

Deactivation and Regeneration of Titania Catalyst Supported on Glass Fiber in the Photocatalytic Degradation of Toluene

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(Received 20 August 2002 • accepted 7 October 2002)

Abstract—Two titania photocatalysts supported on glass fiber (GF) were prepared by using anatase-type crystalline P25 powder and dilute titanium isopropoxide solution (DTS). Chemical compositions and characteristics of the surface of the P25/GF and DTS/GF catalysts were examined with an XPS method, and their activities in the photocatalytic degradation of toluene under UV irradiation were discussed. Although a large amount of titania was stably impregnated on glass fiber on the DTS/GF catalyst, low-temperature calcination brought about insufficient oxidation of titanium atoms resulting in a heavy deposit of carbonaceous materials. Both catalysts (P25/GF and DTS/GF) were active in photocatalytic degradation, while their catalytic activity was lowered because of the accumulation of reactant and carbonaceous materials on the surface. Hydrogen peroxide completely regenerated the deactivated P25/GF catalyst by removing contaminants. However, the activity of the used DTS/GF catalyst was considerably enhanced by exposing it to hydrogen peroxide vapor to a level higher than the fresh catalyst due to the increase in the surface concentration of active oxidizing species as well as the removal of carbonaceous materials.

Key words: Photocatalysis, Titania, Toluene, Glass Fiber, Hydrogen Peroxide

INTRODUCTION

Wide use of chemicals as solvents, diluents, and stabilizers in industry and homes brings about a significant increase in the concentration of volatile organic compounds (VOCs) in the air. However, since VOCs are harmful and unpleasant materials their concentrations are strictly regulated. Although various methods such as absorption, adsorption, catalytic combustion and biodegradation are applicable for VOCs removal [Khan et al., 2000], employed methods are carefully selected on the basis of their physico-chemical properties, concentration and regulation limits.

Photocatalytic degradation of VOCs has several advantages as a removal method: low operation cost, variety in catalyst shapes and supports, and high removal efficiency even at a low concentration of VOCs [Choi et al., 2001; Yamazaki et al., 1999; Sopyan et al., 1996]. Since active species such as O^- , O_2^- , and OH radicals formed on the surface of photocatalysts by sunlight degrade VOCs, photocatalytic degradation does not require any chemicals. Furthermore, continuous long-term photocatalytic operation without any treatment enhances its economic feasibility when deactivation of photocatalysts is negligible. Partially oxidized and polymerized materials formed during the photocatalytic degradation, however, deposit on the surface of photocatalysts and cover active sites, resulting in catalyst deactivation. Aromatic compounds such as benzene, toluene and xylene, and their partially oxidized materials are strongly adsorbed

on the photocatalyst surface compared to paraffins and olefins, and thus they easily form high-boiling materials through polymerization. Therefore, deactivation of photocatalysts is relatively serious in the degradation of aromatic compounds rather than that of paraffins and olefins [Rafael et al., 1998; Blount et al., 2001; Blanco et al., 1996].

Although titania photocatalysts dispersed on various solid supports have conventionally been used, transparent supports such as glass fiber and glass bead improve photocatalytic efficiencies of titania because of their low absorption of visible light [Robert et al., 1999; Nishikawa et al., 2001; You et al., 2001; Li et al., 2001]. Easy shaping of glass fiber makes it possible to produce various shapes of photocatalysts. The low melting point of glass, however, limits calcination temperature, requiring inorganic binder to ensure high stability of supported titania particles. A direct hydrolysis of titanium alkoxide on the surface of support can be employed to enhance the stability of supported titania on glass fiber. This preparation method using a dilute titanium alkoxide solution is effective in terms of high stability and easy control of loading amounts. Nevertheless, the low-temperature calcination may bring about a partially heterogeneous and incomplete arrangement at the surface of supported titania. Therefore, the insufficient calcinations of the photocatalysts prepared by direct hydrolysis of titanium alkoxide cause catalytic properties different from conventional photocatalysts prepared by using crystalline titania powder because of low-temperature calcination.

A titania photocatalyst supported on glass fiber was prepared using a dilute titanium isopropoxide solution to investigate the photocatalytic activity of low-temperature-calcined titania in the photocatalytic degradation of toluene. Deactivation of titania photocatalysts

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*This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

was discussed in relation to their surface states investigated through X-ray photoelectron spectroscopy, then compared with a photocatalyst prepared by using a commercially available crystalline anatase-type titania powder. Also examined was the regeneration efficiency of deactivated catalysts with hydrogen peroxide.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

Titanium isopropoxide (Aldrich, 99.9%) was diluted into anhydrous ethanol (Fluka, 99.9%) to obtain 10 wt% solution based on titania in a dehumidified glove box. This solution was stirred at ambient temperature for 24 h without adding water or acid, and we named it dilute titanium alkoxide solution (DTS). Glass fiber (F58-C30) purchased from Hankook Fiber Glass Company was used as a support for photocatalysts after being sonicated in anhydrous ethanol by using an ultrasonic cleaner (Branson 5210) for 30 min. Dried glass fiber was dipped in the DTS solution at 25 °C for 30 min and pulled out slowly. After drying at 100 °C for 1 h, DTS-coated glass fiber was heated to 500 °C in the air with a ramping rate of 1 °C/min and maintained at the temperature for 4 h. The prepared catalyst was denoted as the DTS/GF catalyst.

A crystalline titania photocatalyst was prepared by using anatase-type titania powder (Degussa P25). P25 powder was suspended in anhydrous ethanol to reach 3 wt%. P25-impregnated (P25/GF) catalyst was obtained by dipping the dried glass fiber into P25 suspension. The same drying and calcination heating methods were used as those of the DTS/GF catalyst.

The impregnated state of titania was examined by using an FE-SEM (Hitachi, S-470: Korea Basic Science Institute/Gwangju Branch) and loading amounts of titania were determined by using an attached EDX unit. X-ray diffraction patterns of titania photocatalysts supported on glass fiber were recorded on an X-ray diffractometer (Rigaku, D/Max-1200) with CuK α ray at 40 kV and 20 mA.

Chemical states of surface atoms were investigated with an X-ray photoelectron spectrometer (XPS, PHI Model 5700). Samples were irradiated with monochromated AlK α X-rays, and XPS spectra were recorded at 10 kV and 8 mA under 1×10^{-7} Torr. Fresh and used photocatalysts were put in a 28% hydrogen peroxide solution (Ducksan) for 5 min. After rinsing with distilled water and drying in a vacuum oven at 60 °C, the surface state of photocatalysts was examined with the XPS. The deposit amount of carbonaceous materials on used photocatalysts was deduced from their TG results obtained by using a thermogravimetric analyzer (Seiko). The decrease in mass was measured by raising the temperature from ambient temperature to 600 °C with a ramping rate of 10 °C/min.

2. Photocatalytic Degradation of Toluene

A cylindrical pyrex reactor (280 mL volume) with three UV-black light tubes (Sankyo Denki, F8T5BLB, 8 W) was employed for photocatalytic degradation of toluene (Fig. 1). The reactor was connected to a vacuum manifold to remove adsorbed materials on the surface of photocatalysts. The reactor temperature was maintained at 35 °C by removing heat generated from UV irradiation with a fan. A filter-type (3 $\times$ 15 cm) catalyst of 3 g was mounted perpendicularly at the center of the reactor and was evacuated to 10^{-4} Torr for 30 min under UV irradiation. A small amount of toluene was

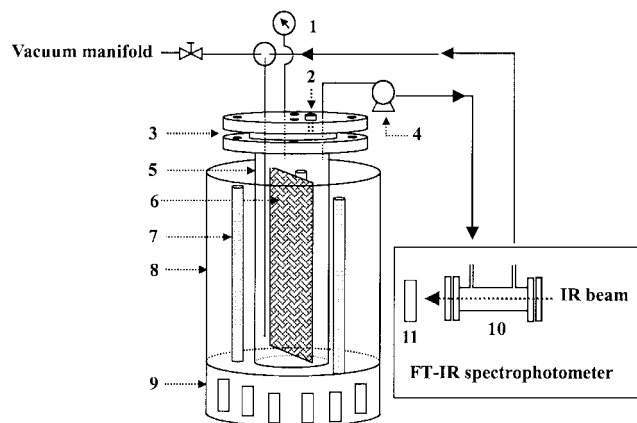


Fig. 1. Schematic diagram of a batch reactor for the photocatalytic degradation of toluene over titania catalysts supported on glass fiber.

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|-------------------------|----------------|
| 1. Pressure gauge | 7. UV lamp |
| 2. Injection septum | 8. Reflector |
| 3. Flanges and O-ring | 9. Cooling fan |
| 4. Circulating pump | 10. IR cell |
| 5. Photoreactor | 11. Detector |
| 6. Filter-type catalyst | |

injected into the reactor, and then the reactor was charged with dry air to 1 atm. Partial pressure of toluene in the reactor was controlled by adjusting its injection amount. The reactant gas in the reactor was circulated at 50 ml/min speed by using a small gas pump through a home-built IR cell located in the cell compartment of an FT-IR spectrophotometer (Mattson ATI). The changes in toluene concentration were continuously monitored by IR spectra recorded with 4 cm^{-1} resolution. The conversion of toluene, defined as a percentage of degraded toluene to supplied one, was calculated from the amount of carbon dioxide produced. The integrated areas of absorption bands at 2,400-2,240 cm^{-1} of the IR spectra provided amounts of carbon dioxide produced through photocatalytic degradation of toluene.

The extent of deactivation was deduced from the catalytic behaviors of photocatalysts obtained from repeated runs over the used photocatalysts for 60 min after rough evacuation of the reactor for 20 min. The same composition of the reactant was supplied, and the photocatalytic degradation started again by irradiation of UV light. For the regeneration of deactivated photocatalysts used in the previous run, hydrogen peroxide was simultaneously co-fed with toluene. Initial concentrations of toluene and hydrogen peroxide for the second and successive runs were adjusted to 3,800 ppm and 3,680 ppm, respectively.

RESULTS AND DISCUSSION

1. Characterization of Titania Photocatalysts Supported on Glass Fiber

Particle sizes of titania photocatalysts supported on glass fiber varied according to their precursors. Fig. 2 shows SEM photos of the DTS/GF and P25/GF catalysts. Titania particles of the DTS/GF catalyst were very fine, less than 15 nm, while dispersed titania particles were relatively large - above 30 nm on the P25/GF catalysts. In addition, the amount of titania loaded on glass fiber also varied

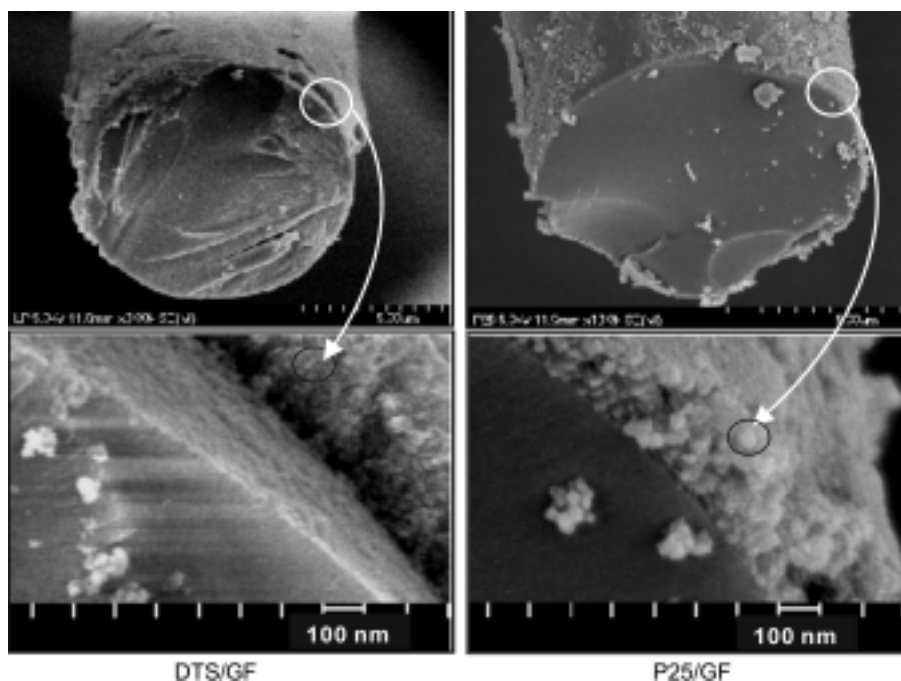


Fig. 2. SEM photos of titania catalysts supported on glass fiber.

with the precursors; titania loading was large at 8.5% on the DTS/GF catalyst, while it was quite small, only 2.2%, on the P25/GF catalyst.

Since P25 titania is composed of crystalline anatase particles, its particle size and shape are not altered with impregnation on glass fiber. The loading amount of P25 titania was small due to the small amount of polar groups which interacted with hydroxyl groups of glass fiber surface. Therefore, weak interaction of P25 particles with glass fiber as well as weak interaction among particles themselves resulted in a low loading of titania on the P25/GF catalyst. Direct

hydrolysis of titanium alkoxide led to numerous hydroxyl groups, and thus strong interaction involving a large amount of hydroxyl groups caused a relatively large loading of titania on the DTS/GF catalyst. The low-temperature calcination to prevent glass melting also contributed to the suppression of particle aggregation, resulting in small particles.

The crystalline structures of titania supported on glass fiber were deduced from their X-ray diffraction patterns shown in Fig. 3. P25 titania itself shows strong diffraction peaks assigned to an anatase type of titania [Wilke et al., 1999], while the P25/GF catalyst shows only the weak peaks. The amount of impregnated P25 powder loaded on the P25/GF catalyst was only 2.2 wt%, and thus, its diffraction peaks must be small. Although the amount of titania loaded on the DTS/GF catalyst was 8.5% larger than the P25/GF catalyst by about 4 times, the diffraction patterns of both catalysts were

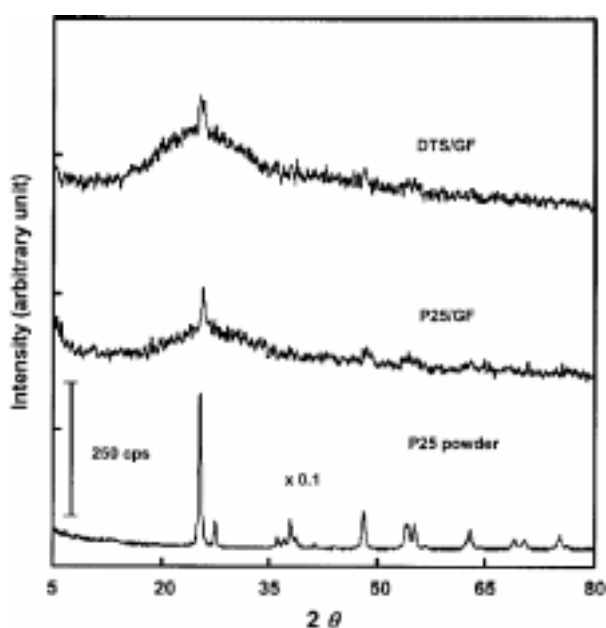


Fig. 3. XRD patterns of titania catalysts supported on glass fiber.

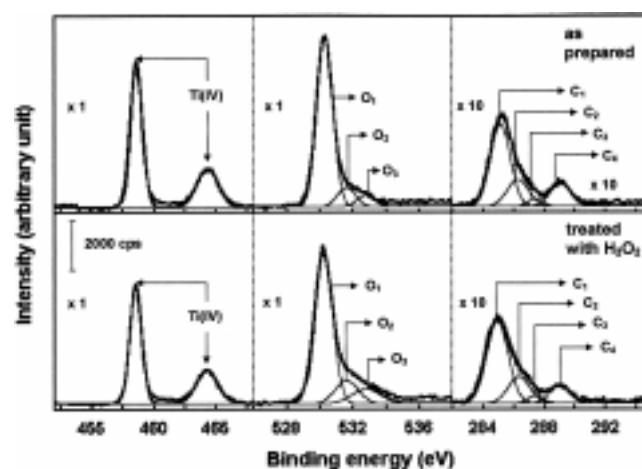


Fig. 4. XPS spectra of the P25/GF catalyst: as received and treated with hydrogen peroxide.

similar. This means that most of the titania supported on the DTS/GF catalyst was highly dispersed without forming any crystalline phase. Only a small part of titania formed an anatase phase and brought about weak diffraction peaks. The calcination at 500 °C was not sufficient to obtain a highly crystalline anatase-type titania phase.

The XPS spectra of these photocatalysts clarify the differences in chemical states of surface atoms according to their precursors. Fig. 4 shows the XPS spectra of the P25/GF catalyst as prepared and after having been treated with hydrogen peroxide. The spectra of the P25/GF catalyst as prepared are in good agreement with those of anatase-type titania [Kumar et al., 2000]. Doublet peaks ($2p_{1/2}$ and $2p_{3/2}$) of titanium atoms were observed at binding energies of 458.5 eV and 464.2 eV, exhibiting anatase-type titania in a +4 oxidation state. Oxygen peaks of the P25/GF catalyst could be deconvoluted into three peaks; the highest peak at 530.3 eV was ascribed to lattice oxygen (Ti-O), and small peaks at 531.6 and 532.8 eV were attributed to Ti-OH and Ti-OH₂ groups, respectively [Kumar et al., 2000; Hasegawa et al., 2001]. Oxygen atoms included in C-OH groups also show peaks at binding energies similar to those in Ti-OH and Ti-OH₂ groups, while those with higher binding energies may be ascribed to more oxidized states.

The C_{1s} XPS spectrum requires four deconvoluted peaks for a best fit. The highest peak at 285.1 eV was usually observed on graphite and ascribed to carbon atoms bound to other carbon atoms. On the other hand, peaks with higher binding energies are attributed to carbon atoms bound to oxygen atoms; the peak at 286.2 eV is assigned to the carbon atoms of C-OH groups, and the peak at 287.4 eV to the carbon atoms of C-O-C groups. The carbon peak at 289.1 eV with further higher binding energy is considered to be related to highly oxidized carbon atoms in ketone and carboxylic acid groups. These oxidized carbon peaks were usually observed on titania photocatalysts because of their oxidizing property. The low-peak height of carbon, when compared to those of oxygen and titanium, however, suggested that carbon deposit on the P25/GF catalyst was not serious.

Hydrogen peroxide treatment - an effective way to remove contaminated carbonaceous materials on the surface-provided no significant change in XPS spectra of the P25/GF catalyst. Only a small

increase in the deconvoluted oxygen peak, which is attributed to Ti-OH species, indicated that the surface of the P25/GF catalyst was stable, and thus, the effect of hydrogen peroxide treatment on its surfaces was negligible.

On the other hand, the XPS spectra of the DTS/GF catalyst prepared through *in-situ* hydrolysis of dilute titanium alkoxide at the surface of glass fiber differed considerably from those of the P25/GF catalyst. As shown in Fig. 5, titanium peaks were very weak compared to oxygen and carbon peaks, assuming that its surface was covered with a large amount of oxygen and carbon atoms. In addition, a half of titanium atoms had a +3 oxidation state, indicating insufficient calcinations for obtaining fully oxidized titania. Predominance of oxygen peaks (O₂ and O₃) with binding energies higher than the oxygen peak (O₁) exhibited that most of the oxygen atoms formed hydroxyl groups or bound to carbon atoms. The carbon peak was also very complicated, as expected. The carbon peak with the lowest binding energy 285.1 eV assigned to graphite carbon was small. On the other hand, the carbon peaks assigned to carbon atoms included in hydroxyl groups and ether groups were extraordinarily high, suggesting that most deposited contaminants on the DTS/GF photocatalyst were oxidized carbonaceous materials, not graphite-type carbon materials.

The treatment of the DTS/GF catalyst with hydrogen peroxide brought about considerable changes in its XPS spectra; titanium peaks, especially the Ti(IV) peaks, extremely increased, accompanying a large decrease in carbon peaks (C₁ and C₂) and a considerable increase in oxygen peaks (O₁ and O₂). Since hydrogen peroxide is a powerful oxidizing reagent, titanium atoms with a +3 oxidation state of the DTS/GF catalyst oxidized to those with a +4 oxidation state through hydrogen peroxide treatment. Oxidation resulted in the increase in the number of oxygen atoms composing hydroxyl groups. These observations led us to discover that hydrogen peroxide removes carbonaceous contaminants on the surface of the DTS/GF catalyst through further oxidation.

The low-temperature calcinations for the DTS/GF catalyst bring about the differences in the surface states from the P25/GF catalyst. Since P25 powder is crystalline anatase-type titania having Ti(IV)-O-Ti(IV) skeletal, its surface is so stable that there is no significant change effected by the hydrogen peroxide treatment. On the other hand, the DTS/GF catalyst was prepared with a reacting dilute titanium alkoxide solution with glass fiber, and then calcined at 500 °C to prevent the melting of glass fiber. Its XPS spectra revealed, therefore, numerous titania atoms in a low oxidation state and many carbonaceous contaminants. A partial oxidation of Ti(III) to Ti(IV) occurred during the hydrogen peroxide treatment. Furthermore, hydrogen peroxide effectively removed carbonaceous contaminants from the surface the DTS/GF catalyst.

2. Photocatalytic Degradation of Toluene

Toluene reacts with oxidizing species generated on the surface of photocatalysts under UV irradiation, converting itself into carbon dioxide and water. Fig. 6 shows IR spectra recorded during the photocatalytic degradation of toluene on the DTS/GF catalyst. Absorption bands assigned to water and carbon dioxide gradually increase with the time on stream, while those related to toluene decrease. Because absorption bands attributed to carbon monoxide are extremely small at 2,177 and 2,120 cm⁻¹ and those attributed to carbon dioxide are large at 2,360 and 2,342 cm⁻¹, most of the tol-

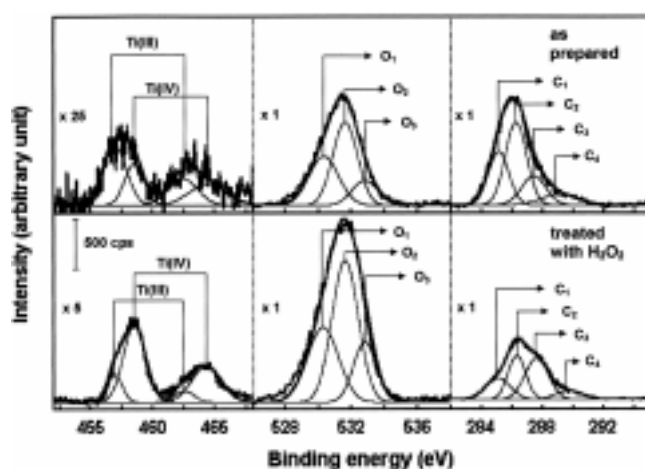


Fig. 5. XPS spectra of the DTS/GF catalyst: as received and treated with hydrogen peroxide.

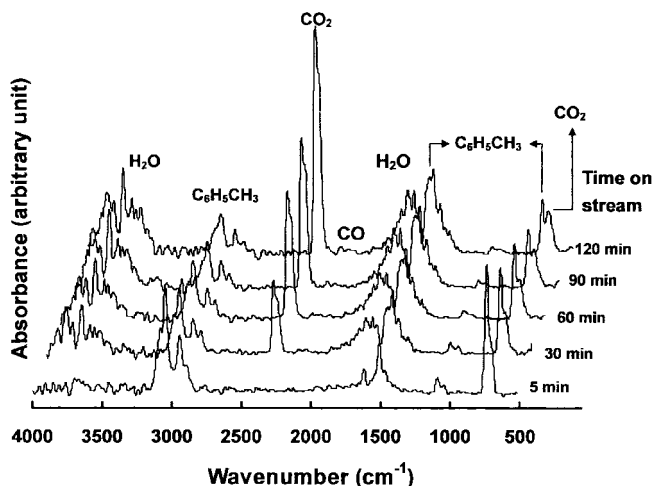


Fig. 6. Photocatalytic degradation of toluene over the DTS/GF catalyst monitored by IR spectra. $[\text{Toluene}]_0 = 3,800$ ppm.

uene was oxidized to harmless water and carbon dioxide. The formation of partially oxidized products such as benzaldehyde, benzoic acid and phenol was also possible, but no absorption bands related to carbonyl groups and phenolic OH groups reflected their extremely low contents, because of the high feasibility of the complete oxidation producing carbon dioxide and water.

The increase in the concentration of carbon dioxide with the time on stream is suitable to represent the process of photocatalytic degradation of toluene over titania photocatalysts. As a toluene molecule produces seven carbon dioxide molecules throughout the photocatalytic degradation, the axis of ordination multiplied by 1/7, as shown in Fig. 7, directly corresponds to the decrease in the concentration of toluene. The concentration lines in Fig. 7 indicate that both the P25/GF and DTS/GF catalysts are active in the photodegradation of toluene. The large production of carbon dioxide at a higher initial concentration of toluene indicates that the increase in the surface concentration of toluene due to the high concentration

of gas phase causes a large amount of toluene degradation. In addition, the lowering of the slopes in the concentration lines with increasing time on stream shows the reduction of the photodegradation rate due to the decrease in toluene concentration and catalytic deactivation.

Although amounts of degraded toluene were large at a higher concentration of toluene, the conversions of toluene, representing a percentage of toluene degraded to toluene fed, show an opposite trend. The conversion of toluene on the P25/GF catalyst was about 27% at the time on stream of 120 min when the initial concentration of toluene was 760 ppm, but the conversion was a low 10% when the initial concentration was high 7,600 ppm. Even though toluene molecules react with oxidizing species at adsorbed state, high concentration of adsorbed toluene on the surface reduces the surface concentration of oxidizing species on photocatalysts, resulting in low conversion. Furthermore, the high concentration of adsorbed toluene may cause the deactivation of photocatalysts by reducing the concentration of oxidizing species and accelerating the polymerization of adsorbed toluene producing carbonaceous materials.

The conversion profiles of toluene with the time on stream over the P25/GF and DTS/GF photocatalysts become lower with repeated reuse as shown in Fig. 8. Since the evacuation at the intervals of successive runs of the photocatalytic degradation was mild, adsorbed materials on the surface of photocatalysts remained. The conversion of toluene, therefore, becomes lower with repeated successive runs, and thus the accumulation of adsorbed materials on the surface brings about the deactivation of photocatalysts. The general features for the catalyst deactivation of both photocatalysts were similar, while the deactivation was slightly severe on the DTS/GF catalyst compared to the P25/GF catalyst.

In order to regenerate the activity of deactivated photocatalysts, they were evacuated and exposed simultaneously to hydrogen peroxide and toluene vapor. As shown in Fig. 8, the activity of the P25/GF catalyst was completely recovered when it was exposed to hydrogen peroxide vapor. On the other hand, the conversion profile at the 2nd and 3rd runs over the regenerated DTS/GF catalyst becomes

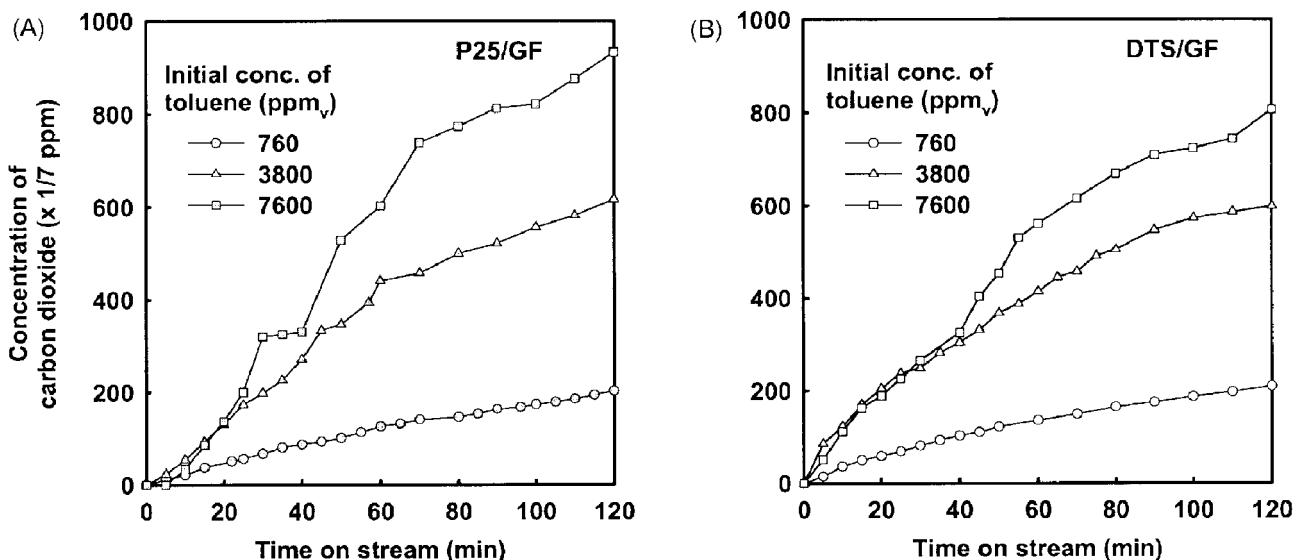


Fig. 7. Photocatalytic degradation of toluene over the P25/GF (A) and the DTS/GF (B) catalysts at 35 °C with different initial concentration of toluene.

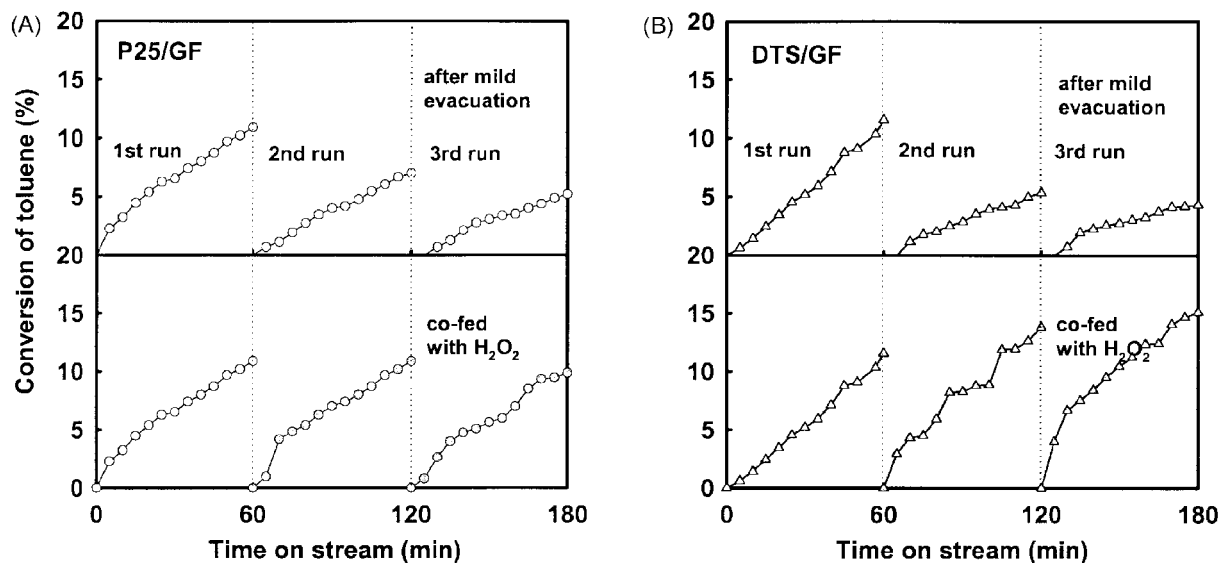


Fig. 8. Deactivation and regeneration of the P25/GF (A) and DTS/GF (B) catalysts in the photocatalytic degradation of toluene. Used catalysts were regenerated by co-fed hydrogen peroxide. $[\text{Toluene}]_0 = 3,800 \text{ ppm}$, $[\text{H}_2\text{O}_2]_0 = 3,680 \text{ ppm}$.

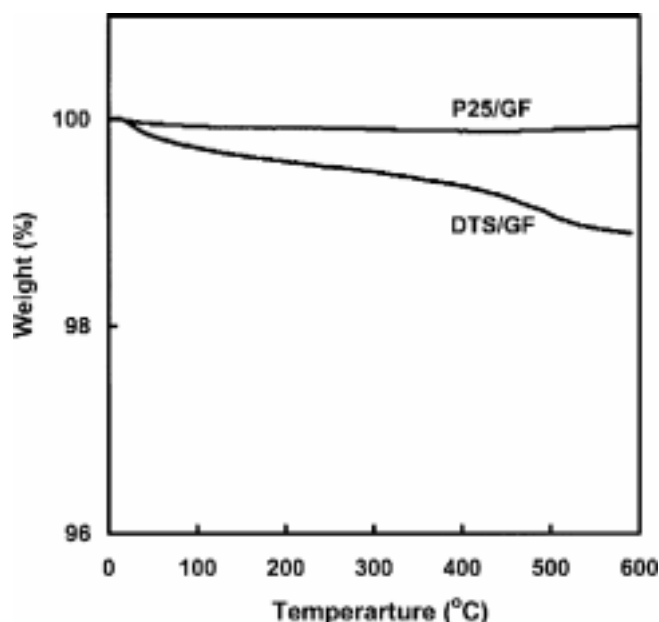


Fig. 9. TG curves of the used P25/GF and DTS/GF catalysts.

higher with the exposure to hydrogen peroxide vapor, compared to that at the 1st run over the fresh DTS/GF catalyst. Deactivation of the DTS/GF catalyst in the photocatalytic degradation was slightly rapid compared to that of the P25/GF catalyst, but the activity of the used DTS/GF catalyst was considerably enhanced with the exposure to hydrogen peroxide vapor.

The TG curves of used catalysts, shown in Fig. 9, provide a plausible explanation for the different deactivation behaviors of the photocatalysts. The photocatalysts samples were used in the photocatalytic degradation of toluene for 2 h when the initial concentration toluene was 3,800 ppm. The weight loss of the used P25/GF catalyst attributed to the combustion of carbonaceous materials was negligible, while that of the used DTS/GF catalyst was considerable. The strong adsorption of toluene on the titanium atoms with

insufficient coordination of the DTS/GF catalyst brings about a large amount of carbonaceous materials, which remain on the photocatalyst surface even after being exposed to the air. The titanium atoms on the crystalline surface of the P25/GF catalyst, however, interact weakly with adsorbed toluene molecules, preventing the formation of carbonaceous materials.

The exposure of the used P25/GF and DTS/GF catalysts to hydrogen peroxide vapor is effective in regenerating their activity, while regeneration efficiencies are considerably different. As mentioned earlier, hydrogen peroxide vapor recovers the activity of the P25/GF catalyst up to its original level. Easy removal of adsorbed toluene on the P25/GF catalyst by hydrogen peroxide, therefore, completely restores its activity.

On the other hand, the activity of the used DTS/GF catalyst considerably improved when exposed to hydrogen peroxide vapor. This means that hydrogen peroxide induces some changes in the surface of the used DTS/GF catalyst as well as the removal of carbonaceous materials. The XPS spectra of the used DTS/GF catalyst shown in

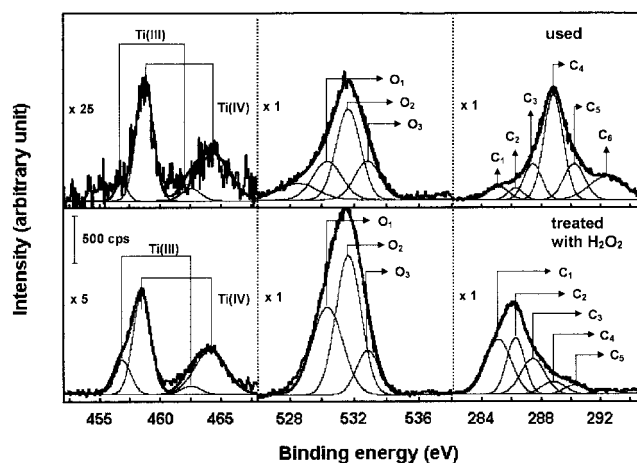


Fig. 10. XPS spectra of the DTS/GF catalysts: used and treated with hydrogen peroxide.

Fig. 10 supported this suggestion. A significant decrease in highly oxidized carbon peaks indicates the removal of carbonaceous contaminants. In addition, the simultaneous increases in the titanium peak with the oxidation state of +4 and O_1 peak indicate a further oxidation of surface titanium atoms with low oxidation states. The increase in active titanium atoms with a +4 oxidation state causes enhancement of the photocatalytic activity of the DTS/GF catalyst. High concentration of oxidizing species on the catalyst surface with higher binding energy - related to O_2^- species formed on tetrahedrally coordinated titanium atoms - may also contribute to the enhancement of photocatalytic degradation [Kim et al., 2001].

Although the high transparency of glass fiber is a valuable advantage as a support for photocatalysts, its low melting point limits the calcination temperature, resulting in poor impregnation stability and small loading of crystalline anatase particles. Direct hydrolysis of dilute titanium alkoxide solution on the surface of glass fiber brings about a high loading of titania with good stability. Low temperature calcination, however, causes heterogeneity in titanium coordination. Insufficiently coordinated titanium atoms induce a heavy accumulation of carbonaceous materials on the surface, resulting in a rapid deactivation of the DTS/GF catalysts. Hydrogen peroxide, however, removes carbonaceous materials from the surface of photocatalysts and regenerates their activity up to the original level or better.

CONCLUSIONS

Titania can be dispersed on glass fiber by impregnating anatase-type powder and by direct hydrolysis of dilute titanium isopropoxide solution. Titania particles dispersed on the DTS/GF catalyst were less than 15 nm, and the amount of titania loaded on it was 8.5 wt%. The surface of the DTS/GF catalyst was covered with a large amount of carbonaceous materials due to titania atoms with insufficient coordination, but the P25/GF catalyst prepared by using stable anatase powder had a considerably small carbon deposit due to the high regularity of surface atoms.

Both the DTS/GF and P25/GF catalysts are active in the photocatalytic degradation of toluene, while their activities become lower because of the accumulation of reactant or carbonaceous material on the catalyst surface. Hydrogen peroxide not only regenerates the deactivated P25/GF catalysts completely by removing contaminants, but also enhances the activity of the used DTS/GF catalyst better than fresh catalyst by increasing the surface concentration of active oxidizing species as well as removing carbonaceous materials.

ACKNOWLEDGMENTS

This work was supported by The Brain Korea 21 Project.

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