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Influence of solution concentration on the hydrothermal preparation of titania crystallites

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Nano/micro-sized titania powders were prepared by a hydrothermal method using an aqueous solution of $TiCl_4$ as precursor. The influence of the concentration of the aqueous $TiCl_4$ solution on the formation, phase, morphology, and grain size of the products was investigated at various reaction temperatures and times. Increasing the concentration of $TiCl_4$ favored the formation of rutile type TiO_2. When $[TiCl_4] < 0.5\ \mathrm{mol\ dm^{-3}}$, the products were a mixture of rutile type and anatase type powders, the percentage of rutile type powders in all crystalline products varied with reaction time. When $[TiCl_4] = 0.5\ \mathrm{mol\ dm^{-3}}$, the product was a pure rutile type powder. The powder size was related to the concentration based on the nucleation and growth theory of supersaturated solutions. A growth unit model was proposed to explain the phase formation.

Introduction

Recently, nanocrystalline materials have attracted increasing attention in the scientific community because of their wide applications in pigments, solar cells,[1] semiconductors,[2] *etc.* Titanium dioxide powders with a rutile structure are the most widely used because of their high refractive index, tinting strength, and inert chemical properties. The anatase form is preferred for titania membrane applications in dye-sensitized titanium oxide solar cells. Thus, the crystallographic phase of nanocrystalline titanium dioxide is of great importance from the viewpoint of potential applications.[3]

It has been found that the precursor species used for the hydrothermal reaction and the pretreatment method have a special relationship with the crystallographic phase of the powders obtained. Oguri *et al.* pioneered the processing of anatase powders using the hydrothermal technique to crystallize hydrous titania derived from alkoxides.[4] Other researchers have studied the influence of water content, time and temperature on the hydrothermal crystallization of anatase from hydrous titania.[5,6] Bacsa *et al.* investigated the hydrothermal crystallization of unpeptized and peptized titania sols and found that hydrothermal processing of unpeptized titania precipitated from alkoxide formed a highly crystallized anatase powder in all cases.[3] However, when the precursor was peptized, *i.e.*, precipitates were redispersed in nitric acid and refluxed to obtain transparent sols, varying amounts of rutile powders were obtained together with anatase powders from ethoxide and isopropoxide whereas the powder from *tert*-butoxide showed only an anatase phase.[3] Cheng *et al.* studied the preparation of uniform nanosize rutile and anatase particles by the hydrothermal method using titanium tetrachloride as precursor, and made the conclusion that high acidity and concentrations of titanium tetrachloride solution favor the formation of a rutile phase, whereas solutions with pH values in the range of 3.4 to 8.2 favor the anatase phase.[7] Wang *et al.* prepared nanosize anatase powders from a mixture of titanium tetrachloride and sulfuric acid solutions.[8]

The aim of the present work is to research the influence of the concentration of the $TiCl_4$ solution, from $0.05\ \mathrm{mol\ dm^{-3}}$ to $4.0\ \mathrm{mol\ dm^{-3}}$, and reaction temperature and time on the formation, phase, morphology and particle size of titania powders formed by a hydrothermal route.

Experimental

Hydrothermal synthesis of titania crystallites

Titanium tetrachloride was added slowly into ice water with stirring to prepare an aqueous $TiCl_4$ solution. The concentration of the $TiCl_4$ solution was determined by gravimetric analysis. The concentration of $TiCl_4$ in the precursor was varied from $0.05\ \mathrm{mol\ dm^{-3}}$ to $4.0\ \mathrm{mol\ dm^{-3}}$. The feedstock of 30 mL was charged into a 43 mL Teflon-lined stainless steel autoclave which was then placed in a heated furnace maintained at the desired temperature (between 100 and 300 °C). The autoclave was kept in the furnace for a set time interval and then removed to be cooled in water.

XRD and TEM characterizaton

After the autoclave was cooled to room temperature, the product was allowed to stand for 12 h and then filtered, after removing the supernatant, washed with deionized water, and dried at 110 °C. The prepared TiO_2 powders were analyzed by X-ray diffraction (XRD) using Cu-Kα radiation (XRD, RAX-10, JAPAN RIGAKU) to determine the phase of the crystalline powders. The contents of the rutile and anatase phases were determined semiquantitatively from the XRD spectra by measuring the height of the (110) peak of rutile and the (101) peak of anatase. The morphology of the powders was observed using transmission electron microscopy (TEM, JEM-2010, JEOL). Where required electron diffraction (ED, JEM-2010, JEOL) of selected crystallites was used to specify rutile and anatase phases.

Results

Titanium dioxide has three crystalline forms: rutile, anatase and brookite. Titanium dioxide powders prepared by the hydrothermal method can have different crystal structures and various morphologies, depending on the hydrothermal condi-

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tions used, which would influence the composition and structure of the Ti(IV) complex ion in hydrothermal solution.

The phase composition characterized by XRD

Influence of concentration. The phase composition depends on the concentration of the $TiCl_4$ solution when the hydrothermal process is carried out at 200 °C for 24 h. When [$TiCl_4$] is less than 0.5 mol dm^{-3}, the crystalline phases are a mixture of rutile and anatase. The content of the rutile phase increased with $TiCl_4$ concentration (as shown in Fig. 1). When the concentration is increased to 0.5 mol dm^{-3}, the products consist of only the rutile phase. However, when the concentration is 1.0 mol dm^{-3}, a small amount of brookite phase is found in the product. However, when the concentration is 2.0 or 4.0 mol dm^{-3}, again only the rutile phase product is observed.

Influence of reaction time. Crystallizing time also influences the phase composition of the products. Taking 0.3 mol dm^{-3} $TiCl_4$ solution as an example, the rutile phase content varies with increasing crystallizing time (see Fig. 2). When the solution is crystallized for 6 h, the rutile phase content is lowest, then it rises with prolonged crystallizing time. Using the 0.1 mol dm^{-3} $TiCl_4$ solution, the rutile phase content also rises with prolonged crystallizing time, reaching 97% after 44 h of reaction.

Influence of reaction temperature. The effect of reaction temperature, or so-called crystallizing temperature, on the phase composition of the products has also been investigated. Taking a 0.3 mol dm^{-3} $TiCl_4$ solution as an example, crystallizing times of 12 h and 24 h were selected. In the 24 h reactions, the rutile phase content in the crystalline product is found to increase with increasing crystallizing temperature (shown in Fig. 3). However, in the 12 h reactions, the rutile phase content in the reaction at 250 °C is slightly less than that at 200 °C.

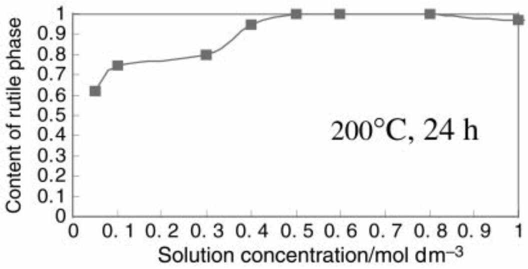

Fig. 1 The rutile phase content in the hydrothermal products obtained using different concentration $TiCl_4$ solutions as precursors.

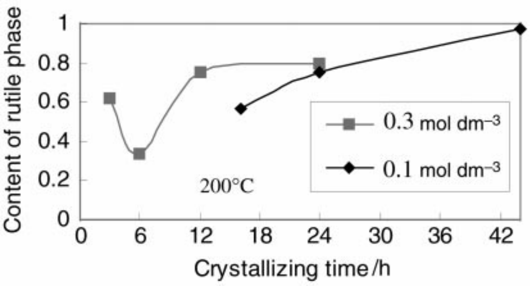

Fig. 2 The rutile phase content in the hydrothermal products obtained after various crystallizing times.

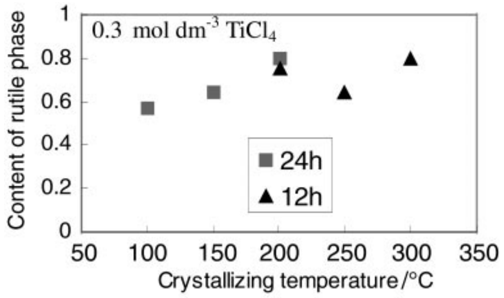

Fig. 3 The rutile phase content in the hydrothermal products obtained using various crystallizing temperatures.

The product morphologies characterized by TEM

Character of products prepared from different concentration solutions. From the TEM observation, it is shown that crystallites of the rutile phase are apt to grow into long prisms when the concentration of the $TiCl_4$ solution is greater than 0.3 mol dm^{-3} (shown in Fig. 4). In Fig. 4(a), the majority of the crystallites are prisms of rutile phase, while a few crystallites are small spheres of anatase phase. In Figs. 4(b) and 4(c), all crystallites are rutile phase and prism-like. The growth habit of rutile crystallites under hydrothermal conditions has been reviewed elsewhere.[17] The crystallites of anatase phase grow as polyhedrons and are much smaller in size than those of rutile phase in most cases.

Contrast of products with increasing reaction time. For the 0.1 mol dm^{-3} $TiCl_4$ solution, the morphology of the crystallites changes greatly with increasing time. As shown in Fig. 5, the crystallites are small short columns after 16 h of crystallization, including both rutile and anatase crystallites (Fig. 5(a)); some crystallites grow to be large polyhedrons (identified to be the rutile phase by ED) after 24 h of crystallization, the others retain their sizes and shapes (identified to be anatase) (Fig. 5(b)); over 44 h of crystallization, the majority of crystallites grow to be large rutile polyhedrons (Fig. 5(c)). For the 0.3 mol dm^{-3} solution, the morphological differences of the products with increasing reaction time are not so obvious.

The average crystallite sizes

From the above TEM micrographs, it can be found that the crystallite sizes vary with the concentration of $TiCl_4$ used. In order to determine the relationship between crystallite size and solution concentration, the lengths of the crystallites were measured directly from the TEM micrographs (here, the largest size of a particle is taken as its length). A total of 300 crystallites were measured in several fields of TEM view to obtain the average size of a sample. The arithmetic average is taken as the average size. Fig. 6 shows the average sizes of crystallites of the products crystallizing from solutions of different concentrations after 24 h reactions at 200 °C. When [$TiCl_4$] is 0.1 mol dm^{-3}, the rutile crystallites are much larger than the anatase crystallites. When [$TiCl_4$] is raised to 0.2 mol dm^{-3}, the lowest average size crystallites are obtained. After this point the average crystallite size increases with $TiCl_4$ concentration. The curve of crystallite growth kinetics is shown in Fig. 7. It is seen that the average crystallite size has a logarithmic-like relation with crystallizing time.

Discussion

A formation model for titania polymorphs

From the viewpoint of energy, the driving force for this hydrothermal crystallization reaction is the free energy

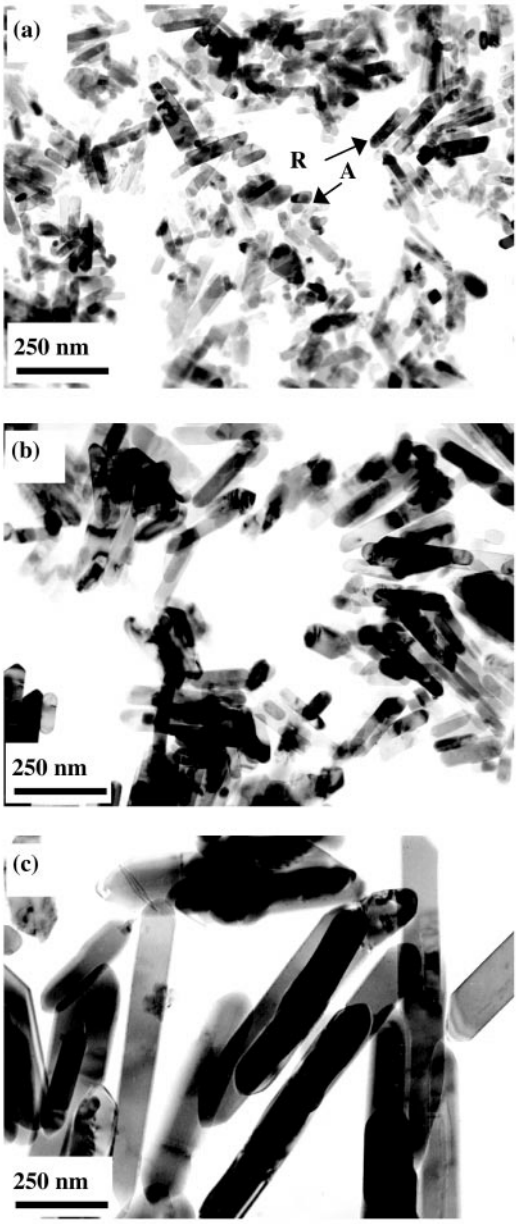

Fig. 4 TEM micrographs of the hydrothermal reaction (24 h reaction at 200 °C) products of (a) 0.4 mol dm^{-3} $TiCl_4$, containing rutile phase (labeled as R) and anatase phase (labeled as A), (b) 0.8 mol dm^{-3} $TiCl_4$, pure rutile phase, and (c) 4.0 mol dm^{-3} $TiCl_4$ solutions, pure rutile phase.

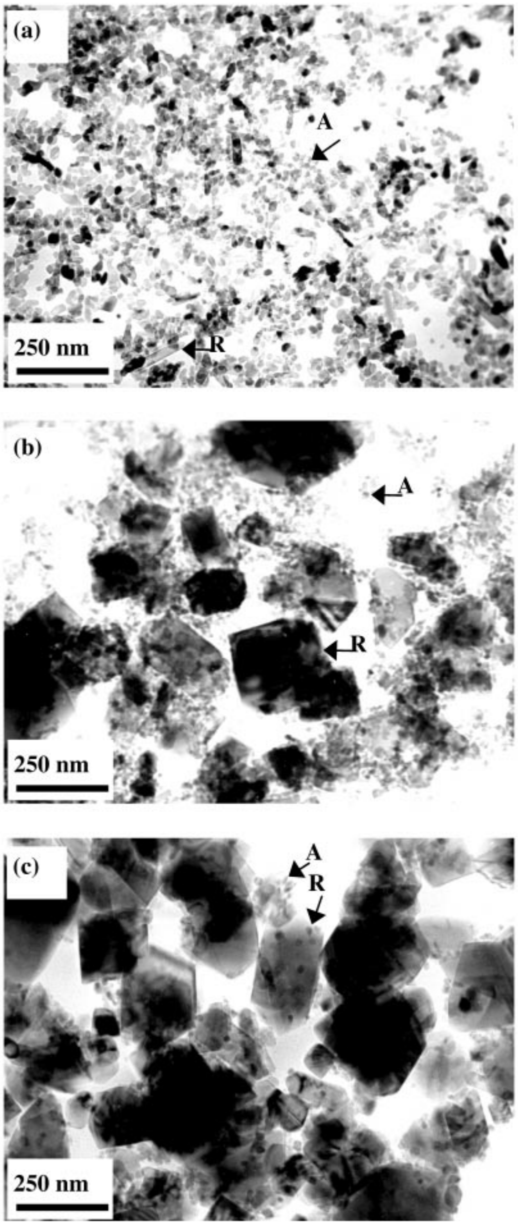

Fig. 5 TEM micrographs of the hydrothermal crystallization products of 0.1 mol dm^{-3} $TiCl_4$ solution after (a) 16 h, (b) 24 h and (c) 44 h reaction at 200 °C. The rutile and anatase phases are indicated with arrows, R representing rutile and A representing anatase phases.

difference generated by the relative supersaturation which occurs on increasing the temperature from room temperature to hydrothermal temperatures. Adair *et al.* have shown that the solubility of zirconia in hydrothermal systems is decreased with increasing hydrothermal temperature.[9] From the similarity of titania and zirconia, it can be assumed that titania has a similar solubility–temperature relationship. Hence, the formation of titania here obeys a dissolution–precipitation mechanism. Here we will discuss the microscopic model from a molecular level.

In aqueous $TiCl_4$ solution, Ti(IV) doesn't exist in the form of the Ti^{4+} cation, but exists as a six-fold coordinated monomer: $[Ti(OH_x)_6]^{(8-6x)-}$, which can form polynuclear complexes by olation or oxolation depending on the concentration of the solution. Hildenbrand *et al.* investigated 2.17, 3.39 and 4.98 mol dm^{-3} aqueous $TiCl_4$ solutions and revealed that corner-sharing titanium–oxygen octahedral dimers and trimers exist in solution.[10]

A microscopic formation procedure is proposed to explain the polymorphs partition behavior here, described as follows: (a) At room temperature, a low concentration $TiCl_4$ solution contains a large amount of disperse octahedral $[Ti(OH)_2(OH_2)_4]^{2+}$ monomers or edge-sharing dimers. As the concentration rises, the Ti(IV) species exist in another form, $[TiO(OH)_5]^{2+}$.[11,12] (b) When the temperature rises to the

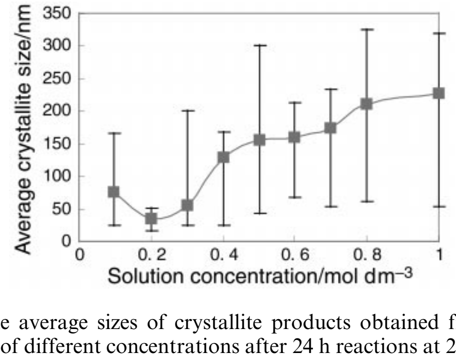

Fig. 6 The average sizes of crystallite products obtained from $TiCl_4$ solutions of different concentrations after 24 h reactions at 200 °C. The error bars indicate the range of size distributions.

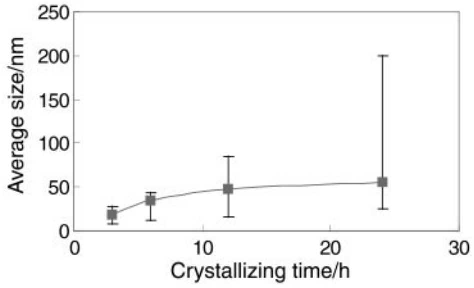

Fig. 7 The relationship between the crystallizing time and the average sizes of crystallites obtained from 0.3 mol dm^{-3} $TiCl_4$ solutions after hydrothermal reaction at 200 °C. The error bars indicate the range of size distributions.

reaction temperature, the solution is in a saturated state, the species in solution are unstable and prone to combine together through oxolation or olation, forming original nuclei. As these nuclei grow to exceed the critical nuclei size they become stable and further growth continues. During the formation of original nuclei, the $[Ti(OH)_2(OH_2)_4]^{2+}$ monomers can form different structures of polymers by sharing equatorial or apical edges, while the $[TiO(OH)_5]^{2+}$ monomers can only form linear chain polymers by sharing equatorial edges[13] (as shown in Fig. 8). Bearing the structures of the titania polymorphs in mind, it is obvious that linear chains can only form rutile type nuclei, while skewed chains can only form anatase type nuclei. The nuclei then grow to rutile and anatase type crystallites, respectively. In high concentration solution ($[TiCl_4] > 0.4$ mol dm^{-3}), only rutile crystallites are developed because only rutile type nuclei exist in the solution. (c) In the prolonged reaction, anatase crystallites grow larger and larger and become unstable relative to the rutile phase, which is, as known, more stable than the anatase phase.[14] Anatase crystallites then migrate and align themselves and undergo an *in situ* rearrangement of the lattice, transforming to larger rutile crystallites.

Based on the above microscopic model, the experimental results can be easily explained. As shown in Fig. 1, pure rutile crystallites crystallize from 0.5–0.8 mol dm^{-3} $TiCl_4$ solutions, this can be explained by the fact that in those solutions only linear chains of polymers exist. As for 0.1 mol dm^{-3} solution, from the XRD and TEM characterization results, it can be concluded that procedure (c) occurs in the prolonged reaction, in which small anatase crystallites transform to huge rutile polyhedral crystallites. The influence of the hydrothermal reaction temperature may be due to its effect of increasing the growth rate of crystallites, which is, to some extent, equal to lengthening the reaction time except that higher temperatures favor the formation of the more stable phase.

In the crystallization process, anatase type crystallites seem to form earlier than the rutile type, but when the rutile type crystallites begin to crystallize, the former seem to be inhibited or even transform to rutile type crystallites. This conclusion can be deduced from Fig. 2.

The relationship between the crystallite size and the supersaturation ratio

Considering the growth rate of nanosize crystallites from solution for low supersaturation solutions ($\sigma < \sigma_1$), volume diffusion is the rate determining step, so a second parabolic law is obtained according to Bennema,[15]

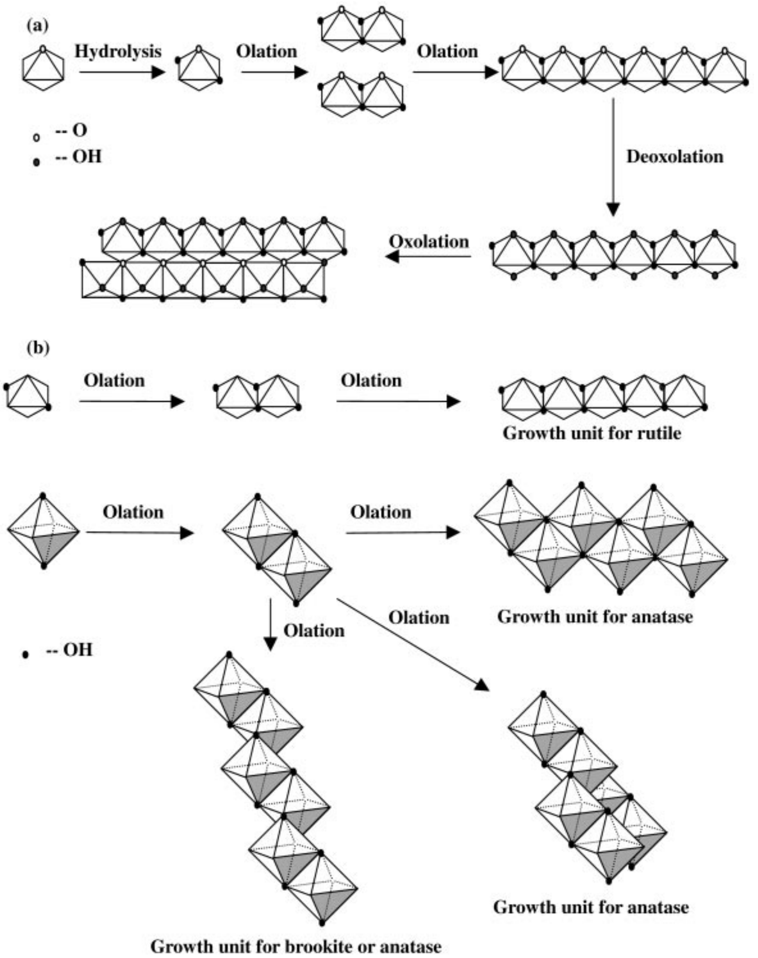

Fig. 8 A possible condensation pathway for the titania nuclei of rutile, anatase or brookite type nuclei starting from octahedral cations $[TiO(OH_2)_5]^{2+}$ and $[Ti(OH)_2(OH_2)_4]^{2+}$.

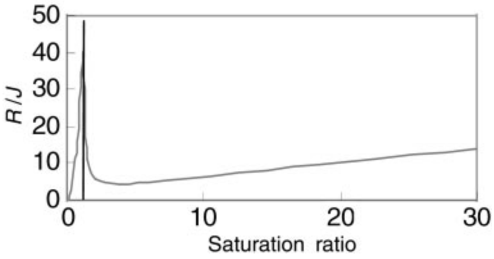

Fig. 9 The relationship between the ratio of growth rate to nucleation rate *R*/*J* and the saturation ratio in a solution growth system.

$$R = C'\sigma^2$$

For high supersaturation solutions ($\sigma > \sigma_1$), surface diffusion is the rate determining step, so a linear law is obtained as follows:

$$R = C\sigma$$

The nucleation rate can be deduced as:[16]

$$J = K_1 R\sigma^{-3/2}(\ln\sigma)^2$$

In the above equations, C', C and K_1 are constants of a determined system. Thus, whether the growth rate obeys the second parabolic law or the linear law, the ratio of the growth rate to the nucleation rate is,

$$R/J = K_1^{-1}\sigma^{-3/2}(\ln\sigma)^{-2}$$

While $\sigma > 3.79$, the ratio *R*/*J* increases monotonously *versus* σ. When the concentration of the solution is increased, the saturation ratio rises, thus both the growth rate and nucleation rate rise. But when the saturation ratio rises, the growth rate increases more quickly than the nucleation rate. Then the crystallites are precipitated from solution, the saturation ratio decreases, and so the growth rate and nucleation rate are reduced. Until the saturation ratio is decreased to a value near to one, the growth and nucleation of crystallites stop. Therefore, the mean size of the crystallites increases with the saturation ratio or concentration of the solution when the saturation ratio is higher than 3.79 (shown in Fig. 9). Of course, this is just an approximate treatment of the complex question of multiple crystallite growth.

Conclusions

The crystalline phase of titania prepared by a hydrothermal route is found to be influenced by the concentration of the $TiCl_4$ precursor solution and, in some cases, by the reaction time. A formation model is proposed for titania polymorphs and used to explain the experimental results.

The relationship between the crystallite size and solution concentration is explained by a semiquantitative equation deduced from the solution nucleation and growth theory.

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