Research paper

Insights into effects and mechanism of pre-dispersant on surface morphologies of silica or alumina coated rutile TiO₂ particles

Xiongbo Dong, Zhiming Sun *, Yangyu Liu, Lei Jiang, Shuilin Zheng *

School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, PR China

A B S T R A C T

Silica and alumina coated rutile TiO₂ samples with various surface morphologies were fabricated using four different pre-dispersants. Using sodium silicate nonahydrate (SSNH) as pre-dispersant, the received sample displayed the best acidic stability. The addition of SSNH could induce layer-by-layer growth of hydrous silica via enhancing the dispersion of hydrous silica nucleus and accelerating the dehydration condensation rate of silica film. Alumina coated rutile TiO₂ sample obtained by polyethyleneglycol 1000 (PEG) presented the highest dispersion stability. The existence of PEG can induce the formation of fibrous hydrous alumina film, which would increase the steric hindrance and the promotion of dispersion stability.

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1. Introduction

As one of the most important inorganic filler, the rutile TiO₂ particles have been widely used in rubber, paints, ink, plastic, papermaking and pharmaceutical industries over the past decades. The addition of rutile TiO₂ particles could essentially enhance the weatherability of rubber, prolong the life span of paint films, increase the whiteness of paper, improve the dispersion stability of ink, and so on [1–5]. However, the uncoated rutile TiO₂ particles were prone to corrosion and agglomeration because of their unique photocatalytic activity and highly surface energy, which evidently restricted their practical application [6–8]. To address aforementioned issues, considerable research efforts have been devoted to decrease the corrosion and agglomeration of rutile TiO₂ particles via coating with silica or alumina on the surface of rutile TiO₂ particles. Generally, the silica film was mainly adopted to decrease the corrosion of rutile TiO₂ particles, while the alumina film was used to improve their dispersion stability [9–12].

Among of previous researches, the silica and alumina coated rutile TiO₂ particles were usually synthesized by precipitation or co-precipitation methods [9,13,14], sol–gel methods [15,16], chemical vapor deposition methods [17], and so on [18]. To the best of our knowledge, the precipitation or co-precipitation coating methods are extensively applied in the previous researches and practical production in comparison with other coating methods

due to their relative simple process and low cost. It is notable that precipitation and co-precipitation coating methods were composed of two parts: pre-dispersion process and coating process [19–21]. At present, most of the previous studies mainly paid attention to the coating process. For instance, Taylor et al. [22] synthesized the alumina coated rutile TiO₂ samples by co-precipitation methods, and the optimal coating process was obtained as well. Li et al. [23] fabricated hydrous alumina/silica coated rutile TiO₂ samples by precipitation method, and investigated the optimal conditions through a single-factor test. However, only few researches focused on the pre-dispersion process. As an essential part in pre-dispersion process, it must also be mentioned that the pre-dispersant played an important role in the surface morphology of silica or alumina films [24–26]. Nevertheless, the influence of pre-dispersant on the surface morphology of silica and alumina films is seldom reported. The mechanism for pre-dispersant to affect the surface morphology of silica and alumina films has not yet been clear. Furthermore, the formation kinetics of silica and alumina films would be also investigated for the first time.

In this study, the alumina and silica coated rutile TiO₂ samples were synthesized via precipitation coating method. And sodium hexametaphosphate, sodium silicate nonahydrate, sodium dedecylbenzene sulfonate and polyetheyleneglycol 1000 were selected as pre-dispersant in the pre-dispersion process, respectively. The dispersion stability and acidic stability were applied to measure the properties of alumina or silica coated rutile TiO₂ samples, respectively. Effect of the species and dosage of pre-dispersant on the dispersion stability and acidic stability of samples was

* Corresponding authors.
E-mail addresses: zhimingsun@cumtb.edu.cn (Z. Sun), shuilinzheng8@gmail.com (S. Zheng).

studied, and effect of the species of pre-dispersant on the surface morphology of samples was investigated by transmission electron microscope (TEM). The nitrogen absorption-desorption isotherms were used to estimate the specific surface areas and pore size distribution of the coating rutile TiO$_2$ samples. Furthermore, the mechanism for various pre-dispersant to affect the surface morphology of film was also discussed.

2. Experimental

2.1. Materials

The rutile TiO$_2$ was obtained from Jinzhou Titanium Industry Co. Ltd, which was prepared by chloride process. The TEM image of pure rutile TiO$_2$ sample is presented in Fig. S1, it can be seen that the surface of rutile TiO$_2$ particle is smooth. Sodium hexametaphosphate (SHP), sodium silicate nonahydrate (SSNH), sodium dodecylbenzene sulfonate (SDBS), polyethyleneglycol- 1000 (PEG) were applied as pretreatment pre-dispersant, and their chemical structures were illustrated in Scheme S1. Sodium silicate nonahydrate (Na$_2$SiO$_3$·9H$_2$O) and aluminum sulfate octadecahydrate (Al$_2$(SO$_4$)$_3$·18H$_2$O) were adopted as silica and alumina sources, respectively. Hydrochloric acid (HCl) (10 wt%) and sodium hydroxide (NaOH) (10 wt%) were employed as precipitating agent. All chemicals used in this study were of analytical pure grade without further purification, which were purchased from Beijing Reagent Co. (Beijing, China).

2.2. Sample preparation

The silica coated rutile TiO$_2$ samples were synthesized by a facile precipitation coating method. Firstly, the pure rutile TiO$_2$ sample was dispersed in de-ionized water at a concentration of 25 wt% which was then transferred into the thermostat water bath at 90 °C. The pH of rutile TiO$_2$ suspension was adjusted to 9.0 with sodium hydroxide solution. Simultaneously, the pre-dispersant was added into the suspension. After continuously stirring for 20 min, sodium silicate solution was drop-wise added into the suspension, at the same time, 10% of hydrochloric acid solution was used to keep the pH value at 9.0. The mass ratio of SiO$_2$ to TiO$_2$ was 2.5%. After aging for 120 min, the suspension was filtered, washed with de-ionized water and dried at 105 °C for 12 h. The prepared silica coated rutile TiO$_2$ samples with the use of various pre-dispersant were labeled as SSNH-Si-TiO$_2$, SHP-Si-TiO$_2$, SDBS-Si-TiO$_2$ and PEG-Si-TiO$_2$, respectively. In addition, when there is no pre-dispersant, the obtained silica coated rutile TiO$_2$ sample was labeled as Si-TiO$_2$.

The alumina coated rutile TiO$_2$ samples were prepared with the same precipitation coating method. Wherein, the coating agents were changed to aluminum sulfate solution and sodium hydroxide solution, respectively. In addition, the temperature of bath water and mass ratio of Al$_2$O$_3$ to TiO$_2$ were changed to 60 °C and 3.2%, respectively. The prepared alumina coated rutile TiO$_2$ samples were labeled as Al-TiO$_2$, SSNH-Al-TiO$_2$, SHP-Al-TiO$_2$, SDBS-Al-TiO$_2$ and PEG-Al-TiO$_2$, respectively.

The contents of SiO$_2$ and Al$_2$O$_3$ of silica or alumina coated rutile TiO$_2$ samples are displayed in Table S1. It is found that the content of SiO$_2$ and Al$_2$O$_3$ remain steady with the addition of various pre-dispersant, suggesting that pre-dispersant will not change the content of SiO$_2$ and Al$_2$O$_3$ of alumina or silica coated rutile TiO$_2$ samples.

2.3. Characterizations

The specific surface areas and pore size distribution of the samples were measured by the nitrogen absorption-desorption

isotherm measurements at the liquid nitrogen temperature [27]. Before the actual measurements, all the samples measured were degassed at 250 °C for 60 min. The G2 F20 transmission electron microscope (Tecnai, America) was applied to observe the surface morphology of alumina and silica coated rutile TiO$_2$ samples. Where the samples were first dispersed in ethanol and then deposited onto a carbon-coated copper grid for TEM imaging. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to measure the chemical compositions. The dispersion stability of samples was evaluated by WZS-186 turbidity meter. The acidic stability of samples was indirectly measured by the UV–vis spectrophotometer (UV-9000S, Shanghai Yuanxi). Malvern ZEN 3600 Zeta-sizer was used to determine Zeta potentials of the samples, the pH of solution was adjusted by sodium hydroxide (10%) and hydrochloric (10%).

2.4. Measurement of acidic stability

The acidic stability was applied to evaluate the photocorrosion resistance of silica coated rutile TiO$_2$ particles. The pure rutile TiO$_2$ particles could be dissolved at high-temperature concentrated sulphuric acid, while the silica film could prevent the rutile TiO$_2$ particles from being dissolved. At first, 0.1 g of rutile TiO$_2$ sample and 20 mL of concentrated sulphuric acid were simultaneously added into a flask and then heated to 180 °C in an oil bath for 60 min. Then the ice was poured into the above suspension, and diluted to 100 mL. At the same time, 10 mL of the above diluted solution and 2 mL of hydrogen peroxide were poured into a 100 mL volumetric flask, and diluted to 100 mL. The yellow solution was monitored with an UV–vis spectrophotometer (UV-9000S, Shanghai Metash, China) at the maximum absorption wavelength of 410 nm. The acidic stability of silica coated rutile TiO$_2$ samples could be indirectly evaluated by the absorbance of yellow solution, and the sample with lower absorbance presented the higher acidic stability.

2.5. Dispersion stability test

In our previous study, it has been proofed that the dispersion stability of rutile TiO$_2$ could be elevated markedly via coating with alumina film [9]. Hence, the dispersion stability was used to measure the performance of alumina coated rutile TiO$_2$ sample by a turbidity meter. Firstly, 0.01 g of rutile TiO$_2$ was dispersed into 200 mL of deionized water with ultrasonic cleaner for 1 min. Then, 25 mL of the above suspension was poured into turbidity meter, and the value of turbidity was counted automatically. Finally, the removal rate of turbidity was calculated using the following equation:

$$W_t = \frac{NTU_0 - NTU_t}{NTU_0} \times 100\%$$

where, NTU_0 and NTU_t are turbidity of rutile TiO$_2$ sample at initial time and at time of t, respectively. All the removal data of turbidity was obtained by parallel experiments.

3. Results and discussion

3.1. Acidic stability

The acidic stability of silica coated rutile TiO$_2$ samples obtained with the use of different pre-dispersant (SSNH, SHP, SDBS, PEG) was determined by measuring the solubility of samples at the atmosphere of high temperature concentrated sulphuric acid. The silica coated rutile TiO$_2$ sample with lower solubility presented the higher acidic stability. Firstly, the influence of the pre-dispersant dosage on acidic stability of samples was investigated