Research Article

Photocatalytic Degradation of Chlorobenzene by TiO$_2$ in High-Temperature and High-Pressure Water

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A fluidized-bed-type flow reactor available for the photocatalytic treatment of the suspension of model soil under high-temperature, high-pressure conditions was designed. An aqueous suspension containing hydrogen peroxide (H$_2$O$_2$) as an oxidizer and inorganic oxides as a model soil, titania (TiO$_2$), silica (SiO$_2$), or kaoline (Al$_2$Si$_2$O$_5$(OH)$_4$) was continuously fed into the reactor with the temperature and the pressure controlled to be $T = 20$–400°C and $P = 30$ MPa, respectively. The degradation of chlorobenzene (CB) in water was chosen as a model oxidation reaction. It appeared that most of the model soils are not so harmful to the SCWO treatment of CB in solutions. When the TiO$_2$ suspension containing H$_2$O$_2$ was irradiated with near-UV light, the promotion of the degradation caused by photocatalytic actions of TiO$_2$ was observed at all temperatures. Persistence of the photocatalytic activity in the oxidation reaction in high-temperature, high-pressure water would open up a possibility of the development of the hybrid process based on the combination of SCWO process and TiO$_2$ photocatalysis for the treatment of environmental pollutants in soil and water, which are difficult to handle by conventional SCWO process or catalytic SCWO process alone.

1. INTRODUCTION

Since the discovery of the Becquerel effect in 1839, photochemistry and photocatalytic reactions of inorganic solids including semiconductors and photoconductors have been an important subject in solid-state photochemistry and catalytic chemistry. Focusing on electronic and ionic processes at the solid solution interface, the work by Brattain and Garrett on semiconductor electrochemistry of germanium (Ge) in 1955 pioneered a great deal of work in the United States, Germany, and Russia [1]. 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, which triggered a lot of activities to find photoelectrochemical systems capable of splitting water into H$_2$ and O$_2$ [2, 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, recovery of natural resources [4, 5]. At the present time, TiO$_2$ is still efficient, practical, and the most studied photocatalyst despite extensive efforts to find photocatalytic materials overcoming TiO$_2$. At the same time, numerous efforts have been devoted to the improvement of TiO$_2$ photocatalyst. However, those applications have been based on the premise that the photocatalyst is used under mild conditions near ambient temperature and pressure. On the other hand, from a wider viewpoint related to hydrothermal processes in geochemistry and earth sciences, it is of substantial interest how the photocatalytic actions of inorganic solids are influenced by the extreme conditions of the surroundings, particularly in the high-temperature, high-pressure water [6].

Supercritical water has been used as a reaction medium for chemical synthesis, fuel production, waste treatment by oxidation, and so on [7]. The supercritical water oxidation (SCWO) process for wastewater treatment has been extensively studied. Recently, there has been increasing interest in the use of heterogeneous catalysts in SCWO (catalytic SCWO) [8]. However, there has been no attempt to combine photocatalysis with SCWO. As a part of the project of extended applications of photocatalyst to environmental

problems, we have concentrated on the extensive use of photocatalytic reactions involving photoelectrons and photoholes under ambient ~ extreme conditions. An aqueous suspension of TiO_2 illuminated with near-UV light under ambient conditions has been known to oxidize many chlorinated hydrocarbons to carbon oxide under oxygenated or air-equilibrated conditions [9]. In this study, we chose chlorobenzene (CB) as a model compound for the photocatalytic oxidation as it is listed as a priority pollutant in water because of the low biodegradability and accumulation potential in soil and water [10]. Degradation of CB was undertaken in the aqueous suspension containing inorganic oxides: titania (TiO_2), colloidal silica (SiO_2), or kaoline ($Al_2Si_2O_5(OH)_4$), which are regarded as the model soil contaminated with organochlorine compounds. To this end, we designed a fluidized-bed-type flow reactor available for the study of photocatalytic reactions of aqueous suspensions and slurry of inorganic oxides. A remarkable observation of this study is that TiO_2 can maintain the efficient photocatalytic activity even in high-temperature, high-pressure water up to $T = 400°C$ and $P = 30$ MPa. A qualitative consideration of the reaction mechanism was discussed briefly.

2. EXPERIMENTAL METHODS

Inorganic oxides used in this study were TiO_2 powder (JRC-TIO-01) from Catalysis Society of Japan (Japan), SiO_2 from Nissan Chemical Industry Co. (Tokyo, Japan) and kaoline from Kishida Chemicals Co. (Osaka, Japan). CB, hydrogen peroxide (H_2O_2), and n-decane were of special grade purchased from Kishida Chemical Co. The photocatalytic activity of TiO_2 at room temperature in air was tested with respect to the photobleach of methylene blue (MB, Kishida Chemical Co.) in the TiO_2 suspension [11]. A 50 mL aqueous suspension containing TiO_2 and MB was illuminated with near-UV light from a 500 W high-pressure mercury lamp UI-501C (Ushio Denki Co., Tokyo, Japan) combined with a UV-D35 glass filter (Toshiba Co., Japan). The intensity of incident light was made almost equal to that used in the following experiments. The variations of the absorption spectrum were recorded on a V-560 spectrophotometer (JASCO Co., Tokyo, Japan). It appeared that about 90% of MB, existed at the beginning, was photobleached after 60 minutes irradiation, which ensured regular photocatalytic activity of the TiO_2 powder.

A fluidized-bed-type flow reactor equipped with sapphire windows was designed and tested. The schematic diagram of the reactor and the combination of experimental apparatus are illustrated in Figure 1. The basic structure of the reactor was the same as described in [12]. It was made of Hastelloy (inner volume ~$1.0 \, cm^3$) and was equipped with two sapphire windows whose diameter was 6.0 mm. The reactor could be heated at desired temperature $T = 20$–$400°C$ by an electric furnace. Pressure was kept at $P = 30$ MPa by a back pressure regulator (SCF-Bpg, JASCO Co., Tokyo, Japan). Typically, an aqueous suspension was composed of 1 mM CB and 0.1 wt% inorganic oxide in water, with or without 0.1 wt% H_2O_2. The suspension was injected into the reactor by a slurry type HPLC pump PU-2086 Plus
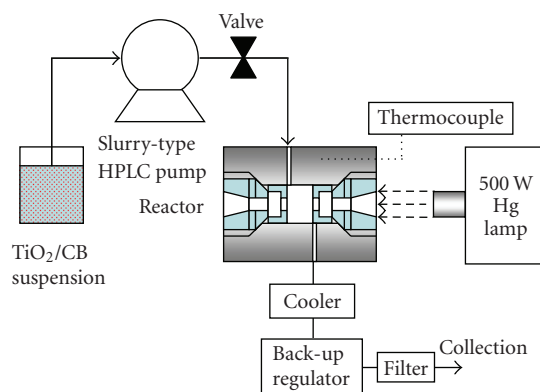

Figure 1: Schematic diagram of the fluidized-bed-type reactor designed for the study of photocatalytic reactions of TiO_2 suspension under high-temperature, high-pressure conditions.

(JASCO Co.) with the flow rate 0.2–1 $cm^3 min^{-1}$, the average residence time being 1–5 minutes. To avoid the precipitation of inorganic oxides from the solution phase, the flow rate should be larger than 0.2 $cm^3 min^{-1}$. The suspension was illuminated through the sapphire window with near-UV light ($\lambda = 300$–400 nm) from a 500 W high-pressure mercury lamp (USH-500D) with a Type HB-501A power supply (Ushio Denki Co.). Near-UV light was selected by the combination of a glass filter and a $CuSO_4$ solution filter. As the surface area of the window was small, the high-power lamp was used as the light source. The reaction mixture after cooling was first passed through a filter SS-4TF-0.5 (Swagelok Co., Ohio, USA) to remove TiO_2 powder larger than 0.5 μm in diameter before flowing into the back pressure regulator.

To trace the photocatalytic reactions, the reaction mixture was collected from the outlet of the back pressure regulator and then subjected to gas chromatographic analysis. Either a gas chromatograph mass spectrometer, GC/MS-QP 1000 (Shimadzu Co., Japan), or a G2800-F gas chromatograph (Yanagimoto Co., Koyto, Japan) was employed. CB was extracted from the reaction mixture with n-decane before being submitted to gas chromatograph mass spectrometer analysis.

3. RESULTS AND DISCUSSION

It has been reported that in the absence of suitable oxidants, some of the aromatic compounds like CB and phenol in water are tolerant to decomposition even under high-temperature, high-pressure conditions [13]. We at first tested the degradation of CB in aqueous suspensions containing model soils. The suspension containing 1 mM CB and model soil was supplied to the flow reactor with the rate 1 $cm^3 min^{-1}$ at the temperature $T = 20$–$400°C$. The fraction of residual CB collected at the outlet after passing through the reactor at each temperature is shown in Figure 2. The effects of the model soils on the degradation of CB were not straightforward. Kaoline promoted the reaction at all temperatures, while titania and silica suppressed the reaction at $T = 20$–$200°C$. At the elevated temperature, certain promotion effect
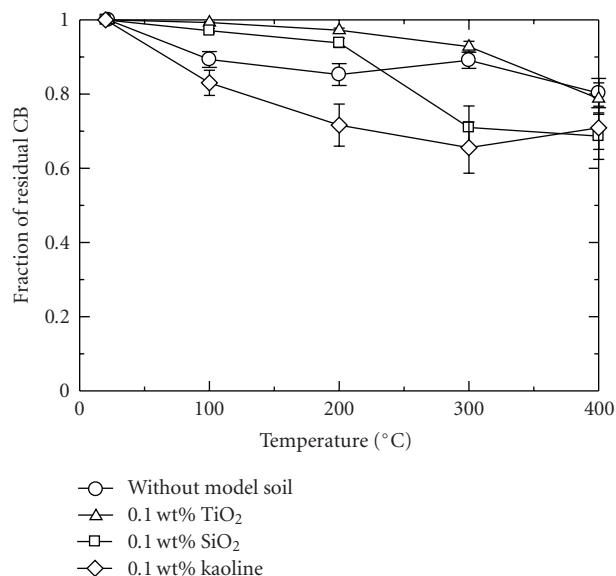
FIGURE 2: The fraction of residual chlorobenzene (CB) at different temperatures. Fluidized-bed-type reactor with the flow rate $1.0\,\mathrm{cm^3min^{-1}}$ and $P = 30$ MPa. CB = 1 mM. ○: without model soil; △: 0.1 wt% TiO_2; □: 0.1 wt% SiO_2; ◊: 0.1 wt% kaoline.

○— Without model soil
△— 0.1 wt% TiO_2
□— 0.1 wt% SiO_2
◊— 0.1 wt% kaoline

FIGURE 3: The fraction of residual chlorobenzene (CB) at different temperatures. Flow rate $1.0\,\mathrm{cm^3min^{-1}}$ and $P = 30$ MPa. CB = 1 mM, $[H_2O_2] = 0.1$ wt%. ●: without model soil; ▲: 0.1 wt% TiO_2; ■: 0.1 wt% SiO_2; ◆: 0.1 wt% kaoline.

●— 0.1 wt% H_2O_2
▲— 0.1 wt% TiO_2, 0.1 wt% H_2O_2
■— 0.1 wt% SiO_2, 0.1 wt% H_2O_2
◆— 0.1 wt% kaoline, 0.1 wt% H_2O_2

was observed in the silica suspension. We next examined the influence of oxidant, H_2O_2, on the degradation of CB. The fraction of residual CB in the aqueous solutions containing 1 mM CB and 0.1 wt% H_2O_2, together with or without model soils at each temperature, is given in Figure 3. Despite the rather short residence time of about 1 minute in the reactor, more than 40% of CB disappeared at $T = 200–400°C$, indicating the hydrothermal oxidation by H_2O_2 [14]. Although the reaction temperature (T) is not so much higher than critical temperature of water $T_c = 374.2°C$, this is regarded as a kind of SCWO process. Yu and Savage chose several metal oxides, which are known to be active catalysts for aqueous-phase oxidation and examined catalytic activity during H_2O_2 oxidation of phenol in supercritical water [13]. Indeed they observed catalytic SCWO of phenol over bulk TiO_2, but the reaction temperature, $T = 380–440°C$, was somewhat higher than what we detected. It was observed that the presence of model soils has little effect on the SCWO process at all temperatures within the experimental errors. The observations in Figures 2 and 3 are summarized as follows: the addition of H_2O_2 brings about the degradation of CB at $T = 200–400°C$. However, most of the model soils are not harmful to the SCWO treatment of CB at the temperature range studied here.

Considering the photocatalytic activity of TiO_2, it is expected that titania is capable of decomposing CB on irradiation with near-UV light. We therefore focused on the influence of irradiation of near-UV light on the degradation of CB. We firstly examined the effects of irradiation under ambient conditions. The aqueous solution of 1 mM CB with or without 0.1 wt% titania was put in the quartz cell and irradiated with near-UV light, whose intensity was the same as that used in the photobleach of MB. The variations of the
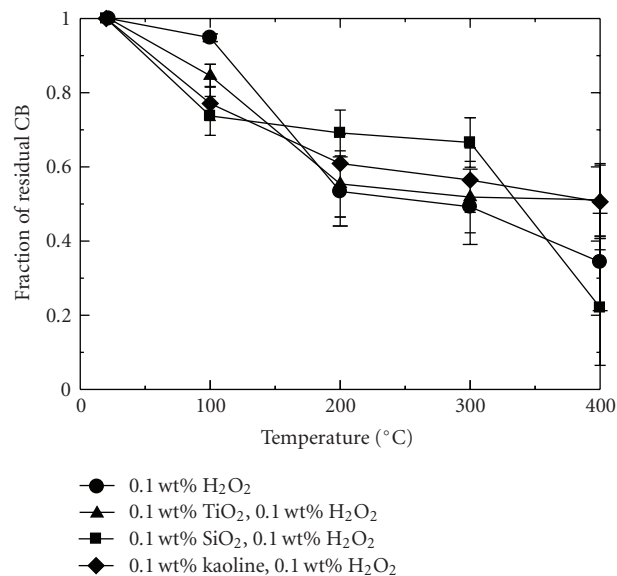
fraction of residual CB with irradiation time are shown in Figure 4. In the titania suspension, a rapid decrease of CB at the beginning was followed by a slower decrease with prolonged irradiation. About 25% of CB existed at the beginning disappeared after 1-minute irradiation. Photocatalytic degradation of CB under ambient conditions in Figure 4 is consistent with the works of Matthews [9] and Bhatkhande et al. [15]. On the other hand, degradation of CB did not proceed efficiently in the absence of titania. The fraction of CB disappeared after 60-minute irradiation was about 1/3 of that in the titania suspension. In view of the development of a hybrid process available for the extensive treatment of contaminated soil and water, the combination of the catalytic degradation by illuminated TiO_2 and SCWO process would attract much attention. The aqueous suspension comprising 1 mM CB, 0.1 wt% titania, and 0.1 wt% H_2O_2 was supplied to the flow reactor and irradiated with near-UV light through the sapphire window. The intensity of light incident to the reactor was managed to be nearly equal to that used in the photobleach of MB. The fraction of residual CB in the suspension at $T = 20–400°C$ collected at the outlet is given in Figure 5. Irradiation of the suspension with near-UV light caused efficient degradation of CB at all temperatures. Even if the average reaction time was 1 minute, about 60% of CB disappeared at $T = 200–400°C$. It is noted that the fraction of CB decomposed at $T = 20°C$ and $P = 30$ MPa in Figure 5, about 25%, in which average reaction time is 1 minute, is not so much different from the corresponding value after 1-minute irradiation in ambient conditions (Figure 4). Accordingly, we may employ the fractional residues of CB at each temperature in Figure 5 as a measure of the rate of degradation of CB. This is a necessary approximation because it was difficult for us to trace ordinary kinetics curves, that is, variations of the
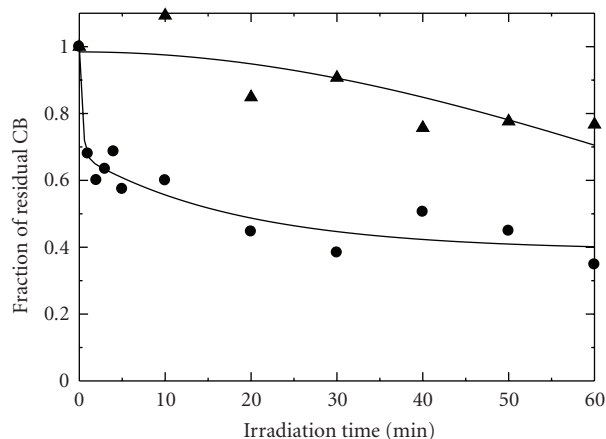
FIGURE 4: The time course of the fraction of residual chlorobenzene (CB) under near-UV irradiation at room temperature and atmospheric pressure. CB = 1 mM; ●: 0.1 wt% TiO_2; ▲: without TiO_2. The solid lines are drawn to guide the eyes.

-△- 0.1 wt% TiO_2 without irradiation
-▲- 0.1 wt% TiO_2 with irradiation
-○- 0.1 wt% TiO_2, 0.1 wt% H_2O_2 without irradiation
-◑- 0.1 wt% TiO_2, 0.1 wt% H_2O_2 with irradiation

FIGURE 5: The fraction of residual chlorobenzene (CB) with and without near-UV irradiation at different temperatures. Flow rate 1.0 cm^3min^{-1} and P =30 MPa. CB = 1 mM; △: 0.1 wt% TiO_2 without near-UV irradiation (taken from Figure 2); ▲: 0.1 wt% TiO_2 with near-UV irradiation; ○: 0.1 wt% TiO_2+ 0.1 wt% H_2O_2 without near-UV irradiation (taken from Figure 3); ◑: 0.1 wt% TiO_2 + 0.1 wt% H_2O_2 with near-UV irradiation.

concentration of CB as the continuous function of time, for catalytic/photocatalytic reactions in the high-temperature, high-pressure reactor. To examine the persistence of the photocatalytic activity of TiO_2 in the absence of H_2O_2, the aqueous suspension containing 1 mM CB and 0.1 wt% TiO_2 was fed to the reactor and irradiated with near-UV light. The fraction of residual CB for T =20–300°C is added to Figure 5. We could confirm that photocatalytic degradation of CB proceeds in high-temperature, high-pressure water in the absence of H_2O_2, too. Judging from the dependence of the fractional residues of CB at each temperature in Figure 5, an ordinary Arrhenius-type relation between the rate of degradation and temperature does not seem to be realized in such complex reactions. We finally note that the near-UV irradiation of the aqueous solutions containing only 1 mM CB or 1 mM CB and 0.1 wt% H_2O_2 has practically no effect on the degradation of CB at all temperatures, and the results were almost identical to "○" in Figure 2 and "●" in Figure 3, respectively.

To obtain further evidence of the photocatalytic activity of TiO_2, we constructed a fixed-bed-type flow reactor having a holder of the inorganic powder [16]. A TiO_2 pellet was set in the holder and an aqueous solution, containing 1 mM CB, was injected into the reactor by an HPLC pump (PU-1580, JASCO Co.) at the flow rate of 0.2 cm^3min^{-1} and the decomposition of CB by illumination with near-UV light was examined. It was found that near-UV irradiation surely promotes the reaction at T = 20–400°C in the absence of H_2O_2, that is, fractional residues of CB after average reaction time of 5 minutes were 0.9(T = 20°C), 0.8(100°C), 0.4(200°C), and 0.5(300°C). These observations would reconfirm the photocatalytic activity of TiO_2 in the high-temperature, high-pressure water.

The photocatalytic reactions of TiO_2 are initiated by absorbing UV or near-UV light that can excite valence band electrons to the conduction band. Photoelectrons in conduction band and positive holes in valence band undergo subse-
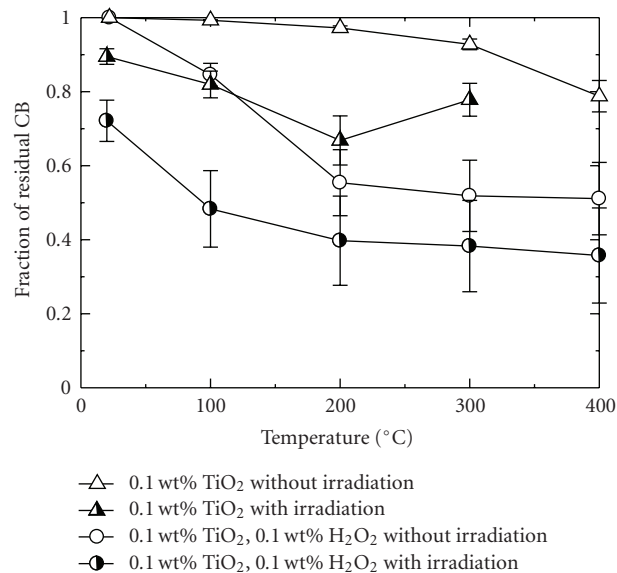
quent interfacial electron transfers and thermal reactions at the surface [17]. In a previous article [18], we have examined photocatalytic reduction of Ag^+ ions by TiO_2 and observed that the photoreduction of Ag^+ ions evident at room temperature is maintained in high-temperature, high-pressure water as well. Although reaction mechanism of the degradation of CB has not been well established, photoholes and OH radicals seem to be the oxidative species [9, 11, 15]. We have found for the first time that photocatalytic reactions of TiO_2, oxidation by holes and reduction by electrons, persist in subcritical ∼ supercritical water, contrary to the conventional view that it should be depressed due to the preferred electron and hole recombination at higher temperatures. However, despite the important role of the structure and energy states at the semiconductor-solution interface [19], the nature of the TiO_2 surface and redox pairs in subcritical ∼ supercritical water, for example, the energy band positions of TiO_2, electronic redox levels of redox pairs, as well as the structure of the electric double layer at the interface, are still beyond our scope. Concerning the properties of water, 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 [20, 21]. The dielectric constant of water at P = 30 MPa is a decreasing function of temperature from T = 20°C to 400°C, which may cause the decrease of the solvation energy for ionic species. Taking those features into consideration, we will make a speculative consideration of the persistence of the photocatalytic activity in high-temperature, high-pressure
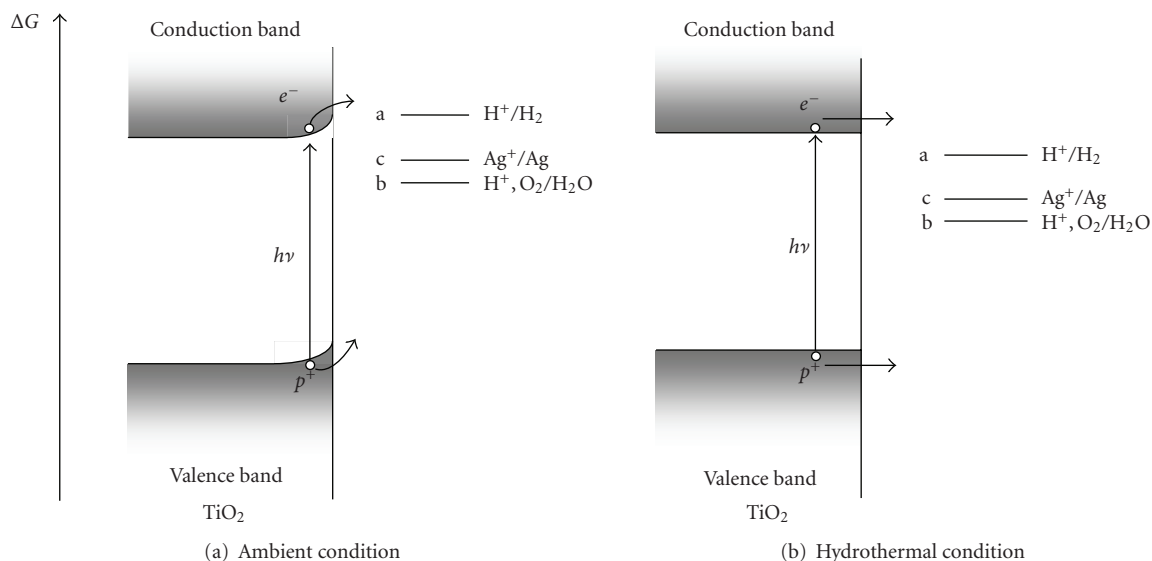
FIGURE 6: Schematic energy-level diagram showing photoreduction and photooxidation at the TiO_2-aqueous solution interface. Symbols $h\nu$ denote the photon energy of near-UV light, e^- and p^+ the conduction-band electron and positive hole, respectively. a; H^+/H_2, b; H^+, O_2/H_2O, and c; Ag^+/Ag: electronic redox levels. (a) Aqueous solution in ambient conditions; $T = 25°C$, $P = 0.1$ MPa. (b) Aqueous solution in hydrothermal conditions; $T = 100–400°C$, $P = 30$ MPa.

water. We sketch a schematic energy-level diagram at the TiO_2-aqueous solution interface in hydrothermal conditions Figure 6(b) with reference to the conventional diagram in ambient conditions Figure 6(a) [22]. The reduced electric field in the space-charge layer at the TiO_2 surface due to high-temperature conditions and the positive shift of the electronic redox levels as a result of reduced solvation energy have been assumed. In Figure 6, some of the conduction-band electrons in TiO_2, which are in contact with subcritical $\sim$ supercritical water, can contribute to the reduction of, for example, Ag^+ and H^+, while positive holes may contribute to the oxidation of certain molecular species like OH^- and H_2O. The higher concentration of OH^- ions may promote the consumption of positive holes. The increase in OH radicals would be a favorable condition for the oxidative degradation of CB. Furthermore, higher temperature in subcritical, supercritical water can in itself promote a variety of chemical reactions characterized by relatively large activation energy. However, to substantiate these considerations, further experimental and theoretical works are needed particularly on photochemistry and electrochemistry in high-temperature, high-pressure water [23].

In the last decade, much effort has been devoted to treat wastewater containing organic compounds such as aromatic compounds, chlorinated compounds. Conventional SCWO processes rely on free-radical reactions to convert organics to CO_2 and heteroatoms such as chlorine, sulfur to mineral acids with the help of concomitant oxygen or H_2O_2 and higher temperature $T > T_c$ [14, 24]. On the other hand, it was reported that the oxidation of a number of aromatic compounds to CO_2 takes place in aqueous suspensions of UV-irradiated TiO_2 at room temperature in air [9, 15]. In this study, we have observed that the addition of H_2O_2 to

the TiO_2 suspension promotes the degradation of CB at all temperatures. In certain temperature range, it looks as if a synergic effect comes out by the addition of H_2O_2 and the irradiation with near-UV light. However, due to experimental error, the detailed relation between the photocatalytic activities in the presence and absence of H_2O_2 has not been well established. According to the studies on the effect of H_2O_2 on the TiO_2 photocatalysis [25, 26], the combination of photocatalysis and SCWO would be attractive for the development of the innovated process capable of continuous treatment of wastewater at temperature $T < T_c$.

4. SUMMARY

An examination of inorganic semiconductors tolerant to corrosion under extreme conditions, irradiation with UV or near-UV light and contact to high-temperature, high-pressure water, is important to develop remediation processes for environmental and energy problems based on the photocatalysis in hydrothermal conditions. In this study, we constructed a fluidized-bed-type flow reactor available for the photocatalytic treatment of the model soil, titania, silica, or kaoline, contaminated with organochlorine compound, chlorobenzene (CB). We firstly examined the effect of the model soil on the SCWO treatment of CB with H_2O_2 and found that the presence of the model soils was not so harmful to this process. We next focused on the photocatalytic reaction of TiO_2. The TiO_2 suspension containing CB and H_2O_2 was continuously fed to the reactor under high-temperature ($T = 20–400°C$), high-pressure ($P = 30$ MPa) conditions and irradiated with near-UV light through the sapphire window installed to the reactor. It was observed that the degradation of CB was enhanced by irradiation at all temperatures.

Similar effects were observed in the absence of H_2O_2 or in case that the TiO_2 pellet was fixed inside the reactor. Based on these observations, we have concluded that the photocatalytic activity of TiO_2 persists in the high-temperature, high-pressure water. This finding is of great significance because the efficient photocatalytic activity of TiO_2 in the oxidation reaction in high-temperature, high-pressure water would open up a possibility of the development of the hybrid process based on the combination of SCWO process and TiO_2 photocatalysis for the treatment of environmental pollutants in soil and water, which are difficult to handle by conventional SCWO process or catalytic SCWO process alone.

ACKNOWLEDGMENT

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