

Photocatalytic Activity of TiO₂ Powders Synthesized by Supercritical Gas Antisolvent Method

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Synthesis of nanocrystalline, spherical, and anatase type TiO₂ photocatalyst were performed by supercritical gas antisolvent process in the range of 50–150 °C and 100–150 bar. As-prepared samples were calcined at 500 °C and characterized by X-ray diffraction, scanning electron microscopy, Brunauer–Emmett–Teller method, differential thermal analysis/thermal gravimetry. In X-ray diffraction analysis, the anatase crystalline phase of titanium dioxide has been detected. The mean crystalline size of powders is about 13 nm. The photoactivity test of the powders was evaluated by the photodegradation of aqueous RR 180 (reactive red 180) solution under UV light. While the photocatalytic performance of TiO₂ powders (Brunauer–Emmett–Teller surface area of 69.2 m²/g) produced at 150 bar and 150 °C was found to be 98%, only 25% degradation was observed with powder produced at 150 bar and 100 °C. Results showed that the powder properties and photocatalytic activity can be tuned by controlling the supercritical conditions such as temperature and pressure.

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1. Introduction

Titanium oxide (TiO₂) has been important ceramic oxide in point of view of both industrial and academic area for many years because of unique physical and chemical properties such as semiconductor, biocompatibility, low cost and optical [1, 2]. TiO₂ ceramics are employed in various applications such as sensor, photovoltaic, electrodes and UV blocks. One of the novel applications of TiO₂ is the photocatalytic decomposition of harmful organic pollutions [3, 4].

A number of methods such as sol–gel, hydrothermal and precipitation have been proposed for TiO₂ synthesis [4–6]. One of these methods is supercritical fluid process [7–9]. Over the past few years, it has been widely researched for preparing inorganic powders in material science. It is a new approach in powder processing because nanopowders with desired physical and chemical properties can be easily designed by this method. In this regard, powder performance in applications is enlarged [10, 11].

Supercritical fluids (SCF) also present a novel combination of liquid-like and gas-like physical and chemical properties, which composes these fluids unique as solvents, reaction and drying media. These properties are continuously variable with changes in pressure and temperature, which allows a tailoring of the properties of SCF for applications to improve the formation of nanocrystalline powders [12, 13]. CO₂ is widely used as supercritical fluid due to chemically stable, environmentally benign, non-flammable, especially at low critical temperature (31 °C) and pressure (7.38 MPa) [10].

Several processes for particle formation by supercritical fluids have been performed in the literature. The supercritical antisolvent process (known in a variety forms in literature such as GAS, SAS, ASES, PCA, or SEDS) is based on the precipitation of solid by antisolvent effect. It uses the supercritical CO₂ due to its antisolvent effect to precipitate the substrate initially dissolved in solvent. When antisolvent is introduced into solvent, it decreases solubility limit of solvent through volumetric expansion and finally solvent becomes highly supersaturated, forcing solute to forming as particle through nucleation and growth [14, 15].

The purpose of this research is to report the synthesis of nanocrystalline TiO₂ under supercritical conditions, as well as to test the photocatalytic performance of TiO₂ in photodegradation of aqueous reactive red 180 (RR 180) solution.

2. Experimental procedure

The solid precipitate precursor of TiO₂ was obtained via supercritical gas antisolvent method using titanium isopropoxide (TTIP, 97%, Aldrich Chemical Co.). Isopropanol alcohol (Fluka, analytic reagent) and CO₂ were used as a solvent and an antisolvent, respectively. TTIP were dissolved in alcohol to obtain highly transparent ceramic solutions to be precipitate under the supercritical condition. The obtained solution was then stirred for 30 min at room temperature and then filtered. The experiments were performed in a 300 ml 316 stainless steel autoclave (autoclave engineering reactor controller unit, USA) with teflon liner, equipped with a magnetically stirring unit. High pressure pump (LabAlliance, model SFC-24) was used for delivering CO₂ into reactor. The solid precipitates were obtained as previously reported in detail [16]. After collecting solid precipitate from bottom of the vessel, it was washed with water and ethanol, cen-

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trifuged at 9000 rpm for 5 min, dried at 90 °C overnight and finally heated at 500 °C for 2 h. X-ray diffraction (XRD) patterns (Rigaku, Miniflex) were recorded to determine the crystallite size and phases of the powders using Cu K_α radiation. The surface area of the powders was determined with the Brunauer–Emmett–Teller (BET) equation from the N₂ adsorption obtained with Quantachrome instrument (Nova 2200 E). The mass and heat flow of the samples were monitored by thermal analysis (Perkin Elmer) in argon atmosphere at a heating rate of 10 °C/min. The morphology and particle size of powders are characterized by a Zeiss Supra 50 VP SEM. Photocatalytic studies were performed in a photoreactor containing the required TiO₂ powder and aqueous solution of dye. More details and explanation of the procedure, setup and characterization were given elsewhere [17].

3. Results and discussion

Different operating conditions (pressure and temperature from 100 to 150 bar and from 50 to 150 °C, respectively) have been performed to produce TiO₂ powders. Supercritical conditions are shown in Table.

TABLE

Experimental conditions for TiO₂ synthesis via supercritical fluid precipitation.

Sample	Supercritical conditions		Powder formation
	Temperature [°C]	Pressure [bar]	
T1	50	100	no
T2	100	100	no
T3	100	150	yes
T4	150	150	yes

Whereas the precipitation was not observed at 50 and 100 °C, it was achieved after both pressure and temperature was increased (in case of T3 and T4). This means that temperature and pressure are key parameters to be considered for producing powder.

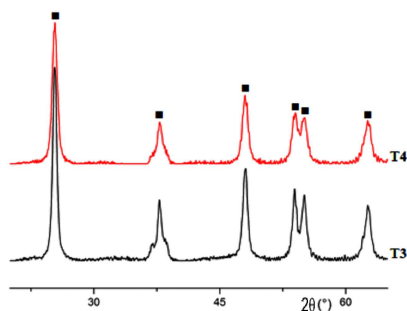


Fig. 1. XRD patterns of powders calcined at 500 °C (■ anatase).

Figure 1 shows the XRD patterns of the calcined TiO₂ powders. At 500 °C, both powders are in the anatase-

-type structure, which shows high photocatalytic efficiency. The crystal size of both powders was found to be 13.5 nm. According to XRD results, there is no effect of supercritical condition on the phase formation.

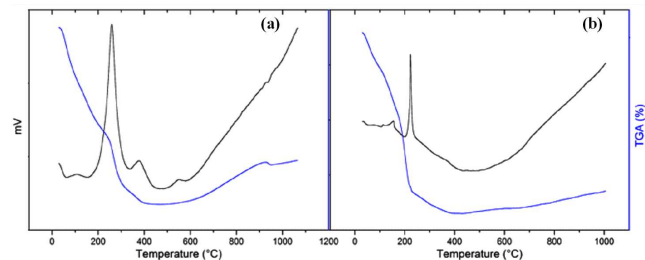


Fig. 2. DTA–TG curves of as precipitated (a) T3 and (b) T4 powders.

Typical differential thermal analysis/thermogravimetry (DTA/TG) curves of the as precipitated — TiO₂ powders are shown in Fig. 2. According to DTA traces, the dominant peaks of endothermic reactions centered at between 200 and 300 °C were observed at both powders. This stage corresponds to the loss of bonded water and organics, during which approximately 15% of the original mass is lost. The crystallization peak was expected to occur below 500 °C (confirmed by the XRD in Fig. 1) where the powder crystallizes (from an amorphous state).

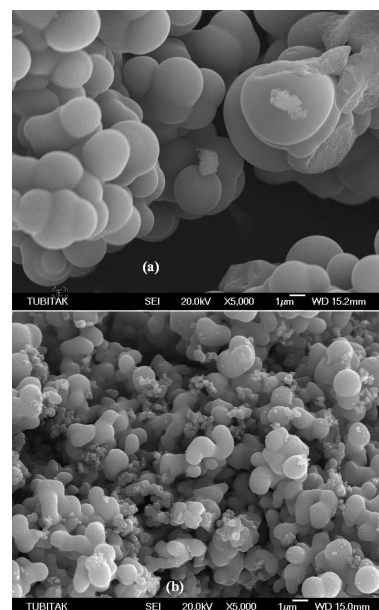


Fig. 3. SEM images of the TiO₂ powders (a) T3, (b) T4.

SEM micrographs of the morphology and particle size of the calcined powders are shown in Fig. 3. The results show that the temperature and pressure of supercritical conditions during particle formation affected the powder characteristics (agglomeration, size and morphology). In

case of T3 powder precipitated at 150 bar and 100 °C, the micrograph shows agglomerates consisting of fine spherical primary particles having monomodal size distribution (2–3 μm). As temperature increases to 150 °C at constant pressure, powders (T4) with size changing from 200 nm to 2 μm were produced. It had weak agglomeration and surface area value of 69.2 m^2/g . While increase in temperature induced higher nucleation rate, it hindered the growth rate of crystallites during supercritical precipitation. Furthermore, the weak agglomerations were obtained.

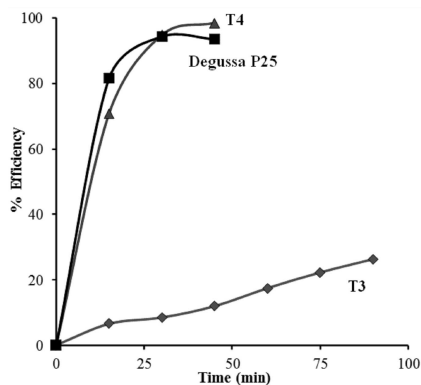


Fig. 4. Photocatalytic activity of TiO_2 powders precipitated at various supercritical conditions.

Dye (red 180) decomposition curves are shown in Fig. 4. As can be seen, the efficiency of TiO_2 strongly depends on supercritical condition and it can be tuned by changing the supercritical temperature. Photocatalytic performance of T4 is higher than that of T3 in the same conditions. While T3 powders had 25% of performance after 90 min, that of T4 was found to be 98% after 45 min. Also, T4 powders have the same value when compared to commercial form of TiO_2 (Degussa P 25), which is known as a highly efficient photocatalyst. It is thought that higher performance can result from high surface area and soft agglomeration of powders. Thus, powders were homogeneously dispersed in dye solution. As a result of high interaction between spherical powder and dye molecules, the photocatalytic activity was increased.

4. Conclusion

In the present work, titania (TiO_2) powders were successfully prepared by supercritical gas antisolvent method and tested their photocatalytic performance. All the obtained powders are nanocrystalline anatase phase, which have the crystalline size of 13 nm. The powders (surface area of 63.2 m^2/g) produced under the conditions of 150 bar and 150 °C exhibited the higher photoactivity than those obtained at 150 bar and 100 °C and

commercial Degussa P25. The increase in photocatalytic activity could be attributed to the higher surface area, smaller particle size, and weak agglomeration in the powders. As a result, the supercritical fluid process can be successfully used to control the properties powder and, hence to tune performance for final use.

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