

Photocatalytic Degradation of Gaseous Formaldehyde Using TiO₂ Film

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The photocatalytic degradation of gaseous formaldehyde—a major cause of sick building syndrome—was studied using a TiO₂ thin film. TiO₂ thin films have many unique photoinduced properties, for example, self-cleaning, anti-fouling, and anti-bacterial functions. UV illumination of the TiO₂ thin film placed in a gaseous formaldehyde/air environment resulted in the total mineralization of formaldehyde to CO₂ and H₂O. We invoked a Langmuir–Hinshelwood kinetic model to analyze the dependence of reaction rates on the concentration of formaldehyde. In addition, the overall decomposition rate constant for formaldehyde was comparable to that of acetaldehyde (a standard test reactant) for initial concentrations of up to 1000 ppmv. However, the apparent adsorption constant K_{app} of formaldehyde onto TiO₂ was ca. 2.5 times larger than that of acetaldehyde. Thus in the low concentration regime, the reactivity of formaldehyde appeared to be greater than that of acetaldehyde. In like manner, a dark adsorption experiment also showed the high adsorption capacity of TiO₂ for formaldehyde. Therefore, we conclude that TiO₂ serves as both a good adsorbent and a photocatalyst for the elimination of gaseous formaldehyde.

Introduction

Much work has been done in recent years on the photocatalytic treatment of environmental pollutants found in the gas phase for possible application to decontamination, purification, and deodorization of the atmospheres (1–9). In addition, new TiO₂-based self-cleaning materials such as TiO₂-coated glass (10–13), tile, paper (14), etc. have been developed or are under development. One of the possible targets for these materials is the elimination of indoor air pollution, for example, the destruction of formaldehyde. This is because the intensity of ultraviolet (UV) light in a typical indoor environment is considered to be adequate for the

decomposition of very low concentrations of pollutants (15, 16). Formaldehyde is one of the major sources of indoor air pollution. Formaldehyde is an irritant that produces allergic symptoms at very low levels, and it is also a carcinogen. In recent years, formaldehyde emission from building renovations (new carpets, painting, etc.) is considered to be one of the major causes of the problem known as “sick building syndrome”. This condition is characterized by drowsiness, headaches, sore throats, and mental fatigue in many occupants of modern office buildings, shopping centers, schools, and newly built houses (17). We report herein a study of the TiO₂-mediated photodecomposition of formaldehyde in the gas phase. The decomposition of acetaldehyde photocatalyzed by TiO₂ was used as a standard test reaction (13) for the evaluation of the efficiency of the TiO₂ thin film photocatalyst.

Experimental Section

The TiO₂ thin film on soda lime glass was prepared from a STS-21 sol (40 wt % anatase TiO₂, pH 8.5, 20 nm particle diameter, 50 m² g⁻¹ surface area) by a spin coating method (18). The sol was obtained from Ishihara Sangyo Co. After being spin coated, the film was calcined at 450 °C for 1 h. The thickness of the translucent anatase TiO₂ film was ca. 1.7 μm.

All photodecomposition experiments were conducted at room temperature using a sealed Pyrex glass photocatalytic reaction vessel (500 cm³). The TiO₂ thin film (3 × 3 cm²) was placed at the bottom of the reaction vessel, and an appropriate concentration of formaldehyde (prepared by heating paraformaldehyde) or acetaldehyde was injected into the vessel. Typical initial reactant concentrations were in the range of 30–2000 ppmv (parts per million by volume). After adsorption equilibrium was attained (approximately 1 h), UV light from a Hg–Xe lamp (Hayashi Tokei, Luminar Ace 210) passed through a 365-nm band-pass filter was irradiated onto the TiO₂ film through a transparent silica plate window. The UV light that uniformly illuminated the whole area of the TiO₂ film was transferred from the light source using a 1-m fiber light pipe. The UV light intensity at the film surface was approximately 1.0 mW/cm² (measured by a UV intensity meter: TOPCON UVR-1). The photodecomposition processes were followed by gas chromatography [Shimadzu GC-8A equipped with a 2 m Porapak-Q column and a flame ionization detector (FID)]. N₂ was used as the carrier gas. Due to the lack of response of the FID to formaldehyde and CO₂, an additional methanizer (Shimadzu MTN-1 loaded with reduced shimalite-Ni catalyst) that reduces formaldehyde to methanol (HCHO + H₂ → CH₃OH) and CO₂ and/or CO to methane (CO₂ + 4H₂ → CH₄ + 2H₂O) was attached to the GC system between the column and the detector. The experimental error in the determination of formaldehyde and CO₂ was approximately 5%, respectively. Residual byproducts that remained on the TiO₂ surface were extracted with a 0.01 M NaOH aqueous solution and were measured using a liquid chromatograph (Toyosoda HPLC system with a UV-8010 optical detector and a Shodex Ionpak KC-811 column).

Results and Discussion

Typical results for the photodecomposition of formaldehyde (280 ppmv) are shown in Figure 1. The decomposition reaction was initiated by UV illumination of the TiO₂ film. As the initial concentration of formaldehyde decreased, a parallel increase in the concentration of CO₂ was observed. There were no traces of formaldehyde (in the photoreactor)

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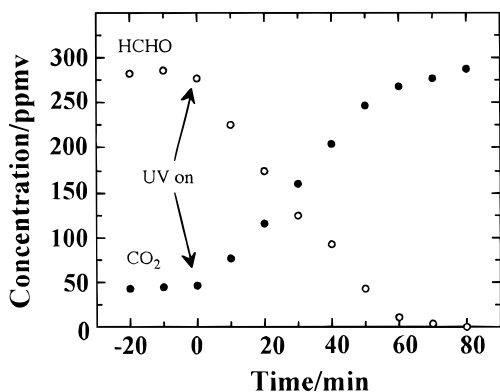


FIGURE 1. Plot of concentration versus irradiation time for the degradation of formaldehyde photocatalyzed by a TiO_2 film. Open circles (○) represent the disappearance of formaldehyde whereas filled circles (●) show the evolution of CO_2 with reaction time, respectively. Reaction conditions were as follows: initial concentration of formaldehyde, ca. 280 ppmv, incident light intensity, $I = 1.0 \text{ mW cm}^{-2}$; temperature, $\approx 22^\circ\text{C}$; and relative humidity, 40%.

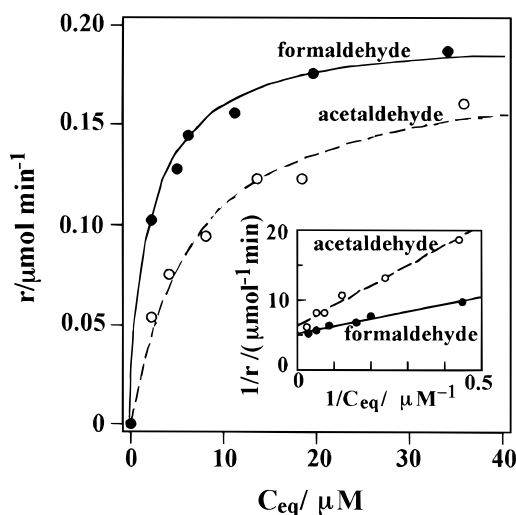


FIGURE 2. Dependence of reaction rates on the initial reactant concentrations. Open circles (○) represent acetaldehyde whereas the filled circles (●) represent formaldehyde. The reaction rates were calculated within 10 min of reaction. The initial concentration of formaldehyde and acetaldehyde was varied from 30 to 2000 ppmv, respectively, under otherwise standard reaction conditions, i.e., $I = 1.0 \text{ mW cm}^{-2}$; temperature, $\approx 22^\circ\text{C}$; and relative humidity, 40%. The inset shows the reciprocal plot of eq 1. The following data were extracted from the least-squares fit of the curves: (a) formaldehyde, intercept = $5.3 \mu\text{mol min}^{-1}$, slope = $10.3 \text{ dm}^{-3} \text{ min}^{-1}$, and $r = 0.986$; (b) acetaldehyde, intercept = $6.2 \mu\text{mol min}^{-1}$, slope = $28.9 \text{ dm}^{-3} \text{ min}^{-1}$, and $r = 0.992$. These data were used to estimate the surface rate constant k and the apparent adsorption coefficient K_{app} for the respective compounds on TiO_2 (see text for details).

after about 80 min reaction. Accordingly, the expected stoichiometric CO_2 concentration was generated.

Next, we investigated the influence of initial reactant concentration on the rate of decomposition of formaldehyde. Furthermore, we compared the rate of decomposition of formaldehyde with that of a standard test reactant, acetaldehyde (13), using the same TiO_2 film sample. In Figure 2 the dependence of initial decomposition rates on the initial gas concentrations for formaldehyde and acetaldehyde are presented. It is evident that formaldehyde decomposed faster than acetaldehyde in the low concentration region. To analyze these differences in detail, we used a Langmuir–Hinshelwood (L–H) kinetic model. The L–H model has been shown to provide a quantitative kinetics treatment of many

TABLE 1. Product Distribution at about 75% Reaction during the Photodegradation of Formaldehyde and Acetaldehyde Mediated by a TiO_2 Film, Respectively^a

	product (%)			
	CO_2	HCOOH	CH_3COOH	others
HCHO	80	20		
CH_3CHO	50	20	25	5

^a Reaction conditions as outlined in Figure 1.

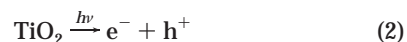
solid–gas-phase reactions (19). The rate r of a unimolecular surface reaction will obey the following equation:

$$r = \frac{kK_{\text{app}}C_{\text{eq}}}{1 + kK_{\text{app}}C_{\text{eq}}} \quad (1)$$

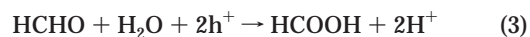
where k is the surface rate constant, K_{app} is the apparent adsorption coefficient, and C_{eq} is the reactant equilibrium concentration. By fitting plots of Figure 2 to the linear form of eq 1 as shown in the inset in Figure 2, we obtained k values of 0.19 and $0.16 \mu\text{mol min}^{-1}$ and K_{app} values of 0.51 and $0.21 \mu\text{mol dm}^{-3}$ for formaldehyde and acetaldehyde, respectively. The calculated results emphasize the differences in K_{app} values which are related to the adsorption strength of each compound onto TiO_2 . On the contrary, there are no remarkable differences in k values that directly correspond to the reactivity of each compound. These results suggest that the differences in decomposition rates in the low concentration region between formaldehyde and acetaldehyde can be attributed to the differences in adsorption strength. That is, in the low reactant concentration region, the reaction kinetics is “mass-transfer limited”. Mass transfer is increased for higher K_{app} values because the driving force for mass transfer from the air to the solid surface is greater. As a result, formaldehyde decomposition in the low concentration region proceeds faster than the decomposition of acetaldehyde due to its greater adsorption onto TiO_2 promoted by a higher adsorption strength (20).

Although CO_2 is the final oxidation product, intermediates and/or byproducts are however generated. Byproducts were extracted from the TiO_2 surface by aqueous NaOH solution, and the extracts were analyzed by HPLC. The product distribution in the photocatalytic reactions of formaldehyde and acetaldehyde at ca. 75% reaction are shown in Table 1. Formic acid in the case of formaldehyde and acetic acid, formic acid, etc. in the case of acetaldehyde remained on the TiO_2 surface as partial oxidation byproducts. Nevertheless, with prolonged UV illumination, all of the intermediates and byproducts were oxidized to CO_2 .

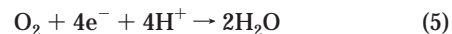
The major oxidative and reductive processes in the photodegradation of formaldehyde can be written as follows (1, 21):



oxidation



reduction



Thus, the complete oxidation of one formaldehyde molecule to CO_2 requires four holes stoichiometrically. Furthermore, we estimated the apparent quantum yield ($\phi_{\text{app}} = [4 \text{ mol of HCHO degraded}] / [\text{incident photons (365 nm)}]$) for the

TABLE 2. Adsorption Constants (K) and Maximum Adsorption Quantities per Unit Surface Area (Q_m) for the Dark Adsorption of Formaldehyde^a

	P25	activated carbon
K (μM^{-1})	0.57	0.11
Q_m ($\mu\text{mol m}^{-2}$)	5.0	2.0

^a Dark adsorption experiments were conducted at room temperature using the same vessel used in the photodegradation experiments. The powder form of TiO_2 (Degussa P25, surface area: $50 \text{ m}^2/\text{g}$) and activated carbon (surface area: $700 \text{ m}^2/\text{g}$) were used as adsorbents.

decomposition of formaldehyde based on the initial decrease of formaldehyde concentration shown in Figure 1. ϕ_{app} was ca. 27%.

We also performed dark adsorption experiments to determine the adsorption capacity of TiO_2 for formaldehyde. Compared to a familiar adsorbent (activated carbon), TiO_2 powder (Degussa P25) showed a high adsorption affinity for formaldehyde as shown in Table 2. Moreover, in terms of unit surface area, P25 even surpassed the adsorption capacity of activated carbon.

In summary, we have demonstrated that formaldehyde can be efficiently photooxidized to CO_2 on a TiO_2 thin film photocatalyst. In the concentration range we investigated, our findings suggest that the rate of photooxidation of formaldehyde is greater than that of acetaldehyde in the low concentration region. This phenomenon is attributed to the higher adsorption capacity of TiO_2 for formaldehyde. Interestingly, TiO_2 also shows a greater adsorption capacity for formaldehyde as compared to a conventional adsorbent, activated carbon.

Acknowledgments

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