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Degradation of Chlorobenzene by the Hybrid Process of Supercritical Water Oxidation and TiO_2 Photocatalysis

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A novel hybrid process of hydrothermal or supercritical water oxidation and TiO_2 photocatalysis was developed to examine the degradation of chlorobenzene as a model of the oxidative decomposition of organic pollutants. Aqueous solutions of chlorobenzene containing H_2O_2 as the oxidizing agent and/or colloidal TiO_2 nanoparticles as catalyst, were fed into the reactor with the temperature and the pressure controlled to be $T = 25$–$400°C$ and $P = 30\,MPa$, respectively. Chlorobenzene was considerably decomposed in the presence of H_2O_2 under hydrothermal conditions for $T \geqq 300°C$. It appeared that photocatalytic decomposition of chlorobenzene takes place at all temperatures by colloidal TiO_2 nanoparticles under irradiation with near-UV light. We have realized the synergic decomposition of chlorobenzene by the coexistence of H_2O_2 and TiO_2 in which maximum conversion is more than 80% under irradiation at $T = 200°C$.

Keywords chlorobenzene; photocatalysis; supercritical water oxidation; titanium dioxide

INTRODUCTION

Subcritical water and supercritical water (SCW) have been used as a reaction medium for chemical synthesis, fuel production, waste treatment by oxidation, and so on (1). The critical temperature and pressure of water are rather severe; $T_c = 374.2°C$ and $P_c = 22.1\,MPa$. Supercritical water oxidation (SCWO), a promising technique for the treatment of hazardous wastewater, takes advantage of the complete miscibility of organic compounds and oxidizing agent such as oxygen (O_2) and hydrogen peroxide (H_2O_2) with SCW so that there is a single phase at reaction conditions. Moreover, as the temperature is sufficiently high (400–600°C, $T > T_c$), intrinsic reaction rates are rapid and essentially complete mineralization of ordinary organic compounds to CO_2 and H_2O occurs within a reasonable residence time in the reactor. However, for certain persistent organic compounds, higher reaction temperature is usually necessary. In the practical processes, the low operation temperature is frequently desirable and to meet the needs, heterogeneous catalytic oxidation in high-temperature, high-pressure water has received attention as a new approach (catalytic SCWO). In this process, such catalysts as can increase the oxidation rate, reduce the residence time and reaction temperature required for the treatment is demanded (2).

In 1972, Fujishima and Honda found that O_2 is produced without being accompanied with corrosion when a titanium dioxide (TiO_2) single crystal electrode is illuminated with near-UV light (3). By virtue of high photocatalytic activity as well as chemical stability, TiO_2 photocatalyst is promising for a variety of applications such as solar energy conversion, treatments of organic-containing wastewater, and the recovery of natural resources (4,5). The photocatalytic degradation of pollutants in aqueous solution is attracting considerable attention for application to environmental problems. Photoexcitation of TiO_2 generates conduction-band electrons and positive holes, which triggers a series of reactions that ultimately lead to mineralization of the pollutants. To improve the performance of such photoprocess and put into practical use, the photocatalysis has been often combined with some physical and chemical operations (6).

Until now, most applications of TiO_2 photocatalysis have been based on the premise that the photocatalyst is used under mild conditions near ambient temperature and pressure. We have recently examined the photocatalytic reduction of silver ions by colloidal TiO_2 nanoparticles in high-temperature ($T = 25$–$400°C$), high-pressure ($P = 30\,MPa$) water (7). It has been found that photocatalytic reduction takes place even under hydrothermal conditions as efficiently as at room temperature. In this connection, it is of substantial interest how the photocatalytic oxidation reactions are influenced by such conditions

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of the surroundings. In a preceding article on the treatment of soil contaminated with organic pollutant, we have examined the oxidative decomposition of chlorobenzene (CB) in the slurry of model soils, silica, kaolin, and titania under hydrothermal conditions (8). In the present study, we have chosen CB as a model compound because it is listed as a priority pollutant in water due to low biodegradability and accumulation potential in soil and water (9,10). A flow type reactor available for the study of photocatalytic reactions of the aqueous suspension has been constructed and the degradation of CB by H_2O_2, photocatalytic oxidation by TiO_2 and the treatment of CB by the combination of H_2O_2 and TiO_2 have been examined using this reactor. One distinctive feature of this study is that the combination of hydrothermal oxidation with TiO_2 photocatalysis has achieved the synergic decomposition of CB.

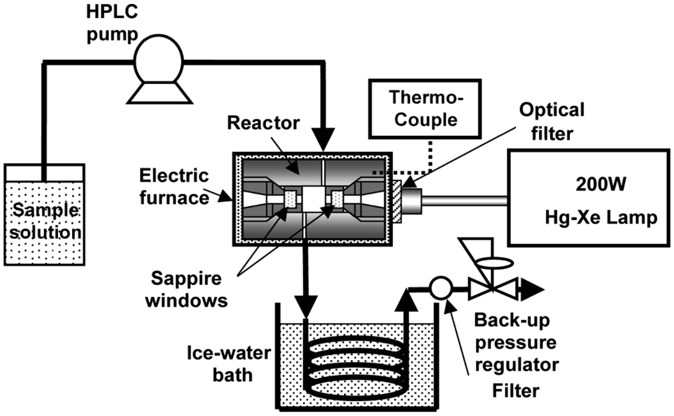


FIG. 1. Schematic diagram of the flow reactor designed for the study of photocatalytic reactions of aqueous suspensions under high-temperature, high-pressure conditions.

EXPERIMENTAL

Materials

Colloidal TiO_2 nanoparticles were synthesized by hydrolysis of titanium(IV) tetraisopropoxide (Ti(*i*-OPr)$_4$) as in the preceding paper (11) and then purified by dialysis with an aqueous HNO_3 (pH = 1.5) for 24 h in a dialysis tubing (VISKASE Co.). According to X-ray diffraction pattern, the obtained TiO_2 nanoparticles were of anatase-type. TiO_2 powder (JRC-TIO-01) was generously supplied from the Catalysis Society of Japan, which was also of anatase type with a nominal diameter of the primary particle being about 21 nm. Ti(*i*-OPr)$_4$, 2-propanol, HNO_3, chlorobenzene (CB), hydrogen peroxide (H_2O_2), nitrobenzene, and *N,N′*-dimethylformamide were purchased from Kishida Chemicals Co. and used as received.

Experimental Methods

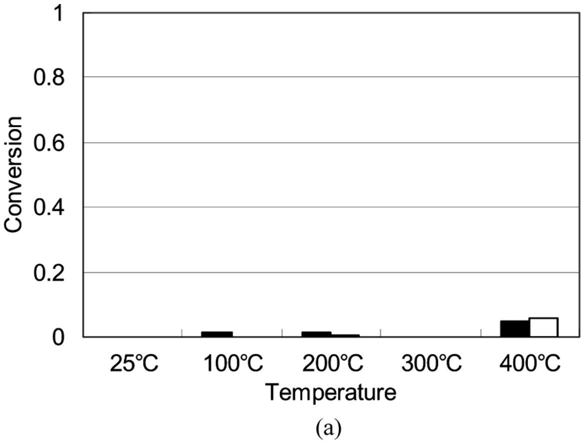
A flow type reactor equipped with sapphire windows was designed. The schematic diagram of the reactor and the combination of experimental apparatus are illustrated in Fig. 1. The basic structure of the reactor was the same as described in Ref (12). It was made of Hastelloy (inner volume $\sim 1.0\,cm^3$) and was equipped with two sapphire windows whose diameter was 6.0 mm. The reactor could be heated at desired temperature $T = 25$–$400°C$ by an electric furnace. Pressure was kept at $P = 30$ MPa by a back-up pressure regulator (SCF-Bpg, JASCO Co.). Typically, four kinds of CB solutions were prepared and tested; A: CB solution, B: CB + H_2O_2 solution, C: CB+TiO_2 suspension, D: CB + H_2O_2 + TiO_2 suspension. The solution was injected into the reactor by a HPLC pump, PU-1580 (JASCO Co.), with the flow rate $0.3\,cm^3\,min^{-1}$, the average residence time being about 3.3 min. The solution was illuminated through the sapphire window with near-UV light ($\lambda = 300$–400 nm) from a 200 W Hg/Xe lamp (MUV-202U, Moritex Co.). A fraction of UV light ($\lambda < 300$ nm) was cut off by an optical filter. To minimize the effect of adsorption of CB inside of the reactor, the solution was let to flow for more than 60 min in the reactor for aging before the start of the reaction. The reaction mixture ejected from the reactor was passed through an ice-water bath for cooling and a filter SS-4TF-0.5 (Swagelok Co.) and then finally collected from the outlet of a back-up pressure regulator.

To monitor the degradation of CB quantitatively, organic compounds in the reaction mixture were extracted with nitrobenzene and then submitted to gas-chromatographic analysis by a G2800-F gas chromatograph with a TCD detector (Yanagimoto Co.). *N,N′*-dimethylformamide (1 vol%) was added to the nitrobenzene solution as the internal standard to determine the amount of remaining CB in the reaction mixture.

RESULTS AND DISCUSSION

Chlorobenzene/H_2O_2 Solution

It has been known that CB is tolerant to decomposition in the absence of suitable oxidants in water even under hydrothermal conditions. We began by examining the degradation of CB itself. The aqueous solution of 1 mM CB (solution A) was supplied to the reactor with the rate $0.3\,cm^3\ min^{-1}$ for $T = 25$–$400°C$. The conversion of CB after passing through the reactor in the dark and under near-UV irradiation at each temperature is shown in Fig. 2(a). It appeared that CB is fairly stable for $T = 25$–$300°C$ irrespective of irradiation with light. Even at the elevated temperature $T = 400°C$, only 4–5% of CB was decomposed, reflecting the recalcitrant properties of CB. We next examined the influence of the oxidizing agent H_2O_2 on the degradation of CB. The conversion of CB in the aqueous solution containing 1 mM CB and 0.1 wt% H_2O_2 (solution B) is given in Fig. 2(b). While less than 5% of CB was decomposed for $T \leqq 200°C$, higher temperature $T \geqq 300°C$ caused more than 20% decomposition.



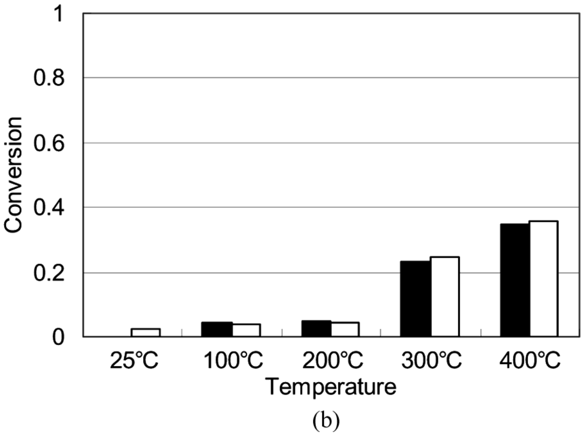


FIG. 2. The conversion of CB after passing through the reactor in the dark (filled bars) and under near-UV irradiation (open bars) at each temperature for (a) 1 mM CB solution, and (b) 1 mM CB + 0.1 wt% H_2O_2 solution. Flow rate 0.3 $cm^3 min^{-1}$ and $P = 30$ MPa.

Despite the rather short residence time, nearly 40% of CB disappeared at $T = 400$°C, indicating a typical hydrothermal oxidation by H_2O_2 (13). In our study, only the experiments at $T = 400$°C met the conditions of SCWO and the reaction temperature of $T = 100$–300°C was lower than T_c. However, for the sake of convenience, we may call hydrothermal oxidation for $T \geqq 100$°C in Fig. 2(b) the SCWO in a wide sense.

Chlorobenzene/Colloidal TiO_2 Nanoparticle Suspension

The aqueous suspension containing 1 mM CB and 0.8 mM TiO_2 (solution C) was injected into the reactor and the conversion of CB in the dark and under irradiation was examined. Figure 3 shows the conversion of CB at each temperature. In the dark, the conversion of CB was less than 5% for $T \leqq 300$°C but it amounted to around 35% at $T = 400$°C. The irradiation of the suspension with near-UV light caused enhanced degradation at all temperatures ($T = 25$–400°C) (Fig. 3). This is a second example of the persistence of the photocatalytic activity of TiO_2 under hydrothermal conditions. Apparent photocatalytic activity, as defined by the magnitude of increment of the conversion caused by irradiation, does not change so much for $T = 100$–400°C, except a sink at $T = 300$°C. The drop at $T = 300$°C may be due to the coagulation of TiO_2 nanoparticles in the reactor (7). We should note that considering the decrease in the density of subcritical and supercritical water, which affects the residence time in the reactor, photocatalytic activity at $T = 300$–400°C is higher than what it looks in Fig. 3.

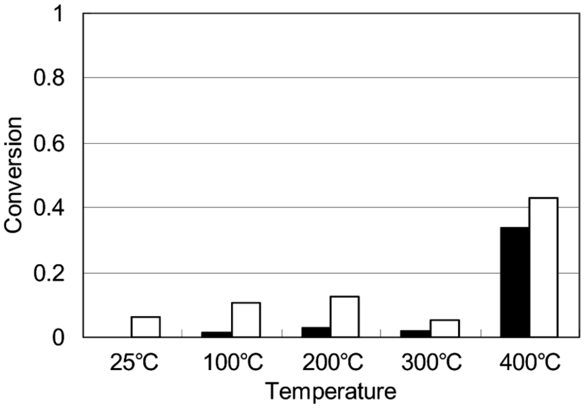
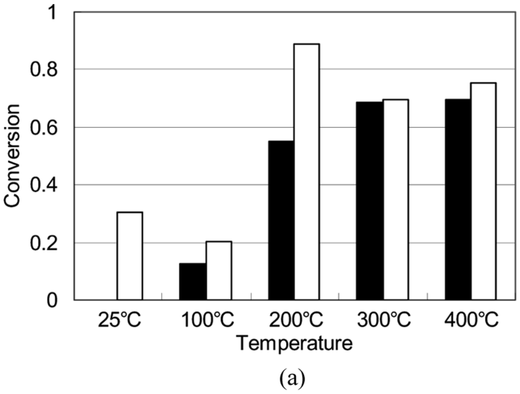


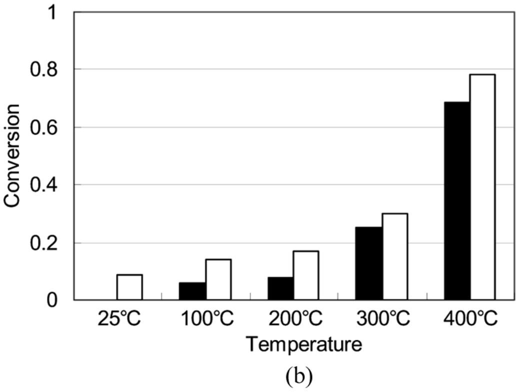
FIG. 3. The conversion of CB after passing through the reactor in the dark (filled bars) and under near-UV irradiation (open bars) at each temperature for 1 mM CB + 0.8 mM colloidal TiO_2 solution. Flow rate 0.3 $cm^3 min^{-1}$ and $P = 30$ MPa.

The aqueous suspension containing 1 mM CB, 0.1 wt% H_2O_2 and 0.8 mM TiO_2 (solution D) was supplied to the reactor and irradiated with near-UV light. The conversion of CB at each temperature is shown in Fig. 4(a). As a comparison, a simple sum of the conversion of CB by oxidation process of the CB + H_2O_2 solution at each temperature (Fig. 2(b)) and photocatalytic degradation of the CB + TiO_2 suspension at each temperature in Fig. 3 is given in Fig. 4(b). Even in the dark, the conversion of CB in the CB + H_2O_2 + TiO_2 suspension (Fig. 4(a)) is considerably larger than the conversion in Fig. 4(b) for $T = 100$–300°C. Particularly, the increase in the conversion for $T = 200$–300°C is remarkable. The irradiation of the CB + H_2O_2 + TiO_2 suspension with near-UV light surely increased the conversion. At $T = 200$°C, more than 80% conversion was attained in Fig. 4(a), indicating the synergic decomposition of CB by the coexistence of H_2O_2 and TiO_2 in the solution.

We carried out a preliminary analysis of the reaction byproducts. The reaction mixture at the outlet of the back pressure regulator was collected and diluted by 10 times with ethanol. The solution was subjected to GC/MS analysis with a gas chromatograph mass spectrometer, GC/MS-QP1000 (Shimadzu Co.). The reaction mixture of the CB + H_2O_2 + TiO_2 suspension after the treatment contained the remainder of the CB and a small amount of



(a)



(b)

FIG. 4. (a) The conversion of CB after passing through the reactor in the dark (filled bars) and under near-UV irradiation (open bars) at each temperature for 1 mM CB + 0.1 wt% H_2O_2 + 0.8 mM colloidal TiO_2 solution. (b) The sum of the conversion of CB by hydrothermal oxidation process shown in Fig. 2(b) and the photocatalytic degradation given in Fig. 3 at each temperature. Flow rate 0.3 $cm^3 min^{-1}$ and $P = 30$ MPa.

aliphatic C2 ~ C4 ketone, aldehyde, alcohol, and carboxylic acid and no aromatic hydrocarbons and their derivatives, e.g., benzene and phenol, were detected. Those results strongly suggest that except for the remainder of the CB and a small amount of short-chain aliphatic compounds, most of CB is converted to CO_2 and H_2O.

Chlorobenzene/ TiO_2 Powder Suspension

To obtain further evidence of the photocatalytic activity of TiO_2 under hydrothermal conditions, TiO_2 powder was used in place of colloidal TiO_2 nanoparticles. A newly designed piston separator (inner volume 180 cm^3) was installed between the HCLP pump and the reactor in Fig. 1 to ensure continuous and stable supply of TiO_2 suspension to the reactor. The filter SS-4TF-0.5 between the ice-water bath and the back-up pressure regulator was effective to trap TiO_2 particles larger than 0.5 μm. The conditions of temperature, pressure, and flow rate were set equal to those employed in the colloidal TiO_2 nanoparticles. We at first tested an aqueous suspension composed of 1 mM CB and 0.1 wt% (ca. 13.8 mM) TiO_2 powder.

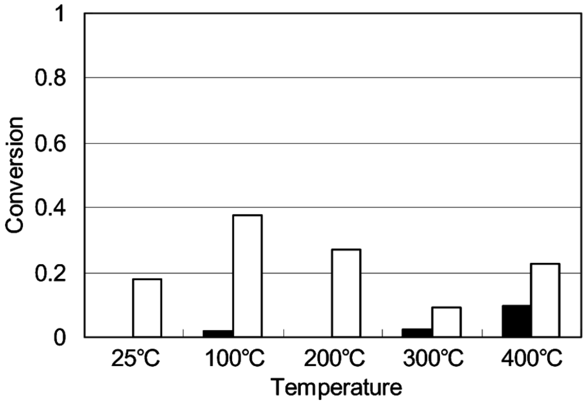


FIG. 5. The conversion of CB after passing through the reactor in the dark (filled bars) and under near-UV irradiation (open bars) at each temperature for the aqueous suspension composed of 1 mM CB and 0.1 wt% TiO_2 powder. Flow rate 0.3 $cm^3 min^{-1}$ and $P = 30$ MPa.

The conversion of CB at each temperature is shown in Fig. 5. The conversion in the dark is on the whole smaller than that in the colloidal TiO_2 nanoparticles. On the other hand, it appeared that apparent photocatalytic activity is larger than colloidal TiO_2 nanoparticles. Photocatalytic activity is most pronounced around $T = 100$–200°C. We next examined the aqueous suspension composed of 1 mM CB, 0.1 wt% H_2O_2 and 0.1 wt% TiO_2 powder. The conversion of CB at each temperature is shown in Fig. 6(a). The simple sum of the conversion of CB by oxidation process in Fig. 2(b) and photocatalytic degradation of the CB + TiO_2 suspension in Fig. 5 at each temperature is given in Fig. 6(b). The conversion of CB in Fig. 6(a) for $T = 200$–300°C is substantially larger than the conversion in Fig. 6(b). Near-UV irradiation surely promotes the degradation (Fig. 6(a)). The conversion amounts to nearly 80% at $T = 200$°C. These results are qualitatively in accordance with those in the case of colloidal TiO_2 nanoparticles, indicating that the synergic degradation of CB observed for the first time in this study is the common phenomenon for the combination of hydrothermal oxidation and TiO_2 photocatalysis.

Mechanism of CB Degradation

In this study, we have made several attempts to decompose CB under hydrothermal conditions. We shall here make qualitative discussion on the reaction mechanism with reference to some related papers. Although elementary reactions for the oxidation of organic compounds in the aqueous solution are rather complex, hydroxyl radicals $^{\bullet}OH$ are undoubtedly primary oxidative species. We have therefore focused on the generation of $^{\bullet}OH$ radicals, which will subsequently attack adsorbed pollutant molecules. The conversion of CB in the aqueous solution containing H_2O_2 is increased for $T \geqq 300$°C in the dark (Fig. 2(b)). Such

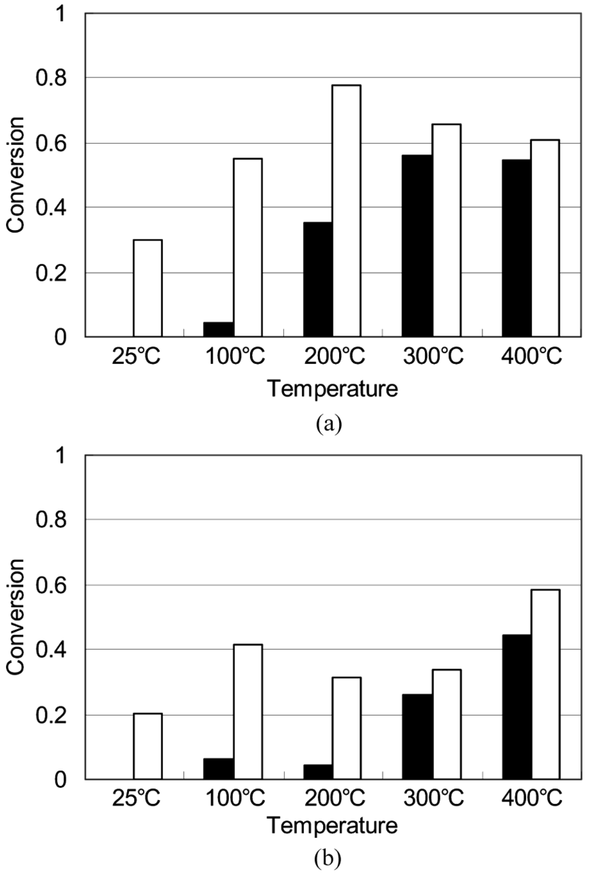


FIG. 6. (a) The conversion of CB after passing through the reactor in the dark (filled bars) and under near-UV irradiation (open bars) at each temperature for the aqueous suspension composed of 1 mM CB, 0.1 wt% H_2O_2 and 0.1 wt% TiO_2 powder. (b) The sum of the conversion of CB by hydrothermal oxidation process shown in Fig. 2(b) and the photocatalytic degradation given in Fig. 5 at each temperature. Flow rate 0.3 cm^3 min^{-1} and $P = 30$ MPa.

observations are consistent with thermal decomposition of H_2O_2 in SCWO as discussed by Savage (1).

$$H_2O_2 \rightarrow 2\ {}^{\bullet}OH \tag{1}$$

${}^{\bullet}OH$ radicals undergo succeeding reactions yielding O_2 and ${}^{\bullet}HO_2$ radical. It has been known that irradiation of H_2O_2 with UV light yields ${}^{\bullet}OH$ with relatively high quantum efficiency (14,15).

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \tag{2}$$

However, reaction (2) is almost negligible in this study because H_2O_2 does not significantly absorb the near-UV light of the range of $\lambda = 300$–400 nm (16).

Although photocatalytic actions have been the principal issue of wide bandgap metal oxide semiconductors like TiO_2, generation of charge carriers in the dark could also play significant role at high temperatures. Mizuguchi & Shinbara have reported on a complete decomposition of polycarbonates that utilizes thermally-excited holes in TiO_2 powder at about 500°C (17). According to the DSC measurements by them, the onset temperature of the polycarbonate decomposition is lower than 400°C. Accordingly, the contribution of thermally-excited holes has to be taken into account to interpret considerable extent of CB degradation in the dark at $T = 400°C$ (Fig. 3). Positive holes in the valence band (V.B.) oxidize H_2O molecules on the surface to produce ${}^{\bullet}OH$ radicals.

$$TiO_2 \rightarrow e^-(C.B.) + h^+(V.B.) \tag{3}$$

$$H_2O + h^+(V.B.) \rightarrow \bullet OH + H^+ \tag{4}$$

Electrons in the conduction band (C.B.) can react with O_2 molecules on the surface and produce $\bullet O_2^-$.

$$O_2 + e^-(C.B.) \rightarrow \bullet O_2^- \tag{5}$$

Photocatalytic reactions on the TiO_2 surface are initiated by absorbing UV ~ near-UV light that can excite valence band electrons to the conduction band. Photoelectrons in the conduction band and positive holes in the valence band undergo subsequent interfacial electron transfers and thermal reactions at the surface (11).

$$TiO_2 + h\nu \rightarrow e^-(C.B.) + h^+(V.B.) \tag{6}$$

The photocatalytic degradation of organic compounds in aqueous solutions is the process in which photoinduced holes oxidize H_2O molecules (reaction (4)) or hydroxide ions (OH^-) on the surface to produce ${}^{\bullet}OH$ radicals (9,18,19).

$$OH^- + h^+(V.B.) \rightarrow \bullet OH \tag{7}$$

Formation of H_2O_2 from ${}^{\bullet}OH$ radicals has been known (20).

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{8}$$

Some of the charge carriers may disappear by electron-hole recombination

$$e^-(C.B.) + h^+(V.B.) \rightarrow \text{recombination} \tag{9}$$

In Fig. 3, we have shown the persistence of the photocatalytic activity of colloidal TiO_2 nanoparticles in high-temperature, high-pressure water. Moreover, Fig. 5 demonstrates the photocatalytic action of TiO_2 powder for $T = 25$–$400°C$. In conjunction with our former study on the reduction of Ag^+ ions by TiO_2, we can conclude that the photocatalytic activity of TiO_2; oxidation by positive holes as well as reduction by conduction-band electrons, are maintained in subcritical ~ supercritical water. These results could open up the way to new applications of TiO_2 photocatalyst under extreme environments, e.g., treatments of environmental pollutants, recovery of natural resources, gasification of biomass, and so forth. The ionic product of water is known to increase from $K_W = 10^{-14}$ at ambient conditions to about $K_W = 10^{-11}$ at $T = 200$–300°C and $P = 25$–50 MPa, and then it starts to decrease with increasing temperature higher than $T = 350°C$ (21,22). The dielectric constant of water at $P = 30$ MPa is a decreasing function of temperature from $T = 20°C$ to 400°C, which may reduce the solvation energy for ionic species. The nature of the TiO_2 surface and redox pairs under hydrothermal conditions, e.g., the energy band positions of TiO_2, electronic redox levels of redox pairs, have not been well-established to date. We have assumed that conduction-band electrons and positive holes in TiO_2 in contact with subcritical ~ supercritical water can contribute to the reduction of O_2 (reaction (5)) and oxidation of OH^- or H_2O (reaction (4),(7)), respectively. The increased concentration of OH^- in subcritical water seems to be a favorable condition for the oxidation by positive holes. Higher temperature under hydrothermal conditions in itself can promote a variety of chemical reactions having large activation energy, such as chemical reactions involving $^{\cdot}OH$ radicals and CB. To substantiate those considerations, direct experimental and theoretical works on the electrochemistry and photochemistry under hydrothermal conditions are needed, which have not been advanced so much until now (23).

Synergic degradation of CB has been found in the aqueous suspension containing TiO_2 and H_2O_2 (Fig. 4). Yu and Savage have reported the catalytic SCWO of phenol by H_2O_2 over bulk TiO_2 for $T = 380$–440°C, which is higher than T_c (24). In this study, we have employed physicochemically well-defined colloidal TiO_2 nanoparticles as the catalyst. Efficient decomposition of H_2O_2 by colloidal metals and oxides has been known since early times as "Anorganische Fermente" (25). It is likely that colloidal TiO_2 nanoparticles can catalyze the Fenton-type reaction (26), producing a large amount of $^{\cdot}OH$ radicals in the dark under hydrothermal conditions.

$$H_2O_2 + (\text{active site}) \rightarrow .OH + OH^- + (\text{deactivated site}) \qquad (10)$$

It is probable that a certain surface site at the TiO_2 surface, such as an oxygen-deficient site or Ti(III) site (27), can play the role of the active site for catalytic decomposition of H_2O_2.

It has been reported by several research groups (28–32) that the addition of H_2O_2 to the aqueous TiO_2 suspension can drastically increase the quantum efficiency of $^{\cdot}OH$ radical generation. In this process, added H_2O_2 acts as an electron acceptor, which competes with O_2 molecules in reactions (5), as well as electron-hole recombination (reaction (9)).

$$H_2O_2 + e^-(\text{C.B.}) \rightarrow .OH + OH^- \qquad (11)$$

The increase in $^{\cdot}OH$ radical concentration by reaction (11) may be a favorable condition for the enhanced conversion seen in Fig. 4(a) under near-UV irradiation. However, the origin of maximum conversion efficiency at $T = 200°C$ (Fig. 4(a)), which is practically most important because it enables us to degrade CB at lower temperature than T_c, still remains unsolved. The interaction between H_2O_2 and TiO_2 surface seems to be rather complicated. Recently, visible-light induced photodecomposition of H_2O_2 from the surface complex, $\equiv Ti(IV){-}OOH$, has been reported (33).

In the last decade, much effort has been devoted to treat wastewater containing organic compounds such as aromatic compounds, chlorinated compounds, and so on. The combination of hydrothermal oxidation or SCWO with TiO_2 photocatalysis proposed in this study is attractive for the development of the innovated process capable of the treatment of wastewater at temperature $T < T_c$. As an extension of conventional SCWO and catalytic SCWO, we may call the novel hybrid process photocatalytic supercritical water oxidation (photocatalytic SCWO).

Chlorinated compounds like CB typically eliminate chlorine atoms under hydrothermal conditions. Chloride ions in solutions often lead to a corrosive environment. We made a preliminary examination of the analysis of chloride ions with a help of ion chromatography (DX-500, Dionex Co.) and proved that almost all chlorine is converted to chloride ions in the reaction mixture. Because of the continuous process with relatively short residence time, practically no corrosion of the Hastelloy reactor was noticed. However, detailed analysis of the reaction products, those included in the organic phase, the aqueous phase, and the gaseous phase, is necessary to establish the mechanism of the degradation of CB, which is ultimately related to the improvement of photocatalytic SCWO process to decompose up to 100% of organic pollutants in wastewater and soil.

Finally, we would like to emphasize that the efficient photocatalytic activity of TiO_2 in the oxidation reaction as well as the reduction reaction under hydrothermal conditions can open up a possibility to develop a novel hybrid process based on the combination of conventional hydrothermal technology and photocatalysis. Besides the photocatalytic SCWO which has proved quite useful for the treatment of environmental pollutants in this study, it has recently been revealed that a certain type of model biomass such as glucose and ethanol could be effectively converted to low-molecular gases like hydrogen and methane by the hybrid process of hydrothermal gasification and TiO_2 photocatalysis (34,35).

SUMMARY

We have designed a flow type reactor available for the study of photocatalytic treatment of wastewater under high-temperature, high-pressure conditions. Degradation of chlorobenzene (CB) was taken up as a model of oxidative decomposition of organic pollutants. Aqueous solutions containing CB, H_2O_2, and/or colloidal TiO_2 nanoparticles were fed into the reactor with the temperature and the pressure controlled to be $T = 25$–$400°C$ and $P = 30\,MPa$, respectively. The conversion of CB in aqueous solution containing H_2O_2 was increased for $T \geqq 300°C$ by the broad-sense SCWO. The irradiation of the TiO_2 suspension with near-UV light caused the enhanced degradation of CB for $T = 25$–$400°C$. In conjunction with the former work on the reduction of Ag^+ ions by TiO_2, it has been concluded that photocatalytic activity of TiO_2; oxidation by positive holes as well as reduction by conduction-band electrons, are maintained in subcritical ~ supercritical water. By using physicochemically well-defined colloidal TiO_2 nanoparticles as the catalyst, we have realized the synergic degradation of CB, in which maximum conversion was achieved at $T = 200°C$. The effects of the coexistence of TiO_2 and H_2O_2 have been interpreted in terms of Fenton-type reaction by TiO_2 nanoparticles and electron acceptor properties of H_2O_2 towards conduction-band electrons, both of which would promote the production of $^{\cdot}OH$ radicals, the primary oxidative species of the degradation.

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REFERENCES

1. Savage, P.E. (1999) Organic chemical reactions in supercritical water. *Chem. Rev.*, 99: 603–621.
2. Yu, J.; Savage, P.E. (2001) Catalyst activity, stability, and transformations during oxidation in supercritical water. *Applied Catalysis B: Environmental*, 31: 123–132.
3. Fujishima, A.; Honda, K. (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238: 37–38.
4. Hoffmann, M.R.; Martin, S.T.; Choi, W.Y.; Bahnemann, D.W. (1996) Environmental applications of semiconductor photocatalysis. *Chem. Rev.*, 95: 69–96.
5. Serpone, N.; Pelizzetii, E. (1989) *Photocatalyst: Fundamentals and Applications*; Wiley: New York.
6. Augugliaro, V.; Litter, M.; Palmisano, L.; Soria, J. (2006) The combination of heterogeneous photocatalysis with chemical and physical operation: A tool for improving the photoprocess performance. *J. Photochem. Photobiol. C: Photochem. Rev.*, 7: 127–144.
7. Kometani, N.; Sugimoto, K.; Fujita, A.; Yonezawa, Y. (2007) Photocatalytic activity of TiO_2 nanoparticles in hydrothermal and supercritical water. *J. Chem. Eng. Jpn.*, 40: 463–467.
8. Kometani, N.; Inata, S.; Shimokawa, A.; Yonezawa, Y. (2008) Photocatalytic degradation of chlorobenzene by TiO_2 in high-temperature, high-pressure water. *Int. J. Photoenergy*, 2008: 512170.
9. Bhatkhande, D.S.; Sawant, S.B.; Schouten, J.C.; Pangarkar, V.G. (2004) Photocatalytic degradation of chlorobenzene using solar and artificial UV radiation. *J. Chem. Technol. Biotechnol.*, 79: 354–360.
10. Stavarache, C.; Yim, B.; Vinatoru, M.; Maeda, Y. (2002) Sonolysis of chlorobenzene in Fenton-type aqueous systems. *Ultrasonics Sonochem.*, 9: 291–296.
11. Yonezawa, Y.; Kometani, N.; Sakaue, T.; Yano, A. (2005) Photoreduction of silver ions in a colloidal titanium dioxide suspension. *J. Photochem. Photobiol. A: Chem.*, 171: 1–8.
12. Amita, F.; Okada, K.; Oka, H.; Kajimoto, O. (2001) A high-temperature high-pressure optical cell for general-purpose spectrometers designed for supercritical water experiments. *Rev. Sci. Instrum.*, 72: 3605–3609.
13. Portela, J.R.; Nebot, E.; de la Ossa, E.M. (2001) Kinetic comparison between subcritical and supercritical water oxidation of phenol. *Chem. Eng. J.*, 81: 287–299.
14. Gibson, J.F.; Ingram, D.J.E.; Symons, M.C.R.; Townsend, M.G. (1957) Electron resonance studies of different radical species formed in rigid solutions of hydrogen peroxide after u.-v. irradiation. *Trans. Faraday Soc.*, 53: 914–920.
15. Fujihira, M.; Satoh, Y.; Osa, T. (1981) Heterogeneous photocatalytic oxidation of aromatic compounds on TiO_2. *Nature*, 293: 206–208.
16. Ondrey, G.; van Veen, N.; Bersohn, R. (1983) The state distribution of OH radicals photodissociated from H_2O_2 at 193 and 248 nm. *J. Chem. Phys.*, 78: 3732–3737.
17. Mizuguchi, J.; Shinbara, T. (2004) Disposal of used optical disks utilizing thermally-excited holes in titanium dioxide at high temperatures: A complete decomposition of polycarbonate. *J. Appl. Phys.*, 96: 3514–3519.
18. Matthews, W. (1987) Carbon dioxide formation from organic solutes in aqueous suspensions of ultraviolet-irradiate TiO_2. Effect of solute concentration. *Aust. J. Chem.*, 40: 667–675.
19. Izumi, I.; Dunn, W.W.; Wilbourn, K.O.; Fan, F.R.F.; Bard, A.J. (1980) Heterogeneous photocatalytic oxidation of hydrocarbons on platinized TiO_2 powders. *J. Phys. Chem.*, 84: 3207–3210.
20. Harbour, J.R.; Tromp, J.; Hair, M.L. (1985) Photogeneration of hydrogen peroxide in aqueous TiO_2 dispersions. *Can. J. Chem.*, 63: 204–208.
21. Marshall, W.L.; Franck, E.U. (1981) Ion product of water substance, 0–1000°C, 1–10000 bars new international formulation and its background. *J. Phys. Chem. Ref. Data*, 10: 295–304.
22. Editorial board, Adschiri, T. (1997) *Handbook of Hydrothermal Science* (in Japanese); Gihoudo Shuppan: Tokyo.
23. McDonald, A.C.; Fan, F.R.F.; Bard, A.J. (1986) Electrochemistry in near-critical and supercritical fluids. 2. Water. Experimental techniques and the copper(II) system. *J. Phys. Chem.*, 90: 196–202.
24. Yu, J.; Savage, P.E. (2000) Kinetics of catalytic supercritical water oxidation of phenol over TiO_2. *Environ. Sci. Technol.*, 34: 3191–3198.
25. Bredig, G. (1901) *Anorganische Fermente*; Engelmann: Leipzig.
26. Walling, C. (1975) Fenton’s reagent revisited. *Acc. Chem. Res.*, 8: 125–131.
27. Breckenridge, R.G.; Hosler, W.R. (1953) Electrical properties of titanium dioxide semiconductors. *Phys. Rev.*, 91: 793–802.

28. Tanaka, K.; Hisanaga, T.; Harada, K. (1989) Efficient photocatalytic degradation of chloral hydrate in aqueous semiconductor suspension. *J. Photochem. Photobiol. A: Chem.*, 48: 155–159.
29. Tanaka, K.; Hisanaga, T.; Harada, K. (1989) Photocatalytic degradation of organohalide compounds in semiconductor suspension with added hydrogen peroxide. *New J. Chem.*, 13: 5–7.
30. Auguliaro, V.; Davì, E.; Palmisano, L.; Schiavello, M.; Sclafani, A. (1990) Influence of hydrogen peroxide on the kinetics of phenol photodegradation in aqueous titanium dioxide dispersion. *Appl. Catal.*, 65: 101–116.
31. Sun, L.; Bolton, J.R. (1996) Determination of the quantum yield for the photochemical generation of hydroxyl radicals in TiO_2 suspensions. *J. Phys. Chem.*, 100: 4127–4134.
32. Hirakawa, T.; Nosaka, Y. (2002) Properties of $O_2^{\cdot -}$ and $OH^{\cdot}$ formed in TiO_2 aqueous suspensions by photocatalytic reaction and the influence of H_2O_2 and some ions. *Langmuir*, 18: 3247–3254.
33. Li, X.; Chen, C.; Zhao, J. (2001) Mechanism of photodecomposition of H_2O_2 on TiO_2 surfaces under visible light irradiation. *Langmuir*, 17: 4118–4122.
34. Kometani, N.; Sugimoto, K.; Okuno, Y.; Yonezawa, Y. (2008). Photocatalytic Enhancement of Hydrogen Evolution from Ethanol by TiO_2 in High-temperature High-pressure Water. *Proc. 15th Int. Conf. on the Properties of Water and Steam*, VDI-Gesellschaft Energietechnik: Berlin.
35. Nakatani, A.; Kometani, N. (2010) Photocatalytic Effect of TiO_2 on the Hydrothermal Gasification of Glucose. *J. Phys.: Conf. Ser.*, 215: 012091.