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Highly Efficient TiO_2 Film Photocatalyst. Degradation of Gaseous Acetaldehyde

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A glass-supported pure anatase film with an extremely high photocatalytic activity has been prepared. Photocatalytic properties of the film were investigated by measuring the degradation of gaseous acetaldehyde under relatively strong (black fluorescent light) and weak (white fluorescent light) UV light irradiations. It was found that the photocatalytic efficiency was higher than that of Degussa P25, one of the most efficient commercial TiO_2 powders.

It is well known that irradiation of a semiconductor with a light whose energy is greater than the band gap would give rise to a strong redox power that is capable of promoting a wide variety of chemical reactions.1) Starting with the photocatalytic splitting of water into hydrogen and oxygen in a photoelectrochemical cell,2) studies in this area have been of continuous interest. The applicabilities to a wide range of industrially valuable chemical processes have been suggested, including organic synthesis, photodestruction of toxic materials, purification of drinking water, and so on.

TiO_2 powder, particularly in anatase form, has been the most extensively employed in such photocatalytic reactions because of its high activity and chemical stability. Recently, several publications concerning the photodegradation of organic compounds by photoassisted TiO_2 films have also appeared.3-12) The film photocatalyst system has various practical benefits that are not attainable in the powder system : 1) the catalyst filtration step after photocatalysis of the organics is not necessary, and 2) measurement of the photocatalytic effect can be repeated. So, it is of a high technological importance that a TiO_2 film with high photoactivity can be prepared. We have recently reported that TiO_2 film coated on a ceramic tile showed a photocatalytic deodorizing reaction even under room light illumination.13)

This report presents an extraordinarily efficient TiO_2 film coated onto a glass substrate and its photocatalytic properties. The photoactivity was investigated in terms of the photodecomposition of gaseous acetaldehyde under various UV light intensities, and the results were then compared with that of one of the most active commercial TiO_2 powder catalysts.

The preparation of the TiO_2 thin film from sol was carried out according to the method that has been reported previously.[14,15] TiO_2 sol was prepared by the thermal hydrolysis of titanyl sulfate. To neutralize the adsorbed sulfuric acid, the resultant was treated with an alkali and washed until free of sulfates. The sol was then dispersed by adding concentrated nitric acid to give a titanic acid sol (Ishihara Sangyo Kaisha Ltd., trade mark CS-N). In order to obtain a sol that is better for preparing a film, this titanic acid sol was aged in an autoclave for 15 min at 180 °C. The transmission electron micrograph (TEM) of the sol is presented in Fig.1; the average diameter of each particle is ca. 20 nm. Finally, the TiO_2 sol was smeared onto a glass plate substrate (6 cm x 8 cm) followed by sintering in air at 450 °C for 30 min. The film thickness is ca. 10 μm and its scanning electron micrograph (SEM) is shown in Fig. 2. The film is rather porous and consists of small crystalline particles with a diameter of ca. 50 nm, i.e., the particles enlarged slightly during the heat treatment. The photocatalytic activity of this film was evaluated by measuring the concentration change of acetaldehyde as a function of irradiation time under black fluorescent light (BL) and regular white fluorescent light (FL) irradiations. The UV light (λ = 300 - 400 nm) fluxes of these lights were 1.80 and 0.12 mW/cm^2, respectively. Saturated gaseous acetaldehyde was injected into a 1 L ABS resin vessel, whose bottom was replaced with a silica glass plate (transmission 95% in the UV light, λ > 260 nm). The concentrations of gaseous acetaldehyde used were 3000 and 50 ppm for BL and FL radiations, respectively. The irradiations were conducted at room temperature after the equilibrium was reached between the gaseous and adsorbed acetaldehyde, which was indicated by a constant gaseous acetaldehyde concentration. The acetaldehyde concentration was measured using a gas chromatograph, Ohkura Model C-103 equipped with 2-m TCP Column and flame ionization detectors, with helium as the carrier gas. Similar experiments using commercial TiO_2 powder (Degussa P25, Nippon Aerosil Co.Ltd.) was also carried out. In this case, ca. 1.0 g of the powder was spread inside a glass Petri dish with a diameter of 8.5 cm, and it was placed in the reaction vessel described above. The photocatalytic activities of both catalysts were then compared.

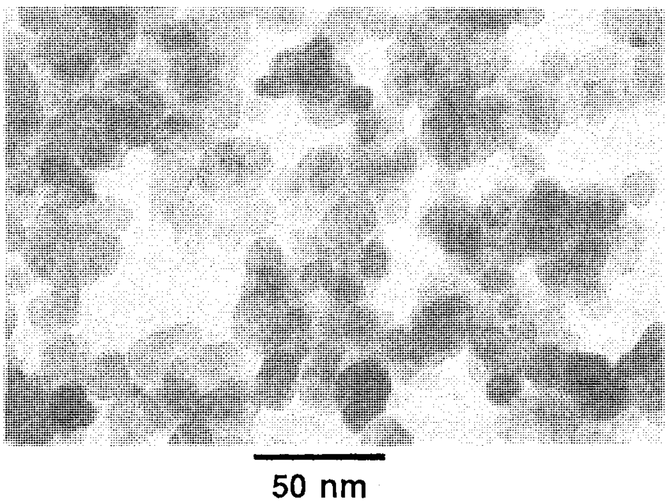

Fig. 1. The Transmission Electron Micrograph of TiO_2 Sol.

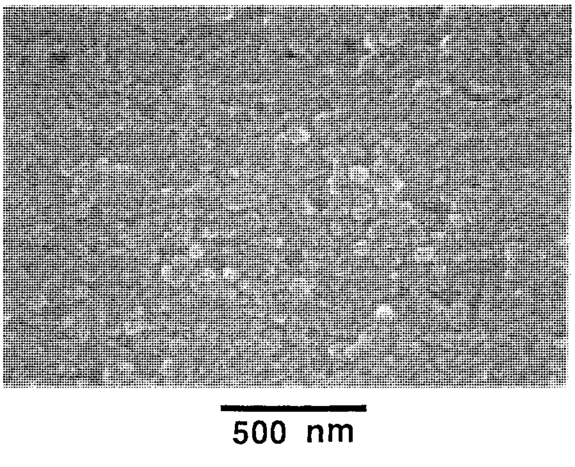

Fig. 2. The Scanning Electron Micrograph of TiO_2 Film.

Figure 3 shows the semilogarithmic plots of the change in the concentration of acetaldehyde as a function of irradiation time. Results for the photodegradation of acetaldehyde over both the thin film and P25 powder are shown. The initial concentration for each case was 3000 ppm, and BL was used for both experiments. Approximately, 30 - 50 min after the injection of saturated gas into the vessel, adsorption equilibrium was reached, and the irradiation was started. For both cases, the concentration change did not show an exponential decay as shown in the figure. This was probably because the initial concentration was too high as compared to the incident photon number so that the reaction initially proceeded with zero-order kinetics, i.e., light intensity - controlled kinetics. At low concentrations, the reaction obeyed mass transfer-controlled first-order kinetics. When the initial concentration was set at several hundreds ppm and BL light was used, an exponential concentration decrease was observed just after the irradiation. The first-order rate constant *k* was calculated from the data shown in Figure 3 by analyzing experimental points at low concentrations by means of a linear least-square fit. The results are indicated as the dashed line in each plot. On the other hand, the apparent quantum yield (QY) was evaluated from the initial decomposition rate (nearly zero-order kinetics region). If the number of molecules is much larger than the number of photon, acetaldehyde is oxidized only to CH_3COOH,

$$CH_3CHO + H_2O + 2\,h^+ \longrightarrow CH_3COOH + 2\,H^+ \qquad (1)$$

In this case the apparent quantum yield is calculated by the following equation.

$$QY = 2 \times (\text{ number of acetaldehyde molecules degraded }) / (\text{ number of incident photons }) \qquad (2)$$

However, when the number of the holes produced in TiO_2 is much larger than the number of acetaldehyde molecules adsorbed on the surface, acetaldehyde is oxidized completely to CO_2 as follows,

$$CH_3CHO + 3\,H_2O + 10\,h^+ \longrightarrow 2\,CO_2 + 10\,H^+ \qquad (3)$$

Both CH_3COOH and CO_2 were detected as reaction products. Since 10 holes are consumed in reaction (3) as compared to the 2 holes in reaction (1), the values calculated using equation (2) are lower than the true ones.

Table 1 lists the first-order rate constant *k* and the quantum yield for the photodegradation over both catalysts with 3000 and 50 ppm initial acetaldehyde concentrations under black and white fluorescent light irradiations. It can be confirmed from this table that the film coated on the substrate exhibits a very high photocatalytic activity; it is higher in both *k* and QY values than the P-25 powders. This result is rather surprising, because the number of reaction site is thought to be smaller on a film than on powders.

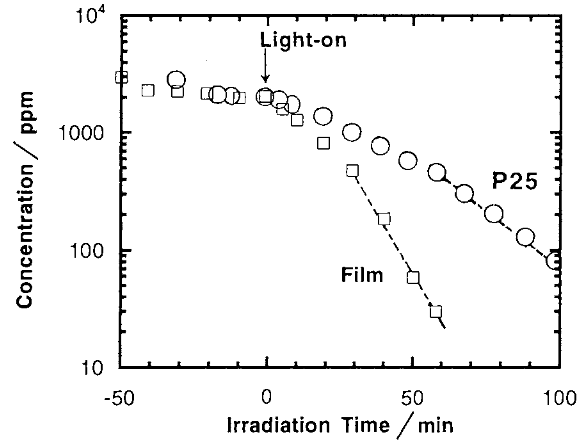

Fig. 3. The Plots of the Change in Concentration vs Radiation Time on the Photodegradation of Acetaldehyde under BL Radiation.

The photocatalytic reaction yield reached nearly maximum in the present system. It was also shown that the photooxidative decomposition of several tens of ppm of gaseous acetaldehyde proceeded efficiently even by very weak UV light contained in a regular fluorescent light. These concentrations are much higher than the detection limit of human smell sense. Therefore, the present results suggest that the TiO_2 film system can be applied as a new efficient technique for air purification.

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Table 1. First-Order Rate Constants (k) and Quantum Yields (QY) of Acetaldehyde Photodegradation over the TiO_2 Thin Film and P25 Powder Catalysts[a)]

Light Source	UV Intensity	Acetaldehyde Conc.	Thin Film		P25 Powder	
	mW/cm^2	ppm	$k/x10^{-3}$ min^{-1}	QY /%	$k/x10^{-3}$ min^{-1}	QY /%
Black fluorescent light	1.80	3000	1.37	28.9	0.81	19.3
White fluorescent light	0.12	50	0.51	7.6	0.41	3.2

a) Rate constants were calculated for the catalyst surface area of 1 cm^2.

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