Synthesis of Nanosized Titanium Dioxide Using a Hydrothermal Method and Their Photocatalytic Activity

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Abstract: TiO₂ nanoparticles were prepared through the hydrolysis of titanium tetraisopropoxide (TTIP) using TMA (tetramethylamine) as a peptizer via a hydrothermal method. The photocatalytic degradation of orange II was studied using a batch reactor in the presence of UV light. The particle sizes were similar after hydrothermal treatment at 120 °C ~ 170 °C, but it increased to 23 nm at 200 °C. The titania particles prepared at 170 °C had the highest activity, and the titania particles calcined at 600 °C also had the highest activity for the photocatalytic decomposition of orange II. The degradation rate of orange II increased upon increasing the catalyst weight, but no further increase occurred above 2.0 g/L. In addition, the decomposition rate was higher under acidic conditions than under neutral or the basic conditions.

Keywords: nanosized titania, hydrothermal method, TMA, photocatalytic degradation of orange II

Introduction

Nanocrystalline powders of titania are widely used as catalysts in photocatalytic reactions, gas sensors, and white pigment materials [1]. The preparation of nanosized TiO₂ is mainly performed using the sol-gel method, whose main disadvantages is that costly organic solvents are required. The direct hydrolysis of titanium salt and chemical vapor deposition procedure, in which TiCl₄ vapor is oxidized at very high temperatures, can be used to prepare nanosized TiO₂. In addition, water-in-oil (W/O) microemulsions have been successfully employed to obtain ultrafine particles of controlled size for a variety of materials [2]. However, this method gives rise to environmental problems because of the use of solvents. Thus, an improved method, using carbon dioxide instead of oil, has been studied to prepare nanosized materials [3].

Hydrothermal synthesis, in which chemical reactions take place in aqueous or organo-aqueous media with the generation of pressure upon heating, has been used to prepare nano-crystalline titania at low temperature [4]. Highly crystalline anatase or rutile nanoparticles have been synthesized by hydrothermally treating TEOH and HNO₃ peptized titania sols [5]. The peptizing agents influence the physical properties of titania, such as its particle size, shape, and the ratio of the anatase and rutile phases.

In this study paper, we prepared nanosized TiO₂ particles by hydrolysis of TTIP (titanium tetraisopropoxide) with TMA (tetramethylamine) as a peptizer using a hydrothermal method. The physical properties of these nanosized TiO₂ particles were investigated. We also investigated the effects that the synthesis temperature and calcination temperature have on the physical properties of the nanosized TiO₂ particles, and examined the activities of these TiO₂ particles as photocatalysts for the decompositions of orange II.

Experimental

Nanosed TiO₂ powders were derived through sol-gel hydrolysis precipitation of titanium isopropoxide (TTIP, Aldrich) under hydrothermal conditions. A specific amount of titanium isopropoxide was mixed at a water/TTIP molar (R) ratio of 100.

Titanium isopropoxide solution was added into the aqueous solution consisting of water and trimethylamine
Table 1. Physical Properties of Nanosized TiO₂ Powders Prepared at Different Temperatures

<table>
<thead>
<tr>
<th>Synthesis Temperature (°C)</th>
<th>XRD</th>
<th>TEM</th>
<th>BET</th>
<th>Activity $k \times 10^{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Structure</td>
<td>Crystallite Size [nm]</td>
<td>Crystallite Size [nm]</td>
<td>Surface Area (m²/g)</td>
</tr>
<tr>
<td>120</td>
<td>anatase</td>
<td>20</td>
<td>23</td>
<td>44</td>
</tr>
<tr>
<td>150</td>
<td>anatase</td>
<td>18</td>
<td>24</td>
<td>59</td>
</tr>
<tr>
<td>170</td>
<td>anatase</td>
<td>19</td>
<td>22</td>
<td>73</td>
</tr>
<tr>
<td>200</td>
<td>anatase</td>
<td>23</td>
<td>28</td>
<td>41</td>
</tr>
</tbody>
</table>

* R ratio(H₂O/TTIP)=100; dried at 105°C. Obtained using the Scherrer equation. Apparent first-order constants ($k$) of orange II.

Figure 1. XRD patterns of nanosized TiO₂ powders prepared at different temperatures.

with rigorous stirring at room temperatures. A white precipitate of hydrous oxides was produced instantly, and the mixture was stirred for at least 2 h. This solution of 200 mL was taken into a 250-mL Teflon container held in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 120~200 °C for 4 h. After hydrothermal treatment, the TiO₂ particles were separated in a centrifuge at 10000 rpm for 10 min and then were washed with distilled water. The particles were dried at 105 °C for 12 h and then calcined at 200~800 °C for 3 h.

The chemical structures of the prepared particles were examined using a Fourier transform infrared spectrophotometer (FTIR, Bruker, IFS-88). The major phase of the obtained particles was analyzed by X-ray diffraction (Rigaku D/MAXIIIC) using CuKα radiation. The crystallite size of the prepared particles was determined from the broadening of the anatase main peak at $2\theta=25.3^{\circ}$ using the Scherrer equation [6]. The particle size and external morphology of the prepared particles were observed using a transmission electron microscope (TEM, JEOL, JEM-2020) operated at an accelerating voltage of 200 kV.

A biannular quartz glass reactor with a lamp immersed in the inner part was used for all of the photocatalytic experiments. The batch reactor was filled with 500 mL of an aqueous dispersion, in which the concentrations of titania and orange II were 1.0 g/L and 100 mg/L, respectively, and magnetically stirred to maintain both uniformly 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 cooling of the lamp and warming of reactor at the desired temperature. Nitrogen was used as a carrier gas and pure oxygen was used as an oxidant. The samples were immediately centrifuged and the quantitative determination of orange II was performed using a UV-vis spectrophotometer (Shimazu UV-240).

Results and Discussion

Figure 1 shows the XRD patterns of the TiO₂ particles prepared at different temperatures. These particles were only dried at 105 °C without calcination. The major phase of all the prepared particles is an anatase structure, regardless of synthesis temperature. This result indicates that the titania sol was successfully crystallized to the anatase phase at relatively low temperatures through hydrothermal aging.

The crystallite size of the particles can be determined by using the Scherrer equation; the sizes of the titania particles are shown in Table 1. The particle sizes were similar after hydrothermal treatment at 120~170 °C. It is well known that the particle size increases upon increasing the synthesis temperature when using the hydrothermal method [7]. From the TEM micrographs (Figure 3), we observe that the titania nanoparticles have a needle-like or polygonal shapes when prepared below 150 °C; however, the micrographs show that the particles were spherical and had a narrow size distribution when prepared at temperatures above 170 °C. It is thought that the rate of nucleus formation is slower than that of particle growth at the low synthesis temperature and that the shape of the particle changes to spherical with an increase of temperature. Therefore, the particle size prepared at 170 °C did not increase as a result of a transformation of its shape, even though it was synthesized at
high temperature. However, a nanocrystalline anatase material, with a grain size of 23 nm, was obtained after hydrothermal treatment at 200 °C because of aggregation of the particles. In addition, when compared to the sol-gel method using a calcination process, titania with much finer crystallite sizes can be obtained via the hydrothermal method.

Figure 2 shows the XRD patterns of the TiO₂ particles calcined at different temperatures. The major phase of each of the prepared particles an anatase structure; a rutile peak was observed at temperatures above 900°C.

It is well known that calcination improves the crystallinity of the particles, and that the amorphous TiO₂ changes into the anatase phase and the anatase phase changes into the rutile phase upon increasing the calcination temperature. It is reported that the transformation of the anatase phase into the rutile phase occurs at temperatures above 600 °C and that the differences in the transformation temperatures depend on the kind of precursors, the preparation conditions of the particles, and the properties of the particles [8]. As shown in Figure 2, the particles calcined at 600–800°C were identified as nanocrystalline anatase. It is also confirmed that the titania prepared using the hydrothermal method has high thermal stability, which results in suppression of the phase transformation of titania from anatase to rutile. In addition, this high thermal stability made it possible to calcine the TiO₂ particles at higher temperature without forming the rutile phase.

Figure 3 shows the IR spectra for the nanosized TiO₂ particles calcined at different temperatures. When the prepared particles were dried at 105 °C without calcination, no bands that are due to residual organic surfactants are observed.

The peak appearing at 580 cm⁻¹ relates to absorption of the Ti-O bonds. The weak absorption peak appearing near 3400 cm⁻¹ relates to a stretching vibration of the hydroxy groups. At 1620 cm⁻¹, a weak band, assigned to water, also appears. The hydroxyl group band intensities are significantly decreased when calcination was performed at high temperature. It has been reported that physisorbed water is easily removed from the surface, but the decrease of those units OH hydroxyl group band intensities of those units bonded to the TiO₂ may be attributed to the OH population produced by dehydroxyla-
Table 2. Physical Properties of Nanosized TiO₂ Powders Prepared at Different Calcination Temperatures

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Structure</th>
<th>XRD Crystallite Size [nm]</th>
<th>Activity ($k(min^{-1}) \times 10^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>anatase</td>
<td>20</td>
<td>4.6</td>
</tr>
<tr>
<td>700</td>
<td>anatase</td>
<td>25</td>
<td>3.4</td>
</tr>
<tr>
<td>800</td>
<td>anatase</td>
<td>28</td>
<td>2.8</td>
</tr>
<tr>
<td>900</td>
<td>anatase/rutile</td>
<td>40/-</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* R ratio(H₂O/TiCl₄)=100; synthesis temperature=170°C; ² Obtained using the Scherrer equation. ³ Apparent first-order constants ($k$) of orange II.

Figure 5. Effect of catalyst weight on the photocatalytic decomposition of orange II: synthesis temperature = 170 °C; calcined at 600 °C.

Figure 4 shows TEM micrographs of the nanoparticles prepared at different synthesis temperatures. The titania nanoparticles have needle-like or polygonal shapes when prepared at temperatures below 150 °C but they were spherical and had a narrow size distribution when prepared at temperatures above 170 °C. This result is consistent with the knowledge that particle shapes can be affected by the preparation conditions, such as the synthesis temperature, the pH, and the nature of additives [10]. The crystallite size was determined by counting the number of particles and their sizes in a given area; it was 23 nm when prepared below 170 °C, but it increased to 28 nm when prepared at 200 °C. This result shows the same tendency as that from XRD analysis.

It is well known that photocatalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics [11]. Therefore, this kind of reaction can be represented as follows:

\[-dc/dt = kC\]  \hspace{1cm} (1)

In addition, it can be integrated as follows:

\[C = C_o \exp(-kt)\]  \hspace{1cm} (2)

where $C_o$ is the initial concentration of orange II and $k$ is a rate constant related to the reaction properties of the solute, which depends on the reaction conditions, such as the reaction temperature and the pH of the solution; the photocatalytic activity increases upon increasing this value.

The photocatalytic activity for the decomposition of orange II was examined; the results are shown in Tables 1 and 2. The titania particles prepared at 170 °C had the highest activity for the photocatalytic decomposition of orange II. This result suggests that the photocatalytic activity of the decomposition of orange II depends on the particle size, at the same particle shape, and increases with a decrease of the particle size. This finding is consistent with the knowledge that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases upon decreasing the particle size [12]. It can be also confirmed that a small particle has a larger illuminated surface area because the particles have constant density at the same structure.

The titania particles calcined at 600 °C had the highest activity for the photocatalytic decomposition of orange II; the photocatalytic activity decreased according to an increase of the calcination temperature. This finding is also consistent with the result that the photocatalytic reaction has a small particle-size effect, wherein the photocatalytic activity increases upon decreasing the particle size. Titanium dioxide can take on any of the following three crystal structures: rutile, anatase, or brookite. Anatase-type titanium dioxide generally exhibits a higher photocatalytic activity than do the other types of titanium dioxide, with regard to the decomposition of organic pollutants, by suppressing electron-hole recombination [13]. In the case of our titania particles calcined at 900 °C, the anatase and rutile phases were combined therefore, this sample shows low photocatalytic activity.

Figure 5 shows the effect that the catalyst weight had on the photodegradation of orange II. The degradation rate increased upon increasing the catalyst weight, but no further increase occurred above 2.0 g/L.

As shown in Figure 5, we also observe that the degradation rate of orange II increased proportionally with the mass of the catalyst; almost complete degradation occurred within 1 h in the case of the 1 g/L
catalyst weight. It is believed that the absorption of photons increases proportionally with the mass of the catalyst and that the reactants can easily react over the catalyst surface corresponding to an increasing residence time. However, the degradation rate shows no further increase above 2.0 g/L. It is believed that the initial reaction rate increases proportionally with the mass of TiO₂ up to a plateau, corresponding to the complete absorption of the photons potentially absorbable by TiO₂, and that the excess mass of the catalyst interferes with the transmission of light. This result shows a similar tendency to that reported for the photodegradation of 4-chlorophenol by Al-Sayyed and coworkers [14].

Figure 6 shows the effect of the initial pH of the solution on the photocatalytic decomposition of orange II. The decomposition rate was highest under acidic condition than it was under neutral or basic conditions.

The isoelectric point for TiO₂ in water is ca. pH 6; positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH [15,16]. Therefore, at basic pH, the surface charge is negative and tends to repel electron-sufficient materials from the surface and, consequently, the decomposition rate decreases by prohibiting the adsorption of orange II. Because orange II has a sulfuric group in its structure, which is negatively charged, the acidic solution favors the adsorption on the surface of TiO₂; thus, it is expected that the decomposition rate of orange II should increase.

We must also consider the photocatalytic degradation of orange II in acidic solution, which probably is due to the formation of OH radicals as can be inferred from the following reactions [Eqns. (3)–(6)] [17]:

\[ e^{-} + O_{2}(ads) \rightarrow O_{2}(ads) \]  \hspace{1cm} (3)

\[ O_{2}(ads) + H^{+} \rightarrow HO_{2}^{\cdot} \]  \hspace{1cm} (4)

\[ 2HO_{2}^{\cdot} \rightarrow O_{2} + H_{2}O \]  \hspace{1cm} (5)

\[ H_{2}O_{2} + O_{2}(ads) \rightarrow \cdot OH + \cdot OH + O_{2} \]  \hspace{1cm} (6)

This explanation favors an increase in the degradation of orange II when changing the initial pH of the suspension from 10 to 3.

**Conclusions**

Titania nanoparticles were prepared through the hydrolysis of titanium tetraisopropoxide (TTIP), using TMA (tetramethylammonium) as a peptizer, via a hydrothermal method. The photocatalytic degradation of orange II was studied using a batch reactor in the presence of UV light. The particle sizes were similar after hydrothermal treatment at 120–170 °C, but it increased to 23 nm at 200 °C. The titania nanoparticles had needle-like or polygonal shape when prepared below 150 °C, but they were spherical and had a narrow size distribution when prepared above 170 °C. The titania particles prepared at 170 °C had the highest activity; the titania particles calcined at 600 °C also had the highest activity for the photocatalytic decomposition of orange II. The degradation rate increased upon increasing catalyst weight, but no further increase occurred above 2.0 g/L. In addition, the decomposition rate was higher under acidic conditions than it was under neutral or basic conditions.

**Acknowledgments**

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**References**