

## Support Effect of Silica on Photocatalytic Degradation of Dibutyl Phthalate by TiO<sub>2</sub> Nanoparticles in Water Containing Chloride Anion

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Employing silica as a support of TiO<sub>2</sub> reduced the inhibition effect of chloride anion on photocatalytic activity for degradation of dibutyl phthalate in water. This support effect was largely observed in the cases of silica having larger surface area and of smaller TiO<sub>2</sub> particles.

Photocatalysis on TiO<sub>2</sub> should be one of the most promising systems that are able to degrade many kinds of organic compounds in water,<sup>1</sup> because diluted organic pollutants can be decomposed without separation from water. However, it is also known that inorganic anion such as chlorine anion in water reduced the photocatalytic performance in many cases,<sup>2</sup> which is explained by the competition with organics for adsorption or reaction.

In order to avoid the direct use of TiO<sub>2</sub> powder, which entails later separation from the water, support materials are often used.<sup>1</sup> Silica is often employed as catalyst support since it has high specific surface area. In addition, silica shows good transmittance of UV light, which is better for photocatalyst. Especially, mesoporous silica, which has large specific surface area such as 1000 m<sup>2</sup>·g<sup>-1</sup> and shows high transmittance of UV light,<sup>3</sup> might be an excellent support for photocatalyst.<sup>4</sup> In the present study, we examined three kinds of silica support including mesoporous silica, and found that the silica support could effectively decrease the inhibitive effect of chloride anion in water.

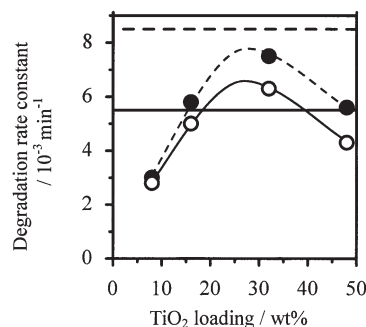
The mesoporous silica (FSM-16)<sup>5</sup> was prepared in the same manner as previous works.<sup>6</sup> The sample of TiO<sub>2</sub> supported by FSM-16, which is referred to as TiO<sub>2</sub>/FSM, was prepared as follows; as-synthesized FSM-16 containing template surfactant was impregnated by an aqueous (NH<sub>4</sub>)<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> at 353 K and evaporated to dryness in the ambient air, followed by drying and calcination in a flow of N<sub>2</sub> at 523 K for 1 h and successively in flowing dry air at 773 K for 5 h. The Ti content was 8, 16, 32, and 48 wt %. Although X-ray diffraction (XRD) intensity of the samples due to hexagonal structure at low angle decreased with increasing Ti content, it was confirmed that the diffractions clearly remained, meaning that the hexagonal structure maintained even the sample of 48 wt % Ti. Other series of silica-supported TiO<sub>2</sub> samples (8, 16, 32, and 48 wt %) were prepared in conventional impregnation method by employing sol-gel prepared silica<sup>7</sup> (540 m<sup>2</sup>·g<sup>-1</sup>) and fumed silica (Cab-o-sil, 200 m<sup>2</sup>·g<sup>-1</sup>), referred as to TiO<sub>2</sub>/SG and TiO<sub>2</sub>/Cab, respectively. ST-01 (Ishihara, 200 m<sup>2</sup>·g<sup>-1</sup>) was employed as unsupported TiO<sub>2</sub>. Although the silica-supported TiO<sub>2</sub> were also powder, it was obvious that the silica-support contributed to the easy separation.

The BET specific surface area of catalyst was calculated from N<sub>2</sub> adsorption amount at 77 K. The surface area of exposed

TiO<sub>2</sub> particle was estimated by BAT (benzaldehyde–ammonia titration) method<sup>8</sup> and the particle size was calculated.<sup>9</sup> Although the mean particle size of supported TiO<sub>2</sub> on the 8 wt % TiO<sub>2</sub>/FSM sample (2.1 nm) was smaller than the mesopore size (ca. 2.5 nm), that of higher loading TiO<sub>2</sub>/FSM sample was larger, implying the particles existed both inside and outside of mesopores. The BET surface area of TiO<sub>2</sub>/FSM was in range from 520 to 950 m<sup>2</sup>·g<sup>-1</sup>. Diffuse reflectance UV–vis spectra showed that the band gap of supported TiO<sub>2</sub> particle became small with an increase of Ti content, indicating an increase of the particle size.

The adsorption and photodegradation test was carried out at room temperature.<sup>10</sup> Dibutyl phthalate (DBP) was employed as a model compounds for endocrine disruptors.<sup>11</sup> After aqueous solution of DBP (17 mg·dm<sup>-3</sup>, 30 cm<sup>3</sup>) was magnetically stirred in the dark for 1 h, the catalyst (15 mg) was introduced into the flask made of borosilicate glass and again stirred in the dark. The DBP concentration in the solution was sometimes measured by gas chromatography (GC). After DBP concentration achieved to the adsorption equilibrium (200 min), the light from Xe-lamp (300 W, 0.1 W·cm<sup>-2</sup> measured at the range from 360 to 470 nm) was irradiated through a small window (5 mm diameter) after passing a cooling water filter, and the DBP concentration was monitored by GC. The wavelength of irradiated light to the sample should be more than 280 nm, which was limited by borosilicate reactor. It has been confirmed that the complete mineralization of DBP occurs in the system employing TiO<sub>2</sub> photocatalyst.<sup>10</sup> NaCl was added for the experiments in the presence of chloride anion (70 mg·dm<sup>-3</sup>). The pseudo-first-order rate constant of photodegradation<sup>12</sup> was evaluated in the similar way to the previous work.<sup>10</sup>

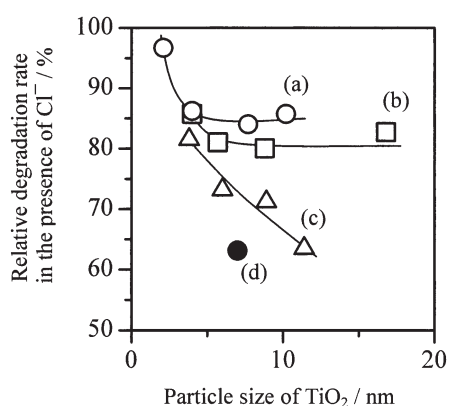
Photocatalytic activity was confirmed on each sample. In Figure 1, shown was the pseudo-first order rate constant of pho-



**Figure 1.** Effect of Cl<sup>-</sup> on DBP degradation rate constant over TiO<sub>2</sub> (ST-01) (straight lines) and TiO<sub>2</sub>/FSM with various loading amount (curves). Broken line/curve shows the results in the absence of Cl<sup>-</sup>, solid line/curve shows the results in the presence of Cl<sup>-</sup>.

todegradation in the absence and presence of  $\text{Cl}^-$  over unsupported  $\text{TiO}_2$  (lines) and  $\text{TiO}_2/\text{FSM}$  of various Ti content (curves) as representatives. In the absence of  $\text{Cl}^-$  (broken line/curve), each  $\text{TiO}_2/\text{FSM}$  exhibited lower activity than unsupported  $\text{TiO}_2$ , owing to less amount of  $\text{TiO}_2$ .<sup>13</sup> The order of the photoactivity was: unsupported  $\text{TiO}_2 > \text{TiO}_2/\text{FSM} > \text{TiO}_2/\text{Cab} > \text{TiO}_2/\text{SG}$ .<sup>14</sup> In the presence of  $\text{Cl}^-$ , the activity of unsupported  $\text{TiO}_2$  much reduced (solid straight line), while the activity of  $\text{TiO}_2/\text{FSM}$  scarcely decreased (solid curve). As a result, the  $\text{TiO}_2/\text{FSM}$  of 32 wt %  $\text{TiO}_2$  showed higher activity than unsupported one in the presence of  $\text{Cl}^-$ .

From the rate constant in the absence and presence of  $\text{Cl}^-$ , relative rate of DBP degradation in the presence of  $\text{Cl}^-$  was evaluated<sup>15</sup> for each samples and plotted as a function of particle size of  $\text{TiO}_2$  (Figure 2). It is clearly shown that almost all silica-supported  $\text{TiO}_2$  samples exhibited higher relative rate than that unsupported  $\text{TiO}_2$ . In other words, employing silica support reduced the inhibition effect of  $\text{Cl}^-$  on the photocatalytic activity of  $\text{TiO}_2$ .



**Figure 2.** Plots of relative rate of DBP degradation in the presence of  $\text{Cl}^-$  to that in absence of  $\text{Cl}^-$  versus particle size of  $\text{TiO}_2$  over (a)  $\text{TiO}_2/\text{FSM}$ , (b)  $\text{TiO}_2/\text{SG}$ , (c)  $\text{TiO}_2/\text{Cab}$ , and (d) non-supported  $\text{TiO}_2$  (ST-01).

Note that the silica-supported samples were differently influenced by  $\text{Cl}^-$ . The inhibition effect depended on the support material and  $\text{TiO}_2$  particle size. For any size of  $\text{TiO}_2$ , this support effect of silica materials was in order of  $\text{FSM-16} > \text{SiO}_2(\text{sol-gel prepared}) > \text{SiO}_2(\text{Cab-o-sil})$ , which was the same order as that of the specific surface area of the support ( $1100$ ,  $540$ , and  $200 \text{ m}^2 \cdot \text{g}^{-1}$ , respectively). Since the surface charge of  $\text{TiO}_2$  was almost neutral (the point of zero charge,  $\text{pH}_{\text{pzc}}$ , of  $\text{TiO}_2$  was measured to be  $6.9$ ),<sup>16</sup> there would be less repulsion between  $\text{Cl}^-$  and surface, which would bring about much inhibition effect of  $\text{Cl}^-$ . On the other hand, since the surface charge of  $\text{SiO}_2$  was negative in the neutral water ( $\text{pH}_{\text{pzc}}$  of  $\text{FSM-16}$  was  $2.2$ , and that of  $\text{Cab-o-sil}$  was  $2.4$ ), the larger surface area and negative charge of surface might reduce the accessibility of  $\text{Cl}^-$  to  $\text{TiO}_2$  nanoparticles on it.

In Figure 2, it was also found that smaller  $\text{TiO}_2$  particles were less subject to the effect of  $\text{Cl}^-$ . The smaller particle might be more influenced by the surface property of the support. Further study is required to discuss the mechanism of this support effect.

In conclusion, the use of silica support for  $\text{TiO}_2$  nanoparticle

was effective to reduce the inhibition effect of  $\text{Cl}^-$  on photocatalytic degradation of DBP in water. This support effect was intensely observed in the cases of smaller  $\text{TiO}_2$  particles on the silica having larger surface area such as mesoporous silica.

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- 9 The particle size was estimated from the surface area of  $\text{TiO}_2$  measured by BAT method (Ref. 8) on an assumption that the particle was hemisphere on the silica surface, because XRD and TEM were not suitable for determination of the particle size of low loading samples.
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- 12 The following equation was assumed;  $v = k [\text{DBP}]$ , where  $v$  is the decrease rate of DBP,  $k$  ( $\text{min}^{-1}$ ) is the rate constant and  $[\text{DBP}]$  is the concentration of DBP.
- 13 When they were compared in the rate per  $\text{TiO}_2$ -weight, the activities of silica-supported  $\text{TiO}_2$  were higher than that of unsupported  $\text{TiO}_2$ ; the order of the photocatalytic activity was:  $\text{TiO}_2/\text{FSM} > \text{TiO}_2/\text{Cab} > \text{TiO}_2/\text{SG} > \text{unsupported TiO}_2$ . On each support, smaller nanoparticles of  $\text{TiO}_2$  showed higher specific activity per  $\text{TiO}_2$ -weight.
- 14 The samples of less loading amount showed lower rate due to less amount of  $\text{TiO}_2$ . On the other hand, the highest loading sample did not show the maximum rate, which might be due to the larger particle size of  $\text{TiO}_2$ . These are common observations in both the absence and presence of  $\text{Cl}^-$ .
- 15 Relative rate of DBP degradation ( $R$  (%)) was defined as follows;  $R = k_{\text{Cl}}/k_0 \times 100$ , where  $k_{\text{Cl}}$  is the rate constant in the presence of  $\text{Cl}^-$ ,  $k_0$  was that in the absence of  $\text{Cl}^-$ .
- 16 The  $\text{pH}_{\text{pzc}}$  was defined as the intersection point of two HCl ( $0.1 \text{ mol} \cdot \text{dm}^{-3}$ ,  $25 \text{ cm}^3$ )-NaOH ( $0.1 \text{ mol} \cdot \text{dm}^{-3}$ ) titration curves in the absence and presence of catalyst ( $0.5 \text{ g}$ ).