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Formation of Hydrogen Peroxide in Photocatalytic Reactions

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To characterize the formation of H_2O_2 in photocatalytic reactions, HCHO and HCOOH have been photocatalytically decomposed by use of TiO_2 and Pd/TiO_2 under irradiation with the UV light emitted from a blacklight blue fluorescent lamp (BL) or germicidal lamp (GL). An enzymatic method has been introduced to accurately measure the H_2O_2 concentration. The photocatalyst irradiated with the UV light emitted from the GL produces H_2O_2 from water at a larger rate and amount. Deposition of Pd on TiO_2 increases the rate and amount of the formation of H_2O_2 from water. In the absence of the photocatalyst, no HCOOH is decomposed under irradiations with both the UV lights from the BL and GL, whereas the decomposition becomes possible in the presence of the photocatalyst. H_2O_2 is formed in parallel with the photocatalytic decomposition of HCOOH. In the presence of the photocatalyst, the concentration of the H_2O_2 formed during the decomposition of HCHO is smaller than that formed from water alone. In contrast, this relationship is reversed with the decomposition of HCOOH. This is considered due to the formation of H_2O_2 in the process of the decomposition of HCOOH to carbon dioxide and water. The rates of decomposition of HCHO and HCOOH are directly proportional to their respective rates of formation of H_2O_2, indicating that there is a close relationship between the photocatalytic activity and the capability of the photocatalyst to form H_2O_2.

1. Introduction

In the decomposition of organic compounds by titanium dioxide (TiO_2) irradiated with UV light, various kinds of reactive radicals are formed.[1] From the mechanisms of the photocatalytic reactions described in a number of papers,[2−9] it is easy to notice that among these, only a few kinds of radicals, such as superoxide radicals and hydroxyl radicals ($HO^\bullet$), are directly related to the photocatalytic decomposition.

We recently investigated the time courses of the formic acid (HCOOH) concentration in its photocatalytic decompositions, where two kinds of enzymes were individually added to the reaction mixture.[10] Addition of superoxide dismutase (SOD), catalyzing a conversion of superoxide into hydrogen peroxide (H_2O_2), did not affect the time course of the HCOOH concentration. On the other hand, addition of catalase, catalyzing a decomposition of H_2O_2 into O_2 and H_2O, caused a temporary stop of the photocatalytic reaction. This is probably because H_2O_2 was rapidly decomposed by catalase and consequently, the concentration of $HO^\bullet$, which is usually produced greatly and allowed to aggressively react with HCOOH, was significantly reduced. This experimental result suggests that H_2O_2 is closely related to the photocatalytic decomposition of HCOOH, or organic compounds.

However, there is little report on the concentration level of H_2O_2 formed during the photocatalytic decomposition or on the time course of the H_2O_2 concentration. This is considered due to low sensitivities of the analytical methods[11−17] that have been used to measure the H_2O_2 concentration in the photocatalytic reaction. That is, in these analytical methods, it is difficult to accurately measure a very low concentration of H_2O_2 that is likely encountered in the photocatalytic reaction, so that it is supposed that the researchers were unable to pay much attention to the presence of a relationship between the hydrogen peroxide and photocatalytic reaction.

The photocatalytic reaction may drastically be promoted or retarded by doping TiO_2 with a certain kind of metal. In the past two decades, numerous reports have been published on the photocatalytic activities that were enhanced in the production of hydrogen and oxygen from a mixture of water and alcohol by platinum- and/or ruthenium-doped TiO_2 photocatalysts.[18−22] The use of RuO_2-doped TiO_2 powder or RuO_2 and Pt-doped TiO_2 particles induced water cleavage by visible light in water photolysis systems.[23−26] In addition, many reports are available on metal-doped or metal-depositing TiO_2 photocatalysts to efficiently decompose toxic compounds. Several of the preparations showed positive effects,[27−29] while others presented negative ones.[27,28,30−32] We also photodeposited palladium (Pd) on a thin film of TiO_2 covering the surface of a glass tube to examine its performance in the photocatalytic decompositions of several kinds of organic compounds in water.[33] As a result, this Pd/TiO_2 photocatalyst was found to decompose the organic compounds, especially formaldehyde (HCHO), at a higher rate than does the TiO_2 photocatalyst. In general, such an increase in the decomposition rate by depositing a certain metal on TiO_2 is explained by an inhibition of the recombination of electrons with holes by the deposited metal. Under such a condition, however, it is unclear which chemical species in the system changes its concentration and why the change results in a change of the decomposition rate.

In the present work, therefore, we examine the formation of H_2O_2 in the photocatalytic reactions under various reaction conditions and then elucidate the relationship between the photocatalytic activity and H_2O_2 concentration. To achieve this goal, we introduce the analytical method using an enzyme, which has an ability to accurately measure a very low

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concentration of H_2O_2 that is encountered in the photocatalytic reaction. First, HCHO is photocatalytically decomposed using TiO_2 and Pd/TiO_2 of different activities, and the time courses of the concentrations of H_2O_2 formed during the photocatalytic decompositions are investigated. Throughout a series of the experiment, two types of low-pressure mercury lamps (blacklight blue fluorescent lamp and germicidal lamp) are used to investigate the effect of the wavelength of UV light on the H_2O_2 formation. Second, the same discussion is carried out on the photocatalytic decomposition of HCOOH, which is an intermediate in the photocatalytic decomposition of HCHO. Finally, the role of the H_2O_2 formed in the photocatalytic reaction is discussed under estimation of the mechanism of the formation of H_2O_2 and $HO^{\bullet}$ in the photocatalytic decomposition of HCHO.

2. Experimental Section

2.1. Reagents and Materials. Palladium(II) nitrate [Pd(NO_3)$_2$], methanol, 2-propanol (IPA), and HCHO (a 37 (v/v)% aqueous solution containing 8 (v/v)% methanol as a stabilizer) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka). Titanium tetra-isopropoxide (TIP) was obtained from Katayama Chemicals, Inc. (Osaka), and a 31 (v/v)% aqueous H_2O_2 solution was from Mitsubishi Chemical Co., Ltd. (Tokyo). All these reagents were at least of laboratory reagent grade. The 6-W UV lamps used as a light source were a blacklight blue fluorescent lamp (BL) with wavelengths of 300−380 nm (FL6BL-B; Matsushita Electric Industrial Co., Ltd., Osaka) and a germicidal lamp (GL) with a wavelength of 254 nm (GL-6; Sankyo Denki, Tokyo).

2.2. Preparation of Amorphous TiO_2 Powder. Amorphous TiO_2 powder was prepared as follows.[34]

(1) TIP and IPA were mixed at a molar ratio of 1:5 (for example, 29.69 g of TIP/ 31.39 g of IPA) at 278 K for 2 h.

(2) To this solution, an aqueous solution of IPA at a molar ratio of 5:4 (for example, 31.39 g of IPA and 7.53 g of ultrarpure water) was slowly added by spending more than 10 min and the resulting solution, consisting of TIP, IPA, and H_2O at a molar ratio of 1:10:4, was mixed for 4 h; consequently, a white-colored solution containing amorphous TiO_2 fine particles was obtained.

(3) The white-colored solution was filtered under suction and the cake of amorphous TiO_2 particles remaining on the filter was dried at 373 K for 5 h, sometimes breaking into pieces with a small hammer.

(4) After being sufficiently pounded in a mortar, the resulting TiO_2 powder was dried at 373 K for 15 h.

(5) The amorphous TiO_2 fine powder thus prepared was kept in a desiccator with silica gel until next use.

2.3. Preparation of a Coating Solution of TiO_2. A coating solution of TiO_2 was prepared as follows.[10,34−38]

(1) The amorphous TiO_2 powder was added to a 31% aqueous H_2O_2 solution (a volume of 2.0×10^{-5} m^3 per one gram of the TiO_2 powder) and well mixed at 298 K for 2 h; the TiO_2 powder was thus completely dissolved in the aqueous solution with generating bubbles.

(2) The mixture was let stand until gelatinization at room temperature.

(3) The gelatinized solution was redissolved by addition of a 31% aqueous H_2O_2 solution (a volume of 1.2×10^{-4} m^3 per one gram of TiO_2) and mixed at 298 K for 12 h.

(4) This solution was let stand for about 50 h until generation of bubbles stopped.

(5) The transparent TiO_2 solution of a pale yellow color thus obtained was used as a coating solution. Since this solution was easily gelatinized after a period of time, it was redissolved prior to use by addition of a small amount of H_2O_2 solution.

2.4. Coating the Inside Surface of a Glass Tube with a Thin Film of TiO_2. The inside surface of a glass tube was coated with a thin film of TiO_2 according to the following procedure.[10,34−38]

(1) A Pyrex glass tube (28.5 mm in inside diameter, 1.8 mm in wall thickness, and 140 mm long) was ultrasonically washed in IPA for 3 min, rinsed in boiling distilled water, and dried at 373 K.

(2) The coating solution of TiO_2 was uniformly applied to the inside surface of the glass tube with a brush, and this glass tube was then heated at 673 K for 30 min. The same procedure was repeated four times.

(3) After one more application of the coating solution, the glass tube was heated at 773 K for 1 h. Consequently, a glass tube was obtained whose inside surface was coated with a transparent thin film of anatase TiO_2.

2.5. Photodeposition of Pd on a Thin Film of TiO_2. Photodeposition of Pd on a thin film of TiO_2 was carried out according to the following procedure,[33] which was constructed on the basis of the literature.[25]

(1) An aqueous solution of 0.4 M methanol and 0.1 M palladium nitrate was prepared.

(2) This solution (1.5×10^{-5} m^3) was poured into the glass tube coated with a thin film of TiO_2, and both the ends of the glass tube were plugged with rubber stoppers.

(3) The glass tube was horizontally attached to a rotary machine and slowly rotated for 5 min at 7 rpm under irradiation with the UV light emitted from two BLs; consequently, Pd was photodeposited on the thin film of TiO_2.

(4) After detachment from the rotary machine, the glass tube was sufficiently washed with distilled water and dried at room temperature.

2.6. Photocatalytic Reactor System and Its Operating Method. An annular-flow photocatalytic reactor,[10,36,39] as illustrated in Figure 1, is a plastic cylindrical vessel with a UV lamp fixed in the center, a quartz glass tube (20 mm in inside diameter and 220 mm long) for protection of the lamp, and a Pyrex glass tube (photocatalytic surface area, 0.0123 m^2) coated with a thin film of TiO_2 or Pd/TiO_2. The Pyrex glass tube was inserted and fixed between the outer surface of the quartz glass tube and the inside wall of the cylindrical vessel. Since the outer surface of the Pyrex glass tube was in close contact with the inside wall of the cylindrical vessel, a reaction mixture was allowed to flow through an annulus of 2 mm in width between the outer surface of the Pyrex glass tube and the inner surface of the Pyrex glass tube. A substantial amount of liquid inside the reactor was 7.0×10^{-5} m^3.

The photocatalytic reactor, a mixed-flow vessel, and a peristaltic pump (RP-1000; EYELA, Tokyo) were connected in a loop, as illustrated in Figure 2. A 5.0×10^{-4} m^3 aqueous solution of HCHO prepared at a given concentration was poured into the mixed-flow vessel and then recirculated at a flow rate of 1.08×10^{-3} m^3 min^{-1} in the batch recirculation reactor system. The reaction was started by switching the UV lamp in the reactor on. A sample liquid was withdrawn at appropriate time intervals from the mixed-flow vessel to determine the HCHO and H_2O_2 concentrations by their respective analytical methods described below. The same experiment was carried out for a 3.0×10^{-4} m^3 aqueous solution of HCOOH at a given concentration, and the HCOOH and H_2O_2 concentrations were measured by the analytical methods described below.

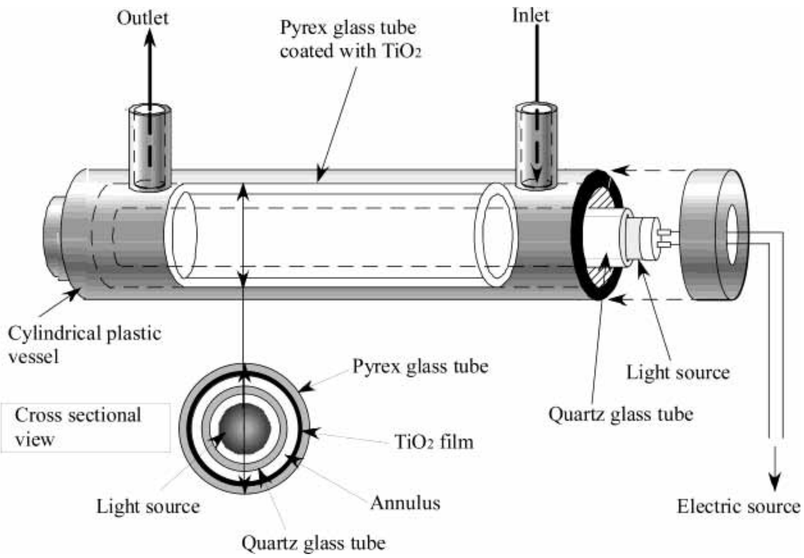


Figure 1. Annular-flow photocatalytic reactor.

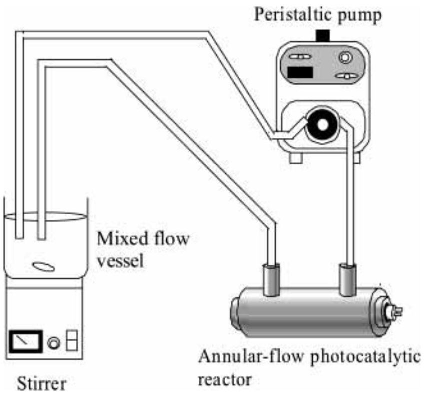


Figure 2. Batch recirculation reactor system.

2.7. Analytical Method for H_2O_2. Different types of analytical methods[11−17] have been used to measure the concentration of H_2O_2 formed in the photocatalytic decompositions of organic compounds in water. From the standpoint of the measurement sensitivity, however, these methods based on chemical reactions seem not to be adequate to accurately measure H_2O_2 at a very low concentration that is encountered in the photocatalytic reaction.

We therefore introduced an enzymatic method using a commercially available analytical reagent (Glucose B Test Wako; Wako Pure Chemical Industries, Ltd.). This reagent is originally used to measure a β-D-glucose concentration. Addition of the analytical reagent to an aqueous solution containing β-D-glucose first causes an oxidation of glucose to β-D-gluconic acid by glucose oxidase. At the same time, H_2O_2 is produced in the oxidation and successively allowed to react with a coloring dye by a catalytic action of peroxidase. Consequently, the β-D-glucose concentration is selectively determined by measuring the absorbance of the colored solution at 505 nm.

It is readily predictable that if only H_2O_2 is contained in a sample solution, addition of the above analytical reagent would cause only the second enzymatic reaction. Although it is not so difficult to prepare such an analytical reagent containing only peroxidase, we used the commercially available analytical reagent without any modification. The minimum measurable concentration of H_2O_2 was about 2×10^{-4} mol m^{-3}. Another advantage of introducing the enzymatic method is utilization of the substrate-specificity of an enzyme's action.[40] That is, an enzyme can distinguish its own reactant from the others and catalyzes a designated reaction. For example, in the kit used in the present work, the peroxidase selectively acts on H_2O_2 to cause the coloring reaction:

$$2H_2O_2 + \text{4-aminoanti-pyrine} + \text{phenol} \rightarrow \text{red quinoneimine dye} + 4H_2O$$

If the solution becomes colored, therefore, the presence of H_2O_2 can be identified. In fact, since the coloring reaction occurred when the analytical reagent was added to the sample solution, there is no doubt that H_2O_2 was formed in the photocatalytic reaction investigated in the present work.

An enzymatic reaction is more or less influenced by the pH of the sample solution. Therefore, aqueous solutions containing H_2O_2 at the same concentration were analyzed in the pH range of 3.5−6.5, corresponding to a pH change of the solution during the HCHO decomposition. As a result, we found that the measured values of the H_2O_2 concentration are changed within only 5%. In the following discussion, therefore, we used the measured values without any correction.

2.8. Analytical Methods for HCHO and HCOOH. The HCHO concentration was determined by coloring the sample solution with an analytical reagent (Formaldehyde Test Wako; Wako Pure Chemical Industries, Ltd.) and then measuring the absorption at 550 nm with a spectrophotometer (UVmini-1240; Shimadzu, Tokyo). The HCOOH concentration was measured by ion chromatography (DX-100; Dionex Corporation, CA).

3. Results and Discussion

3.1. Formation of HCOOH during Decomposition of HCHO. Figure 3 shows the time courses of the HCHO and HCOOH concentrations and pH in the decomposition of HCHO at an initial concentration of 0.271mol m^{-3} by Pd/TiO_2 under irradiation with the UV light emitted from the GL. HCHO is decomposed toward zero concentration. In parallel to this reaction, HCOOH is successively formed. Its concentration initially increases, passing through a maximum and decreasing. Such a time course of the concentration indicates that HCOOH is an intermediate in the decomposition of HCHO. However,

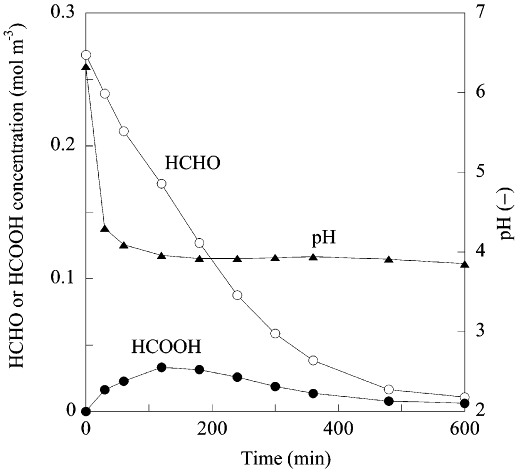


Figure 3. Time courses of HCHO and HCOOH concentrations and pH in decomposition of HCHO at an initial concentration of 0.271mol m^{-3} by Pd/TiO_2 under irradiation with UV light emitted from a germicidal lamp.

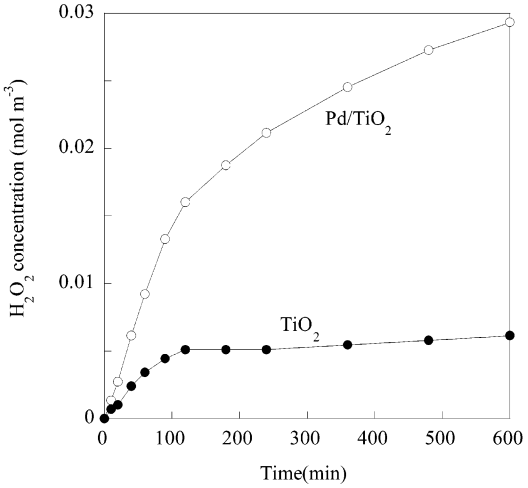
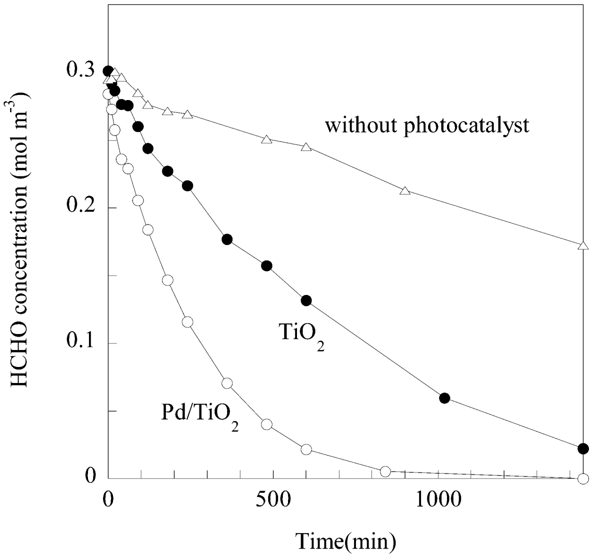


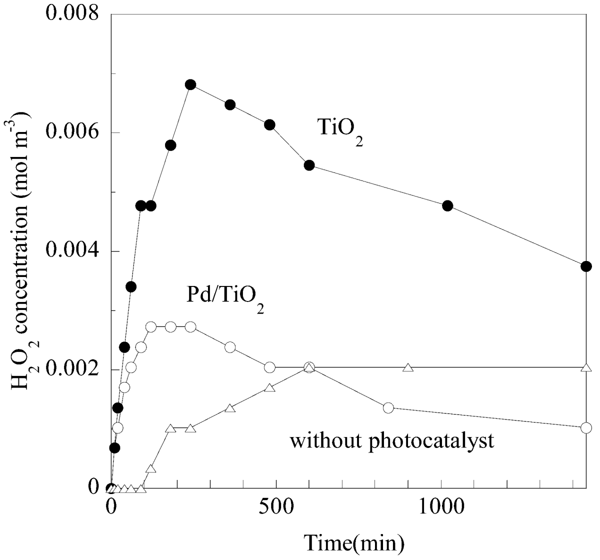
Figure 4. Formation of H_2O_2 from water by photocatalyst under irradiation with UV light from a blacklight blue fluorescent lamp.

since the HCOOH concentration reaches a maximum of about 0.04 mol m^{-3} and this value is rather small compared with the concentration corresponding to the HCHO decomposed, it is supposed that the HCOOH formed on the photocatalyst surface is mostly decomposed on the spot without being released from the surface. The pH of the reaction mixture is decreased from 6.5 to 3.8 as a result of the formation of HCOOH.

3.2. Decomposition of HCHO. *3.2.1. Blacklight Blue Fluorescent Lamp.* Figure 4 shows the time courses of the H_2O_2 concentration in the mixed-flow vessel when water was recirculated through the reactor with the glass tube coated with a thin film of TiO_2 or Pd/TiO_2 under irradiation with the UV light from the BL. In the case of TiO_2 alone, the H_2O_2 concentration increases until 120 min and then levels off at about 0.005 mol m^{-3}. In the case of Pd/TiO_2, the H_2O_2 concentration quickly increases from the initial stage and continues to increase even after 600 min. These results indicate that H_2O_2 is certainly produced in the presence of TiO_2 and the production rate is more increased by depositing Pd on TiO_2.



(a) Change in HCHO concentration



(b) Change in H_2O_2 concentration

Figure 5. Time courses of HCHO and H_2O_2 concentrations in decompositions of HCHO at an initial concentration of 0.3 mol m^{-3} by UV light alone or photocatalyst irradiated with UV light from a blacklight blue fluorescent lamp. (a) Change in HCHO concentration, (b) change in H_2O_2 concentration.

Figure 5 shows the time courses of the HCHO and H_2O_2 concentrations in the mixed-flow vessel when an aqueous solution of 0.3 mol m^{-3} HCHO was recirculated through the photocatalytic reactor under irradiation with the UV light from the BL. The HCHO concentration decreases even in the absence of the photocatalyst, indicating that HCHO is easily decomposed by just irradiating with UV light. The decomposition of HCHO is certainly increased in the presence of the photocatalyst, which increase is significant with Pd/TiO_2. It should be noted that there is a remarkable difference between the concentrations of H_2O_2 formed from water alone and from water containing HCHO. As a result of the decomposition of HCHO, the H_2O_2 concentration is lowered by about one-half with TiO_2 and one-fourth with Pd/TiO_2. This result clearly indicates that a considerable amount of H_2O_2 is steadily consumed throughout the decomposition of HCHO.

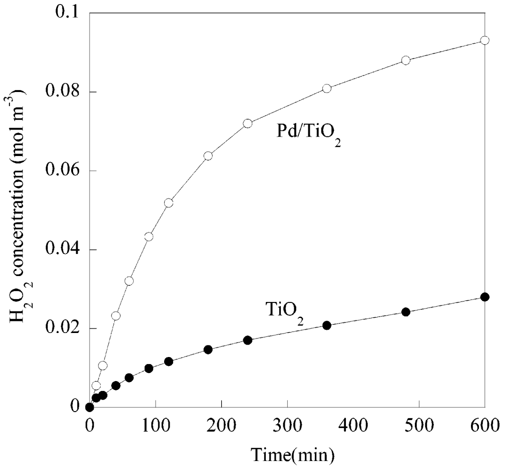
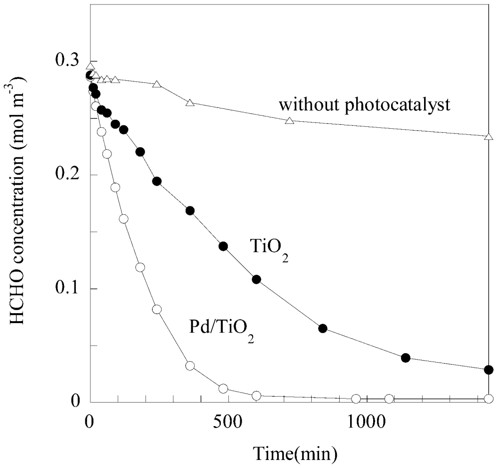
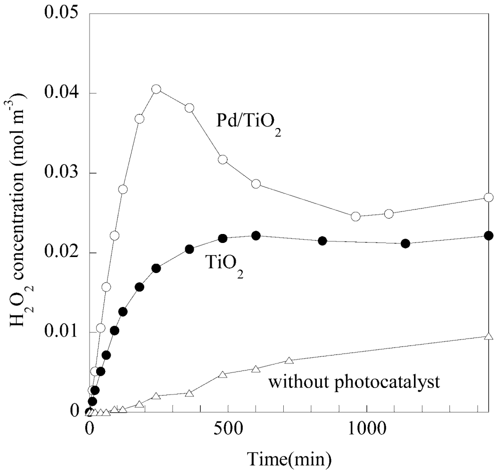


Figure 6. Formation of H_2O_2 from water by photocatalyst under irradiation with UV light from a germicidal lamp.



(a) Change in HCHO concentration



(b) Change in H_2O_2 concentration

Figure 7. Time courses of HCHO and H_2O_2 concentrations in decompositions of HCHO at an initial concentration of 0.3 mol m^{-3} by UV light alone or photocatalyst irradiated with UV light from a germicidal lamp. (a) Change in HCHO concentration, (b) change in H_2O_2 concentration.

3.2.2. Germicidal Lamp. Figure 6 shows the time courses of the H_2O_2 concentration when water was recirculated through the reactor under irradiation with the UV light from the GL. As in the case of the BL, H_2O_2 is certainly produced in the presence of the photocatalyst and the capability of the photocatalyst to form H_2O_2 is enhanced by depositing Pd on TiO_2.

Figure 7 shows the time courses of the HCHO and H_2O_2 concentrations in the mixed-flow vessel when an aqueous solution of 0.3 mol m^{-3} HCHO was recirculated through the photocatalytic reactor under irradiation with the UV light emitted from the GL. As in the case of the BL, the decomposition of HCHO is caused even in the absence of TiO_2 or Pd/TiO_2 and is accelerated in the presence of the photocatalyst, especially with Pd/TiO_2. The H_2O_2 concentration is lowered compared to the case of water alone in Figure 6, implying that H_2O_2 is steadily consumed during the decomposition of HCHO.

The rate of decomposition of HCHO is clearly proportional to the rate of formation of H_2O_2. It should be noted that the H_2O_2 concentration for Pd/TiO_2 passes through a maximum at 240 min and then decreases rapidly from 360 min, where most HCHO has been decomposed. As discussed later, such a time course of the H_2O_2 concentration is closely related to the H_2O_2 formed in parallel with the decomposition of HCOOH, which is produced as an intermediate in the decomposition of HCHO.

3.3. Decomposition of HCOOH. A formation mechanism of H_2O_2 has been proposed in the photolytic decomposition of HCOOH.[41−43] Also, Figure 3 gives a proof for the formation of HCOOH in the photocatalytic decomposition of HCHO. In this photocatalytic decomposition, thus, there is a possibility that H_2O_2 is formed in parallel with the decomposition of HCOOH. If this is true, it is clear that this formation more or less affects the time course of the H_2O_2 concentration during the photocatalytic decomposition. To clarify the formation mechanism of H_2O_2 in the photocatalytic decomposition of HCHO, therefore, the photocatalytic reaction was carried out using HCOOH as an initial reactant.

3.3.1. Formation of H_2O_2 in Photocatalytic Decomposition of HCOOH. Although several research groups have studied the photocatalytic decomposition of HCOOH,[44−46] there is no report on the formation of H_2O_2 in this photocatalytic reaction. To confirm the formation of H_2O_2, therefore, we investigated if the H_2O_2 concentration is changed when the HCOOH concentration is instantaneously increased in the process of the decomposition of HCOOH. The result is shown in Figure 8, where a 3.0×10^{-4} m^3 aqueous solution of HCOOH, at an initial concentration of 0.45 mol m^{-3}, was treated by TiO_2 irradiated with the UV light from the BL and a 5.0×10^{-5} m^3 aqueous solution of HCOOH at 0.45 mol m^{-3} was added after 720 min. The H_2O_2 concentration initially increases with the decrease in the HCOOH concentration, passing through a maximum at around 180 min and then decreasing. It is apparent that the H_2O_2 concentration temporarily increases just after the addition of HCOOH at 720 min, which clearly shows that the formation of H_2O_2 occurred in parallel with the photocatalytic decomposition of HCOOH.

3.3.2. Blacklight Blue Fluorescent Lamp. Figure 9 shows the time courses of the H_2O_2 concentration in the mixed-flow vessel when water was recirculated through the reactor with the glass tube coated with a thin film of TiO_2 or Pd/TiO_2 under irradiation with the UV light from the BL. This experimental result is fundamentally the same as that in Figure 4. However, we dare

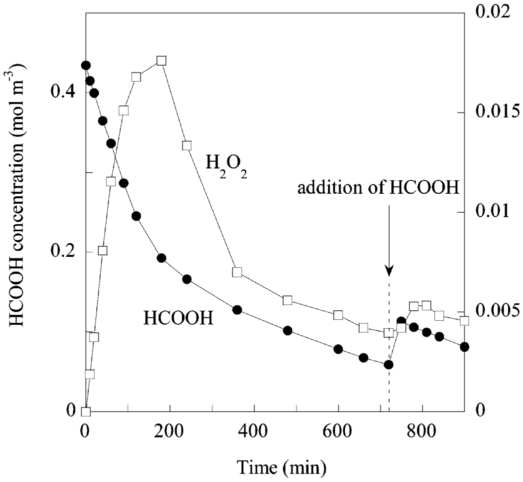


Figure 8. Time courses of HCOOH and H_2O_2 concentrations in treatment of a 3.0×10^{-4} m^3 aqueous solution of HCOOH at an initial concentration of 0.45 mol m^{-3} by TiO_2 under irradiation with UV light from a blacklight blue fluorescent lamp. A 5.0×10^{-5} m^3 aqueous solution of HCOOH at 0.45 mol m^{-3} was added after 720 min.

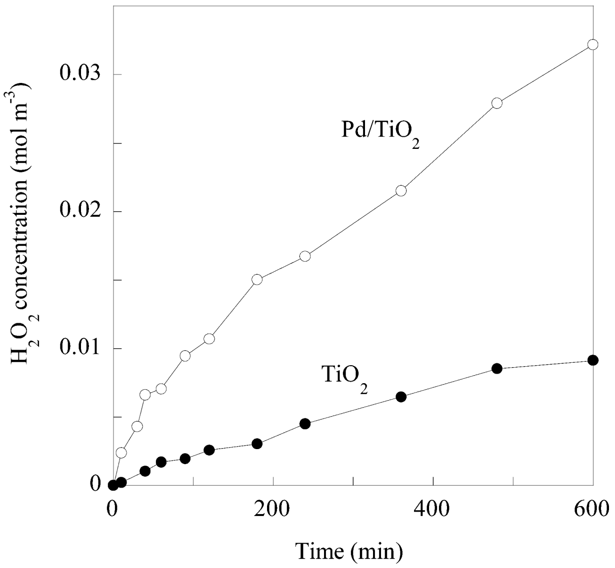
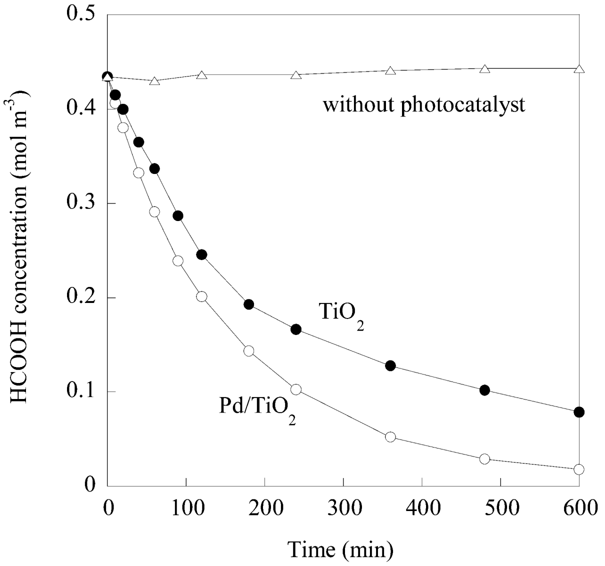
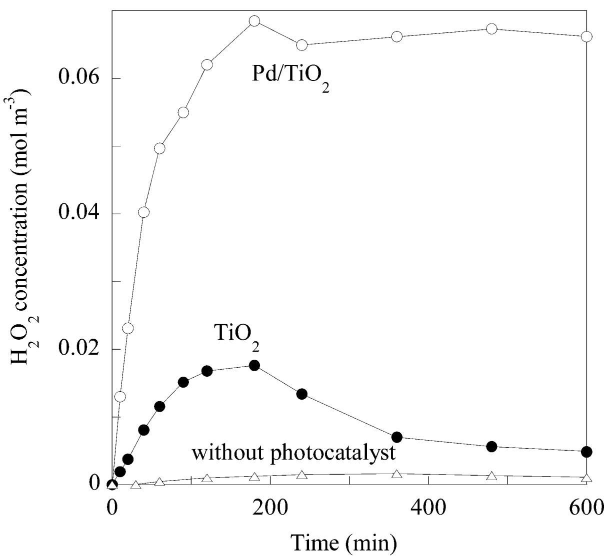


Figure 9. Time courses of H_2O_2 concentration under irradiation of water with UV light from a blacklight blue fluorescent lamp.



(a) Time courses of HCOOH concentration



(b) Time courses of H_2O_2 concentration

Figure 10. Time courses of HCOOH and H_2O_2 concentrations in decomposition of HCOOH at an initial concentration of 0.45 mol m^{-3} by UV light alone or by photocatalysts irradiated with UV light from a blacklight blue fluorescent lamp. (a) Time courses of HCOOH concentration, (b) time courses of H_2O_2 concentration.

to show the experimental data because the volume of the reaction mixture was different between the decompositions of HCHO and HCOOH. In addition, we used different lots of the glass tubes coated with TiO_2 and Pd/TiO_2 and the BLs. In the case of TiO_2 alone, the H_2O_2 concentration is steadily increased from the start of the reaction to 600 min and becomes almost constant at about 0.009 mol m^{-3}. The rate of formation of H_2O_2 for Pd/TiO_2 is more than three times larger than that for TiO_2 and the H_2O_2 concentration still continues to increase even after 600 min.

Figure 10 shows the time courses of the HCOOH and H_2O_2 concentrations in the mixed-flow vessel when an aqueous solution of 0.45 mol m^{-3} HCOOH was recirculated through the photocatalytic reactor under irradiation with the UV light from the BL. In the absence of TiO_2 or Pd/ TiO_2, there is little decrease in the HCOOH concentration, indicating that HCOOH cannot easily be decomposed by just irradiating with the UV light from the BL, whereas HCHO was decomposed under the same reaction condition, as shown in Figure 5. It is evident that HCOOH is certainly decomposed in the presence of the photocatalyst and the rate of decomposition for Pd/TiO_2 is larger than that for TiO_2. The higher the rate of decomposition of HCOOH, the larger the concentration of the H_2O_2 formed. Moreover, the H_2O_2 concentration measured is larger in water containing HCOOH than in water alone. In the photocatalytic decomposition of HCHO, on the other hand, this relation was reversed. These experimental results clearly show that when HCOOH is used as a reactant, the formation of H_2O_2 occurs in parallel with the decomposition of HCOOH. Since the decom-

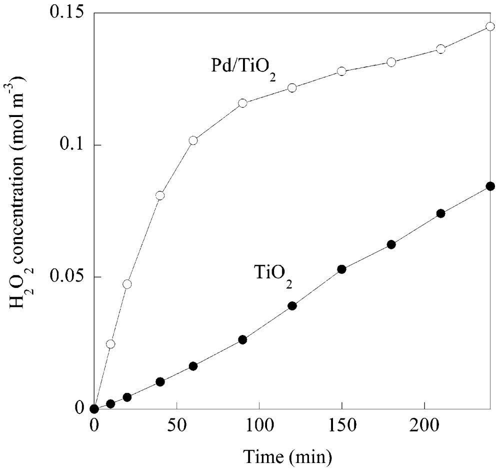


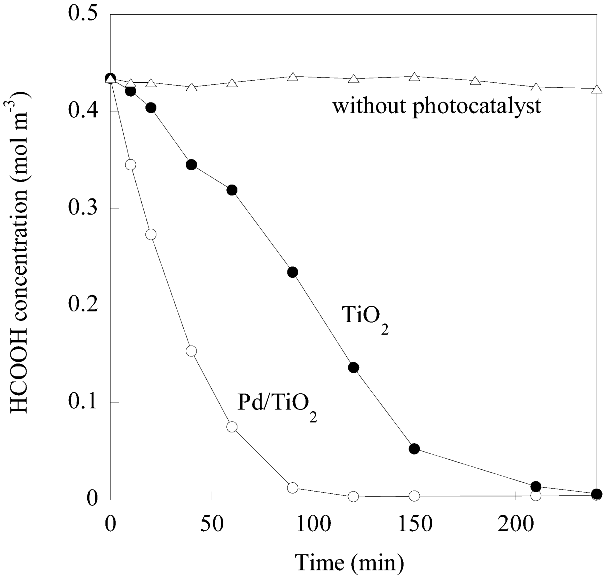
Figure 11. Time courses of H_2O_2 concentration under irradiation of water with UV light from a germicidal lamp.

position of HCHO causes a successive formation of HCOOH (Figure 3), it is thus considered that H_2O_2 is simultaneously formed with the decomposition of HCOOH, while the H_2O_2 formed is consumed in the oxidation of HCHO to HCOOH, leading to a lowering in the H_2O_2 concentration compared with the concentration of the H_2O_2 formed from water alone.

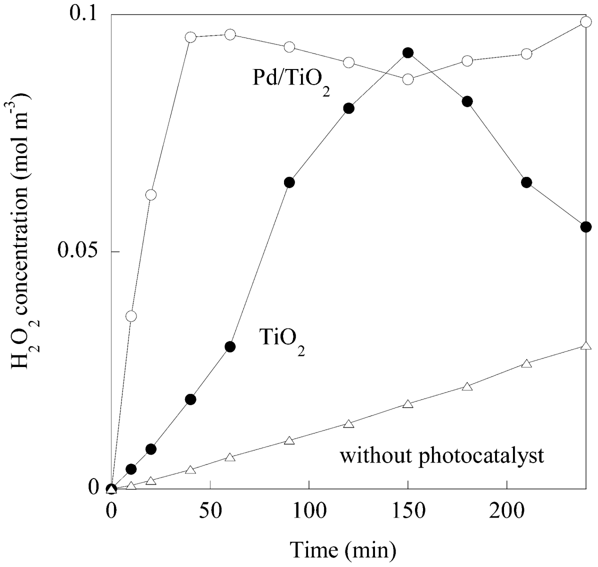
3.3.3. Germicidal Lamp. Figure 11 shows the time courses of the H_2O_2 concentration in the mixed-flow vessel when water was recirculated through the reactor with the glass tube coated with a thin film of TiO_2 or Pd/TiO_2 under irradiation with the UV light from the GL. This experimental result is fundamentally the same as that in Figure 6. Again, we dare to show the experimental data because the volume of the reaction mixture was different between the decompositions of HCHO and HCOOH and we used different lots of the glass tubes coated with TiO_2 and Pd/TiO_2 and the GLs. It is clear that depositing Pd on TiO_2 certainly increases the capability of the photocatalyst to form H_2O_2.

Figure 12 shows the time courses of the HCOOH and H_2O_2 concentrations in the mixed-flow vessel when an aqueous solution of 0.45 mol m^{-3} HCOOH was recirculated through the photocatalytic reactor with a glass tube of TiO_2 or Pd/TiO_2 under irradiation with the UV light from the GL. The rate of decomposition of HCOOH with the GL is 1.6 times larger than that with the BL in the presence of TiO_2, and 3.2 times larger in the presence of Pd/TiO_2. There is little decomposition of HCOOH in the absence of the photocatalyst, as found with the use of the BL. In contrast, HCOOH is remarkably decomposed in the presence of the photocatalyst. The rate of decomposition is larger with Pd/TiO_2.

3.4. Relationship between Rates of HCHO Decomposition and of H_2O_2 Formation. Figure 13 shows a plot of the initial rate of decomposition of HCHO against the initial rate of formation of H_2O_2 in the photocatalytic decomposition of HCHO. These values were calculated from Figures 5 and 7. It is apparent that there is a proportional relationship between the two initial rates. That is, the higher the ability to form H_2O_2, the higher the ability to decompose HCHO.



(a) Time courses of HCOOH concentration



(b) Time courses of H_2O_2 concentration

Figure 12. Time courses of HCOOH and H_2O_2 concentrations in decomposition of HCOOH at an initial concentration of 0.45 mol m^{-3} by UV light alone or by photocatalysts irradiated with UV light from a germicidal lamp. (a) Time courses of HCOOH concentration, (b) time courses of H_2O_2 concentration.

Likewise, the initial rate of decomposition of HCOOH is plotted against the initial rate of formation of H_2O_2 in the decomposition of HCOOH in Figure 14. These values were calculated from Figures 10 and 12. As in the case of the decomposition of HCHO, there is a proportional relationship between the two initial rates, indicating that the higher the ability to form H_2O_2, the higher the ability to decompose HCOOH.

Consequently, the data plots for the decompositions of HCHO and HCOOH suggest that the photocatalytic activity of TiO_2 is strongly dependent on the ability of the photocatalyst to form H_2O_2. It is thus concluded that the higher the ability to form H_2O_2, the higher the photocatalytic activity.

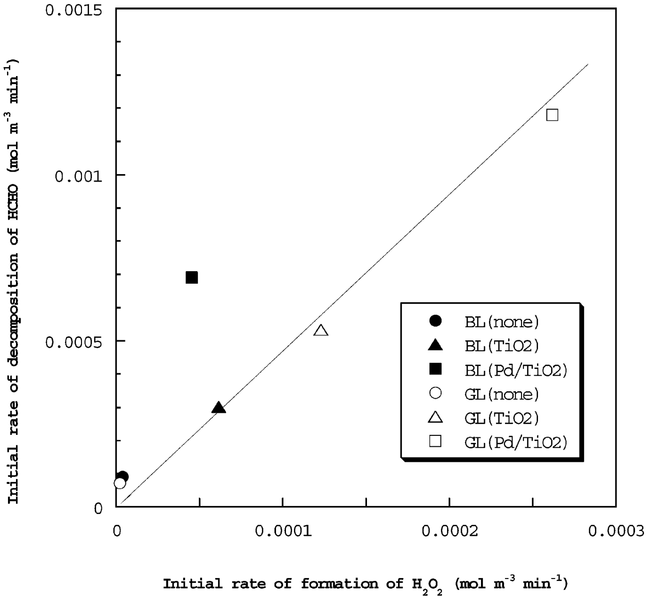


Figure 13. Relationship between initial rates of formation of H_2O_2 from water and initial rates of decomposition of HCHO in photocatalytic decomposition of HCHO.

3.5. Estimation of Reaction Mechanism. *3.5.1. Formation of Radicals in Photocatalytic Reactions.* The mechanism of the formation of radicals from water on the photocatalyst is generally described as[47,48]

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+) \qquad (1)$$

$$H_2O + h^+ \rightarrow HO^\bullet + H^+ \qquad (2)$$

$$OH^- + h^+ \rightarrow HO^\bullet \qquad (3)$$

$$O_2 + e^- \rightarrow O_2^{-\bullet} \qquad (4)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \qquad (5)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (6)$$

$$O_2^{-\bullet} + HO_2^\bullet \rightarrow HO_2^{\bullet-} + O_2 \qquad (7)$$

$$HO_2^\bullet + H^+ \rightarrow H_2O_2 \qquad (8)$$

$$H_2O_2 + e^- \rightarrow HO^\bullet + OH^- \qquad (9)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^\bullet + OH^- + O_2 \qquad (10)$$

$$H_2O_2 \xrightarrow{h\nu} 2HO^\bullet \qquad (11)$$

This reaction mechanism indicates that several kinds of radicals are successively produced as a result of the formation of electrons and holes on the TiO_2 irradiated with UV light.

3.5.2. Formation of H_2O_2. From the above reaction mechanism, it is considered that the formation of H_2O_2 in the presence of TiO_2 occurs in the following way. First, water molecules are decomposed by the action of holes on the photocatalytic surface excited with UV light to produce $HO^\bullet$ (eq 2). This radical is consumed for the decomposition of organic compounds if they are present. On the other hand, the dissolved O_2 is converted to $O_2^{-\bullet}$ by the action of electrons (eq 4). Finally, $HO_2^\bullet$ is produced via several steps, followed by the formation of H_2O_2 (eqs 6 and 8).

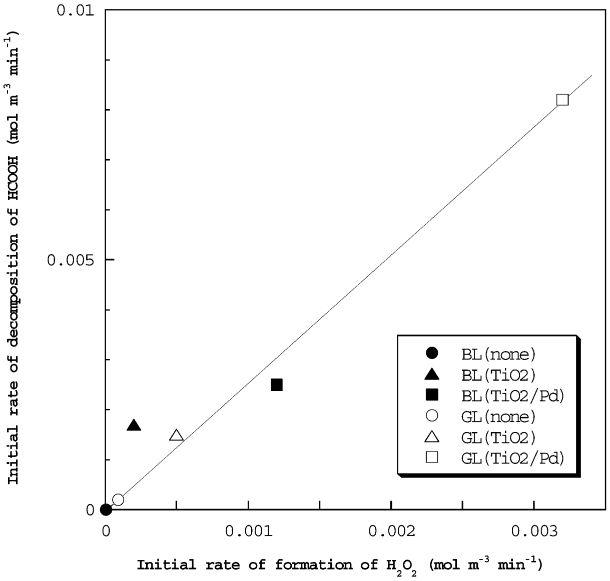


Figure 14. Relationship between initial rates of formation of H_2O_2 from water and initial rates of decomposition of HCOOH in photocatalytic decomposition of HCOOH.

It is known that an oxygen molecule is decomposed into oxygen atoms under irradiation with UV light of a wavelength shorter than 240 nm[49] (eq 12). The oxygen atom thus produced easily reacts with an oxygen molecule to become ozone (eq 13, which subsequently reacts with water to give H_2O_2 (eq 14):

$$O_2 \xrightarrow{\text{UV(185 nm)}} O^\bullet + O^\bullet \qquad (12)$$

$$O^\bullet + O_2 \rightarrow O_3 \qquad (13)$$

$$H_2O + O_3 \rightarrow H_2O_2 + O_2 \qquad (14)$$

However, the wavelengths of the light sources used in the present work are above 240 nm, and therefore it is considered that the formation of H_2O_2 does not occur according to the reaction mechanism given by eqs 12−14. In fact, when the BL was used as a light source, there was little formation of H_2O_2 by just irradiating the UV light (300−380 nm). Likewise, the formation of H_2O_2 was slight when the GL was used.

3.5.3. Decomposition of H_2O_2. It is considered that the photocatalytic and photolytic decompositions of H_2O_2 occur in parallel with the formation of H_2O_2. The former decomposition proceeds according to eqs 9 and 10, and the latter decomposition proceeds under irradiation with UV light according to eq 11. Moreover, the experimental result for the UV photolysis of H_2O_2[42] suggested the following mechanism for the photolysis of H_2O_2 in an aqueous solution:

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (15)$$

$$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \qquad (16)$$

Also, the following reaction may proceed:

$$2HO^\bullet \rightarrow H_2O_2 \qquad (17)$$

3.5.4. Formation Mechanism of $HO^\bullet$. The following three pathways may be possible for the formation of $HO^\bullet$:

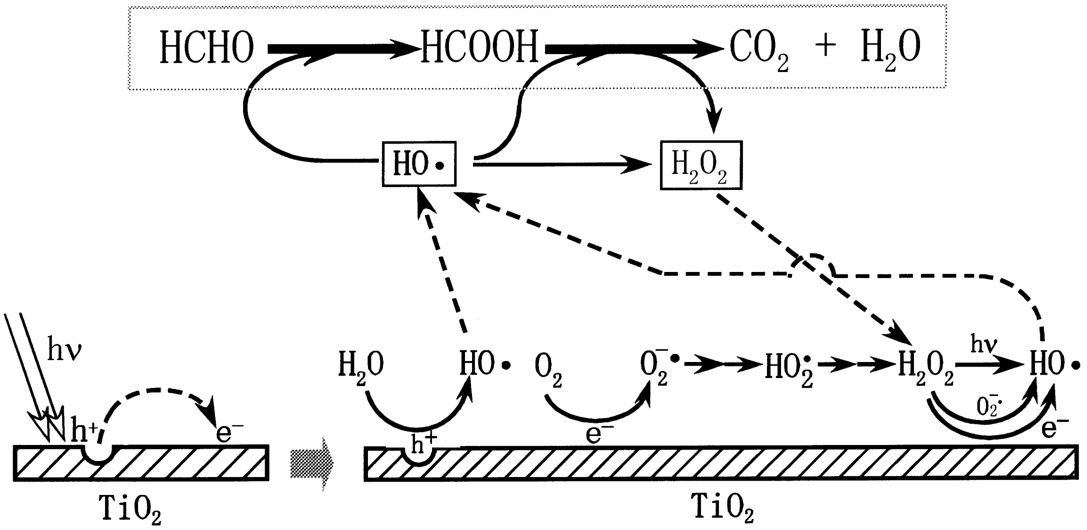


Figure 15. Reaction mechanism proposed for photocatalytic decomposition of HCHO.

Pathway 1: formed as a result of the decomposition of H_2O_2 by UV light (eq 11).

Pathway 2: formed as a result of the decomposition of H_2O_2 by the action of radicals densely existing in the very neighborhood of the photocatalyst surface (eqs 9 and 10).

Pathway 3: formed after several reaction steps including the photocatalytic decomposition of water (eqs 2 and 3).

To elucidate which pathway among pathways 1−3 is the main route to the $HO^\bullet$ formation in the photocatalytic reaction, H_2O_2 at almost the same concentration level as produced in the photocatalytic decomposition of HCOOH was added to the HCOOH solution and a change in the HCOOH concentration was investigated under irradiation with the UV light from the GL. Unlike in the presence of photocatalyst, however, HCOOH was slowly decomposed under this condition. Therefore, the H_2O_2 concentration was increased by 10 times and HCOOH was likewise decomposed. As a result, such a high concentration of H_2O_2 made it possible to decompose HCOOH rapidly, suggesting that the decomposition of HCOOH occurs in the very neighborhood of the photocatalyst surface and the formation of $HO^\bullet$ is mainly carried out through pathway 2 or 3. A further study is necessary to judge which of pathway 2 and 3 is more utilized.

3.5.5. Mechanism of Photocatalytic Decomposition of HCHO. Figure 15 shows a mechanism estimated for the decomposition of HCHO including the formations of H_2O_2 and $HO^\bullet$. HCHO is finally decomposed into carbon dioxide and water via the formation of HCOOH. $HO^\bullet$ is formed according to the mechanism described above and is directly related to the decompositions of HCHO and HCOOH. In parallel, formation of H_2O_2 occurs in the photocatalytic reaction. This is carried out through two pathways; the inherent pathway of the photocatalyst and the pathway included in the process of the decomposition of HCOOH. H_2O_2 is gradually accumulated in the solution with the progress of the reaction, while it is decomposed by the actions of UV light and radicals. Consequently, the increase in the H_2O_2 concentration terminates at a certain concentration level.

An increase in the photocatalytic activity when a certain metal is deposited is generally explained by attraction of electrons to the metal particles on TiO_2 followed by reduction in the recombination rate of electrons with holes. Thus, it is concluded that the increase of the H_2O_2 concentration by depositing Pd on TiO_2 was caused by promotion of each elementary reaction owing to a decrease in the recombination rate of electrons with holes.

3.6. Significance of the Measurement of H_2O_2 Concentration. There is little report on the time course of the H_2O_2 concentration during the photocatalytic reaction. This is probably because the concentration of the H_2O_2 formed by the photocatalyst is remarkably reduced by the autodecomposition or the consumption in the decomposition of organic compounds, thereby becoming difficult to detect H_2O_2. In fact, this was confirmed in our experiment. When HCHO was used as a reactant, the H_2O_2 concentration was lower than that formed from water alone under UV-irradiation, because H_2O_2 was unilaterally consumed in the oxidation of HCHO to HCOOH, which makes it difficult to accurately measure the H_2O_2 concentration by the conventional analytical methods based on chemical reactions.[11−15,17] When HCOOH was used as a reactant, on the other hand, the H_2O_2 concentration became higher because H_2O_2 was formed in the process of the decomposition of HCOOH. In the photocatalytic decompositions of most organic compounds, H_2O_2 would not be formed unless HCOOH is produced as an intermediate, leading to a remarkably low H_2O_2 concentration and then causing a difficulty in the measurement of the concentration. However, the use of the enzymatic method introduced in the present work would enable us to characterize the formation of H_2O_2 in the photocatalytic reaction.

The result of the measurement of H_2O_2 concentration indicates that the photocatalytic activity is directly proportional to the capability of the photocatalyst to form H_2O_2. This new finding would be useful to understand the mechanism of the photocatalytic reaction more clearly. Moreover, the concentration of the H_2O_2 produced in the photocatalytic treatment of water alone could be used as an index to identify the performances of the photocatalysts prepared by various methods.

4. Conclusions

In the present work, the photocatalytic decompositions of HCHO and HCOOH were performed by use of TiO_2 and Pd/TiO_2 under irradiation with the UV light emitted from a UV lamp (BL and GL) and the formation of H_2O_2 in their photocatalytic decomposition was investigated by introducing a highly accurate method for measurement of H_2O_2 based on an enzymatic reaction. As a result, the following conclusions were drawn.

(1) The photocatalyst irradiated with the UV light from the GL produces H_2O_2 from water at a larger rate and amount.

(2) Deposition of Pd on TiO_2 increases the rate and amount of the formation of H_2O_2 from water.

(3) In the absence of the photocatalyst, no HCOOH is decomposed under irradiations with both the UV lights from the BL and GL, whereas the decomposition becomes possible in the presence of the photocatalyst.

(4) H_2O_2 is formed in parallel with the photocatalytic decomposition of HCOOH.

(5) In the presence of the photocatalyst, the concentration of the H_2O_2 formed during the decomposition of HCHO is smaller than that formed from water alone. In contrast, this relationship is reversed with the decomposition of HCOOH. This is considered due to the formation of H_2O_2 in the process of the decomposition of HCOOH to carbon dioxide and water.

(6) The rates of decomposition of HCHO and HCOOH are directly proportional to their respective rates of formation of H_2O_2, indicating that there is a close relationship between the photocatalytic activity and the capability of the photocatalyst to form H_2O_2.

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