Photocatalysis of SiO2-loaded TiO2

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Abstract

SiO_2 was loaded to TiO_2 by sol–gel method, and the resulting SiO_2/TiO_2 was calcined at different temperatures. The loading of SiO_2 improved photocatalytic activity of TiO_2. The optimum calcination temperature was 300 °C, and the optimum amount of loaded SiO_2 was 1.5–4.8 wt.%. This modified photocatalyst was tested for the degradation of nitrobenzene (NB), benzyltrimethylammonium chloride (BTMA), phenol and propionic acid. The highest effect was observed for BTMA, and attributed to electrostatic interaction between BTMA and SiO_2/TiO_2. Whereas simple mechanical mixing of TiO_2 and SiO_2 was not effective.
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1. Introduction

There have been intensive studies on TiO_2 photocatalysis in the past two decades [1,2] and its practical use are in progress for air purification and related fields. However, still several technical breakthroughs are required for water purification. Major improvement to be achieved is an increase in the degradation efficiency. One of the factors to determine the efficiency is adsorption of substrate to TiO_2. Incorporation of silica [3–10], alumina [4], zeolite [8,11–14] and activated carbon [8,9,15,16] into TiO_2 have been studied to increase the adsorption. It was demonstrated that most of the TiO_2-covered adsorbents are more efficient than bare TiO_2. In those works the authors aim also to support TiO_2 on the larger adsorbent particle, so that the recovery of photocatalyst is facilitated. Partly because of this reason, in the most studies TiO_2 was formed on the surface of adsorbent instead of vice versa. However, it is advantageous to modify existing highly efficient TiO_2 to a better photocatalyst. One of the present author reported that the improved efficiency of SiO_2-loaded TiO_2 (SiO_2/TiO_2) resulted from sodium silicate. The modified catalyst was effective for cationic pollutants. In the possible reaction mechanism of SiO_2-loaded TiO_2 photocatalyst the substrate is concentrated on SiO_2 near the surface of TiO_2 and thereby increases the degradation of the substrate. This mechanism suggests that adsorbent should be finely distributed on the surface of TiO_2 to achieve the high efficiency and accordingly the subtle difference in the preparation process affects the photocatalytic activity. On the other hand, it has been demonstrated that simple mechanical mixing of TiO_2 and adsorbent increases the efficiency [17,18]. The comparison between two systems, loaded TiO_2 and mechanically mixing, provides some insights into the mechanism of the adsorbent effect.

In the present study SiO_2 was loaded to TiO_2 by sol–gel method and the optimization of this photocatalyst was studied.

2. Experimental

2.1. Chemicals

The TiO_2 used is TP-2 (anatase) purchased from Fujititan Co. [19]. Nitrobenzene (NB), benzyltrimethylammonium chloride (BTMA), phenol and propionic acid tested for the degradation are of reagent grade. Silica OX-50 was a product of Nihonaerosil Co.

2.2. Loading of SiO2

General procedure is as follows. 0.5–1.5 ml of TEOS (tetraethoxysilane) in 24 ml of methanol was added to 3 g

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TiO_2 and stirred magnetically until complete evaporation of methanol. Then distilled water was added to the TiO_2. After stirring for several seconds, the TiO_2 was separated by decantation. It was suspended in 50 ml of water again and stirred for up to 3 h for hydrolysis of TEOS. The suspension was centrifuged, washed by water and then methanol (each washing was followed by centrifugation). TiO_2 was dried at 120 °C and calcined at 200–500 °C for 1 h. This process can be summarized by the following diagram: mixture of TiO_2, TEOS and methanol → evaporation of methanol → washing by water → hydrolysis by stirring in water → washing by water and methanol → dry at 120 °C → calcination.

The amount of loaded SiO_2 was measured by Kyushu Techno Service Co., using IPC.

2.3. Photocatalytic degradation

The amount of TiO_2 suspended in 25 ml of 5×10^{-5} mol/l solution was 75 mg. The suspension was illuminated by 500 W super-high pressure mercury lamp through a water filter with Pyrex glass windows and a neutral filter (attenuated to 6% intensity for BTMA, 10% for NB and phenol, and 20% for propionic acid). A small amount of sample solution was withdrawn at fixed times and filtered to separate TiO_2 powder, and the filtrate was subjected to the analysis of HPLC (Shimadzu LC-10AD system) for NB, BTMA and phenol, and that of IC (Yokogawa IC7000) for propionic acid, respectively. Degradation rate represented by degraded substrate concentration per minute was calculated for the first 20 min.

2.4. Characterization of photocatalyst

Isoelectric point (IEP) was measured using ζpotential meter PEN KEM Model 501. pH was adjusted by adding small quantity of HCl and NaOH solutions.

3. Results and discussion

Fig. 1 shows the effect of calcination temperature on the nitrobenzene degradation. The activity increases at higher temperature than 300 °C and the optimum was 300 °C. Similar trend was obtained for BTMA in the previous study in which the optimum temperature was 300–400 °C [20]. This temperature dependence may be attributed to the highest adsorbability of TiO_2 sample calcined at 300 °C as reported for Na^+ adsorption [21].

The degradation curves of nitrobenzene on SiO_2/TiO_2 were shown for different hydrolysis times in Fig. 2. It was demonstrated that the rate remained nearly unchanged for 30 min–3 h of hydrolysis. But even in the absence of this hydrolysis procedure the activity was already improved to some extent, suggesting the hydrolysis occurrence during the decantation and/or evaporation of methanol. The activity increased with the initially added TEOS concentration and the optimum value was 0.67 ml TEOS/g TiO_2 (Fig. 3). The amount of SiO_2 loaded to TiO_2 under different conditions was analyzed quantitatively. The results were listed in Table 1 and the activity of the sam-
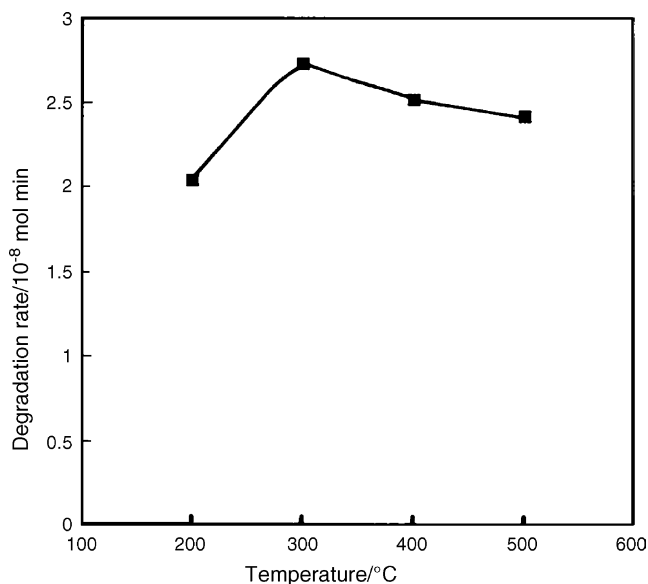

Fig. 1. Effect of calcination temperature on the photocatalytic activity.

ple (degradation rate) was plotted against the amount of SiO_2 in Fig. 4. The optimum amount ranges from 1.5 to 4.8%. The relatively wide range may suggest that the samples contain unbound SiO_2. Scanning electron microscopic observation and FT-IR measurement did not distinguish between bound and unbound SiO_2. The effect of unbound SiO_2 will be discussed later. It can be noted that the preparation method affects the photocatalytic activity. Based on the above results, the standard procedure hereafter for the preparation of SiO_2/TiO_2 is determined to be as mentioned in the experimental section: 0.5 ml TEOS/g TiO_2, 1 h hydrolysis and 300 °C calcination.

Three other substrates, BTMA, phenol and propionic acid, were studied to assess the effect of SiO_2-loading. Table 2 com-
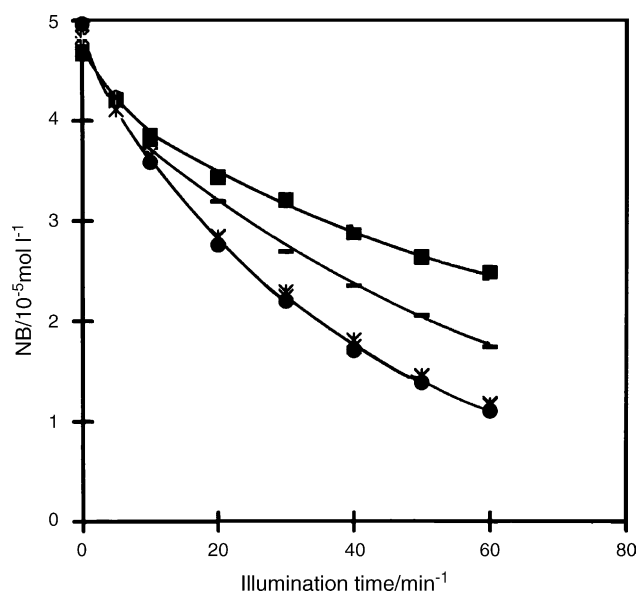

Fig. 2. Degradation of NB on SiO_2/TiO_2 prepared by different hydrolysis times after washing by water and decantation (see Section 2). Hydrolysis time: (■) 0, (*) 30 min, (×) 1 h, (●) 3 h, and (■) TiO_2 (control).
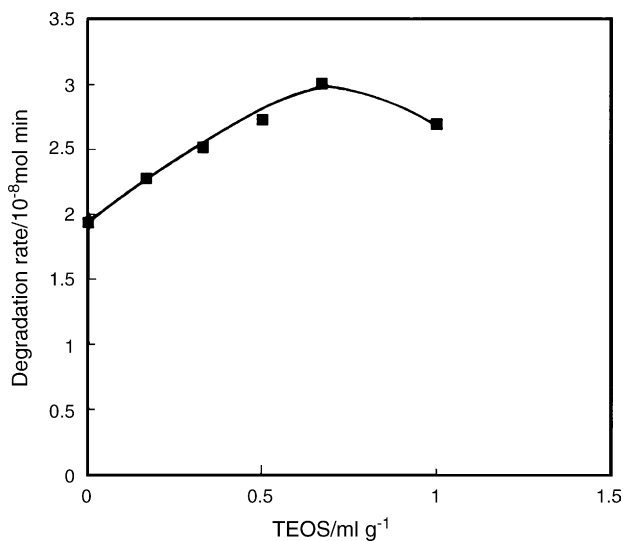
Fig. 3. Initial amount of TEOS vs. photocatalytic activity.

Table 1
Relationship between the amount of loaded SiO_2 and degradation rate

Amount of initially added TEOS (ml g^{-1})	Amount of loaded SiO_2 (%)	Degradation rate (mol min^{-1})
0.17	1.68	2.26
0.33	1.39	2.52
0.5	3.1	2.73
0.67	1.72	3.01
1	4.82	2.7
0.5[a]	7.74	1.42
0.5[b]	2.12	0.5
0.5[c]	1.48	2.26

[a] Without the first washing or hydrolysis (see Section 2).
[b] Without the first washing and with hydrolysis for 1 h.
[c] With the first washing but hydrolysis.

pares the degradation rate of the four compounds measured under the same conditions. The effect of SiO_2-loading was evaluated by the ratio of the degradation rate on SiO_2/TiO_2 per that on bare TiO_2. SiO_2-loading enhanced the degrada-
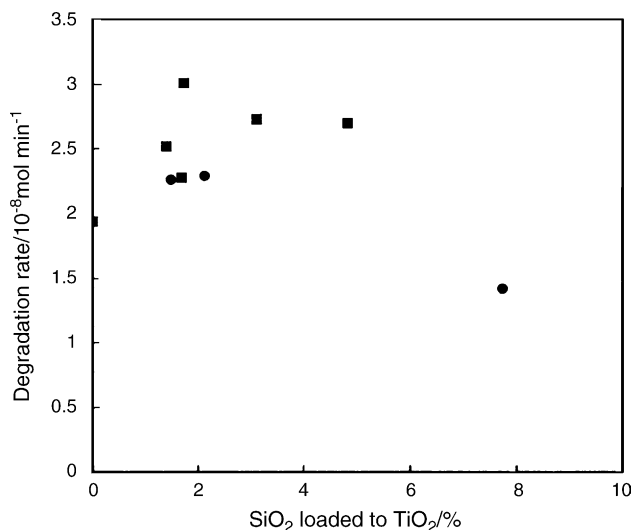
Table 2
Effect of silica-loading on the degradation of different substrates

Substrate	r_0 ($\times 10^{-8}$ mol min^{-1}) (TiO_2)	r ($\times 10^{-8}$ mol min^{-1}) (SiO_2/TiO_2)	r/r_0
BTMA	1.12	2.60	2.32
NB	1.94	2.73	1.41
Phenol	2.14	3.32	1.55
Propionic acid	3.12	3.93	1.26

tion of all these compounds. The highest ratio was observed for BTMA. The significant rate enhancement can be caused by the shift in isoelectric point (IEP) of TiO_2 from 6.0 to 2.8 as a result of SiO_2-loading (0.4%) (Fig. 5), which increases the electrostatic interaction between TiO_2 and BTMA: TiO_2 is negatively charged around pH 6.0 of the BTMA solution, and BTMA is a cationic compound. The large IEP shift suggests also that substantial part of TiO_2 surface is covered by silica, for the IEP of silica is around 2.0–3.0 [22]. One of the present authors reported previously that by controlling the TiO_2 surface charge the photocatalytic activity for the degradation of cationic compound could be increased [23]. Among the studied compounds the smallest rate enhancement was observed for propionic acid. Electrostatic repulsion between negatively charged SiO_2/TiO_2 (pH of the solution is 5.3) and propionate anion may be responsible for the relatively small effect. It is significant from practical viewpoint that SiO_2-loading is effective to different species of pollutants, because their mixture commonly occurs in wastewater.

The effect of SiO_2-loading was also affected by the substrate concentration, as already pointed out [6,10]. At the lower concentration (10^{-5} and 2×10^{-5} mole/l), the effect was larger ($r/r_0 = 1.84$ and 1.86, respectively).

It was reported previously that simple mechanical mixing of TiO_2 and adsorbent promoted the degradation of several aqueous pollutants [17,18]. One of the present authors reported that loading of zeolite to TiO_2 is less effective than the mechanical mixing of the two [24]. Therefore, it is important to confirm
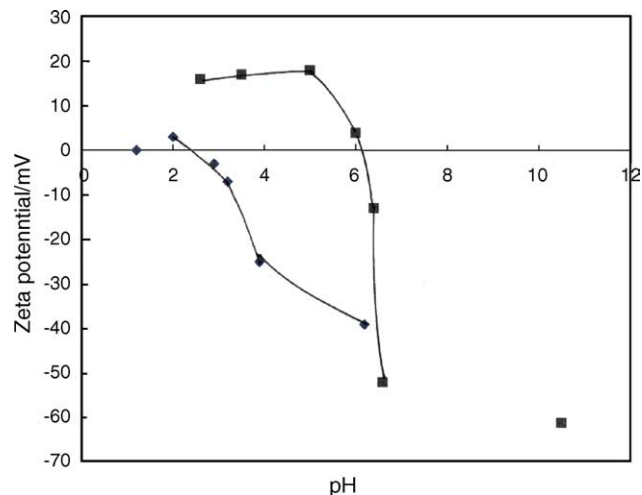

Fig. 4. Photocatalytic activity vs. amount of SiO_2 loaded to TiO_2.
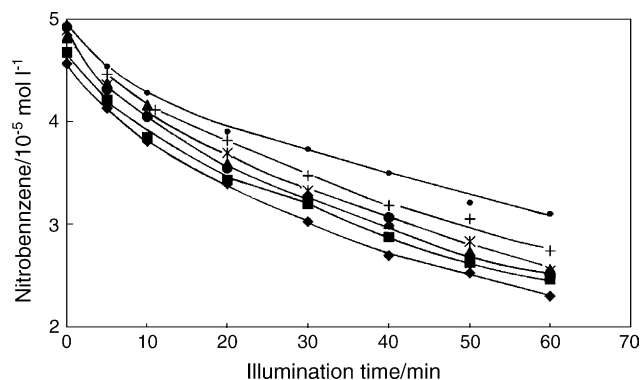

Fig. 5. Variation of zeta potential with pH.

Fig. 6. Mechanical mixing of SiO$_2$ with TiO$_2$: (■) TiO$_2$, (♦) OX-50 0.5%, (▲) OX-50 2%, (+) synthesized SiO$_2$ 10%, (●) synthesized SiO$_2$ 2%, and (●) synthesized SiO$_2$ 2% ground.

the effect of unbound adsorbent (not loaded to TiO$_2$) which may be contained in the present SiO$_2$/TiO$_2$ sample. SiO$_2$ powder was prepared separately in a similar way to SiO$_2$ loaded to TiO$_2$. The mechanical mixing of this SiO$_2$ (0.5 and 2 wt.%) with TiO$_2$ exhibited no effect on the degradation, and 10% SiO$_2$ even retarded the degradation (Fig. 6). The same experiment with commercially obtained silica OX-50 (2 and 0.5%) resulted in no effect. It was thus implicated that loading of silica to TiO$_2$ is significant. To study further the effect of loading, silica (synthesized) and TiO$_2$ were ground in a mortar by which two powder samples might be loaded partly to each other. This modification resulted in even negative effect. It appears that the method of loading is important. Negative effect may be due to the filtering effect by silica to incident light.

It has been established that photocatalytic reaction is initiated by OH radical created on UV illuminated TiO$_2$ surface. For the reaction of adsorbed substrate with OH radical two processes may be proposed: adsorbed substrate moves to the active site of TiO$_2$, and conversely OH radical diffuses to the substrate. The previous report [8,15] that strong adsorption of substrate suppresses the degradation appears to support the first process. However, further study is needed for the clarification of the adsorbent effect mechanism.

4. Conclusion

SiO$_2$-loading to TiO$_2$ accelerated the degradation rate of the different substrates. The highest effect was observed for BTMA (cationic substance). The optimum amount of loaded SiO$_2$ was 1.5–4.8 wt.%. Activity can be affected by loading method. Loaded sample calcined at 300 °C resulted in the best effect. Unbound SiO$_2$ mechanically mixed with TiO$_2$ was not effective at least up to 10 wt.%.

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