

Effect of hydrolysis conditions on morphology and crystallization of nanosized TiO₂ powder

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Abstract

Nanosized titania powders were prepared by controlling the hydrolysis of TiCl₄ in aqueous solution. The powders were characterised by TEM, HREM, XRD, ED, and BET techniques. In the presence of a small amount sulphate ions, when TiCl₄ solution hydrolysed at 70°C, the obtained powder was pure anatase and its primary particle size was 3.5 nm, which is finer than that of alkoxide-derived powders, moreover, its anatase-rutile transformation was retarded. However, at the same temperature, in the absence of SO₄²⁻ the synthetic powder was a mixture of the anatase and rutile, the primary particle size in the rutile phase was 4.3 nm. When TiCl₄ solution hydrolysed at 20°C, the prepared TiO₂ powder was amorphous and its BET surface area was as high as 501 m²/g. The results of UV–Vis absorption spectra indicate that the presence of sulphate ions accelerated the growth of TiO₂ clusters to anatase. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Calcination; Electron microscopy; Powders-chemical preparation; TiO₂

1. Introduction

Titania has been studied extensively because of its wide applications in pigments, catalyst supports, fillers, coatings, photoconductors, dielectric materials and so on. In recent years, TiO₂ is well known as a semiconductor with photocatalytic activities and has a great potential for applications such as environmental purification, decomposition of carbonic acid gas, and generation of hydrogen gas.^{1,2} A key requirement to improving its activity is to increase the specific surface area and decrease the primary particle size of the catalyst. Generally, titania is obtained either from minerals or from a solution of titanium salts or alkoxides. It is also known that the transformation behaviour from amorphous to anatase or rutile phase is influenced by the synthesis conditions. However, to our knowledge, most of the literature shows that alkoxide-based sol–gel or precipitation process yield amorphous titania precursors, or powders in the anatase phase with a primary

particle size in the range 4–6 nm.^{3–5} Phase transformation to the rutile structure takes place when the temperature is raised at least above 450°C.^{5,6} As precursors of nanocrystalline oxide powders, however, inorganic compounds are more economical than alkoxides. At present, there are a few studies on preparation of mono-dispersed titania powders from TiCl₄ or Ti(SO₄)₂.^{7,8} Also, gas-phase synthesis of titania by TiCl₄ oxidation in the presence of dopants was investigated,^{9,10} but effects of hydrolysis conditions on morphology and crystalline of nanosized titania from such inorganic compounds solutions are still unclear.

In this work, nanosized TiO₂ powder was prepared by controlling the hydrolysis of TiCl₄ in aqueous solution. The effects of the temperature of hydrolysis and sulphate ions on the anatase–rutile transformation and crystalline morphology were investigated. In a typical process, XRD result shows a sample dried at room temperature under vacuum was in anatase phase and its primary particle size was 3.5 nm, which is finer than that of alkoxide-derived powders. By varying hydrolysis conditions, a mixture of rutile and anatase in good crystallinity was prepared and it was potential to be applied as photocatalyst with high photocatalytic activities since its quantum-size effect, high BET surface

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area, and it can be excited by the light $\lambda=365$ nm, which is the strongest peak emitted by medium or high pressure Hg lamp.

2. Experimental procedure

2.1. Preparation of titania powders

Titanium tetrachloride (98% TiCl_4) was used as a main starting material without any further purification. When TiCl_4 dissolved in water, the heat of the exothermic reaction explosively generated the formation of orthotitanic acid $\text{Ti}(\text{OH})_4$. Since the formation of that species disturbed homogeneous precipitation, the appreciated amount TiCl_4 was dissolved in distilled water in an ice-water bath. The concentration of titanium was adjusted to 3 M. This aqueous solution was then mixed with distilled water or $(\text{NH}_4)_2\text{SO}_4$ solution in a temperature-controlled bath. The hydrolysis temperatures were varied in the 20–95°C range. The mixture was stirred at high speed while the amount of TiCl_4 solution necessary for the desired $[\text{H}_2\text{O}]:[\text{Ti}]$ molar ratio was added dropwise. Maintaining at the same temperature for 1 h, the mixed solution was treated with 2.5 M dilute NH_4OH until the pH value was 7. Subsequently, the precipitated titanium hydroxide/hydrous titanium oxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) was separated from the solution by using filtration and repeatedly washed with distilled water to make $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ that was free of chloride ions. The hydrous oxide was dried at room temperature (~30°C) under vacuum and ground to fine powder. The hydrous TiO_2 powders were calcined at various temperatures for 2 h.

2.2. Characterisation

X-ray diffraction (XRD) patterns were obtained on an automated diffractometer RAX-10. The fraction of rutile in each sample was determined via the usually accepted quantitative method. This method consists of measuring the relative XRD intensities of the anatase [101] ($d=3.520$ Å) and rutile [110] ($d=3.247$ Å) from the following equation:¹¹

$$\chi = 1/[1 + 0.8(I_A/I_R)] \quad (1)$$

where χ is the mass fraction of rutile in the powder, while I_A and I_R are the X-ray integrated intensities of the (101) reflection of anatase and (110) reflection of rutile, respectively.

The morphology of the powder as well as electron diffraction patterns obtained by transmission electron microscopy (TEM) in a Jeol JEM2010 ultra high resolution TEM operating at 200 kV. The primary particle

size was calculated using the Scherrer formula and obtained by TEM observation. The Brunauer–Emmett–Teller (BET) surface area was determined using a micromeritics ASAP 2010 nitrogen adsorption apparatus. Adsorption spectra were obtained on a dual beam Shimadzu UV-1601 spectrophotometer.

3. Results and discussion

A summary of the properties and preparation conditions of TiO_2 powders is shown in Table 1. When TiCl_4 solution hydrolysed at 70°C, the addition of sulphate is quite effective in promoting the formation of the anatase phase and the primary particle size is 3.5 nm, which is finer than those of alkoxide-derived titania powders.^{3–5} However, at the same hydrolysis temperature, in the absence of SO_4^{2-} , the obtained powder was a mixture of anatase and rutile, the fraction of rutile was 63.4%. The primary particle size in the rutile and the anatase phase was 4.3 and 5.9 nm, respectively. When TiCl_4 solution hydrolysed at 20°C, either the presence of SO_4^{2-} or not, as-prepared powders were amorphous, but, the product prepared by sulphate-process had a BET surface area as high as 501 m²/g, which is potential to be used as catalyst supports.

Fig. 1 shows XRD patterns of some nanocrystalline TiO_2 powders prepared by the hydrolysis of TiCl_4 solution. TEM micrographs confirmed the 4–5 nm size of the crystallites and their crystallinity: anatase electronic diffraction ring patterns were observed, as well as continuous lattice fringes on many particles. Fig. 2 gave the morphology of sample 1 dried at room temperature under vacuum. Electron diffraction (ED) pattern shows that the brightness and intensity of polymorphic ring is weak, so titania particle is poorly crystallised and partly amorphous.

When these samples were calcined at 400°C for 2 h, they crystallised completely, ED patterns as well as intensity of XRD patterns increased. Fig. 3 are their TEM micrographs, the morphology of these samples is different from each other: the primary particle size of sample 1 is finer than the rest, some particle was bottle-fused. But, for sample 2, as same as for sample 1, it was all anatase, particles were discrete. The morphology of samples 4 and 5 calcined at 400°C was similar to sample 2 calcined at the same temperature, their TEM micrographs were not provided in Fig. 3. By the TEM observation of Fig. 3, for sample 3, we noticed that the larger particles were cubic-shaped while the finer particles were polyhedral, recalling Table 1, the primary particle size was 10.7 and 14.2 nm calculated from Scherrer formula for anatase and rutile, respectively. We conclude that larger cubic-shaped particles are crystallites of rutile. In strong acidic environment generated by hydrolysis of TiCl_4 , the nucleation and the growth of TiO_2 clusters

Table 1
Comparison of powders prepared under various hydrolysis conditions

	[Ti]/[SO ₄ ²⁻]	Hydrolysis temperature (°C)	Particle size ^a /nm, dried at RT	Particle size ^a /nm, calcined at 400°C	BET surface area dried at RT (m ² /g)
Sample 1	1:2	95	3.8(A)	6.8(A)	290
Sample 2	20:1	70	3.5(A)	9.5(A)	383
Sample 3	1:0	70	5.9(A), 4.3(R)	10.7(A), 14.2(R)	271
Sample 4	20:1	20	Amorphous	10.2(A)	470
Sample 5	1:0	20	Amorphous	10.5(A)	501

^a Calculated by XRD; A denotes anatase, R denotes rutile.

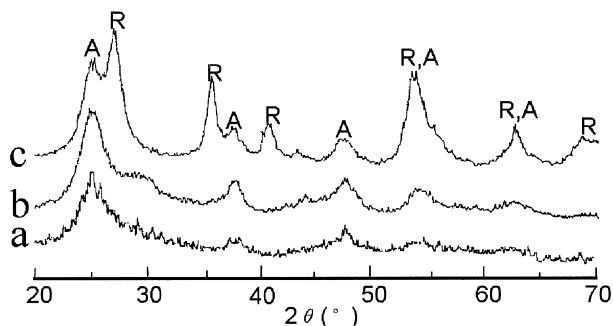
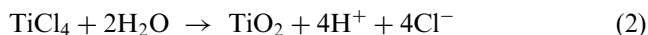


Fig. 1. XRD patterns of three titania powders, taken after dried at room temperature under vacuum: (a) sample 1, (b) sample 2, and (c) sample 3.

are at a mediate rate. The equilibrium between the nucleation and the growth make the formation of TiO₂ particles in the rutile possible, and the morphology of rutile is cubic-shaped, which different from the crystallites grown from clusters of rutile short-range ordered [TiO₆] octahedral by an aggregative growth process.¹² Since titanium atoms in the rutile link each other in the straight chains rather than the kinked chains of edge-sharing octahedral typical of anatase, the formation of rutile requires a relative low rate; in other words, the formation of rutile are kinetically controlled in the strong acidic solution. After the neutralisation of NH₄OH, the equilibrium between the nucleation and the growth was broken, the growth rate accelerated, the formation of anatase in the kinky chains of edge-sharing octahedral possible. Without the neutralisation of NH₄OH, and maintaining the temperature for a longer time, we have obtained TiO₂ powder in the pure rutile phase.

Fig. 4 shows the UV absorption spectra of TiCl₄ solutions, which has been diluted with HCl solution (pH=1) to 1 mM. Both solutions were clear, and titania clusters in these solutions were too ultra small to be detected by TEM. Therefore, the scattering effect of these clusters could be neglected. The spectra were shown after subtraction of the background spectrum of the TiCl₄-lacking solution. When TiCl₄ hydrolyses, it generates TiO₂ particle as well as H⁺ and Cl⁻ ions, the process is described as Eq. (2):



In the present work, the concentration of TiCl₄ before diluting was much high than those employed to preparation of TiO₂ colloidal particles.^{13,14} The absorption spectra of the TiO₂ particles in the solution exhibit an onset of absorption (determined by the linear extrapolation of the steep part of the UV absorption toward the base line), $\lambda_{\text{os}} = 336$ nm for the solution in absence of SO₄²⁻ ions and $\lambda_{\text{os}} = 345$ nm for which in presence of SO₄²⁻ ions. Although the concentration of SO₄²⁻ ions as low as 1/20th to that of Ti⁴⁺, it can be observed that this onset of absorption shifted to longer wavelength. The onset of absorption and the corresponding bandgap energy of bulk TiO₂ are $\lambda_{\text{os}} = 385$ nm and $E_g = 3.2$ eV for anatase, or $\lambda_{\text{os}} = 415$ nm and $E_g = 3.0$ eV for rutile. As both polymorphs (rutile or anatase) have been found in TiO₂ colloids, depending on the conditions employed for preparation. In the strong acidic solution of TiCl₄ (pH < 1), we had obtained titania powder in the pure rutile phase by hydrolysis of TiCl₄ solution. We propose that in the absence of sulphate ions, the nucleated TiO₂ particles either rutile or amorphous before diluting with NH₄OH solution. In the case $\lambda_{\text{os}} = 345$ nm, the calculated bandgap shift of the TiO₂ particles in the solution is then 0.33 or 0.54 eV, as compared to bulk anatase or rutile, respectively. A mathematical treatment using a quantum mechanical approach yields the relationship between bandgap shift (ΔE_g) and radius (R) of quantum-size particles, expressed in Eq. (3):¹⁵

$$\Delta E_g = \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{\epsilon R} \quad (3)$$

where h is Plank's constant, μ is the reduced mass of the electron and the hole ($1/\mu = 1/m_e^* + 1/m_h^*$) in the semiconductor, e is the electron charge, and ϵ is the dielectric constant of the semiconductor, Kormann et al. cited $\epsilon = 184$ and calculated a value of $\mu = 1.63 m_e$ (m_e is the electron rest mass).¹⁴ As an approximation, in the presence of SO₄²⁻ ions, we estimate the diameter of our particle is $2R = 2.2$ nm and $2R = 1.8$ nm for anatase and rutile, respectively. On the other hand, in the absence of SO₄²⁻ ions, the diameter is 1.8 nm or 1.6 nm, respec-

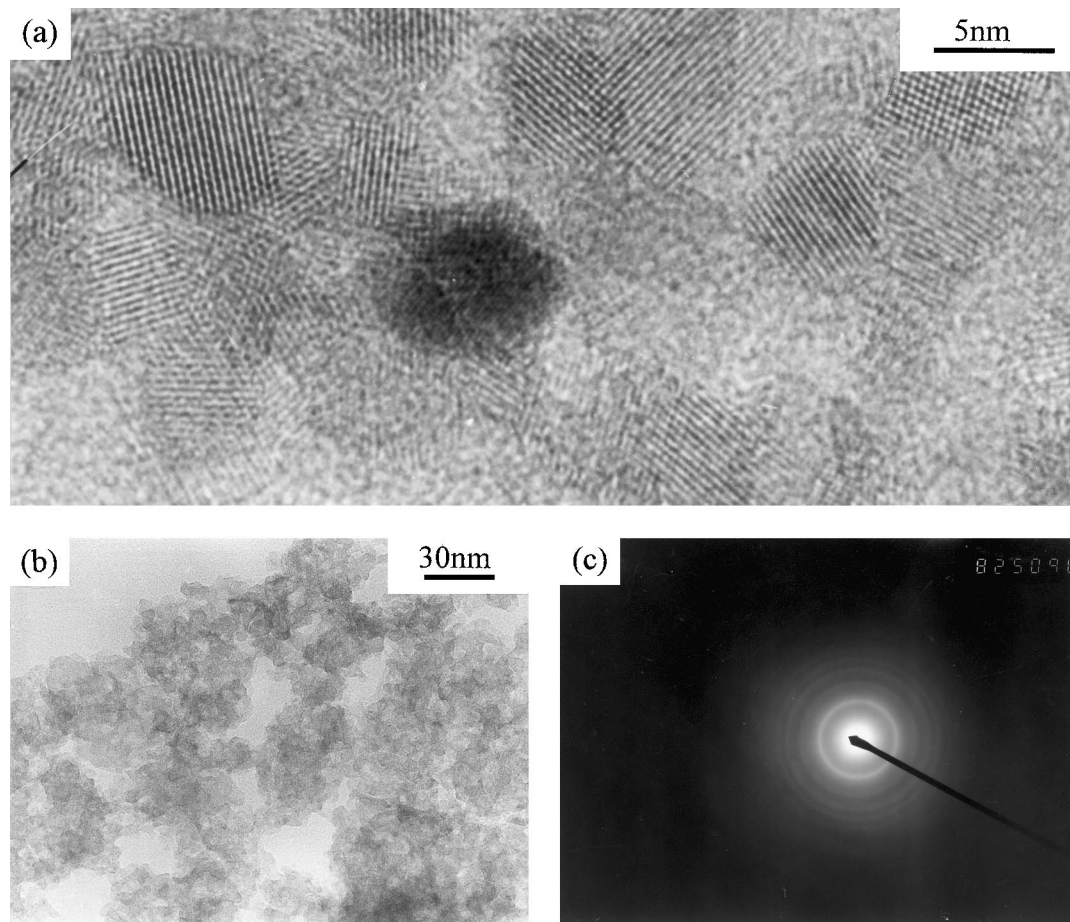


Fig. 2. Bright field (a) HREM and (b) TEM image, (c) ED patterns of sample 1 dried at RT under vacuum.

tively. It is clear that the TiO_2 particles in the solution containing sulphate ions are larger than that in absence of SO_4^{2-} . Unfortunately, TEM image was not sharp enough to allow probe determination of the particle size, so it remains an approximation.

The mechanism of that the addition of a small amount of SO_4^{2-} ions promotes anatase may be that SO_4^{2-} ions induce the growth of TiO_2 clusters to anatase phase, which is supported by the red-shift of λ_{os} in the absorption spectra and XRD results. Moreover, in the presence of SO_4^{2-} ions, as-prepared powders had a higher BET surface area than those prepared in the absence of SO_4^{2-} ions. The surface of precipitate prepared by hydrolysis of TiCl_4 solution is described by acid-base equilibria involving surface hydroxyl groups.¹⁴ The pH of zero point of charge (pH_{zpc}) is in the range between 5.1 and 6.7.^{14,16} Below the pH_{zpc} , TiO_2 particles is of positive charge, during the competitive adsorption process, sulfate ions in the larger size as well as of more negative charge is in dominant position comparing to Cl^- . The precipitate adsorbed sulphate ions results in both electrostatic and steric repulsion to keep from agglomeration and result in these titania particles in finer size. The BET surface area of the powder prepared

by hydrolysis of TiCl_4 solution at 20°C in the presence of SO_4^{2-} was 501 m^2/g , its total pore volume was 0.495 cm^3/g and with the mesoporous diameter in the range 1–5 nm.

The transformation behaviour of anatase to rutile in alkoxide-derived nanocrystalline titania powders can be effected by many factors, such as impurities, preparation conditions and so on.^{5,17} In this work, the anatase-rutile transformation temperature in the range 650–700°C and below 600°C for sample 1 and sample 3, respectively. Curve (a) in Fig. 5 shows that, the anatase-rutile transformation of sample 1 in air increased as the temperature increased. After calcination at 900°C, it is in pure rutile phase. Gennari et al reported a commercial TiO_2 powder (consisting of 95% anatase and 5% rutile) in larger size (about 200nm by SEM) started to the anatase-rutile transformation at 875°C by adding some Fe_2O_3 which was applied as to enhance the anatase-rutile transformation.¹⁸ As compared to this commercial TiO_2 , the anatase-rutile transformation starting temperature decreased 150°C, but compared to those of alkoxide-derived nanosized TiO_2 powders,^{3–5,17} it increased 100°C. We ascribe increment of the anatase-rutile transformation starting temperature to inhibition

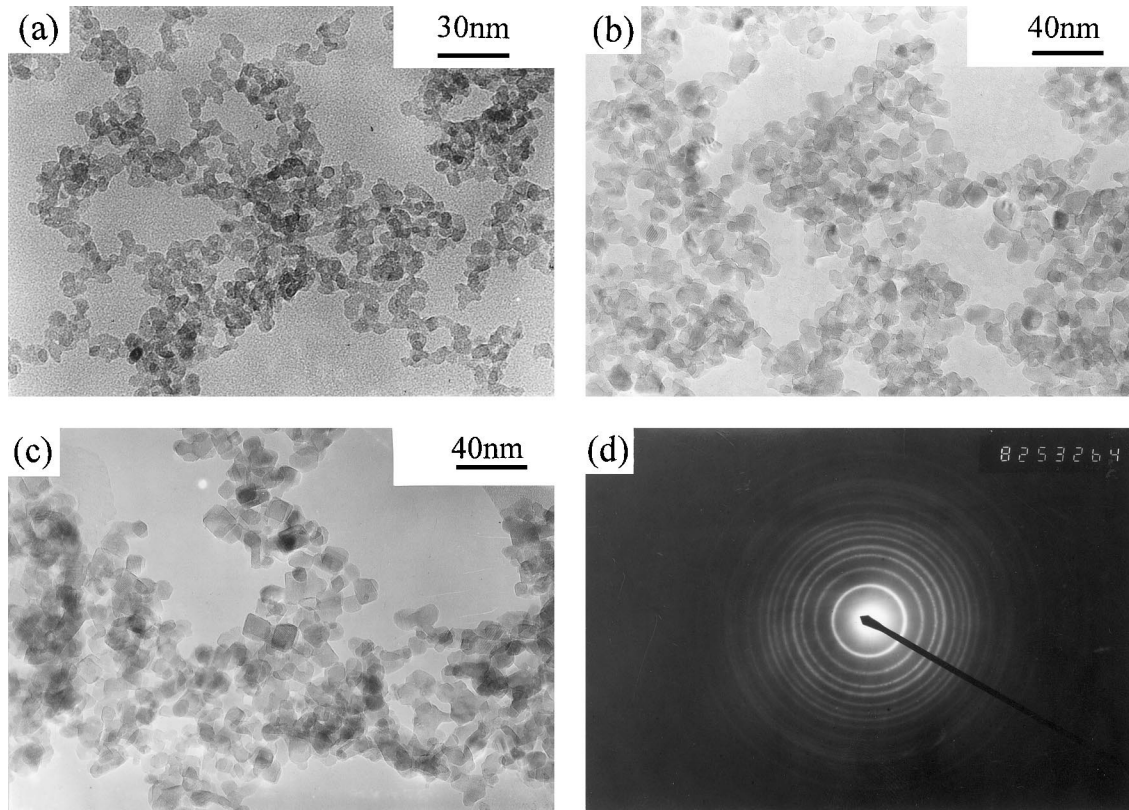


Fig. 3. Bright field TEM image of three samples calcined at 400°C for 2 h: (a) sample 1, (b) sample 2, (c) sample 3, and (d) ED pattern of sample 1 under same condition.

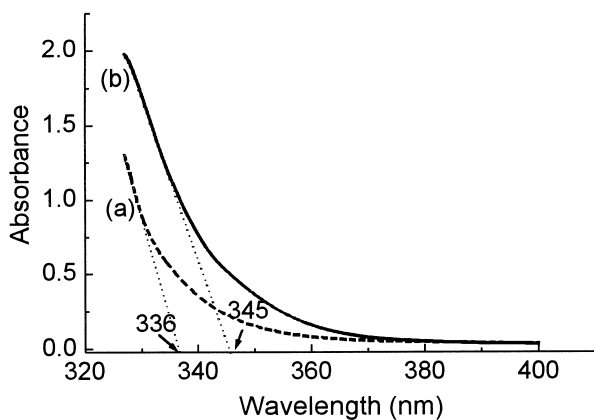


Fig. 4. UV-Vis absorption spectra of 3 M TiCl_4 diluted to 1 mM at 20°C: (a) without SO_4^{2-} ions, (b) addition 1/20th SO_4^{2-} to titanium.

effect of trace sulphate ions. The fraction of rutile in sample 3 dried at room temperature is 0.634, after calcination at 400°C, χ decreased to 0.582, indicate some amorphous TiO_2 existed in sample dried at RT under vacuum, this amorphous solid transformed to anatase as the temperature increased. Curve (b) in Fig. 5 shows that, after calcination at 600°C, χ increased to 0.723, the anatase–rutile transformation started. The lower rutile fraction temperature for sample 3 may due to rutile nanocrystals seeding the anatase to rutile transforma-

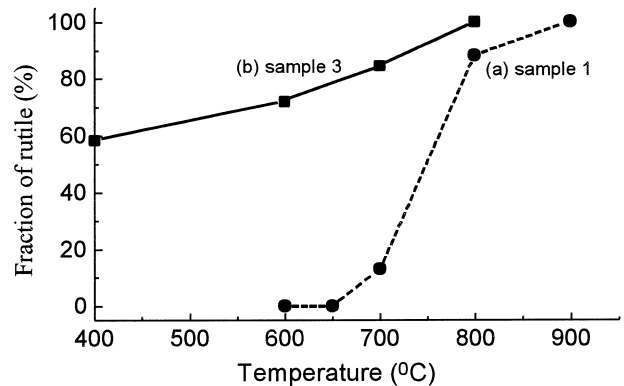


Fig. 5. Effect of calcination temperature on the fraction of rutile (a) sample 1, (b) sample 3.

tion. At 800°C, the anatase–rutile transformation completed. The temperature of the anatase–rutile transformation of sample 3 is comparable to those of the alkoxide-derived nanosized TiO_2 powders.

4. Conclusion

An economic inorganic compound TiCl_4 was used as precursor of nanosized TiO_2 powder. By controlling the

hydrolysis conditions, either nanocrystalline or amorphous TiO₂ powders can be prepared. The particle size in the crystalline samples is ultra fine (3.5 nm for anatase and 4.3 nm for rutile, respectively.) and the BET surface area of this powders is much higher than that of alkoxide-derived powders. The amorphous powders have mesoporous structure as well as high BET surface area. The addition of a small amount of (NH₄)₂SO₄ promotes the formation of anatase phase and inhibits the anatase–rutile transformation such that the powder is in completely anatase phase after calcining at 650°C for 2 h, and rutile occurs at around 700°C. However, in the absence of SO₄²⁻ ions, the powder prepared by hydrolysis of TiCl₄ solution at 70°C is in both rutile and anatase phase. When it was calcined at 600°C, anatase starts to transform to rutile. While aqueous solution of TiCl₄ hydrolyses at 20°C, either the presence of SO₄²⁻ ions or not, the rate of nucleation is too slow to form crystalline TiO₂ powders. This amorphous TiO₂ powders have a BET surface area in the range 470–501 m²/g, after calcining at 400°C, they transform to anatase completely.

Acknowledgements

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