Korean J. Chem. Eng., **20**(6), 1149-1153 (2003)

Characterization and Photocatalytic Performance of Nanosize TiO_2 Powders Prepared by the Solvothermal Method

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(*Received 3 April 2003 • accepted 4 July 2003*)

Abstract−The solvothermal reaction of titanium tetra-isopropoxide (TTIP) in different alcohol solvents was investigated in the pressure range 40±2 bar to prepare Titanium (IV) oxide. The results show that the physical properties of the products, such as crystal size, shape, and structure, are strongly influenced by the types of solvents and temperature during the reaction. The effects of reaction conditions on the physical properties and the crystal structure of powder were investigated by using XRD, SEM, DLS, DSC and BET. The obtained TiO_2 powder prepared at an organic solvent condition exhibited submicron size and huge surface area with a narrow size distribution but some agglomeration. TiO_2 powder prepared at 1,4-butanediol and 623 K shows the highest photoactivity on the photodegradation rate of methyl orange.

Key words: Solvothermal Method, TiO_2, Photocatalyst, Photodegradation, Methyl Orange

INTRODUCTION

Solid inorganic materials are often employed to promote high efficiency chemical processes including both catalytic and photocatalytic reactions [Domen et al., 2001; Park et al., 2001]. Among the large number of inorganic materials, titania has been the most extensively used in modern technologies including solar energy conversion, and photocatalysis because of its high photocatalytic activity, stability, suitable band-gap energy, and so on [Kominanmi et al., 2001]. These properties are dictated to a large extent by control of its crystal phase, morphology, and particle size. In recent years, researchers have reported a variety of nano-size TiO_2 materials as nano-particles, nano-wires, nano-tubes, and so on. As we know, titania has three main crystal phases: anatase, rutile and brokite [Hoffmann et al., 1995; Linsebigler et al., 1995]. Among them, anatase phase is chemically and optically active, and thus is suitable for catalysts and supports. Crystal structures have their own stabilization temperature ranges and can be controlled by heat treatment and sometimes, by dopants [Calza et al., 1997; Mills and Wang, 1997]. Nanocrystallite sizes and high surface areas have attracted interest due to the unusual photocatalytic properties. However, nanosized titanium dioxide particles have a strong tendency to agglomerate to larger particles, which leads to a decrease of thermal stability and exerts an influence on its applications. Therefore, this study is focused on the synthesis and characterization of ultrafine TiO_2 particles with nanosize, crystal phase, narrow size distribution and minimal agglomeration.

A solvothermal method was employed for this purpose. The solvothermal method, a powerful route for preparing materials, is similar to the hydrothermal method except that organic solvents are used instead of water [Qian, 1999; Wang et al., 2001; Zhu et al., 1995]. In comparison with the hydrothermal method, the solvothermal method might allow the product to be free from foreign anions because the organic solution, having a low relative permittivity, is free from ionic species [Chen and Xu, 1998]. So, this method will be defined as chemical reactions or transformations in an organic solvent under supercritical or sub-critical pressure with temperature conditions. Solvothermal processing provides for excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. As expected, the prepared TiO_2 nanoparticles exhibited photocatalytic activity much higher than those of commercial products of TiO_2. In this study, we first attempted to compare a characterization and photocatalytic activities of synthesized nanocrystalline TiO_2 in various organic solvents.

The prepared TiO_2 photocatalysts were evaluated on the photocatalytic activity by using a simple photoreactor system. Photooxidation of methyl orange was chosen to test the photocatalytic activity of TiO_2 powders prepared by solvothermal method. The photocatalytic activity of the catalysts was analyzed by a UV-VIS spectrophotometer [Chen, 2000; Nam et al., 2003]. The photocatalytic activity of TiO_2 powders prepared by the hydrothermal method was compared with Degussa P-25 TiO_2 powder.

EXPERIMENTAL

1. Preparation of Titania

The preparation procedure for TiO_2 powder was as follows: 0.1 mole of TTIP (99.9%, $Ti[OCH(CH_2)_2]_4$, Junsei Chemical) 0.10 mole was slowly, respectively, added into three different kinds of 1.0 mole of solvents (1-Butanol 99%; 1,4-Butanediol 99%; Glycerol 99.5+%) to obtain a white precipitate. Before the solvothermal treatment, the solutions were sonicated for distribution of conglomerated amorphous phase TiO_2 with 140 W, 15,000 Hz for 2 min. And the solutions were heated to 573 K or 623 K with a ramping rate of 5 K/min and maintained these temperatures with auto-generative pressure of 40 bars in a stirred autoclave system for 1 hr. During the solvothermal treatment, a white precipitation was formed to anatase phase TiO_2 nano powder. The stirring velocity of magnetic drive in the stirred autoclave was maintained at about 300 rpm. The ob-

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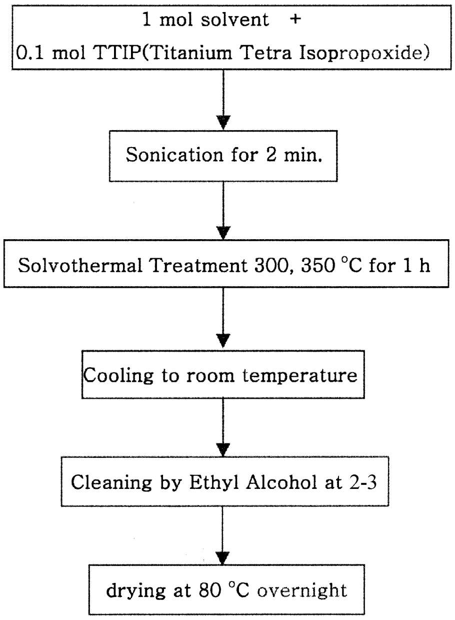

Fig. 1. Procedure for preparing the nanocrystalline TiO_2 powder by solvothermal method.

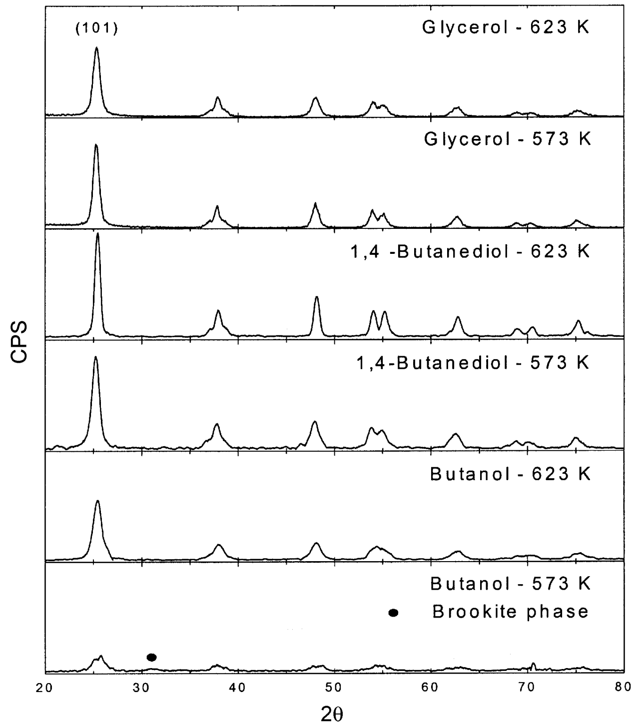

Fig. 2. The powder XRD patterns of nanocrystalline TiO_2 powders prepared by the solvothermal method at various stirring velocities and pH of solutions.

tained TiO_2 powders were rapidly washed with ethanol repeatedly, and then dried at 353 K for overnight. This preparation procedure is given in Fig. 1.

2. Photooxidation of Methyl Orange

The photooxidation of methyl orange was carried out in a simple photocatalytic reactor to test the activity of catalyst. The methyl orange solution was prepared by mixing 30 ppm of methyl orange and 100 ml of distilled water (MilliPore Q). 0.1 g of the prepared TiO_2 catalyst was added into a pyrex cylindrical reactor with the methyl orange solution. A 400 W Osram metal halide lamp, built into aluminum lamp housing with rear reflectors, was used as the light source which was located 30 cm in front of the reactor. A magnetic stirrer at 300 rpm was used to mix the TiO_2 suspension with reactant and air bubbling of 200 ml/min was used for source of oxygen in the solution. The reaction rate was analyzed by a UV-VIS spectrometer (Hitachi Co. U-3210) at 462 nm.

RESULTS AND DISCUSSION

1. Characterization of TiO_2 Powders

The TiO_2 powder was analyzed by powder X-ray diffraction (XRD, Rigaku Co. Model DMax) with nickel filtered CuK_α radiation (30 kV, 30 mA) and with the 2θ range from 20 to 80°. The scan speed was 10°/min and the time constant was 1 sec. The diffraction angle of 25.4° was selected to discuss the crystallinity of the prepared TiO_2. The powder XRD patterns of the products are shown in Fig. 2.

The analysis of the XRD pattern revealed that the TiO_2 powders were successfully crystallized to the anatase phase through solvothermal treatment by JCPDS files (card number 9-29). The average particle size was determined from the full width at half maximum (FWHM) of anatase peak by using Sherrer's equation. The crystallite sizes were calculated at 5.6-11.4 nm for the TiO_2 powders. These results are summarized in Table 1. The number of -OH in the moleculer structure might be one of the factors that affect the crystallization reaction. The titania gels in the 1,4-butanediol and

Table 1. The measured physical properties of TiO_2 prepared by the solvothermal method at various conditions

Properties \ Solvents		Butanol		1,4-butanediol		Glycerol	
		573 K	623 K	573 K	623 K	573 K	623 K
BET (m^2/g)		96	102	99	122	107	111
DSC (kcal/mol)	Heat of physisorption of H_2O	0.43	1.44	0.70	1.66	0.57	0.98
	Heat of chemisorption of H_2O	17.17	17.62	28.96	29.15	27.64	28.47
Crystalline phase		anatase, brookite	anatase	anatase	anatase	anatase	anatase
Calculated crystal size by BET (nm)		15.9	15.1	15.4	12.6	14.2	14.0
Calculated crystal size by XRD (nm)		11.8	6.8	8.3	5.6	6.0	5.9
Measured average particle size by DLS (nm)		102	89	66	59	113	104

glycerol solvents showed higher crystallinity to the anatase phase than titania gel in the butanol through solvothermal treatment. The -OH facilitated the condensation of hydrolyzed precipitates, and, 1,4-butanediol and glycerol solvents have more plentiful -OH in the molecule structure than butanol. However, the crystalline size of TiO_2 was slightly decreased with increasing the cystallinity of TiO_2.

The effect of reaction temperature during the solvothermal treatment was examined. Fig. 2 shows that the primary particle size at 623 K is smaller than that at 573 K and has higher crystallinities. We know that reaction temperature might be one of the factors that affect the initial nucleation and crystallization reactions. This result indicates that the solvothermal method could be effective for obtaining the comparatively small sizes but high crystallinity of TiO_2 powder by controlling the temperature and the number of -OH in the formula of solvents. It is believed that the reaction temperature controlled the morphologies and crystalline size of the TiO_2. The higher temperatures of solvothermal treatment of TiO_2 precipitates were beneficial to promote initial nucleation and crystallization of particles and to slightly decrease the particle size of the primary particles. In addition, a weak peak of the brookite phase was observed for the sample in the butanol at the 573 K because of competitive reaction about the crystallization pathway: dissociation and association [Kivinen, 1965]. The polycrystalline TiO_2 size and shape of the obtained samples were observed by a scanning electron microscope (SEM, JEOL Co. Model JSM 35CF). The SEM picture confirmed the morphologies of agglomerated TiO_2 powders.

Fig. 3 shows the difference of shape and size of the agglomerated TiO_2 powders. It shows the irregular shapes of secondary particles, and that butanol has a weaker solvolysis activity than other solvents because it has one -OH in a formula structure. In addition, the agglomeration of crystallized TiO_2 in the glycerol solvent was highly progressed by plenty of -OH sources. In order to compare the particle size distribution of TiO_2, dynamic light scattering spectrometer (DLS, BI Co. Model 9000AT) analysis was performed. The DLS results reflected the conglomerated particle size distribution of primary TiO_2 crystals. This analysis involved weighing out an appropriate sample, re-dispersing it in 20 ml of distilled water using an ultrasonication for the dispersion and stabilization of the separated for fine powder at 140 W, 20 kHz for 10 min. These results are shown in Fig. 4.

The results show that with the solvothermal method it is difficult to avoid the agglomeration of particles by electrostatic repulsion arising from their surface charge which can be controlled by the pH-value of the suspension. The energy for H_2O desorption was determined by using a differential scanning calorimeter (DSC, Perkin Elmer Co. Model DSC7). Usually, the energy for desorption of

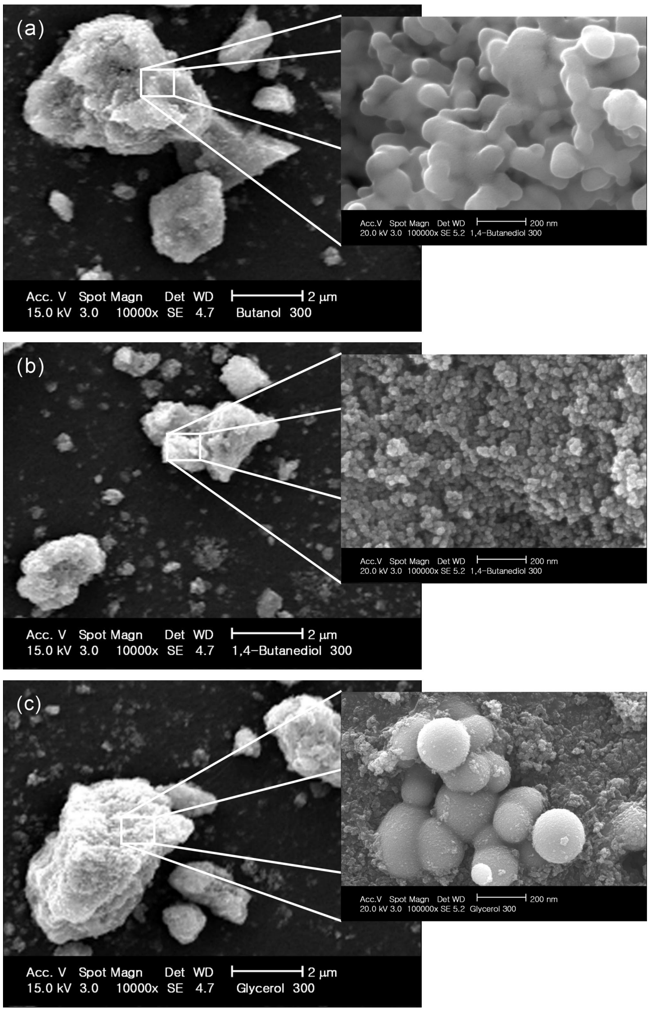

Fig. 3. SEM images for the TiO_2 powders prepared by solvothermal method at various conditions of solutions: (a) ×10,000 and ×100,000, 573 K, butanol, (b) ×10,000 and ×100,000, 573 K, 1,4-butanediol, and (c) ×10,000 and ×100,000, 573 K, glycerol.

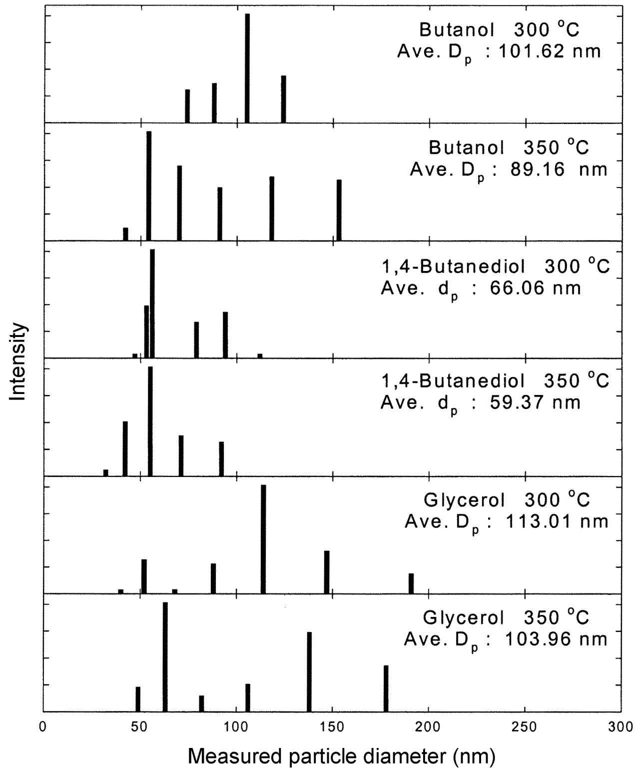

Fig. 4. DLS data for particle size distribution of the TiO_2 powders prepared by the solvothermal method with different solvents at two reaction temperatures.

H_2O on single crystals was below about 10 kcal/mol. The DSC data show that all of these prepared TiO_2 have a high surface area and pores with a hydrophilic character. And the surface area of the TiO_2 was measured by nitrogen adsorption with continuous flow method by using a BET surface area analyzer (Gemini model 2375) after heat treatment at 280 °C for 1 hr. These results are summarized in Table 1.

The particle sizes as measured by various experimental techniques (calculation of crystal size by BET, XRD by Sherrer's equation, and average particle size by DLS) are given in Table 1. We can see the difference of crystal size calculated by BET and XRD and average particle size measured by DLS techniques.

From these results, it is noted that the dominant particle size and crystallinity are affected by the number of -OH. During the solvothermal treatment, the metal alkoxides were partially hydrolyzed with -OH sources such as alcohols, -diols and so on. Generally, titanium alkoxides were fully hydrolyzed and condensed to TiO_2 amorphous powder by -OH. Finally, these powders formed gelled anatase phase titania through solvothermal treatment. However, excessive -OH accelerate condensation of hydrolyzed titanium alkoxides and growth of particles at high temperatures. Similarly, the thermal treatment involves the formation of metal-oxo-polymer network from the metal alkoxides with H_2O [Lee et al., 2001]. Especially, it is believed that the butanol solvent will be partially hydrolyzed at 573 K. Others were fully hydrolyzed. If the sources with much -OH take part in the condensation of hydrolyzed titanium alkoxides, these immediately nucleate titania amorphous powder. Subsequently, powdered should be crystallized from amorphous phase to anatase phase by the auto-generated high pressure in the stirred autoclave system. And glycerol solvent will accelerate the agglomeration of crystalline titania.

2. Photooxidation of Methyl Orange

The photocatalytic activity of TiO_2 powder was examined by measurement of the photodegradation rate of methyl orange. As shown in Fig. 5, the photodegradation rate of methyl orange slightly increased with increasing the temperature of solvothermal treatment. It also showed that the catalyst activity prepared through 1,4-butanediol and glycerol was higher than the commercial Degussa P-25 TiO_2 powder.

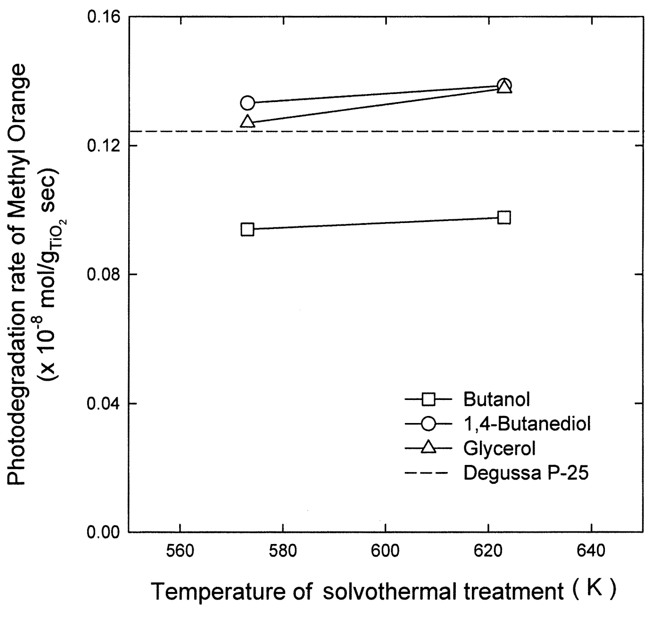

Fig. 5. Comparison of Photooxidation rate of Methyl Orange using the TiO_2 powders prepared by hydrothermal method: volume 0.1 L, concentration 30 ppm, air flow rate 0.5 L/min.

From the results of photodegradation rate of methyl orange with different TiO_2 catalysts, it can be said that the temperature of crystallization and the number of -OH in synthesizing solution highly affected physical properties of the TiO_2 powders and their catalytic activity.

CONCLUSIONS

In summary, nanocrystalline titania could be successfully prepared through solvothermal method with three different kinds of solvents. Anatase phase secondary powders (about 100 nm) were obtained with some grain growth and particle agglomeration in various conditions. In addition, the stirring of solution prevents agglomeration of TiO_2 powder during the solvothermal treatment, but agitation energy has little effect of dispersion of powders. The catalytic activity of TiO_2 powders was examined in a simple photoreaction system, and their photocatalytic activities were observed to be higher or similar to the Degussa P-25 TiO_2 powder. It was observed that the reaction temperature and number of -OH in the molecular structure of solvents affected the physical properties of TiO_2 powders and thus affected the catalytic activity.

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