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Surfactant removal from mesoporous TiO_2 nanocrystals by supercritical CO_2 fluid extraction

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ABSTRACT

In this study, mesoporous TiO_2 crystals were synthesized with a sol–gel process in the presence of hexadecylamine which was used as a structure-directing agent. The neutral template was removed by either supercritical CO_2 extraction (SCE) or conventional calcinations to produce mesopores, and the pore characteristics of mesoporous TiO_2 were investigated with TGA, XRD, FT-IR, SEM and N_2 sorption analysis. The results showed that hexadecylamine was completely combusted by a thermal treatment above 400 °C, whereas SCE successfully removed more than 62% of the surfactant with methanol used as a modifier. However, in contrast to SCE, calcination at 400 °C accompanied a reduction in surface area and pore volume, as well as the partial collapse of the mesostructure. The combination of SCE and subsequent heat treatment at 400 °C not only improved the porosity but also retarded the structure destruction due to much less exothermal behavior. The SCE approach provided mesoporous TiO_2 nanocrystals with remarkably high mesoporosity. The SCE technique can result in numerous advantages such as high mesoporosity, short processing time, low energy consumption, and environmental benefit.

1. Introduction

During the past few decades, TiO_2 materials with low cost, non-toxicity, strong oxidizing power and high resistance to chemical or photo-induced corrosion have been widely investigated. TiO_2 has large potential for the clean-up of environmental pollutants, including photocatalysis applications [1–4]. Moreover, smaller TiO_2 nanoparticles are also beneficial for more effective separation of photogenerated carriers (electron–hole pair) and greater photocurrent, resulting in higher photocatalytic and photoelectrical chemical conversion [5,6]. Nevertheless, TiO_2 nanoparticles are insufficient for industrial purposes, mainly limited by the low specific surface area and detrimental electron–hole recombination within nanoseconds.

Since the discovery of the mesoporous silicate molecular sieve family (M41S) in 1992 [7,8], and subsequently, mesostructured transition metal oxides [9–13], mesoporous TiO_2 materials have drawn much attention due to the high surface area and pore volume, well-defined structure, increased active sites, and tunable pore size [13]. Mesoporous TiO_2 has been synthesized by several techniques [11,14–17]. Stable mesoporous TiO_2 with a large surface area was first prepared in 1995 by Antonelli and Ying [10] via a modified sol–gel method in the presence of a phosphate surfactant, which illustrated a new technique for the synthesis of mesoporous TiO_2. Additional synthetic strategies have since been developed to prepare mesoporous TiO_2 using cationic, anionic and non-ionic surfactants as mesopore-forming agents due to the electrostatic and hydrogen bonding interactions [11,15,18–23].

Alternatively, removing the organic template from the pores is one of several key factors that cause mesoporous materials to function as efficient adsorbents or catalysts, as the template directly influences the textural properties and structural characteristics. Calcination and polar solvent extraction have been utilized in the final step of synthesis of mesoporous TiO_2 to liberate the structure-directing agent from the pore space while maintaining the desired stability of the inorganic network [15,16,21–25]. Calcination at moderate temperatures (350–450 °C) has been most commonly used as an efficient and valuable method due to the valuable crystallization in the channel wall. However, this is an energy consuming process that indispensably leads to the emission of a large amount of noxious gases during combustion. Moreover, severe damage to the mesoporous structure by thermal treatment may occur in the form of pore contraction, distortion or collapse of mesoporous TiO_2 [7,26–28]. In addition, an important aspect to engineer is the possible combination of template removal and recovery as these organic molecules constitute 30–50% of the total manufacturing cost of mesoporous materials. Unfortunately, an expensive template cannot be recovered by thermal treatment.

Critical fluid extraction at low temperature has attracted considerable attention for recovering templates due to the unique

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physicochemical characteristics and tremendous capacity for dissolving surfactants. The combination of the gas-like mass transfer and liquid-like solvating characteristics has led to considerable potential for use as mobile phases to extract analysts [29–31]. The use of supercritical CO_2 for extraction originates from the environmentally benign nature of CO_2 as well as the quality and purity of the final product compared to other methods. CO_2 was chosen because of its nonflammability, non-toxicity, low cost, near-ambient critical temperature and low pressure (304.1 K and 73.8 bar). The efficient method has been widely applied for the removal of cationic, anionic and neutral templates from silica-based mesoporous materials [31–35], however few from mesoporous TiO_2 [36,37]. High quality pore structure and removal effectiveness (over 80%) have been attained through supercritical fluid extraction with the promotion of physical properties of the products compared to calcined materials.

In our present work, mesoporous TiO_2 nanocrystals were obtained via sol–gel processing of titanium alkoxide in the presence of micellar hexadecylamine. The neutral template molecules were removed from the as-synthesized powders by either conventional calcination or supercritical CO_2 extraction (SCE). Comparisons of the mesoporosity and structural properties of mesoporous TiO_2 created from two treatment conditions were investigated via TGA analysis, wide-angle powder XRD patterns, FT-IR spectra, FE-SEM images and nitrogen sorption measurements.

2. Experimental

2.1. Materials

Titanium isopropoxide ($Ti(O–C_3H_7)_4$, TIP), 1-hexadecylamine ($C_{16}H_{33}NH_2$, HDA). Acetylacetone ($CH_3COCH_2COCH_3$, AcAc), *iso*-propanol (C_3H_7OH, IPA) and all other chemicals were purchased from Aldrich and used as received without any further purification.

2.2. Methods

2.2.1. Synthesis of as-synthesized mesoporous TiO_2

Mesoporous titania was prepared using titanium isopropoxide (TIP) as the titanium source and 1-hexadecylamine as the structure-directing agent. In a typical process, a yellow mixture of TIP and Acetylaceton with equal molar ratio was stirred vigorously. Surfactant and an aqueous solution of HCl (0.1 M) were dissolved in excess deionized water at 313 K until a homogeneous solution was obtained. The precursor mixture was then added drop-wise to the surfactant solution under stirring at room temperature. After 1 h, the yellow suspension was stirred at 40 °C for 48 h, and allowed to age at 80 °C for 8 days. The product was dried at 80 °C overnight and was subsequently centrifuged, and washed with *iso*-propanol (IPA) several times. Acetylacetone was used as a chelating agent to slow down the rapid condensation from the high reactivity of the Ti(IV) precursor. The dried, as-synthesized material was designated as TiO_2-*H*.

2.2.2. Template removal

The alkylamine surfactant was removed by two methods: thermal treatment and supercritical fluid extraction. Using a conventional method, the as-synthesized mesoporous TiO_2 was calcined in air for 24 h at 400 °C with a heating rate of 0.5 °C min^{-1}. The sample was designated TiO_2-*H-673*. Alternatively, SCE was employed to remove the surfactant. A schematic diagram for the SCE unit is shown in Fig. 1. After pre-treatment overnight, 0.5 g TiO_2-*H* was placed in a stainless reactor that was wrapped with heating tape and controlled by RKC REX-P100 with 0.1 °C resolution. The pressure was monitored by a pressure gauge using a PSI-TRONIX model 68922-16. Liquid CO_2 was supplied to the stainless reactor by a high pressure metering pump with a flow rate of 1 ml min^{-1}. After two hours of stabilizing the system, methanol as a polar modifier was introduced to the reactor at 0.1 ml min^{-1} by a liquid metering pump along with CO_2 flow. When the equilibrium was reached, the template extraction was then performed for three hours at constant pressure (2000 psi) and temperature (60 °C) under mild stirring. A mixture of CO_2, surfactant and solvent fluid in the outlet was isolated, released and dissolved in a deionized water reservoir. After extraction, the product was dried overnight at 80 °C, designated TiO_2-*H-SCE*, and characterized. For the comparison, TiO_2-*H-SCE* sample was subsequently calcined under the same condition and the final sample was designated TiO_2-*H-SCE-673*.

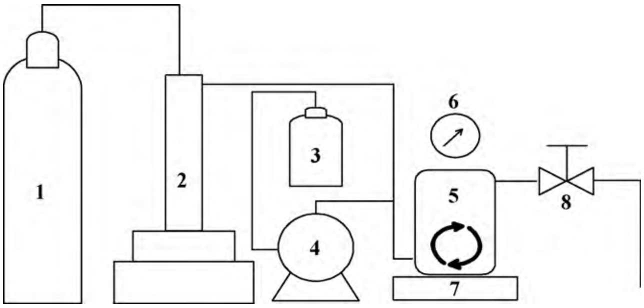

Fig. 1. A schematic diagram for the experimental apparatus of supercritical CO_2-modifier extraction: (1) liquid CO_2 cylinder, (2) CO_2 metering pump, (3) methanol reservoir, (4) liquid metering pump, (5) stainless reactor with *in situ* magnetic stirrer bar, (6) pressure gauge, (7) hot plate with magnetic driver, and (8) switching valve.

2.2.3. Physicochemical characterizations

The removal efficiency of the template was determined using thermogravimetric analysis (TGA) by comparing the weight loss of the as-synthesized sample with that of the powder after SCE. The TG profiles were performed on a TA Q50 instrument combined with Universal Analysis 2000 in a N_2/air flow rate of 40/60 ml min^{-1}. The samples were heated from room temperature to 800 °C at a rate of 10 °C min^{-1}, and maintained for 30 min in air. A trace of amine surfactant and functional groups of the solid samples were identified by Fourier transform-IR spectra, performed on a Nicolet 380 FT-IR spectrometer (Thermo Electron Corporation, USA) in the 4000–400 cm^{-1} at a resolution of 4 cm^{-1} and a 200 scan average using the KBr pellet technique. Powder X-ray diffraction patterns were recorded on a Rigaku D/MAX 2200 Diffractometer (Japan) using a Cu Kα radiation source (λ = 1.5418 Å) at a scan rate of 2° (2θ)/min over the 2θ region of 10–80°, operated at 35 kV and 20 mA. The anatase crystallite size was calculated from the Scherrer equation, $L = k\lambda/\beta\cos\theta$, where $k = 0.89$ is the shape factor, θ is the Bragg angle and β is the full-width at half-maximum (FWHM) value of the anatase (1 0 1) diffraction. The surface morphology and particle size of mesoporous TiO_2 were studied by field-emission scanning electron microscopy (JEOL JSM-6500FE, Japan) operating at 10 kV. The mesoporosity was revealed by N_2 adsorption–desorption analysis at −196 °C using a Micromeritics ASAP 2020 apparatus (USA). Prior to measurement, the samples were degassed at 150 °C for two hours. The specific surface area, pore volume and pore size distribution were determined using Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods. The porosity was calculated from $P = V_P/(V_P + V_S)$, where V_P is the volume of the liquid nitrogen corresponding to the total pore volume and V_S is the skeleton specific volume of TiO_2 taken as 0.27 and 0.235 cm^3/g for anatase and rutile, respectively [38].