Activity of nanosized titania synthesized from thermal decomposition of titanium (IV) n-butoxide for the photocatalytic degradation of diuron

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Received 12 January 2005; revised 15 February 2005; accepted 15 February 2005
Available online 17 June 2005

Abstract

Nanoparticles of anatase titania were synthesized by the thermal decomposition of titanium (IV) n-butoxide in 1,4-butanediol. The powder obtained was characterized by various characterization techniques, such as XRD, BET, SEM and TEM, to confirm that it was a collection of single crystal anatase with particle size smaller than 15 nm. The synthesized titania was employed as catalyst for the photodegradation of diuron, a herbicide belonging to the phenylurea family, which has been considered as a biologically active pollutant in soil and water. Although diuron is chemically stable, degradation of diuron by photocatalyzed oxidation was found possible. The conversions achieved by titania prepared were in the range of 70–80\% within 6 h of reaction, using standard UV lamps, while over 99\% conversion was achieved under solar irradiation. The photocatalytic activity was compared with that of the Japanese Reference Catalyst (JRC-TIO-1) titania from the Catalysis Society of Japan. The synthesized titania exhibited higher rate and efficiency in diuron degradation than reference catalyst. The results from the investigations by controlling various reaction parameters, such as oxygen dissolved in the solution, diuron concentration, as well as light source, suggested that the enhanced photocatalytic activity was the result from higher crystallinity of the synthesized titania.

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Keywords: Titania; Thermal decomposition; Nanoparticle; Photocatalytic activity; Diuron; Degradation

1. Introduction

Titanium (IV) dioxide or titania (\(\text{TiO}_2\)) is one of the most common metal-oxides recognized in various industries. Due to its good physical and chemical properties, such as catalytic activity \cite{1}, photocatalytic activity \cite{2}, good stability toward adverse environment \cite{3}, sensitivity to humidity and gas \cite{4}, dielectric character \cite{5}, nonlinear optical characteristic \cite{6} and photoluminescence \cite{7}, titania has been used in many fields of application including the use as catalysts, catalyst supports, electronics, cosmetics, pigments and filler coating. Nevertheless, photocatalyst is one of the most important applications of titania. Although titania is known to have three natural polymorphs, i.e. rutile, anatase, and brookite, only anatase is generally accepted to have significant photocatalytic activity \cite{8–10}.

Many factors affect the photocatalytic activity of titania. Particle size is one of the most important factors. It has been reported that photocatalytic activity is increased with the decrease in titania particle size, especially into nanometer-scale, because of high surface area and short interface migration distances for photoinduced holes and electrons \cite{11–13}. Nanocrystalline titania can be synthesized by many methods, such as sol-gel method, hydrothermal method, vapor-phase hydrolysis, laser-induced decomposition, chemical vapor deposition and molten salt method. In this work, nanocrystalline anatase titania was synthesized via the thermal decomposition of titanium alkoxide in organic solvent, which has been employed to synthesize various nanocrystalline metal-oxides \cite{14–19}. It has been
demonstrated that the activity of titania synthesized by this method is much higher than those of commercially available titania for photocatalytic decomposition of simple compound, such as acetic acid, in aqueous solutions [20]. However, it has never been used for the decomposition of more complex substance. In this study, photodegradation of complex substance, i.e. diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], is employed to investigate the activity of titania prepared by this method.

Diuron has been one of the most commonly used herbicides for more than 40 years. It is bio-recalcitrant and chemically stable with half-life in soil over 300 days. Since, diuron is slightly soluble (solubility of 36.4 mg/l at 25 °C), it can slowly penetrates through soil and contaminates underground water. Photodegradation using titania as catalyst is therefore one potential option for contaminated water remediation.

2. Materials and methods

2.1. Synthesis of titania

Titanium (IV) n-butoxide (TNB) was used as starting material for titania synthesis. 15 g of TNB was suspended in 100 ml of 1,4-butanediol, which was used as reaction medium, in a test tube. The test tube was then placed in a 300 ml autoclave. The gap between the test tube and the autoclave wall was also filled with 1,4-butanediol. The autoclave was purged completely by nitrogen before heating up to 300 °C at a rate of 2.5 °C/min. Autogeneous pressure during the reaction gradually increased as the temperature was raised. The system was held at 300 °C for 2 h before cooling down to room temperature. The resulting powders in the test tube were repeatedly washed with methanol and dried in 110 °C oven overnight. Subsequently, the obtained product was calcined at 500 °C for 2 h in a box furnace with a heating rate of 10 °C/min.

Synthesized powders were characterized by various techniques, i.e. powder X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). Powder X-ray diffraction (XRD) analysis was done by using a SIEMENS D5000 diffractometer with CuKα radiation. The crystallite size of the product was determined from the broadening of its main peak, using the Scherrer equation. Specific surface area of the samples was also measured by using the BET multipoint method.

2.2. Photocatalytic experiments

Photodegradation of diuron in aqueous solution was employed to investigate the photocatalytic activity of the synthesized titania. The initial concentrations of diuron used were 1 and 10 ppm, respectively. The solution was mixed with titania in the ratio of 1 mg titania to 10 ml of solution and kept in the dark for at least 15 min to allow the complete adsorption of diuron on the surface of titania. The photocatalytic reaction was initiated by exposing test tubes to light from UV lamps (Phillips Cleo 15 W). Diuron degradation was periodically monitored by using a reverse phase HPLC system. The HPLC system included Hyperclone column (150×8 mm inner diameter; 5 μm particle size) (Phenomenex, USA) with a mobile phase of 70% acetonitrile–29.5% water–0.5% phosphoric acid; a flow rate of 0.5 ml/min and a UV detector at 254 nm. The photocatalytic activity of the synthesized catalyst was compared with that of the Japanese Reference Catalyst titania, JRC-TIO-1, which is also pure nanocrystalline anatase.

3. Results and discussion

3.1. Properties of synthesized titania

The particles obtained from the decomposition of TNB in 1,4-buteneol at 300 °C was confirmed to be titania. The XRD analysis, as shown in Fig. 1, revealed that the synthesized product before calcination was already anatase phase. This result was in agreement with the results from our previous work that anatase crystals were formed by crystallization when the temperature in the autoclave reached 250 °C [21]. The crystallite size of the as-synthesized product calculated from the Scherrer equation was approximately 13 nm, while that of the calcined product was 15 nm. It should be noted that the crystallite sizes calculated were in agreement with TEM observation (Fig. 2). Therefore, it was suggested that the synthesized product synthesized was nanosized single crystal titania.

As shown in Table 1, the BET surface area measured by nitrogen adsorption (SBET) of the as-synthesized products was comparable with the surface area calculated from the particle size (SXRD), which was assumed that the particles were spherical and nonporous. It was therefore suggested
that the primary particles were not heavily agglomerated. It was also confirmed by SEM micrographs (Fig. 3a) that the synthesized powder was an irregular aggregates of nanometer particles. According to Park et al. [22], agglomeration of the precipitates is influenced by dielectric constant of the reaction medium. The lower the dielectric constant, the higher the degree of agglomeration. Since, 1,4-butanediol has quite high dielectric constant ($\varepsilon = 32$ at 25 °C [23]), the repulsive force between anatase particles formed in this reaction medium is more pronounced than the attraction force, resulting in low degree of agglomeration.

After calcination at 500 °C, the calcined powder was still in anatase phase, as previously proved that anatase synthesized by this method is thermally stable [21]. Nevertheless, the crystallite size of titania increased due to crystal growth. Agglomeration of primary particles was also observed, according to the fact that the BET surface area was notably decreased. Despite of the smaller surface area, calcined titania has shown higher photocatalytic activity than as-synthesized titania. This is due to the fact that the crystallinity of titania was improved by calcination and the crystallinity predominantly influenced the activity rather than surface area [24].

### 3.2. Photodegradation of diuron

It has been reported that titania synthesized by the thermal decomposition of titanium alkoxide in organic solvent has high activity in photocatalytic decomposition of various compounds [20]. In this work, titania synthesized by this method was employed as catalyst in the photodegradation of diuron, which is chemically stable pollutant. Since, the photocatalytic activity depends upon the conditions of the reaction, such as temperature, light intensity, initial concentration of the compound to be degraded and amount of catalyst used, it is difficult to directly compare the results obtained in this work to those reported in literatures. Therefore, in order to investigate activity of the in-house synthesized catalyst, the results were compared to that of the reference catalyst (JRC-TIO-1) from the Catalysis Society of Japan. It should be noted that mass of the reference catalyst used was the same as the mass of the in-house synthesized catalyst.

Fig. 4 shows the disappearance of diuron by photocatalytic degradation using the synthesized titania or reference titania as catalyst. It should be noted that $C$ is the concentration of diuron at time $t$, while $C_0$ is the initial diuron concentration. The results shown in Fig. 4a indicate

| Crystallite size, $d$ (nm) | $S_{\text{BET}}$ (m$^2$/g) | $S_{\text{XRD}}$ (m$^2$/g) |
|----------------------------|-----------------------------|-----------------------------|
| Synthesized titania         |                             |                             |
| Before calcination          | 13                          | 113                         | 120                         |
| After calcination           | 15                          | 68                          | 103                         |
| Reference titania           | 9                           | 53                          | 174                         |

*a* Crystallite size calculated from XRD peak broadening.
that although both catalysts yielded approximately the same degradation after the reaction time of 6 h, the synthesized titania showed almost twice as much in the initial degradation rate than the reference catalyst. The amount of diuron was reduced to 30% of its initial value within 4 h of the reaction using the synthesized catalyst, while almost 6 h was required for the reference catalyst.

It has been recognized that the efficiency of titania in photocatalytic reaction is influenced by many factors such as crystallinity of the anatase phase \[9\], particle size \[11\] and surface area \[11\]. Since, the synthesized and reference titania are both anatase with roughly same particle size and surface area, the main factor accountable for the enhanced activity of the synthesized titania is its crystallinity. Although there has been no consensus on the detailed mechanism of the photocatalytic reaction on titania, it is generally agreed that the reaction involves generation of electron-hole pairs upon illumination of UV light on titania. The photogenerated holes can be subsequently scavenged by oxidizing species such as H\(_2\)O or OH\(^{-}\) and result in highly reactive hydroxyl radicals, which are the key for decomposition of most organic contaminants. Therefore, the separation of the photogenerated electron-hole pairs is considered to have a predominant role in photocatalytic reaction. The longer the separation period, the higher the activity. Crystallinity, including quality and quantity of both bulk and surface crystal defects, is one factor that affects the electron-hole separation \[25\]. It has been reported that negligible photocatalytic activity of amorphous titania is attributable to the facilitated recombination of photoexcited electrons and holes in the amorphous structure. Therefore, the result in Fig. 4a suggests that titania synthesized by thermal decomposition of TNB in 1,4-butanediol has structure with high crystallinity that prevents electron-hole recombination. This result supports the findings in our previous work that titania synthesized by this method was formed via crystallization pathway \[21\].

When all oxygen dissolved in the solution was purged by thoroughly bubbling with nitrogen gas, the conversion of diuron photodegradation dramatically decreased. As shown in Fig. 4(b), only about 30% of diuron was degraded within 6 h of the reaction with either the synthesized or the reference catalyst. This is in agreement with the generally accepted mechanism of the photocatalytic reaction that the presence of oxygen as an electron scavenger in the system is required for the course of the reaction \[26–28\]. Without electron scavenger, the electron-hole recombination spontaneously took place on the surface of titania. The enhanced effect from crystallinity of the synthesized titania was therefore compromised and the progress of the photocatalytic reactions from both catalysts were roughly the same. However, regardless of the depletion of dissolved oxygen in the solution, the reaction still slowly progressed. This was expected to be the results from chlorine radicals produced during diuron degradation. Several studies involving photocatalytic decomposition of chlorinated organic materials have proposed that chlorine radicals may be generated during photocatalysis \[29\] and these radicals participate in radical chain reactions \[30–32\].

Further, investigations on the enhanced activity of the synthesized titania were conducted by using solar irradiation, which had much higher light intensity than UV lamps. It should be noted that the concentration of
diuron employed was increased to 10 ppm in order to investigate the effect of the initial concentration as well. Fig. 5 shows the results comparing the photodegradation using sunlight to that using UV lamps. Furthermore, since rates of photooxidation of various organic contaminants over illuminated titania have been suggested to follow the Langmuir–Hinshelwood kinetics model [27,33,34], which can be simplified to the apparent first-order kinetics at low concentration, the plot of \( \ln \left( \frac{C_0}{C} \right) \) versus time was expected to be a straight line with the slope equal to the apparent rate constant, \( k_{\text{app}} \), of the degradation. The first-order linear transforms of the results shown in Fig. 5 are given in Fig. 6 and the rate constants are reported in Table 2.

Regarding the effect of diuron concentration, it was found that the degradation rate under UV light shown in Fig. 5 (\( C_0 = 10 \) ppm) was only slightly less than that was given in Fig. 4 (\( C_0 = 1 \) ppm). This is in general agreement with the pseudo first-order nature, according to the Langmuir–Hinshelwood kinetics, of the photooxidation on titania.

It can be seen from Figs. 5 and 6 that titania synthesized from thermal decomposition of titanium alkoxide has higher photocatalytic activity than the reference catalyst, especially under solar irradiation. Although it was not surprise to observe higher degradation rate under higher light intensity, it was particularly interesting to find that the enhancement in the activity from the synthesized titania increased with an increase in light intensity. According to Table 2, the reaction rate constant obtained from the synthesized titania was roughly 45% higher than that of the reference titania, when UV lamps were used. On the other hand, the rate from the synthesized titania was about 60% higher, under solar irradiation.

In general, under higher light intensity, more photoelectron-hole pairs are generated. However, it has been reported that a rate of the electron-hole recombination increases with increasing light intensity more progressively than the rates of charge transfer reaction [35]. Therefore, titania with high crystallinity, which prolongs the separation lifetime of the photogenerated electron-hole pairs, would utilize these greater amount of photoexcited electrons and holes with higher efficiency. Consequently, the enhancement in the photocatalytic activity under high light intensity is more pronounced than that from titania with lower crystallinity. This feature supports the aforementioned discussion that thermal decomposition of titanium alkoxide resulted in anatase titania with much higher crystallinity than the conventional preparation techniques.

Results discussed above have demonstrated that titania synthesized by thermal decomposition of TNB in 1,4-butanediol is potentially applicable for the photodegradation of diuron. However, the operating conditions for photocatalytic reaction in this work have not been optimized. Further, investigation on effects of degradation parameters on the degradation efficiency as well as the intermediates resulted from diuron degradation will be discussed in our next paper.

### 4. Conclusion

Nanocrystalline anatase titania can be prepared via thermal decomposition of TNB in 1,4-butanediol. The synthesized titania has shown higher photocatalytic activity comparing to the reference catalyst. It is suggested that the enhanced activity is resulted from high crystallinity of the synthesized powder, which consequently reduces the recombination of photogenerated electron-hole pairs. The synthesized titania also shows the potential for the degradation of chemically stable compound such as diuron. Nevertheless, conditions for photodecomposition need to be optimized.

### Acknowledgements

The author would like to thank the Thailand Research Fund (TRF) and the Thailand-Japan Technology Transfer Project (TJITTP) for their financial support.
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