

Preparation of porous rutile titania from ilmenite by mechanical activation and subsequent sulfuric acid leaching

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Abstract

Synthesis of porous titania via mechanical activation of natural ilmenite and subsequent simultaneous dissolution and hydrolysis in dilute solutions of sulfuric acid was investigated by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), N₂ adsorption/desorption measurements, energy-dispersive X-ray spectrometry (EDX) and thermogravimetric analysis (TG). This is a novel template-free approach for synthesis of microporous, mesoporous and micro-mesoporous TiO₂ materials. Effects of sulfuric acid concentration and calcination temperature on physicochemical properties of the TiO₂ materials were examined systematically. The results show that both the factors considerably affected the porosity of the materials. In a 15% acid solution a microporous TiO₂ hydrolysate with BET surface area 109.3 m²/g was prepared. With a 10% H₂SO₄, we obtained a more pure micro/mesopore TiO₂ hydrolysate with BET area of 257.6 m²/g. Calcining the hydrolysate at ≥500 °C led to the formation of a mesopore TiO₂. The mesoporous TiO₂ generated at 600 °C still has a BET area of 92.1 m²/g. The high thermal stability is probably related to the presence of H₂SO₄ in the channel walls of hydrolysate. The XRD analysis indicated all the TiO₂ materials prepared in this study being rutile. The mechanism for formation of the porous rutile TiO₂ is mainly via in situ hydrolysis and precipitation of the dissolved titanium on the un-reacted ilmenite surface, where H₂SO₄ may play a very important role.

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1. Introduction

Mobil Corp. researchers firstly demonstrated the syntheses of aluminosilicate and silicate with hexagonal pore array in 1992 [1,2]. Their approach was based on the condensation and polymerization of inorganic species around the organized systems of surfactant molecules, which acted as structure-directing templates. Porous structures were formed after eliminating the surfactant. A variety of silica with different morphologies and porous structures has been synthesized using this strategy. Inspired by the discovery, this approach to porous materials has been extended to

metal oxides. Among porous transition metal oxides, titania is most attractive because of its excellent photochemical, optical and electronic properties.

Mesoporous TiO₂ was firstly synthesized by a modified sol-gel method in the presence of phosphorous surfactant, which acts as a template [3]. Since then, many different routes for preparation of mesoporous TiO₂ have been reported in the framework of sol-gel methods. In those processes, mesoporous TiO₂ was generally synthesized by controlling the high reactivity of Ti(IV) with addition of stabilizing agents, such as phosphate [4–6], amine [7–9], ionic [10–12], block polymer [13–15], or nonionic [16] surfactants as templates, or nonsurfactant templates [17–19]. Removing templates by either calcination or solvent extraction generates high-surface-area mesoporous TiO₂. However, thermal treatment at high temperature may be

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disadvantageous since it causes the collapse of mesoporous framework and loss of surface area due to the facile crystallization of TiO_2 and the subsequent crystal growth [20]. Solvent extraction allows the templates being removed without decomposition, but it is difficult to completely remove the templates from the as-prepared materials. Template-free routes for the synthesis of mesoporous TiO_2 materials include the hydrolysis of titanium butoxide with nitric acid [21] or phosphoric acid [22] as catalyst, the oxidation of TiC with nitric acid [23] and the direct hydrolysis of a titanyl sulfate solution [24].

On the other hand, majority of the porous titania prepared up to now are anatase. Titania exists in three main crystallographic forms e.g., anatase, rutile, and brookite. Each structure exhibits different physical properties, which lead to their different application. It is generally accepted that anatase titania is more efficient as photocatalyst than rutile titania. However, some investigations demonstrated that nanometer rutile [25,26] and mesoporous rutile TiO_2 [27] had better photocatalytic oxidation of some organic pollutants and photocatalytic reduction of heavy transition metal ions than nano-sized anatase and mesoporous anatase TiO_2 . It is well known that the basic requirements for photoactive materials are high crystallinity, large surface area, etc. Thus, high-surface-area porous titania with good crystalline framework is an important material. Up to now, only Luo et al. [28] and Li et al. [27] have reported synthesis of mesoporous rutile titania and their surface areas are 91 and $174.5 \text{ m}^2/\text{g}$, respectively.

Moreover, almost all of the titanium sources used is expensive organic or inorganic raw materials and the approaches to prepare porous TiO_2 often need rigorous reaction conditions, hence limiting its application.

Recently, we found a new template-free method for preparation of porous rutile TiO_2 . Using cheaper natural ilmenite as titanium source, a microporous, mesoporous or micro-mesoporous TiO_2 with large surface area and high crystallinity was synthesized via leaching a mechanically activated ilmenite with dilute sulfuric acid.

It should be noted that preparation of porous materials from natural minerals is not new. Molecular sieves obtained from zeolite type minerals have been widely applied in petroleum and chemical industries. The preparation of porous silica through mechanical pretreatment of silicate minerals and subsequent leaching was also reported [29,30], in which the leaching could selectively remove metallic ions from silicates, leaving pores within the mineral structures.

As well known, ilmenite is very resistant to acid attack. In the sulfate TiO_2 pigment production, a sulfuric acid solution with a concentration of at least $\sim 80 \text{ wt.}\%$ is required for effective decomposition of ilmenite. However, mechanically pretreated ilmenite could be well leached in a $50 \text{ wt.}\%$ sulfuric acid solution [31–33]. Our recent study [34] showed that even a sulfuric acid solution of as low as $5 \text{ wt.}\%$ could effectively dissolve mechanically activated Panzhihua ilmenite. However, the dissolved titanium was

unstable in the dilute acid solution and it rapidly hydrolyzed. We found the hydrolysate being a porous material. Therefore, in the present work synthesis and characterization of the porous TiO_2 were researched in detail.

2. Experimental

2.1. Preparation of porous titania materials

Natural ilmenite from Panzhihua, Southwestern China was used as starting material. Its main chemical compositions were as follows (wt.%): 34.21 FeO, 47.25 TiO_2 , 5.56 Fe_2O_3 , 6.23 MgO, 2.75 SiO_2 , 1.49 Al_2O_3 , and 0.61 MnO_2 . The particle size was 100–150 μm . A vertical planetary ball mill (QM-1SP2, Nanjing, China) with a rotation speed of 200 rpm and a spin rate of 580 rpm was employed in the mechanical activation of ilmenite. Four milling cells were fixed on its platform. Each of the cells was $\sim 420 \text{ ml}$ stainless steel vessel filled with 250 g $\varnothing 10 \text{ mm}$ and 150 g $\varnothing 5 \text{ mm}$ hardened steel balls. The milling operation was conducted under vacuum (residual pressure $\leq 16.3 \text{ kPa}$) with a ball/ilmenite mass ratio of 40:1. After milled for 4 h, 4 g of the milled sample was leached in a 400 ml 5–15 wt.% sulphuric acid solution at $100 \text{ }^\circ\text{C}$ for 4 h. During the dissolution, the slurry was sampled periodically to determine the dissolved rate of titanium and total iron. At the end of leaching, all the suspension was filtered and the resulting solid residual – hydrolysate was washed, dried at $80 \text{ }^\circ\text{C}$ for 3 h, and then calcined at different temperatures for 2 h. The solid samples before and after calcination were characterized.

The effects of sulfuric acid concentration and calcination temperature on the physical–chemical properties of the as-synthesized TiO_2 materials were studied.

2.2. Analysis and characterization

The titanium and iron contents in the leaching solution were directly determined by reduction–oxidation titration [35]. The relative element contents of the solid residuals were determined with a Hitachi S-450 microscope equipped with an energy-dispersive X-ray spectrometer (EDX, Thermo Electron V4105).

X-ray diffraction (XRD) patterns of solid samples were obtained with an X'Pert Pro MPD diffractometer in reflection mode using Cu K_α radiation with a voltage of 40 kV. SEM images were obtained using a JEOL JSM-5900LV scanning electron microscopy at an accelerating voltage of 20 kV. The external features and morphology of the solid residual were observed using a high-resolution transmission electron microscope (HR-TEM, FEI Tecnai F20).

The specific surface area, total pore volume and average pore diameter were measured by the N_2 adsorption/desorption method with a Quantachrome Nova1000e volumetric instrument at liquid nitrogen temperature. The un-calcined and calcined solid samples were degassed, respectively, at $100 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$ for 2 h prior to the measurement. The

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