Influence of Carbon Black as an Adsorbent Used in TiO₂ Photocatalyst Films on Photodegradation Behaviors of Propyzamide

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The photodecomposition of propyzamide in the aqueous solution was investigated using TiO₂-carbon black composite films. It was found that the photodecomposition rate was largely influenced by the content of carbon black in the photocatalyst film. The decomposition rate increased with increasing the carbon black content up to an optimal value, beyond which the photocatalytic activity showed a decreasing tendency. The increase of the photodecomposition rate seems to result from increase of adsorbability for propyzamide in the TiO₂-carbon black composite films. With further increase of carbon black from the optimum value, however, relative occupation of TiO₂ to carbon black decreases, and the time needed for adsorbed propyzamide on carbon black to diffuse to TiO₂ particles becomes great, resulting in the decrease of the apparent photocatalytic activity of the film. Experiments employing a circulating photoreactor system also showed that the TiO₂-carbon black composite films had higher photocatalytic activities than the naked TiO₂ film.   © 1998 **Academic Press**

INTRODUCTION

Photocatalytic degradation of numerous organic pollutants has been studied using TiO₂ as a photocatalyst for remediation of contaminated air and water (1–30). The photodecomposition reaction is usually thought to be initiated by either direct (22–24, 31) or ·OH radical mediated (10–21, 32, 33) hole transfer to the organic molecules. In some cases, conduction band electrons are also postulated to participate in photodegradation processes (25–30). Such TiO₂-photocatalytic processes have important significance when applied to the destruction of target compounds of very low concentrations of ppm level or below: However, there are no efficient and economical techniques available to achieve this. Since TiO₂ itself has low abilities for adsorption of organic compounds, it usually takes a long time to achieve complete decomposition, because the rate of the decomposition reaction in such cases is controlled by the collision probability of the substance with TiO₂.

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Recently it has been demonstrated that the rate of photodegradation at TiO₂ is enhanced by loading TiO₂ onto adsorbents (34–46). The adsorbent supports make a high concentration environment of target compounds around TiO₂, hence, increasing the collision probability between them. So far our studies concerning aqueous solution systems have been carried out using TiO₂-loaded adsorbent particles suspended in solution containing target compounds (34, 37, 39). In practical applications, however, it is desired to prepare TiO₂ in the form of the films which allows easy handling of the photocatalysts (1, 4, 6, 47, 48). We have used TiO₂-carbon black films as photocatalysts for the decomposition of 3,5-dichloro-N-(1,1-dimetyl-2-propynyl) benzamide, which is a typical herbicide having popular name of propyzamide. Photocatalytic activities were investigated as a function of the loading ratio of TiO₂ to carbon black and the thickness of the photocatalyst film. The purpose of this paper is to report these results in detail.

METHODS

Commercially available carbon black (Cabot, VULCAN XC72R) was used as an adsorbent whose specific surface area and average particle diameter were 250 m² g⁻¹ and 20 nm, respectively. Propyzamide was obtained from Wako Pure Chemical Industry and used as received. All the other chemicals used in this study were of reagent grade and purchased from Wako Pure Chemical Industry. Aqueous solutions were prepared using doubly distilled water.

Composite films of TiO₂ and carbon black, which are denoted in this paper as TiO₂/CB, were prepared as follows. Titanium tetraisopropoxide (3.7 cm³) was added dropwise to HNO₃ aqueous solution of 1.0 mol dm⁻³ (15 cm³) followed by agitation for 2 h. This formed a transparent TiO₂ sol containing 1.0 g TiO₂. After adding adequate amounts of carbon black powder to the TiO₂ colloids, the resulting mixed suspension was agitated for 0.5 h at room temperature, followed by dilution with the addition of 40 cm³ of 1.0 mol dm⁻³ HNO₃ aqueous solution. The mixed suspension of TiO₂ and carbon black (CB) was sprayed on a borosilicate glass plate (1.3 × 3.8 cm²) heated on a hot plate

to 300°C, held at 300°C for 2 h, then heated at 400°C for 1 h. The TiO₂ content in the resulting film was determined by colorimetric analysis using sodium 1,2-dihydroxy benzene-3,5-disulfate (Tiron) as a complexing agent (51). Naked TiO₂ films were prepared using the same procedures as described above without using the carbon black powder. We use the term "photocatalyst film" below for both TiO₂/CB and naked TiO₂ films as long as there is no need to discriminate between TiO₂/CB and naked TiO₂ films. Photocatalyst tubes used in the circulating experiment were also prepared using the above procedure. A glass tube (1.0 cm diameter, 16-cm high), instead of using the glass plate, was used as the solid substrate for the photocatalyst films. The morphology of the photocatalyst film was observed by the scanning electron microscope (SEM) (Hitachi S-800). The crystal structure of the TiO₂ particles in the film was determined by electron diffraction analysis with a Hitachi H-800 transmission electron microscope. Apparent transmittance of the photocatalyst film was measured with use of a Hewlett-Packard 8452A diode array spectrophotometer and was not corrected for the reflection and/or scattering of irradiated lights.

In order to purify the prepared photocatalyst films before using them as photocatalysts, they were first immersed in distilled water for more than one day and then taken out of the water and preirradiated in air containing 4.6 Torr (1 Torr = 133.3 N m⁻²) of water vapor. The light source was either a 500-W Xe lamp or a 15-W black light fluorescent lamp. The xenon lamp was used to irradiate the flat plate photocatalyst film by passing the light through a UV cutoff filter ($\lambda > 320$ nm), while the black light fluorescent lamps were used in the circulating reaction system. The preirradiation procedure was repeated several times until CO₂ no longer evolved in appreciable quantities.

The flat plate photocatalyst films were placed vertically inside a Pyrex reaction cell (1.5 cm diameter, 11 cm height, 18 cm³ capacity) and immersed in 10 cm³ of an aqueous solution containing 15 μmol dm⁻³ propyzamide at pH 6.5. The solution was bubbled for 15 min with air (21% O₂ and 79% N₂), followed by sealing the top of the cell with a rubber septum. Sampling was made intermittently through the septum during the photodecomposition experiments. Prior to the irradiation, the solution phase was stirred for more than 12 h in the dark to achieve adsorption equilibrium of the propyzamide to the photocatalyst film. The irradiation was performed at room temperature in such a way that the incident light was normal to the surface of the photocatalyst film. The irradiation intensity was 600 mW cm⁻² as determined by a Coherent Radiation Model 210 power meter. In the case of photodecomposition experiments using the circulating system, sample solutions were circulated through a Pyrex cell for irradiation (1.8 cm diameter, 15 cm height), a solution reservoir (capacity 300 cm³), and a cir-

culating pump. These constituents were connected to each other using glass tubes and Teflon tubes. The Pyrex cell contained the photocatalyst-coated glass tube in the center. The total capacity of these constituents was 350 cm³; 200 cm³ of an aqueous solution containing 15 μmol dm⁻³ of propyzamide was used in each photodecomposition experiment, and the solution was bubbled with dry air for 1 h and circulated from the bottom to top of the catalyst tube in the dark for 12 h. It was found that if the propyzamide solution was circulated for 2 days in this system in the absence of photocatalyst films, no appreciable decrease of propyzamide was detected, indicating that propyzamide did not adsorb on constituents of the circulating reactor. The photocatalyst-coated glass tube which was set vertically in the Pyrex cell was irradiated using five 15-W fluorescent black lamps whose spectrum ranged from 300 to 430 nm, peaking at 352 nm. These lamps were concentrically set around the Pyrex cell which contained the photocatalyst film-coated glass tube. The light intensity at the surface of the photocatalyst tube was 4.0 mW cm⁻², as determined by an Eppley Lab Model E-6 thermopile. The amount of CO₂ produced by the photodecomposition of propyzamide was determined by means of gas chromatography using a Yanaco G2800 gas chromatograph equipped with a thermal conductivity detector and a Porapak T column (Waters) at 100°C. Helium was used as a carrier gas.

The adsorbability of the photocatalyst films for propyzamide was evaluated by determining a decrease in the concentration of propyzamide in the solution with use of a high-performance liquid chromatograph system (HPLC) composed of a Jasco PU-980 pump, a Tosoh UV8011 detector, and a Tosoh TSK-GEL ODS-80T$_M$ reversed phase column. The eluent used was a mixed solvent of acetonitrile and water (55 : 45 by volume). Before sampling the solution, the flat plate photocatalyst film was soaked in 10 cm³ of propyzamide solution of various concentrations for more than 12 h.

In order to measure the photoelectrochemical properties, naked TiO₂ film and TiO₂/CB film having 80 wt% TiO₂ content were immobilized on conducting indium tin oxide (ITO) glass electrode with 0.73 mg cm⁻² TiO₂. The electrolyte solution used was 0.10 mol dm⁻³ HCl (pH 1.0) containing 0.10 mol dm⁻³ 2-propanol as a sacrificial electron donor. A quartz electrolytic cell used had a flat window. A Pt flag was used as the counter electrode. The potential was determined against an Ag/AgCl electrode in a saturated KCl as a reference electrode. Photocurrents were measured under N₂ with a Hokuto Denko HA-301 potentiostat using the lock-in technique. When voltammograms were measured, a function generator (Hokuto Denko HB-104) was combined with the potentiostat. The light from a 500-W Xe lamp was chopped at 8 Hz by a light chopper before irradiating the electrode.
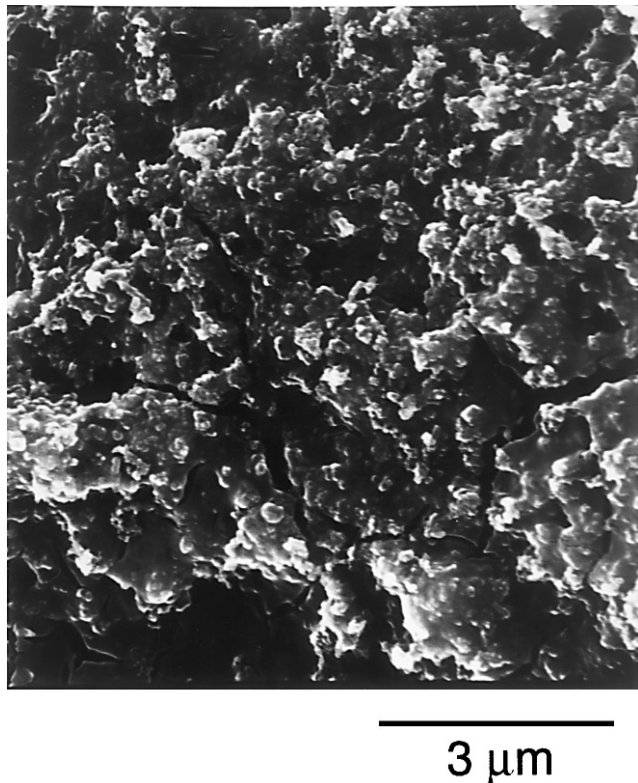
FIG. 1. SEM image of TiO$_2$/CB film with 80 wt% of TiO$_2$ content.

FIG. 2. Relationship between the amount of adsorption of propyzamide (S_{ads}) and its equilibrium concentration in solution (C_{eq}). The TiO$_2$ content in the film was 50 ($\square$), 65 ($\triangle$), 80 ($\bigcirc$), and 100 ($\bullet$) wt%. Photocatalyst film containing 0.73 mg-TiO$_2$ cm^{-2} on 4.9 cm^2 glass plate were immersed in the 10 cm^3 aqueous solution of propyzamide having various concentrations.

Fig. 2 to Langmuir adsorption isotherm given by Eq. [1],

$$\frac{C_{eq}}{S_{ads}} = \frac{C_{eq}}{S_{ads}^{max}} + \frac{1}{K_{ads} S_{ads}^{max}}, \quad [1]$$

where K_{ads} is the adsorption constant and S_{ads}^{max} is the maximum value of S_{ads}. The results are given in Fig. 3a, which shows Eq. [1] holding fairly satisfactorily with our

RESULTS AND DISCUSSION

Characterization of TiO$_2$-Carbon Black Composite Photocatalyst Films

Figure 1 shows a typical SEM image of the TiO$_2$/CB film surface containing 80 wt% TiO$_2$. The surface of the film was very rough and porous and seemed to be consisted of aggregated TiO$_2$ particles of less than 0.2 μm. X-ray microanalyses (Horiba EMAX-1770) of the film suggested that TiO$_2$ and carbon black were well mixed. Electron diffraction analyses revealed that TiO$_2$ particles consisted mostly of anatase (52).

TiO$_2$/CB films had abilities of adsorption for propyzamide dissolved in solution, as in the case of TiO$_2$-loaded activated carbon (34, 37). Figure 2 shows the relationships between the amount of adsorbed propyzamide on the photocatalyst films (S_{ads}) and the concentration of propyzamide in solution phase (C_{eq}) under equilibrium conditions for photocatalyst films having different contents of TiO$_2$. The amount of adsorption of propyzamide increased with an increase of the concentration of propyzamide, and this tendency was more marked with the increase of the carbon black content in the film.

Quantitative evaluations of the adsorbability of the photocatalyst films were made by applying the results shown in
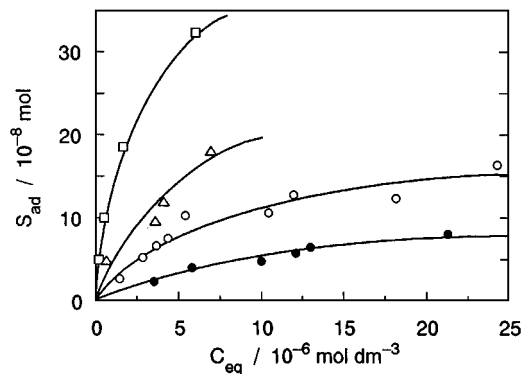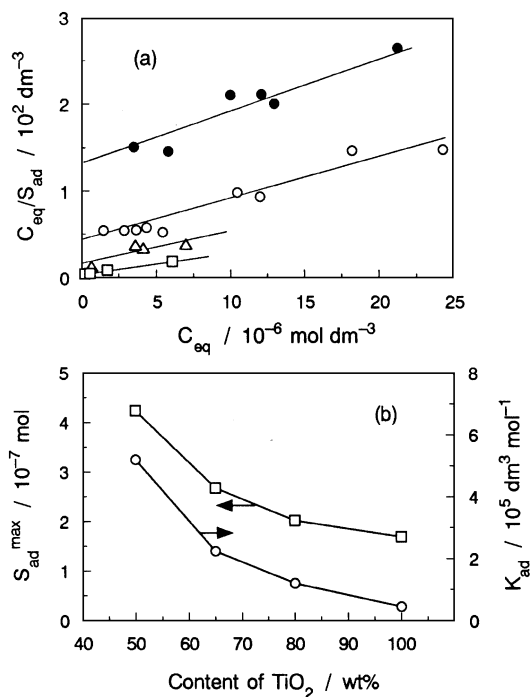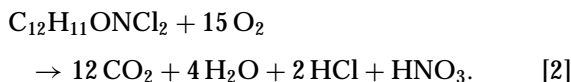

FIG. 3. (a) Plots of the left-hand side of Eq. [1] as a function of C_{eq}. The TiO$_2$ content in the film was 50 ($\square$), 65 ($\triangle$), 80 ($\bigcirc$), and 100 ($\bullet$) wt%. (b) Influence of the TiO$_2$ content on the adsorption constant of propyzamide (K_{ads}) and the maximum amount of adsorbed propyzamide (S_{ads}^{max}).

experimentally obtained results. From the linear relations in Fig. 3a, K_{ads} and S_{ads}^{max} were obtained as a function of the TiO₂ content (Fig. 3b). With an increase of the TiO₂ content, the S_{ads}^{max} and K_{ads} decreased. These results suggest that the adsorption sites in the films increased with an increase of the carbon black content. The K_{ads} values also decreased with an increase of the TiO₂ content in the film, suggesting that carbon black had greater adsorption strength than TiO₂ and that propyzamide was predominantly adsorbed on carbon black in the photocatalyst film.

Influence of the Content of TiO₂ on Photocatalytic Decomposition of Propyzamide

When photoinduced mineralization of propyzamide occurs stoichiometrically using oxygen as an oxidizing agent, the overall reaction is given by

$$C_{12}H_{11}ONCl_2 + 15\,O_2$$
$$\rightarrow 12\,CO_2 + 4\,H_2O + 2\,HCl + HNO_3. \qquad [2]$$

Since 10 cm³ of 15 μmol dm⁻³ of propyzamide was used in the experiments, the production of 1.8 μmol of CO₂ is expected when complete mineralization is achieved. Figure 4a shows the time course of CO₂ evolution with irradiation
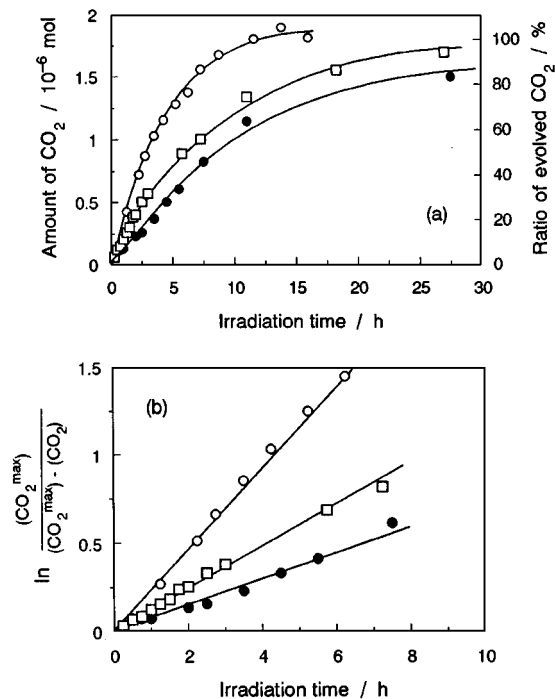

FIG. 4. Time course of CO₂ evolution in photodecomposition of propyzamide over various photocatalyst films (a) and plots of the left-hand side of Eq. [3] as a function of the irradiation time (b). The TiO₂ content in the film was 50 (□), 80 (○), and 100 (●) wt%. Photocatalyst film containing 0.73 mg-TiO₂ cm⁻² on 4.9 cm² glass plate were immersed in the 10 cm³ of 15 μmol dm⁻³ propyzamide aqueous solution. The irradiation was performed with a 500-W Xe lamp ($\lambda > 320$ nm).

of the naked TiO₂ film and TiO₂/CB films having 50 and 80 wt% of TiO₂. The rate of CO₂ evolution was considerably influenced by the content of TiO₂ in the film and the highest decomposition rate was achieved at the TiO₂/CB film having 80 wt% of TiO₂ among three kinds of the photocatalyst films shown in the figure. In the figure, the ratio of the amount of evolved CO₂ to that expected from the complete destruction of propyzamide contained in the cell is also given. Since the experimentally obtained ratio did not exceed 100%, evolution of CO₂ from photodestruction of carbon black is unlikely. In that case complete mineralization was attained with irradiation for 11 h. The obtained films were not stripped off from the glass substrate during the photodecomposition experiments.

Photoelectrochemical measurements of the naked TiO₂ film and TiO₂/CB film having 80 wt% of TiO₂ were performed in the presence of 2-propanol as a sacrificial electron donor at solution pH 1.0. Anodic photocurrents appeared at potentials more positive than -0.40 V versus Ag/AgCl in both photocatalyst films, suggesting that the energy structure of TiO₂ particles was not changed by contacting with carbon black. If the onset potential obtained is assumed to be equal to the flat band potential (E_{fb}), it agrees with the value deduced from the published literatures for anatase TiO₂ with the assumption that E_{fb} varies at the rate of -60 mV per unit increase of pH (49, 50). If the potential of the conduction band edge is approximated to E_{fb}, it is calculated to be -0.73 V versus Ag/AgCl under the present experimental conditions (pH 6.5) and the potential of valence band edge to be 2.5 V versus Ag/AgCl.

If it is assumed that the photodecomposition of propyzamide to CO₂ proceeded with pseudo-first-order kinetics with respect to its concentration, the relationship (18–20, 36, 39)

$$\ln \frac{(CO_2)_{max}}{(CO_2)_{max} - (CO_2)} = Ak_{CO_2}t \qquad [3]$$

holds, where A is the geometrical surface area of photocatalyst film used (4.9 cm²), k_{CO_2} is the apparent rate constant for CO₂ evolution per unit surface area, $(CO_2)_{max}$ is the amount of CO₂ expected from the complete decomposition of propyzamide (1.8 μmol), and (CO_2) is that obtained at a given irradiation time. When the left-hand side of Eq. [3] was plotted as a function of the irradiation time for the results given in Fig. 4a, fairly good linear relations were obtained as shown in Fig. 4b in an early stage of irradiation. Values of k_{CO_2} were determined from these linear fits.

Figure 5a shows k_{CO_2} determined in this way as a function of the TiO₂ content. With an increase of the TiO₂ content, k_{CO_2} increased up to an optimum value, beyond which it showed a decrease. Under experimental conditions employed in the photodecomposition experiments, about 30% of propyzamide was adsorbed on the naked TiO₂ film and with increasing the fraction of carbon black in TiO₂/CB composite films its adsorption was increased, as shown in
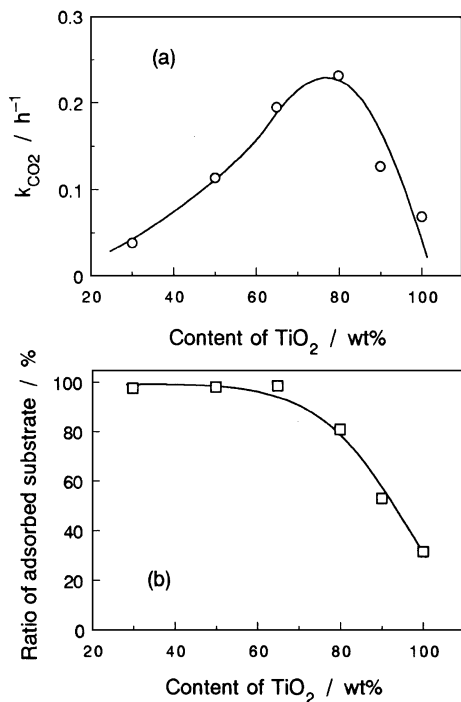
FIG. 5. (a) Relationship between the rate constant of CO_2 evolution and the TiO_2 content in the photocatalyst films. (b) The amount of adsorbed propyzamide on the photocatalyst films as a function of the TiO_2 content determined prior to the photodecomposition experiment.

Fig. 5b. Less than 60 wt% TiO_2 allowed for the adsorption of almost all propyzamide from the solution. The dependence of the adsorption of propyzamide on the TiO_2 content as shown in Fig. 5b agreed with the results shown in Fig. 3b. By comparing the effect of the TiO_2 content on k_{CO_2} (Fig. 5a) and on the ratio of adsorbed propyzamide (Fig. 5b), it is suggested that the decrease of k_{CO_2} with an increase of TiO_2 content above 80 wt% resulted from a decrease in the amount of adsorbed propyzamide. On the other hand, a decrease of k_{CO_2} with decreasing the TiO_2 content below 80 wt% results from different causes. With decreasing the TiO_2 content, the amount of adsorption of propyzamide increases. However, since relative occupation of TiO_2 to carbon black decreases in that case, the diffusion length of adsorbed propyzamide to TiO_2 becomes great on average with decreasing the TiO_2 content (that is, increasing carbon black content). Moreover, an increase in the fraction of carbon black must decrease photoexcitation of TiO_2, because light absorption in the carbon black would not allow the light penetration through the film. Either of these or both would have caused an apparent decrease of the CO_2 evolution rate as observed in Fig. 5a.

Effect of the Amount of Photocatalyst on Decomposition of Propyzamide

Figure 6a shows the effect of the amount of TiO_2/CB film containing 80 wt% TiO_2 on k_{CO_2}. It is obvious that k_{CO_2} in-

creases with an increase of the total amount of the catalyst up to about 0.9 mg cm^{-2}, beyond which a decreasing tendency appears. The total amount of propyzamide used in the photoreaction cell was fixed to 10 cm^3 of 15 μmol dm^{-3} for all cases, and under such conditions the amount of adsorbed propyzamide was also influenced by the total amount of the photocatalyst film as shown in Fig. 6b. Since the thickness of the catalyst film increases with an increase in the amount of the catalyst, the observed dependence is explained in terms of utilization of TiO_2 particles in photoexcitation. It was found that the optimum amount of 0.9 mg cm^{-2} TiO_2/CB film allowed the transmittance of less than 5% at 350 nm. The obtained transmittance does not necessarily give a direct measure of light absorption at TiO_2 particles in the film, because light reflection and/or light scattering at the TiO_2/CB film, if any, were not corrected at all. However, there is no doubt about the fact that all TiO_2 particles contained in the film were photoexcited for the TiO_2/CB loading less than the optimum value. It is suggested by comparing Fig. 6a with 6b that, up to the optimum amount of the photocatalyst film, k_{CO_2} was determined by the amount of adsorbed propyzamide. If the amount of photocatalyst loading is increased from the optimum value, the fraction of photoexcited TiO_2 in the film is decreased, although propyzamide in solution becomes completely removed by adsorption onto the photocatalyst films, resulting in a decrease of
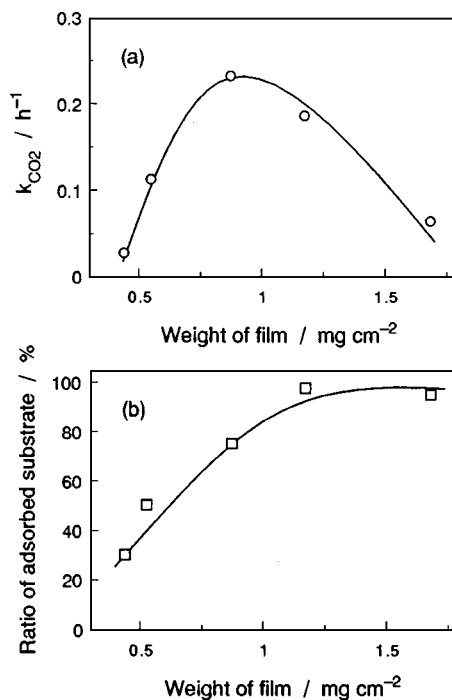

FIG. 6. (a) Dependence of the rate constant of CO_2 evolution on the total weight of TiO_2/CB film with 80 wt% TiO_2 content on glass plate (4.9 cm^2). (b) The amount of adsorbed propyzamide on the photocatalyst films as a function of the total weight of TiO_2/CB film in the condition of the photodecomposition experiment.

k_{CO_2} as shown in Fig. 6a. The optimum amount of the photocatalyst film of 0.9 mg cm^{-2} may be changed by using different kinds of TiO_2 or carbon black, or by using different techniques for the preparation of the photocatalyst films, because the amount of active TiO_2 and that of adsorbed propyzamide per unit thickness and unit apparent area of the photocatalyst films may be changed in such cases.

The apparent photonic yield (*PY*), which is defined here as the ratio of the number of holes consumed in the complete photodecomposition of propyzamide to that of the incident photons, was evaluated for the optimum amount of TiO_2/CB loading of 0.9 mg cm^{-2} using monochromatic irradiation at 365 nm, which was obtained by passing light from a 500-W Hg lamp through a band-pass filter. The monochromatic light contained 3.3×10^{-4} einstein h^{-1} cm^{-2} photons which resulted in CO_2 evolution with its initial rate of 5.9×10^{-8} mol h^{-1}. The *PY* was then determined to be 2.2×10^{-3}, if 60 positive holes are assumed to be involved in the complete photomineralization of one molecule of propyzamide.

Application of TiO_2-Carbon Black Composite Films to a Circulating Reactor

Although the obtained *PY* was rather low, photodecomposition behaviors of propyzamide were further investigated by taking into considerations of practical applications with circulating 15 μmol dm^{-3} aqueous propyzamide solution using the experimental setup described in the experimental section. Two different flow rates of 7.5 or 15 cm^3 s^{-1} were tested. The photocatalyst films used were the TiO_2/CB having 80 wt% TiO_2 and the naked TiO_2; for both cases the amount of TiO_2 contained in the photocatalyst films was 0.73 mg-TiO_2 cm^{-2}. Figure 7 shows the time course of CO_2 evolution given in relative values to that expected

from total decomposition of propyzamide. As shown in this figure, the flow rate did not influence the decomposition rate but the kind of the photocatalyst did, suggesting that the flow rate used in this study was high enough to supply the propyzamide to the irradiated surface of photocatalyst films and that the rate determining step of the photodecomposition reaction is the degradation of adsorbed propyzamide on the photoexcited TiO_2 particles. If Eq. [3] was applied to the results given in Fig. 7, k_{CO_2} of 1.1×10^{-2} and 4.0×10^{-3} h^{-1} cm^{-2} were obtained for the case of the naked TiO_2 and the TiO_2/CB film having 80 wt% of TiO_2, respectively. The latter is about three times greater than the former, indicating that the degree of enhancement of the decomposition rate obtained in the circulating system was the same as that obtained in the batch system described above. Accordingly, the activity difference seems to be related to differences in adsorbability of propyzamide, as discussed above. The amount of adsorbed propyzamide at the TiO_2/CB film was determined to be 47% of the amount contained in the initial sample solution, while that at the naked TiO_2 film was as small as 8.7%. Although the TiO_2/CB film gave higher activities than the naked TiO_2 film, the CO_2 evolution rate obtained at the TiO_2/CB film in the circulating system was about one-fifth that obtained in the batch system which is given in Fig. 5a. Such a difference seems to have resulted from differences in experimental conditions used, especially from differences in the irradiation intensity used in the photodecomposition experiments of propyzamide.

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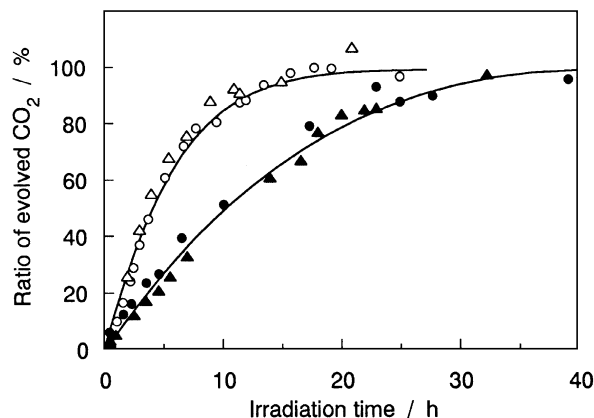
FIG. 7. Time course of CO_2 evolution in photodecomposition of propyzamide with use of circulating photoreactor. The photocatalyst tubes of TiO_2/CB film with 80 wt% TiO_2 content (○, ●) and the naked TiO_2 film (○, ▲) containing 0.73 mg-TiO_2 cm^{-2} were used. The flow rate was 7.5 (○, ●) and 15 cm^3 s^{-1} (△, ▲). The irradiation was performed with five 15-W blacklight fluorescent lamps.

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