Preparation of TiO₂ nanoparticles by supercritical carbon dioxide

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Abstract

Nano-sized titanium dioxide TiO₂ powder was successfully prepared from its precursor titanium (IV) isopropoxide (TTIP) by a system comprising of supercritical fluids microemulsion and supercritical-drying method, in which TTIP reacted in reversed micelles formed by surfactant Zonyl FSJ employing a supercritical carbon dioxide system. The milky white product, collected from the bottom of the pressure cell turned into sol–gel after sitting in the air for 5 days. Amorphous TiO₂ particles with particles size 2–7 nm can be obtained from the sol–gel by the supercritical-drying method. The amorphous TiO₂ particles were converted to anatase phase by calcining at 500 °C. Characterization of the TiO₂ powder consisted of TEM, XRD and EDS methods.
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1. Introduction

Titanium dioxide (TiO₂) of both anatase and rutile phases are usually found in industrial applications. Anatase is a useful catalyst in photochemistry because of its high photoactivity and rutile are common white pigment being employed for its superior optical hiding power. Titanium hydroxide (Ti(OH)₄) or amorphous TiO₂ can be prepared by liquid-phase methods such as by reaction of an alkoxide with water [1] and separately by a chemical vapor deposition process [2]. Both crystalline TiO₂ phases can be obtained by claiming the amorphous phase at different temperatures.

The supercritical fluid (SCF) technique has been applied to the preparation of nano-sized Ti(OH)₄ and TiO₂ particles [3]. In addition, Reverchon et al. [4] prepared TiO₂ particles with a size range of 70 nm–110 nm by using titanium tetra-isopropoxide (TTIP) hydrolysis in a supercritical carbon dioxide system. Furthermore, Chhor et al. [5] obtained submicron TiO₂ particles from supercritical ethanol by thermal decomposition of TTIP. Moreover, Tadros et al. [6] used TTIP to prepare 0.1–2.0 μm TiO₂ particles in supercritical carbon dioxide.

Supercritical fluids microemulsion has shown to be another highly effective SCF technique other than thermal decomposition to prepare nano-sized particles. For example, Ohde et al. [7] suggested that using as PFPE-PO₄ as surfactant in SCF CO₂ and successfully obtained silver nanoparticles by the reduction of Ag⁺. Ohde also noted the critical role of the surfactant for the formation of reversed micelles in SCF CO₂, in which H₂O occupies the central space of micelles and CO₂ on the outer space. Zielinski et al. [8] employed PFPE as surfactant to investigate water-in-carbon dioxide and found that micelles with core radius 20 Å–36 Å could be formed with PFPE at a concentration 2.1 wt.% in CO₂ and D₂O concentration of 0.8–2.0 wt.%.
Hu et al. [9] prepared TiO$_2$ particles with a size range of 70 nm–110 nm by sol–gel technique and a subsequent $n$-butanol supercritical-drying method. Generally speaking, there is no gas–liquid interface in supercritical fluid and the solvent can be beneficially removed without surface tension effect limiting the coagulation of particles. Also, it seems that the functional proportion of ultrafine TiO$_2$ powder may be greatly enhanced by obtaining a product, having a size range of less than 20 nm.

In this paper, the supercritical fluid microemulsion method was applied to the preparation of nano-sized Ti(OH)$_4$ and TiO$_2$ particles by using fluorinated anionic fluorinated anionic Zonyl FSJ as the surfactant. Supercritical-drying technique was subsequently used to dry the particles. With respect to the demand for the lower range of nano-sized TiO$_2$ powder product, our experimental efforts have been aimed to obtain a product with a size range of less than 10 nm.

2. Materials and experiment

2.1. Synthesis

Titanium (IV) isopropoxide (TTIP), ethyl alcohol, and isopropanol (IPA), were purchased from ACROS manufacturer. Zonyl FSJ is a surfactant made by Du Pont, having a formulation of $(F(CF_2CF_2)_{x}CH_2CH_2O)_{y}P(O)(ONH_4)_z$ $(x=1$ or 2, $y=2$ or 1, $z=1–7$), 15 wt.% isopropyl alcohol, and 40 wt. % water. CO$_2$ was obtained from Air Products San Fu Co. Ltd. located in Taiwan.

The autoclave reactor (max. pressure 37.5 MPa), having an inner diameter of 45 mm; length 180 mm; and volume 300 mL, for the preparation of titanium dioxide nanoparticles was Manufactured by Autoclave Engineers Inc.

Fig. 1 shows the schematic drawing of the experimental setup designed by the authors. Generally speaking, the arrangement of the different parts of the reactor systems may be considered to be a viable modification of laboratory design.

50 mL of the 0.4 M TTIP dissolved in isopropanol was stirred in the high pressure cell, and 1 mL of the surfactant ZONYL FSJ was gradually added. An operating procedure included. Close up of the cell; maintaining at temperature to 60 °C; and pumping liquid CO$_2$ so as to give a pressure of 30 MPa; turning off the pump; and finally allowing the reaction to proceed for four hours. The milky white product was collected from the bottom of the pressure cell by a long test tube.

The milky white product became gel at room temperature after setting for 5 days. 10 mL anhydride ethanol was added to mix with the gel and then was stirred by a magnetic stirrer in the autoclave, and temperature was increased to 60 °C. Liquid CO$_2$ was pumped into the cell to give a pressure of 30 MPa. The drying of the product was completed after a duration of four hours. Collections of the ultrafine powders were conducted through the needle valve (at top) at a flaw rate of 1 L/min for 2–3 h.

Fig. 1. The supercritical fluids apparatus drawing A: CO$_2$ tank, B: cooler, C: pump, D: stirrer, E: autoclave, F: flow meter, Pi: pressure gauge, V1, V2: valve and V3: needle valve.

Fig. 2. XRD pattern of TiO$_2$ particles: (A) for amorphous TiO$_2$ before calcinations; and (B) for anatase TiO$_2$ after calcinations.

Fig. 3. EDS of particle before calcinations. (The Au came from the gold plating on the specimen to prevent static discharging.)
The above TiO\textsubscript{2} powder was heated at a heating rate 1 °C/min to a temperature of 500 °C, in an oven under ambient condition, maintaining at this temperature for 30 min.

2.2. Characterization

TiO\textsubscript{2} nanoparticles were characterized by the following: (a) transmission electron microscope (JEM-1200EX), (b) scanning electron microscope (ABT-150 S) with energy dispersive spectrometer (EDS) and (c) X-ray diffraction (RINT 2000 CuK\textsubscript{\alpha} at \( \lambda \) of 1.5405 Å).

A drop of the TiO\textsubscript{2} solution (from a feedstock of 0.01 g TiO\textsubscript{2} powder diluted to 20 mL by EtOH) was placed on a carbon film supported by a 200 mesh copper grid (TED PELLA, INC. Prod No. 01800-F), and the solvent was allowed to evaporate. The size distributions of the TiO\textsubscript{2} particles were obtained by Fig. 4. (A) TEM micrograph of particle prior to calcinations. (For feedstock of 1.0 mL FSJ) (B) TEM micrograph of particle after calcinations. (C) TEM micrograph of particle derived from feedstock of FSJ 2.0 mL. (A') particle size distribution of (A) TiO\textsubscript{2} product. (B') particle size distribution of (B) TiO\textsubscript{2} product. (C') particle size distribution of (C) TiO\textsubscript{2} product.
measuring the digitized micrographs. The mean diameter, $D$, and the standard deviation, $\sigma$, were derived from an average of 200 particles.

3. Results and discussion

A product of nano-sized TiO$_2$ particles has been successfully prepared by a combination of supercritical microemulsion and supercritical-drying processes. Hydrolysis and polycondensation took place in the micelles by the following route [11]:

\[
\text{TiOC}_3\text{H}_7(\text{OH})_4 + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4\text{C}_3\text{H}_7\text{OH}
\]

\[
\text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}
\]

A milky white dispersion was formed after CO$_2$ was released, becoming a gelatinous form after maintaining at room temperature for 5 days.

The particle size distribution has been shown to be controlled by the hydrolysis rate and the amount of water added in reverse micelle and sol–gel techniques [10–12]. Furthermore, water is also an important factor in controlling the hydrolysis rate.

It should be emphasized that the presence of water is considered to be a controlling factor for the formation of micelles in connection to the growth of TiO$_2$ particles. In this regard, the kinetics of TiO$_2$ formation is parallel to the size-growth TiO$_2$ particles whereas, an insufficient supply of water may decrease the formation of TiO$_2$ particles, also leading to the smaller particle size for the TiO$_2$ product. For example, Fig. 4A and C show that the average particle size of TiO$_2$ powder is much smaller for a case of a smaller ratio of (TTIP: TiO$_2$) = 1:1.25 than that of (TTIP: TiO$_2$) = 1:2.5, respectively.

White fine particles were obtained after drying the milky white gel by supercritical-drying method, being necessary for the removal of the solvent without surface tension effect so as to avoid the troublesome effect of the coagulation of particle. Theoretically, this beneficial behavior for powder handling is considered to be due to the non-existence of surface tension in the supercritical fluid state in the system.

The fine particles were amorphous from the analysis of XRD as shown in Fig. 2A and contained elements of Ti, C, and O from EDS analysis as shown in Fig. 3. From Figs. 2 and 3, it may be noted that the particles are amorphous TiO$_2$. The Au in Fig. 3 was due to the gold plating on the specimen to prevent static discharging in the TEM chamber. Fig. 4A shows the TEM micrograph of these particles, giving a particle size range of about 2–7 nm. The distribution of particles size is shown in Fig. 4(A’).

Amorphous TiO$_2$ particles could be transformed to crystalline TiO$_2$ via calcinations [13]. As shown by XRD pattern as given by Fig. 2B after calcinations at 500 °C, the amorphous TiO$_2$ particles have been transformed to crystalline anatase phase. Fig. 4B presented the TEM micrograph for the samples calcined at 500 °C, and the individual particles have a size range of 10–25 nm.

4. Conclusions

Nano-sized titanium dioxide TiO$_2$ powder has been successfully prepared from its precursor titanium (IV) isopropoxide (TTIP) by a combination of supercritical fluids microemulsion and supercritical-drying techniques, in which TTIP reacts in reverse micelles (H$_2$O being surrounded by CO$_2$) formed by surfactant Zonyl FSJ using a medium of supercritical carbon dioxide. The milky white product, collected from the bottom of the pressure cell turned into sol–gel mode after sitting in the air for 5 days. Amorphous TiO$_2$ particles with particles size 2–7 nm can be obtained from the sol–gel by supercritical-drying method. The amorphous TiO$_2$ particles were converted to anatase phase by calcining at 500 °C.

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