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# Photocatalytic Decomposition of Propyzamide Using $TiO_2$ Supported on Activated Carbon

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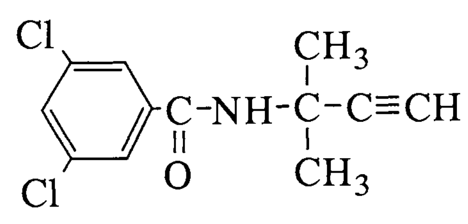
Utility of activated carbon adsorbate as a support for $TiO_2$ photocatalysts was demonstrated for photomineralization of propyzamide, a typical herbicide, in dilute aqueous solution. High adsorptive activity of the activated carbon support enables the organic pollutant to concentrate around the loaded $TiO_2$, resulting in a high photocatalytic degradation rate.

Recently photochemical processes using semiconductor photocatalysts have been intensively studied with purposes of detoxification of organic and inorganic pollutants in water.1) A lot of studies have shown that illumination of semiconductor powders such as $TiO_2$ suspended in aqueous solutions containing organic compounds and oxygen induces oxidative decomposition of the organic compounds, accompanied by reduction of dissolved oxygen. It is believed that the first step of the oxidative decomposition is oxidation of the oganic molecules with hydroxyl radicals produced on the photocatalyst surfaces.2-4) Then, adsorbability of the organic molecules on $TiO_2$ is an important factor to determine its decomposition kinetics. In cases of dilute pollutants of ppm levels, it usually takes a long time to complete their decomposition. In order to perform a rapid and efficient decomposition under such dilute conditions, it may be effective to load photocatalysts on suitable adsorbents to concentrate the pollutants around the photocatalyst. Minero et al.5) examined the effect of the addition of $Al_2O_3$ and $SiO_2$ as inert supports to $TiO_2$ photocatalyst suspensions for photodecompositions of several kinds of organic compounds. However, they observed that the decomposition rates were little affected by the location of the organic compounds, whether in solution, on the photocatalyst or on these inert supports.



Propyzamide

We have obtained very promising results on the use of activated carbon as a support for $TiO_2$ in photocatalytic degradation of 3,5-dichloro-N-(1,1-dimethyl-2-propynyl) benzamide (Propyzamide), a typical herbicide widely used in golf links. The purpose of this

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paper is to describe the first finding of the usefulness of the inert support for semiconductor photocatalyst.

Microcrystalline $TiO_2$ colloids were prepared by dropwisely adding 2.58 $cm^3$ of titanium tetraisopropoxide to 7.74 $cm^3$ of 1 M (1 M = 1 mol $dm^{-3}$) $HNO_3$ aqueous solution under vigorous stirring at room temperature. The resulting slurry was peptized by further stirring for 2 h to give a clear $TiO_2$ sol. 50 $cm^3$ of water was added to the sol and pH was adjusted to 3 by adding 1 M NaOH, resulting in a turbid $TiO_2$ colloid. Then a desired amount of activated carbon particles (AC) (Wako Pure Chemicals) was added to the colloid, followed by stirring for 1 h to attach $TiO_2$ particles on the activated carbon. After repetition of centrifuge and washing with distilled water more than five times until the solutuion pH became 6 – 7, $TiO_2$–loaded activated carbon ($TiO_2$/AC) was vacuum dried. Finally the obtained powders were heated at 300 °C in air for 1 h. The photocatalyst thus prepared will be denoted as $TiO_2$/AC. We prepared three kinds of $TiO_2$/AC with different $TiO_2$ loadings of 33, 56, and 80 wt%, which were determined by a spectrophotometric method using Tiron as a complexing agent. Besides the $TiO_2$/AC, naked $TiO_2$ particles were prepared as a reference using the similar hydrolysis procedures of titaniumtetraisopropoxide.

The naked $TiO_2$ powder showed broad X–ray diffraction patterns assigned to anatase form. Its mean diameter determined by dynamic light scattering was 0.26 μm and the BET surface area was 139 $m^2$ $g^{-1}$. The BET surface area and average particle size of the original active carbon were 749 $m^2$ $g^{-1}$ and 5 μm, respectively. Scanning electron microscopy and energy dispersive X–ray microanalysis of $TiO_2$/AC indicated that fine $TiO_2$ particles of ca. 0.2 μm or their aggregates distributed uniformly over the activated carbon surfaces. The BET surface area of $TiO_2$/AC was 798, 556, and 242 $m^2$ $g^{-1}$ for 33, 56 and 80 wt% $TiO_2$ loadings.

Photocatalytic degradation of propyzamide was carried out using a pyrex glass reacion cell. 10 mg of the photocatalyst powder ($TiO_2$/AC or naked $TiO_2$) was suspended in 10 $cm^3$ of air–saturated aqueous solution containing 7.8 ppm, i.e., 30.5 μM propyzamide. Under magnetically stirring, the cell was illuminated with a 400 W Xenon lamp at irradiance of 135 mW $cm^{-2}$. After a given time of illumination, the photocatalyst was removed by centrifuge, and the solution was filtered off with a 0.2 μm pore size membrane filter. Changes in the concentration of propyzamide were monitored by measuring the optical absorption spectra of the filtrates with use of a photodiode array spectrophotometer. As the decomposition products, $Cl^-$ ions and dissolved $CO_2$ were analyzed by a $Cl^-$ selective electrode (Horiba 8002–06T) and a $CO_2$ electrode (TOA CE–235), respectively.

Figure 1 shows the time course of $Cl^-$ production in the photocatalytic degradation of propyzamide over various amounts of naked $TiO_2$. Almost the same production rate of $Cl^-$ was obtained with the use of 1.0 and 2.0 g $dm^{-3}$ of the photocatalyst, though a lower production rate was seen for 0.5 g $dm^{-3}$. In this figure, the degree of the release of $Cl^-$ ions from propyzamide is also given as the percentage of decomposition. The release of $Cl^-$ ions completed within 2 h of illumination for 1 g $dm^{-3}$ of the suspended $TiO_2$. In contrast the evolution of $CO_2$ from propyzamide took a long time for its completion. As shown in Fig. 2, a long induction period was needed before the $CO_2$ evolution took place. The percentage of the decomposition to $CO_2$ given in Fig. 2 was obtained by assuming that twelve $CO_2$ molecules evolved from one propyzamide molecule. As shown in the figure, the decomposition of propyzamide into $CO_2$ was less than 30 % even after 6h illumination of 1g $dm^{-3}$ naked $TiO_2$ photocatalyst suspension. The results given in Figs. 1 and 2 show that the complete mineralization of propyzamide into $CO_2$ takes a long time, whereas Cl–C bonds are easily cleaved.

To evaluate abilities for popyzamide adsorption of the naked $TiO_2$ and activated carbon, they were suspended in 7.8 ppm propyzamide solution so as to give 1 $gdm^{-3}$, followed by magnetically stirring for 1 h in

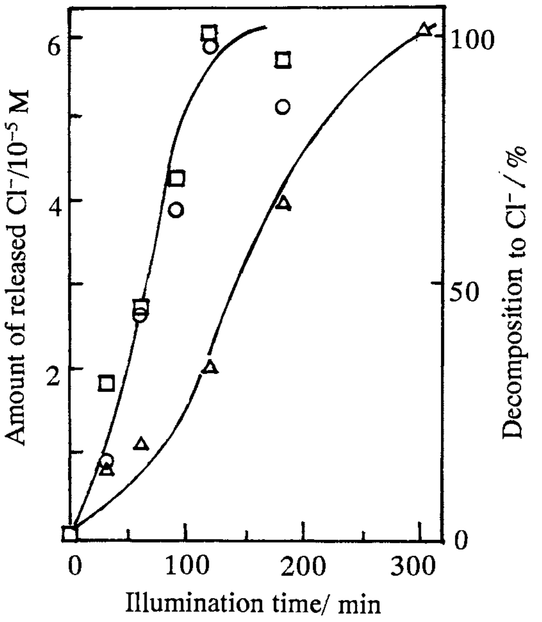

Fig. 1. Time course of $Cl^-$ ion production in photodegradation of 30.5 μM propyzamide over different amounts of naked $TiO_2$. The amount of $TiO_2$ suspended : (▲) 0.5, (○) 1.0, and (□) 2.0 g $dm^{-3}$.

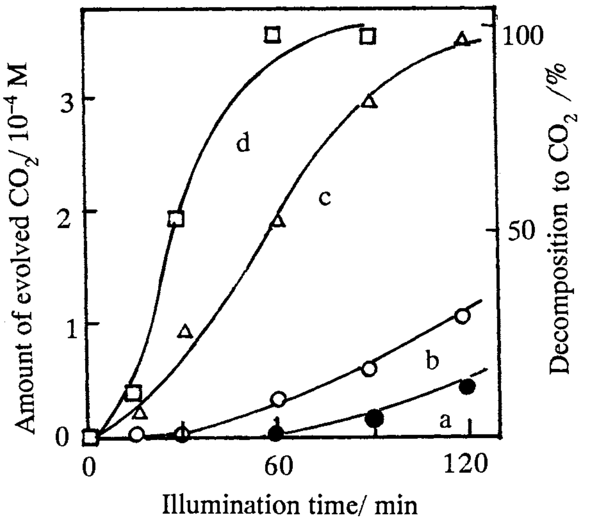

Fig. 2. Time course of $CO_2$ production in photodegradation of 30.5 μM propyzamide over (a) naked $TiO_2$, and (b)– (d) $TiO_2$/AC. The amount of loaded $TiO_2$ : (b) 33, (c) 56, and (d) 80 wt%. The amount of the photocatalyst suspended was 1 g $dm^{-3}$.

the dark. After filtration, the concentration of propyzamide in the filtrates was determined by measuring the absorbance at 208 nm. It was found that as small as 13% of propyzamide in solution adsorbed on the naked $TiO_2$, while 87.6% was removed by the activted carbon. The observed very slow degradation rate of propyzamide at the naked $TiO_2$ may result from such low adsorbability.

It was found by blank tests that a detectable amount of $CO_2$ evolved with illumination of $TiO_2$/AC suspension in the absence of propyzamide. The $CO_2$ evolution in that case is due probably to decomposition of trace amounts of organic impurities adsorbed on the activated carbon. In the results given in Fig. 2, the amount of $CO_2$ obtained in the balnk test is subtracted. It is noticed from Fig. 2 that the induction period for $CO_2$ evolution was shortened and the $CO_2$ evolution rate was dramatically increased by increasing the amount of loaded $TiO_2$. When 80 wt%-loaded $TiO_2$/AC was used, the degradation of propyzamide to $CO_2$ completed with illumination for about 1 h. A series of control experiments showed that such an efficient minerarization was achieved only with the use of $TiO_2$/AC.

All the photodegradation experiments desrcibed above were carried out without regulating the cell temperature. However, illumination of $TiO_2$/AC suspensions raised the cell temperature up to 40 °C by absorbing IR lights in the activated carbon support, while no remarkable rise of temperature was observed for the use of the naked $TiO_2$ suspension. To examine the effect of temperature on the photodegradation rate, the $CO_2$ evolution was measured at two different temperatures of 25 °C and 40 °C. The experiments were carried out by circulating water of regulated temperature through a quartz cell in which the reaction cell was immersed. It was found that 40 °C gave a higher evolution rate of $CO_2$ than 25 °C. However, the activity difference at 40 °C between the naked $TiO_2$ and 80 wt%-loaded $TiO_2$/AC was smaller than that at 25 °C; The activity of the

$TiO_2$/AC was 6.5 times as great as that of the naked $TiO_2$ at 25 °C, while a 4.3 times activity difference was obtained at 40 °C. This seems to suggest that the effect of the activated carbon supports must appear more remarkably at lower temperatures.

To demonstrate further the utility of the activated carbon support for $TiO_2$ loading, photodecomposition of propyzamide to $CO_2$ was studied at 25 °C using the naked $TiO_2$ in the presence of dispersed activated carbon. As shown in Fig. 3, the reaction rate of the naked $TiO_2$ was increased by introducing the active carbon into the $TiO_2$ suspension, but the enhanement was not so great as that obtained at the 80 wt%-loaded $TiO_2$/AC, suggesting that activated carbon worked well as an effective adsorbate to concentrate propyzamide around the loaded $TiO_2$ photocatalysts. The adsorbed propyzamide seems to be supplied to the loaded $TiO_2$ photocatalyst mostly by surface diffusion.5) It is believed that the complete photodecomposition of propyzamide is achieved by several consecutive reactions, as in oxidative decomposition of other organic compounds.6) Studies to elucidate this point are currently in progress in our laboratory. It is concluded that the use of adsorbates as supports for semiconductor photocatalysts is very useful to enhance the apparent activities of the photocatalysts. The results shown here may open a new route for designing semiconductor photocatalysts for detoxification of pollutants of very dilute concentrations.

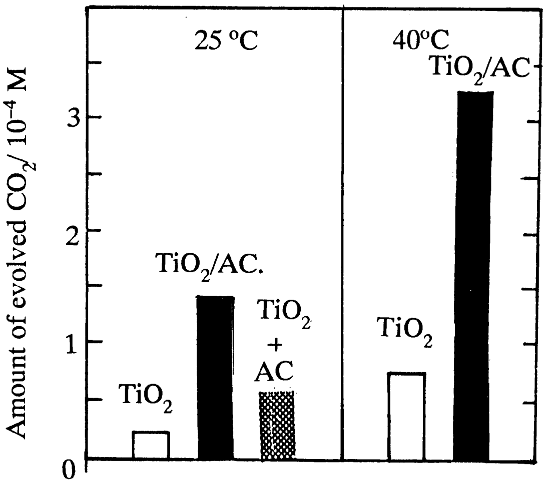

Fig. 3. Amount of $CO_2$ produced by illumination for 1 h at 25 °C and 40 °C. $TiO_2$/AC: 80 wt% loaded $TiO_2$ on AC, $TiO_2$ + AC: mixture of 80 wt% $TiO_2$ and AC. The amount of the catalyst suspended was 1 g $dm^{-3}$ including AC. Illumination time: 1 h.

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## Refeences

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