Hydrothermal Synthesis of Titanium Dioxide Using Acidic Peptizing Agents and Their Photocatalytic Activity

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Abstract—We have prepared TiO_2 nanoparticles by the hydrolysis of titanium tetraisopropoxide (TTIP) using HNO_3 as a peptizing agent in the hydrothermal method. The physical properties of nanosized TiO_2 have been investigated by TEM, XRD and FT-IR. The photocatalytic degradation of orange II has been studied by using a batch reactor in the presence of UV light. When the molar ratio of HNO_3/TTIP was 1.0, the rutile phase appeared on the titania and the photocatalytic activity decreased with an increase of HNO_3 concentration. The crystallite size of the anatase phase increased from 6.6 to 24.2 nm as the calcination temperature increased from 300 °C to 600 °C. The highest activity on the photocatalytic decomposition of orange II was obtained with titania particles dried at 105 °C without a calcination and the photocatalytic activity decreased with increasing the calcination temperature. In addition, the titania particles prepared at 180 °C showed the highest activity on the photocatalytic decomposition of orange II.

Key words: Nanosized Titania, Hydrothermal Method, Peptizing Agent, HNO_3, Photocatalytic Degradation of Orange II

INTRODUCTION

Nanocrystalline powders of titania continues to attract much interest because of its wide variety of applications, such as optical devices, pigment, photocatalyst, etc. [Wold, 1993; Chai et al., 2000]. The synthesis of nanocrystalline particles with controlled size and composition is of technological importance because they have more active sites for achieving enhanced performance. Up to now, many methods have been established for the synthesis of titania [Hong et al., 2003; Lim at al., 2002], the sol-gel technique being the most often used. Unfortunately, the sol-gel derived precipitates are amorphous in nature, which requires further treatment to induce crystallization [Hong et al., 2001].

Hydrothermal synthesis, in which chemical reactions can take place in aqueous or organo-aqueous media under simultaneous generation of pressure upon heating, has been used to prepare nanocrystalline titania at low temperatures. High crystalline anatase or rutile nano-particles were synthesized by hydrothermal treating tetraalkylammonium hydroxides (TENOH) or HNO_3 peptized titania sols, respectively [Yang et al., 2001; Wang and Ying, 1999]. The peptizing agents have an influence on the physical properties of titania, such as, particle size, shape, and the ratio of anatase to rutile phase [Nam and Han, 2003]

Wastewater produced from textile and other dyestuff industrial processes contains large quantities of organic dyes, which are difficult to degrade with standard biological methods. Within the overall category of dyestuffs, azo-dyes constitute a significant portion and probably have the least desirable consequences in terms of surrounding ecosystems. Photocatalysis using TiO_2 semiconductors was irradiated by near UV-light. The complete mineralization of the organic compound without generation of dangerous residual intermediate compounds and the possibility of working over wide ranges of operational conditions make the photocatalytic method preferable or, at least, competitive with the others.

In this paper, we prepared nanosized TiO_2 particles by hydrolysis of TTIP using HNO_3 as a peptizer in the hydrothermal method. The physical properties of prepared nanosized TiO_2 particles were investigated by TEM, XRD and FT-IR. We also investigated the effect of peptizing agents, synthesis temperature and calcination temperature on the physical properties of nanosized TiO_2 particles, and examined the activity of TiO_2 particles as a photocatalyst for the decomposition of orange II.

EXPERIMENTAL

Titanium tetraisopropoxide $(Ti(OC_3H_7)_4$, hereafter abbreviated as TTIP) was used as a precursor without further purification. TiO_2 precipitates were obtained by adding 0.5 M isopropanol solution of the TTIP dropwise into deionized water and rigorously stirred for 30 min. The amount of water was fixed at a [H_2O]/[TTIP]molar ratio of 150. The precipitates were washed with deionized water using a centrifuge. Portions of the white precipitates were peptized by adding diluted solutions of HNO_3 (HNO_3/TTIP=0.2-2.0) at room temperature.

This solution of 100 ml was transferred to a 250 ml Teflon container held in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 180 °C for 5 h. After hydrothermal treatment, the TiO_2 particles were separated in a centrifuge at 10,000 rpm for 10 min and were then washed in distilled water. The particles were dried at 105 °C for 12 h and were then calcined at 300-700 °C for 3 h.

The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIC) using Cu Kα radiation. The crystallite size of the prepared particles was determined from the

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broadening of the anatase main peak where $2\theta=25.3°$ according to the Schrerrer equation [Cullity, 1978]. The chemical structure of the prepared particles was examined by using a Fourier transform infrared spectrophotometer (FTIR, Bruker, IFS-88) in the 400-4,000 cm^{-1} frequency range. The particle size and external morphology of the prepared particles were observed on a transmission electron microscope (TEM, JEOL, JEM-2020) of 200 kV accelerating voltage.

A biannular quartz glass reactor with a lamp immersed in the inner part of the reactor was used for all the photocatalytic experiments. The batch reactor was filled with 500 ml of an aqueous dispersion in which the concentration of titania and of orange II were 1.0 g/L and 100 mg/L, respectively, and magnetically stirred to maintain uniformity of both concentration and temperature. A 500 W high-pressure mercury lamp (Kumkang Co.) was used. The circulation of water in the quartz glass tube between the reactor and the lamp allowed the lamp to stay cool and to warm the reactor to the desired temperature. Nitrogen was used as a carrier gas and pure oxygen was used as an oxidant. The samples were immediately centrifuged and a quantitative determination of orange II was performed by a UV-vis spectrophotometer (Shimazu UV-240).

RESULTS AND DISCUSSION

1. X-ray Diffraction Analysis

Fig. 1 shows the XRD patterns of the TiO$_2$ particles prepared by using different concentrations of nitric acid. These particles were only dried at 105 °C without any calcination.

The evolution (Fig. 1) of the intensities of the (101) reflection of anatase and the (110) reflection rutile, is a function of HNO$_3$ concentration for different solutions. It can be observed that a rutile phase appears from HNO$_3$/TTIP=1.0. According to Gopal et al. [1997], the formation of anatase and rutile TiO$_2$ is determined by the nucleation and the growth of TiO$_2$ clusters. If the condensation starts before completion of hydrolysis, either amorphous or metastable anatase TiO$_2$ will form. Acid environment promotes hydrolysis rate and at the same time decreases the condensation rate. In a strong acid so-
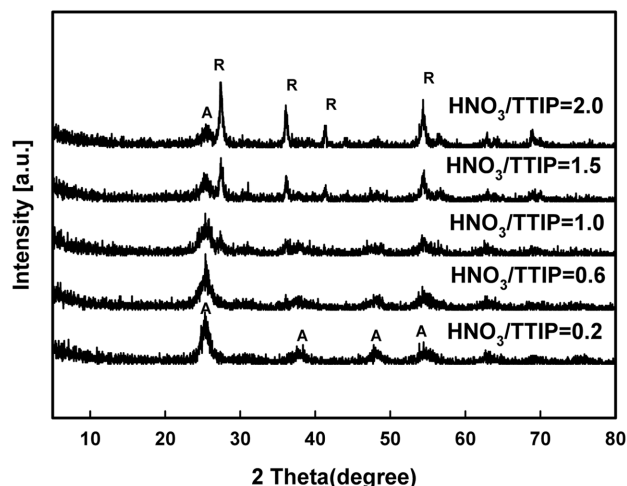

Fig. 1. XRD patterns of nanosized TiO$_2$ powders prepared at different HNO$_3$/TTIP molar ratio; dried at 105 °C, R(H$_2$O/ TTIP) ratio=150.
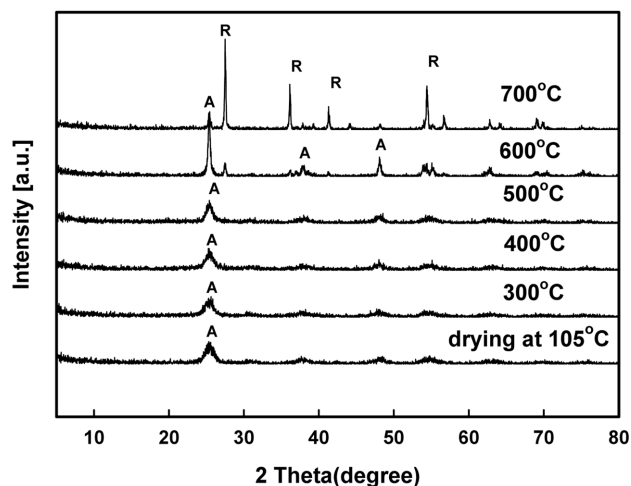

Fig. 2. XRD patterns of nanosized TiO$_2$ powders calcined at different temperature: HNO$_3$/TTIP=0.2, R(H$_2$O/TTIP) ratio= 150.

lution, the condensation rate is slow enough and the formation of rutile phase is kinetically favored, so rutile TiO$_2$ can be obtained at low temperature.

The crystallite size of the particles prepared at different HNO$_3$ concentration can be determined by the Scherrers equation [Cullity, 1978] and is listed in Table 1. The crystallite size of the anatase phase shows similar value from HNO$_3$/TTIP=0.2 to 1.0 but that of rutile phase increases with an increase of HNO$_3$ concentration.

Fig. 2 shows the XRD patterns of the TiO$_2$ particles calcined at a different temperature. These particles are prepared at HNO$_3$/TTIP= 0.2. The major phase of all the prepared particles is an anatase structure, and a rutile peak was observed above 600 °C.

It is well known that calcination improves the crystallinity of the particle, and the amorphous TiO$_2$ changes into the anatase phase and the anatase phase changes into the rutile phase with increasing calcination temperature. It was reported that the transformation of the anatase phase into the rutile phase occurs between 450 °C and 600 °C and the difference in the transformation temperature depends on the kind of precursors, the preparation conditions of the particles, and the properties of the particles [Reddy et al., 2001]. As shown in Fig. 2, the particles calcined at 300-500 °C were identified as nanocrystalline anatase. Upon increasing the temperature to 600 °C, the rutile peak appears. In addition, the crystallinity increases with an increase of the calcination temperature because higher ordering in the structure of titania particles makes X-ray peaks to be sharper and more narrow.

The crystallite size of the particles calcined at different temperature is listed in Table 2. One can see that the crystallite size of the anatase phase is increased from 6.6 to 24.2 nm as the calcination temperature increased from 300 °C to 600 °C. However, the size of rutile crystallites calcined at 600 °C cannot be measured because of small intensity of the peak.

2. FT-IR Analysis

Fig. 3 shows the IR spectra for the TiO$_2$ particles calcined at different temperature in the range of 400-4,000 cm^{-1}.

During the calcination the NO$_3^-$ is removed as indicated by the disappearance of the asymmetric stretching band of NO$_3^-$ ion at 1,383

cm^{-1}. In addition, the broad absorption peak appearing near 3,400 cm^{-1} relates to a stretching vibration of O-H group. At 1,620 cm^{-1}, a band assigned to water also appears. The OH band intensities show a significant decrease in the case of calcination at high temperature. It is reported that the physisorbed water is easily removed from the surface, but the decrea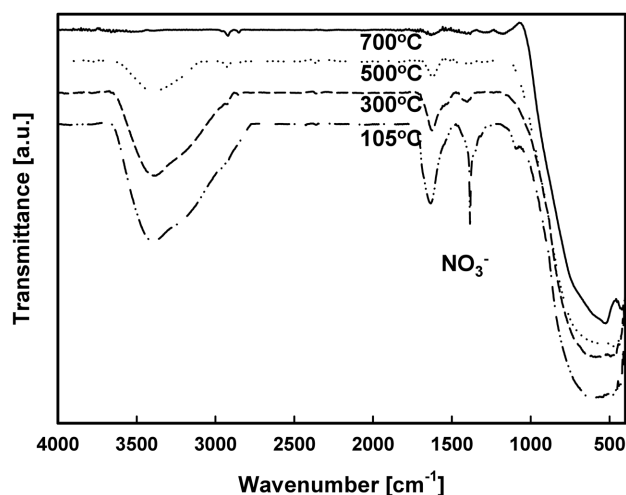se in the OH band intensities bonded to TiO_2 may be attributed to the OH population produced by a dehydroxylation of the surface titania [Pecchi et al., 2001]. The OH band intensities also decrease with an increase of the calcination temperature. This result suggests that this process is also responsible for the sintering of the catalysts, by collapsing the smaller pores of TiO_2, as it is shown in the particle size summarized in Table 2.

3. TEM Analysis

Fig. 4 shows the TEM micrographs of the nanoparticles prepared by different calcination temperatures. The titania nanoparticles are shown to have a spherical shape and uniform size distribution when they are calcined at the low temperature but they aggregate to be large particle with an increase of calcination temperature. The crystallite size was determined by calculating the particle size in a given area and that was 6 nm dried at 105 °C without a calcination. However, the particle size increases with an increase of calcination temperature, which is due to sintering effect.

4. Activity Test

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics [Turchi and Ollis, 1990; Mu et al., 2004]. Therefore, this kind of reaction can be represented as follows:

$$- dc/dt = kC \tag{1}$$

In addition, it can be integrated as follows:

$$C = C_o \exp(-kt) \tag{2}$$

Where C_o is initial concentration of the orange II and k is a rate constant related to the reaction properties of the solute which depends on the reaction conditions, such as reaction temperature, pH of solution. The photocatalytic activity increases with an increase in this value.

When a blank test in the absence of TiO_2 photocatalyst was carried out, orange II was decomposed to about 18% after 3 hs reaction by photolysis reaction. The photocatalytic activity for the decomposition of orange II on the titania particles prepared at different $HNO_3/TTIP$ molar ratio was examined and the result is shown in Table 1 and Fig. 5. The titania particle prepared at $HNO_3/TTIP$ molar ratio=

Fig. 3. FT-IR spectra of nanosized TiO_2 powders calcined at different temperature: $HNO_3/TTIP=0.2$, $R(H_2O/TTIP)$ ratio= 150.
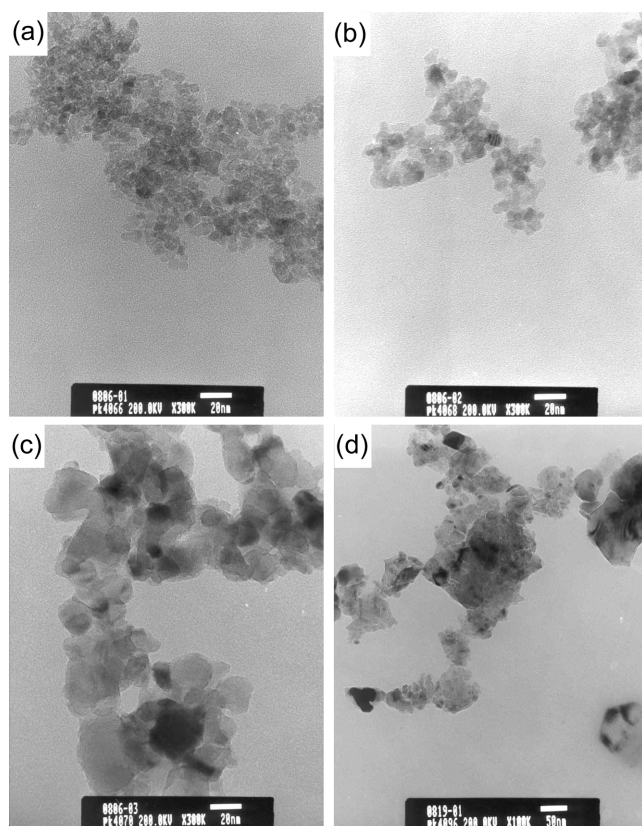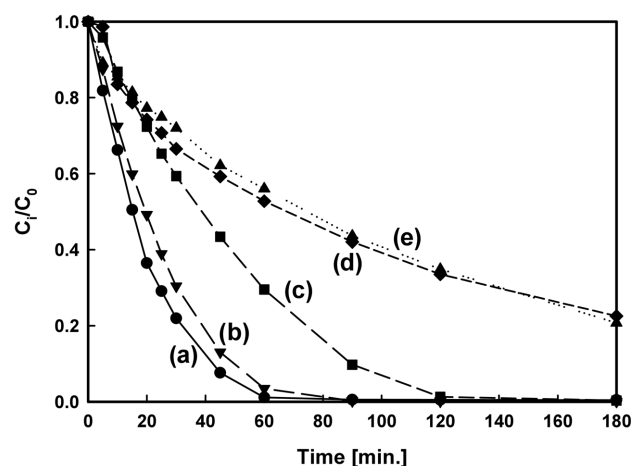

Fig. 4. TEM micrographs of nanosized TiO_2 powders calcined at different temperature: (a) 105 °C (without calcination), (b) 300 °C, (c) 500 °C, (d) 700 °C.

Fig. 5. Photocatalytic decomposition of orange II over TiO_2 prepared at different $HNO_3/TTIP$ molar ratio; dried at 105 °C, $R(H_2O/TTIP)$ ratio=150. C_o=100 mg/L, W=1.0 g/L, (a) $HNO_3/TTIP$=0.2, (b) 0.6, (c) 1.0, (d) 1.5, (e) 2.0.

Fig. 6. Photocatalytic decomposition of orange II over TiO$_2$ calcined at different temperature; HNO$_3$/TTIP=0.2, R(H$_2$O/TTIP) ratio=150. C$_o$=100 mg/L, W=1.0 g/L, (a) 105 °C (without calcination), (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C.

Fig. 7. Photocatalytic decomposition of orange II over TiO$_2$ prepared at different temperature; HNO$_3$/TTIP=0.2, R(H$_2$O/TTIP) ratio=150. C$_o$=100 mg/L, W=1.0 g/L.

0.2 shows the highest activity on the photocatalytic decomposition of orange II. However, the photocatalytic activity steeply decreases on the titania particles prepared at HNO$_3$/TTIP molar ratio=1.0. This result suggests that the photocatalytic activity of the decomposition of orange II depends on crystal structure. Titanium dioxide can take on any of the following three crystal structures: rutile, anatase, or brookite. An anatase-type titanium dioxide generally exhibits a higher photocatalytic activity than the other types of titanium dioxide in regard to the decomposition of organic pollutants by suppressing the electron-hole recombination [Lee et al., 2002]. It is thought that the photocatalytic activity decreases on the titania particles prepared at HNO$_3$/TTIP molar ratio>1.0 owing to the formation of rutile phase of titania.

Table 2 and Fig. 6 show the photocatalytic activity for the decomposition of orange II on the titania particles calcined at different temperature. The highest activity on the photocatalytic decomposition of orange II is shown on titania particles dried at 105 °C without a calcination and the photocatalytic activity decreases with an increasing calcination temperature. This result suggests that the photocatalytic activity of the decomposition of orange II depends on the particle size. That is, the activity increases with a decreasing particle size. This is consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases with a decrease in particle size [Fujishima et al., 1999]. It can be also confirmed that a small particle has a large illuminated surface area as the particles with the same structure have a constant density.

In the case of titania particles calcined above 600 °C, the anatase and rutile phase are combined and it causes a decrease of photocatalytic activity.

Fig. 7 shows the photocatalytic activity for the decomposition of orange II on the titania particles prepared at different temperature. The highest activity on the photocatalytic decomposition of orange II is shown on titania particles prepared at 180 °C. In addition, the titania particle prepared at 180 °C without peptizing agent shows very poor photocatalytic activity. This result suggests that acid pep-
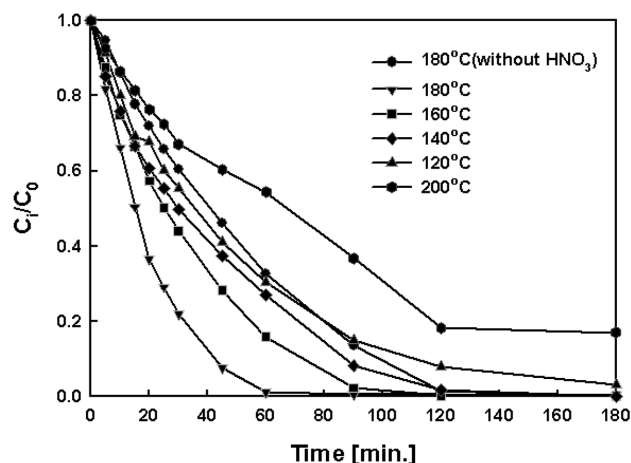
tizing agent has an influence on the property and photocatalytic activity of titania particles. It was also reported that the particle prepared at low temperature showed amorphous shape and the size increased with an increasing temperature through the hydrothermal method [Wang and Ying, 1999]. From the previous work [Ryu et al., 2004], the titania particles showed needle-like or polygonal shape prepared below 150 °C but it changed to spherical shape prepared above 170 °C. These results suggest that the hydrothermal treatment temperature has an influence on shape and size of titania particles. It is thought that the particle hydrothermally treated at low temperature cannot be fully crystallized to anatase structure and high temperature treatment gives a rise to grow to the large particle. Therefore, the pure anatase titania prepared at 180 °C shows the highest activity on the photocatalytic decomposition of orange II.

CONCLUSIONS

In the present work, we have prepared TiO$_2$ nanoparticles by the hydrolysis of titanium tetraisopropoxide (TTIP) using nitric acid as a peptizing agent in the hydrothermal method. The physical properties of nanosized TiO$_2$ have been investigated by TEM, XRD and FT-IR. The photocatalytic degradation of orange II has been studied by using a batch reactor under UV light. The titania nanoparticles are shown to have a spherical shape and uniform size distribution when they are calcined at low temperature, but they aggregate to be large particles with increasing calcination temperature. When the molar ratio of HNO$_3$/TTIP is 1.0, the rutile phase appeared on the titania and the photocatalytic activity decreased with increasing HNO$_3$ concentration. The crystallite size of the anatase phase is increased from 6.6 to 24.2 nm as the calcination temperature increases from 300 °C to 600 °C. The highest activity on the photocatalytic decomposition of orange II was obtained with titania particles dried at 105 °C without a calcination and the photocatalytic activity decreases with increasing calcination temperature.

ACKNOWLEDGMENTS

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in 2003.

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