

Photocatalytic Oxidation of Toluene over TiO_2 Catalysts Supported on Glass Fiber

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Abstract—Titania-impregnated photocatalysts supported on glass fiber (GF) were prepared and employed in the photocatalytic oxidation of toluene. Amorphous titania sol (ATS) prepared from titanium isopropoxide was useful to impregnate titania on glass fiber in the shape of a thin film. TiO_2/GF catalysts prepared by using the ATS showed better stability against water and vibration, but lower catalytic activity in the photo-oxidation of toluene compared to crystalline anatase powder (CAP) impregnated catalyst. Photocatalytic activity of the ATS catalyst was considerably enhanced by the addition of hydrogen peroxide, resulting in high activity comparable to that of the CAP catalyst.

Key words: Photocatalysis, Oxidation, TiO_2 , Toluene, Glass Fiber

INTRODUCTION

Aromatic compounds are widely used in industries for various purposes as solvents, diluents, and stabilizers. However, the content of aromatic compounds in the air of work places is strictly regulated due to their strong toxicity [Robert et al., 1999]. Therefore, various removal methods have been suggested and used to preserve clean air [Khan et al., 2000]. Adsorption and absorption, catalytic combustion and biological degradation have been successfully employed to remove concentrated aromatic compounds from the air, but the efficiency of these methods considerably decreases when they are applied to the treatment of air contaminated with an extremely low concentration. Too huge a treatment system with a slow rate due to its low concentration significantly reduces economic effectiveness.

On the other hand, photocatalytic oxidation using natural light was considered to be suitable for the removal of dilute aromatic compounds [Hennegezel et al., 1998] and N_2O [Anpo et al., 1997]. The removal rate was not fast; however, the decomposition of harmful materials continued on photocatalysts when light - with sufficient energy - was irradiated. In addition, long catalyst durability and no requirement of any working materials made it more feasible economically.

Titania is a typical active material showing photocatalytic activity with an excellent chemical and thermal stability [Chai et al., 2000; Choi et al., 2001; Bacsá et al., 2001]. In order to obtain sufficient surface area and mechanical convenience for application, titania is usually supported on various solids: activated carbon, silica, glass bead etc. [Choi et al., 2001; Lepore et al., 1996]. Since highly active species such as O_2^- and OH^\bullet radicals are formed on the surface of titania during the photocatalytic reaction, the exceptional chemical stability of supports is strongly required to retain their surface structure. Moreover, a high transparency of supports is required for the effective use of light, thereby increasing the efficiency of photo-

energy.

Glass fiber has several strong points as a support of photocatalyst, since it is highly stable against ultraviolet rays, activated oxygen and hydroxyl radical species, convenient to shape in various forms, and highly transparent for natural light [Robert et al., 1999]. In this study, titania-impregnated photocatalysts supported on glass fiber were prepared and employed for the photocatalytic oxidation of toluene. Dispersion and mechanical stability of the impregnated titania were also examined. Their photocatalytic activities toward the complete oxidation of toluene were investigated and discussed relating to their physical properties. The reasons for the activity enhancement by adding water and/or hydrogen peroxide were also proposed.

EXPERIMENTAL

1. Catalyst Preparation

Titanium isopropoxide (Aldrich, 99.9%) of 24 mL was dissolved in 66 mL of anhydrous ethanol (Fluka, 99.9%) in a completely dried glove box. The contents of isopropoxide dissolved in ethanol solution were adjusted to 2.5 wt%, 5 wt%, and 10 wt% of the mass of titania. The solutions were stirred at ambient temperature for 2 h, and then 300 mL of distilled water was dropwise added to initiate hydrolysis. Transparent amorphous titania sol (ATS) was obtained through peptization with the addition of 2 mL of nitric acid as following so-called sol-gel process [Yamashita et al., 1998].

Glass fiber (F58-C30) was purchased from Hankook Fiber Glass Co. and used after washing with anhydrous ethanol, followed by drying at 100 °C overnight. Dried glass fiber was settled in ethanol containing titania sol at ambient temperature for 30 min. Titania was impregnated on glass fiber by drying at 100 °C for 1 h, followed by calcination at 500 °C in the air for 4 h. Impregnated amounts of titania on glass fiber were determined from the increase in mass after calcinations, and they were symbolized in the parenthesis as $\text{ATS}(x)/\text{GF}$. The impregnated amount of titania on three $\text{ATS}(x)/\text{GF}$ catalysts was 1.3 wt%, 2.1 wt%, and 6.1 wt% of GF, respectively.

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A reference photocatalyst with crystalline anatase titania was prepared by using commercially available P25 titania (Degussa). P25 powder was dispersed in anhydrous ethanol. Crystalline titania catalyst supported on glass fiber was obtained by following the same procedure for the preparation of ATS-impregnated catalysts. Since the impregnated amount of P25 titania on glass fiber was 5.1 wt%, the reference catalyst was abbreviated as P25(5.1)/GF catalyst.

2. Characterization

Impregnation of titanium isoperoxide on glass fiber and its conversion to anatase was investigated by using a thermal analyzer (TG/DTA, Shimadzu). Samples were heated in the air flow from ambient temperature to 800 °C with a ramping rate of 10 °C/min. The stability of impregnated titania was estimated from the retained fraction of titania on glass fiber after sonication of supported titania catalysts. The catalysts were suspended in distilled water and treated in an ultrasonic cleaner (BRANSON 5210) for a certain time.

X-ray diffraction patterns of impregnated titania catalysts were recorded on an X-ray diffractometer using a $\text{CuK}\alpha$ ray and nickel filter at 40 kV and 20 mA. Their morphology was examined by a field-emission scanning electron microscope (FE-SEM, S-470, Hitachi; Korean Basic Science Institute/Gwangju Branch). UV-VIS absorption spectra of pressed titania supported catalysts were obtained by using a double-beam UV-VIS spectrometer (Varian Cary 3E) in the range of 190–800 nm with a dehydrated MgO reference.

3. Photocatalytic Oxidation of Toluene

Photocatalytic reaction was carried out in a cylindrical pyrex reactor with three UV-black light tubes (F8T5BLB, 8 W) as shown in Fig. 1. A filter-type (3 × 15 cm) catalyst was perpendicularly mounted in a catalyst holder installed at the center of the reactor. A small gas pump circulated the reactant gas in the reactor with 100 mL/min speed to reduce mass-transfer limitation. The reactor system was connected to a vacuum manifold to introduce reactant gases. An

automatic gas sampler took samples at certain intervals and sent them to a directly connected gas chromatograph (Younglin M600D) with a Supel Q-Plot capillary column and a helium ionization detector (VICI, Valco) for composition analysis. IR spectra of the gas phase of the reactor during the photocatalytic oxidation were recorded on an FT-IR spectrometer (Mattson ATI) by circulating the gas phase through an *in-situ* IR cell (GRASEBY, SPECAC) directly connected to the reactor.

The reactor was evacuated after catalyst charge to remove water and carbon dioxide. Toluene and dried air were introduced to the reactor, and the reactor pressure was adjusted to 1 bar. Water and hydrogen peroxide were supplied to study their promotional effects.

The extent of photocatalytic oxidation was monitored from the changes in the concentration of toluene and carbon dioxide. Since a small part of toluene was adsorbed on glass fiber and carbon monoxide was not observed in the reactor, the extent of photocatalytic complete oxidation was calculated from the produced amount of carbon dioxide. The percentage of the measured amount of produced carbon dioxide to the expected amount of carbon dioxide production from toluene in the reactor was defined as the complete oxidation of toluene.

RESULTS AND DISCUSSION

1. Physical Properties of Titania Catalysts Supported on Glass Fiber

Titanium alkoxide reacts with hydroxyl groups of glass fiber, producing partially hydrolyzed, surface-incorporated titanium alkoxide $[\text{Ti}(\text{OR})_x(\text{OH})_y]$. The partially hydrolyzed titania alkoxide loses its weight during complete hydrolysis. Moreover the condensation of hydroxyl groups at higher temperature, producing ATS, makes a successive weight loss again. Fig. 2 shows the TG/DTA result of the ATS(6.1)/GF catalyst. The first weight loss at 350 °C was attributed to the formation of anatase film from amorphous titania sol on glass fiber, and the second, at 550 °C to the condensation of ATS to anatase film. Since P25 particles were highly crystalline anatase, the P25(5.1)/GF catalyst did not show any weight loss in this tem-

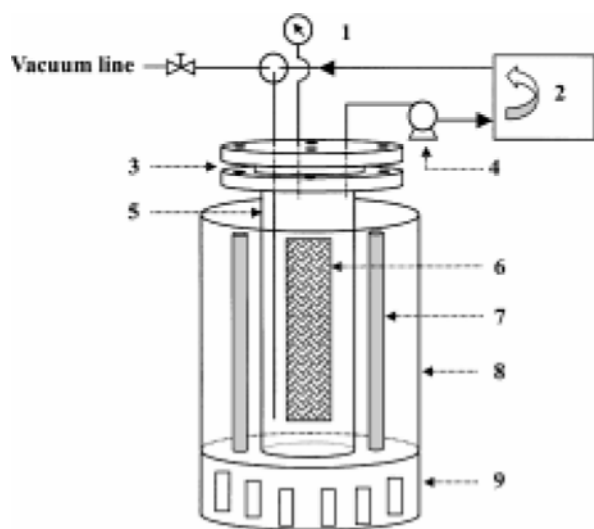


Fig. 1. Schematic diagram of a photocatalytic reactor for toluene oxidation over TiO_2 catalyst supported on glass fiber.

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|----------------------------|-------------------------|
| 1. Pressure gauge | 6. Filter-type catalyst |
| 2. GC with an auto-sampler | 7. UV lamp |
| 3. Flanges and O-ring | 8. Reflector |
| 4. Circulation pump | 9. Cooling fan |
| 5. Photoreactor | |

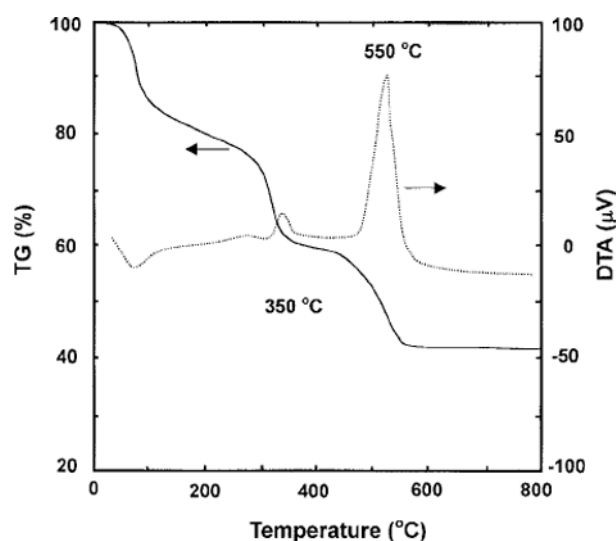


Fig. 2. TG/DTA result of the precursor of ATS(6.1)/GF catalyst.

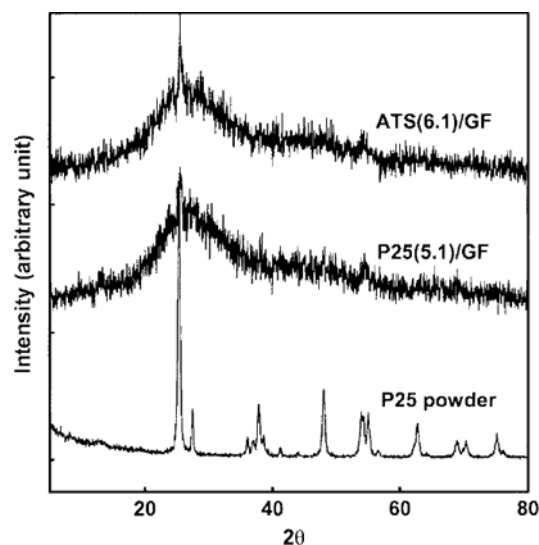


Fig. 3. XRD patterns of TiO_2 catalysts supported on glass fiber.

perature range. Although high crystallinity of anatase titania is helpful for the rapid photocatalytic oxidations due to the increase of the charge transfer rate [Zili et al., 1999], the calcination temperature of ATS/GF catalysts was set at 500°C to prevent excessive treatment at higher temperature inducing decrease in surface area or phase transition.

XRD patterns of the ATS(6.1)/GF and P25(5.1)/GF catalysts are shown in Fig. 3. Intensities of diffraction peaks attributed to anatase were too weak to confirm their crystalline structure; however, these patterns showed a high dispersion of titania on both catalysts. Fig. 4 shows that impregnated titania of the ATS(6.1)/GF catalyst produces a thin film composed of very fine particles (below 20 nm). On the other hand, many aggregates of $0.3\text{--}0.5\text{ }\mu\text{m}$ particles were observed on the P25(5.1)/GF catalyst. In the preparation of ATS/GF catalysts, immobilization of titania sol and its peptization to large material simultaneously proceeded on the surface of glass fiber, resulting in close contact between impregnated titania and glass fiber. Since anatase-type titania is considerably stable, any change in physical shape or the chemical property of P25 particles is not expected during the impregnation, retaining their sphere shapes even in the impregnated state on the glass fiber surface.

The stability of impregnated titania depended on its shape. Most P25 particles of the P25(6.1)/GF catalyst fell apart rapidly from the glass fiber and dispersed when they were sonicated in water as shown in Fig. 5. On the contrary, titania impregnated on glass fiber as a thin film, for instance titania of ATS/GF catalysts, retained their dispersion even after sonication for 120 min. Strong adhesion between impregnated titania and the glass fiber of ATS/GF catalysts supposed their high performance in wet conditions with high vibration.

2. Photocatalytic Oxidation of Toluene

Toluene in the air can be oxidized and decomposed to carbon

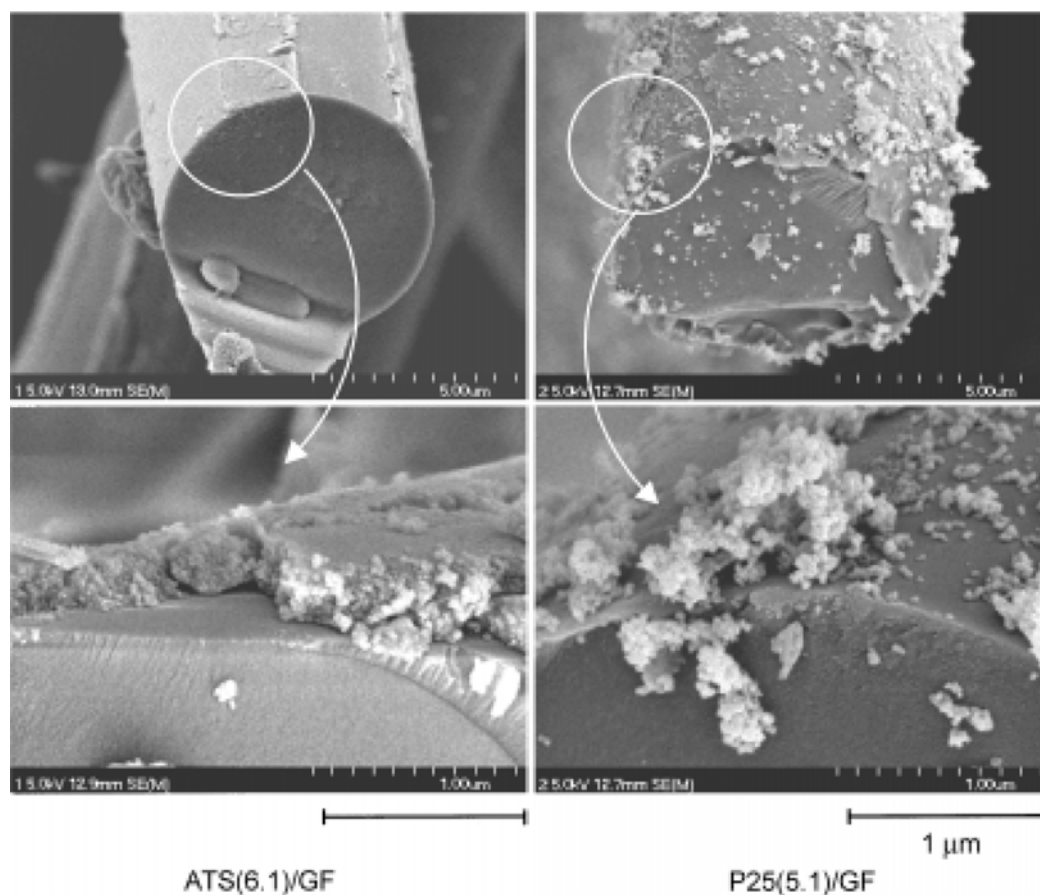


Fig. 4. SEM photos of TiO_2 catalysts supported on glass fiber.

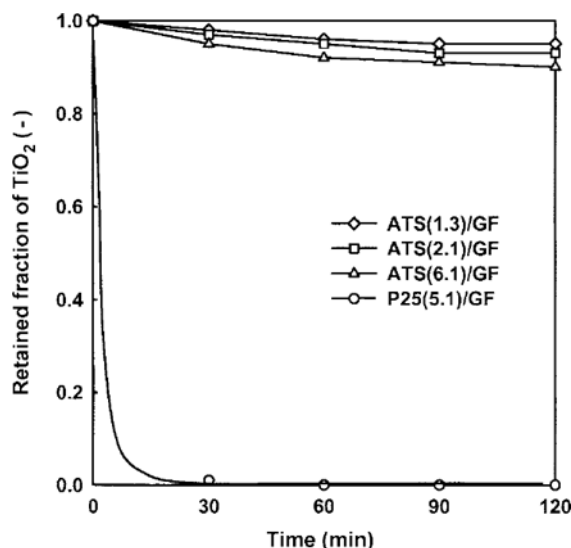


Fig. 5. Mechanical stability of TiO_2 catalysts supported on glass fiber.

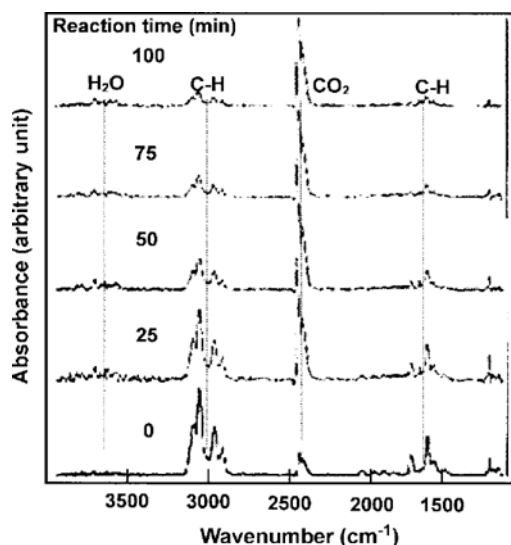


Fig. 6. Photocatalytic oxidation of toluene over ATS(6.1)/GF catalyst monitored by IR spectra.

dioxide and water on titania catalysts through photocatalytic oxidation [Hennezel et al., 1998; Maira et al., 2001]. Fig. 6 shows the oxidation of toluene on the ATS(6.1)/GF catalyst monitored by the FT-IR spectrometer. Reactant at 0 min shows only the absorption band attributed to toluene. As the photocatalytic reaction proceeds, strong absorption bands at $2,300\text{ cm}^{-1}$ assigned to carbon dioxide and weak absorption bands around $3,520\text{ cm}^{-1}$ assigned to water appeared accompanying the decrease in the absorption bands of toluene at $2,800\text{--}3,200\text{ cm}^{-1}$, $1,650\text{--}1,500\text{ cm}^{-1}$ and $\sim 1,200\text{ cm}^{-1}$. The change in IR spectra according to reaction time clearly showed the oxidation of toluene to carbon dioxide and water. The absence of the absorption band at around $1,700\text{ cm}^{-1}$ related to carbon monoxide, therefore suggesting toluene is mainly oxidized to carbon dioxide and water through complete oxidation over the photocatalysts.

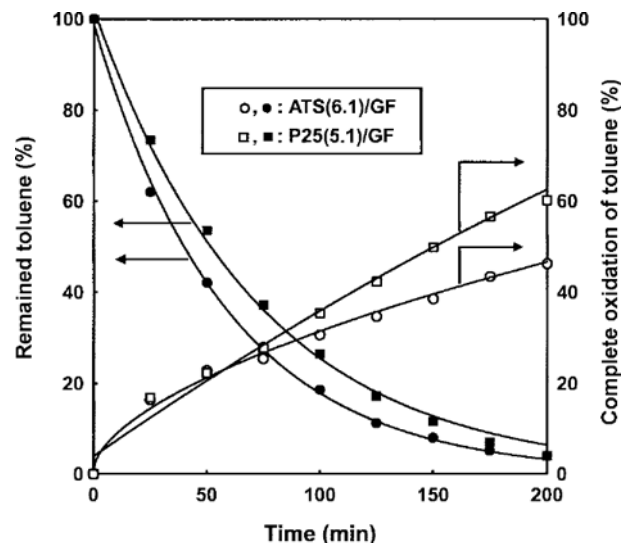


Fig. 7. Photocatalytic oxidation of toluene over TiO_2 catalysts supported on glass fiber at $35\text{ }^{\circ}\text{C}$.

$P_{\text{CH}_4} = 0.61\text{ Torr}$, $P_{\text{O}_2} = 160\text{ Torr}$

Photocatalytic oxidation of toluene brings about a decrease in its concentration and simultaneous increase in the concentration of carbon dioxide as shown in Fig. 7. However, the produced amount of carbon dioxide was not stoichiometrically coincident with the consumed amount of toluene. This discrepancy is due to the formation of intermediates and their adsorption on glass fiber [Blount and Falconer, 2001; Rafael et al., 1998]. Supposed intermediates in the photocatalytic oxidation of toluene are benzaldehyde and benzoic acid, and their accumulation on the catalyst surface induces a blocking of active sites. As the removal of toluene using photocatalytic oxidation means its complete oxidation producing carbon dioxide and water, complete oxidation of toluene was calculated from the change in carbon dioxide concentration. Although the toluene concentration decreased over both the ATS(6.1)/GF and P25(5.1)/GF catalysts, the decreasing rate was slightly more rapid over the ATS(6.1)/GF catalyst. On the other hand, complete oxidation of toluene was slightly higher over the P25(5.1)/GF catalyst. This discrepancy between the decrease in toluene concentration and the increase in carbon dioxide concentration is assumed to be the differences in their photocatalytic activity and adsorption capacity. The adsorbed amounts of toluene and its partially oxidized products were larger on the ATS(6.1)/GF catalyst due to its nanoscale titania particles, but the photocatalytic activity was higher over the P25(5.1)/GF catalyst due to its high crystallinity of anatase.

The photocatalytic activity of ATS/GF catalysts was compared in Fig. 8 according to the impregnated amount of titania. The figure shows the variation of the complete oxidation of toluene at 200 min with the impregnated amount of titania. The extent of complete oxidation over ATS/GF catalysts increases with the impregnated amount of titania, while the increase in the complete oxidation of toluene is very small when the impregnated amount is larger than 2 wt%. Excessive titania above this value may form a thicker film on glass fiber, and thus, is not effective for the photocatalytic activity.

Since toluene molecules adsorbed on titania catalysts react with active species such as oxygen and hydroxyl radicals, the presence

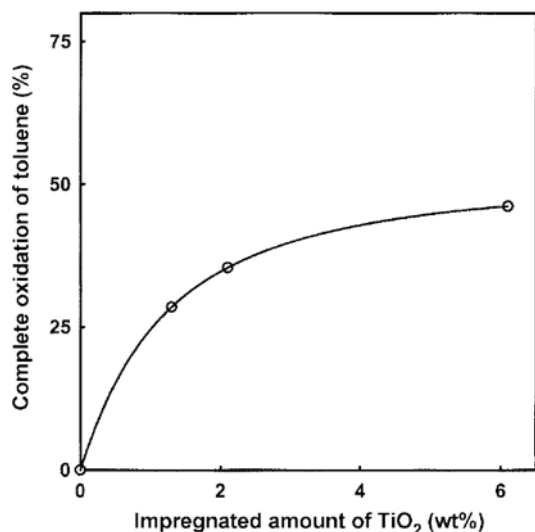


Fig. 8. Variation of complete oxidation of toluene at 200 min with the impregnated amount of TiO₂ in the photocatalytic oxidation of toluene over ATS/GF catalysts at 35 °C.

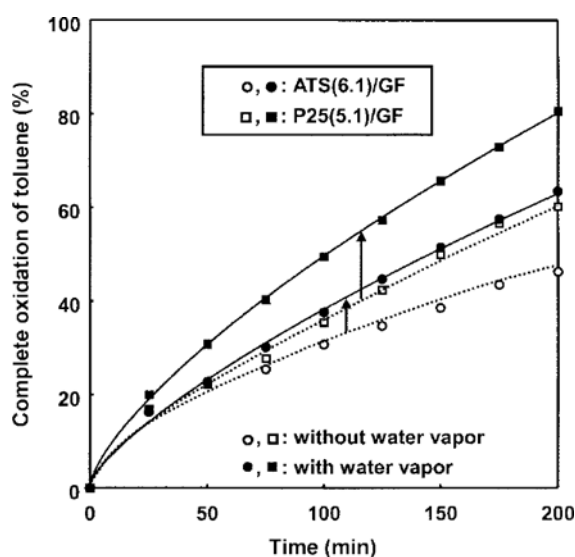


Fig. 9. The effect of water addition on the photocatalytic complete oxidation of toluene over TiO₂ catalysts supported on glass fiber at 35 °C.

$P_{CH_3} = 0.61$ Torr, $P_{H_2O} = 0.91$ Torr, $P_{O_2} = 160$ Torr

of water vapor with reactants generally enhances the photocatalytic reaction by increasing the formation of active hydroxyl radicals [Marta et al., 1999]. The introduction of water vapor was helpful for complete oxidation of toluene on both the ATS(6.1)/GF and P25 (5.1)/GF catalysts as shown in Fig. 9. The increase in the extent of complete oxidation due to the addition of water was similar over both catalysts.

Hydrogen peroxide is a better electron acceptor than molecular oxygen and can also form hydroxyl radicals more easily than water by the catalyst and photo-energy [Dionysiou et al., 2000]. The minimum energy requirement of oxygen reduction to produce hydroxyl radical is 3.0 eV, while that of hydrogen peroxide is 2.2 eV. Fig. 10 shows a significant increase in the complete oxidation of toluene

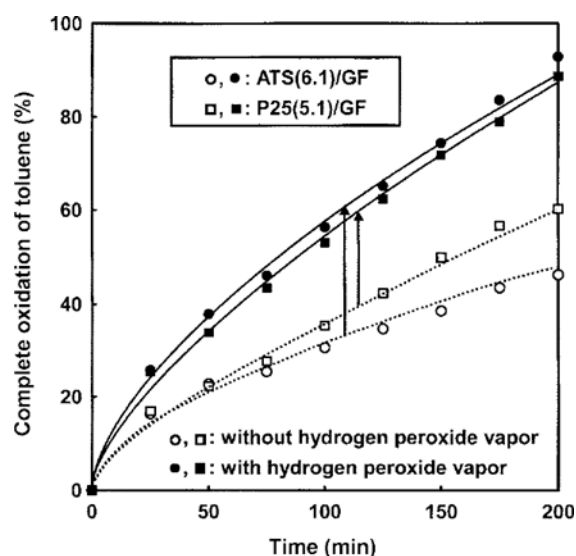


Fig. 10. The effect of water and hydrogen peroxide addition on the photocatalytic complete oxidation of toluene over TiO₂ catalysts supported on glass fiber.

$P_{CH_3} = 0.61$ Torr, $P_{H_2O} = 0.91$ Torr, $P_{H_2O_2} = 0.27$ Torr, $P_{O_2} = 160$ Torr

over the ATS(6.1)/GF catalyst by adding hydrogen peroxide vapor. The required amount of oxygen to oxidize toluene completely continuously in the reactor to carbon dioxide was estimated to be about 85 μ mole; however, the supplied amount of hydrogen peroxide 4.4 μ mole was extremely small. Hydrogen peroxide, therefore, must be considered as a promoter for complete oxidation. Although hydrogen peroxide itself can directly participate in the complete oxidation of toluene, its added amount is too small to induce such a significant increase in the extent of complete oxidation of toluene. The promotional mechanism of hydrogen peroxide to titania catalysts is not clear yet; however, the superoxide ions formed on tetra-

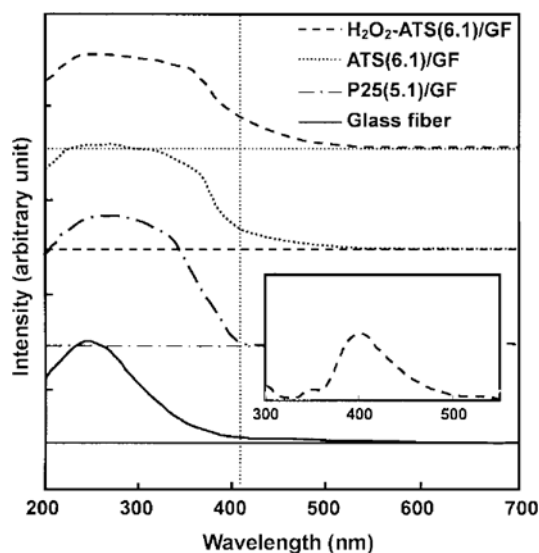


Fig. 11. Diffuse reflectance UV-VIS spectra of TiO₂ catalysts supported on glass fiber. Inset: dotted line is the differential spectrum of ATS(6.1)/GF catalyst with hydrogen peroxide treatment.

hedrally coordinated titanium atoms are considered to be a plausible cause of oxygen activation.

UV-VIS absorption of titania varies with its coordinated state and crystalline structure as shown in Fig. 11. The appreciable absorption by the P25(5.1)/GF catalyst was not observed above 415 nm. However, the absorption limit wavelength of the ATS(6.1)/GF catalyst was shifted from 415 nm to 440 nm. In addition, its absorption above 415 nm was considerably enhanced with the addition of hydrogen peroxide as clearly shown in the inset of Fig. 11. The strong yellow color confirms the formation of a superoxide ionic species (O₂⁻) on tetrahedrally coordinated titanium atoms [Geobaldo et al., 1992; Kim et al., 2001]. The increase in the photoenergy absorption by active superoxide species may be responsible for the increase in the photocatalytic activity of the ATS(6.1)/GF catalysts.

The complete oxidation of toluene over the P25(5.1)/GF catalyst was also enhanced by the addition of hydrogen peroxide, but the increase over the P25(5.1)/GF catalyst was relatively small compared to that over the ATS(6.1)/GF catalyst. The amount of superoxide ions formed on the ATS(6.1)/GF catalyst was relatively large on the P25(5.1)/GF catalyst due to the difference in their particle sizes. The photocatalytic activity of ATS/GF catalysts was lower than that of the P25/GF catalyst because of low crystallinity, but the ATS/GF catalyst had better stability toward water and vibration and a similar level of high photocatalytic activity by adding hydrogen peroxide.

CONCLUSIONS

Titania sol made from titanium isopropoxide is useful to impregnate titania on glass fiber in the shape of a thin film composed of about 20 nm particles. Although the activity of the ATS(6.1)/GF catalyst was slightly lower in the photocatalytic oxidation of toluene, the mechanical stability of ATS/GF catalysts was better than that of the P25(5.1)/GF catalyst. The low activity of the ATS(6.1)/GF catalyst, however, could be significantly enhanced by the addition of hydrogen peroxide. Amorphous titania sol synthesized by the sol-gel process was suitable for the preparation of titania impregnated photocatalysts with high activity and mechanical stability.

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