JOURNAL OF
Materials
CHEMISTRY

Formation of uniform size anatase nanocrystals from bis(ammonium lactato)titanium dihydroxide by thermohydrolysis

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Received 5th July 1999, Accepted 13th September 1999

Bis(ammonium lactato)titanium dihydroxide decomposes in neutral aqueous solution at temperatures above 100 °C to produce anatase nanocrystals of preferentially oblate habitus, and with a very narrow size distribution. There is almost no dependence of size on precursor concentration, and a time dependence is observed only in the very beginning of crystal growth. The crystal size is mainly determined by the reaction temperature, increasing from *ca.* 2 nm at 120 °C to about 20 nm at 300 °C. We assume the temperature dependent formation of a layer of byproduct ammonium lactate at the crystallite surface where it interferes with growth reactions. After removal of this layer, continued heating yields larger crystallites in typical anatase shapes, indicating that Ostwald ripening has now become effective.

Introduction

Nanocrystalline TiO_2 can be prepared in various ways. One of the most common is hydrolysis and polycondensation of titanium tetraalkoxides (*e.g.* isopropoxide) or $TiCl_4$.[1–10]

We have found bis(ammonium lactato)titanium dihydroxide (ALT) to be an interesting and quite convenient starting material in TiO_2 crystallite synthesis. Recently, ALT has also been mentioned as a new base material in preparing catalysts,[11] in making electrodes for medical treatment and diagnosis,[12] and in generating UV-protective films on various surfaces.[13] While titanium alkoxides hydrolyse rapidly, ALT is stable at ambient temperature in neutral solution. Aqueous NaOH decomposes ALT to yield TiO_2, NH_3 and sodium lactate. High pH hydrolysis of ALT is slower and more easily controlled than titanium alkoxide decomposition. We will report on this reaction elsewhere.[14] Acid decomposition of ALT has recently been described by Baskaran *et al.*[13]

Thermohydrolysis of ALT appeared particularly interesting since preliminary experiments yielded good, almost monodisperse nanocrystals. Nanocrystalline TiO_2 having well defined size and narrow size distribution would be desirable for making thin films. The present work was carried out in order to investigate the possible influence of various experimental parameters (concentration of precursor ALT and of byproduct ammonium lactate, temperature and time exposed to high temperature) on crystal growth and size distribution. The products were analyzed using transmission electron microscopy (TEM).

Experimental

ALT is available (Aldrich) as a 50% (w/w) aqueous solution (ALT50). It was used as received or diluted as necessary with de-ionized water. [ALT, $M = 294.12$; ALT50, $d = 1.222$ kg L^{-1}, $C = 2.08$ mol L^{-1}]. Ammonium lactate (HAL) was obtained (Aldrich) as a 20% aqueous solution [HAL, $M = 107.11$, $d = 1.054$ kg L^{-1}].

Thermal decomposition experiments up to 300 °C were performed in sealed glass ampoules, or, in a few cases, in a 15 mL titanium autoclave at higher temperature. A sealed ampoule was placed in an empty HPLC column, 125 × 20 mm SS (pressure tube). The tube was filled with water and pressurized by an HPLC pump (Knauer 64), using a discarded HPLC column (250 × 4 mm, 5 μm packing) or a sufficient length of 0.1 mm I.D. capillary as a restrictor. The pressure was adjusted *via* the flow rate to a value above the vapor pressure of water at the desired temperature. The pressure tube was suspended vertically in an adjustable temperature oven, and heated to 200 °C within 15 min. During heating and cooling periods, strong pressure changes occur due to the thermal expansion behaviour of water. To avoid ampoule cracking, these changes were compensated for by manually adjusting the flow rate. Ampoules from high temperature (~250–300 °C) reactions have to be opened cautiously because the internal pressure might be very high due to secondary reactions.

HPLC tests were performed on a 250 × 4 mm ODS column (Nucleosil 10 μm grain, 10 nm pores) with MeOH–H_2O (80 : 20) eluent and UV detection at 254 nm.

In some experiments, organic components were removed from the product. An aqueous solution of ALT (0.415 mol L^{-1}) was heated to 260 °C for 24 h. The product was centrifuged and the liquid decanted. The precipitate was washed using ultrasound and centrifugation, first with diluted NH_3 and methanol in water, then with water.

For yield determination, samples were ultrasonically treated for maximum homogeneity. Aliquots of 50 μL were dried at 100 °C, then baked at 300 °C for 19 h and, after weighing, at 400 °C for another 19 h. There was no further weight decrease after the 300 °C treatment, indicating that all organic material had been removed.

The TiO_2 samples were examined using a Philips CM12 (accelerating voltage 120 kV) electron microscope equipped with a super twin lens and EDAX analyzer. High resolution images were taken using a slow scan CCD camera under Scherze defocus conditions.[15] For the HRTEM studies the sample was adsorbed on electron microscopic grids coated with a very thin (50 Å) amorphous carbon film.

Results

General

Under mild reaction conditions (0.153 g ALT mL^{-1}, 200 °C for 3 days) there was no indication of new compounds being formed except for TiO_2 and probably ammonium lactate. In particular, no new absorptions were seen in the UV-VIS spectrum, except for some transmission decrease due to scattering. A yield determination gave 90% of what was expected from the reaction ALT→$TiO_2 + 2$ HAL. Considering losses through washing of precipitate, this value indicates complete conversion.

At high reaction temperatures (>250 °C) an additional organic layer is formed. The byproducts smell like pyridine derivatives; preliminary HPLC tests showed the formation of at least six polar aromatic compounds, absorbing strongly at 254 nm and eluting well ahead of reference phenyl alkanes.

Influence of precursor (ALT) concentration

The precursor concentration dependence of nanocrystal formation was investigated at 200 °C in 72 h runs. The experimental range was 2.08 mol L^{-1} through 2.08×10^{-3} mol L^{-1} in aqueous solution. As can be seen from the TEM pictures [Fig. 1(a)], we obtained the same average crystal size of 5 nm throughout the whole ALT concentration range.

The only change observed was a distinct yield increase at higher concentrations, as estimated from the height of the precipitate layer in the reaction tube. No real quantification was attempted. The particles all appear very similar. In electron diffraction experiments they show Debye–Scherrer rings characteristic of the anatase modification of TiO_2. Some single particles from different concentrations of ALT imaged by high resolution TEM are shown in Fig. 1(b).

The most frequently observed crystal contours are close to hexagons and squares. The narrow size distribution appears to be typical for anatase crystals made by thermohydrolysis of neutral ALT solutions. Many experiments yielded products looking practically monodisperse.

Several tests at higher temperatures and different initial concentrations confirmed the negligible influence of the precursor concentration on the crystal size.

Influence of reaction time

The time dependence of the growth of anatase nanocrystals from ALT solution was investigated in four sets of experiments:

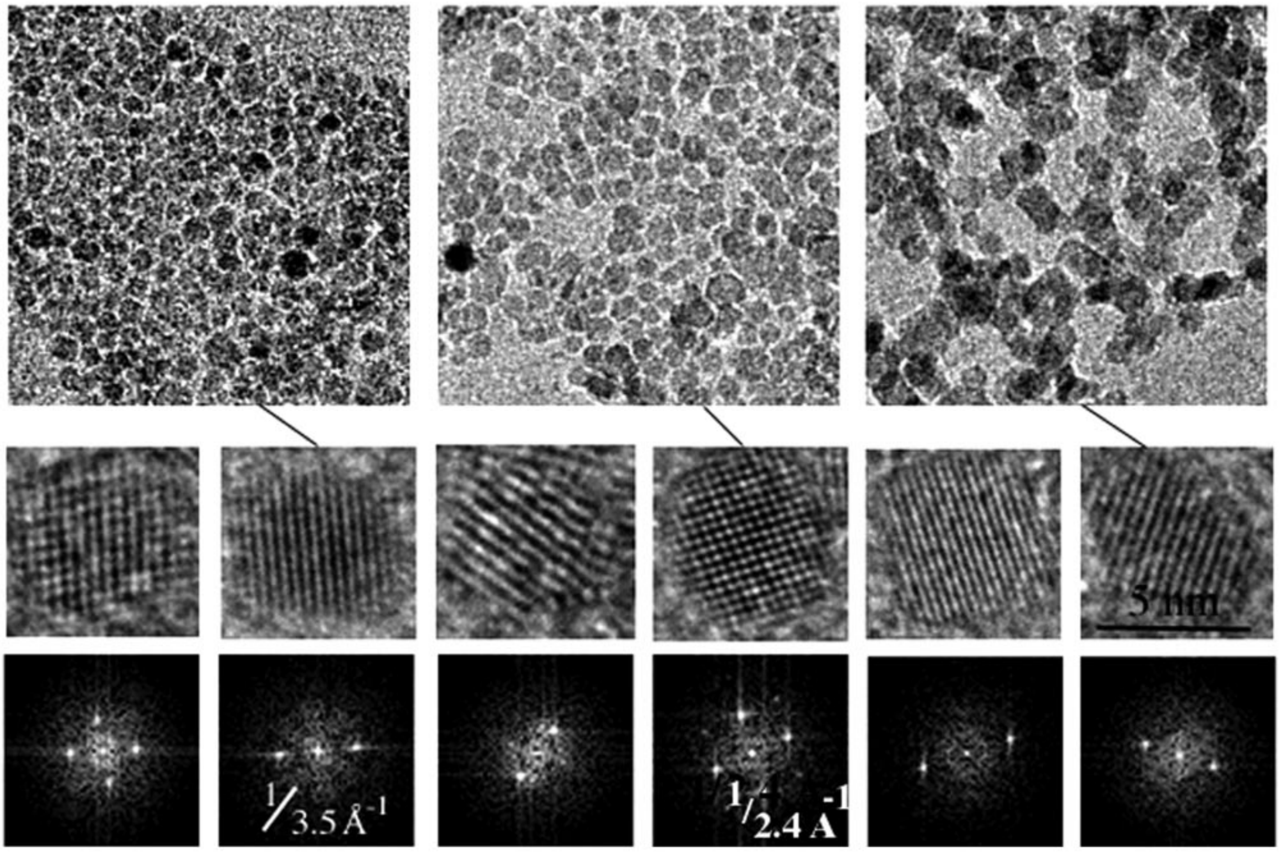
(1) undiluted ALT50 at 200 °C, from 3 h to 3 d,
(2) 1 : 5 diluted at 250 °C, from 2 h increasing in 2 h steps,
(3) 1 : 5 diluted at 200 °C, 1 day and 10 days,
(4) 1 : 5 diluted at 300 °C, 1 day and 6 days.

In set (1), the particle size increased slightly from about 3 nm after 3 h to 5 nm. Set (2) showed that growth is practically complete after ~4 h at 250 °C. From sets (3) and (4) it was found that, after 1 day, 300 °C crystals are larger than 200 °C crystals, but no further growth was seen for longer time periods. After a relatively short initial period, the reaction time seems to be less important in the growth of anatase nanocrystals from ALT.

Influence of reaction temperature

The influence of the temperature on crystal growth was measured by heating 1 : 5 diluted ALT50 solutions (0.415 mol L^{-1}) for 24 hours at various temperatures from 120 °C to 300 °C. The crystal size increases non-linearly with increasing temperature, as can be seen from the TEM pictures in Fig. 2(a) and HRTEM images in Fig. 2(b). Fig. 3 shows the size–temperature dependence as a continuous curve over the investigated range.

In preliminary experiments at very high temperature (around 400 °C) in a titanium autoclave we observed large crystals with



Concentration 1 0.5 0.25 0.1 0.01 0.001

Fig. 1 (a) Typical low magnification TEM images of TiO_2 particles produced at different ALT concentrations of 1.04, 2.08 and 2.08×10^{-3} mol L^{-1}. (b) High resolution TEM images of single particles of TiO_2 with the corresponding powder spectra. The characteristics for orientations (*hkl*) 101 and 103 lattice plane distances of 3.5 and 2.4 Å are very well resolved. Concentration factor 1 refers to 2.08 mol L^{-1}.

varying shapes with a wide size distribution. Besides species exhibiting typical anatase forms, characteristic rutile needles were also found.

Influence of byproduct (HAL) concentration

The influence of HAL concentration was tested in three experiments. 1 mL ALT50 was mixed with 4 mL of 20% ammonium lactate solution, so that the sample was about 0.4 mol L^{-1} in HAL. After heating at 250 °C for 24 h, the crystals formed had the same shape as seen without added HAL, but their size was reduced by almost 50%, indicating that growth is hampered by the presence of HAL.

In order to reduce the HAL concentration at the crystal surface, the second sample (0.415 mol L^{-1} ALT) was brought to pH < 1 with nitric acid before heating. After reaction at 200 °C for 1 d, the pressure in the ampoule was very high, the product brownish. The pH was 5, indicating that the added HNO_3 had been used up. The average crystal size had increased from 5 nm (without acid) to 8 nm.

In the third experiment, water soluble components (HAL and, if present, some unreacted ALT) were removed from the reaction products of a 24 h 260 °C run as described in the experimental section.

Fig. 4(a) shows a suspension of washed nanocrystals in water. HNO_3 (2 M) was added to the suspension pH 1 in order to avoid excessive agglomeration, and the suspension was heated to 260 °C for 5 d. The resulting nanocrystals [Fig. 4(b)] have increased in size and look different. There are new shapes, and the size distribution is wider now, from less than 10 nm to more than 50 nm. Since there was no precursor present in the system, the crystal growth must be due to Ostwald ripening which obviously had been suppressed in the presence of HAL.

The crystal shapes found in the acidified suspension are more

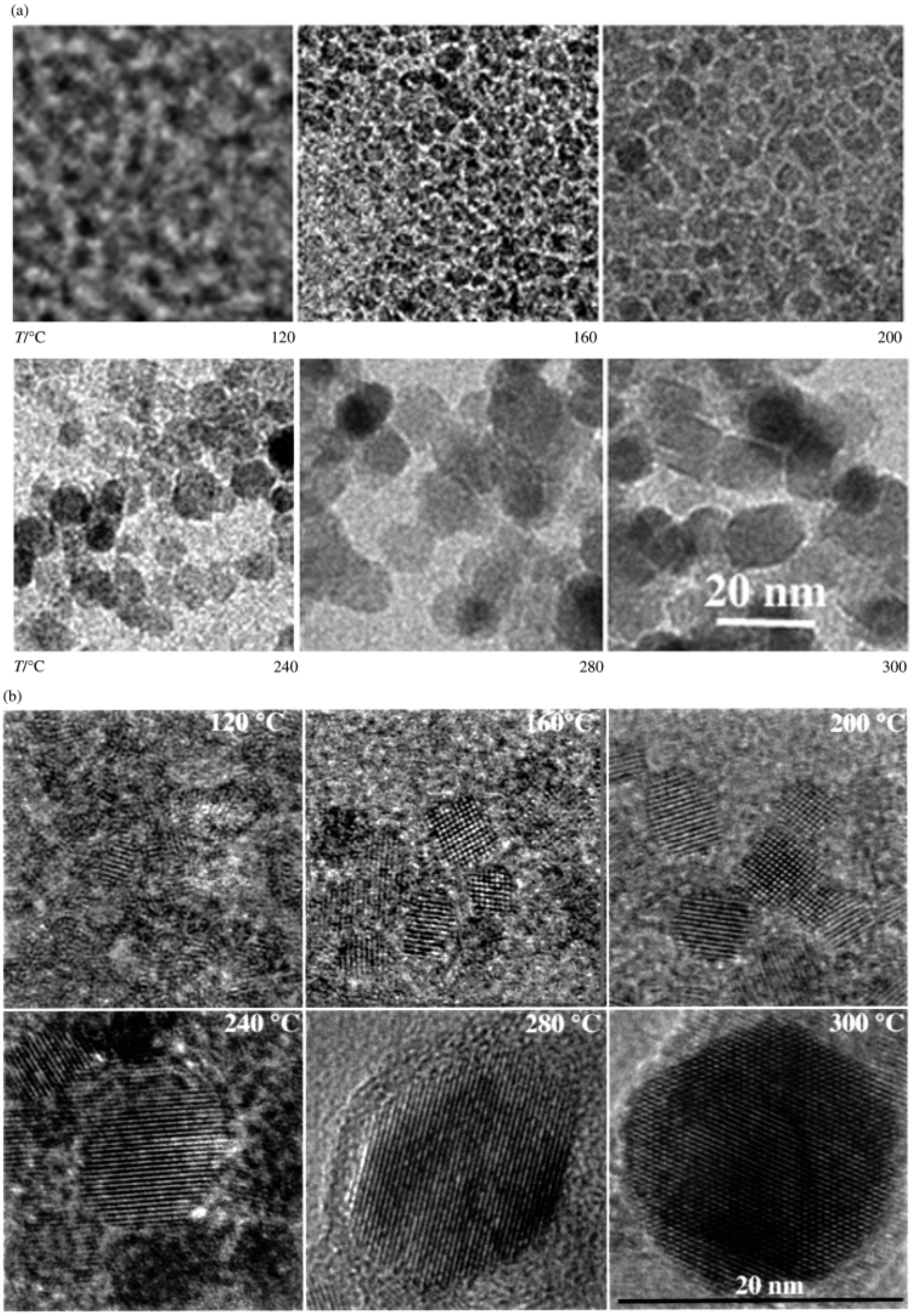


Fig. 2 (a) Low magnification TEM micrographs of TiO_2 prepared at different temperatures as indicated. (b) HRTEM images of the same samples.

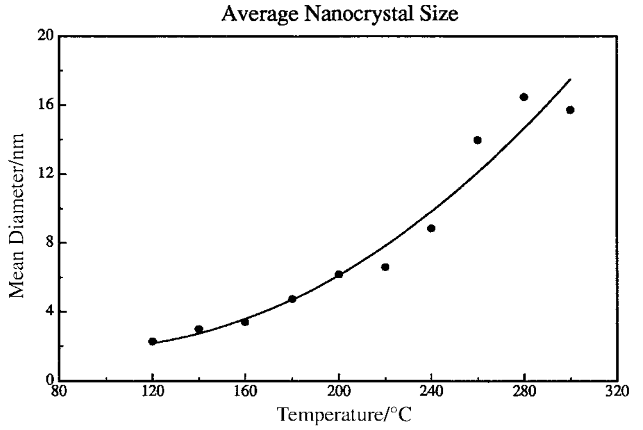


Fig. 3 Dependence of approximate average crystal size (diameter of hexagons and squares) on formation temperature. (ALT in water 0.415 mol L^{-1} heated for 24 h at temperatures as shown).

typical of anatase than those observed in the original ALT solution. The crystal contours are sharp in acid suspension, while they often appear slightly blurred before acid treatment.

Discussion

The high stability of ALT, as compared to Ti alkoxides, towards hydrolytic attack follows from its different structure. ALT is a chelate compound[13] in which all six-coordinate positions of Ti are occupied. Bonding between ammonium and the remainder of ALT should be similar to that in ammonium lactate which is a weak acid/weak base salt. From conductivity data[14] we found that ALT is partly dissociated into an anion plus NH_4^+, but a substantial fraction is not ionized. The structure of that fraction is probably similar to the model shown in Fig. 5.

The addition of chelating or other complexing agents to Ti alcoholate solutions prior to hydrolysis is a well known way to moderate the reactivity or to modify the reaction modes of the titania precursor.[5,8,9,16–19]

The overall reaction of ALT to finally yield anatase is

$$n\mathrm{ALT} \rightarrow n\mathrm{TiO_2} + 2n\mathrm{HAL} \qquad (1)$$

Decomposition of ALT may involve hydrolysis in which the number of chelating ligands is reduced [eqn. (2)]:

$$\mathrm{(AL)(OH)_2Ti{-}AL + H{-}O{-}H \rightarrow (AL)(OH)_3Ti + HAL} \qquad (2)$$

(AL = ammonium lactate radical, CH_3–HC(O$^\bullet$)–$COONH_4$ followed by condensation with another ALT:

$$\begin{aligned}&\mathrm{(AL)(OH)_2Ti{-}OH + HO{-}Ti(AL)_2(OH)}\\&\rightarrow \mathrm{(AL)(OH)_2Ti{-}O{-}Ti(AL)_2(OH) + H_2O} \qquad (3)\end{aligned}$$

or a more direct reaction (4) in which condensation releasing HAL leads to larger sized species:

$$\begin{aligned}&\mathrm{(AL)(OH)_2T{-}AL + HO{-}Ti(AL)_2(OH)}\\&\rightarrow \mathrm{(AL)(OH)_2Ti{-}O{-}Ti(AL)_2(OH) + HAL} \qquad (4)\end{aligned}$$

Subsequent reaction sequences like (5) have a multitude of reaction pathways.

$$\begin{aligned}&\mathrm{2ALT \rightarrow \{Ti_2\} + HAL\{Ti_2\} + ALT \rightarrow \{Ti_3\}}\\&\mathrm{+ HAL\{Ti_3\} + ALT \rightarrow \{Ti_4\}}\\&\mathrm{+ HAL\{Ti_{\mathit{x}}\} + ALT \rightarrow \{Ti_{\mathit{x}+1}\} + HAL}, \mathit{etc.} \qquad (5)\end{aligned}$$

(x, rank of oligomerization)

The third step of the above sequence may be a branching process, giving way to the formation of three-dimensional clusters. In addition, oligomers $\{Ti_x\}$ might react with each other or with growing clusters, according to their concentration. Besides growth reactions by which additional ALT or $\{Ti_x\}$ is incorporated, intramolecular reactions occur forming more oxo bridges[8] and releasing HAL.

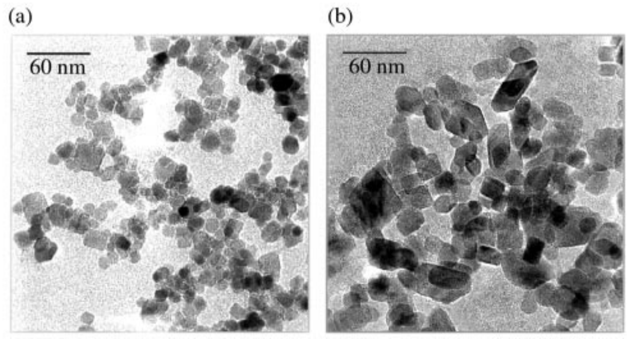


Fig. 4 (a) Low magnification TEM image of washed product from ALT 0.415 mol L^{-1} 24 h at 260 °C. (b) Aqueous suspension of sample from Fig. 4(a) at pH = 1 with HNO_3 heated at 260 °C for 5 days.

The exceedingly complex system of possible reactions is prohibitive for a quantitative treatment of anatase formation from ALT. Instead, a simple descriptive model accounting for the observed effects shall be proposed.

It has been pointed out[9] that coordinative unsaturation of Ti in $Ti(OR)_4$ or similar precursors is the ultimate driving force towards crystalline TiO_2 in which Ti is octahedrally surrounded by oxygen. There is no indication of an activation barrier in these reactions.

The situation is different with ALT thermal decomposition. The starting compound has octahedral coordination and is apparently stable in water at ambient temperature. In reactions (2)–(5) *etc.* the octahedral coordination is successively replaced by less stable surroundings which are probably closer to tetrahedral, as OTi_3 and TiO_4 groups have been identified spectroscopically in growing clusters from $Ti(OPr)_4$.[20] Activation energy has to be supplied for this process. Only the final step of crystallite X formation stabilizes the system.

Necessarily, $2\mathrm{ALT} \rightarrow \{Ti_2\} + \mathrm{HAL}$ is the first step in the formation of X, which does not imply that each $\{Ti_2\}$ finally produces a crystal.

Reactions analogous to (4) build a three-dimensional cluster. Intramolecular reactions successively remove –AL and –OH residues from the cluster core, while on the outside the cluster grows by reacting with ALT and oligomers.

When the core has reached a sufficient size, the Ti and O atoms rearrange to form an anatase crystallite X, the surface composition of which is probably very different from plain TiO_2. Poor crystalline order and a high surface concentration of OH[10,21] as well as residual AL groups are expected, comparable to the composition of the original cluster. Slightly blurred contours of nanocrystal TEM images might be attributed to this outer layer.

A nanocrystal grows by increasing its TiO_2 content:

$$\mathrm{X}_n + \mathrm{ALT} \rightarrow \mathrm{X}_{n+1} + \mathrm{HAL} \qquad (6)$$

Possible reaction of oligomers from (5) will not be considered explicitly at present. In reaction (6), a surface site (–AL or –OH) reacts with one ALT. The concentration of surface sites may be defined as the number of sites per particle

$$[\mathrm{S}] = Cd^2\sigma \qquad (7)$$

where d is the linear size of crystal X; C is a factor converting d^2 into surface area, and σ is the surface density of sites in nm^{-2}.

It has been shown that lactic acid adsorbs strongly at titania surfaces,[22] and HAL has basically the same properties. The ability of HAL to form hydrogen bonds to the –AL and –OH surface sites of the growing crystal X is evident. Adsorption of

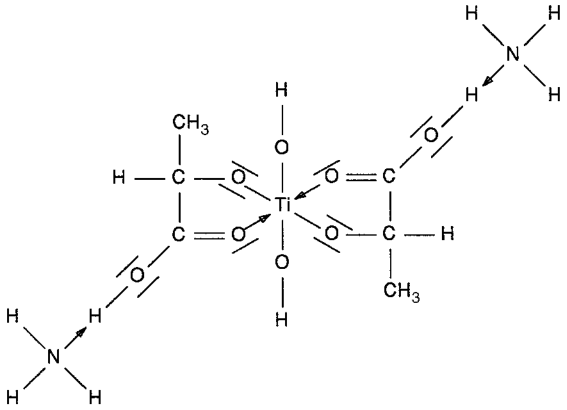


Fig. 5 Assumed molecular structure of non-ionized form of ALT. Arrows indicate donated electron pairs.

HAL makes a fraction α of surface sites inaccessible to reaction with ALT.

The growth rate may then be expressed as

$$\boldsymbol{v}=\boldsymbol{k}(1-\alpha)[\mathrm{S}][\mathrm{ALT}] \quad (8)$$

Experiments show that nanocrystal growth stops at a certain (temperature dependent) size. This effect may be related to surface deactivation *via* HAL adsorption.

HAL is produced in high yield, 2 HAL per TiO_2. The number of HAL molecules emerging from X is

$$n(\mathrm{HAL})=2Dd^3 \quad (9)$$

where D is a factor converting d^3 into the number of TiO_2.

The smallest identifiable anatase nanocrystals obtained from ALT solution have a size of about 2 nm and, to a rough approximation, a volume of 8 nm^3, containing some 200 TiO_2, corresponding to 400 HAL. These values agree with other estimates of very small anatase nanocrystals.[23]

There is no information about the adsorption of HAL at growing anatase nanocrystals, but the existence of a limiting size indicates that practically the whole surface may eventually be covered, *i.e.*, α in eqn. (8) approaches unity, and the growth rate approaches a value of zero.

The adsorption of HAL at growing X is opposed by HAL diffusion into the bulk, and only a fraction of HAL produced from a species will be adsorbed. As can be seen from eqn. (7) and (9), the number of HAL produced by a nanocrystal per unit area of its surface increases linearly with size. The concentration of HAL at the surface must reach a critical value in order to reach practically complete deactivation at a given temperature.

The crystallite size at which [HAL] (locally produced plus background from bulk) reaches this critical value is the observed limiting size. The growth of smaller crystals ($d<d_{\max}$) is gradually slowed down, due to increasing numbers of inaccessible surface sites α. As a consequence, the reaction of ALT (and perhaps oligomers) is shifted to smaller X which increase in size. The size of the nanocrystallites produced is finally focused to a fairly narrow range around $d_{\max}$.

Fraction α is related to an adsorption process. It should therefore depend mainly on the local HAL concentration, sorption energy and temperature. The temperature and [HAL] influence HAL adsorption in opposite directions. Adsorption is reduced with increasing T. Since less adsorption means less surface coverage, crystallites can grow further at higher T. When they have reached a certain size, additionally produced HAL is sufficient to compensate for the T increase, and growth is stopped at larger crystal sizes.

After practically complete conversion there are many small X at low temperatures while at high T species are larger but less numerous.

In producing anatase crystallites from ALT solution, the reaction time has no further influence on the species size after an initial, relatively short period. This behaviour follows directly from the proposed mechanism.

The practically nonexistent dependence of the crystal size on the precursor concentration [ALT] is also a consequence of surface blocking. Since growing crystallites produce much more HAL than is needed for complete coverage, the effect occurs even at the lowest investigated ALT concentration.

When HAL is added to the ALT sample at the highest possible concentration, $d_{\max}$ is reduced. Because HAL is present now from the beginning of the reaction, the concentration gradient between the growing species and the bulk is smaller, and diffusion of produced HAL from the surface is less effective. More HAL is available for adsorption, and complete coverage is reached at an earlier growth stage. Partial removal of HAL from the reaction has the opposite effect. Practically complete removal of HAL changes the growth mechanism to what is usually observed in crystal development.

The above considerations are very approximate and omit other effects which may also be important. In particular, the possible role of reaction equilibria has been disregarded, as well as mutual interference of diffusion of ALT and HAL at high concentration. Equilibria conditions have been mentioned in hydrolysis–condensation reactions of titanium tetrabutylate.[24]

Conclusion

Bis(ammonium lactato)titanium dihydroxide in aqueous solution is hydrolyzed at temperatures between 120 °C and 300 °C to yield titania nanocrystals in pure anatase form. The crystallite size is determined by the reaction temperature, and the crystallite size distribution is unusually narrow. This simple process can be utilized to produce almost monodisperse anatase particles of predetermined size with high yield. The product is not contaminated by non-volatile components (*e.g.* Cl^-, Na^+) used in other processes.

Acknowledgements

The authors wish to thank Mrs. U. Michalczik and Mrs. S. Schadow for most of the preparative work, and Mrs. U. Bloeck for excellent TEM measurements. We greatly acknowledge outstanding technical support by Mr. U. Fischmann in building the high temperature equipment.

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Paper 9/05373E