



Calcination intensity on rutile white pigment production via short sulfate process

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ABSTRACT

The rutile titanium dioxide pigment was produced via short sulfate process from unenriched industrial titanyl sulfate solution as raw material. The effects of calcination intensity after crystal transformation on the crystal structure, particle size distribution and pigment performances were investigated. The samples were characterized by TG-DSC, XRD, SEM, particle size distribution test and pigment properties test. The crystal grain size and content for rutile pigment gradually grew as the calcination intensity increasing, with a positive linear correlation. While the blue phase index is negative linear correlation with calcination time. The optimized calcining time at 860 °C for rutile pigment production is of 40 min, corresponding calcination intensity of 1,34,277 K min, and the as-prepared rutile pigment is with the grain size of 110.8 nm, rutile content of 98.3%, suitable and narrow particle size distribution, and the best pigment performances.

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1. Introduction

Titanium dioxide (TiO₂) occurs in several polymorphs, among them anatase and rutile are manufactured in the chemical industry as microcrystalline. With the properties of higher opacity, smaller crystal size, inertness, higher refractive index, it is the best choice of white pigment, and has been used in many fields such as paints, paper, fibers, cosmetics, sunscreen products, toothpaste, food stuffs, pharmaceutical additives, energy industries, and so on [1–5]. Anatase and rutile pigments are produced on industrial scale by means of either the chloride or the sulfate method. The TiO₂ pigment production via the hydrolytic precipitation of titanyl sulfate, more commonly known as the sulfate process, is one of the most important methods. In the self-seeded precipitation sulfate process, the formation of hydrated TiO₂ goes through a series of steps involving ionic reactions to form precursors for polymerisation, during which olation and oxolation gives birth to nuclei, which continue to grow and aggregate to the final form [6], and the effects of solution composition and acidity on the precipitation rate and yield have been investigated widely [7–10]. There are many hydroxyl groups (-OH) adsorbed on the crystallite surfaces,

hydrolyzed from TiOSO₄ bearing liquid by addition of steam causing anatase crystallites of about 5–15 nm size to precipitate, and the overall composition TiO(OH)₂ is achieved [11]. Due to incomplete desulphurization, about 5–10 wt % of the solid is still present as residual TiOSO₄·H₂O and TiOSO₄·2H₂O [12]. The hydrolysate is dewatered by means of vacuum rotary drum filters until a water content of about 55% (wt%) is reached. The resultant paste-like filter cake is calcined in a rotary kiln where moisture, adsorbed water and remaining sulfate groups are removed before finally the phase transition from anatase to rutile (rutilisation) occurs between 800 and 1000 °C [13]. The last process step of the sulfate process, named calcination, is carried out in a rotary kiln with feed of paste-like consistency and mainly contains anatase-crystallites. Within the kiln the material is dried and desulphurised before the phase transition from anatase to rutile occurs. The residence time of the material in the kiln is about 5–6 h. Ginsberg investigated the chemical reactions that occur during Calcination by means of simultaneous DTA-TG-MS-measurements in order to provide a 5-step reaction schematic, and developed a rigorous one-dimensional dynamic model of a rotary kiln for calcination of titanium dioxide white pigment, and the predictive accuracy of the model was estimated by means of a sensitivity analysis considering uncertainties of model parameters and measured input values [14,15]. Our previous work had also investigated the effects of calcining temperature on the structure and

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photo-catalytic properties of porous TiO₂ prepared from industrial TiOSO₄ solution [16,17]. The traditional sulfate process had been developed in industry since 1918, using concentrated TiOSO₄ solution by concentrating the unenriched TiOSO₄ solution as hydrolysis raw material after acid decomposing and leaching from ilmenite and titanium slag. But there was no try by using unenriched TiOSO₄ solution (namely low concentration) as titanium source to produce TiO₂ white pigment, which was called short sulfate process. It is the best way to significantly lower the cost, reduce the energy consumption and shorten the process. While the decrease of titanium concentration, acidity and hydrolysis temperature would lead to the change of hydrolysis rate, particle growth and aggregation, even the doping and Calcination conditions, resulting in difference in structure and pigment properties for the TiO₂ white pigment. Herein, rutile TiO₂ white pigment was prepared by using unenriched TiOSO₄ solution as hydrolysis raw material via short sulfate process, and the effects of calcining time on the structure and pigment properties were investigated.

2. Experimental

2.1. Pigment preparation

Unenriched low concentration industrial TiOSO₄ solution was used as the hydrolysis raw material to produce rutile pigment, obtained after acid decomposing, leaching and purifying from titanium slag and ilmenite via short sulfate process, and its typical composition was TiO₂ of 181.4 g/L, F value (effective H₂SO₄)/TiO₂ of 1.84 (mass ratio), Fe/TiO₂ of 0.27 (mass ratio), Ti³⁺ of 1.58 g/L. All other reagents were A-grade without any further purification, and the water was distilled water. To prepare a good fine uniform dispersion precipitates and control its structure, in a typical synthesis, unenriched industrial TiOSO₄ solution and pre-adding water was warmed up to 96 ± 1 °C, with volume ratio of 1: 0.15, respectively. Then the preheated TiOSO₄ solution was dropped into the pre-adding water at constant speed in about 20 min under stirring and reflux conditions. After feeding off, the hydrolysis solution was heated to the first boiling point (104 °C) in 10 min. When the reacting system turned into grey color (namely the grey point) after a few minutes, heating and stirring was immediately stopped in order to obtain the uniform hydrated metatitanic acid particles. After aging for 25 min, the hydrolysis mixture was then heated to the second boiling point (about 105 °C) under stirring, and the mixture was gradually changed into milky white. After 120 min from the second boiling point, 2% distilled water was added dropwise to the hydrolysis slurry to increase the hydrolysis and recovery rate of titanium. Then 4% rutile calcined seed (wt% to TiO₂) was added to the hydrolysis slurry. And the hydrolysis process was completed for another 30 min. The metatitanic acid denoted as PTS was obtained after the slurry was filtered and washed with diluted sulfuric acid solution and distilled water at about 65 °C. Then PTS was salt-treated at the optimized value with zinc salt (ZnO of 0.28% (wt%) as to TiO₂), potassium salt (K₂O of 0.55%) and phosphate salt (P₂O₅ of 0.15%), then calcined in a muffle furnace. The calcining conditions was as follows: room temperature to 420 °C in 60 min and holding for 30 min at 420 °C, then 420 °C to 780 °C in 60 min and holding for 60 min at 780 °C, at last 780 °C to 860 °C in 120 min and holding for different time at 860 °C. The holding time at 860 °C was of 10 min, 20 min, 30 min, 40 min, 50 min, and the obtained rutile pigments were marked as R1, R2, R3, R4 and R5, respectively.

2.2. Characterization

The TG–DSC thermal analysis was performed on a synchronous comprehensive thermal analyzer (STA 449C, NETZSCH) using

purified nitrogen flow. The crystal structure was determined by XRD (D8 Advance, Bruker). The average crystallite size ($L_{(110)}$) was calculated from the rutile plane (110) according to Debye-Scherrer equation [18] (Equation (1)), and rutile content (X_R) was calculated as Equation (2) [19].

$$\text{Crystallite size : } L = \frac{K\lambda}{\beta \cdot \cos \theta} \quad (1)$$

$$\text{Rutile phase content : } X_R = \frac{I_R}{0.884I_A + I_R} \quad (2)$$

In Equation (1), K was the constant (0.8900), λ is the wavelength of CuK α_1 (0.15418 nm), β was the full width at half maximum intensity (FWHM) of crystal plane (110) for rutile peak in radians, and θ was the Bragg's diffraction angle, respectively. In Equation (2), I_A and I_R represented the integrated intensity of the anatase (101) main peak and the rutile (110) main peak, respectively. Particle size distribution test was carried out on a Malvern particle size analyzer instrument (Zetasizer Nano ZS90). The surface morphology was observed through a JEOL electron microscope (JSM-7100F). The pigment properties was conducted on ultra-precise spectral color measurement instrument (LabScan EX, American Hunter), and chromatic power indicators (TCS), blue phase (SCX), brightness (J_{asn}) was obtained using R930 as the standard sample according to the industry standard.

3. Results and discussion

The thermal analysis (TG–DSC) patterns of the dried PTS were shown in Fig. 1. It is obvious that the weight has gradually lost as the temperature increasing, with total weight loss of 17.6%. The significant weight loss of 13.8% has happened at the range of 25.3 °C to 546 °C, owing to the removal of free water, bound moisture and some volatile materials at lower temperature. And the primary sulfur removal has been occurred at 546–780 °C, with the value of 2.9%, suggesting that the SO₄²⁻/TiO₂ mole ratio of 0.029:1. After 780 °C, the weight loss of PTS is only 0.9%, corresponding to the decomposition and removal of some high temperature resistant material. The DSC curve shows that the first endothermic peak is mainly due to the loss of free water and bound moisture at 25.3–226 °C, the second endothermic peak due to the removal of surface hydroxide radicals at 226–500 °C, the third exothermic peak at 560–780 °C due to removal of sulfur compound, and the

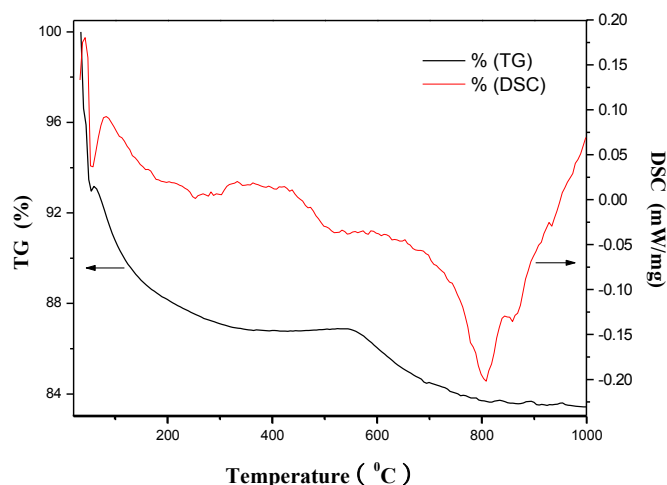


Fig. 1. TG–DSC patterns for PTS.

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