

Evaluation of Diffusibility of Adsorbed Propionaldehyde on Titanium Dioxide-Loaded Adsorbent Photocatalyst Films from Its Photodecomposition Rate

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Photocatalytic degradation of gaseous propionaldehyde over TiO₂-loaded adsorbent films was investigated after adsorption equilibrium was obtained using silica, alumina, activated carbon, and several kinds of zeolites as adsorbents. Irradiation of one-tenth of the TiO₂-loaded adsorbent film caused complete mineralization of the adsorbed substrate in the entire film, although the rates obtained in that case were much lower than one-tenth of the rates obtained with the total area irradiation, indicating a considerable contribution of supply of the adsorbed substrate from the nonirradiated part of the film to the irradiated part. The apparent diffusion coefficient D_{app} of adsorbed substrate was evaluated by applying the time course of CO₂ evolution obtained in the area-selective photodecomposition reaction to a one-dimensional diffusion model. The D_{app} values estimated for various kinds of TiO₂-loaded adsorbent supports explain well the differences in the photodecomposition rates obtained at these photocatalysts. On the basis of experimental results, the effect of diffusion of the adsorbed substrate on the photodecomposition kinetics is quantitatively discussed.

Introduction

Photocatalytic degradation of numerous organic pollutants has been extensively studied using TiO₂ as a photocatalyst for remediation of contaminated water and air.^{1–20} It is postulated that the photodegradation reaction is initiated with attack of the target substrate by photogenerated active oxygen species such as O₂^{•−} and OH[•].^{5,21–28} However, the photodegradation rates to be expected in practical applications are usually very low, because in most cases the concentration of target substances is low and TiO₂ particles do not have high adsorbabilities for them. Thus one of the promising approaches to enhance the decomposition rate will be to concentrate the target substances around TiO₂ particles.

We reported previously that the use of inert supports such as activated carbon and zeolites for TiO₂ loading is effective in enhancing the photodecomposition rate of propylamide dissolved in water,²⁹ gaseous pyridine,³⁰ and propionaldehyde.³¹ In those cases, the inert supports concentrate the substrates around TiO₂ particles, thereby enhancing the decomposition rate. Recently similar enhancement effects were reported by other investigators for photodecomposition of rhodamine with use of a SiO₂ support,³² and acetophenone and 4-chlorophenol with use of ZSM5 and zeolite A supports.³³ On the contrary, if the adsorbability of the inert support for a target substrate is very high, a null effect of the use of inert supports may appear, as demonstrated for the photodegradation of decafluorobiphenyl adsorbed on alumina particles with cosuspended TiO₂ photocatalysts, where the decomposition rate was lower than that obtained with use of TiO₂ alone.³⁴ According to our previous study on photodecomposition of gaseous propionaldehyde, the reaction rate was influenced by adsorbability of the adsorbents used, and the highest rate was observed at the supports of moderate adsorbability.³¹ The results seem to suggest that the supports having moderate adsorbability form fairly high concentration environments of the adsorbate around the loaded TiO₂

TABLE 1: Fraction of Initial Adsorption to the Injected Gaseous Propionaldehyde (f_{ads}), Apparent Photodecomposition Rate Constant Obtained by Total-Area Irradiation (k_{obs}), and Apparent Diffusion Coefficient (D_{app}) of Adsorbed Propionaldehyde for Various TiO₂-Loaded Adsorbent Photocatalyst Films

photocatalyst ^a	weight of the film, mg cm ^{−2}	f_{ads} ^b	k_{obs} , ^c 10 ^{−3} s ^{−1}	D_{app} , 10 ^{−4} cm ² s ^{−1}
TiO ₂ /mordenite	0.33	0.71	0.98	2.3
	0.58	0.82	1.4	2.4
	1.0	0.92	1.5	2.5
	1.7	0.98	1.0	2.1
	2.5	0.98	0.67	2.0
TiO ₂ /silica	1.0	0.83	1.3	1.9
TiO ₂ /ferrierite	1.0	0.98	0.77	1.0
TiO ₂ /alumina	1.0	0.84	0.97	0.96
TiO ₂ /activated carbon	1.0	0.95	0.68	0.91
TiO ₂ /zeolite X	1.0	0.83	0.33	0.40
TiO ₂ /zeolite A(4)	1.0	0.84	0.25	0.28
TiO ₂ /zeolite A(3)	1.0	0.65	0.22	0.26
TiO ₂ /zeolite A(5)	1.0	0.66	0.15	0.25

^a TiO₂ content is 50 wt %. ^b Calculated for a total of 1.22 μmol of propionaldehyde from an adsorption isotherm reported previously.³¹

^c Obtained from photodecomposition experiments with total-area irradiation.

and allow a fairly easy supply from the support to the loaded TiO₂. The present study has been carried out to confirm this view by quantitatively evaluating the diffusibility of adsorbed propionaldehyde for various kinds of inert supports.

Experimental Section

Adsorbents used as the supports for TiO₂ were the same as those used in the previous study.³¹ TiO₂-loaded (50 wt %) adsorbents were prepared and fixed on a borosilicate glass plate (0.8 mm thick) of 1 cm wide × 4 cm long using the same procedures described previously in detail.³¹ The TiO₂-loaded adsorbents prepared are described as photocatalysts in this paper, which are given in Table 1 together with the amount of coating.

The experimental setups used in the present study were basically the same as those reported before,³¹ and the essence

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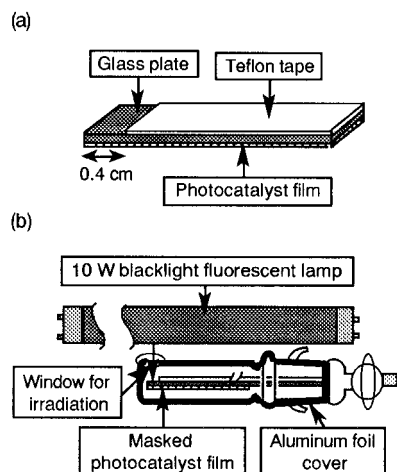


Figure 1. Schematic illustration of apparatus for area-selective photodecomposition experiment: (a) masked photocatalyst-coated glass plate; total area of photocatalyst was $1.0 \times 4.0 \text{ cm}^2$ and unmasked area was $1.0 \times 0.4 \text{ cm}^2$; (b) experimental setup for photodecomposition experiments. Area-selective irradiation was performed by irradiation from the back side of the photocatalyst-coated glass plate through a small window of the cell.

of them is briefly described here. The photodecomposition experiments were carried out using a Pyrex glass cell (1.4 cm diameter, 9.5 cm long, and 15 cm^3 capacity), which is schematically illustrated by Figure 1. The photocatalyst-fixed glass plate was placed horizontally in the cell, and dry air (21% O_2 and 79% N_2) passed through a water tank kept at 0°C was flowed through the cell for 10 min. Prior to the photodecomposition experiments, the photocatalyst film was irradiated with a 10 W black light fluorescent lamp (NEC) until organic impurities adsorbed on the photocatalyst surface were completely photodecomposed. Then the wet air was introduced again into the cell, and 0.1 cm^3 of propionaldehyde vapor prepared by holding a propionaldehyde container at 15°C was injected. The amount of the injected propionaldehyde was $1.22 \mu\text{mol}$. The cell was kept for more than 2 h in the dark to ensure the attainment of the adsorption equilibrium of propionaldehyde. The amount of adsorbed propionaldehyde was determined using the same technique as that reported previously.³¹ Then the entire surface of the photocatalyst film was irradiated using the 10 W black light fluorescent lamp with a light intensity of 1.8 mW cm^{-2} from the front side of the normal to the film surface. A sampling of the gas was made intermittently during the course of photodecomposition experiments to obtain the time course of CO_2 evolution, the amount of which was determined by means of gas chromatography.

To obtain information on the diffusion of adsorbed propionaldehyde, area-selected irradiation of the photocatalyst film was also performed. In that case, the back side of the photocatalyst-fixed glass plate was masked with a Teflon tape so as to leave a 0.4 cm length from the edge of one corner as illustrated in Figure 1a. The Teflon tape did not allow penetration of the UV light used in the present study. The cell was covered with aluminum foil except a small window ($1 \text{ cm} \times 0.4 \text{ cm}$; see Figure 1b) through which the photocatalyst film was irradiated from the back side. The cell wall absorbed light of wavelengths shorter than 330 nm, and the same was true for the glass plate used for fixing the photocatalyst. Accordingly it is believed that the incident photon flux per unit area of the irradiated part was essentially the same between the irradiation of the entire surface (from the front side) and the area-selective irradiation (from the back face).

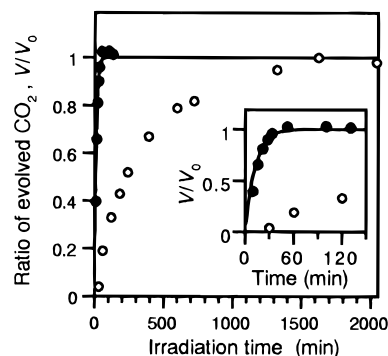


Figure 2. Time course of CO_2 evolution observed for photodecomposition of $1.22 \times 10^{-6} \text{ mol}$ of propionaldehyde over 1.0 mg cm^{-2} of $\text{TiO}_2/\text{mordenite}$ photocatalyst film: (filled circles) total-area irradiation; (open circles) area-selective irradiation. Inset: magnification for the initial 150 min period.

Results and Discussion

Photodecomposition of Propionaldehyde. The fraction of the amount of adsorbed substrate to the injected amount is listed as f_{ads} in Table 1 for all the photocatalyst films used. Figure 2 shows the ratio of the amount of evolved $\text{CO}_2(V)$ to that expected from complete decomposition of injected propionaldehyde (V_0) as a function of irradiation time. The results are given for irradiation of both the entire surface (solid circles) and the restricted surface (open circles) of the TiO_2 -loaded mordenite photocatalyst film of 1.0 mg cm^{-2} coating. The complete decomposition of injected propionaldehyde was achieved with irradiation of the entire surface for about 50 min. Even when one-tenth of the entire surface was irradiated, the amount of CO_2 expected from the complete decomposition of injected propionaldehyde was obtained with irradiation for about 1600 min, and further irradiation did not change the amount of CO_2 evolved. It should be noted that the time required in that case was much more than 10 times the irradiation time needed in the total area irradiation, suggesting that the adsorbed propionaldehyde was supplied from the nonirradiated surface to the irradiated surface, because a large fraction of the injected propionaldehyde was adsorbed on the photocatalyst film. As long as the photocatalysts given in Table 1 are concerned, the area-selective irradiation allowed complete degradation of propionaldehyde introduced into the cell, although the irradiation time required was different among the photocatalysts. The apparent rate constant for CO_2 evolution was evaluated for all the photocatalysts used by applying the pseudo-first-order rate equation (eq 1) to the initial stage of CO_2 evolution obtained with the entire-surface irradiation.³¹

$$\frac{d(\text{CO}_2)}{dt} = k_{\text{obs}}\{(\text{CO}_2)_{\text{max}} - (\text{CO}_2)\} \quad (1)$$

where $(\text{CO}_2)_{\text{max}}$ is the amount of carbon dioxide expected for the complete degradation of propionaldehyde injected into the cell. The rate constants obtained in this way are also included in Table 1.

Diffusion Model of Adsorbed Substrate from Nonirradiated Surface to Irradiated Surface. As shown in Table 1, more than 80% of injected propionaldehyde was adsorbed on the photocatalyst films in most cases. Then let it be assumed for simplicity that all of the propionaldehyde introduced into the cell was adsorbed on the photocatalyst film in such a way as to give the same concentration throughout the entire film. When one-tenth of the photocatalyst film (up to 0.4 cm from the edge) is irradiated, the photodecomposition of the adsorbed propionaldehyde on that part occurs, resulting in a difference in the concentration of adsorbed propionaldehyde between the

irradiated and the dark part. It is important to remark here that the photocatalyst films used in the present study were thin enough to allow penetration of irradiated photons used for excitation of the loaded TiO₂ particles. If the adsorbed propionaldehyde is mobile, then it moves from the nonirradiated part by diffusion. Here, the assumption is made that the diffusion occurs only along the horizontal plane of the film and not in a vertical direction of the photocatalyst film surface. This assumption is rationalized for the photocatalyst films of 1.0 mg cm⁻² or less used in most of the experiments, because the thickness of the film in that case was ca. 5 μm or less, which was negligibly small as compared to the diffusion length along the film plane. If it is assumed that the photodecomposition rate is proportional to the concentration of the adsorbed propionaldehyde in the irradiated part, the one-dimensional diffusion equation given by Fick's second law³⁵ holds both for the irradiated and for the dark part,

$$\frac{\partial C(x,t)}{\partial t} = D_{\text{app}} \frac{\partial^2 C(x,t)}{\partial x^2} - kC(x,t), \quad 0 \leq x \leq 0.4 \text{ (irradiated part)} \quad (2)$$

$$\frac{\partial C(x,t)}{\partial t} = D_{\text{app}} \frac{\partial^2 C(x,t)}{\partial x^2}, \quad 0.4 < x \leq 4.0 \text{ (dark part)} \quad (3)$$

where $C(x,t)$ (mol cm⁻³) is the concentration of adsorbed substrate at distance x (cm) from the edge of the irradiated part after the irradiation of given time t (s), D_{app} (cm² s⁻¹) represents its apparent diffusion coefficient in the photocatalyst film, and k (s⁻¹) represents the rate constant of the photodecomposition in the irradiated part.

The length of the photocatalyst film used in the present study limits the length of the diffusion layer, and under such condition eqs 2 and 3 cannot be solved analytically.³⁵ Therefore we adopt the explicit finite-difference method to obtain numerical solutions, which is commonly used for solving practical diffusion problems.^{36a} The procedures of numerical calculations are described in the Appendix. The concentration of adsorbed substrate as a function of the distance from the edge of the area-selective irradiation and the time course of photoproducted CO₂ were obtained using eqs A7–A12 and A16 of the Appendix.

Numerical calculations using these equations required D_{app} and k values. Since the area-selective photodecomposition experiments were carried out under the same conditions as those chosen in the total-area irradiated experiments, it is not unreasonable to employ the photodecomposition rate constants obtained by the total-area irradiation experiments, which are given in Table 1. Then the numerical calculations were performed using D_{app} as the only adjustable parameter.

Figure 3a shows the time course of CO₂ evolution obtained by the area-selective irradiation of 1.0 mg cm⁻² TiO₂/mordenite photocatalyst film together with those obtained by the digital simulation with use of the k_{obs} value given in Table 1 and a variety of D_{app} values. As clearly shown in this figure, numerical calculations predict that the photodegradation rate becomes great with increase of D_{app} values and the use of D_{app} of 2.5×10^{-4} cm² s⁻¹ gives the best fitted curve with the experimentally obtained one. Figure 3b shows concentration profiles of adsorbed propionaldehyde for different irradiation time with the use of this best fitted D_{app} . As shown in this figure, the concentration of the adsorbate decreases rapidly with time in the irradiated part, and simultaneously the concentration gradient develops. According to the experimental results shown in Figure 3a, about 30% of propionaldehyde was photodecomposed by irradiation for 100 min, and the concentration profiles of adsorbed propionaldehyde given in Figure 3b show that with

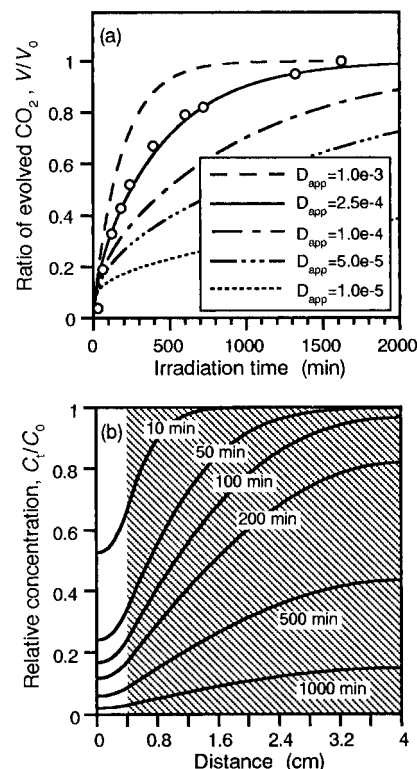


Figure 3. (a) Time course of CO₂ evolution obtained by the area-selective irradiation of 1.0 mg cm⁻² TiO₂/mordenite photocatalyst film. The amount of propionaldehyde injected into the cell was 1.22 μmol. Open circles are experimentally obtained results, and curves are theoretically predicted time courses obtained by simulations with use of various D_{app} values given in the figure. $k = 1.5 \times 10^{-3}$ s⁻¹ was used. (b) Ratio of the concentration of adsorbed propionaldehyde at various irradiation times (C_i) to the initial concentration (C_0) obtained by simulations with use of the best fitted $D_{\text{app}} = 2.5 \times 10^{-4}$ cm² s⁻¹ and $k = 1.5 \times 10^{-3}$ s⁻¹. Blank parts show the irradiated part, and shaded parts show the dark part of the film.

irradiation for that time period the concentration gradient is extended up to the most distant part of the photocatalyst film.

In the numerical calculations to give Figure 3, we assumed that all of the substrates were adsorbed on the photocatalyst film before irradiation. However, this was not the case. As shown in Table 1, 10–20% of propionaldehyde injected into the cell remained in the gas phase in most cases. Accordingly, the supply of the reactant from the gas phase to the photocatalyst film seems to have influenced the decomposition behaviors. To obtain information about this, we performed the photodecomposition experiments using photocatalyst films of different amounts of TiO₂/mordenite under the same conditions as those chosen in the above-mentioned experiments. Results obtained are also given in Table 1. As shown in this table, the amount of adsorbed propionaldehyde became high with increasing the weight of the film up to 1.7 mg cm⁻², beyond which the amount of adsorption seemed almost complete. This implies that the amount of propionaldehyde in the gas phase was higher for thinner photocatalyst films. However, the rate constant obtained does not reflect such a situation. As already reported,³¹ the apparent rate constant k_{obs} was determined by the amount of photoexcited TiO₂ if the photocatalyst films were less than 1.0 mg cm⁻², which gave a threshold value for light penetration, and if the film thickness became thicker than this, photoexcitation of TiO₂ in the film became incomplete, resulting in a decrease in the apparent rate constant. Although the k_{obs} values obtained were different in this complicated manner depending on the amount of photocatalyst loading, the digital simulations gave almost the same D_{app} values for the photocatalyst films of different thickness, suggesting that the propionaldehyde in the

gas phase does not seriously affect the diffusion of the adsorbed propionaldehyde on the photocatalyst film.

Evaluation of the Diffusion Coefficient for Various Photocatalyst Films. The time courses of CO₂ evolution as shown in Figure 3a were obtained for all photocatalyst films to determine the best fitted D_{app} , and obtained values are given in Table 1. Changes in the concentration profiles as a function of distance from the edge of the photocatalyst film with irradiation time as shown in Figure 3b were found to be different among the kinds of photocatalysts used, although not shown in this paper.

As shown in Table 1, the estimated D_{app} values range from 0.25×10^{-4} to 2.5×10^{-4} cm² s⁻¹ depending on the kind of adsorbents used. In our previous report, it was predicted that the supports having a very high adsorption strength retard the diffusion of the adsorbed substrate, resulting in a low photodecomposition rate. As far as the results obtained for photocatalysts having relatively high f_{ads} are concerned, this hypothesis seems valid. By comparing f_{ads} obtained for the same amount of photocatalyst loading of 1.0 mg cm⁻², it is noticed that TiO₂/ferrierite and TiO₂/activated carbon possessed high adsorbability for propionaldehyde, but their D_{app} was much smaller than that of TiO₂/mordenite, which had a little lower adsorbability. However, TiO₂/zeolite X and three kinds of TiO₂/zeolite A, which had relatively low f_{ads} , gave relatively small D_{app} , suggesting that the diffusibility of the adsorbed substrate is not necessarily determined by the adsorbability alone. Differences in physical conditions of the supports such as porosity, pore diameter, particle diameter, and particle shape also seem to be important in determining D_{app} values. Anyway it is important to note that the order of D_{app} values given in Table 1 almost agreed with the order of observed rate constant k_{obs} .

The D_{app} values given in Table 1 are 3–4 orders of magnitude smaller than the diffusion coefficients reported for gaseous molecules in air.³⁷ The diffusion of the adsorbed substrate will occur through pores at intergranular contacts and/or micropores (<2 nm) which the adsorbent supports originally have. Such complicated diffusion paths, which are different depending on the kind of adsorbent supports used, must influence greatly the value of D_{app} determined. Consequently the obtained diffusion coefficient is regarded to be an “apparent” one. It is not easy to correlate the obtained diffusion constant to the genuine diffusion constant which is determined in homogeneous media. Nevertheless, the obtained values are useful as a measure of diffusibility of the adsorbed substrate in the photocatalyst films.

Effect of Diffusibility on Photodecomposition Rate. It is suggested from the above discussion on D_{app} that the apparent photodecomposition rate constant of propionaldehyde k_{obs} is determined mostly by D_{app} . In the following, we obtain more insight into relations of the diffusibility of adsorbed substrate to the photodecomposition rate. As described in the preceding section, the area-selective irradiation allowed the determination of D_{app} with use of the one-dimensional diffusion model. To have more generalities, however, attempts are made to derive the decomposition rate with radial diffusion of the adsorbed substrate from the adsorbent support to a loaded TiO₂ particle having a spherical shape. The photodecomposition of the adsorbed substrate under such conditions will be valid for the case of irradiation of the entire surface of the photocatalyst film.

It may be assumed that the loaded TiO₂ particles are embedded in adsorbent supports. If the adsorbent support could be regarded as a homogeneous medium for the loaded TiO₂ particle, then the diffusion of the adsorbed substrate can be analytically solved in a similar way to that reported for interfacial electron transfer between a semiconductor particle and electron donors (or acceptors) in solution systems.^{21a,38} If

the loaded TiO₂ particle is irradiated, the adsorbed substrate is photodecomposed at a rate proportional to its concentration at the surface of the TiO₂ particle. When the steady state is reached, the rate of photodecomposition reaction is determined by the flux of the substrate at the surface,³⁸ which is given by

$$J_{particle} = C_{bulk}/(1/k_{photo} + R/D) \quad (4)$$

where C_{bulk} is the bulk concentration of adsorbed substrate, k_{photo} the actual rate constant of photodecomposition reaction, R the radius of the loaded TiO₂ particle, and D the diffusion coefficient of the adsorbed substrate around the TiO₂ particle. The bulk concentration of adsorbed substrate C_{bulk} may be regarded to be unchanged by irradiation in an initial stage for a short time. Then the photodecomposition rate is equal to the sum of $J_{particle}$ obtained at individual TiO₂ particles present in the photocatalyst film and is given by

$$-(dS/dt)_{init} = 4\pi R^2 N J_{particle} \quad (5)$$

where S is the total amount of remaining propionaldehyde and N is the number of TiO₂ particles present in the photocatalyst film.

At the same time, since complete photodecomposition of one propionaldehyde molecule yields three carbon dioxide molecules, the photodecomposition rate of propionaldehyde can be correlated to the rate constant of CO₂ evolution. With use of eq 1 and the relation $S = \{(CO_2)_{max} - (CO_2)\}/3$, the following equation is obtained.

$$-\frac{dS}{dt} = \frac{1}{3} \frac{d(CO_2)}{dt} = k_{obs} S \quad (6)$$

At an initial stage of photodecomposition, S can be assumed to be equal to S_0 , and then eq 7 holds.

$$-(dS/dt)_{init} = k_{obs} S_0 \quad (7)$$

The initial amount of adsorbed substrate S_{ads} is equal to $C_{bulk} V_{film}$, where V_{film} is the volume of the photocatalyst film. By inserting eqs 4 and 7 into eq 5, followed by rearrangements, eq 8 is obtained.

$$\frac{1}{k_{obs}} \frac{S_{ads}}{S_0} = \frac{V_{film}}{4\pi R^2 N} \left(\frac{1}{k_{photo}} + \frac{R}{D} \right) \quad (8)$$

Equation 8 can be reduced to eq 9, using the fraction of initial adsorption f_{ads} , which is equal to S_{ads}/S_0 .

$$\frac{f_{ads}}{k_{obs}} = \frac{1}{k_{max}} + \frac{V_{film}}{4\pi R N D} \quad (9)$$

$$k_{max} = \frac{4\pi R^2 N k_{photo}}{V_{film}} \quad (10)$$

where k_{max} gives the maximum apparent rate constant obtained when all of the substrates are adsorbed on the adsorbent ($f_{ads} = 1$) and the diffusion occurs so fast that the overall photodecomposition rate is determined solely by the reaction at the surface of TiO₂ particles.

Considering that f_{ads} and D are variables independent of each other, eq 9 predicts that k_{obs} increases with an increase of D if f_{ads} is constant and also increases with an increase of f_{ads} if D is constant. By using D_{app} values given in Table 1 for D in eq 9, plots of f_{ads}/k_{obs} vs $1/D_{app}$ were made for various kinds of photocatalyst films of the same amount (1.0 mg cm⁻²). As shown in Figure 4, a linear relation is established between the

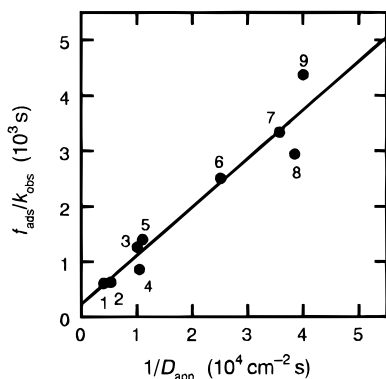


Figure 4. Plots of $f_{\text{ads}}/k_{\text{obs}}$ vs $1/D_{\text{app}}$ for a variety of TiO_2 /adsorbent photocatalyst films using parameters shown in Table 1. Solid line is a least squares fit applied to eq 9. (1) TiO_2 /mordenite; (2) TiO_2 /silica; (3) TiO_2 /ferrierite; (4) TiO_2 /alumina; (5) TiO_2 /activated carbon; (6) TiO_2 /zeolite X; (7) TiO_2 /zeolite A(4); (8) TiO_2 /zeolite A(3); (9) TiO_2 /zeolite A(5).

two, indicating that k_{obs} is governed by both the amount of adsorbed substrate and the diffusion of the adsorbed substrate when the entire photocatalyst film is irradiated after the adsorption equilibrium is attained. Extrapolation to the y axis of a solid line drawn by least squares fits to the experimentally obtained data gives $k_{\text{max}} = 4.2 \times 10^{-3} \text{ s}^{-1}$. The obtained k_{max} value is about 3 times greater than the rate constant obtained at the TiO_2 /mordenite and about 9 times greater than that obtained at the naked TiO_2 photocatalyst film ($k_{\text{obs}} = 4.7 \times 10^{-4} \text{ s}^{-1}$)³¹ having the same amount of TiO_2 (0.5 mg cm^{-2}).

Conclusions

The area-selective photodecomposition experiments evidenced that the adsorbed propionaldehyde was certainly involved in the decomposition reaction. The one-dimensional diffusion model of the adsorbate allowed successfully the estimation of the apparent diffusion coefficient of the adsorbed propionaldehyde on TiO_2 -loaded adsorbent supports of various kinds, and it is concluded from the results obtained in this study that the diffusion process of the adsorbed substrate plays a key role in the decomposition reaction of propionaldehyde at the TiO_2 -loaded adsorbent photocatalysts.

Another important suggestion obtained in the present study is that since the diffusion process of the adsorbed substrate determines the decomposition rate, the rate enhancement effect of the adsorbent support can be increased by decreasing the diffusion length of the adsorbate. Decrease of the diffusion length of the adsorbate will be experimentally achieved by improving the dispersiveness of TiO_2 particles. Since the diffusibility, adsorbability and then the net photodecomposition rate of substrates will be different among different kinds of adsorbents, it is important to properly select the adsorbent support for the photodecomposition of target substances.

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Appendix

To solve the diffusion problem by numerical calculations, discretized forms of eqs 2 and 3 are needed, which are given by eqs A1 and A2.

$$\frac{C(x,t+\Delta t) - C(x,t)}{\Delta t} = D_{\text{app}} \frac{C(x+\Delta x,t) - 2C(x,t) + C(x-\Delta x,t)}{(\Delta x)^2} - kC(x,t), \quad 0 < x \leq 0.4 \quad (\text{A1})$$

$$\frac{C(x,t+\Delta t) - C(x,t)}{\Delta t} = D_{\text{app}} \frac{C(x+\Delta x,t) - 2C(x,t) + C(x-\Delta x,t)}{(\Delta x)^2}, \quad 0.4 < x < 4.0 \quad (\text{A2})$$

where Δt denotes a time interval and Δx denotes a distance between the neighboring sections. Since the supply of adsorbed substrate is terminated at the edge of the photocatalyst film (at $x = 0$ and 4.0 cm), the flux of species by diffusion is null at the edges. The boundary conditions for the discretized equations are then given by eqs A3 and A4.

$$\frac{C(x,t+\Delta t) - C(x,t)}{\Delta t} = D_{\text{app}} \frac{C(x+\Delta x,t) - C(x,t)}{(\Delta x)^2} - kC(x,t), \quad x = 0, t > 0 \quad (\text{A3})$$

$$\frac{C(x,t+\Delta t) - C(x,t)}{\Delta t} = D_{\text{app}} \frac{C(x-\Delta x,t) - C(x,t)}{(\Delta x)^2}, \quad x = 4.0, t > 0 \quad (\text{A4})$$

Calculations of these equations were made by dividing the photocatalyst film into box elements of intervals δx along the x axis and the time intervals δt . If the coordinate of the center of the i th box is given by x_i and the irradiation time of the j th time increment by t_j , then x_i and t_j are given by eqs A5 and A6.

$$x_i = (i - 0.5)\delta x \quad (\text{A5})$$

$$t_j = j\delta t \quad (\text{A6})$$

where i and j are integers. For the calculations in present study, the photocatalyst film was divided into 100 boxes, having $\delta x = 0.04 \text{ cm}$. In that case the irradiated part of the photocatalyst film is given by the first to the 10th box element ($1 \leq i \leq 10$) and the nonirradiated part by the 11th to the 100th element ($11 \leq i \leq 100$). If the substrate concentration at x_i and t_j is denoted by $C(i,j)$, insertion of the latter after rearrangements of eq A1 gives eq A1'.

$$C(i,j+1) = (1 - k\delta t)C(i,j) + \frac{D_{\text{app}}\delta t}{(\delta x)^2} \{C(i+1,j) - C(i,j)\} \quad (\text{A1}')$$

Similarly, eqs A2'–A4' are obtained.

$$C(i,j+1) = (1 - k\delta t)C(i,j) + \frac{D_{\text{app}}\delta t}{(\delta x)^2} \{C(i+1,j) - 2C(i,j) + C(i-1,j)\} \quad (\text{A2}')$$

$$C(i,j+1) = C(i,j) + \frac{D_{\text{app}}\delta t}{(\delta x)^2} \{C(i+1,j) - 2C(i,j) + C(i-1,j)\} \quad (\text{A3}')$$

$$C(i,j+1) = C(i,j) + \frac{D_{\text{app}}\delta t}{(\delta x)^2} \{C(i-1,j) - C(i,j)\} \quad (\text{A4}')$$

Here, dimensionless parameters $c(i,j) = C(i,j)/C_0$ and $\alpha = D_{\text{app}}$

$\delta t/(\delta x)^2$ are introduced, where C_0 is the initial concentration of the adsorbed substrate, and the value of c at (x_i, t_j) is denoted by $c(i, j)$. Then eqs A7–A10 are obtained.

$$c(i, j+1) = (1 - k\delta t)c(i, j) + \alpha\{c(i+1, j) - c(i, j)\}, \quad i = 1 \quad (\text{A7})$$

$$c(i, j+1) = (1 - k\delta t)c(i, j) + \alpha\{c(i+1, j) - 2c(i, j) + c(i-1, j)\}, \quad 2 \leq i \leq 10 \quad (\text{A8})$$

$$c(i, j+1) = c(i, j) + \alpha\{c(i+1, j) - 2c(i, j) + c(i-1, j)\}, \quad 11 \leq i \leq 99 \quad (\text{A9})$$

$$c(i, j+1) = c(i, j) + \alpha\{c(i-1, j) - c(i, j)\}, \quad i = 100 \quad (\text{A10})$$

The initial condition is given by

$$c(i, j) = 1, \quad 1 \leq i \leq 100, \quad j = 0 \quad (\text{A11})$$

because at $t = 0$ ($j = 0$), $C = C_0$ ($c = 1$) holds all over the photocatalyst film. Besides this, there is a limitation on the value of α in order to get solutions within acceptable accuracy. It is suggested that $\alpha = 0.5$ is critical, and errors become significant when the value of α used is greater than the critical value.^{35,36} In the present study we chose $\alpha = 0.4$. Then together with the value of $\delta x = 0.04$ cm, the time interval of calculation δt is given by

$$\delta t = 6.4 \times 10^{-4} / D_{\text{app}} \quad (\text{A12})$$

By inserting k and D_{app} into eqs A7–A12 for the case of $j = 0$, one can calculate the values of c for $i = 1-100$. By iterating the calculations for successive j values, concentration profiles at given times as shown in Figure 3b are obtained.

The fraction of photodecomposition at a given time t_j , which is denoted by $P(j)$, is obtained by dividing the sum of the amount of photodecomposed propionaldehyde by the total amount of propionaldehyde used for destruction.

$$P(j) = (M_0 - M_j) / M_0 \quad (\text{A13})$$

where M_0 is the total amount of substrate and M_j is the amount of undecomposed substrate adsorbed on the film. M_0 is given by summing the initial amount of substrate over the total boxes,

$$M_0 = nC_0(i, j) \delta v \quad (\text{A14})$$

where n is the total number of boxes ($n = 100$ in present case) and δv is the volume of each box. On the other hand M_j is given by summing $C(i, j) \delta v$ for all boxes in the photocatalyst film:

$$M_j = \sum_{i=1}^n C(i, j) \delta v \quad (\text{A15})$$

By inserting eqs A14 and A15 into eq A13, we get

$$P(j) = 1 - \frac{1}{n} \sum_{i=1}^n c(i, j) \quad (\text{A16})$$

Calculations of this equation with successive j give the time courses of CO_2 evolution as shown in Figure 3a.

References and Notes

- (1) Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Photocatalysis—Fundamentals and Applications*; Serpone, N., Pelizzetti, E., Eds.; John Wiley & Sons: New York, 1989; Chapter 18.
- (2) Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Environ. Sci. Technol.* **1991**, 25, 1522.
- (3) Ollis, D. F.; Al-Ekabi, H., Eds. *Photocatalytic Purification and Treatment of Water and Air*; Elsevier: Amsterdam, 1993.
- (4) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, 93, 341.
- (5) Wold, A. *Chem. Mater.* **1993**, 5, 280.
- (6) Pelizzetti, E.; Minero, C. *Electrochim. Acta* **1993**, 238, 47.
- (7) Mills, A.; Davies, R. H.; Worsley, D. *Chem. Soc. Rev.* **1993**, 22, 417.
- (8) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, 95, 69.
- (9) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, 95, 735.
- (10) Heller, A. *Acc. Chem. Res.* **1995**, 28, 503.
- (11) Stafford, U.; Gray, K. A.; Kamat, P. V. *Heterogeneous Chem. Rev.* **1996**, 3, 77.
- (12) (a) Matthews, R. W. *J. Phys. Chem.* **1987**, 91, 3328. (b) Matthews, R. W. *J. Catal.* **1988**, 111, 264.
- (13) (a) Terzian, R.; Serpone, N.; Minero, C.; Pelizzetti, E. *J. Catal.* **1991**, 128, 352. (b) Minero, C.; Pelizzetti, E.; Terzian, R.; Serpone, N. *Langmuir* **1994**, 10, 692.
- (14) (a) Morris, S.; Mills, A. *J. Photochem. Photobiol. A: Chem.* **1993**, 71, 75. (b) Mills, A.; Holland, C. E.; Davies, R. H.; Worsley, D. *J. Photochem. Photobiol. A: Chem.* **1994**, 83, 257.
- (15) Dagan, G.; Tomkiewicz, M. *J. Phys. Chem.* **1993**, 97, 12651.
- (16) Sopyan, I.; Murasawa, S.; Hashimoto, K.; Fujishima, A. *Chem. Lett.* **1994**, 723.
- (17) Choi, W.; Termin, A.; Hoffmann, M. R. *J. Phys. Chem.* **1994**, 98, 13669.
- (18) Vinodgopal, K.; Kamat, P. V. *Environ. Sci. Technol.* **1995**, 29, 841.
- (19) Dagan, G.; Sampath, S.; Lev, O. *Chem. Mater.* **1995**, 7, 446.
- (20) Wong, J. C. S.; Linsebigler, A.; Lu, G.; Fan, J.; Yates, J. T., Jr. *J. Phys. Chem.* **1995**, 99, 335.
- (21) (a) Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, 95, 5261. (b) Wang, C.-M.; Heller, A.; Gerischer, H. *J. Am. Chem. Soc.* **1992**, 114, 5230. (c) Schwitzgebel, J.; Ekerdt, J. G.; Gerischer, H.; Heller, A. *J. Phys. Chem.* **1995**, 99, 5633.
- (22) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, 83, 3146.
- (23) Anpo, M.; Shima, T.; Kubokawa, Y. *Chem. Lett.* **1985**, 1799.
- (24) Turchi, C. S.; Ollis, D. F. *J. Catal.* **1990**, 122, 178.
- (25) Peterson, M. W.; Turner, J. A.; Nozik, A. J. *J. Phys. Chem.* **1991**, 95, 221.
- (26) Stafford, U.; Gray, K. A.; Kamat, P. V.; Varma, A. *Chem. Phys. Lett.* **1993**, 205, 55.
- (27) Mills, G.; Hoffmann, M. R. *Environ. Sci. Technol.* **1993**, 27, 1681.
- (28) Lawless, D.; Serpone, N.; Meisel, D. *J. Phys. Chem.* **1991**, 95, 5166.
- (29) (a) Uchida, H.; Itoh, S.; Yoneyama, H. *Chem. Lett.* **1993**, 1995. (b) Torimoto, T.; Itoh, S.; Kuwabata, S.; Yoneyama, H. *Environ. Sci. Technol.* **1996**, 30, 1275.
- (30) Sampath, S.; Uchida, H.; Yoneyama, H. *J. Catal.* **1994**, 149, 189.
- (31) Takeda, N.; Torimoto, T.; Sampath, S.; Kuwabata, S.; Yoneyama, H. *J. Phys. Chem.* **1995**, 99, 9986.
- (32) Anderson, C.; Bard, A. J. *J. Phys. Chem.* **1995**, 99, 9882.
- (33) Xu, X.; Langford, C. H. *J. Phys. Chem.* **1995**, 99, 11501.
- (34) Minero, C.; Catozzo, F.; Pelizzetti, E. *Langmuir* **1992**, 8, 481.
- (35) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, 1975.
- (36) (a) Feldberg, S. W. *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; Vol. 3. (b) Richtmeyer, R. D. *Difference Methods for Initial Value Problems*; Wiley Interscience: New York, 1957.
- (37) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 75th ed.; CRC Press: Boca Raton, 1994.
- (38) Grätzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC Press: Boca Raton, 1989.