1. INTRODUCTION

Titanium dioxide (TiO$_2$) 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 TiO$_2$ only occurs under ultraviolet (UV) light intensity, due to its wide band-gap energy (3.2 eV), showing semiconducting characteristics. It is known that electrons and holes (e$^-$/h$^+$) are generated under UV irradiation on TiO$_2$, resulting in the formation of highly active radicals such as ·OH, HO$_2^-$ and O$_2^-$ (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 TiO$_2$ photocatalysts, having strong absorption in the visible light region. Previous studies showed that doping of TiO$_2$ 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
other hand, non-metal doping on TiO$_2$ turned out to be promising for visible light active photocatalysts. Asahi et al. (2001) reported that N-doped TiO$_2$ shifted the absorption edge to a lower energy, thereby increasing the photocatalytic activity potential in the visible light region. Similarly, S-doped TiO$_2$ has also proved to have strong photocatalytic activity under irradiation at wavelengths longer than 440 nm, compared with those of pure TiO$_2$ (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 TiO$_2$ or placed in an interstitial position. Among various combinations, co-doping of TiO$_2$ such as Zr,S-TiO$_2$ 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 TiO$_2$ but also retards the $e^-/h^+$ recombination, while sulfur was to reduce the band-gap energy of TiO$_2$, 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 TiO$_2$ significantly increased visible light absorption and showed better photocatalytic activities for the degradation of methyl tert-butyl ether (MTBE) than those of undoped TiO$_2$. 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 TiO$_2$ and boron-doped TiO$_2$ (B-TiO$_2$) catalysts as well as their photocatalytic activities and physical properties. The photocatalytic activity measurements are performed using a batch photoreactor and compared between pure TiO$_2$ and B-TiO$_2$ catalysts under UV and visible lights. Particularly, the photocatalytic activity using B-TiO$_2$ 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 (TiO$_2$) and boron-doped TiO$_2$ photocatalysts (B-TiO$_2$) 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 precursored in ethanolic solution where a mixture of HCl/C$_2$H$_5$OH/H$_2$O was added and then NH$_4$OH added drop wise for TiO$_2$ preparation. More detailed procedure was previously well described by Khan et al. (2008). Different B-doped TiO$_2$ catalysts (1~3wt%) were prepared in the same manner as above where weighed amount of H$_3$BO$_3$ as B-precursor was added, and particularly 1wt% B-TiO$_2$ 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 TiO$_2$ (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 cm$^3$/min. The reactor containing the catalyst was equipped with a UV lamp (Philips TUV 10 W/G10T8, 254 nm) and a visible lamp (Oslam 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 $1.47 \times 10^{-6}$
Einstein/s for UV light and $3.9 \times 10^{-6}$ 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),

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

where $C_0$ is the initial concentration, $C$ is the concentration after a time ($t$) of the toluene degradation. And here the half-life time ($t$) 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 TiO$_2$ catalysts

The photocatalytic activity tests were performed in order to compare the photocatalytic decomposition of toluene using commercially available P25, and synthetized TiO$_2$, and boron-doped TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ catalysts up to 70%. However, under visible light, those degradation efficiencies only reach less than 10%, and show little difference between commercial and synthetic TiO$_2$. As similar characteristics observed in Table 1, the rate constants of P25 ($8.79 \times 10^{-3}$ min$^{-1}$) and TiO$_2$
(1.13 × 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 (hv) 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 recombination 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 (OH\cdot, O\cdot_{2} or HO\cdot_{2}) 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 × 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, specifically (101) plane.

**Table 1. The physical properties of selected TiO_{2} catalysts.**

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

^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.}

Fig. 2. Photocatalytic degradation of toluene with adopting different catalysts under UV and visible light conditions; $C_{0}$=145 ppm, calcination temperature=500°C, catalyst amount=0.46 g/L.
and an O ion, or in an interstitial position. The co-presence of boron substitutional to oxygen (B\textsubscript{Ti}) and interstitial boron (BO\textsubscript{3} or BO\textsubscript{4}) is generally agreed, favoring the formation of B species, e.g. B\textsuperscript{3+} ions in B-TiO\textsubscript{2} structure, while boron substitutional to Ti is energetically less favorable (Finazzi \textit{et al.}, 2009; Chen \textit{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-TiO\textsubscript{2} 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-TiO\textsubscript{2}) reached $k = 1.64 \times 10^{-2}$ min\textsuperscript{-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 $k = 2.41 \times 10^{-2}$ min\textsuperscript{-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-TiO\textsubscript{2}) 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 TiO\textsubscript{2} is prominently effective in photocatalytic decomposi-

### Table 2. Comparison of reaction kinetics with boron-doped TiO\textsubscript{2} catalyst under different catalyst amount and light sources.

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Catalyst amount (g/L)*</th>
<th>Rate constant, $K$ (min\textsuperscript{-1})</th>
<th>Half-life time, $\tau$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt% B-TiO\textsubscript{2}</td>
<td>0.23</td>
<td>$1.29 \times 10^{-2}$</td>
<td>53.3</td>
</tr>
<tr>
<td>UV</td>
<td>0.46</td>
<td>$1.64 \times 10^{-2}$</td>
<td>43.3</td>
</tr>
<tr>
<td></td>
<td>0.69</td>
<td>$1.78 \times 10^{-2}$</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>$2.41 \times 10^{-2}$</td>
<td>28.8</td>
</tr>
<tr>
<td>1wt% B-TiO\textsubscript{2}</td>
<td>0.46</td>
<td>$2.78 \times 10^{-2}$</td>
<td>25.6</td>
</tr>
</tbody>
</table>

*: the ratio of catalyst amount over gaseous volume.

Similar results can be found in previous studies (Ryu \textit{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 \textit{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/cm\textsuperscript{2} through a dip coating process, the decomposition rate constants were $3.10 \times 10^{-3}$ min\textsuperscript{-1} and $1.02 \times 10^{-1}$ min\textsuperscript{-1} respectively. However, these results must remain effective...
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 summerizes 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 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 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.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Decomposition (irradiation time)</th>
<th>Model pollutant (concentration)</th>
<th>Light source (reaction)</th>
<th>Rate constant k (min⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1wt% B-TiO₂</td>
<td>100% (3.5 hr)</td>
<td>Toluene (145 ppm)</td>
<td>Visible (gaseous)</td>
<td>2.78 × 10⁻²</td>
<td>This study</td>
</tr>
<tr>
<td>1wt% B-TiO₂</td>
<td>100% (4 hr)</td>
<td>Toluene (500 ppm)</td>
<td>Visible (gaseous)</td>
<td>4.71 × 10⁻²</td>
<td>Khan et al., 2008</td>
</tr>
<tr>
<td>N,S-TiO₂</td>
<td>64% (3 hr)</td>
<td>Formaldehyde (200 ppm)</td>
<td>Daylight (gaseous)</td>
<td>–</td>
<td>Yu et al., 2006</td>
</tr>
<tr>
<td>3wt% Zr,S-TiO₂</td>
<td>77%</td>
<td>Toluene (530 ppm)</td>
<td>Visible (gaseous)</td>
<td>0.60 × 10⁻²</td>
<td>Kim et al., 2008</td>
</tr>
<tr>
<td>0.01mol% B-TiO₂</td>
<td>53.6% (80 min)</td>
<td>Azo-dye (50 mg/L)</td>
<td>Visible (aqueous)</td>
<td>1.03 × 10⁻²</td>
<td>Xu et al., 2009</td>
</tr>
<tr>
<td>9mol% B-TiO₂</td>
<td>95% (4 hr)</td>
<td>Methylene blue (19 mg/L)</td>
<td>Visible (aqueous)</td>
<td>–</td>
<td>Bettinelli et al., 2007</td>
</tr>
<tr>
<td>0.01mol% B-TiO₂-Fer(0.01)/SiO₂</td>
<td>52% (3 hr)</td>
<td>Phenol (50 mg/L)</td>
<td>Visible (aqueous)</td>
<td>–</td>
<td>Ling et al., 2008</td>
</tr>
<tr>
<td>1mol% B,C-TiO₂</td>
<td>60% (3 hr)</td>
<td>Acid orange 7 (20 mg/L)</td>
<td>Visible (aqueous)</td>
<td>–</td>
<td>Wu et al., 2010</td>
</tr>
</tbody>
</table>

Table 3. Photocatalytic decomposition characteristics with various TiO₂-based catalysts under visible light conditions.
kinetics, having the rate constant of $2.78 \times 10^{-2}$ min$^{-1}$ with boron-doped TiO$_2$ (0.46 g/L), which tends to increase with increasing the catalyst weight.

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