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Adsorption and Photocatalytic Decomposition of Volatile Organic Compounds on Photocatalyst of TiO_2—Silica Beads

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Abstract. Photocatalyst of TiO_2 coated on silica beads was prepared, and the adsorption isotherms and kinetics of photocatalytic decomposition of acetone and acetaldehyde on the photocatalyst were studied at room temperature (ca. 298 K). Adsorption isotherms of both acetone and acetaldehyde conformed to the Langmuir isotherm. FTIR spectra of the gas phase showed that these volatile organic compounds were mainly oxidized to CO_2 and H_2O. The time courses of concentration change due to photocatalytic decomposition under UV-irradiation were well represented by a proposed model by using the values of Langmuir parameters and the kinetic parameters determined.

Keywords: adsorption, acetone, acetaldehyde, photocatalyst, decomposition

1. Introduction

Titanium dioxide is noted as a desirable photocatalyst to decompose harmful organic compounds in air and in water. In recent years photocatalytic decomposition of various volatile organic compounds (VOCs) has been extensively investigated (Daniel, 2001). However, kinetic studies on photocatalytic decomposition of VOCs were limited. The Langmuir-Hinshelwood kinetic model was often used to explain the photocatalytic decomposition rate of VOCs (Kim and Hong, 2002; Bouzaza and Laplanche, 2002; Obuchi et al., 1999; Jian-Hua et al.,1999; Xu and Shiraishi, 1999; Sopyan et al., 1996; El-Maazawi et al., 2000; Sauer and Ollis, 1996). However, photocatalytic decomposition rate was influenced by many factors such as activity and surface area of photocatalyst, light intensity, adsorption and desorption of reactants/products, presence of oxygen, humidity, etc.

In the present work, photocatalyst of TiO_2 coated on silica beads was prepared, and photocatalytic decomposition rate of acetone and acetaldehyde were investigated in air atmosphere. While, adsorption isotherms of these VOCs were also examined. It was shown that the time courses of concentration change due to photocatalytic decomposition were well represented by the kinetic model proposed.

2. Material and Methods

Photocatalyst of TiO_2 coated on silica beads was prepared by immersing silica beads (beads diameter, 75–150 μm; pore diameter, 30 nm) in titania sol. obtained from Photocatalytic Materials Inc. (Aichi, Japan) under reduced pressure, followed by calcining the beads at 825 K for one hour in air atmosphere. The titanium dioxide was confirmed to be anatase form from the XRD pattern shown in Fig. 1. The BET-surface area of the prepared TiO_2-SiO_2 photocatalyst was determined to be 103 m^2/g by nitrogen physi-adsorption.

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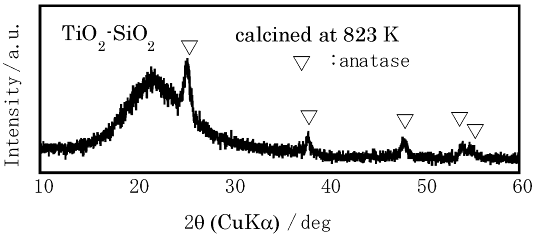

Figure 1. X-Ray diffraction pattern of TiO_2 coated on silica beads heat-treated at 823 K.

The molar ratio of Ti to Si was determined to be 0.25 with a X-ray Fluorescence Spectrometer (JEOL JSX-3202M).

The photocatalyst beads (0.5 g) were placed in a FTIR gas cell equipped with CaF_2 windows (25 mm diameter), and then a fixed volume of cold liquid acetone/acetaldehyde was injected into the cell (volume: 136 cm^3). The adsorption isotherms of these VOCs were measured in dark room. Photocatalytic decomposition rate was measured under UV-irradiation with a low pressure mercury lamp (light intensity at cell surface: 940 mW/cm^2). The gas phase composition in the cell was analyzed at a fixed time interval with a FTIR spectrophotometer (Biorad FTS3000). The concentrations of acetone and acetaldehyde in the gas phase were determined from the peak area of the bands at 1366 and 2737 cm^{-1}, respectively (see Fig. 3).

3. Results and Discussion

3.1. Adsorption Isotherms of Acetone and Acetaldehyde on TiO_2-SiO_2 Photocatalyst Beads

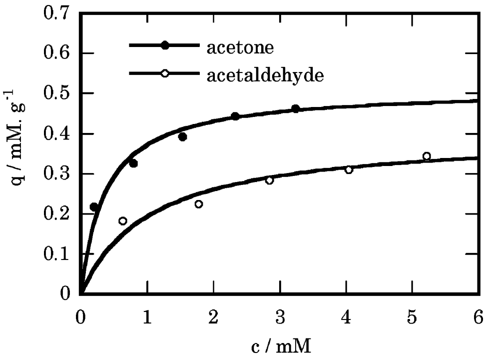

Figure 2. Adsorption isotherms of acetone and acetaldehyde on photocatalyst of TiO_2-SiO_2.

After introducing a fixed volume of cold acetone or acetaldehyde into the FTIR gas cell, the concentration in the gas phase immediately rose due to evaporation. The concentration then decreased gradually through adsorption onto the photocatalyst, and reached a steady after 210 minutes. Therefore, the concentration in the gas phase after 210 minutes was taken as the equilibrium concentration. The amount of acetone or acetaldehyde adsorbed was evaluated from the change in the concentration in the gas phase. As shown in Fig. 2, adsorption isotherms of both acetone and acetaldehyde were well represented by the following Langmuir equation:

$$q = q_m Kc/(1 + Kc) \tag{1}$$

The values of adsorption capacity, q_m, and equilibrium constant, K, were evaluated by conventional Langmuir plots. They are summarized in Table 1.

3.2. FTIR Study on Photocatalytic Decomposition of Acetone and Acetaldehyde

Figure 3 shows the FTIR spectra of the gas-phase in the FTIR gas cell at different irradiation times. The bands at 1738, 1435, and 1366 cm^{-1} assigned to acetone decreased with an increase in irradiation time. On the other hand, the bands at 2361 and 2340 cm^{-1} attributed to CO_2 increased with increasing irradiation time, and the bands at 3550–3780 cm^{-1} assigned to H_2O appeared slightly. These results imply that acetone was decomposed mainly to CO_2 and H_2O, but the amount of observed CO_2 was stoichiometrically less than that of decomposed acetone. This may be due to the adsorption of produced CO_2 on the photocatalyst beads and/or the formation of any unidentified intermediates. As seen from the FTIR spectra shown

Table 1. The values of Langmuir parameters and kinetic parameters determined.

	q_m	K	$\langle \beta I \rangle_0$	μ
	(mol.g^{-1})	(m^3.mol^{-1})	(m^3.kg^{-1}.min^{-1})	(–)
Acetone	0.51	2.66	1.35g× 10^{-3}	1.07
Acetaldehyde	0.40	0.94	2.40 g× 10^{-3}	1.13

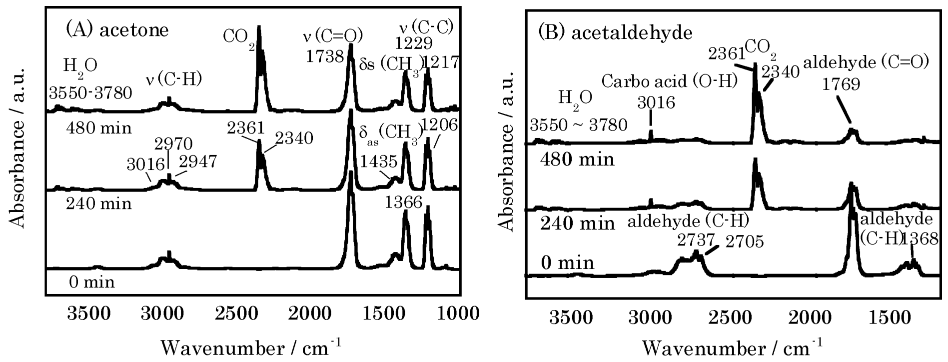

Figure 3. FTIR spectra of gas phase irradiated for different times: (A) acetone, (B) acetaldehyde.

in Fig. 3(B), acetaldehyde was also oxidized mainly to CO_2 and H_2O.

Figures 4(A) and (B) show time courses of the concentration changes of acetone and acetaldehyde at different initial concentrations, respectively. For both cases of acetone and acetaldehyde, the concentrations in the gas phase decreased monotonically with the irradiation time. The initial slope of the curve corresponds to the initial rate of photocatalytic decomposition. It increased with an increase in the initial concentration in the gas phase. This implies that the controlling step of the photocatalytic decomposition is reaction on the photocatalyst surface.

3.3. Analysis of Photocatalytic Decomposition Rate

Assuming that the decomposition rate is proportional to the concentration in the gas phase, c, and the amount of photocatalyst, m, decomposition rate is expressed by the following equation:

$$-\left(m\frac{dq}{dt}+V\frac{dc}{dt}\right)=m\,\langle\beta I\rangle\,c \tag{2}$$

where q and V are the amount of the VOC adsorbed and the cell volume, respectively. $\langle\beta I\rangle$ denotes an overall rate constant of photocatalytic decomposition including the light intensity, quantum yield, surface area of the photocatalyst, etc.

As described above, the adsorption isotherm was represented by Langmuir equation. Therefore, Eqs. (3) is derived from Eqs. (1) and (2).

$$\int_{c_t}^{c_0}\left\{\frac{q_m K}{(1+Kc)^2}+\frac{V}{m}\right\}\frac{dc}{c}=\langle\beta I\rangle\,t \tag{3}$$

where c_t is the concentration at irradiation time, t, and c_0 is the initial concentration in the gas phase. Consequently, the value of $\langle\beta I\rangle t$ can be obtained by

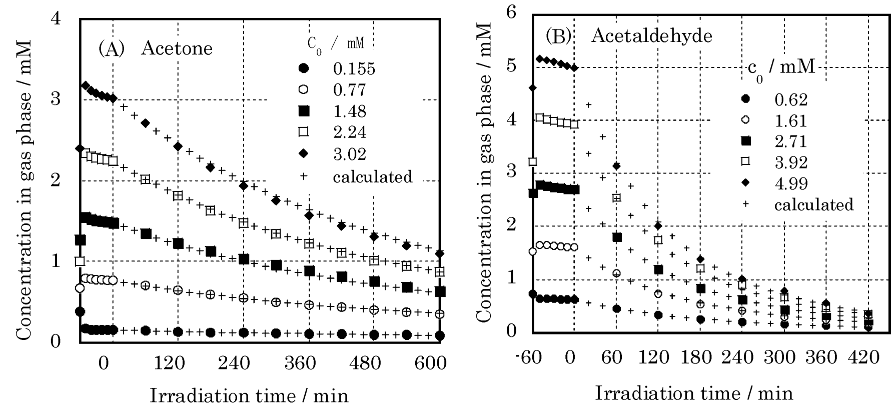

Figure 4. Time courses of concentration change by photocatalytic decomposition: (A) acetone, (B) acetaldehyde.

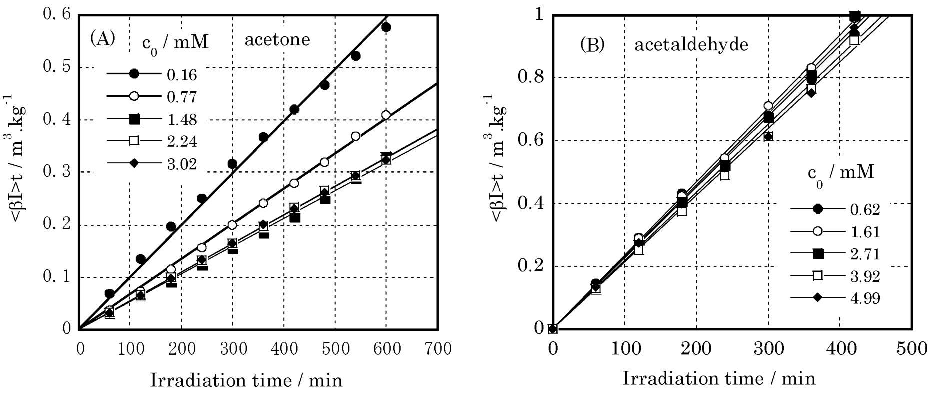

Figure 5. Relation between $\langle \beta I \rangle_t$ and t for photocatalytic decomposition: (A) acetone, (B) acetaldehyde.

integrating the function in left hand side of Eq. (3) from c_t to c_0. As shown in Fig. 5, plotting the calculated values of $\langle \beta I \rangle t$ against the irradiation times gives a straight line through the origin. Thus, the value of $\langle \beta I \rangle$ could be evaluated from the slope of each straight line.

Figure 6 shows the relation between $\langle \beta I \rangle$ and the initial coverage defined by the following equation:

$$\textit{Initial Coverage} = Kc_0/(1 + Kc_0) \qquad (4)$$

As seen from the figure, good relations were obtained for acetone and acetaldehyde. Each line was represented reasonably well by the following equation:

$$\langle \beta I \rangle = \langle \beta I \rangle_0 \exp\{-\mu K c_0/(1 + Kc_0)\} \qquad (5)$$

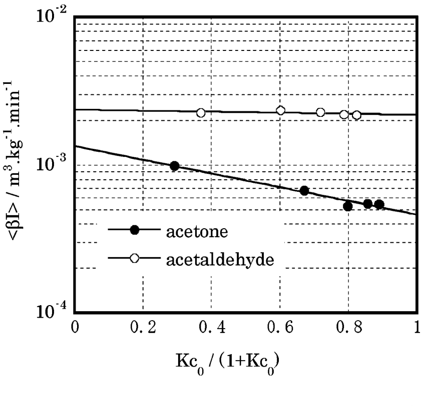

Figure 6. Relation between $\langle \beta I \rangle$ and initial coverage of photocatalyst with reactant.

The values of $\langle \beta I \rangle_0$ and μ were determined from the intercept and the slope of each straight line, respectively. They are summarized in Table 1.

The time courses of concentration changes due to photocatalytic decomposition could be estimated from Eqs. (3) and (5) by using the Langmuir parameters and the kinetic parameters of $\langle \beta I \rangle_0$ and μ given in Table 1. As shown in Fig. 4, the calculated time courses agreed well with the experimental ones at every initial concentration in the gas phase of both acetone and acetaldehyde, indicating a good validity of the present model for photocatalytic decomposition rate. It is concluded that $\langle \beta I \rangle_0$ and μ seem to be characteristic parameters for the photocatalyst and/or photocatalytic decomposition system.

Nomenclature

c = concentration in gas phase (mol·m^{-3})
c_0 = initial concentration in gas phase (mol·m^{-3})
K = adsorption equilibrium constant (mol·m^{-3})
m = amount of photocatalyst (kg)
q = amount of adsorbed species per unit weight of photocatalyst (mol·kg^{-1})
q_m = adsorption capacity of photocatalyst (mol·kg^{-1})
t = irradiation time (s)
V = cell volume (m^3)
$\langle \beta I \rangle$ = overall photocatalytic decomposition rate constant (m^3·kg^{-1}·s^{-1})
$\langle \beta I \rangle_0$ = intrinsic overall photocatalytic decomposition rate constant (m^3·kg^{-1}·s^{-1})
μ = attenuation coefficient (−)

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