Powder Technology 287 (2016) 256–263

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Preparation of nano-titanium dioxide from ilmenite using sulfuric acid-decomposition by liquid phase method

Zenghe Li, Zhencui Wang, Ge Li *

Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form 27 July 2015
Accepted 5 September 2015
Available online 12 September 2015

Keywords:
Ilmenite
H_2SO_4
Liquid phase method
Direct hydrolysis
Nano-TiO_2

ABSTRACT

In this study, high purity nano-TiO_2 was prepared from Panzhihua ilmenite using sulfuric acid-decomposition by liquid phase method. The effects of H_2SO_4 molar volume, reaction time, initial pre-heating temperature and H_2SO_4 concentration on the decomposition rate of ilmenite were investigated in detail. The results showed that the decomposition rate reached 95.21% under the optimal conditions. The resulting titanium solution was qualified with 121 g/L Ti^{4+}. Since the initial pH value of hydrolysis system was below 3, the precipitation of metatitanic acid was obtained by direct hydrolysis of the titanium solution. On the other hand, the well-crystallized anatase and rutile were achieved at different calcination temperatures. The purity of the as-prepared TiO_2 was above 99% with an average particle size of about 40–100 nm. The ilmenite ore, intermediates and final products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray fluorescence spectrometer (EDS), X-ray fluorescence spectroscopy (XRF), thermal gravimetric analysis (TG), inductive coupled plasma emission spectrometer (ICP) and spectrophotometer. The results demonstrated that the process was suitable for industrial production because it was inexpensive, environment-friendly and promising in the preparation of high purity nano-TiO_2.

1. Introduction

Nano-TiO_2 is widely used in photocatalysis, solar cells, sensors, coatings and other areas of chemical industry, owing to its nontoxicity, chemical stability, excellent color effect and strong ability for UV-shielding [1]. Currently, there are many methods to produce nano-TiO_2, such as chemical vapor deposition (CVD), oxidation of titanium tetrachloride, sol–gel technique, and thermal decomposition or hydrolysis of titanium alkoxides [2–5]. The titanium sources in these processes are expensive. Moreover, the reactions often require rigorous conditions. Therefore, these processes are restricted in the further applications. As is known to all, ilmenite is cheap, non-toxic and widely distributed in the world, primarily in North America (USA, Canada), South America (Brazil), Australia, Europe (Norway, Ukraine), Africa (South Africa, Mozambique) and Asia (China, India). Panzhihua is one of the important mineral deposits in China [6]. Thus, it would be very desirable for Panzhihua ilmenite to adapt to the industrial preparation of nano-TiO_2.

Nano-TiO_2 is commercially manufactured by sulfuric acid-decomposition method and chlorination method. The chlorination method is complex, and it requires high quality ilmenite feedstock. Therefore, sulfuric acid-decomposition method is still an important way for the preparation of nano-TiO_2 from Panzhihua ilmenite, all of which are associated with magnetite and high-level CaO and MgO. Sulfuric acid-decomposition method can be divided into solid-phase method and liquid-phase method via the way of decomposition. Several researches have published the sulfuric acid-decomposition treatment to produce TiO_2 from ilmenite by solid-phase method [7,8]. However, it requires high reaction temperature (above 200 °C) and high concentration of H_2SO_4 (above 15.5 M). Moreover, it discharges large amount of waste gas such as SO_2 and SO_3, leading to severe environmental problems. However, liquid-phase method needs lower acid concentration below 15.5 M and lower reaction temperature at the range of 130–160 °C. The reaction is more moderate and it's beneficial for reducing waste gas emission. Besides, it is easy to achieve continuous production without the need of the leaching process. Therefore, it is necessary and urgent to study the liquid-phase process deeply to simplify the sulfate process and reduce environmental pollution.

In this paper, nano-TiO_2 was prepared from Panzhihua ilmenite using sulfuric acid-decomposition by liquid phase method. The factors affecting the decomposition rate were investigated. The initial pH value of the resulting $TiOSO_4$ solution was below 3, which could not reach the acid precipitation of Mg^{2+} and Al^{3+} during the hydrolysis. Therefore, it effectively prevented the small amount of impurities precipitating. H_2TiO_3 precipitate was obtained by direct hydrolysis without the addition of any surfactant. The well-crystallized nano-TiO_2 with high purity was obtained via calcination from the as-prepared H_2TiO_3

* Corresponding author.
E-mail address: ligebuct@gmail.com (G. Li).

http://dx.doi.org/10.1016/j.powtec.2015.09.008
0032-5910/

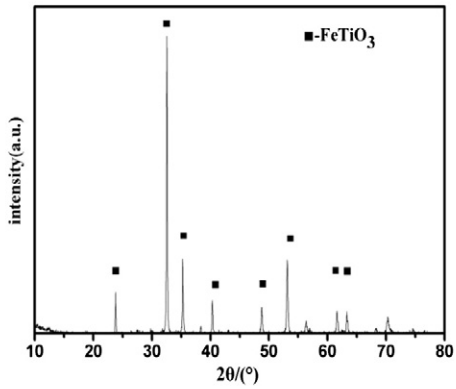

Fig. 1. XRD pattern of the ilmenite ore.

precipitate. In addition, the effects of calcination temperature on polymorphs and particle size of TiO_2 were investigated.

2. Experimental

2.1. Materials and analysis

All the chemical reagents employed were of analytical grade, and deionized water was used throughout. The ilmenite used in the research was supplied by titanium company of Panzhihua Honor and Trade Corporation. Its particle size was about 100 μm. Iron powder was purchased from Beijing Chemical Company. Its effective iron content was 98% and the particle size was about 80 μm.

X-ray diffraction (XRD) characterization was carried out with a diffractometer D/Max-RA (Rigaku, Japan) using Cu Kα radiation with a step size of 0.02° and a scan range from 10° to 80°. SEM images were taken from the S-4700 scanning electron microscope (Hitachi, Japan), which operated at 20 kV. TEM images were taken from the H-800 transmission electron microscope (Hitachi, Japan), which operated at 200 kV. HRTEM images were taken from the JEM-3010 high-resolution transmission electron microscope (Hitachi, Japan). JEOL J-3010 (Japan) energy dispersive X-ray spectroscopy (EDS) and X-ray fluorescence spectroscopy (XRF) system was used for chemical composition analysis. Thermal analysis experiments were carried out on a simultaneous thermogravimetric and differential thermal analyzer (Diamond TG/DTA, PERKINELMER) with a heating rate of 10 °C/min and an air flow rate of 300 ml/min. ICP analysis was performed on ICPS-7500 inductive coupled plasma emission spectrometer (Shimadzu, Japan). The concentration of titanium in the solution was analyzed by 722 N spectrophotometer (China).

2.2. Characterization of the ilmenite ore

XRD and chemical composition for the ilmenite ore used in this study were shown in Fig. 1 and Table 1, respectively. Fig. 1 indicated that the ore mainly contained ilmenite ($FeTiO_3$, PDF NO.29-0733), which is consistent with its chemical composition analysis (Table 1). Based on the mass balance principle, the mineral content of the ore included 86.79 wt.% ilmenite, 5.32 wt.% rutile, 4.40 wt.% quartz, 3.11 wt.% hematite and 0.38 wt.% microcline [9].

2.3. Preparation of nano-TiO_2 from ilmenite

This process was carried out in a 250 ml three-necked flask employed with a thermometer, stirrer and reflux condenser. Firstly, the concentrated H_2SO_4 was heated to certain temperature, and then 20 g of ilmenite was added to the solution under continuous stirring. After 1 h, in order to keep the reaction in the liquid condition, 50 ml of 1.0 mol/L dilute H_2SO_4 at 90 °C was added to the reaction system. This article mainly focused on the effects of H_2SO_4 molar volume, reaction time, initial pre-heating temperature, and H_2SO_4 concentration on the decomposition rate of ilmenite.

The existence of Fe^{3+} would reduce the purity of TiO_2, thus, affecting the whiteness of the product. Therefore, it should be reduced to Fe^{2+} via the addition of an appropriate amount of iron powder late into the reaction. Titanium solution was obtained by filtration, then crystallized at 5 °C for two days. Finally, $FeSO_4 \cdot 7H_2O$ crystal and $TiOSO_4$ filtrate solution were obtained by filtration. The titanium concentration in the solution was analyzed by a spectrophotometer. The decomposition rate of ilmenite was calculated by the following formula [5]:

$$x\% = (V \times C_{Ti}/m \times w_{Ti}\%) \times 100\% \quad (1)$$

where $x\%$ denotes the decomposition rate of ilmenite, C_{Ti} denotes the titanium concentration in the titanium solution ($g \cdot L^{-1}$), m denotes the total mass of the ilmenite (g), $w_{Ti}\%$ denotes the mass fraction of soluble titanium in the ilmenite, and V denotes the volume of titanium solution (L).

The resulting concentrated $TiOSO_4$ solution was used for hydrolysis in a 250 ml three-necked flask employed with a thermometer, stirrer and reflux condenser. Firstly, 25 ml of deionized water was added to the three-necked flask, and 5 ml of $TiOSO_4$ solution was slowly dropped to the reaction system under continuous stirring at room temperature. Then the solution was heated to 90 °Cand kept for 3 h. The precipitate was obtained during aging at room temperature for 6 h, filtered, washed with deionized water and ethanol, and then dried at 80 °C. The as-prepared H_2TiO_3 precipitate was calcined at various temperatures in a tubular furnace for 4 h to synthesize nano-TiO_2. The experimental procedure was shown in Fig. 2.

3. Results and discussion

3.1. Decomposition of ilmenite with H_2SO_4

The ilmenite ore was composed of a variety of minerals, and the decomposition of ilmenite with H_2SO_4 was a complex heterogeneous reaction. The main reactions were expressed by Eqs. (2)–(6) [9]:

$$FeTiO_3(s) + 4H^+(aq) = TiO^{2+}(aq) + Fe^{2+}(aq) + 2H_2O \quad (2)$$

$$Fe_2O_3(s) + 6H^+(aq) = 2Fe^{3+}(aq) + 3H_2O(l) \quad (3)$$

$$MgO(s) + 2H^+(aq) = Mg^{2+}(aq) + H_2O(l) \quad (4)$$

$$Al_2O_3(s) + 6H^+(aq) = 2Al^{3+}(aq) + 3H_2O(l) \quad (5)$$

$$CaO(s) + 2H^+(aq) = Ca^{2+}(aq) + H_2O(l). \quad (6)$$

Table 1
The chemical composition analysis of ilmenite (wt.%).

Composition	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
Wt.%	4.78	43.6	2.10	3.11	34.45	0.69	4.73	1.15	0.20	0.13	0.05	5.01