42]. In agreement with this, brookite is stable against recrystallization into rutile and particle size does not evolve during aging.

Conclusion

The nature of counter ions appears to be a major and determinant factor, with acidity, on the synthesis of titanium dioxide polymorphs. Even if the nitrate ions are known to be poorly complexing towards the metal cations, they play a central role to obtain the different polymorphs of TiO_2. In this way, spherical particles of anatase, platelets of brookite and rod-shaped rutile particles with nanometric size can be easily obtained.

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