

Photocatalytic Degradation Characteristics of Organic Compound by Boron-doped TiO₂ Catalysts

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Abstract

Boron-doped TiO₂ photocatalysts were synthesized by a modified sol-gel method and their photocatalytic activities were performed and compared with those of pure synthetic and commercial TiO₂ catalysts under UV or visible light conditions. Pure TiO₂ itself exhibited very negligible photocatalytic performance under visible light conditions in the aspects of toluene decomposition reactions, although significant decomposition potential was observed as expected with UV light conditions. However, boron doping over TiO₂ significantly improved photocatalytic activity particularly under visible conditions, where over 95% degradation of toluene was achieved with 1wt% B-TiO₂ within 2 hrs. All the decomposition reactions seemed to follow pseudo first-order kinetics. The effects of boron-doping and its characteristics are further discussed through the kinetic studies and comparison of results.

Key words : Photocatalytic, Visible light, Titanium dioxide, Degradation, Toluene

1. INTRODUCTION

Titanium dioxide (TiO₂) has been well known to have strong photocatalytic characteristics, and widely used for the removal of organic pollutants (Bettinelli *et al.*, 2007; Nakamura *et al.*, 2004; Fujishima *et al.*, 2000). Physical properties such as anatase, nanocrystalline particles proved to be critical for effective photocatalytic reactions, and reported are various advantages such as strong oxidation/reduction power, relatively low expense, high stability under light and biological process (Cho *et al.*, 2007; Murakami *et al.*, 2007). However, photocatalytic activity using TiO₂ only occurs under ultraviolet (UV) light intensity, due to its wide band-gap energy (3.2 eV), showing semi-

conducting characteristics. It is known that electrons and holes (e⁻/h⁺) are generated under UV irradiation on TiO₂, resulting in the formation of highly active radicals such as ·OH, HO₂· and O₂⁻· (superoxide anion), which can initiate various decomposition reactions (Konstantinou and Albanis, 2004).

Practically the natural solar energy radiates only 3~4% UV light onto the ground, that numerous investigations have been recently conducted to develop metal or nonmetal-doped TiO₂ photocatalysts, having strong absorption in the visible light region. Previous studies showed that doping of TiO₂ with transition metal such as V, Cr, Fe, Ni or Mn seemed to retard the recombination of e⁻/h⁺ pairs as demonstrated by diffuse reflection spectroscopy (Yang *et al.*, 2007; Yu *et al.*, 2006). Particularly V-doping showed the highest absorption effectiveness in the red shift, which leads to higher photocatalytic activity. On the

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other hand, non-metal doping on TiO₂ turned out to be promising for visible light active photocatalysts. Asahi *et al.* (2001) reported that N-doped TiO₂ shifted the absorption edge to a lower energy, thereby increasing the photocatalytic activity potential in the visible light region. Similarly, S-doped TiO₂ has also proved to have strong photocatalytic activity under irradiation at wavelengths longer than 440 nm, compared with those of pure TiO₂ (Yu *et al.*, 2006; Ohno *et al.*, 2003). It is noted that the dopants such as N or S are usually incorporated as anions replacing O sites or even cations for Ti sites in the lattice of TiO₂ or placed in an interstitial position. Among various combinations, co-doping of TiO₂ such as Zr,S-TiO₂ proved to have been effective for photocatalytic activities more than doping with sulfur or zirconium alone under visible light conditions. They insisted that zirconium increases not only the surface area and the thermal stability of TiO₂ but also retards the e⁻/h⁺ recombination, while sulfur was to reduce the band-gap energy of TiO₂, thus moving the absorption band toward the visible region (Kim *et al.*, 2008; Umebayashi *et al.*, 2003). More recently, many investigations report that boron-doping is another promising alternative in gaseous and aqueous photocatalytic applications (Wu *et al.*, 2010; Zaleska *et al.*, 2009; Bettinelli *et al.*, 2007). Lambert and coworkers (2007) mentioned that low level of B-doping on TiO₂ significantly increased visible light absorption and showed better photocatalytic activities for the degradation of methyl tert-butyl ether (MTBE) than those of undoped TiO₂. Similar studies show that boron doping extends absorption edge to visible light region, increasing the degradation potential of toluene, phenol and other refractory dye compounds (Xu *et al.*, 2009; Khan *et al.*, 2008).

This paper presents further experimental results concerning the syntheses of pure TiO₂ and boron-doped TiO₂ (B-TiO₂) catalysts as well as their photocatalytic activities and physical properties. The photocatalytic activity measurements are performed using a batch photoreactor and compared between pure TiO₂ and B-TiO₂ catalysts under UV and visible lights. Particularly, the photocatalytic activity using B-TiO₂ is focused on the decomposition of toluene

through visible light application, and further discussed through the kinetic studies.

2. EXPERIMENTAL

2.1 Catalyst preparation

Titanium dioxide (TiO₂) and boron-doped TiO₂ photocatalysts (B-TiO₂) were synthesized by a modified sol-gel method, which particularly involved a gradual change of pH from 0.8 ~ 9.0 during the sol-gel transition. Titanium butoxide [Ti(OBu)₄] was initially precursors in ethanolic solution where a mixture of HCl/C₂H₅OH/H₂O was added and then NH₄OH added drop wise for TiO₂ preparation. More detailed procedure was previously well described by Khan *et al.* (2008). Different B-doped TiO₂ catalysts (1 ~ 3wt%) were prepared in the same manner as above where weighed amount of H₃BO₃ as B-precursor was added, and particularly 1wt% B-TiO₂ is focused for the present study. The resulted dry powders were only calcined particularly at 500°C for 3 hr in air, known as the best calcination temperature to obtain the anatase nanocrystalline catalysts (Khan *et al.*, 2008). Commercially available Degussa P-25 TiO₂ (P25) is also provided for comparison of photocatalytic activities.

2.2 Photocatalytic activity measurement

The photocatalytic activity was investigated by the photodegradation of gaseous toluene under UV and visible light irradiation using a closed circulation reactor (batch type) at ambient conditions (Fig. 1). A pyrex-glass tubular reactor with a volume of 1 L, containing the catalysts (300 ~ 1,200 mg) uniformly spread over the irradiation area, was connected to a peristaltic pump through tubing where the gas flow rate was around 320 cm³/min. The reactor containing the catalyst was equipped with a UV lamp (Philips TUV 10 W/G10T8, 254 nm) and a visible lamp (Osram halogen lamp 150 W with 400 nm cutoff filter) as the light sources, which was housed in a black colored, rectangular glass box (30 cmD × 42 cmW × 27 cmH). The photon flux emitted from these lamps was determined actinometrically using the potassium ferrioxalate method and found to be 1.47 × 10⁻⁶

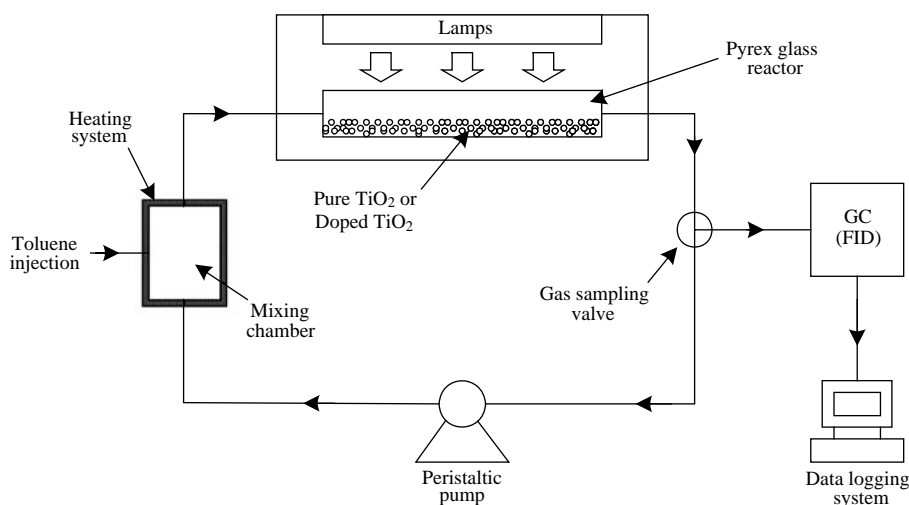


Fig. 1. A schematic diagram of the photocatalytic reactor for the degradation of toluene.

Einstein/s for UV light and 3.9×10^{-6} Einstein/s for visible light. The distance between the lamp and the catalyst was fixed by 10 cm. To introduce toluene for photodegradation measurements, the reactor was connected to a glass mixing chamber, where the temperature was fixed at 70°C to ensure the evaporation of toluene, and the total volume of the circulation reactor was 1.3 L. The initial concentration of toluene used in all experiments reached about 145 ppm. The photoreactor was kept in the dark until the gas concentration remained constant, which indicated that toluene resulted in the steady state between the adsorption and desorption on the catalyst surface. In order to monitor the degradation of toluene at regular interval, Gas Chromatograph (Shimadzu GC-17A, Shimadzu Corporation) equipped with a gas sampler operating with a flame ionization detector (FID) was connected to gas exiting the reactor. The rate of photodegradation was estimated to obey pseudo-first-order kinetics and hence the rate constant (k) was obtained from the first-order plot according to equation (1),

$$\ln \frac{C}{C_0} = -k \cdot t \quad (1)$$

where C_0 is the initial concentration, C is the concen-

tration after a time (t) of the toluene degradation. And here the half-life time (τ) of the reactant is defined as the time required for the toluene concentration to reach half of its initial value.

3. RESULTS AND DISCUSSION

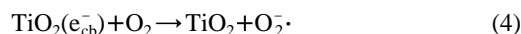
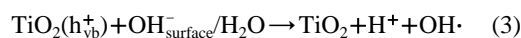
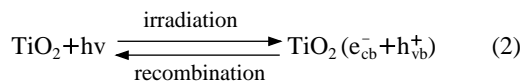
3.1 Effect of pure and B-doped TiO₂ catalysts

The photocatalytic activity tests were performed in order to compare the photocatalytic decomposition of toluene using commercially available P25, and synthesized TiO₂, and boron-doped TiO₂ catalysts. Fig. 2 shows the comparison of the photocatalytic decomposition potentials with adopting different catalysts under UV and visible light sources. With commercial P25 and TiO₂ catalysts under UV light, the degradation efficiency of toluene with P25 increases with increasing reaction time, and reaches almost 60% within 2 hrs, which is further improved by adopting synthetic TiO₂ catalysts up to 70%. However, under visible light, those degradation efficiencies only reach less than 10%, and show little difference between commercial and synthetic TiO₂. As similar characteristics observed in Table 1, the rate constants of P25 ($8.79 \times 10^{-3} \text{ min}^{-1}$) and TiO₂

($1.13 \times 10^{-2} \text{ min}^{-1}$) catalysts under UV light are about 39~43 times higher than those of visible light, which resulted in higher photocatalytic activities, and can be explained by strong UV energy and such physical properties as nanocrystalline size, sufficient surface area and anatase structures.

Photocatalytic reactions are initially induced by the absorption of photons ($h\nu$) with sufficient energy to overcome large band gap, through which electrons (e^-) are excited to the conduction band, leaving holes (h^+) in the valence band on the catalyst surface by reaction (2) (Akpan and Hameed, 2009; Konstantinou and Albanis, 2004). And here, the reverse reaction should be prevented due to the cause of the re-

combination of electrons and holes.



Then, photogenerated electrons and holes (e^-/h^+) can react with water vapor and electron acceptors and donors (O_2 and OH^-) on the catalyst surface to form highly active radicals ($\text{OH}\cdot$, $\text{O}_2\cdot^-$ or $\text{HO}_2\cdot$) by reactions (3) and (4). These radicals eventually contribute to the photocatalytic decomposition reactions.

Encouragingly, boron-doping onto TiO_2 (B- TiO_2) turned out to be very effective particularly under visible light, and sharply increased the photocatalytic activities. When 1wt% B- TiO_2 was adopted with visible light, the toluene decomposition almost completed within 3.5 hrs where the toluene concentration overall decreased exponentially with time, presumably following the first-order kinetics. More boron-loading like 3~5wt% B- TiO_2 showed similar removal potential to 1wt% B- TiO_2 , but made photocatalytic activities slightly fluctuated as the reaction time proceeded. Therefore, those results using 1wt% B- TiO_2 are more reproducible and the highest rate constant ($k=2.78 \times 10^{-2} \text{ min}^{-1}$) was achieved under visible light conditions (Table 1). Boron-doping over TiO_2 could effectively inhibit the crystalline growth and thus slightly increases the surface area, which must be related to the photocatalytic activities. Many studies report that boron may have three possible structures in the anatase lattice, substituting a Ti ion,

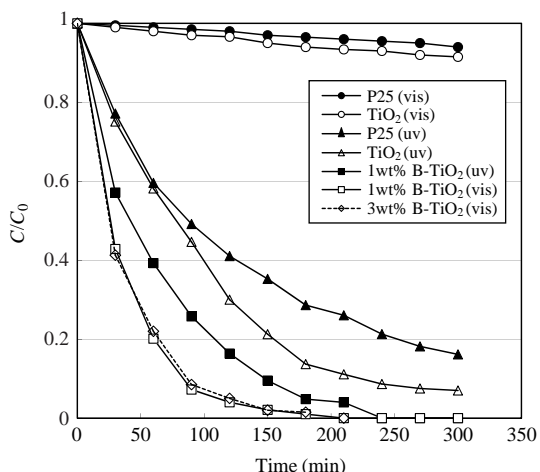


Fig. 2. Photocatalytic degradation of toluene with adopting different catalysts under UV and visible light conditions; $C_0=145 \text{ ppm}$, calcination temperature= 500°C , catalyst amount= 0.46 g/L .

Table 1. The physical properties of selected TiO_2 catalysts.

Type of oxides	Crystalline size (nm) ^a	S_{BET} (m^2/g) ^b	Pore volume (cm^3/g) ^c	Rate constant, K (min^{-1}) (UV) ^d	Rate constant, K (min^{-1}) (Vis) ^d
P25	21	50	—	8.79×10^{-3}	2.01×10^{-4}
TiO_2	18	63	0.12	1.13×10^{-2}	2.89×10^{-4}
1wt% B- TiO_2	15	72	0.16	1.64×10^{-2}	2.78×10^{-2}
3wt% B- TiO_2	15	71	0.15	3.30×10^{-2}	1.10×10^{-2}

^a: Measured by the Scherrer's equation.

^b: Measured by BET method.

^c: Taken from the volume N_2 adsorbed at $P/P_0=0.995$.

^d: Calculated from the linear fitting of $\ln(C/C_0)$ vs. reaction time with catalyst amount of 0.46 g/L .*.

and an O ion, or in an interstitial position. The copresence of boron substitutional to oxygen (BTi₃) and interstitial boron (BO₃ or BO₄) is generally agreed, favoring the formation of B species, e.g. B³⁺ ions in B-TiO₂ structure, while boron substitutional to Ti is energetically less favorable (Finazzi *et al.*, 2009; Chen *et al.*, 2006). Substitutional and interstitial borons introduce new states in the midgap of the catalysts, believed to narrow the band gap energy, which shifts absorption edge to visible light region, increasing the degradation potential of toluene.

3.2 Catalyst amount and their kinetics

Fig. 3 shows the effects of catalyst amount with 1wt% B-TiO₂ and different light sources on the photocatalytic decomposition of toluene and their kinetics. It proves that all reactions well follow pseudo-first order kinetics. The decomposition rate and removal efficiency of toluene generally increased with increasing catalyst weight, but no further optimization was unfortunately achieved for the given range. More precisely in Table 2, the reaction rate constant with 0.46 g/L catalyst (1wt% B-TiO₂) reached $k=1.64 \times 10^{-2} \text{ min}^{-1}$ under UV light source, where the half-life time of toluene took about $\tau=43.3$ minutes. When the catalyst amount increased two times up to 0.92 g/L, the rate constant and half-time were $k=2.41 \times 10^{-2} \text{ min}^{-1}$ and $\tau=28.8$ minutes respectively, which represent about 50% faster than those with 0.46 g/L catalyst. As the catalyst amount increases from 0.23 ~ 0.92 g/L, the decomposition rate proportionally increases as well, but the photocatalytic activity and half-life time are inversely diminished. However, two folds of catalyst amount does not represent two times increase in the reaction rate, although the reactivity almost tends to depend on the catalyst amount. Thus, it is important that particles must be well dispersed uniformly to form possible active sites on the catalyst surface. As these trends compared with visible light conditions, the same amount of catalyst 0.46 g/L (1wt% B-TiO₂) with visible light was producing more degradation potential even than those of 0.92 g/L with UV light. Consequently, this implies that B-doping on TiO₂ is prominently effective in photocatalytic decomposi-

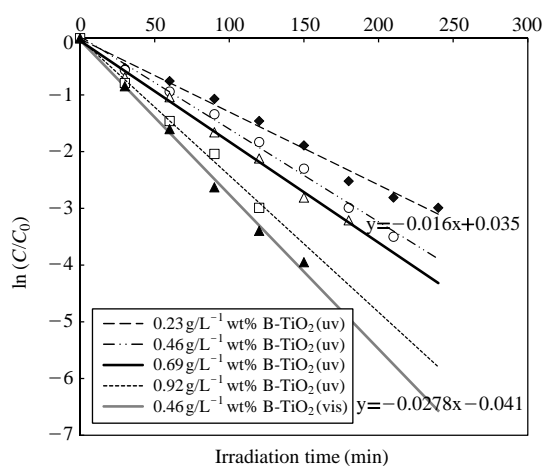


Fig. 3. Effects of catalyst amount on the photocatalytic decomposition of toluene and kinetic studies with 1wt% B-TiO₂ under UV and visible conditions; C₀= 145 ppm, calcination temperature=500°C, catalyst amount=0.23 ~ 0.92 g/L.

Table 2. Comparison of reaction kinetics with boron-doped TiO₂ catalyst under different catalyst amount and light sources.

Operating condition	Catalyst amount (g/L)*	Rate constant, K (min ⁻¹)	Half-life time, τ (min)
1wt% B-TiO ₂ UV	0.23	1.29×10^{-2}	53.3
	0.46	1.64×10^{-2}	43.3
	0.69	1.78×10^{-2}	38.5
	0.92	2.41×10^{-2}	28.8
1wt% B-TiO ₂ VIS	0.46	2.78×10^{-2}	25.6

*: the ratio of catalyst amount over gaseous volume.

tion of organic pollutants.

Similar results can be found in previous studies (Ryu *et al.*, 2006) where the photocatalytic degradation rate of orange II became higher with increasing catalyst weight in a liquid batch reactor under UV conditions. Park (2007) and An *et al.* (2006) also reported in their practical formaldehyde decomposition experiments that as the amount of catalyst coated on glass was fixed at 6 and 32.6 mg/cm² through a dip coating process, the decomposition rate constants were $3.10 \times 10^{-3} \text{ min}^{-1}$ and $1.02 \times 10^{-1} \text{ min}^{-1}$ respectively. However, these results must remain effective

Table 3. Photocatalytic decomposition characteristics with various TiO₂-based catalysts under visible light conditions.

Photocatalysts	Decomposition (irradiation time)	Model pollutant (concentration)	Light source (reaction)	Rate constant k, (min ⁻¹)	Reference
1wt% B-TiO ₂	100% (3.5 hr)	Toluene (145 ppm)	Visible (gaseous)	2.78×10^{-2}	This study
1wt% B-TiO ₂	100% (4 hr)	Toluene (500 ppm)	Visible (gaseous)	4.71×10^{-2}	Khan <i>et al.</i> , 2008
N,S-TiO ₂	64% (3 hr)	Formaldehyde (200 ppm)	Daylight (gaseous)	–	Yu <i>et al.</i> , 2006
3wt% Zr,S-TiO ₂	77%	Toluene (530 ppm)	Visible (gaseous)	0.60×10^{-2}	Kim <i>et al.</i> , 2008
0.015mol% B-TiO ₂	53.6% (80 min)	Azo-dye (50 mg/L)	Visible (aqueous)	1.03×10^{-2}	Xu <i>et al.</i> , 2009
9mol% B-TiO ₂	95% (4 hr)	Methylene blue (19 mg/L)	Visible (aqueous)	–	Bettinelli <i>et al.</i> , 2007
0.01mol% B-TiO ₂ -Fe(0.01)/SiO ₂	52% (3 hr)	Phenol (50 mg/L)	Visible (aqueous)	–	Ling <i>et al.</i> , 2008
1mol% B,C-TiO ₂	60% (3 hr)	Acid orange 7 (20 mg/L)	Visible (aqueous)	–	Wu <i>et al.</i> , 2010

in application systems, and thus increasing catalysts sometimes require too many layers of coatings from which active sites can be agglomerated to produce less activity. So there must be trade-off between catalyst amount and activities for which the previous studies had suggested the optimum catalyst amount as 30 mg/cm² (Kwon *et al.*, 2005; Esplugas *et al.*, 2002).

3.3 Visible light-active B-TiO₂ characteristics

The effects of dopants and their photocatalytic activities have been investigated concerning the decomposition of possible pollutants from many gaseous and aqueous reaction conditions (Khan *et al.*, 2008; Ling *et al.*, 2008). Apart from gaseous organic pollutants, most of synthetic textile dyes in wastewater seem more resistant to be decomposed or decolorized by traditional wastewater treatment technologies because of their chemical stability (Wu *et al.*, 2010; Xu *et al.*, 2009). Table 3 summarizes the comparison of photocatalytic decomposition characteristics using various dopants of TiO₂ catalysts with the present results, particularly showing visible light-active, optimum loaded B-TiO₂ catalysts. Again, B-doped TiO₂ catalysts turned out to be the most effective for the photocatalytic degradation of most synthetic textile dyes. As mol% of boron increases, the degradation potential tends to increase more or less where 95% degradation of methylene blue was photocatalytically achieved with 9mol% B-TiO₂. Similarly in gaseous toluene reactions, about 1wt% B loading seems to be located near the optimum B

range, which is compared with those of nonmetal dopants such as Zr, N, and S components. As mentioned above, 1wt% B-TiO₂ shows the best photocatalytic decomposition performance of toluene (100% in 3.5 ~ 4 hr), compared with those of N,S-TiO₂ (64%) and Zr,S-TiO₂ (77%) catalysts. Consequently, this study again confirms that B-doped TiO₂ is the most promising catalyst for the photocatalytic degradation of possible organic pollutants, particularly even for the lower energy band of the day-time and visible light applications.

4. SUMMARY

The present results show that under UV light conditions, pure TiO₂ itself also shows significant photocatalytic performance, which ranges from about 60~70% degradation of toluene within 2 hrs, while those were negligible presumably under visible light conditions. However, boron doping over TiO₂ significantly improved photocatalytic activity particularly under visible light irradiation, compared with those of pure TiO₂. Decomposition efficiency of toluene sharply increased more than 95% within 2 hrs, and complete decomposition was possible within several hours. The lower B doping (1wt%) seems to approach optimum B loading, favoring the formation of B³⁺ species in B-TiO₂ structure as discussed, which is believed to narrow the band gap energy, resulting in the increase of photocatalytic activity. All the decomposition reactions approached pseudo first-order

kinetics, having the rate constant of $2.78 \times 10^{-2} \text{ min}^{-1}$ with boron-doped TiO₂ (0.46 g/L), which tends to increase with increasing the catalyst weight.

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