The Promoting Effect of Sulfate Ions on the Nucleation of TiO₂ (Anatase) Nanocrystals

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The effect of sulfate ions on the nucleation of anatase nanocrystals during the hydrolysis of TiCl₄ solution was investigated. The resulting titania powders were characterized by DSC, FT-Raman spectroscopy, X-ray diffraction and UV-Vis spectroscopy. In the presence of sulfate ions as low as one twentieth to Ti⁴⁺, the precipitate prepared at room temperature contained 17.8% anatase nanocrystalline titania. The promoting effect of sulfate ions on the nucleation of anatase at higher temperature was more significant. For example, at 343 K, anatase powder was synthesized in the presence of a small amount of sulfate ions, while mixed-phase (the fraction of rutile was 0.634) powder was prepared in the absence of sulfate ions. Small amount of sulfate ions also modified the pore size distribution effectively and stabilized anatase to convert into rutile during calcining process, and powders with narrow pore size distribution (average pore diameter 3.8 nm) and mesoporous nature were prepared in the presence of sulfate ions.

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1. Introduction

Nanosized titania has wide applications in pigments, catalyst supports, fillers, coatings, photocatalysts and so on. These applications are correlated with the properties of TiO₂ powders such as crystalline phase, specific surface area, particle size, and pore size distribution. Titanium dioxide is known to exist in three crystalline polymorphs: rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal). In addition, there are two high-pressure phases, TiO₂-II (which has the α -PbO₂ structure) and TiO₂-III. Anatase and rutile are the two kinds of phases most intensively studied, and their commercial micrometer-sized products are also available. It is well known that quantum size effect can be observed when the particle size of titania crystallites is less than 10 nm.¹⁾ The quantum-sized TiO₂ nanoparticles is expected to have higher photocatalytic activity than those in larger size. Amorphous titania had some special applications such as visible light inducing photocatalyst.²⁾ Generally, titania is obtained either from minerals or from a solution of titanium salts or alkoxides. There are many works on the preparation and characterization of alkoxide-derived nanocrystalline or amorphous TiO₂.³⁻¹²⁾ As precursors of nanocrystalline oxide powders, however, inorganic compounds are more economical than alkoxides. At present, there are a few studies on preparation of monodispersed titania powders from TiCl₄ or Ti(SO₄)₂.^{12,13)} Also, gas-phase synthesis of titania by TiCl₄ oxidation in the presence of dopants was investigated.^{14,15)} Preparation of ultrafine TiO₂ nanoparticles by hydrolysis of TiCl₄ solution may be an economical route, however, how to improve the crystallinity of the resulting powder and modify its pore size distribution is a crucial problem to overcome.

We have reported the preparation of ultrafine (less than 10 nm) TiO₂ nanoparticles in the anatase, rutile, or mixed-phases by the hydrolysis of TiCl₄ solution.¹⁶⁾ In this

work, DSC analysis, FT-Raman and UV-Vis spectra were applied as sharper techniques than XRD to characterize the promoting effect of sulfate ions on the nucleation of anatase. Sulfate ions also modified the pore size distribution significantly, and powders with narrow mesoporous nature were obtained by introducing a small amount of sulfate ions into TiCl₄ solution.

2. Experimental Procedure

2.1 Preparation of titania powders

Titanium tetrachloride (98% TiCl₄) was used as a main starting material without any further purification. When TiCl₄ dissolved in water, the heat of the exothermic reaction explosively generated the formation of orthotitanic acid Ti(OH)₄. Since the formation of that species disturbed homogeneous precipitation, the appreciated amount of TiCl₄ was dissolved in distilled water within an ice-water bath. The concentration of titanium was adjusted to 3 kmol/m³. This aqueous solution was then mixed with distilled water or (NH₄)₂SO₄ solution in a temperature-controlled bath. The hydrolysis temperature varied in the range of 293–368 K. The mixture was stirred at high speed while the amount of TiCl₄ solution necessary for the desired [H₂O]:[Ti] molar ratio was added dropwise. After the holding time of 1 h at the same temperature, the mixed solution was treated with 2.5 kmol/m³ dilute NH₄OH until the pH value was 7. Subsequently, the precipitated hydrous titanium oxide (TiO₂·nH₂O) was separated from the solution by using filtration and washed several times with distilled water to make TiO₂·nH₂O that was free of chloride ions and sulfate ions. The hydrous oxide was dried at 383 K for 24 h and ground to fine powders. Sample RT-ns and sample 70-ns presented TiCl₄ solution hydrolyzed at room temperature (RT) and 343 K (70°C), respectively; ns denoted no sulfate ions added into TiCl₄ solution. Analogously, sample RT-s and sample 70-s presented TiCl₄ solution hydrolyzed at room

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temperature (RT) and 343 K, respectively; *s* denoted 1/20 th sulfate ions to titanium added into TiCl₄ solution.

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained by means of an automated diffractometer RAX-10. The fraction of rutile phase in each sample was determined via the usually accepted quantitative method. This method consisted of measuring the relative XRD intensities of the anatase (101) ($d = 0.3520$ nm) and rutile (110) ($d = 0.3247$ nm), and then the fraction of rutile phase was calculated from the following equation:¹⁷⁾

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

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 powder morphology as well as electron diffraction patterns were obtained by transmission electron microscopy (TEM) of JEOL JEM-2010 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. UV-Vis absorption spectra were carried out on a PE Lambda-2 spectrophotometer.

The precipitates after dried at 383 K were studied by the DSC analysis, UV-Vis absorption spectra, and FT-Raman. The Raman measurement were performed on a Bio-Rad FT-Raman spectrometer with exciting source Nd:YAG laser at the wavelength 1064 nm. In order to eliminate heating effects, the output power of the laser was kept at 200 mW, so the laser power at the samples was about 20 mW. DSC experiments were carried out by an equipment of Shimadzu 50-DSC at a heating rate of 10 K/min, in the atmosphere of dried nitrogen.

3. Results and Discussion

FT-Raman spectra of TiO₂ precipitates dried at 383 K are shown in Fig. 1. The principle features of the precipitates prepared by the hydrolysis of TiCl₄ solution at room temperature are three broad bands at Raman shifts of 160, 407, and 613 cm⁻¹, appearing to consist of multiple components, which are anatase-like but different dynamically from alkoxide-derived amorphous titania.^{6,8)} It is notable that titania powder (RT-s) prepared in the presence of a small amount of sulfate ions shows relative sharp bands at 160 cm⁻¹ and 630 cm⁻¹ compared to RT-ns, indicating the presence of anatase phase in the sample RT-s.^{18–20)} Sample 70-ns and 70-s show sharper Raman bands than RT-ns and RT-s. XRD patterns also show that the crystallinity was improved significantly by increasing the hydrolytic temperature from room temperature to 343 K. For the sample 70-ns, Raman shifts of 447 cm⁻¹ and 610 cm⁻¹ are attributable to rutile phase.^{21–23)}

The properties of prepared powders were summarized in Table 1, the fraction of rutile phase in the powder 70-ns is 0.634. However, the Raman spectra of 70-s show no bands attributed to rutile phase and reveal only anatase phase as the crystalline phase. Raman shifts of ultrafine anatase crystallites are somewhat different from the Raman spectra of

Fig. 1 Raman spectra of the resulting precipitates dried at 383 K. Arrows denotes the Raman bands at 447 cm⁻¹ and 610 cm⁻¹ corresponding to the E_g and A_{1g} modes of rutile, respectively. The Raman band at 235 cm⁻¹ also occurred in other works and might result from the appearance of the second-order spectrum of rutile.

the anatase single crystal. The strongest E_g mode of 70-s shifts to high frequency about 9 cm⁻¹ (for sample 70-s, its strongest E_g mode is 153 cm⁻¹, greater than 144 cm⁻¹ for its single crystal.) in comparison with the anatase single crystal. Other works on Raman spectra of ultrafine anatase also showed the shift of E_g mode at band 153 cm⁻¹.^{24,25)} The non-stoichiometry and phonon confinement effects should be taken into account to explain the change of the lowest-frequency E_g Raman mode.^{26,27)} We also carried out a series of experiments to investigate the particle size effect on the Raman spectra, and found that phonon confinement effects play a more significant role on the change of the lowest-frequency E_g Raman mode. Anatase TiO₂ particles in larger size were obtained by the calcinations of ultrafine TiO₂ particles at 673 K, 873 K and above, respectively, for several hours. During the calcination at high temperature, more non-stoichiometry might be introduced to samples, however, the strongest E_g mode was still in good agreement with that of anatase single crystal. In this paper, we are interested in characterization of the promoting effect of a small amount of sulfate ions on the nucleation of anatase phase, and did not discuss on the shift of Raman band for the ultrafine TiO₂ nanoparticles in detail.

It is notable that the Raman spectra shape of the sample RT-ns is different from that of the sample RT-s. As assuming the sample RT-ns was completely amorphous, the Raman spectra of RT-s can be deconvoluted. The deconvoluted Raman spectra with Raman shifts at the band 160 cm⁻¹ and 638 cm⁻¹ were presented in Fig. 2. This result indicates that a small amount of sulfate ions promoted the nucleation of anatase nanocrystals.

For semiconductor clusters, such as ZnS, CdS, ZnO and TiO₂, a simple and effective method to detect their quantum size effect is UV-Vis spectroscopy.^{28–30)} The UV absorption

Table 1 Properties of TiO₂ powders dried at 383 K and calcined at 673 K for 2 h.

Samples	Dried at 383 K			Calcined at 673 K for 2 h		
	Phase composition	Particle size d/nm	Surface area $S_a/\text{m}^2\cdot\text{g}^{-1}$	Phase composition	Particle size d/nm	Surface area $S_a/\text{m}^2\cdot\text{g}^{-1}$
RT-ns	Amorphous	3.5	449.5	Anatase	10.5	132.1
RT-s	Amorphous + Anatase (17.8%)	3.1	501.3	Anatase	10.2	139.3
70-ns	Anatase + Rutile (63%)	5.9 (Anatase) 4.3 (Rutile)	271.3	Anatase + Rutile (58%)	10.7 (Anatase) 14.2 (Rutile)	77.5
70-s	Anatase	3.5	388.0	Anatase	9.5	146.2

Fig. 2 The deconvoluted FT-Raman spectra of RT-s. The mass fraction in sample RT-s was 0.178 calculated from the DSC analysis.

Fig. 3 Normalized absorption spectra derived from UV-Vis diffuse reflectance spectroscopy of mainly amorphous titania.

threshold, or the optical band gap, is a strong function of titania cluster size. It was reported that titania in diameters less than 10 nm shows a well-known quantum size effect.²⁾ Actually, the quantum size effect of the anatase TiO₂ clusters is less significant than that of rutile particles in the same size.³¹⁾ When the particle size is finer than the quantum size, the blue shift of optical absorption band edge even superfine structures can be observed. The UV-Vis absorption spectra of powdered samples are presented in Fig. 3. The absorption band edge of the sample RT-ns was blue-shifted about 15 nm compared to that of RT-s. Scherrer formula is not suitable to calculate the primary particle size of RT-ns and RT-s since no distinct diffraction peaks was observed in their XRD patterns. TEM images showed that they were aggregates of

Fig. 4 DSC curves of TiO₂ powders obtained by the hydrolysis of TiCl₄ solution at varying temperature in the absence or presence of sulfate ions.

micropores, mesopores and nanoparticles. The surface areas of RT-ns and RT-s were 449.5 m²/g and 501.3 m²/g, respectively (Table 1). Assuming all particles are spherical, these values correspond to a particle size of 3.5 nm for RT-ns and 3.1 nm for RT-s, respectively. Thus, this blueshift of UV-Vis absorption in sample RT-ns could not be assigned to the quantum particle size. Some characteristic features with absorption peaks at wavelength 307 nm and 238 nm occurred in the spectra of the sample RT-s. This may be related to the structural difference between amorphous tetrahedral (TiO₄)³²⁾ rather than and the crystalline octahedral (TiO₆). So, the blueshift of the absorption band edge in RT-ns' absorption spectra was resulted from the amorphous titania or the formation of tetrahedral structure. This result also throws a light on investigations of the size effect in TiO₂ colloidal systems. The effect of amorphous content on the blueshift must be taken into account, since the complete amorphous titania also blueshifted significantly. The sample 70-ns consisted of anatase phase and rutile phase, while its UV-Vis absorption spectra also shows mixed feature of anatase and rutile. The onset of the absorption band edge was 402 nm, which blueshifted 8 nm compared to wavelength 410 nm of the bulk rutile phase.

From the above section, it is clear that the crystallinity of the TiCl₄ derived precipitates depend on the hydrolytic temperature greatly. At a higher temperature (such as 343 K), the nucleation rate of anatase is much faster than that at room temperature, resulting crystalline TiO₂ in the ultrafine size. Figure 4 shows DSC curves of these samples, both sample RT-ns and RT-s exhibited strong exothermal peak at-

tributable to amorphous-anatase transformation. The crystallization temperature of sample RT-ns and RT-s was 709.8 K and 688.9 K, respectively. The position of amorphous-anatase transformation exothermal peak of sample RT-s shifted to lower temperature. From the deconvoluted Raman of RT-s (Fig. 2), it is clear that RT-s had some anatase nanocrystals. The fraction of anatase phase in the sample RT-s was determined by DSC quantitatively. The crystallization heat of RT-ns was determined from the average of peak area in the several measurements to be $218.6 \text{ J} \cdot \text{g}^{-1}$. This crystallization heat was used as a standard to determine the weight fraction of amorphous titania (f_{amor}) in RT-s, 70-ns and 70-s. The mass of titania was normalized after subtraction the mass fraction of water (the decrease in mass after DSC measurements). The weight fraction of anatase (f_{ana}) was estimated by the following equation:

$$f_{\text{ana}} = 1 - f_{\text{amor}} \quad (2)$$

The heat of amorphous-anatase transformation of the sample RT-s was $180.5 \text{ J} \cdot \text{g}^{-1}$, as the weight fraction of anatase phase in the sample RT-s was calculated to be 0.178. No distinctively exothermal peaks were detected for samples 70-ns, 70-s, and RT-ns after calcined at 683 K, which indicates they were crystallized completely.

Based on the above discussions, we assumed that the shift of crystallization temperature toward lower direction because of the seeding effect of anatase, which induced amorphous-anatase transformation at a relatively low temperature.

Sulfate ions also modified the pore distribution significantly. The N₂ adsorption-desorption isotherms and inserted pore size distribution are presented as Fig. 5. The shape of the isotherms corresponded to the type IV classification with hysteresis, which is a combination of H2 and H1. H2 represents the hysteresis with a sloping adsorption branch and a steep desorption branch, which is perpendicular to the relative pressure axis. The H2 type is often associated with a distribution of pore sizes in mesopores and the area of the hysteresis may relate to the condensation of N₂ in the pore.³³⁾ The most important difference between them is that the decline in the desorption branch of its N₂ isotherms of sample RT-s in the range from $P/P_0 = 0.50$ to 0.40 is steeper than that of the sample RT-ns. For the sample RT-s, the decline is $59.1 \text{ cm}^3/\text{g}$, much greater than $27.7 \text{ cm}^3/\text{g}$ for the sample RT-ns. From its pore size distribution inserted in Fig. 5, it is notable that the pore size distribution of the sample RT-s is relatively narrower compared with that of the sample RT-ns. The former has a sharp peak at 3.8 nm illustrated the narrow pore size distribution and mesoporous nature of the sample RT-s, while the pore size distribution of the sample RT-ns was within the range from 2 nm to more than 10 nm and its pores consisted of the inhomogeneous intra-aggregates pores and inter-aggregates pores. The modifying effect of a small amount of sulfate ions on the pore size distribution was also observed in the sample 70-s. It had similarly uniform pore size distribution as that of the sample RT-s. As shown in Fig. 6, when the sample RT-s was calcined at 673 K for 2 h , the pore size distribution was still with a sharp peak at 3.8 nm indicating that the mesopores were thermally stable during the calcination and the amorphous-to-anatase transformation.

The promoting effect of a small amount of sulfate ions

Fig. 5 Nitrogen adsorption-desorption isotherms and pore-size distribution plots (insets) for TiO₂ powders. (a) sample RT-s and (b) sample RT-ns.

Fig. 6 Pore-size distribution plots for sample RT-s after calcination at 673 K for 2 h .

on nucleation of anatase phase was evidenced by the Raman spectra, UV-Vis absorption spectra and XRD patterns. Moreover, SO_4^{2-} ions absorbed by TiO₂ nanoparticles also retard the phase transition of anatase into rutile and slow down the growing rate of anatase-typed nanocrystals. When both 70-s and RT-s were calcined at 873 K for 2 h , they had BET surface areas as high as $70 \text{ m}^2/\text{g}$ and $65 \text{ m}^2/\text{g}$ respectively, and no rutile was found in the calcined samples. These surface areas and the temperature of anatase-to-rutile transformation were much higher than that of TiO₂ crystallites derived from titanium alkoxides.^{3-6,9)} Banfield *et al.* reported if particle size decrease to 14 nm , anatase is more stable than rutile.³⁵⁾ Thus, we assume the stabilization of anatase may result from the retardation of crystal growth of anatase-typed titania dur-

Fig. 7 The zeta potential of 70-ns and 70-s.

ing calcining process. In addition, in the presence of sulfate ions, as-prepared powder had a higher BET surface area and a narrower pore size distribution than those prepared in the absence of sulfate ions. The surface of precipitate prepared by hydrolysis of TiCl_4 solution is described by acid-base equilibrium involving surface hydroxyl groups. The pH of zero point of charge (pH_{ZPC}) of titania is in the range from 5.1 to 6.7.³⁴ Below the pH_{ZPC} , titania particles are of positive charge. Compared with chloride ions, sulfate ions more preferentially adsorb on the titania particles due to its larger size and more negative charges. The precipitates adsorbed sulfate ions result in both electrostatic and steric repulsion to keep from agglomeration and result in these titania particles in finer size. As shown in Fig. 7, shift in pH_{ZPC} has been observed for sample 70-s (the pH_{ZPC} of 70-ns and 70-s was 5.6 and 4.5, respectively). Additionally, the zeta (ζ) potential of 70-s in the range of pH values below pH_{ZPC} is less positive than that of 70-ns. Both shift in pH_{ZPC} and lower ζ potential of 70-s below pH_{ZPC} are evidences of strong specific ion adsorption.³⁶⁾

The complex capacity of sulfate ions to titania ions also plays an important role for the formation of anatase phase. It is well known that the chains of titanium atoms in rutile phase are straight and adjacent units of (TiO_6) are edge-shared. However, the chains of titanium atoms in anatase phase are zigzag and adjacent units of (TiO_6) are corner-shared. When a small amount of sulfate ions are added, the orient growth resulting from non-symmetrical coordination of sulfate ions with titania formed anatase phase with zigzag chains of titanium rather than straight chains of titanium (rutile) dominantly.

4. Conclusions

Sulfate ions were found to play an important role in the preparation of nanosized TiO_2 powder from TiCl_4 solution. While the concentration of the sulfate ions was as low as 1/20 th to titanium, it promoted the formation of anatase phase at room temperature. UV-Vis absorption spectra indicated a blueshift about 15 nm for complete amorphous titania compared to the titania consisted of 17.8% anatase phase. This result throws a light on the investigation works of the quan-

tum size effect of titania clusters, since the contents of amorphous part also had a significant effect on the optical band gap edge. A small amount of sulfate ions also modified the pore size distribution. In the presence of small amount of sulfate ions, the resulting powder showed more uniform and a narrower pore size distribution.

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