



# Photocatalytic decompositions of gaseous HCHO over thin films of anatase titanium oxide converted from amorphous in a heated air and in an aqueous solution of hydrogen peroxide

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## ABSTRACT

This work investigates photocatalytic decompositions of HCHO in air over thin films of titanium oxide prepared on inside surfaces of glass tubes by the following two methods: Method I (the inside surface of a glass tube was covered with an aqueous H<sub>2</sub>O<sub>2</sub> solution containing amorphous titanium oxide, followed by calcination at 500 °C to convert amorphous titanium oxide to anatase one) and Method II (the inside surface of a glass tube was covered with an aqueous H<sub>2</sub>O<sub>2</sub> solution containing anatase titanium oxide, followed by heating at 100 °C). All the experiments were conducted in a photocatalytic reactor with a parallel array of nine light sources. It is found that there is no remarkable difference between the permeabilities of UV light through glass tube walls coated with the photocatalyst films, although the photocatalyst film prepared by Method I is more transparent than that by Method II. As previously observed with the photocatalyst film prepared by Method I, therefore, the photocatalyst film by Method II is found to increase the rate of decomposition of HCHO as a result of action of the UV light emitted from the light source in a given glass tube on the photocatalyst films that coat adjacent glass tubes. Observation by SEM reveals that the photocatalyst film prepared by Method I has a very smooth surface, whereas that by Method II has a rugged one. This is because anatase titanium oxide particles prepared by Method II possesses much larger crystal sizes and is therefore estimated to have a very large specific surface area. As a result, the photocatalytic reactor equipped with the photocatalyst glass tubes prepared by Method II is found to rapidly decompose HCHO especially in the region of its high concentration and also even when the humidity is very high. Kinetic analyses indicate that the photocatalytic decompositions of HCHO on the titanium oxide films prepared by the two methods obey Langmuir–Hinshelwood type kinetics. It is also found that the rate constant for Method II is 53 times larger than that for Method I, implying that the higher activity for Method II is due to its larger specific surface area.

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## 1. Introduction

The indoor air contains various volatile organic compounds (VOCs), usually on the order of parts per billion in volume (ppbv) [1]. A long-term exposure to VOCs at such very low concentrations gradually threatens human health. Formaldehyde (HCHO) is one of the typical VOC compounds causing this problem. Therefore, various approaches to photocatalytically decompose HCHO have been studied [2–15].

In general, it is not easy to photocatalytically decompose VOCs at such a low concentration level because a large film diffusional resistance in the neighborhood of photocatalyst surface interferes

significantly with further photocatalytic decompositions of VOCs to their lower concentrations [14]. To solve this problem, the authors [13,15] previously developed a photocatalytic reactor with a parallel array of nine 6-W blacklight blue fluorescent lamps. Experimental results revealed that this reactor can quickly and certainly decompose trace HCHO in air toward a zero concentration. To treat a large amount of air, furthermore, this reactor was coupled with a continuous adsorption-and-desorption concentrator [12,13,16]. The air purifier thus developed was found to be capable of decreasing the concentration of trace HCHO in 10 m<sup>3</sup> air to the WHO guideline of 80 ppbv within 10 min.

It is reasonable to even more increase the performance of the air purifier by enhancing the decomposition activity of the photocatalytic reactor. So far, the authors have used a coating solution prepared by dissolving amorphous titanium oxide in an aqueous solution of H<sub>2</sub>O<sub>2</sub> in order to coat the inside surface of a glass tube

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with a transparent thin film of anatase titanium oxide [17]. In this case, the glass tube covered with the coating solution was heated for 1 h at 500 °C to convert amorphous titanium oxide to anatase one (Method I). On the other hand, such a conversion can be made by heating the above coating solution in a boiling water bath [18]. Therefore, if this coating solution is employed, it may be possible to readily coat the surface of a glass tube with a thin film of anatase titanium oxide by heating at a lower temperature, around 100 °C (Method II).

The present work elucidates both experimentally and theoretically the performance of such a thin film of anatase titanium oxide prepared on the inside surface of a glass tube by Method II. A comparison is made between decompositions of HCHO in photocatalytic reactors equipped with nine glass tubes whose inside surfaces are coated with photocatalyst films by the above two methods.

In the present work, the HCHO concentration will be expressed by the unit of  $\text{mg m}^{-3}$  instead of the unit of parts per million in volume (ppmv); conversion factors from ppmv to  $\text{mg m}^{-3}$  are 1.2 and 0.81, respectively, at 20 °C.

## 2. Theory

Let us consider the oxidative decomposition of HCHO in air in a closed room by use of a photocatalytic reactor with a parallel array of nine light sources. Titanium oxide irradiated with UV light decomposes HCHO according to the following mechanism;  $\text{HCHO} \rightarrow \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  [19]. In our reactor with a parallel array of nine light sources, however, HCHO was instantaneously decomposed to carbon dioxide and water hardly producing formic acid [14]. In general, the photocatalytic decomposition obeys Langmuir–Hinshelwood kinetics [20–27]. When air of the volume  $V$  ( $\text{m}^3$ ) containing HCHO at the initial concentration  $C_0$  ( $\text{mg m}^{-3}$  air) is treated in the photocatalytic reactor equipped with glass tubes of the total photocatalyst geometric surface area  $S$  ( $\text{m}^2$ ), the rate of decomposition of HCHO  $\nu$  ( $\text{mg m}^{-3}\text{-air min}^{-1}$ ) is expressed by

$$\nu = -\frac{dC}{dt} = \alpha \frac{k K_H C}{1 + K_H C} \quad (1)$$

with the initial condition:

$$C = C_0 \text{ at } t = 0$$

where  $C$  is the HCHO concentration ( $\text{mg m}^{-3}$  air) at a given time  $t$  (min),  $k$  the rate constant ( $\text{mg m}^{-2} \text{cat min}^{-1}$ ),  $K_H$  the adsorption equilibrium constant ( $\text{mg}^{-1} \text{m}^3 \text{air}$ ), and  $\alpha$  ( $=S/V$ ) is the ratio of the geometric surface area of catalyst  $S$  to the air volume  $V$  ( $\text{m}^2 \text{cat m}^{-3} \text{air}$ ). The air is allowed to flow through an annulus in each glass tube at a linear velocity that is sufficiently high to offer a reaction condition of negligible film-diffusional resistance. Numerical solution to Eq. (1) gives a time course of HCHO concentration. For this calculation, it is necessary to experimentally determine the kinetic parameters,  $k$  and  $K_H$ , in Eq. (1). Therefore, the initial rates of decomposition  $\nu_0$  must be measured for various initial reactant concentrations and the measured values must then be applied to the following linearized equation.

$$\frac{C_0}{\nu_0} = \frac{1}{\alpha} \left( \frac{1}{k K_H} + \frac{1}{k} C_0 \right) \quad (2)$$

Consequently, the slope and intercept of this linearized plot gives the kinetic parameters.

## 3. Experimental method

### 3.1. Materials

Titanium tetraisopropoxide (TIP) was purchased from Katayama Chemicals, Co., Ltd. (Osaka, Japan). Amorphous titanium oxide prepared according to the procedure described elsewhere [17,28,29] was dissolved in a 31% aqueous solution of HCHO (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Pyrex glass tubes of 28 mm in inside diameter, 210-mm long, and 2 mm in wall thickness were used as a support. Nine 6-W blacklight blue fluorescent lamps with wavelengths of 300–380 nm (FL6BL-B; Matsushita Electric Industrial Co., Ltd., Osaka) were used as a light source. The HCHO concentration was determined by use of a commercially available analytical reagent (Formaldehyde Test Wako, Wako Pure Chemical Industries, Ltd., Osaka, Japan).

### 3.2. Preparation of coating solutions

#### 3.2.1. Coating solution I

Mixing of 29.69 g of TIP in 31.39 g of isopropanol (IPA), at a molar ratio of 1:5, was carried out for 2 h at 5 °C. A mixture of 7.53 g of ultrapure water and 31.39 g of IPA was gently poured into this solution under vigorous mixing and the resulting solution at a molar ratio of 1:10:4 for TIP:IPA:H<sub>2</sub>O was further mixed for 4 h at 5 °C. A white cake of amorphous titanium oxide was collected by suction filtration and dried for 5 h at 100 °C. This cake was broken into fine powder and further dried for 15 h at 100 °C. The resulting amorphous titanium oxide powder was stored in a desiccator until used.

After dissolving 0.5 g of amorphous titanium oxide powder in 10 mL of a 31% aqueous solution of H<sub>2</sub>O<sub>2</sub>, the resulting solution was well-mixed for 2 h at a room temperature and kept stationary for 1 h to form a gel. This gel was re-dissolved by addition of 60 mL of a 31% aqueous solution of H<sub>2</sub>O<sub>2</sub>. The solution thus obtained was constantly mixed for 50–60 h at a room temperature until foaming stopped. As a result, a yellow-colored transparent solution containing amorphous titanium oxide fine particles was obtained (Fig. 1). This solution, referred to as *coating solution I*, gradually gelled with time. Prior to using for coating, the gel was dissolved by addition of a small amount of aqueous solution of H<sub>2</sub>O<sub>2</sub>.

#### 3.2.2. Coating solution II

A pH value of the coating solution I was adjusted to 4.0 by addition of a small amount of ammonium solution. This solution was

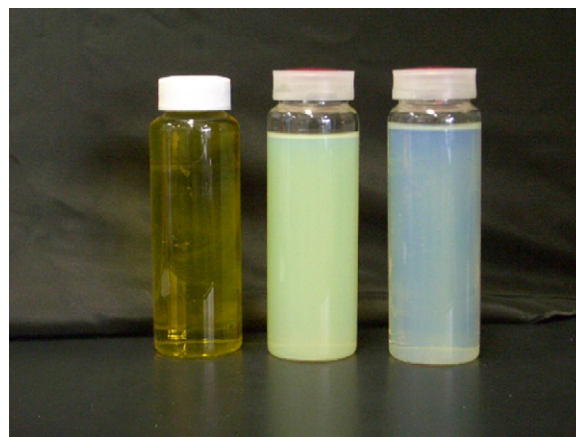


Fig. 1. Aqueous H<sub>2</sub>O<sub>2</sub> solutions containing titanium oxide fine particles. Percentage of conversion of amorphous titanium oxide into anatase: left, 0%; middle, about 50%; right, about 100%.

kept in a boiling water bath for 9 h to convert amorphous titanium oxide to anatase one. In this treatment, the color of the solution turned from light yellow toward white according to the anatase crystallinity of titanium oxide (Fig. 1). The coating solution thus prepared, referred to as *coating solution II*, was stable at a room temperature at least for 1 month, whereas the coating solution I was stored in a refrigerator until used.

### 3.3. Coating of a glass tube surface with a thin film of titanium oxide

#### 3.3.1. Method I

Glass tubes were ultrasonically washed in an IPA solution. The coating solution I was poured into the glass tubes to cover their inside surfaces with the solution. The glass tubes were inclined for a while to remove an excess solution from their surfaces and then calcined for 1 h at 400 °C. After repeating the same procedure four times, the glass tubes were again covered with the solution and calcined for 1 h at 500 °C. Consequently, the glass tubes coated with a transparent thin film of anatase titanium oxide were obtained. The experimental proof that this coating method provides anatase form is available elsewhere [30,31].

#### 3.3.2. Method II

As in Method I, glass tubes were ultrasonically washed in an IPA solution and their inside surfaces were covered with the coating solution II. After removal of an extra coating solution, the glass tubes were kept in a dryer at 100 °C for 30 min. The same procedure was repeated five times. Consequently, the glass tubes coated with a thin film of anatase titanium oxide were obtained. The experimental proof that this coating method provides anatase form is available elsewhere [18].

### 3.4. Photocatalytic reactor and its operational method

A 6-W blacklight blue fluorescent lamp was inserted and fixed in each of nine glass tubes coated with titanium oxide (the total photocatalyst geometric surface area  $S = 0.166 \text{ m}^2 \text{ cat}$ ). These glass tubes with lamps were arranged in parallel in three lines and three rows and an electric fan was fixed above their arrangement. This photocatalytic reactor was placed in a closed 1- or 10- $\text{m}^3$  room covered with transparent vinyl chloride sheets (Fig. 2). The room air was vigorously agitated using two electric fans. A fixed amount of aqueous solution of HCHO was dropped on an electrically heated plate and evaporated instantaneously. The room air was sampled after 2 min to determine the initial concentration of HCHO. Immediately, every

light source in the photocatalytic reactor was switched-on to start the reaction. The air that entered the reactor from its bottom was allowed to flow up through an annulus in each glass tube at a linear velocity above  $709 \text{ m min}^{-1}$  [15], so that HCHO was decomposed on the titanium oxide film excited by UV irradiation, in the absence of diffusional resistance. At time intervals, a small amount of air was sampled to determine the time course of HCHO concentration.

### 3.5. Analytical method

To accurately measure the HCHO concentration at a level of ppbv, air was bubbled into distilled water to trap HCHO. The water containing HCHO was colored using a coloring reagent based on the AHMT (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) method [32] and its absorbance was measured with a spectrophotometer at 550 nm to determine the HCHO concentration. The detailed procedure for this analytical method is described elsewhere [14].

### 3.6. Measurement of permeabilities of UV light through glass tube wall coated with titanium oxide films

Permeabilities of UV light through the glass tube walls coated with titanium oxide films by Methods I and II were determined as follows. A glass tube, wherein a 6-W blacklight blue fluorescent lamp was inserted, was fixed horizontally at a height of about 20 cm. The head of a cylindrical sensor connected to a spectro multi-channel photo detector (MCPD-3000; Otsuka Electronics Co., Ltd., Tokyo, Japan) was fixed close to the outer surface of the glass tube. This whole apparatus was covered with a box to shade the light from outside. The blacklight blue fluorescent lamps were switched-on, followed by the detector. A distribution of UV intensity per unit surface area over a wavelength range of 300–400 nm was measured just after UV light permeated through the glass tube wall and its maximum value at 350 nm was used as a representative value.

## 4. Results and discussion

### 4.1. Observation of photocatalyst films on glass tube surfaces

Fig. 3 shows photographs of the glass tubes coated with titanium oxide films by Methods I and II. The glass tube preparation by Method I is almost transparent, whereas the glass tube preparation by Method II somewhat lacks transparency. Our previous work [15] revealed that the decomposition activity of the photocatalytic

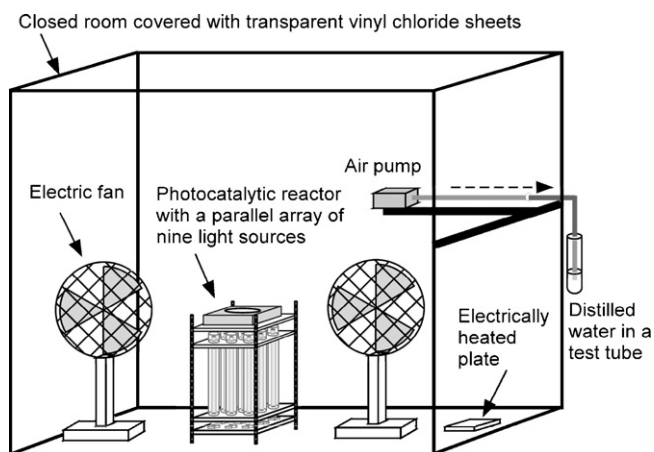


Fig. 2. Experimental system.

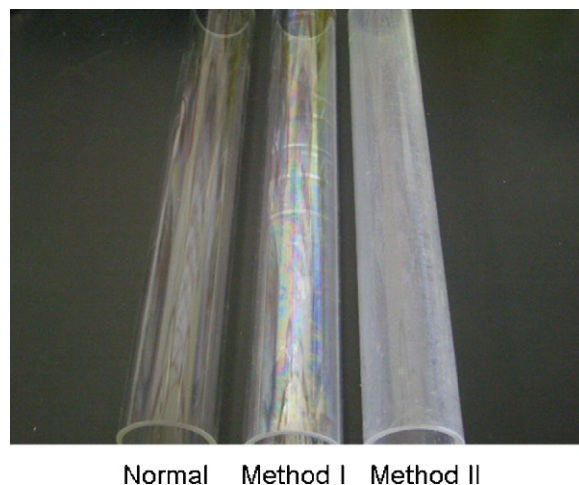


Fig. 3. Glass tubes coated with a thin film of titanium oxide by Methods I and II: (left) not coated; (middle) coated by Method I; (right) coated by Method II.

**Table 1**

A comparison between UV permeabilities of glass tube walls with and without being coated with a thin film of titanium oxide by Methods I and II

	Without being coated	With being coated	
		Method I	Method II
UV intensity ( $\mu\text{W}/\text{cm}^2$ )	221.1	195.8	199.5
Permeability (%)	100	88.5	90.3

reactor with a parallel array of light sources is enhanced by action of the UV light emitted from a light source in a given glass tube on the photocatalyst films of adjacent glass tubes. Obviously, such an enhancement occurs when the glass tube coated with titanium oxide has a high UV permeability. Therefore, UV permeabilities of the glass tube preparations by Methods I and II are compared in Table 1, where the permeability is defined as a ratio of the UV intensities for the glass tubes coated and not coated with titanium oxide. There is no marked difference between the UV permeabilities of the two glass tube preparations. Therefore, it is considered that the glass tube preparation by Method II also has an increase in the decomposition activity by neighboring light sources, as does the glass tube preparation by Method I. In fact, as is described later using experimental data, the photocatalytic reactors equipped with the glass tube preparations by Methods I and II provided almost the same decomposition activity.

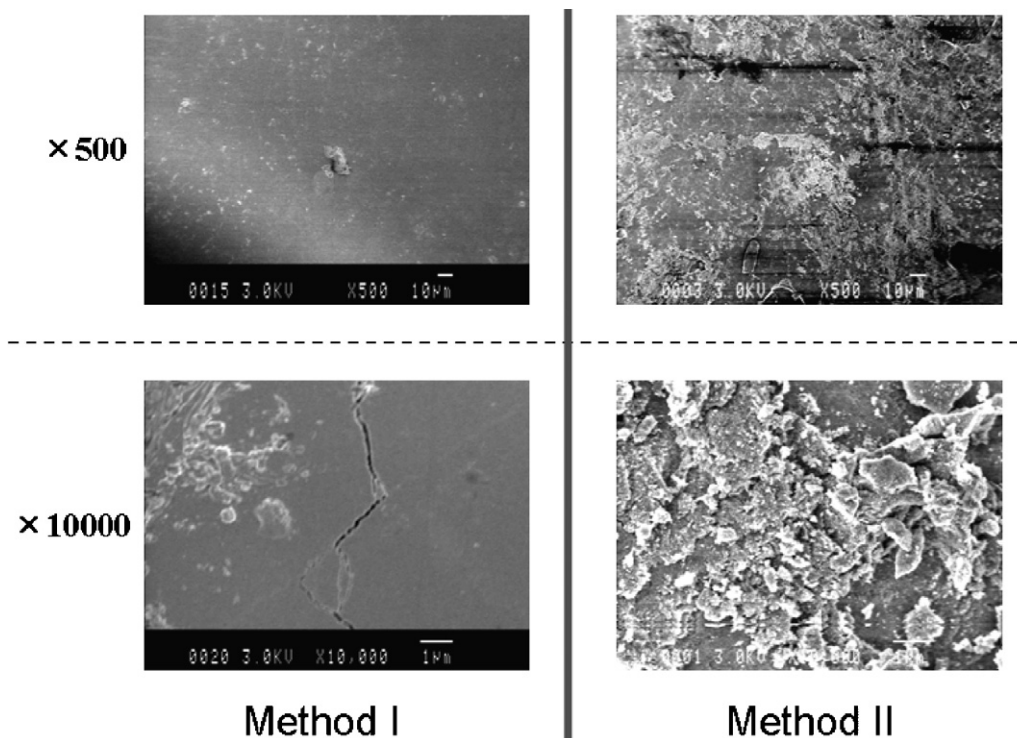
Fig. 4 shows SEM photographs of the thin films of titanium oxide coated on the glass tube surfaces by Methods I and II. There is obviously a remarkable difference between the features of the photocatalyst films prepared by Methods I and II. The photocatalyst film prepared by Method I has a very smooth surface, whereas that by Method II has a rugged one because of much larger sizes of anatase crystal particles. In Method I, amorphous titanium oxide fine particles (about 10 nm in average diameter) dissolved in an aqueous solution of  $\text{H}_2\text{O}_2$  are rapidly converted to anatase on the glass tube surface by calcination at  $500^\circ\text{C}$ . Therefore, the sizes of

anatase crystal particles do not increase. In Method II, on the other hand, amorphous titanium oxide particles in an aqueous solution of  $\text{H}_2\text{O}_2$  are slowly converted to anatase by heating in a boiling water bath for 9 h. As a result, the sizes of anatase crystal particles increase and the coating solution II gets cloudy. When this coating solution is used, therefore, such large sizes of anatase titanium oxide particles (above  $1\ \mu\text{m}$ ) form a rugged film on the glass tube surface. From the SEM photographs, it can be estimated that the titanium oxide film prepared by Method II has an overwhelmingly large specific surface area compared to that prepared by Method I.

#### 4.2. Decomposition of HCHO in air

Fig. 5 compares the time courses of HCHO concentration in decompositions of HCHO at low and high initial concentrations of  $0.65\text{--}1.3$  and  $4.0\text{--}24\ \text{mg m}^{-3}$ , respectively, in an  $1\ \text{m}^3$  room by use of the photocatalytic reactors equipped with glass tube preparations by Methods I and II. At such low and high initial HCHO concentrations, the photocatalyst film prepared by Method II decomposes HCHO more promptly than does the photocatalyst film by Method I. This difference is significant in the high concentration region of HCHO. For example, the photocatalyst film by Method II decomposes HCHO at an initial concentration of  $25\ \text{mg m}^{-3}$  to the WHO guideline ( $0.1\ \text{mg m}^{-3}$ ) in 60 min. On the other hand, the photocatalyst film by Method I spends 3 h on reducing the HCHO concentration from 25 to  $10\ \text{mg m}^{-3}$  at most.

The initial rate of decomposition of HCHO,  $\nu_0$ , is useful to efficiently understand an effect of initial HCHO concentration,  $C_0$ , on the rate of the photocatalytic decomposition. In the Langmuir–Hinshelwood equation,  $\nu_0$  increases linearly in the region of low  $C_0$  and levels off at the value of  $k$  in the region of large  $C_0$ . Fig. 6 shows plots of the initial rates of decomposition of HCHO calculated from experimental data in Fig. 5 against the initial concentrations of HCHO. With the photocatalyst film prepared by Method I, the initial rate of decomposition of HCHO



**Fig. 4.** SEM photographs of thin films of titanium oxide prepared on glass tube surfaces by Methods I (left column) and II (right column). The upper and lower photographs were taken at  $500\times$  and  $10,000\times$  magnifications, respectively.

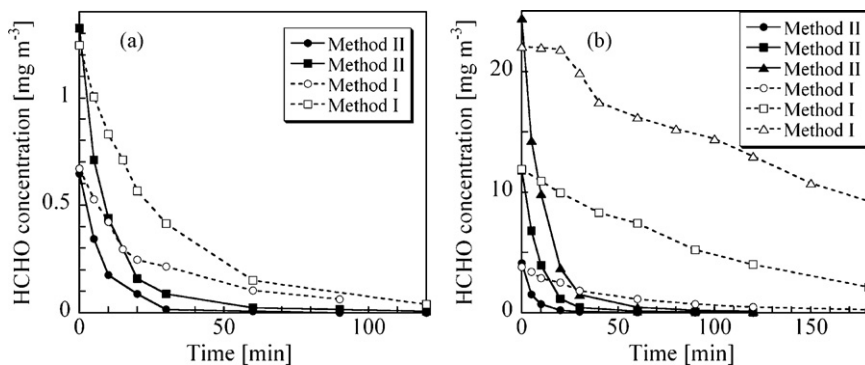


Fig. 5. Time courses of HCHO concentrations in decompositions of HCHO in  $1 \text{ m}^3$  air by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by Methods I and II in regions of (a) low initial concentration and (b) high initial concentration.

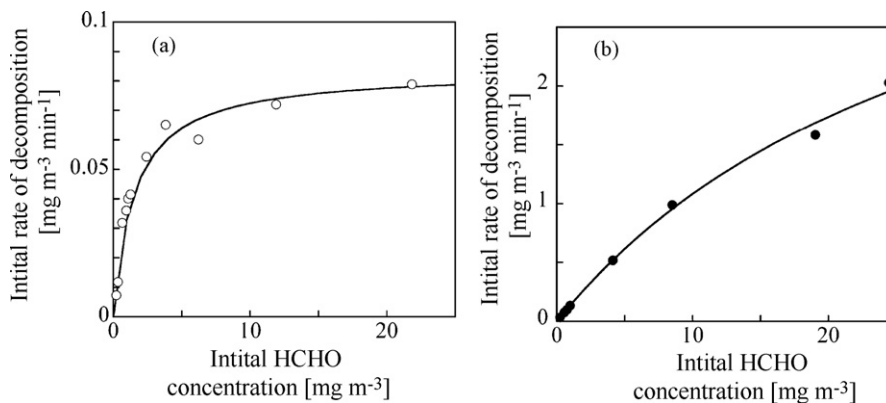


Fig. 6. Relationships between initial rates of decomposition of HCHO calculated from experimental data in Fig. 5 and initial HCHO concentrations in decompositions of HCHO in  $1 \text{ m}^3$  air by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by (a) Method I and (b) Method II. The solid lines show calculated results by Eq. (1).

quickly increases in the region of low HCHO concentration and then approaches its maximum when the HCHO concentration exceeds  $5 \text{ mg m}^{-3}$ . With the photocatalyst film prepared by Method II, on the other hand, it increases almost linearly with the initial concentration of HCHO; surprisingly, this increase occurs even when the initial concentration is increased up to  $25 \text{ mg m}^{-3}$ . It is thus clear that the photocatalyst films prepared by Methods I and II provide entirely different performances as the HCHO concentration is high.

Fig. 7 shows the time courses of HCHO concentration in decompositions of HCHO in  $10 \text{ m}^3$  air by use of the photocatalytic reactor equipped with the glass tubes coated with titanium oxide by Method II. For comparison, the experimental data for the glass tube preparation by Method I is also plotted in Fig. 7(a). It is clear that the

glass tube preparation by Method II exhibits an excellent decomposition performance even when the amount of air is increased up to  $10 \text{ m}^3$ . Again, it can quickly decompose HCHO at low and high initial HCHO concentrations.

Fig. 8 shows the time courses of HCHO concentration in decompositions of HCHO by use of the photocatalytic reactor when the relative humidity in an  $1 \text{ m}^3$  room is adjusted to 50% and when it is abnormally increased up to 100% with a humidifier. Under a condition of the latter high humidity, the HCHO concentration in the air gradually was found to decrease even when the photocatalytic reactor was switched-off, because the moisture in the air caught HCHO molecules and then condensed on the wall of the room or the moisture condensed on the wall caught HCHO. Nevertheless,

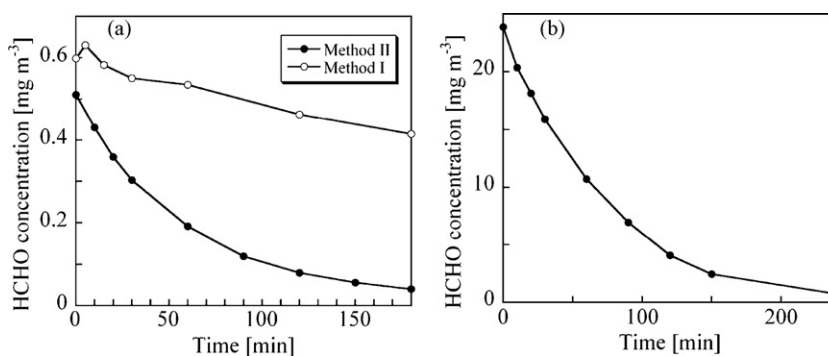
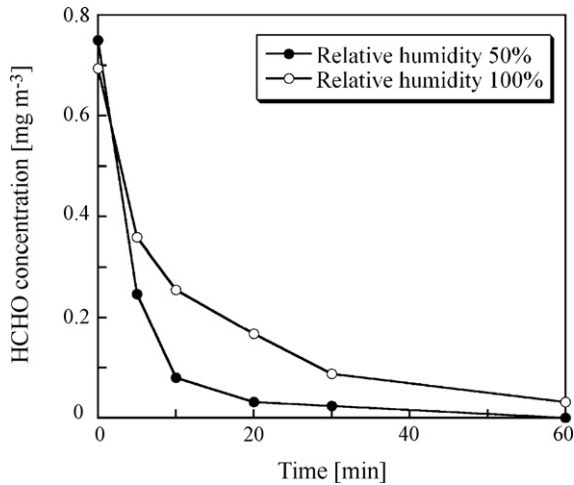


Fig. 7. Time courses of HCHO concentrations in decompositions of HCHO in  $10 \text{ m}^3$  air by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by Methods I and II in regions of (a) low initial concentration and (b) high initial concentration.



**Fig. 8.** Effect of relative humidity on decomposition of HCHO in 1 m<sup>3</sup> air by use of a photocatalytic reactor equipped with glass tubes coated with a thin film of titanium oxide by Method II.

the HCHO concentration at the relative humidity of 100% decreases more slowly than that at the relative humidity of 50%. This may be explained by either of the following two reasons. Firstly, at the relative humidity of 100%, the photocatalyst surface is covered with the moisture, which remarkably increases a mass-transfer resistance and in turn results in a slower decomposition. Secondly, the decomposition of HCHO slows down because under such a high humidity condition, a drop in the UV intensity results from the moisture

**Table 2**

Values of rate constants and adsorption equilibrium constants for photocatalyst films prepared by Methods I and II

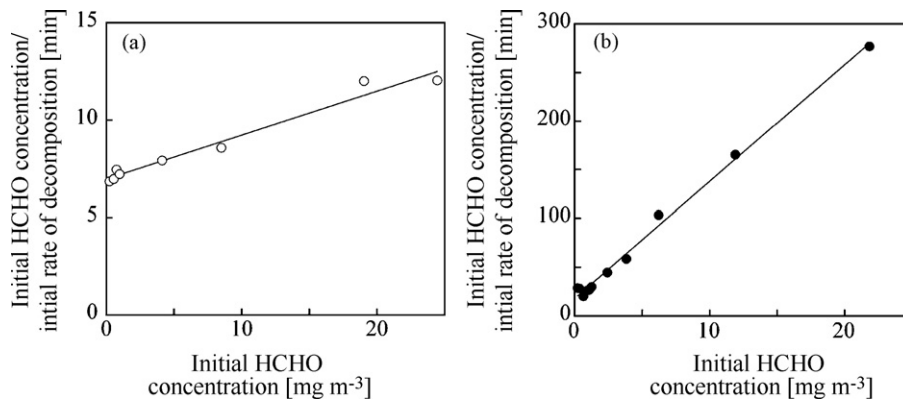
	$k$ (mg m <sup>-2</sup> min <sup>-1</sup> )	$K_H$ (m <sup>3</sup> mg <sup>-1</sup> )
Method I	0.458	0.654
Method II	24.3	0.032

film formed on the photocatalyst surface. Nevertheless, even under such a severe condition, the photocatalytic reactor equipped with the glass tubes coated with the photocatalyst film by Method II can decompose HCHO in a relatively short time, indicating that the activity of the photocatalyst film is sufficiently high.

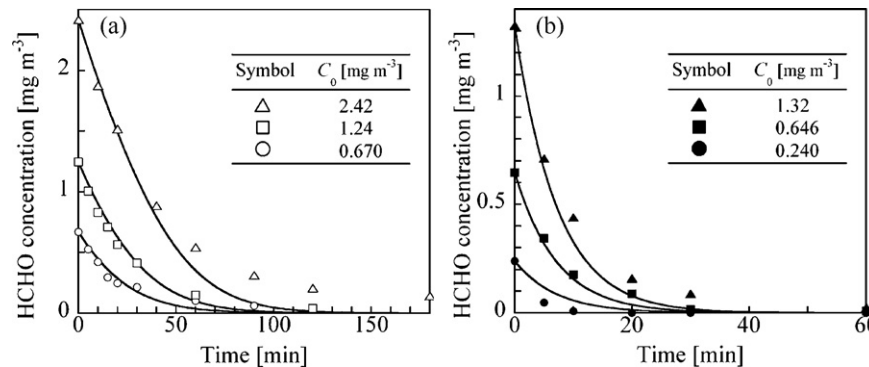
The high performance of the glass tube preparation by Method II is probably based on the rugged structure of the titanium oxide film formed on the glass tube surface. As can easily be predicted from Fig. 4, the titanium oxide film prepared by Method II possesses a sufficiently large specific surface, which provides a much larger field for the photocatalytic reaction and significantly increases the rate of photocatalytic decomposition of HCHO.

4.3. Computer simulation using a mathematical model

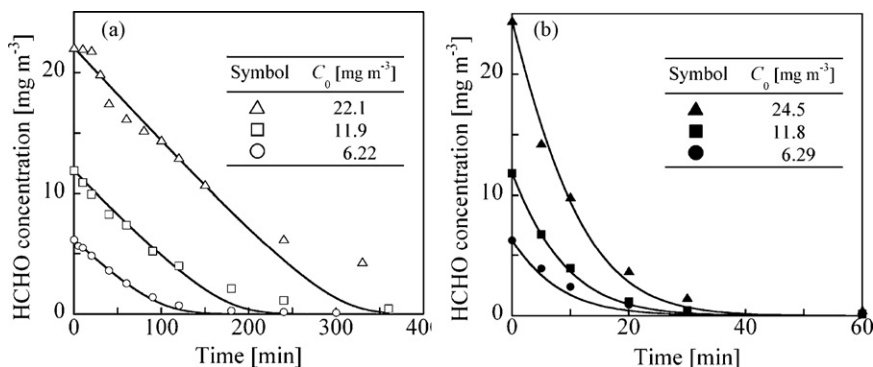
Fig. 9 shows linearized plots of the initial rates of decomposition of HCHO calculated from the experimental values in Figs. 5 and 6. The straight lines were obtained by a least-square regression and the values of  $k$  and  $K_H$  were then calculated from the slope and intercept of each straight line. The result is shown in Table 2. The value of  $k$  for Method II is 53 times larger than that for Method I. In contrast, the value of  $K_H$  for Method II is about one-twentieth



**Fig. 9.** Linearized plots of experimental data taken in decompositions of HCHO in 1 m<sup>3</sup> air by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by (a) Method I and (b) Method II. The solid lines show calculated results.



**Fig. 10.** Comparisons between experimental data and calculated results for time courses of HCHO concentrations in decompositions of HCHO in 1 m<sup>3</sup> air in a region of low initial concentration by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by (a) Method I and (b) Method II. The solid lines show calculated results by Eq. (1).



**Fig. 11.** Comparisons between experimental data and calculated results for time courses of HCHO concentration in decompositions of HCHO in 1 m<sup>3</sup> air in a region of high initial concentrations by use of photocatalytic reactors equipped with glass tubes coated with thin films of titanium oxide by (a) Method I and (b) Method II. The solid lines show calculated results by Eq. (1).

of that for Method I, implying that the photocatalyst film prepared by Method II has a lower affinity with HCHO. However, this negative effect on the rate of decomposition is offset because the value of  $k$  is sufficiently large. Consequently, the rate of decomposition of HCHO for Method II becomes overwhelmingly larger than that for Method I. The value of  $k$  obtained here includes an effect of the specific surface area. Therefore, the significant increase in the photocatalytic activity for Method II is considered to be mainly due to the specific surface area significantly increased.

The kinetic parameters determined were substituted into Eq. (1) to obtain relationships between the initial rate of decomposition of HCHO and the initial HCHO concentration in the photocatalytic decompositions of HCHO over the titanium oxide films prepared by Methods I and II. As is obvious from Fig. 6, both the calculated lines are in good agreement with their respective experimental data.

Eq. (1) was numerically solved to obtain the time courses of HCHO concentration in the photocatalytic decompositions of HCHO over the titanium oxide films prepared by Methods I and II. As is obvious from Figs. 10 and 11, the calculated lines are in good agreement with the experimental data at both low and high initial HCHO concentrations. The result of the kinetic analysis thus indicates that the decomposition of HCHO in the photocatalytic reactor with a parallel array of nine light sources obeys Langmuir–Hinshelwood type kinetics.

## 5. Conclusions

In the present work, the performances of the thin films of titanium oxide prepared by two methods were investigated both experimentally and theoretically by decomposition of HCHO in air in the photocatalytic reactor with a parallel array of nine light sources. As a result, the following conclusions were withdrawn.

- (1) There is no marked difference between the permeabilities of UV light through glass tube walls coated with the photocatalyst films, although the photocatalyst film prepared by Method II is somewhat less transparent than that by Method I. As was previously observed with the photocatalyst film prepared by Method I, therefore, the photocatalyst film prepared by Method I also has an increase in the rate of decomposition of HCHO because the UV light emitted from the light source in a given glass tube acts on the photocatalyst films on adjacent glass tubes.
- (2) The photocatalyst film prepared by Method I has a very smooth surface, whereas that by Method II has a rugged surface. This is because anatase titanium oxide particles prepared by Method II possesses very large crystal sizes and is therefore estimated to have a very large specific surface.

- (3) The photocatalytic reactor equipped with the glass tube preparations by Method II rapidly decomposes HCHO in the region of high HCHO concentration.
- (4) The photocatalyst film prepared by Method II can rapidly decompose HCHO even when the humidity is very high.
- (5) The decomposition of HCHO in the photocatalytic reactor with a parallel array of nine light sources obeys Langmuir–Hinshelwood type kinetics.

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