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Decomposition of gaseous formaldehyde in a photocatalytic reactor with a parallel array of light sources

1. Fundamental experiment for reactor design

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Abstract

To develop a high-performance photocatalytic reactor for purification of indoor air, photocatalytic decomposition of HCHO at a very low concentration is investigated both experimentally and theoretically in two papers. This first paper reports the result of fundamental experiment that is necessary to design the photocatalytic reactor in the second paper. A combination of the absorption of trace HCHO into water with the quantitative analysis of HCHO by the 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) method is found to be useful to accurately measure the HCHO concentration at a ppb level (less than 1.23 mg m^{-3}). The experimental results obtained using three types of annular-flow photocatalytic reactors with different inside diameters (22–120 mm) and light sources (6 and 20 W blacklight blue fluorescent lamps) indicate that the photocatalytic reactor with a 6 W lamp and a glass tube of 28 mm in inside diameter (the distance between the light source and photocatalyst surface; 6.5 mm) gives a maximum rate of decomposition; HCHO at a ppb concentration level is rapidly decomposed to zero concentration when the photocatalyst surface kept at a low temperature (45 °C) is irradiated with UV light of a high light intensity.

Keywords: Photocatalytic decomposition; Formaldehyde; Film-diffusional resistance; Annular-flow reactor; Sick-building syndrome

1. Introduction

The housing industry of Japan aggressively promoted development of houses with highly thermal insulation and airtightness to save energies for floor heating and air conditioning [1]. Consequently, many types of houses that satisfy these conditions are now commercially available. However, lack of adequate ventilation has unexpectedly caused a serious social problem called a sick-building syndrome [2,3], in which inhabitants suffer from the damage by volatile organic compounds (VOCs), such as formaldehyde (HCHO) and toluene, released from building materials or furniture [1,4,5]. Thus, it is desired to rapidly develop a high-performance air-purification system that is capable of certainly removing VOCs from the indoor air.

A photocatalytic process for purification of the indoor air has a potential of solving such a problem [6–10] because of the following advantages: (1) the purification apparatus is not dangerous since the photocatalytic reaction occurs at a room temperature; (2) the structure of the apparatus is not complicated; (3) the apparatus can easily be combined with other treatment methods such as an adsorption method [11] and (4) VOCs are finally decomposed into carbon dioxide, water and minerals. On the other hand, the photocatalytic process has the following disadvantages: (1) there is a limitation to securing a sufficiently large area of the reaction field in a reactor space because the photocatalytic reaction occurs only at the photocatalyst surface irradiated with UV light; (2) it is not easy therefore to dramatically increase the photocatalytic activity of the reactor per unit volume even when depositing precious metals on titanium oxide [12,13] and (3) the HCHO concentration in the indoor air is usually less than 300 ppb[1], in which range the photocatalytic reaction does not proceed efficiently owing to high film-diffusional resistance. Consequently, the photocatalytic processes have not come in practice as much as they were expected despite of many energetic photocatalytic studies.

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Little report has been published on the photocatalytic decomposition of the HCHO concentration at a ppb (parts per billion by volume) level. This is probably due to a difficulty in accurate measurement of HCHO at such a concentration level. As indicated later, the efficiency of the photocatalytic decomposition of HCHO markedly decreases at a concentration below 1 ppmv (parts per million by volume). To evaluate the reactor performance properly, therefore, the photocatalytic decomposition must be investigated at an actual indoor concentration level.

The final goal of the present work is to develop a high-performance photocatalytic reactor that is capable of rapidly reducing gaseous HCHO in a large amount of air to a level below the WHO guideline, 80 ppbv [2]. A series of experimental results will be described in two papers. In this first paper, we report the result of fundamental experiment that is necessary to design a high-performance photocatalytic reactor. In the second paper [14], we will discuss the performance of the photocatalytic reactor with a parallel array of nine light sources constructed on the basis of the result of the fundamental experiment.

In the following, the HCHO concentration will be expressed in unit of mg m^{-3}; the factors of the conversion from ppbv to mg m^{-3} and from mg m^{-3} to ppbv at 25 °C are 0.00123 and 814, respectively.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TIP) and isopropyl alcohol (IPA) were purchased from Katayama Chemicals Co., Japan. An aqueous solution of formaldehyde (37%) used as a reactant was purchased from Wako Pure Chemical Industries Ltd., Japan. Blacklight blue fluorescent lamps with wavelengths of 300–400 nm (FL6BL for 6 W and FL20SBLB for 20 W) used as a light source were products of Matsushita Electric Co. Ltd., Japan. Formaldehyde-Test Wako used for measurement of the HCHO concentration was purchased from Wako Pure Chemical Industries Ltd.

2.2. Coating with titanium oxide

A mixture of 29.69 g of TIP and 31.39 g of IPA, at a molar ratio of 1 and 5, was agitated in a glass vessel for 2 h at 5 °C [15–17]. A mixture of 7.53 g of water and 31.39 g of IPA was slowly added by dripping on the wall surface of the vessel to the mixture of TIP and IPA under vigorous mixing. The solution at a molar ratio of 1:10:4 for TIP, IPA and H_2O was further agitated for 4 h at 5 °C. A white cake of titanium oxide was filtered by suction and dried in an oven for 5 h at 100 °C; it was sometimes taken out and then roughly broken to pieces in order to shorten the drying time. The cake pieces were further finely powdered and dried in an oven for 15 h at 100 °C. The amorphous titanium oxide powder thus prepared was stored in a desiccator.

The amorphous titanium oxide powder (0.5 g) was dissolved in 1.0×10^{-5} m^3 of an aqueous H_2O_2 solution and kept under vigorous mixing for 2 h at 25 °C. To the solution solidified for 1 h, 6.0×10^{-5} m^3 of an aqueous H_2O_2 solution was added and then mixed vigorously for 2 days at 25 °C until bubbling stopped. As a result, a transparent yellow-colored solution was obtained.

Pyrex glass tubes were ultrasonically washed in IPA and the yellow-colored solution was poured into each glass tube so as to cover the inner surface entirely. After tilting for 1 h to remove excessive liquid by dripping, the glass tubes were kept in a furnace for 1 h at 400 °C. The same procedure was repeated five times, except that the fifth calcination was carried out at 500 °C. As a result, we obtained glass tubes whose inner surfaces were coated with a transparent thin film of titanium oxide in *anatase* form.

2.3. Photocatalytic reactors and experimental procedure

Reactor A consists of one of three Pyrex glass tubes (210 mm long) with different inside diameters (22, 28 and 35 mm) and a 6 W blacklight blue fluorescent lamp (15 mm in diameter) inserted and fixed in the center of the glass tube. The surface areas of the photocatalyst for the glass tubes of 22, 28 and 35 mm in inside diameter are 166, 211 and 264 cm^2, respectively. As shown in Fig. 1, the photocatalytic reactor was connected with an air pump and placed in a transparent plastic box with an inlet volume of 0.056 m^3. A small amount of the aqueous HCHO solution was dropped on a heated plate to instantaneously evaporate. The UV lamp was immediately turned on to start the reaction. A gas sample was collected in water by absorption at time intervals to measure the HCHO concentration. An effect of temperature on the rate of photocatalytic decomposition of HCHO was investigated using the reactor covered with a ribbon heater. A thermocouple was fixed on the inside surface of the reactor to continuously monitor the temperature. The reaction was performed by maintaining the inside surface at a constant

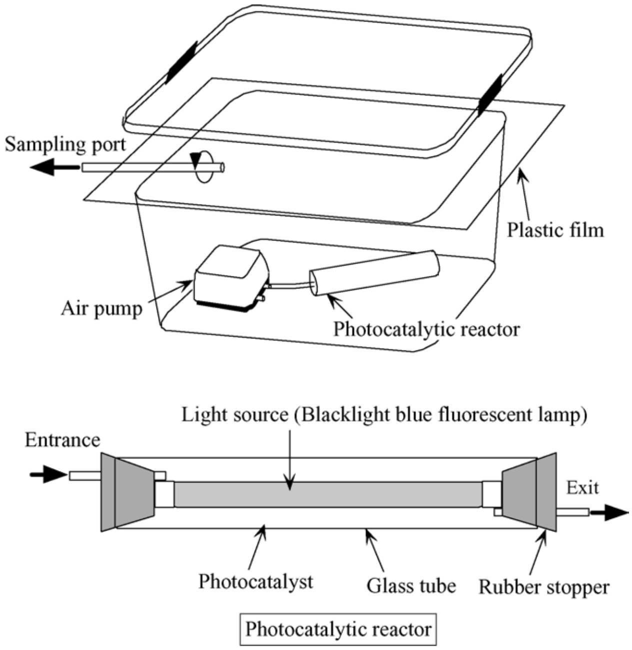

Fig. 1. Experimental system for decompositions of HCHO using Reactor A. The inlet volume of the plastic container is 0.056 m^3.

temperature between 45 and 90 °C with a process controller (GK101-10; CHINO Co. Ltd., Japan).

Reactor B consists of a Pyrex glass tube (44 mm in inside diameter and 580 mm long) with a total photocatalyst surface area of $0.16\,\text{m}^2$ and a 20 W blacklight blue fluorescent lamp (32 mm in diameter and 56 cm long) inserted and fixed in the center of the glass tube. The distance between the light source and photocatalyst is 6 mm. The air was introduced into the reactor by rotation of a fan (electric power consumption; 13 W) fixed at the bottom of the reactor. This reactor system was placed in a closed room with an inlet volume of $1.0\,\text{m}^3$. The fan was switched on to circulate the air through the inside of the reactor at a constant flow rate of $2.8\,\text{m}^3\,\text{min}^{-1}$. The air in the closed room was well mixed with two fans placed at different positions in the room. A small amount of the HCHO solution was instantaneously evaporated by dropping it on a heated plate. After several minutes, the UV lamp was turned on to start the photocatalytic reaction. HCHO in the air was collected in water by absorption at time intervals to measure its concentration. The initial concentration of HCHO was set up at a concentration less than $1.11\,\text{mg}\,\text{m}^{-3}$ (900 ppbv).

Reactor C (120 mm in inside diameter and 600 mm long) was constructed using a thin stainless steel plate coated with titanium oxide (the photocatalyst surface area; $0.226\,\text{m}^2$) according to the same procedure as described above. This plate was round and then fixed to the inside surface of a thin cylinder made of copper, as shown in Fig. 2. A 20 W blacklight blue fluorescent lamp (32 mm in diameter and 560 mm long) was inserted and fixed in the center of the cylinder. The distance between the light source and photocatalyst is 44 mm. The air was introduced from the bottom of the cylinder by rotation of a fan (the electric power consumption; 13 W) fixed at the bottom of the cylinder. This reactor was placed in a closed room with an inlet volume of $1.0\,\text{m}^3$. The fan was switched on to circulate the air through the inside of the reactor at a constant flow rate of $2.8\,\text{m}^3\,\text{min}^{-1}$. The air in the closed room was well mixed with two fans placed at different positions. A small amount of aqueous HCHO solution was dropped on a heated plate and instantaneously evaporated. After several minutes, the lamp was turned on to start the photocatalytic reaction. The initial concentration of HCHO was set up at a concentration less than $1.11\,\text{mg}\,\text{m}^{-3}$ (900 ppbv). HCHO in the room was corrected in water by absorption to measure its concentration.

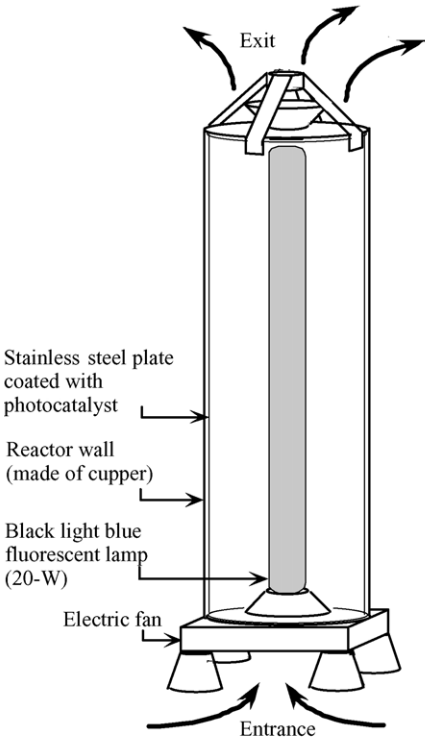

Fig. 2. A schematic structure of Reactor C with an internal diameter of 12 cm and a length of 60 cm.

2.4. Analytical procedure

The HCHO concentration at a level of ppbv ($<1.23\,\text{mg}\,\text{m}^{-3}$) was determined according to the following procedure. A test tube containing $4.0 \times 10^{-6}\,\text{m}^3$ of distilled water was immersed into a constant temperature bath at 30 °C. After 10 min, the air was bubbled through the distilled water for 5 min at a flow rate of $1.0 \times 10^{-4}\,\text{m}^3\,\text{min}^{-1}$ with an air pump to collect HCHO by absorption. To $1.0 \times 10^{-6}\,\text{m}^3$ of this solution, $1.0 \times 10^{-6}\,\text{m}^3$ of the alkaline reagent (5N potassium hydroxide) and $1.0 \times 10^{-6}\,\text{m}^3$ of the coloring reagent (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole, AHMT) were added. The reaction mixture was immediately mixed by shaking for 15 s and then kept for 15 min in the constant temperature bath. Immediately after addition of $1.0 \times 10^{-6}\,\text{m}^3$ of oxidizing reagent (potassium periodate), the reaction mixture was mixed by shaking until foaming stopped and then kept for 5 min in the constant temperature bath. The absorbance of the reaction mixture was measured at 550 nm with a spectrophotometer (UV-240; Shimadzu Co. Ltd., Japan). The HCOOH concentration was measured by ion chromatography (DX-100; Dionex Corporation, CA).

2.5. Measurement of permeability of UV light through a glass tube

A 6 W blacklight fluorescent lamp was inserted into a Pyrex glass tube (28 mm in inside diameter and 1.5 mm in wall thickness) and fixed in its center. The optical sensor connected with the UV spectrometer (Model MCPD-2000; Otsuka Electronics Co. Ltd., Japan) was fixed to the outer surface of the glass tube. The whole reactor system was placed in a paper box to shield from the natural light. After switching on the light source, the light intensity data were collected over a wavelength range of 200–500 nm.

3. Results and discussion

3.1. Calibration curves

Fig. 3 represents the calibration curves for the HCHO concentration at the water temperatures of 20, 25 and 36 °C. We approximated the intercepts of the calibration curves by straight

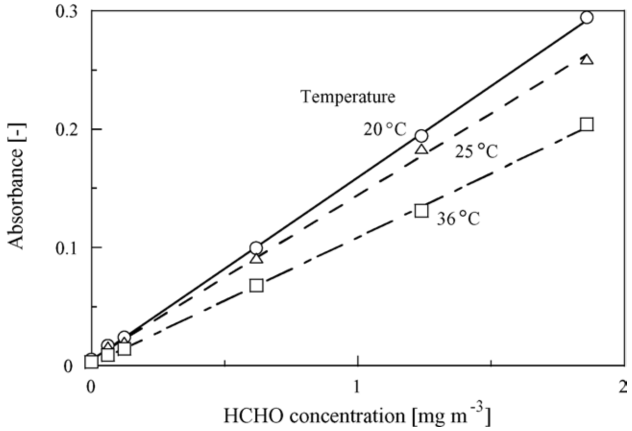

Fig. 3. Calibration curves for determination of HCHO concentration at different water temperatures.

lines and obtained an average value of 0.00403. Furthermore, using this value as the intercept value of each calibration curve, we applied the least-square method again to the experimental data in Fig. 3. As a result, the following expressions were obtained.

$$y = 0.155x + 0.00403 \quad \text{at } 20\,^{\circ}\mathrm{C} \tag{1}$$

$$y = 0.139x + 0.00403 \quad \text{at } 25\,^{\circ}\mathrm{C} \tag{2}$$

$$y = 0.106x + 0.00403 \quad \text{at } 36\,^{\circ}\mathrm{C} \tag{3}$$

where x is the HCHO concentration and y is the absorbance. Fig. 4 represents a plot of the slope of each expression against the water temperature. The least-square method was applied again to the plotted data, so that the following expression was obtained.

$$y = (0.217 - 0.003086\theta)x + 0.00403 \quad \text{at } 20\text{–}36\,^{\circ}\mathrm{C} \tag{4}$$

where θ is the temperature. In Figs. 3 and 4, the plotted data are less scattered and in good agreements with the calculated lines, indicating that the quantitative analytical method used here is highly accurate and useful to measure the HCHO concentration at a ppbv level. In the following experiments, we fixed the water temperature for absorption at 25 °C.

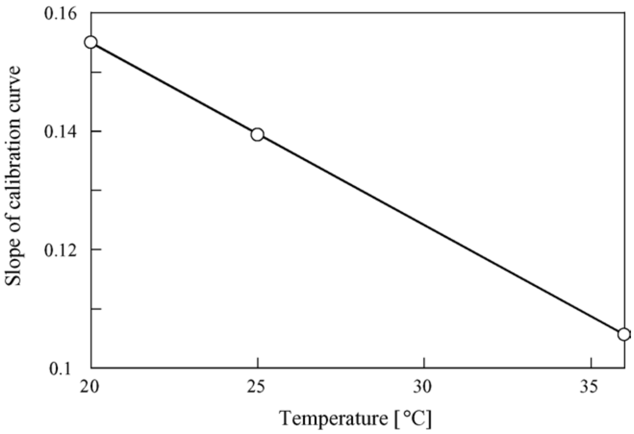

Fig. 4. Relationship between slope of calibration curve and water temperature.

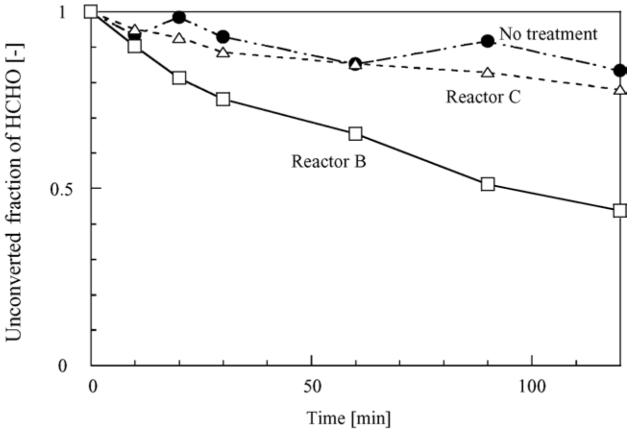

Fig. 5. Comparison of photocatalytic decompositions of HCHO using Reactors B and C.

3.2. Comparison of decompositions of HCHO using Reactors B and C

Fig. 5 represents the experimental results for the decompositions of HCHO in the closed room of 1.0 m^3 using Reactors B and C. The initial HCHO concentrations were set at 1.11 mg m^{-3}. Although the air in the room was circulated through Reactor C without irradiation of UV light, the HCHO concentration was slightly decreased. This is maybe due to either adsorption of HCHO onto the plastic wall of the closed room or leakage of HCHO from the room. There is no marked difference between the time-transient behaviors of HCHO in Reactor C with and without UV-irradiation, suggesting that Reactor C hardly decomposes HCHO. In Reactor B, on the other hand, the HCHO concentration decreases steadily, although the rate of decomposition is not satisfactorily high.

Fig. 6 represents the experimental results for the decompositions of HCHO at different initial concentrations using Reactor B. It is clear that the decomposition of HCHO is relatively high in the region of high HCHO concentration, but it is quickly slowed down in the region of low HCHO concentration. For example, the decomposition of HCHO at the initial concentra-

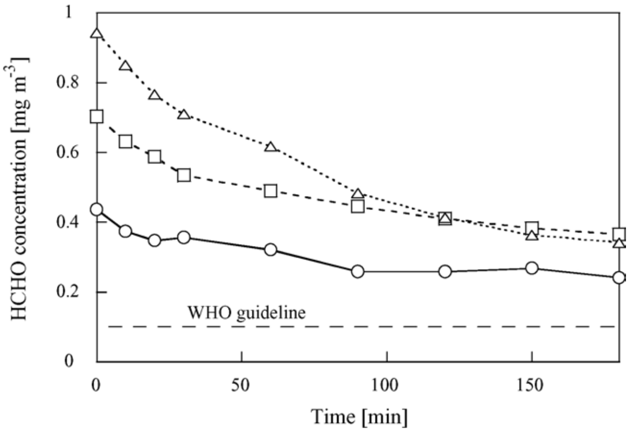

Fig. 6. Effect of initial HCHO concentration on photocatalytic decompositions of HCHO using Reactor B.

tion of 0.44 mg m^{-3} proceeds slowly and almost stops in the neighborhood of 0.25 mg m^{-3}.

3.3. Light intensities of light sources

The experimental results in Figs. 5 and 6 suggest that it is not easy to photocatalytically decompose HCHO at a concentration level of ppbv toward zero concentration. This suggests, in turn, that the photocatalytic decomposition of HCHO in the actual indoor air also causes such a difficulty. In other words, the experimental results indicate that even when HCHO at a high concentration is successfully decomposed using a photocatalytic reactor, there is no guarantee that HCHO in the indoor air can also be decomposed satisfactorily. It is therefore risky to evaluate the reactor performance only by the experimental data for the decomposition of HCHO in the region of high concentration.

When no satisfactory result is obtained for the photocatalytic decomposition of a certain organic compound, one may undertake to introduce a light source with larger electric power consumption. However, it is considered that the relationship between the photocatalyst surface densities of the active species produced as a result of excitement by UV light and the amount of reactant molecules existing at a very low concentration in the air strongly affects the rate of photocatalytic decomposition. It is thus questionable whether or not the above selection is appropriate. For this reason, it is worthwhile to investigate the influence of light intensity on the rate of decomposition of HCHO. Fig. 7 represents the UV light intensity distributions measured for 6 and 20 W blacklight blue fluorescent lamps. It is clear that the light intensity per unit surface area for the 6 W lamp is larger than that for the 20 W lamp. That is, the light intensity is not proportional to the magnitude of the electric power consumption.

Thus, we consider that the decomposition of HCHO existing at a very low concentration in the air should be carried out using the light source with a larger light intensity per unit surface area, by which the densities of the active species on the photocatalyst surface are increased so that the HCHO molecules can have many chances to encounter the active species. In the photocatalytic decomposition of trace HCHO, therefore, the use of several 6 W lamps instead of a 20 W lamp may be advantageous.

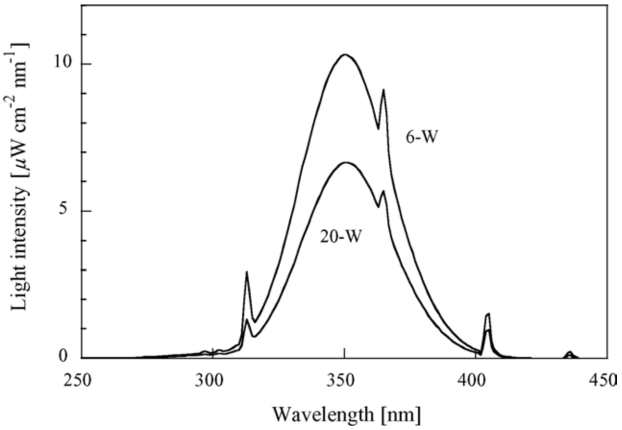

Fig. 7. Distributions of light intensity distributions per unit area for UV lights emitted from 6 to 20 W blacklight blue fluorescent lamps.

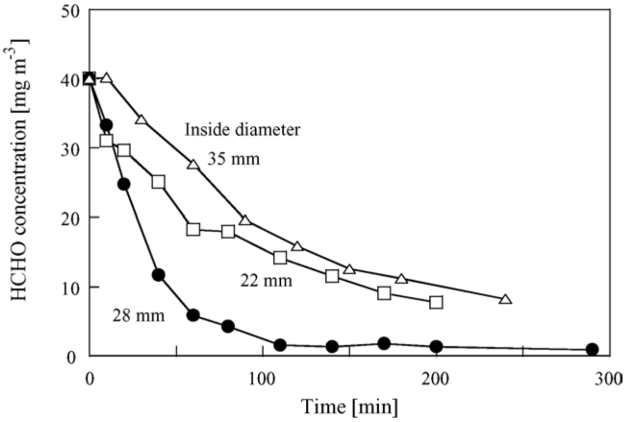

Fig. 8. Effect of inside diameter on photocatalytic decompositions of HCHO using Reactor A.

Fig. 8 represents the experimental results for the decompositions of HCHO at an initial concentration of 40 mg m^{-3} using Reactor A with different inside diameters (22, 28 and 35 mm; the distances between the light source and photocatalyst are 2.0, 6.5 and 10 mm, respectively). The photocatalytic activity for the reactor of 22 mm in inside diameter, which has the largest light intensity per unit surface area, is smaller than that for the reactor of 28 mm in inside diameter. This result is considered due to the difference in the photocatalyst surface area. Also, the photocatalytic activity for the reactor of 35 mm in inside diameter is smaller than that for the reactor of 28 mm in inside diameter, which is considered due to the difference in the light intensity. Thus, in the decomposition of HCHO at a very low concentration using an annular-flow photocatalytic reactor, both the light intensity and photocatalyst surface area must be taken into consideration.

We [18] have previously investigated the photocatalytic decompositions of gaseous acetaldehyde using Reactor A with different inside diameters (28, 35 and 45 mm; the distances between the light source and photocatalyst surface are 6.5, 10 and 15 mm, respectively) and found that the rate of decomposition exponentially decreases with the increase in the distance between the light source and photocatalyst surface. For example, the activity of the reactor of 28 mm in inside diameter was 3.5 times higher than that of the reactor of 35 mm in inside diameter despite the fact that the difference between the distances from the light source to the photocatalyst surface in these reactors was only 3.5 mm. In addition, the reactor activity was not simply proportional to the light intensity.

From Figs. 5, 6 and 8, it is clear that the photocatalytic decomposition of HCHO is also strongly influenced by the distance between the light source and photocatalyst surface. This suggests that the HCHO concentration does not decrease toward a zero value if the light intensity is below a certain level, even under irradiation with UV light. To certainly decompose HCHO, therefore, the photocatalyst surface must be irradiated with UV light of a high light intensity per unit surface area.

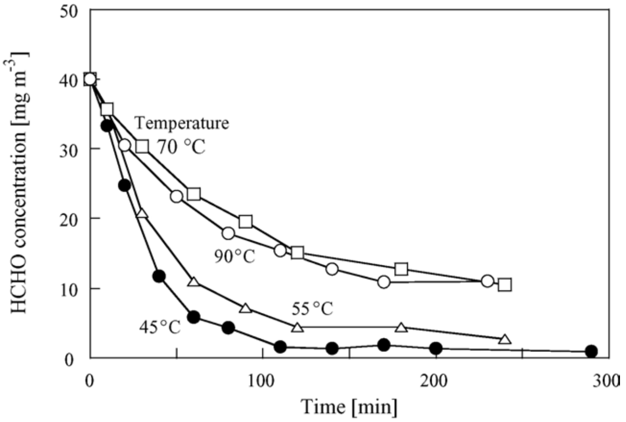

Fig. 9. Effect of temperature on photocatalytic decompositions of HCHO using Reactor A with an inside diameter of 28 mm.

3.4. Effect of reaction temperature

Fig. 9 represents the effect of temperature on the decomposition of HCHO at an initial concentration of 40 mg m^{-3} using Reactor A, where the temperature of the photocatalyst surface was maintained at 45, 55, 70 and 90 °C. The rate of decomposition of HCHO takes a maximum at 45 °C and tends to decrease with the increase in the temperature, indicating that the photocatalytic decomposition of HCHO should be carried out at a lower temperature. In general, the photocatalytic reaction is less influenced by the temperature less that 100 °C, since the photocatalytic reaction utilizes UV light as the energy source. Therefore, the decrease in the rate of decomposition of HCHO may be explained by a decrease in the amount of HCHO adsorbed on the photocatalyst surface with the increase in the temperature.

3.5. Intermediate and final product

HCOOH is an intermediate produced in the photocatalytic decomposition of HCHO into carbon dioxide [19–21]. We attempted to measure the HCOOH concentration in the decomposition of HCHO at an indoor concentration level, but could not detect HCOOH. Therefore, we performed the photocatalytic decomposition by increasing the HCHO concentration up to 1150 mg m^{-3}. The result is shown in Fig. 10. It is clear that during the reaction, the HCOOH concentration stayed below 1 mg m^{-3}, which value would be even smaller if one takes into consideration the fact that the HCHO reagent contained HCOOH of 9.86 mg m^{-3} as an impurity. Furthermore, we monitored the carbon dioxide concentration during the reaction and confirmed that it increases as the HCHO concentration decreases. These experimental results suggest that in the present reactor system, the HCOOH produced as an intermediate tends to be strongly adsorbed on the photocatalyst surface and then quickly converted into carbon dioxide.

The finding that the present reactor system hardly produces HCOOH is very important for the practical use of the reactor, since the HCHO concentration in the indoor air is usually below 0.369 mg m^{-3} (<300 ppbv).

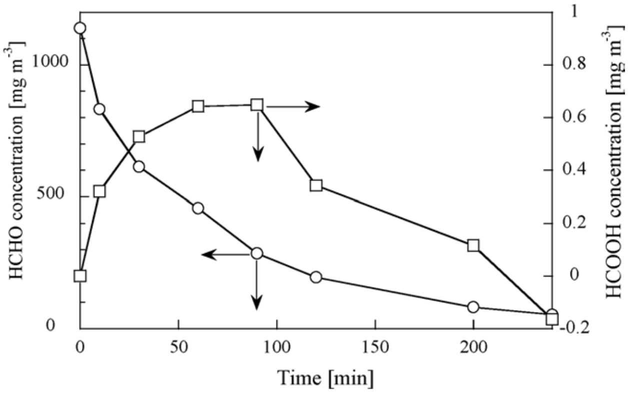

Fig. 10. Formation of HCOOH in a photocatalytic decomposition of HCHO at 1150 mg m^3 using Reactor A with an inside diameter of 28 mm.

3.6. Phenomenological model for photocatalytic decomposition of a VOC at a very low concentration

A photocatalytic reaction proceeds on the titanium oxide surface excited with UV light [22–27]. In a previous work [17], we found that the photocatalytic reaction produces H_2O_2 at a measurable concentration level and the initial rate of formation of H_2O_2 is proportional to the initial rate of decomposition of HCHO. Since H_2O_2 is readily converted to the hydroxyl radicals that are very reactive, it is very important to discuss the relationship between the reactant concentration and the surface density of hydroxyl radicals.

Fig. 11 represents a phenomenological model for the relationship between the light intensity and reactant concentration in the decomposition of reactant molecules on the photocatalyst surface. With a low light intensity, the surface densities of the active species would be low. At a very low reactant concentration, the reaction does not take place remarkably because the reactant

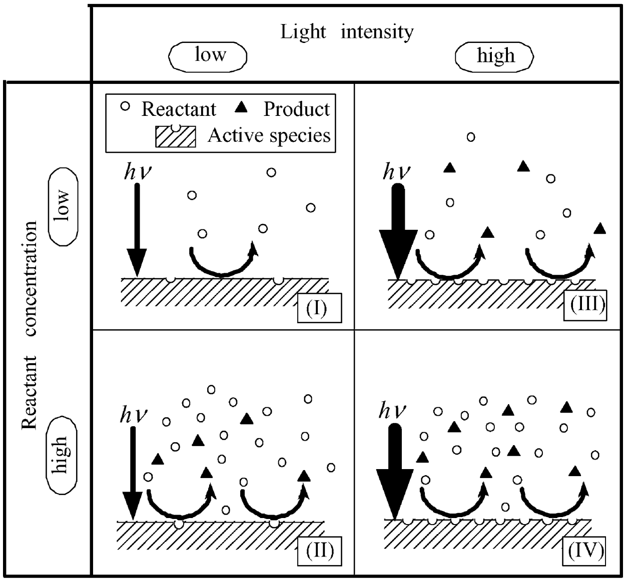

Fig. 11. Phenomenological model for a relationship between light intensity and reactant concentration in a decomposition of reactant molecules on photocatalyst surface.

molecules have little chance to encounter the active species (I). At a high reactant concentration, however, the reaction proceeds smoothly because the reactant molecules are likely to encounter the active species despite their low surface densities (II). With a high light intensity, on the other hand, the active species on the photocatalyst surface would be maintained at high surface densities. Under this condition, the reaction readily takes place without any hindrance when the reactant concentration is high (IV). Likewise, the reaction proceeds smoothly even when the reactant concentration is low because the reactant molecules have many chances to encounter the active species existing at high surface densities (III). This situation corresponds to the reaction condition for the photocatalytic reactor with a parallel array of nine 6 W blacklight blue fluorescent lamps, which will be reported in the second paper.

4. Conclusions

In the present work, we investigated the photocatalytic decompositions of HCHO at very low concentrations, corresponding to the HCHO concentration in the indoor air, and obtained the following conclusions.

(1) A combination of the absorption of trace HCHO into water with the quantitative analysis of HCHO by the AHMT method is useful to accurately measure the HCHO concentration at a ppbv level ($<1.23\,\mathrm{mg\,m^{-3}}$).
(2) In the photocatalytic decomposition of HCHO using an annular-flow photocatalytic reactor with a 6 W blacklight blue fluorescent lamp mounted in the center of the reactor, the use of a glass tube of 28 mm in inside diameter gives a maximum rate of decomposition.
(3) In the photocatalytic decomposition of HCHO at a very low concentration, it is necessary to irradiate the photocatalyst surface with UV light of a high intensity.
(4) A higher rate of photocatalytic decomposition of HCHO is given at a lower temperature between 45 and 90 °C.
(5) The photocatalytic reactor with a parallel array of nine light sources certainly decomposes HCHO at an indoor concentration level (<300 ppbv) toward zero concentration and little produces HCOOH.

Acknowledgments

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