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Effect of surfactants on preparation of nanometer TiO_2 by pyrohydrolysis

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Abstract: The nanometer TiO_2 was prepared by pyrohydrolysis with titanic solution. The effects of species and content of the surfactants on the particle size, morphology and phase of TiO_2 were studied by using LPA, XRD and TEM respectively. The results show that it is beneficial to reducing the aggregation of TiO_2 particles with adding surfactants to the solution. Nanometer TiO_2 powders with the size of 40−55 nm are obtained by adding the anion surfactants in the optimal content of 1.5% (mass fraction). The effect of cationic surfactant for reducing particle aggregation is not as good as that of anion. The crystal phase constitutent of TiO_2 is dependent on the temperature of thermal treatment and complete anatase can be achieved after calcining in the temperature range of 350−750 ℃.

Key words: surfactant; nanometer TiO_2; pyrohydrolysis

1 Introduction

Nano-powder of titanium dioxide has extinguished physicochemical properties, such as large surface area, high activity, nontoxicity, long-term stability, excellent absorbency of light especially for ultraviolet ray, which makes it widely applied in pigments, catalysts, cosmetics, sensor, and environmental protection[1−4]. A lot of methods have been developed for preparing nanometer titanium dioxide powder such as micromusion[5], sonochemical[6], gas pyrohydrolysis[7], and sol-gel[8]. Titanic solution, which was of low cost and easily available raw materials, was adopted in this study to prepare nano titanium dioxide by pyrohydrolysis. However, severe aggregation of hydrolyzed products appeared in the pilot-scale preparation.

ROOSEN and HAUSNER[9] pointed out that the aggregation of powders was mostly caused by the combination of free hydroxyls though hydrogen bonds on the surface of particles in the process of sol reaction. Many methods were developed to disperse the aggregated powders such as organical washing[10], freezing drying[11], and adding surfactants[12]. However, the disadvantage of organical washing method is its high cost and that of freezing drying is great energy consumption. It is the most economical and efficient way to add surfactants for preventing the rigid aggregation of powders up to the present. ZOU et al[13] prepared nano-TiO_2 with small size using $TiCl_4$ as raw material in complex reaction system consisted of HCl, DBS, xylene and H_2O. ZHOU et al[14] adopted DBS as surfactant to prepare the nano-TiO_2 using hydrolysis method, with the result of obtaining TiO_2 particles of the homogeneous dispersion, narrow particle distribution and homogeneous size. HU et al[15] used $Ti(SO_4)_2$ and $CO(NH_2)_2$ to make nano-TiO_2 by harmonious precipitation and it was found to improve the particle size and distribution of TiO_2 by adding complex surfactants.

Therefore, the effects of anionic surfactants D_I, cationic surfactants E_A and non-ionic surfactants P_T on aggregated particle size and phases of TiO_2 in the pyrohydrolysis are investigated in detail in this paper, which is aimed at determining the optimal parameters for preparing dispersed nanometer TiO_2.

2 Experimental

2.1 Preparation of titania powders

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The hydrous titania (H_2TiO_3) from Zhuzhou Chemical Plant, China, was dissolved by hot sulfuric acid to form $TiOSO_4$ solution. And the purified solution was adjusted to a certain concentration of $TiOSO_4$ in the range of 50−56 g/L and H^+ concentration of 2.6−3.0 mol/L and then pyrohydrolyzed in RXQ-SG46-280 of autoclave at 0.14 MPa and the temperature range of 100−130 ℃ with adding some surfactants. The ultra-fine hydrous titania was rinsed using the distilled water and alcohol respectively and filtrated in a centrifugal machine until no existence of sulfuric acid in the filtrated water. Finally, the specimen was dried and calcined.

2.2 Characteristics of powder

The average particle size and size distribution of TiO_2 were measured by using the laser diffraction particle size analyzer(LPA). Phases of sample were detected by using X-ray diffiraction(XRD) with the apparatus of Japanese Rigaku D_{max} rA X-ray diffractometer employing Cu K_α (Ni filtered) radiation of wavelength 15.4 nm. The morphology of the samples was checked by using Hitachi H-800 transmission electron microscopy(TEM) under the accelerating voltage of 200 kV.

3 Results and discussion

3.1 Effect of surfactant type on particle size and distribution of TiO_2

In order to prevent the growth of nano-TiO_2, the influence of the surfactant type on the particle size and distribution of TiO_2, including anionic surfactant D_I, cationic surfactant E_A and non-ionic surfactant P_T were studied respectively. The results are listed in Table 1.

Table 1 Effects of surfactant type on TiO_2 particle size

Type of surfactant	d_{50}/nm	d_{90}/nm
Without surfactant	120	879
Anionic surfactant D_I (1.5%, mass fraction)	40	96
Cationic surfactant E_A (1.5%, mass fraction)	83	240
Non-ionic surfactant P_T (1.5%, mass fraction)	69	191

It can be seen from Table 1 that adding suitable surfactant is helpful to reducing the particle size of TiO_2 due to the sorption of surfactants on the surface of nanometer particles. The reaction of the interfacial energy among particles prevents the aggregation of powders from the static repulsion and special hindrance. The particle with the size of 83 nm is obtained with adding the cationic surfactants E_A, which is larger than that with adding the anion D_I or non-ionic P_T obviously. In addition, from the results of particle size distribution, the effect of adding the anionic surfactant D_I apparently is smaller than others. This means that anionic D_I is the best choice to reduce the aggregation of TiO_2 powders in the hydrolysis process of $TiOSO_4$ solution.

The TEM morphology of TiO_2 powders with various kinds of surfactants is given in Fig.1. It can be seen that particles are in the form of sphere and the samples without adding surfactants are seriously aggregated to the diameter range of 120−130 nm. On the other hand, the aggregation of the samples is alleviated and the particle size is reduced to 40−50 nm with adding anionic surfactant. In general, the preparation of H_2TiO_3 is carried out in the strongly acidic solutions and the particle takes the positive charges from the ionization of the hydroxy groups on the surface of powders. These positive charges are easy to attract the opposite ones to form the electric double layer[16], which is absorbed by the polar groups of surfactants and produces the electrostatic repulsion barrier and steric hindrance. The cationic surfactant shows poor dispersion for the bad absorption of the positive charge. The effect of non-ionic surfactants on the dispersion of nano-TiO_2 is in the range of the above additives.

3.2 Effect of surfactant content on preparation of nanometer TiO_2

Table 2 illustrates the relationship between the content of the anionic surfactant D_I and particle size of TiO_2. It can be found from Table 2 that the hydrolyzed TiO_2 grows up fast without additive. Under this condition there are no covers of surfactant on the surface of hydrolyzed products and no nanometer TiO_2 can be acquired. In addition, the particle size decreases with the increase of the content of anionic additive, especially at 1.5%. The particle size of TiO_2 would rise contrarily when the additive content is over 1.5%. On one hand, no steric hindrance takes place when the content of additive

Table 2 Effect of anionic surfactant D_I content on TiO_2 particle size

$w(D_I)$/%	d_{50}/nm	d_{90}/nm
0	120	879
0.5	87	262
1.0	65	178
1.5	40	96
2.0	53	125
2.5	80	250
3	115	539

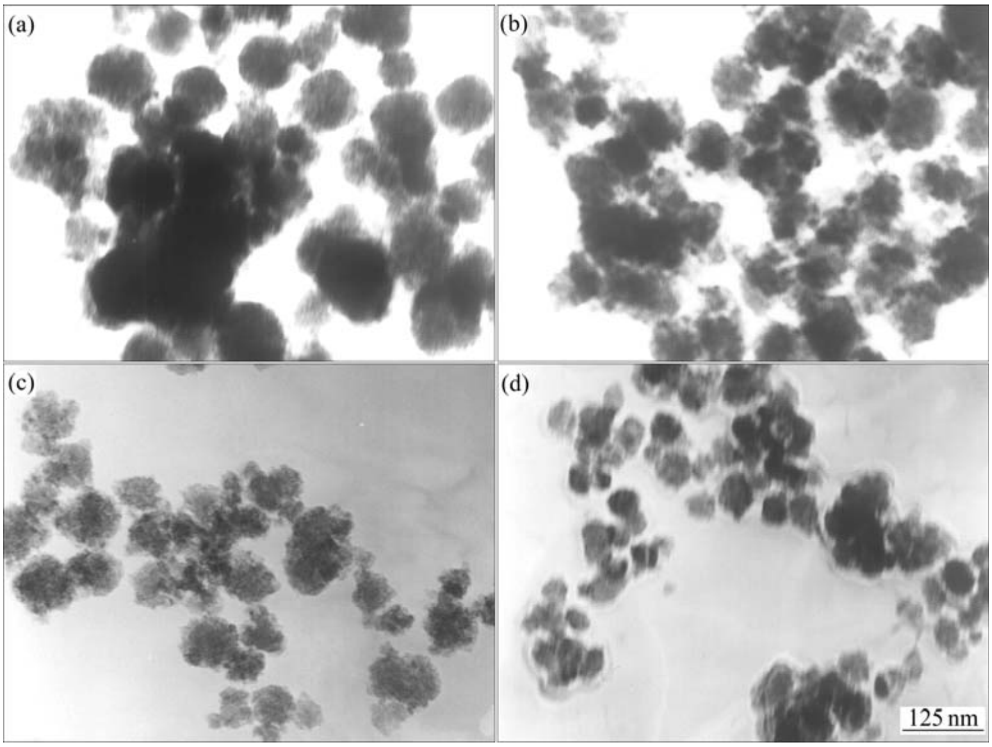

Fig.1 TEM photographs of TiO_2 powder with different surfactants: (a) Without surfactants; (b) 1.5% cationic surfactants E_A; (c) 1.5% non-ionic surfactants P_T; (d) 1.5% anionic surfactants D_I

is too low to cover TiO_2 particles. It is easy to cause the bridging across the particles[17] and the aggregation of powders. On the other hand, the content of surfactant is too high to increase the solubility of active reagent in the strongly acidic system. The viscosity of solution increases, the particle movement becomes difficult and the bridging of the surfactants leads to the increase of the surface tension and large particle size. The TEM photographs of TiO_2 produced with adding different contents of the anionic surfactants are displayed in Fig.2. From these images, it is clear that the lower the content of additive, the bigger the particle size of TiO_2 (Figs.2(a) and (b)). The dispersion of powders would be improved under suitable content and the ultrafine particles would be achieved (Fig.1(d) and Fig.2(c)). The dispersion of samples is reduced under contents of the additive (Fig.2(d)).

3.3 Effect of acidity of solution on particle size and distribution of TiO_2

When the anionic surfactant D_I is introduced into $TiOSO_4$ solution, the concentration of H^+ has an apparent effect on the hydrolysis and particle size of TiO_2[18−19]. The profile of the relationship between TiO_2 crystal dimension and initial concentration of H^+ is shown in Fig.3. The data for the profile are acquired by hydrolyzing with 1.5% of additive D_I and thermal treatment at 550 ℃ for 1 h.

It is found from Fig.3 that the particle size of TiO_2 increases with the increase of H^+ concentration. When the concentration of H^+ is below 3.2 mol/L, the crystal size increases slowly. But when the concentration of H^+ is over 3.2 mol/L, the particles grow up rapidly to large grain. In addition, when the concentration of H^+ is below 3.2 mol/L, the process of hydrolysis can produce the unlayered colloid. This is due to low-level acidity and narrow nucleating region and the time for hydrolysis is so short that a mass of particles are created. The crystal is difficult to grow up and the size is controlled. It is also found that when the concentration of H^+ is over 3.2 mol/L, the ionic concentration of solution increases and the crystalline rate is accelerated, which leads to the increase of particle size and the decrease of nucleation rate. Moreover, the high-level H^+ interferes the reaction and descends the hydrolysis rate. Then the new nuclear has enough time to grow up and aggregates into large-size TiO_2 grains. Fig.4 presents the TEM photograph of TiO_2 sample prepared under the H^+ concentration of 2.6 mol/L. It can be seen that when the concentration of H^+ is kept at low level, the small particle size and favorable dispersion are achieved.

3.4 XRD pattern of TiO_2 powder

Fig.5 shows X-ray diffraction patterns of TiO_2 prepared with adding 1.5% anionic surfactants D_I. It can be concluded that the TiO_2 phase begins to appear in the

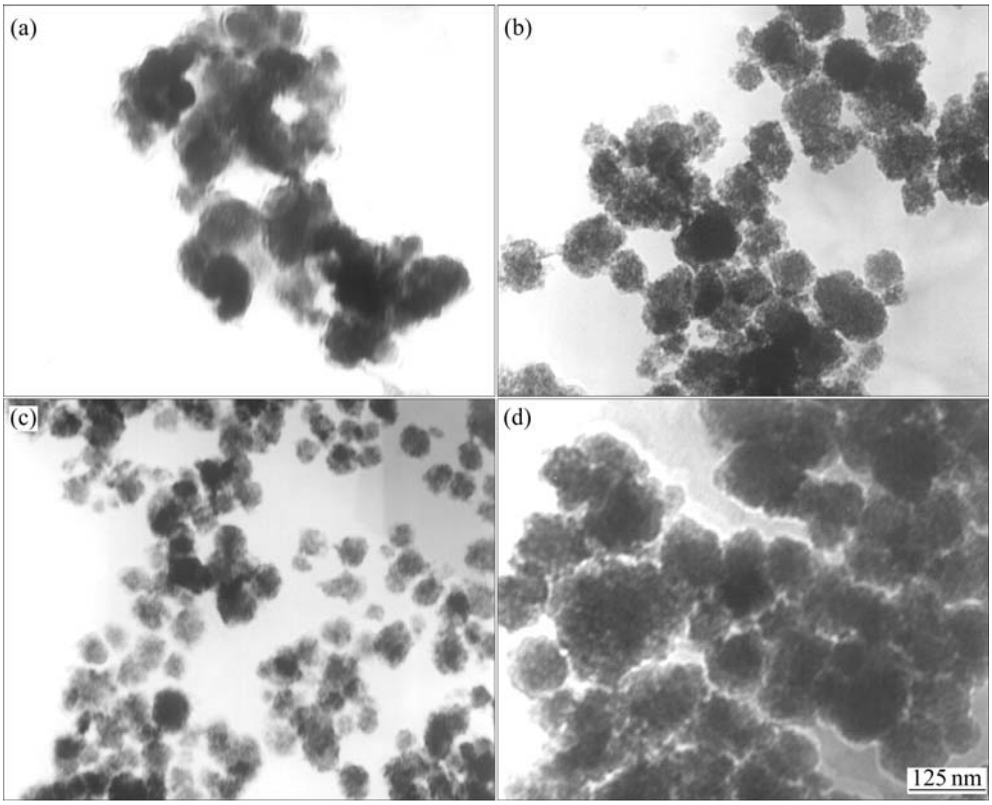

Fig.2 TEM photographs of TiO_2 with adding various contents of surfactant D_I: (a) Without surfactants; (b) 0.5% anion surfactants D_I; (c) 1% anion surfactants D_I; (d) 2% anion surfactants D_I

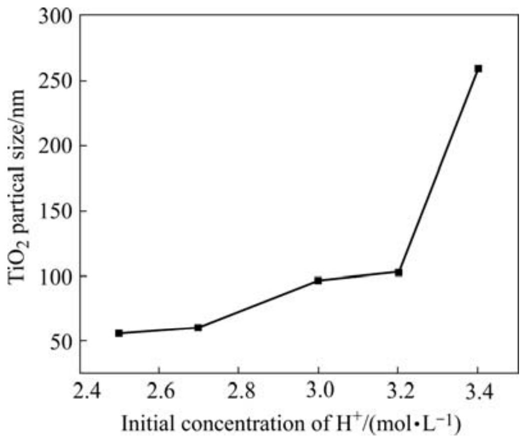

Fig.3 Relationship between TiO_2 particle size and initial concentration of H^+

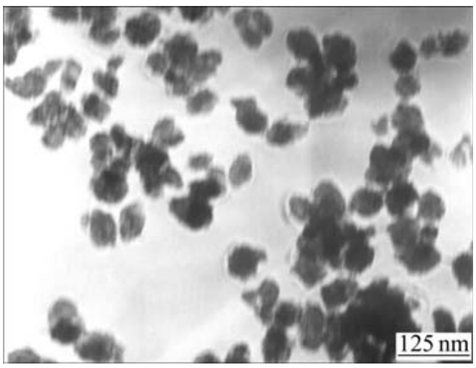

Fig.4 TEM photograph of TiO_2 powders at [H^+] of 2.6 mol/L

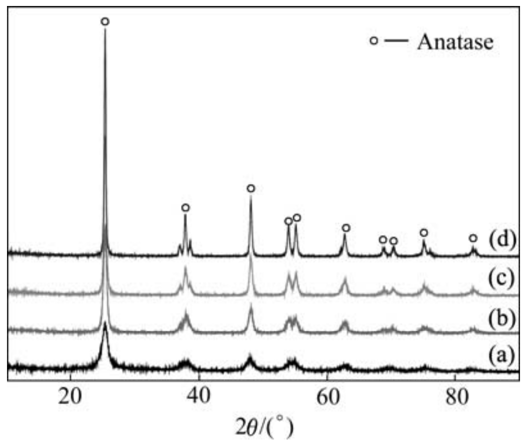

Fig.5 XRD patterns of TiO_2 calcined at various temperatures: (a) 250 ℃; (b) 350 ℃; (c) 550 ℃; (d) 750 ℃

anatase structure at 250 ℃. With increasing calcining temperature, it is easy to find that the width of diffraction peaks becomes narrower. According to Scherrer equation, it is implied that the crystallite size of particles becomes finer. It can be assumed that increasing thermal treating temperature can strengthen the process of re-crystallization and accelerate the crystal growth[20].

This behavior of TiO_2 powders is different from other titanium dioxides. The transformation temperature of the crystal prepared by sol-gel is in the range of 500−650 ℃[21]. This indicates that the type of the crystal is related to not only the thermal treating temperature but also the preparing methods and raw materials. The samples obtained in this research include only one phase of the anatase treated in a wide range of temperature.

4 Conclusions

1) The aggregation and particle size of TiO_2 can be improved with adding surfactants. The anionic additive shows the best result among the additives.

2) The best dispersion is obtained when the content of anionic surfactant is controlled at 1.5%(mass fraction) and the particle size ranges from 40 nm to 55 nm.

3) The crystal phase constituent of TiO_2 is related to thermal treating temperature, fabricating methods and raw materials. The TiO_2 samples in complete anatase can be achieved after thermal treatment at 350−750 ℃.

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