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A Photocatalytic Performance of TiO_2 Photocatalyst Prepared by the Hydrothermal Method

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Abstract−Anatase phase nanocrystalline TiO_2 powders were prepared by hydrothermal method with the TTIP (titanium tetra isopropoxide) at 200 °C in a stirred autoclave system. The effects of synthesis conditions on the physical properties of catalyst were investigated by using XRD, SEM, DLS, DSC and BET. The TiO_2 powders obtained from the optimum condition showed uniform spherical shape, crystalline structure, submicron size with a sharp size distribution and few agglomerates. The optimum synthesis conditions were obtained within the covered experimental ranges. The photocatalytic activity of TiO_2 powders prepared by the hydrothermal method was tested for photooxidation of methyl orange.

Key words: Hydrothermal Method, TiO_2, Photocatalyst, Photooxidation, Methyl Orange

INTRODUCTION

Semiconductors and noble metal catalysts are often employed to promote high efficiency chemical processes including both catalytic and photocatalytic reactions [Domen et al., 2001; Park et al., 2001]. In recent years, researchers have reported a variety of photocatalytic reactions involving several metal oxides, such as ZnO, WO_3, TiO_2, $BaTiO_3$ and so on [Hoffmann et al., 1995; Linsebigler et al., 1995]. Among them, titania has been widely studied for its high photocatalytic properties, such as photoactivity, photochemical stability, suitable band-gap energy, and so on. TiO_2 powders have three common polymorphs: rutile, brookite, and anatase. Among them, rutile phase has the thermodynamically most stable modification of TiO_2 [Hoffmann et al., 1995; Linsebigler et al., 1995]. The anatase phase, on the other hand, has higher photocatalytic activity than the others, thus is suitable for photocatalysts and supports. These crystal structures can be controlled by heat treatment [Calza et al., 1997; Mills and Wang, 1997]. In addition, nanocrystalline sizes and wide surface areas induce higher photocatalytic properties than large particles. However, the nanosized TiO_2 particles have a strong tendency to agglomerate to larger particles, which leads to the decrease of thermal stability and exerts influences on its applications.

There are various methods for preparing TiO_2 powders: sulfate process, chloride route, inert gas condensation, flame synthesis by $TiCl_4$ oxidation, sol-gel method, and so on [Chen et al., 1995; Wang and Ying, 1999]. In this study, we examine a hydrothermal reaction to produce nanocrystalline TiO_2 powders using titanium tetra isopropoxide at 200 °C in a stirred autoclave. Hydrothermal methods are employed in the synthesis of microporous and mesoporous solids and, more generally, sol-gel procedures are widely used in syntheses of high-quality ceramic materials. The fundamental mechanisms are known to involve condensation and polymerization of aqueous solutions or suspensions of precursor fragments in solution at elevated temperature in a pressurized vessel, such as an autoclave. Hydrothermal method provides excellent chemical homogeneity and the possibility of deriving unique stable structures at low reaction temperatures [Chen and Xu, 1998; Ovenstone, 2001].

The prepared TiO_2 photocatalysts were evaluated on the photocatalytic activity by using a simple photoreactor system. In this study, photooxidation of methyl orange was chosen to test the photocatalytic activity of TiO_2 powders prepared by hydrothermal method. Methyl orange, with a simple structure, is one of the azo dyes, which is widely used in the textile industry. In general, azo dyes are stable under visible and near-U.V. light [Walter et al., 1995]. But, in a photocatalytic process, stable structure and chemical properties of azo dyes are changed and big molecules break into smaller fragments. And these results are easily analyzed by a UV-VIS spectrophotometer [Chen, 2000]. The photocatalytic activity of TiO_2 powders prepared by the hydrothermal method was compared with Degussa P-25 TiO_2 powder.

EXPERIMENTAL

1. Anatase TiO_2 Preparation

For nanocrystalline TiO_2 preparation, the TTIP (99.9%, Junsei Chemical) 28.4 ml was slowly added into isopropyl alcohol (99.9%, Carlo Erba) 200 ml. Deionized water was slowly added under vigorous stirring conditions for 10 minutes. During the addition, a white precipitation $Ti[OCH(CH_2)_2]_4$ was formed. Then HNO_3 was added to the mixture for control of pH of 1, 3, 5. Before the hydrolysis, the synthesis solutions were sonicated for distribution of $Ti[OCH(CH_2)_2]_4$ with 140 W, 15,000 Hz for 2 min. Nanocrystalline TiO_2 powder was obtained by hydrolysis under 200 °C and auto-generative pressure of 40 bar in a stirred autoclave. The mixtures, in a stirred autoclave, were heated to 200 °C with 5 °C/min, and then the temperature was kept for 2 hr. The stirring velocity, of the magnetic drive in the stirred autoclave, was controlled between 300, 500 and 800 rpm. The obtained TiO_2 powders were washed with ethanol repeatedly, and then dried at 80 °C for 1 hr.

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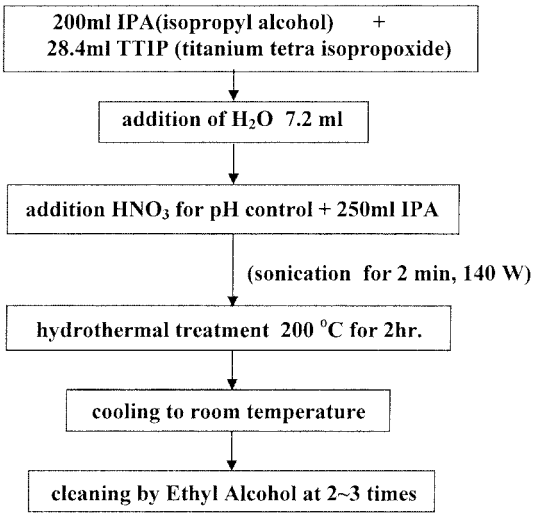

Fig. 1. Procedure for preparing the nanocrystalline TiO_2 powder by hydrothermal method.

2. Photooxidation of Methyl Orange

The photooxidation of methyl orange was carried out in a simple photoreactor as shown in Fig. 2. The methyl orange solution was prepared by mixing 30 ppm of methyl orange and 100 ml of distilled water (MilliPore Q). The prepared TiO_2 powder 0.1 g 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 were analyzed by the 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 are shown in Fig. 3. The analysis of the

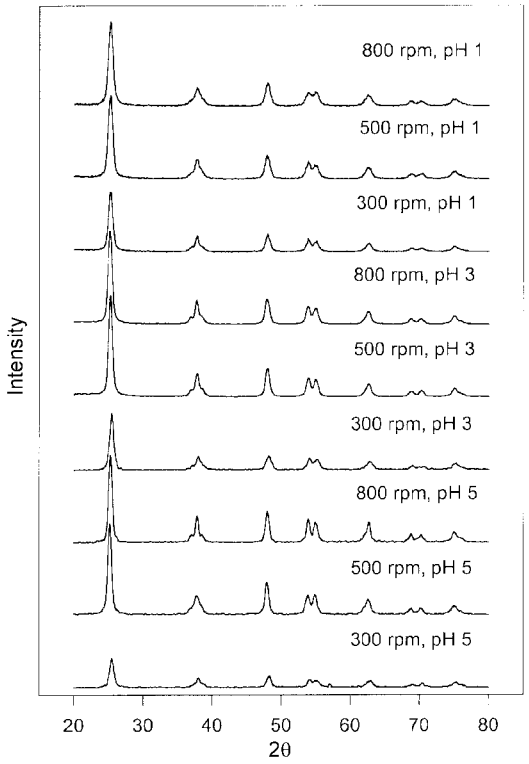

Fig. 3. The powder XRD patterns of nanocrystalline TiO_2 prepared by the hydrothermal method at various stirring velocities and pH of solutions.

XRD pattern revealed that the TiO_2 powders were successfully crystallized to the anatase phase through hydrothermal treatment. By employing Scherrers equation, the average primary particle size was calculated from the half of the maximum intensity. And, the crystallite sizes were calculated at 4.48-20.91 nm for the TiO_2 powders. These results are summarized in Table 1. The peak intensities increase with decreasing the pH of the solution. The pH of the solution affects the state of the hydrolyzed products in the form of sol and precipitates. The presence of acid catalysts promotes the hydrolysis reaction versus the condensation reaction. The nitric acid acts as acid catalyst and electrolyte to prevent particle growth or agglomeration through electrostatic repulsion on the surface between particles. From this the crystalline size of TiO_2 decreased at the low pH condition. In addition, the peak intensity increased with increas-

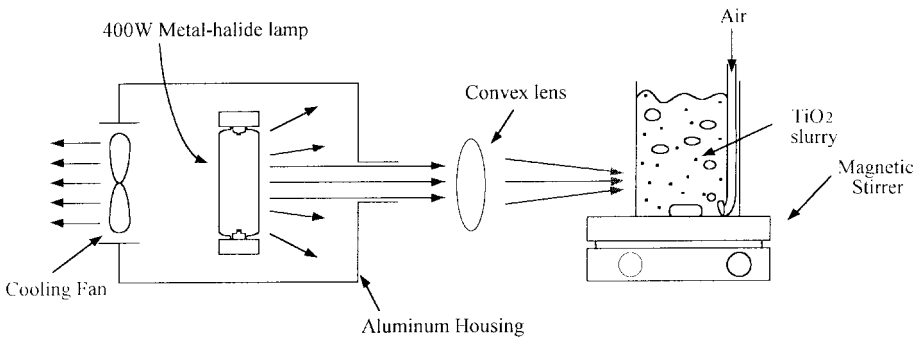

Fig. 2. Schematic diagram of photocatalytic reaction system.

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

		BET (m^2/g)	DSC		Crystalline phase	Crystal size by BET (nm)	Crystal size by XRD (nm)	Average particle size by DLS (nm)
			Heat of physisorption of H_2O (kcal/mol)	Heat of chemisorption of H_2O (kcal/mol)				
300 rpm	pH 1	102.06	0.94	23.29	anatase	14.99	6.67	86.09
	pH 3	96.46	0.15	19.77	anatase	15.95	11.82	97.44
	pH 5	41.82	0.15	11.90	anatase	36.79	20.91	120.8
500 rpm	pH 1	122.31	1.61	27.99	anatase	12.58	5.82	75.40
	pH 3	99.46	1.06	21.12	anatase	15.47	8.28	85.96
	pH 5	58.64	0.14	16.18	anatase	26.24	10.67	99.93
800 rpm	pH 1	172.19	2.72	31.98	anatase	8.93	4.48	71.08
	pH 3	111.01	1.28	27.64	anatase	13.86	5.94	82.38
	pH 5	84.31	0.31	19.42	anatase	18.25	10.98	87.93

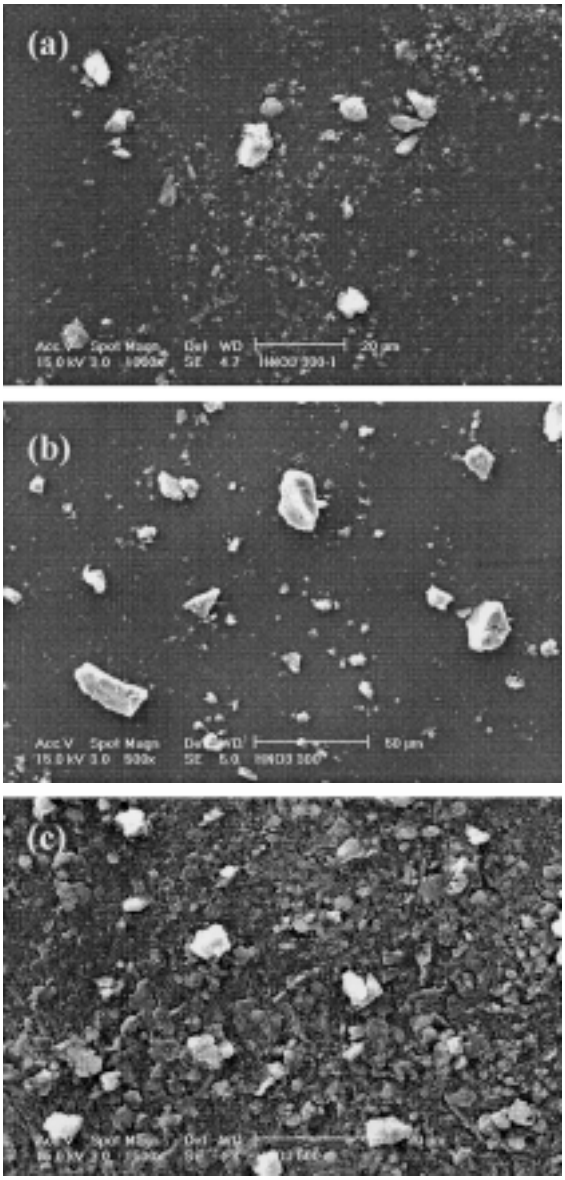

Fig. 4. SEM images for the TiO_2 powders prepared by hydrothermal method at various conditions of solutions: (a) pH 3, 300 rpm, (b) pH 5, 300 rpm, (c) pH 5, 500 rpm.

ing stirring velocity. However, the crystalline size of TiO_2 was slightly decreased with increasing the cystallinity of TiO_2. This result indicates that the hydrothermal method could be effective for obtaining the comparatively small size but high crystallinity of TiO_2 powder by controlling the pH and stirring velocity at low temperatures.

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 analysis confirmed the morphologies of agglomerated TiO_2 powders. Fig. 4 shows the difference of shapes and sizes of the TiO_2 powders. Fig. 4(a) and 4(b) show that the secondary particle size at pH 1 condition is smaller than the particle of pH 5 condition in Fig. 4(b). The acidic solutions supplied electric charges for the TiO_2. These electric charges on the surface of TiO_2 were beneficial to prevent grain growth and decrease the particle size of the primary particles by electrical repulsion. Fig. 4(c) shows that the shear stress of stirring acted on a force for shattering of agglomerated particles.

The particle size distribution of the TiO_2 was measured by dynamic light scattering spectrometer (DLS, BI Co. Model 9000AT). The DLS results reflected the secondary particle size distribution of conglomeration of primary particles. These results, which are shown in Fig. 5, show that the particle size distributions were narrow. In addition, the mean diameters of the agglomerated particles were increased with increasing the pH and decreasing the stirring velocity. From Fig. 5, it is also noted that the dominant particle size is increased with pH of the solution.

The energy for H_2O desorption was determined by using a differential scanning calorimeter (DSC, Perkin Elmer Co. Model DSC7). The surface areas of the TiO_2 were 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. The surface areas were increased with decreasing the pH and increasing the stirring velocity. These results are summarized in Table 1, which shows the particles sizes as measured by various experimental techniques.

During the hydrothermal process at low pH condition, the amorphous TiO_2 sols crystallized to the anatase grains and involved many pores on the surface with some agglomeration to the secondary particles. When the pH of the reaction suspension was higher than pH 1, the amorphous TiO_2 particles may have been changed by the chem-

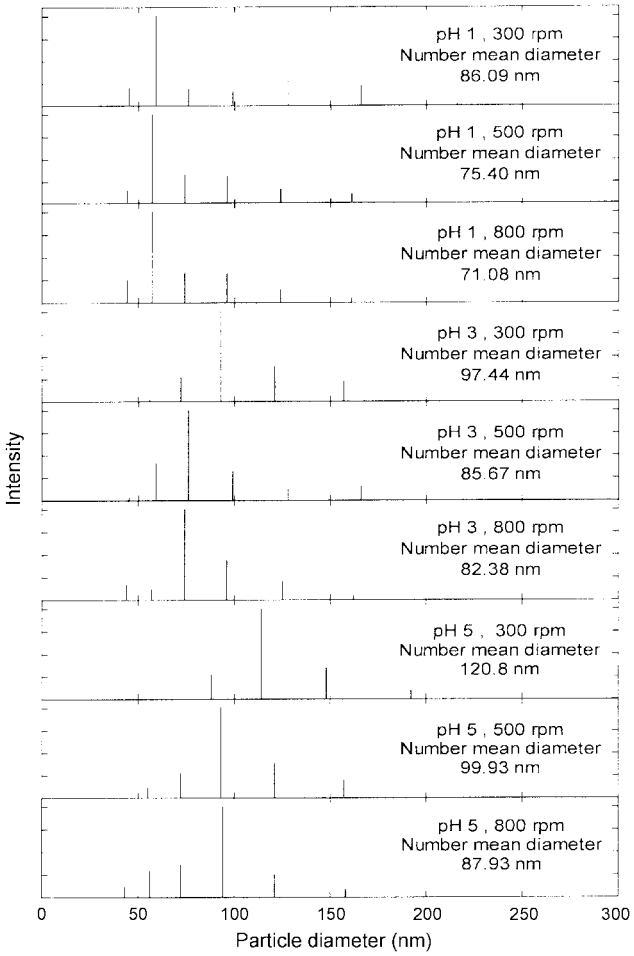

Fig. 5. DLS data for particle size distribution of the TiO_2 powders prepared by the hydrothermal method with different pH and stirring velocities.

isorption of charges. And these particles were rapidly agglomerated to the secondary powders by means of hydrogen bonding each other by OH·radicals on the surface of TiO_2. The surface acidic and basic properties of TiO_2 were described in vicinity of zero point of charge of TiO_2 by Bahnemann, et al. [1984] as follows:

$$\text{For pH<3.5, } TiO_2+nH^+=TiO_2H_n^{n+} \quad \text{(plus counteranions)} \quad (1)$$

$$\text{For pH>3.5, } TiO_2+nOH^-=TiO_2(OH)_n^{n-} \quad \text{(plus counteractions)} \quad (2)$$

The acids should disperse the dense TiO_6 octahedra by offering H^+ to Ti-OH. The generated Ti-OH^+ combined with other TiO_6 octahedra to form Ti-O-Ti by removing the one molecule of H_2O. This mechanism easily induced the anatase structure of TiO_2 [Bahnemann et al., 1984; Yin et al., 2001]. Usually, the energy for desorption of H_2O on single crystal was below about 10 kcal/mol. Therefore, from the DSC data, all of this prepared TiO_2, with a high surface area and pores, has a hydrophilic character.

2. Photooxidation of Methyl Orange

The TiO_2 powders were examined for photocatalytic activity by using the photodegradation rate of methyl orange. As shown in Fig. 6, the photodegradation rate of methyl orange slightly decreased with increasing the pH of synthesis solution. However, these results

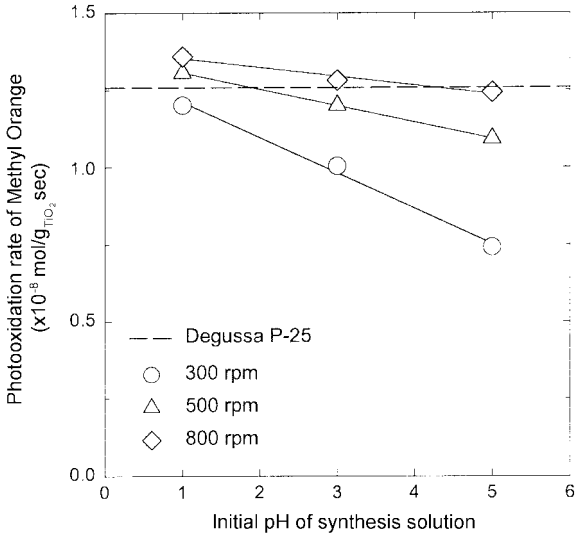

Fig. 6. Comparison of photooxidation rate of methyl orange using the TiO_2 powders prepared by hydrothermal method: volume 0.1 L, concentration 30 ppm, air flow rate 0.5 L/min.

are similar to the performance of the Degussa P-25 TiO_2 powders, which were used to compare the photocatalytic activity with the TiO_2 powders. In addition, Fig. 6 shows the effect of stirring velocity during hydrolysis of TiO_2 solutions. In general, vigorous agitation prevents the particle growth and reduction of surface area by agglomeration during synthesis. But when the stirring velocity was faster than 500 rpm, the prepared TiO_2 powders showed little difference in particle size under the same pH condition. These powders have similar surface areas and photocatalytic activities. A stirring of synthesis solution prevents agglomeration of TiO_2 powder, but excessive agitation energy has little effect on dispersion of powders during hydrolysis. From this result, it appeared that the initial pH of the synthesis solution highly affected physical properties of the photocatalyst.

CONCLUSIONS

The nanocrystalline TiO_2 powders were prepared from TTIP under different conditions through the hydrothermal method. Anatase phase secondary powders (about 100 nm) were obtained through the hydrothermal method with some grain growth and particle agglomeration in various conditions. These TiO_2 powders were examined in a simple photoreaction system, and their photocatalytic activities were observed similar to the Degussa P-25 TiO_2 powder. This is thought to be due to better crystallinity, giving a slower recombination of photoinduced electrons and positive holes. And, the large surface area of prepared TiO_2 supplied activated adsorption sites for reactants.

This study shows an effective means for crystallizing anatase structure without other heat treatments, and confirms that the hydrothermal synthesis of TiO_2 powder highly depends on the pH condition of the initial synthesis solution.

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