

Adsorption and photocatalytic degradation of 1,4-dioxane on TiO₂

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Abstract

1,4-Dioxane in hexane as a solvent was adsorbed on TiO₂ due to an electrostatic interaction. The porous TiO₂ pellets (SG) prepared by sol–gel method were superior adsorbent to ST-B21 and Degussa P-25. Effects of firing temperature of the pellets and the initial concentrations of 1,4-dioxane on the adsorption percents were examined. Photocatalytic degradation of aqueous 1,4-dioxane gave 1,2-ethanediol diformate and formic acid as intermediates. Analysis of total organic carbon indicated that 1,4-dioxane was mineralized effectively in the following order: P-25 > ST-B21 > SG. The photocatalytic degradation of 1,4-dioxane adsorbed on the TiO₂ pellets in air showed that ST-B21 had a higher activity than SG. These facts indicate that SG pellet acts as a good adsorbent because of its high specific surface area but the internal region of the pores is not illuminated and acts only as a support.

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1. Introduction

1,4-Dioxane has been widely used as an industrial solvent and as a stabilizer for chlorinated solvents. Because it is soluble to water, nonvolatile and recalcitrant to microbial degradation, it can migrate swiftly through aquifers and cause widespread contamination in both surface and groundwater [1]. It is a suspected carcinogen and classified as a priority pollutant by the US Environmental Protection Agency.

Several studies have examined the degradation of 1,4-dioxane by using strong oxidants, OH radicals. Treatment processes using the OH radicals are often referred to as advanced oxidation processes (AOPs) [2]. Kleka and Gonsior reported that 1,4-dioxane was rapidly oxidized by a combination of hydrogen peroxide and ferrous iron but the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane [3]. Adams et al. described that ozone in combination with hydrogen peroxide effectively oxidized 1,4-dioxane to more readily biodegradable products that could be treated using conventional biological treatment [4]. Stefan and Bolton studied the degradation of 1,4-dioxane in UV/H₂O₂ process and

proposed the degradation mechanism in order to account for the observed intermediates [5]. Beckett and Hua described that addition of Fe(II) improved the decomposition rate of 1,4-dioxane and mineralization efficiency under ultrasonic irradiation [6].

The use of TiO₂ photocatalysts for environmental cleanup has been of great interest since TiO₂ is stable, harmless, inexpensive, and potentially can be activated by solar energy [7–9]. Especially, the TiO₂ has an advantage over the AOPs because it can be easily reused. Much work has been carried out from the viewpoint of applications for water and air purification [10]. Several researchers have investigated photocatalytic degradation of 1,4-dioxane in water and clarified reaction pathway [11,12]. They have found that 1,2-ethanediol diformate is a main intermediate. Recently, Nakajima et al. investigated synergetic effects of combining sonolysis and photocatalysis for the degradation of 1,4-dioxane and successfully improved the mineralization rate by increasing adsorption capability of TiO₂ to 1,2-ethanediol diformate by the surface treatment with HF [13].

We have investigated the photocatalytic degradation of volatile chlorinated organic compounds by using porous TiO₂ pellets prepared by sol–gel method [14]. We found in the photocatalytic degradation of 1,1,1-trichloroethane in gas phase that 1,4-dioxane, which was contained as a stabilizer in the gas cylinder, adsorbed on porous TiO₂ pellets and was photodegraded to carbon dioxide. This finding leads us to utilize its adsorption

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capability to remove 1,4-dioxane in liquid phase, because this compound has been concerned as a hazardous waste in water rather than in gas phase. In this paper, we examined the adsorption property of the porous TiO₂ pellets for 1,4-dioxane and the photocatalytic activity was compared with that of commercial pellets or powders.

2. Experimental

2.1. Reagent

Porous TiO₂ pellets (SG) were prepared by sol–gel techniques [15]. A mixture of 1.3 ml HNO₃, 180 ml H₂O and 15 ml Ti(OC₃H₇)₄ was peptized at room temperature for 3 days to form a highly dispersed colloidal solution. This sol was then dialyzed in a molecularly porous dialysis tube (molecular weight cut-off: 3500) for 3 days until approximately pH 4 was obtained. The sol was concentrated in a rotary evaporator and dried at 40 °C for 2 days. The obtained gel was fired at 200 °C and then cut into small pellets (ca. 1 mm in diameter). The specific surface area by BET analysis and the mean pore radius obtained by using Kelvin equation [16] were estimated to be 188.5 m² g⁻¹ and 2.6 nm, respectively. Specific surface areas were determined by nitrogen adsorption at 77 K using a Micromeritics apparatus (Gemini 2375). Commercially available TiO₂ pellets, ST-B21 (ceramics covered with TiO₂ (23 wt.%), diameter: 0.3–0.7 mm, specific surface area: 70 m² g⁻¹, Ishihara Sangyo Co.) and Degussa P-25 powders (specific surface area: 50 m² g⁻¹, Japan Aerogel) were also employed.

1,2-Ethanediol diformate (EDDF) was synthesized as reported in the literature [5,17]. Other reagents were of the guaranteed reagent grade and used without further purification. Laboratory grade water was prepared with a Milli-Q water system.

2.2. Measurement of adsorption percent

Adsorption of 1,4-dioxane on the TiO₂ was carried out by adding the TiO₂ to 1.5 ml of 1,4-dioxane solutions under stirring for 1 min and being left in the dark for a certain time. Then, the adsorption percent was calculated by measuring the concentration of 1,4-dioxane in the solution by gas-chromatograph (Shimadzu GC-14B) equipped with DB 624 column.

2.3. Photocatalytic degradation of 1,4-dioxane in aqueous solutions

Fig. 1(A) shows a circulation system consisting of a spiral Pyrex tubing (inner diameter: 5.4 mm, outer diameter: 8.0 mm, total volume: 14.0 cm³) which was packed with 6.65 g of the TiO₂ pellets, SG or ST-B21. Both ends of the TiO₂ bed in the tubing were capped with glass wool. Three 4 W fluorescence black lights were located in parallel, one of them was at a center of the annulus of the tubing and others at a distance of 4.0 cm from it. Two bent Pyrex tubings connected with flexible Tygon tubing through a peristaltic pump were used for recirculating 500 ml of aqueous solutions containing 2×10^{-4} mol dm⁻³ of

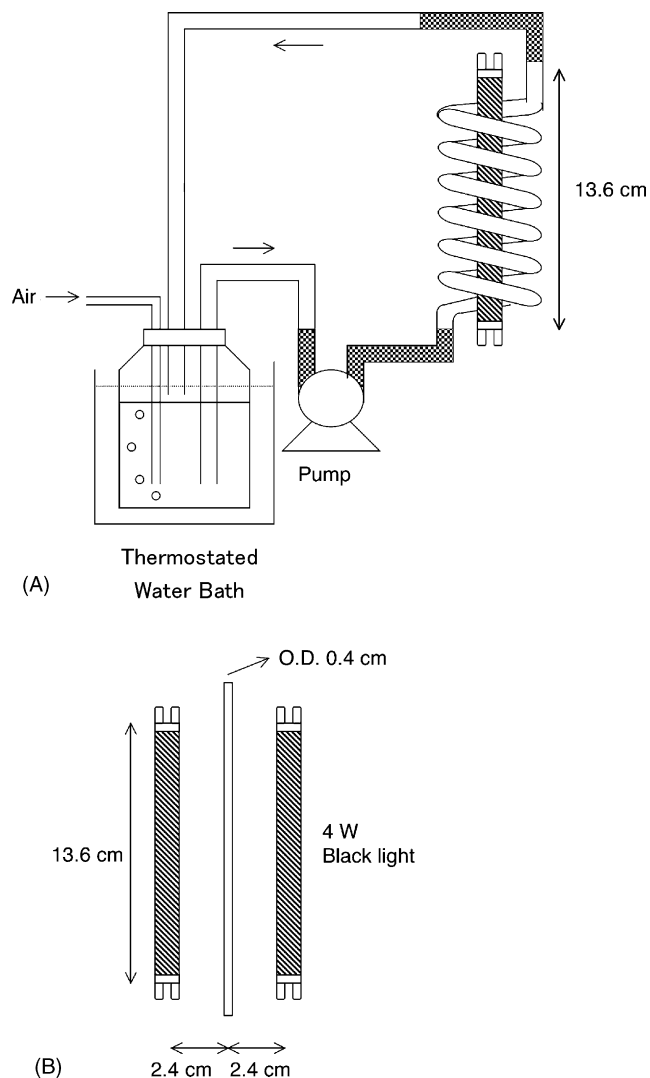


Fig. 1. Schematic illustration of the experimental apparatus for the photocatalytic degradation of 1,4-dioxane in water (A) and adsorbed on the TiO₂ pellets in air (B).

1,4-dioxane at 30 °C under the flowrate of 35 ml min⁻¹. The solution was purged with air throughout experiments in order to keep the oxygen concentration constant. Aliquot samples were withdrawn at appropriate times and analyzed by using GC, ion-chromatograph (Shimadzu PIA-1000) and total organic carbon (TOC) analyzer (Shimadzu 5000A). The photon flux entering into the spiral tubing was estimated to be 1.03×10^{-6} einstein s⁻¹ by potassium tris(oxalato)ferrate(III) chemical actinometer [18]. For comparison, the aqueous solution of 1,4-dioxane was suspended with P-25 and circulated through the system as in Fig. 1(A). Aliquot samples were taken and centrifuged before analyses.

2.4. Photocatalytic degradation of 1,4-dioxane adsorbed on the TiO₂ pellets

The TiO₂ pellets, SG or ST-B21, of 0.25 g were put into 1.5 ml of hexane containing 1.17×10^{-2} mol dm⁻³ of 1,4-dioxane under stirring. The adsorption percent was determined by ana-

lyzing the concentration of 1,4-dioxane in the solution. After filtration, the TiO₂ pellets adsorbing 1,4-dioxane were dried in the dark under flowing air, packed into a Pyrex tubing (inner diameter: 2.4 mm, outer diameter: 4.0 mm, length of the TiO₂ bed of 4.0 cm) and then illuminated with two 4 W fluorescence black lights as shown in Fig. 1(B). The photon flux entering into the Pyrex tubing was estimated to be 2.49×10^{-8} einstein s⁻¹ by potassium tris(oxalato)ferrate(III) chemical actinometer [18]. The TiO₂ pellets exposed to light for 2, 5, 15, 30 or 45 min were immersed into water and concentrations of 1,4-dioxane and formate dissolved were analyzed by using the GC and the ion-chromatograph, respectively.

3. Results and discussion

3.1. Effect of solvents

Adsorption percent of 1,4-dioxane on porous SG pellets was measured in various solvents such as water (dielectric constant [19]: $\epsilon = 78.3$), acetonitrile ($\epsilon = 37.5$), methanol ($\epsilon = 32.7$), ethyl acetate ($\epsilon = 6.02$) and hexane ($\epsilon = 1.88$) and listed in Table 1. The percent was highest with hexane (95.1%) and decreased as the dielectric constant increased except for with methanol. This fact indicates that 1,4-dioxane adsorbed on the TiO₂ due to an electrostatic interaction. It might be between a lone pair on the oxygen atom of 1,4-dioxane and Ti. In fact, we examined the adsorption of methanol (1.97×10^{-3} mol dm⁻³) and ethanol (1.37×10^{-3} mol dm⁻³) on the TiO₂ in hexane and obtained the adsorption percent of 97.1 and 96.0%, respectively. This finding can also explain the low adsorption percent (0.40%) observed with methanol as a solvent although the dielectric constant of methanol is not so different from that of acetonitrile. In this case, methanol competes with 1,4-dioxane to adsorb on the TiO₂.

Fig. 2 shows an effect of time on the adsorption percent, indicating that 15 min was enough. The adsorption percent on 0.5 g of SG and 0.2 g of P-25 was estimated to be 96.7 ± 0.1 and $72.9 \pm 1.0\%$, respectively. Suspension of 0.3 g of the P-25 into hexane became slurry which was not capable of filtering. Fig. 3 depicts an effect of the weight of TiO₂, SG, ST-B21 or P-25, on the adsorption percent which was calculated after leaving in the dark for 30 min. The adsorption on the porous SG pellets was superior to ST-B21 and P-25 under the same conditions.

3.2. Effect of firing temperature of the SG pellets and concentrations of 1,4-dioxane

Fig. 4 indicates that adsorption percent decreased with an increase in the firing temperature of SG pellets. This finding is

Table 1
Adsorption percent of 1,4-dioxane on the porous TiO₂ pellets in various solvents

	H ₂ O	CH ₃ CN	CH ₃ OH	CH ₃ COOC ₂ H ₅	C ₆ H ₁₄
Adsorption (%)	2.33	4.58	0.40	11.2	95.1

Conditions: The porous TiO₂ pellets (1 g) were added to 1.5 ml of solvents containing 2.34×10^{-4} mol dm⁻³ of 1,4-dioxane.

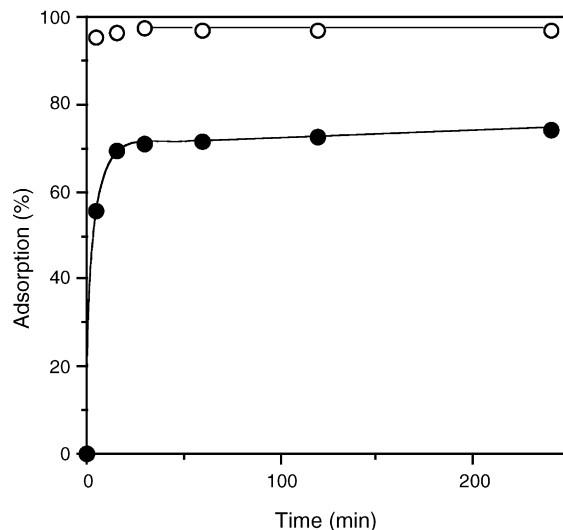


Fig. 2. Effect of time on adsorption percent using 0.5 g of SG pellets (○) or 0.2 g of P-25 (●). The concentration of 1,4-dioxane in hexane was 2.34×10^{-4} mol dm⁻³.

attributable to the decrease of the specific surface area of the pellets with the firing temperature.

Effect of concentration of 1,4-dioxane on the adsorption percent for 0.2 g of SG pellets was examined in the region of 2.34×10^{-4} to 1.17 mol dm⁻³. As shown in Fig. 5(A), the adsorption percent maintained to be $88.0 \pm 2.2\%$ under the 1,4-dioxane concentration below 1.17×10^{-2} mol dm⁻³ and thus, the 1,4-dioxane molecules adsorbed on the pellets increased linearly with the concentration. On the other hand, in the concentration more than 2.34×10^{-2} mol dm⁻³ as shown in Fig. 5(B), the adsorption percent decreased drastically. However, even at the 1.17 mol dm⁻³, the adsorption was not saturated and 9.11×10^{-4} mol of 1,4-dioxane was calculated to adsorb on 1 g of the pellets. The adsorption geometry of 1,4-dioxane on metals

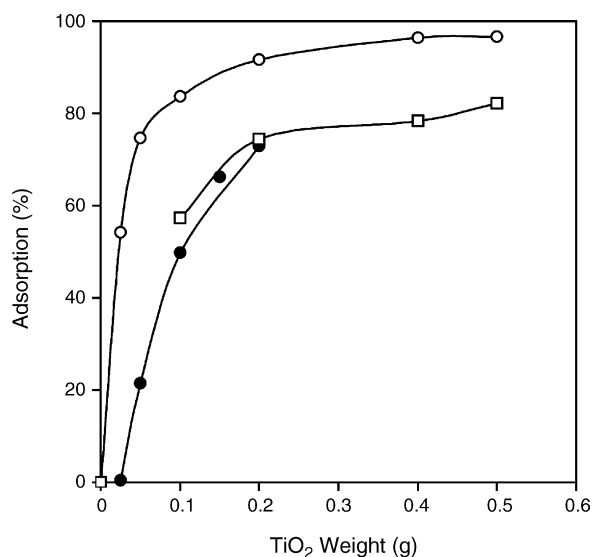


Fig. 3. Effect of weight of SG (○), ST-B21 (□) or P-25 (●) on adsorption percent of 1,4-dioxane. The concentration of 1,4-dioxane in hexane was 2.34×10^{-4} mol dm⁻³.

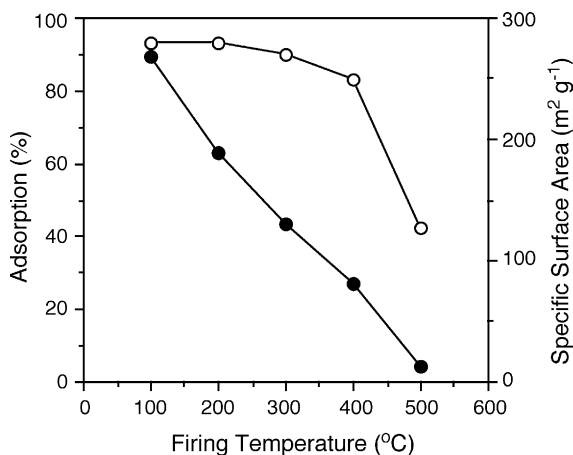


Fig. 4. Effect of firing temperature on adsorption percent (○) and specific surface area of SG pellets (●). Adsorption percent was obtained by placing 0.2 g of the pellets in hexane containing 2.34×10^{-4} mol dm⁻³ of 1,4-dioxane.

such as Cu and Pd has been studied [20,21]. A boat conformation allowing the lone pairs on both oxygen atoms to interact with the metal surface and the chair-form geometry with the ring approximately parallel to the surface were described. We estimated the distance between two oxygen atoms to be 2.829 Å by a theoretical analysis based on density functional theory using B3LYP/6-31G* method [22]. Since the specific surface area of the pellets fired at 200 °C was 188.5 m² g⁻¹, it can be deduced that ca. 5×10^{-3} mol of 1,4-dioxane adsorb on the pellets. Thus, it is reasonable that the adsorption was not saturated even at the concentration of 1.17 mol dm⁻³. Fig. 5(C) indicates that adsorption data in Fig. 5(A and B) fit well with the Langmuir isotherm where Q_{ad} is the specific adsorbed quantity of 1,4-dioxane and C_{eq} is the concentration, both at equilibrium.

3.3. Photocatalytic degradation of 1,4-dioxane in water

The preceding section suggests that the SG pellets is a good adsorbent for 1,4-dioxane. On the other hand, photocatalytic degradation of 1,4-dioxane on TiO₂ in water has been reported and EDDF was observed as the main intermediate [11,12]. Most of the studies employed TiO₂ powder which required a filtration process after mineralizing 1,4-dioxane. The recirculating system of aqueous 1,4-dioxane through a packed bed reactor with TiO₂ pellets is promising since this reactor is free from filtration. We performed the experiments using a closed circulation system as shown in Fig. 1(A) where the spiral tubing was packed with 6.65 g of SG or ST-B21 pellets. For comparison, aqueous 1,4-dioxane solutions suspended with 0.2 wt.% of P-25 was circulated at the flowrate of 500 ml min⁻¹. Fig. 6 indicated that the degradation of 1,4-dioxane accompanied with the formation of HCOO⁻ and EDDF. The amounts of EDDF were plotted as the GC peak area. The maximum concentration of EDDF was roughly estimated to be 1.9×10^{-5} , 4.0×10^{-5} or 1.53×10^{-4} mol dm⁻³ for SG, ST-B21 or P-25, respectively. It is noted that the concentration of EDDF for P-25 was higher by one order of magnitude than others. 1,4-Dioxane was degraded most effectively on P-25 to EDDF which decreased after most

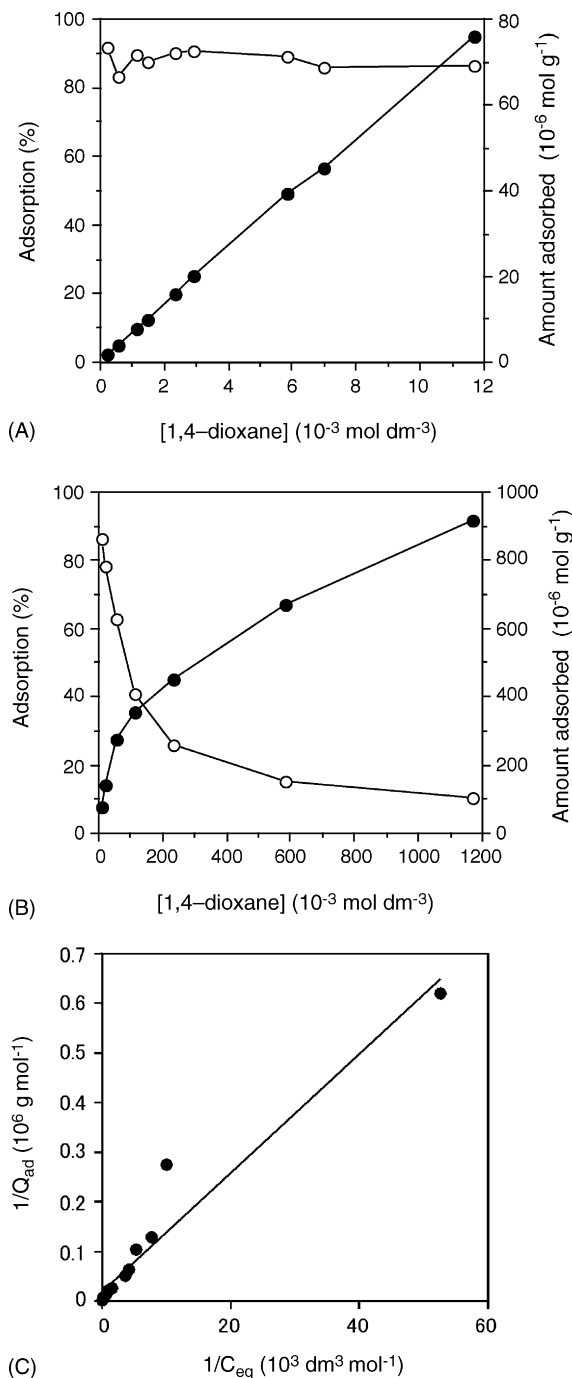


Fig. 5. Dependence of adsorption percent (○) and amount of 1,4-dioxane adsorbed on the pellets (●) on the initial concentration of 1,4-dioxane up to 1.17×10^{-2} mol dm⁻³ (A) and in the range of 2.34×10^{-2} to 11.7 mol dm⁻³ (B). Plots (C) represent the Langmuir adsorption isotherm.

of 1,4-dioxane was degraded. Hill et al. reported that EDDF was accumulated and degraded slowly on P-25 during the degradation of 1,4-dioxane [12]. At the irradiation of 5 h, 92.5% of the initial TOC decreased on P-25 as shown in Fig. 7. Stefan and Bolton described that formic acid was produced from the degradation of EDDF with OH radicals in the UV/H₂O₂ system [5]. As shown in Fig. 6, the maximum concentration of formate was as much as 1.13×10^{-4} mol dm⁻³ on ST-B21, whereas that on SG

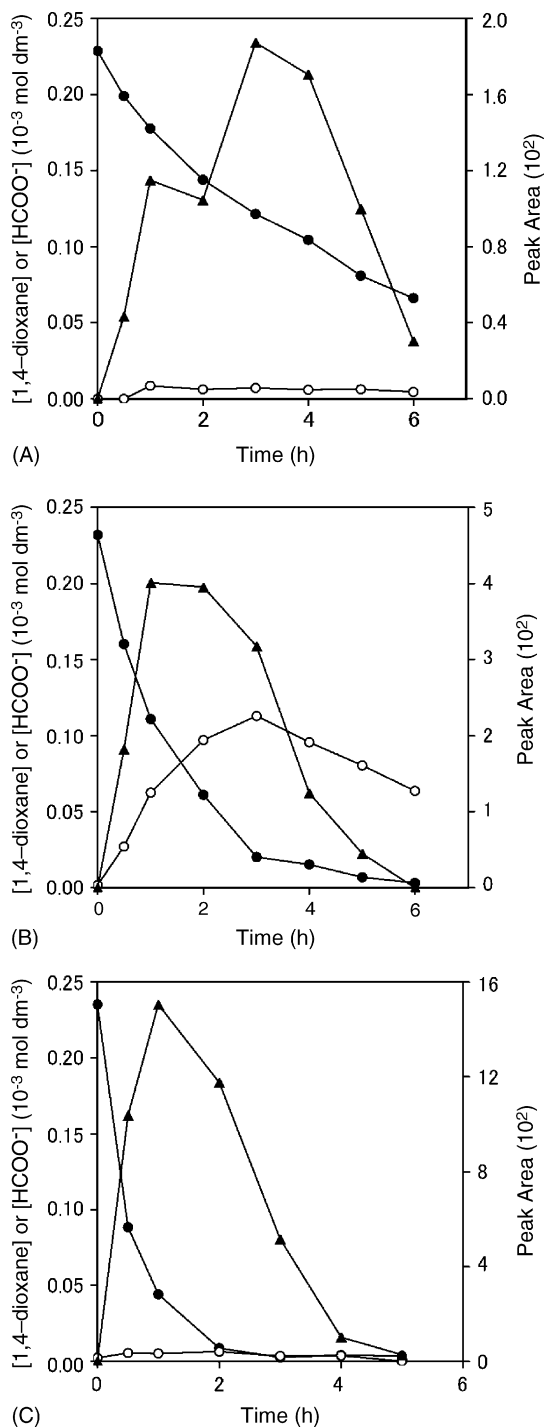


Fig. 6. Concentration change of 1,4-dioxane (●), EDDF (▲) and formate ion (○) in the photocatalytic degradation of 1,4-dioxane in water. (A) SG, (B) ST-B21 and (C) P-25. The data of EDDF are indicated by peak area of GC.

or P-25 was 8.62×10^{-6} or $6.23 \times 10^{-6} \text{ mol dm}^{-3}$, respectively. The photocatalytic activity of TiO_2 for the degradation and mineralization of 1,4-dioxane is in following order: P-25 > ST-B21 > SG although the reaction condition for P-25 was different. The SG has the lowest activity in spite of the highest specific surface area among them. This may suggest that the surface area exposed to illumination of SG is smaller than ST-B21. Thus, the

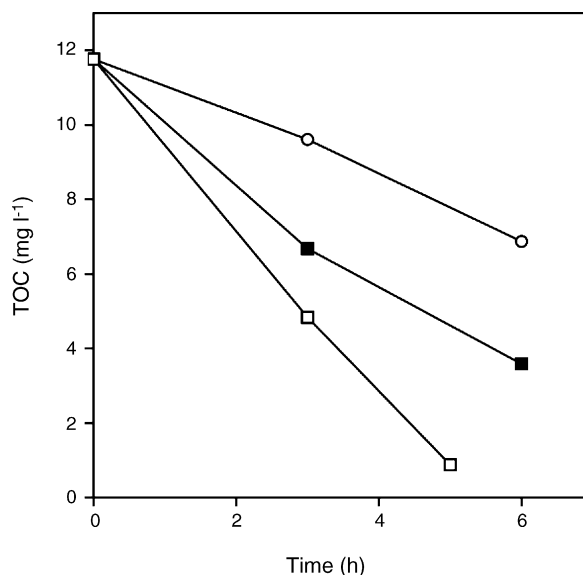


Fig. 7. Variations in TOC vs. the irradiation time using SG (○), ST-B21 (■) or P-25 (□).

internal region of the pores in SG is not illuminated and is not acting as a catalyst but as a support. We have reported in the previous study that the SG turned the color to brown during the photocatalytic degradation of trichloroethylene in water [23]. It was likely that trichloroethylene was photodegraded to form intermediates such as aldehydes or carboxylic acids which did not easily escape out of the pores. This fact also supports that light is not reached at the internal region of the pores.

3.4. Photocatalytic degradation of 1,4-dioxane adsorbed on the TiO_2 pellets in air

We performed the experiments to degrade 1,4-dioxane adsorbed on the pellets in air. Before the experiments, we confirmed that the adsorbed 1,4-dioxane was recovered into water when the TiO_2 pellets adsorbing it were placed into water.

The TiO_2 pellets (0.250 g) were put into 1.5 ml of hexane containing $1.17 \times 10^{-2} \text{ mol dm}^{-3}$ of 1,4-dioxane (17.6 μmol). Analyses of the filtrate indicated that the adsorption percent of 1,4-dioxane was calculated to be 87.6% on SG and 59.0% on ST-B21. The TiO_2 pellets were dried in the dark for 1 h under flowing air and then, 0.16 g of them were packed into a reactor as shown in Fig. 1(B). After the TiO_2 pellets were exposed to the light for a certain time, they were immersed into water to dissolve the 1,4-dioxane and hydrophilic products. Ion chromatography revealed the formation of HCOO^- . No other peak except for 1,4-dioxane was appeared by gas chromatography. The amounts of 1,4-dioxane and formate dissolved from the pellets into water are shown in Fig. 8. The former dissolved from ST-B21 into water at $t=0$ was lower than that from SG because of the lower adsorption percent of ST-B21. Thus, the SG can adsorb more 1,4-dioxane than ST-B21. However, 1,4-dioxane adsorbed on ST-B21 was degraded faster than SG: at the irradiation of 15 min, $4.65 \times 10^{-6} \text{ mol}$ of 1,4-dioxane was degraded on SG, whereas $5.99 \times 10^{-6} \text{ mol}$ on ST-B21. Photo-

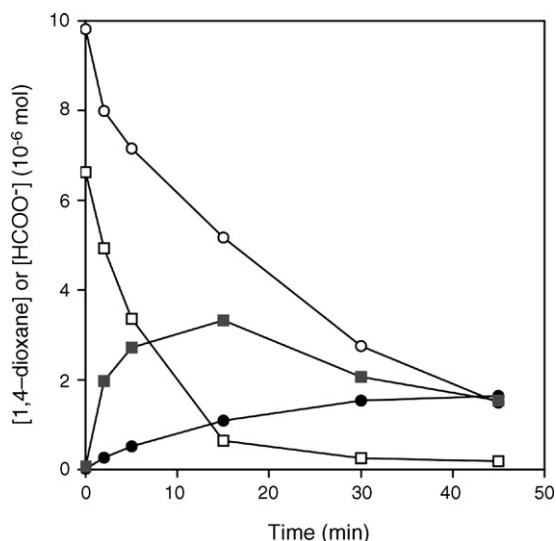


Fig. 8. Variations in the amount of 1,4-dioxane (○) SG, (□) ST-B21 and formate ion (●) SG, (■) ST-B21 which were dissolved from the TiO₂ pellets into water after photodegradation experiments.

catalytic activity for the degradation of the adsorbed 1,4-dioxane on SG is lower than that on ST-B21, which is the similar behavior as observed in water. It is worthy to note that EDDF was not detected as intermediates. This might indicate that EDDF is not formed, which means that the degradation mechanism is different from that in water, or is degraded promptly to formate in the photocatalytic degradation of 1,4-dioxane adsorbed on TiO₂.

4. Conclusions

The TiO₂ adsorbed 1,4-dioxane in hexane due to the electrostatic interaction. The porous TiO₂ pellets prepared by sol-gel techniques act as a superior adsorbent to P-25 and ST-B21. However, the photocatalytic activity of the porous TiO₂ pellets is not good as ST-B21, indicating that the internal region of the pores is not illuminated and is not acting as a catalyst but as a support.

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