In-situ investigations of the photoluminescence properties of SiO2/TiO2 binary and Boron-SiO2/TiO2 ternary oxides prepared by the sol-gel method and their photocatalytic reactivity for the oxidative decomposition of trichloroethylene

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ABSTRACT. Photoluminescence behavior of TiO2, SiO2/TiO2 binary and Boron-SiO2/TiO2 ternary oxides prepared by the sol-gel method was investigated. The differences in their photocatalytic reactivities of TiO2-based photocatalysts were interpreted in terms of the relationship of the difference in their photoluminescence characteristics. The addition of SiO2 into TiO2 matrix induced new photoluminescence sites, which were due to anchored titanium oxide species (i.e., the formation of Ti−O−Si bonds) located on the surface. The photoluminescence was found to be very sensitive to the presence of oxygen. These new photoluminescence completely disappeared by the addition of boron into SiO2/TiO2 binary oxide, since the emitting sites having a Ti−O−Si bond were destroyed and the new sites having B−O−Ti or Si−O−B bonds were constructed on the surface, being in agreement with the results obtained by FT-IR measurements. For all TiO2-based photocatalysts, a significant quenching of photoluminescence was observed by the addition of oxygen. It was found that the photocatalytic reactivity of TiO2-based photocatalysts for the decomposition of trichloroethylene was clearly associated with their relative quenching efficiencies of photoluminescence; photocatalyst showing high quenching efficiency exhibited a high photocatalytic reactivity.

1. INTRODUCTION

TiO2 nano-particles are the best candidate as a photocatalyst having high thermal stability and high activity for the decomposition of various toxic organic materials in aqueous solutions [1-6]. The enhancement of photoreactivity of TiO2 photocatalysts has been a big objective in the research field of photocatalysis. The following factors can be considered to play vital roles in controlling the photocatalytic reactivity of TiO2: particle size, crystal phase, temperature of heat treatment, surface area, surface-bounded species, pH of solution, and the kinds of additives [2, 4, 7-11]. In recent years, the second metal oxide such as SiO2, Al2O3, ZrO2, and WO3 are frequently used as additives to modify the surface or bulk properties of TiO2 photocatalysts [12-16]. Photocatalytic reactions proceed on the surface of TiO2 catalysts, therefore, it is important to know the detailed morphology of the surface active sites which interact with photogenerated electrons and/or holes as well as the reactant molecules.

The measurement of photoluminescence of the photocatalysts is one of the most important and useful ways to elucidate the surface properties related to adsorption, catalysis, and photocatalysis [17]. For example, the photoluminescence spectrum of TiO2 nano-particles is efficiently quenched by the addition of oxygen onto the surface through an increase in the extent of the band bending of TiO2 photocatalyst due to the adsorption of O2− species [18-22]. Thus, it is possible to monitor the changes in the reactivity of the photocatalyst in various atmosphere by measuring the photoluminescence properties of the photocatalysts.

In this work, three kinds of TiO2-based photocatalysts (TiO2, SiO2/TiO2, Boron-SiO2/TiO2) were prepared by the sol-gel method and their characteristics of photoluminescence properties were investigated to elucidate the factors which control the photoactivity of these photocatalysts.

2. EXPERIMENTAL

The conventional sol-gel technique was used to prepare TiO2-based photocatalyst. Titanium ethoxide (TEOT, Aldrich, ~ 20% Ti in excess ethanol) and Tetraethylorthosilicate (TEOS, Aldrich, 98%) were used as TiO2 and SiO2 precursor, respectively. Boric acid (Aldrich, 99.99%) was used as the precursor of boron. Pure TiO2
Table 1. Physicochemical properties of as-prepared TiO₂-based oxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination temperature (K)</th>
<th>Crystal phase</th>
<th>D_{c} (nm)</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>773</td>
<td>Anatase</td>
<td>23.1</td>
<td>45.9</td>
</tr>
<tr>
<td>SiO₂/TiO₂⁴)</td>
<td>1073</td>
<td>Anatase</td>
<td>14.1</td>
<td>189.9</td>
</tr>
<tr>
<td>Boron-SiO₂/TiO₂⁵)</td>
<td>1173</td>
<td>Anatase</td>
<td>14.5</td>
<td>33.5</td>
</tr>
</tbody>
</table>

⁴) Ti/Si = 2.3 (30 at.% of Si), ⁵) Ti/B = 19(5% of Boron) and Ti/Si = 2.3.

The major crystal phase of all TiO₂-based photocatalysts was determined from the X-ray diffraction patterns obtained by using a Rigaku D/MAX-III(3 kW) diffractometer. Surface areas of the prepared Ti-based particles were determined by nitrogen physisorption data at 77 K using a Micrometritics ASAP 2400. FT-IR spectra of the catalysts were obtained by a Bomem MB-100 spectrometer. UV/visible spectra were measured by an UV/visible spectrophotometer (UV-250 1PC, Shimadzu).

Semi-circulation batch reactor of annular shape was used to test the photoreactivity of these TiO₂-based photocatalysts for the decomposition of trichloroethylene (TCE). The photocatalyst used and the initial concentration of TCE were fixed to be 1 g/l and 37 ppm, respectively. The reaction solution suspending photocatalyst particles and solving reactant molecules was irradiated by ultraviolet light (15 W, black light). The change in the TCE concentration was monitored by Cl⁻ electrode (Orion, model 96-17B) as a function of reaction time.

The photoluminescence spectra of these photocatalysts were measured at 77 K using a Shimadzu RF-5000 spectrofluorophotometer. A quartz cell with a window and furnace section connected to a vacuum system (10⁻⁶ Torr) was used for the in situ measurements of the photoluminescence spectra before and after various thermal pretreatments. Prior to spectroscopic measurements, each photocatalyst sample (TiO₂, SiO₂/TiO₂, and 5% Boron-SiO₂/TiO₂) was evacuated at 573 K for 3 hrs then calcined at 473 K with oxygen of 200 Torr for 2 hrs followed by the evacuation at the same temperature.

Figure 1. XRD patterns of TiO₂ (calcined at 773 K), SiO₂/TiO₂ (calcined at 1073 K), and Boron-SiO₂/TiO₂ (calcined at 1173 K) powder prepared by the sol-gel method.

3. RESULTS AND DISCUSSION

The photocatalytic reactivity of these binary and ternary oxide photocatalysts is strongly dependent on the crystal phase of the moiety of TiO₂. Figure 1 shows the XRD patterns of the TiO₂-based photocatalysts prepared by the sol-gel method. All samples exhibit a pure anatase phase even after the calcination of SiO₂/TiO₂ binary and Boron-SiO₂/TiO₂ at 1073 and 1173 K, respectively. The physicochemical properties of these TiO₂-based photocatalysts are summarized in Table 1. It should be noted that the crystallite sizes of TiO₂ which were calculated by the Scherrer equation at 2θ = 23.3° increase in the order of SiO₂/TiO₂ (14.1 nm) < Boron-SiO₂/TiO₂ (14.5 nm) < TiO₂ (23.1 nm).

For the SiO₂/TiO₂ and Boron-SiO₂/TiO₂ catalysts, SiO₂ moiety is embedded into the TiO₂ moiety to form SiO₂/TiO₂ binary oxide and may exist as a segregated amorphous phase of SiO₂ which prevents TiO₂ moiety to form large crystals. In such cases, it is expected
that the Ti–O–Si bonds are formed in some part of the SiO2/TiO2 matrix. Figure 2 shows the FT-IR spectra of TiO2, SiO2, SiO2/TiO2, and Boron-SiO2/TiO2 catalysts as well as SiO2 as a reference. The peak observed at around 1095 cm⁻¹ corresponds to the asymmetric vibration of a Si–O–Si bond [27, 28]. The peak at around 940 cm⁻¹ attributed to the linkage of the Ti–O–Si bond are observed with both SiO2/TiO2 binary and Boron-SiO2/TiO2 ternary oxides, indicating that the Ti–O–Si bonds are formed by mixing SiO2 with TiO2 to form binary oxides [27]. An intrinsic peak at 1393 cm⁻¹ can be seen only with Boron-SiO2/TiO2 ternary oxide. This characteristic peak can be associated with the formation of tri-coordinated boron in the SiO2/TiO2 binary oxide frameworks [29, 30]. These results clearly suggest that Si–O–Ti bonds are successfully produced by mixing TiO2 phase and amorphous SiO2 phase, it resulting in the prevention of the formation of large TiO2 crystals, while boron exists in a tri-coordinated state in the SiO2/TiO2 binary oxides.

Figure 3 shows the UV/Vis reflectance spectra of TiO2, SiO2/TiO2, Boron-SiO2/TiO2 catalysts. TiO2 exhibits a typical absorption band due to the bandgap transition of TiO2 having an anatase phase (λ < 390 nm), while the absorption spectra of SiO2/TiO2 binary and Boron-SiO2/TiO2 ternary oxides were found to shift toward shorter wavelength regions. Since the absorption bands were found to shift toward shorter wavelength regions with a decrease in the TiO2 crystal size of the catalysts (TiO2(23.1 nm) > Boron-SiO2/TiO2 (14.5 nm) > SiO2/TiO2(14.1 nm)), such a spectral shift toward shorter wavelength can be attributed to the size quantization effect due to the presence of TiO2 particles of particularly small size of TiO2 moiety in the SiO2/TiO2 binary oxide.

As shown in Figure 4, TiO2-based photocatalysts shows the photoluminescence spectra at around 450-550 nm upon the excitation when excited with light having energies larger than the bandgap energy of the catalyst. These observed photoluminescence spectra can be attributed to the radiative decay processes from the photoformed electron and hole pair states at the specific surface sites. The difference in the photoluminescence yields of these catalysts can be ascribed to the differences in numbers of the surface sites responsible for the photoluminescence or the different efficiency in the rates of the thermal deactivation process of the photoformed electron and hole pair states. It is notable that the SiO2/TiO2 binary oxide calcined at 1073 K shows a new photoluminescence peak at around 400-480 nm. This peak, however, could not be observed with the Boron-SiO2/TiO2 ternary oxide or pure TiO2 powder. In general, the photoluminescence peak with bulk TiO2 is observed at around 450-550 nm [20, 23]. The peak at around 400-480 nm is not due to bulk TiO2 but highly dispersed TiO2 moiety anchored onto the SiO2 surfaces or into zeolite framework [24-26].
Photocatalysis is a surface phenomenon initiated by the irradiation of UV light of higher energy than the bandgap of the photocatalyst used. It can be seen that the surface properties involving the nature of active sites and their numbers play a key role in determining the photocatalytic reactivity of the catalysts. It is, therefore, important to characterize the surface active sites and their reactivity for various photocatalysts prepared by different preparation methods. The quenching of the photoluminescence of the catalyst can be related to the changes in the surface properties which result from the interaction between the surface and the electron acceptor molecules. In the present work, therefore, the relative reactivity of photocatalysts toward oxygen molecule was estimated by the quenching degree of the photoluminescence by the addition of O₂.

For all TiO₂-based photocatalysts, the addition of 20 Torr of O₂ led to a considerable quenching of the photoluminescence. As shown in Figure 5, in the presence of 20 Torr of O₂, the intensity of the photoluminescence decreased to 89% of its original intensity for SiO₂/TiO₂, 37% for TiO₂ and 26% for Boron-SiO₂/TiO₂, respectively. It has been reported that the addition of O₂ at 298 K onto TiO₂ photocatalyst leads to the formation of O₂⁻ anion radicals stabilized on Ti⁴⁺ sites. The formation of such negatively charged adducts (O₂⁻) results in an increase in the surface band bending of the TiO₂, leading to a quenching of the photoluminescence through a suppression of the efficiency of the radiative recombination of the photoformed electrons and holes at the surface [20]. The photoluminescence can be easily quenched by the addition of O₂ in the case of TiO₂-based catalysts with high photocatalytic reactivity since an efficient formation of surface O₂⁻ anion radicals which play a important role in oxidation reaction can be expected. In line with these arguments, the reactivity of the photocatalysts toward oxygen was found to increase in the order of SiO₂/TiO₂, TiO₂ and Boron-SiO₂/TiO₂. It is notable that the peak at around 400–480 nm, attributed to the photoluminescence from TiO₂ moiety having Ti–O–Si bonds is quenched completely by the addition of oxygen. These results clearly show that the peak at around 400–480 nm is attributed to the photoluminescence from the TiO₂ moiety having Ti–O–Si bonds and these TiO₂ moieties play an important role as the active sites leading to the formation of O₂⁻ anion radicals. On the other hand, with the Boron-SiO₂/TiO₂ ternary oxides, the photoluminescence peak at around 400–480 nm could not be observed. These results showed a good agreement with that the TiO₂ moieties having Ti–O–Si bonds are not formed on the Boron-SiO₂/TiO₂ oxides but the TiO₂ moieties having Ti–O–B or Si–O–B bonds are formed at the surface. However, the FT-IR peak which could be observed at around 940 cm⁻¹, as shown in Figure 2, suggest that the Ti–O–Si bonds still remain in the bulk of the Boron-SiO₂/TiO₂ matrix.

It has been reported that O₂⁻ as well as OH radicals formed on the TiO₂ surface under UV irradiation act as important oxidants in the photodegradation of organic compounds in aqueous solution. As mentioned above, the quenching of the photoluminescence in the presence of O₂ are closely related to the formation of the
Figure 6. Relationship between the quenching efficiency and the intrinsic photoactivity (TCE decomposition) of TiO$_2$, SiO$_2$/TiO$_2$, and Boron-SiO$_2$/TiO$_2$.

O$_2^-$ anion radicals on the TiO$_2$ surface. Figure 6 shows the relationship between the quenching efficiency of photoluminescence and the photocatalytic reactivity of TiO$_2$-based photocatalysts for the decomposition of TCE. The quenching efficiency (QE) is defined as follows:

\[ \text{QE}(/\%) = 100 \times \frac{\text{PL}_{\text{vacuum}} - \text{PL}_{\text{O}_2}}{\text{PL}_{\text{vacuum}}} \]

where \( \text{PL}_{\text{vacuum}} \) is the intensity of photoluminescence under vacuum, and \( \text{PL}_{\text{O}_2} \) is the intensity of photoluminescence in the presence of 20 Torr of O$_2$.

It is clear that there is a close relationship between quenching efficiency and photocatalytic activity, i.e., the higher the quenching efficiency, the higher is the photocatalytic activity. Here, the effect of the crystal structure on the photocatalytic activity can be excluded since all of the prepared TiO$_2$-based photocatalysts have an anatase phase structure. Therefore, it can be considered that O$_2^-$ anion radicals are efficiently formed on the TiO$_2$-based photocatalyst which exhibits the high quenching efficiency, leading to the high decomposition rate of TCE through the efficient reaction of O$_2^-$ anion radicals with TCE. Thus, it is demonstrated that the photoluminescence investigations of the photocatalysts can be applied to estimate the activity of the photocatalysts for the various oxidative reactions, especially by monitoring the quenching efficiency of the photoluminescence in the presence of gaseous oxygen [17].

4. CONCLUSIONS

Three kinds of different photocatalysts such as TiO$_2$, SiO$_2$/TiO$_2$ binary and Boron-SiO$_2$/TiO$_2$ ternary oxides were investigated and applied to interpret the difference in the photocatalytic reactivity of these three types of catalysts for the decomposition of TCE.

For all prepared TiO$_2$-based photocatalysts, a considerable quenching of photoluminescence was observed in the presence of oxygen, which leads to an efficient electron scavenging to form O$_2^-$ anion radicals on the surfaces. It was found that the photocatalytic reactivity of TiO$_2$-based photocatalysts for the decomposition of trichloroethylene is related to their relative quenching efficiency of photoluminescence, i.e., photocatalyst showing larger quenching efficiency in photoluminescence exhibit higher photocatalytic reactivity.

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REFERENCES