초임계 이산화탄소에서 산화티타늄 미세입자 생성

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Formation of Titanium oxide particles in supercritical CO_2

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Introduction

The formation of sub-micro particles by supercritical fluids has been one of the promising research areas. In several cases the key of the process is the formation of very large surface areas. Among the other materials, titanium hydroxide ($Ti(OH)_4$) and titanium oxide(TiO_2) is used widely as a white pigment, opacifier in paper, plastics, paints, inks and cosmetics [1]. Titanium oxide also has many important catalytic applications, as a support for noble metals and other transition metal oxides and as a photocatalyst for water and air purification. Supercritical carbon dioxide is an attractive medium for the synthesis of ceramic powders because it is nontoxic, nonflammable, has a low critical temperature, a high degree of compressibility, and low cost [2]. The major advantage of using such fluids is that they can be efficiently separated, by decompression, from both organic co-solvents and solid products, facilitating single step, clean and recyclable process engineering [3]. Liquid antisolvent processes are based on the use of two liquid solvents that are completely miscible. The solute to be micronized is soluble in the first solvent, but not soluble in the second solvent. Therefore, the addition of the antisolvent induces the formation of a solution of the two liquids and the supersaturation and precipitation of the solute. In the antisolvent processes, this study used the acronym ASES of the process. Titanium alkoxides are reasonably soluble in $SCCO_2$ and titanium isopropoxide(TIP) exhibits the highest solubility of the commercially available compounds[4] . We attempted the production of nanoparticles by optimizing the operating parameters of the process: pressure, solute concentration.

Theory

Submicron TiO_2 particles have been obtained from titanium isopropoxide by thermal decomposition and hydrolysis. In the thermal decomposition method, The alkoxides used as precursors in various TiO_2 syntheses are the ethoxide $Ti(OC_2H_5)_4$ and the isopropoxide $Ti(OC_3H_7)_4$.(TIP) Both are liquids at room temperature but the ehoxide is known to be less volatile because of its higher molecular complexity. This tendency for such compounds to form molecular associations decreases with increasing branching on the alkoxy group. TIP was heated up to 350℃. At 265℃ an important jump of the pressure inside the reactor and the formation of a fine white particles are observed, related with a rapid decomposition of the alkoxide[5].

The hydrolysis of titanium isopropoxide involves two principal reactions;

$$Ti(OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH \quad \text{(hydrolysis)} \quad (1)$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad \text{(condensation)} \quad (2)$$

Both reactions proceed via associative nucleophilic substitution and the condensation step may comprise both water and alcohol elimination reactions. According to the stoichiometry of Eq.(1), four water molecules are required to completely convert one TIP molecule to $Ti(OH)_4$. The reaction time has been estimated by Papet et al.[6] to be about 5second. The relative rate of hydrolysis to condensation dictates the structure of the wet gel and has a direct bearing on the textural properties of the final solid. The stoichiometric hydrolysis level for TiO_2 synthesis from titanium isopropoxide is 2 and higher hydrolysis levels typically favor colloidal titania precipitates rather than polymeric gels.[7,8]

Experiment

Schematic representation of the ASES apparatus is shown in Fig. 1.

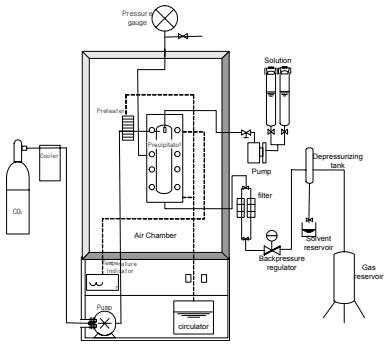
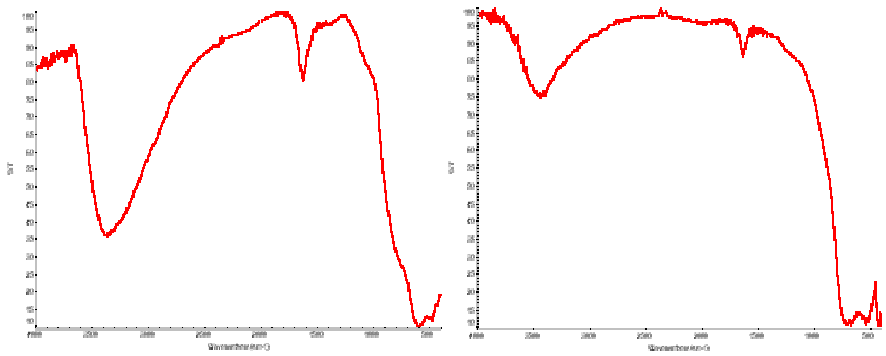


Figure 1. Schematic diagram of Aerosol solvent extraction

It consists of high-pressure precipitator, liquid solution vessel, $SCCO_2$ cylinder, filter and two pumps respectively used to deliver the liquid solution, $SCCO_2$. The pump used for supercritical fluid was modified for compressible-fluid pumping by adding a cooling. In the high-pressure precipitator, stainless steel nozzle was used to produce small droplets of the liquid solution. Reagent-grade TIP($Ti(OC_3H_7)_4$) was supplied by Aldrich; CO_2 at 99% purity was given by Sinyang. Samples of the particle recovered from the precipitator were observed by a scanning electron microscope (SEM), X-ray diffraction pattern, Particles size analyzer (PSA).

Result and discussion

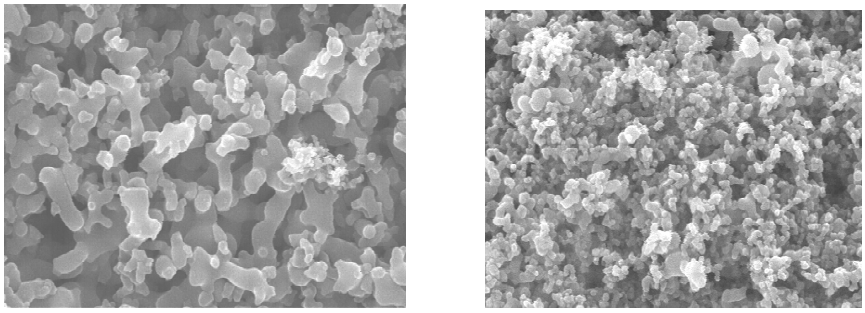
We infer that it was associated with water desorption. The FTIR spectrum (Figure 2(a))of an as-synthesized titania sample confirmed the presence of adsorption water, as evidenced by the characteristic OH stretching(3000-3500㎝$^{-1}$) and HOH bending (1645㎝$^{-1}$) bands. No bands associated with residual TIP are observed.



(a) (b)

Figure 2. FTIR spectrum of a titania particles ; (a) titania particle synthesized using TIP in $SCCO_2$ (b) Reagent TiO_2 particle

we found only a slight decrease of the mean particle size of titanium particles with increasing pressure.



(a) (b)

Figure 3. SEM image of titania particles obtained operating at 35℃; (a) 80bar (b) 150bar

shown in Figure 4 where particle diameter is reported against liquid phase concentration. This result agrees well with particle size and PSA measurements previously performed on other acetates [7]. The increase of polydispersity with liquid solution concentration can be attributed to higher growth rates when compared to nucleation rate.

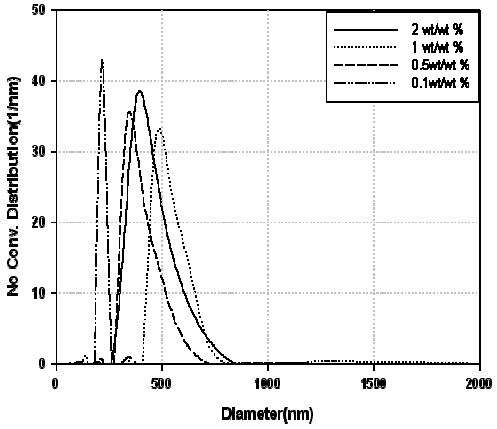


Figure 4. Effect of liquid solution concentration on the PSA of titania particles obtained operating at T=35℃, P=100bar .

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