



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

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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. Although various methods such as absorption, adsorption, catalytic combustion and biodegradation have been adopted for VOCs removal, employed methods are carefully selected on the base of their physico-chemical properties, concentration and regulation limits [1].

Photocatalytic degradation of VOCs using TiO₂ 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. Hydrocarbons are oxidized completely to CO₂ and H₂O by the strong oxidants such as OH, O⁻, and O₂⁻ species formed on the surface of TiO₂ activated by only sunlight without any additives [2]. On the other while, partially oxidized and polymerized materials formed during the photocatalytic degradation of aromatic compounds cover active sites, resulting in catalyst deactivation [3].

In this study, a titania photocatalyst supported on glass fiber was prepared using a dilute titanium isopropoxide solution and employed in the photocatalytic degradation of toluene. Deactivation of titania photocatalyst was discussed in relation to their surface states investigated through X-ray photoelectron spectroscopy. The regeneration efficiency of deactivated catalysts with hydrogen peroxide was also examined.

Experimental

Titanium isopropoxide (Aldrich, 99.9%) was diluted into anhydrous ethanol, named it dilute titanium alkoxide solution (DTS), to obtain 10 wt% solution based on titania in a dehumidified glove box. Glass fiber (Hankook Fiber Glass Co., F58-C30) was used as a support for the photocatalysts after sonicating it in anhydrous ethanol. After drying at 100 °C for 1 h, glass fiber was dipped into DTS for 30 min at 30 °C. A titania photocatalyst supported on glass fiber (DTS/GF photocatalyst) was obtained by calcination at 500 °C for 4 h in the air. A crystalline titania photocatalyst was also prepared using anatase-type P25 powder (Degussa) suspended in ethanol of 3 wt%. The same drying and calcination heating methods were used as those of the DTS/GF catalyst. The physico-chemical properties of titania photocatalysts supported on glass fiber were examined by using an FE-SEM, SEM-EDX, XRD, and XPS apparatus.

Photocatalytic degradation of toluene was carried out in a cylindrical pyrex reactor with three UV-black light tubes. A filter-type catalyst of 3 g was mounted at the center of the reactor and was evacuated to 10⁻⁴ Torr for 30 min. After injection of toluene into the reactor, dry air was charged into the reactor to be 1 atm. 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 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. For the regeneration of deactivated photocatalysts used in the previous run, hydrogen peroxide was simultaneously co-fed with toluene.

Results and Discussion

Particle sizes and loading amounts of titania supported on glass fiber varied according to their precursors. 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. The loading amount of titania impregnated on glass fiber was large at 8.5% on the DTS/GF catalyst, while it was only 2.2% on the P25/GF catalyst. The difference is the small amount of polar groups of crystalline anatase particles which interacted with hydroxyl groups of glass fiber surface. Direct hydrolysis of titanium alkoxide led to a plenty of hydroxyl groups, and this strong interaction involving a large amount of hydroxyl groups caused a relatively large loading of titania on the DTS/GF catalyst.

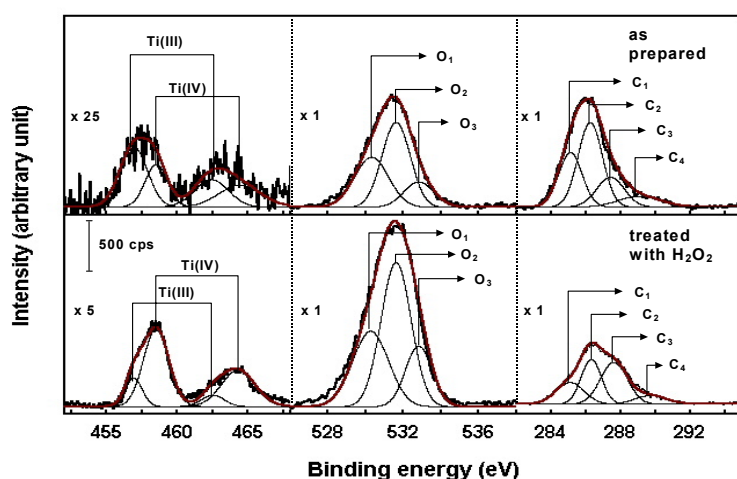


Fig. 1. XPS spectra of the DTS/GF catalyst: as received and treated with hydrogen peroxide.

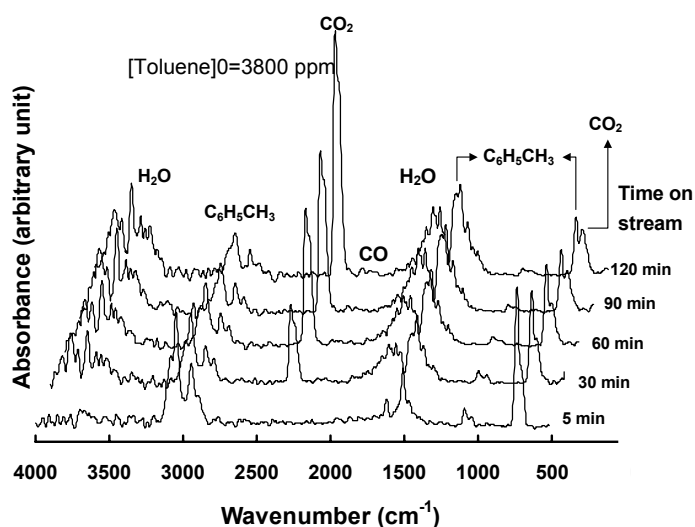


Fig. 2. Photocatalytic degradation of toluene over the DTS/GF catalyst monitored by IR spectra.

The XPS spectra of these photocatalysts clarify the differences in chemical states of surface atoms according to their precursors. Fig. 1 shows the XPS spectra of the DTS/GF catalyst as prepared and after having been treated with hydrogen peroxide. Titanium peaks were very weak compared to oxygen and carbon peaks, assuming that its surface was covered with large amounts of oxygen and carbon atoms. Predominance of oxygen peaks (O_2 ; Ti-OH and O_3 ; Ti-OH₂) with binding energies higher than that the oxygen peak of O_1 exhibited that most of the oxygen atoms formed hydroxyl groups or bound to carbon atoms. 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, considerably increased, accompanying a large decrease in carbon peaks (C_1 and C_2). Further oxidation by hydrogen peroxide treatment resulted in the increase in the number of oxygen atoms composing hydroxyl groups and the removal of carbonaceous contaminants on its surface.

The spectra of the P25/GF catalyst as prepared state are in good agreement with those of

anatase-type titania. Low surface contents of carbon and oxygen atom indicated small contamination with carbonaceous material. Therefore its surface is so stable that there is no significant change effected by the hydrogen peroxide treatment. Toluene reacts with oxidizing species generated on the surface of photocatalysts under UV irradiation, converting itself into carbon dioxide and water. Fig. 2 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 2177 and 2120 cm^{-1} and those attributed to carbon dioxide are large at 2360 and

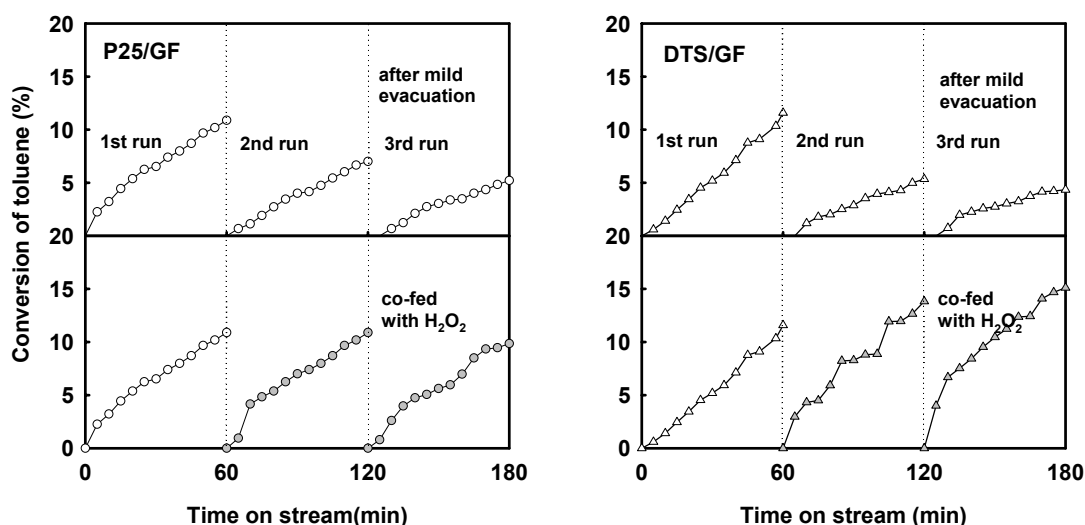


Fig. 3. Deactivation and regeneration of the P25/GF and DTS/GF catalyst in the photocatalytic degradation of toluene. Used catalysts were regenerated by co-fed hydrogen peroxide.

$[\text{Toluene}]_0=3800 \text{ ppm}$, $[\text{H}_2\text{O}_2]_0=3680 \text{ ppm}$

2342 cm^{-1} , most of the toluene was oxidized to harmless water and carbon dioxide.

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. 3. Since the evacuation at the intervals of successive runs of the photocatalytic degradation was mild, adsorbed materials on the surface of photocatalysts were remained. The conversion of toluene becomes lower with successive runs due to the accumulation of adsorbed materials on the surface bringing 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 (B) compared to the P25/GF catalyst (A). In order to regenerate the activity of deactivated photocatalysts, they were evacuated and exposed to simultaneously to hydrogen peroxide and toluene vapor. The activity of the P25/GF catalyst was completely recovered by the exposure 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 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 enhancement of photocatalytic activity of the DTS/GF catalyst suggest that hydrogen peroxide induces some changes in the surface of the used catalyst as well as the removal of carbonaceous materials. The XPS spectra of the used DTS/GF catalyst shown in Fig. 4 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 the enhancement of the photocatalytic activity of the DTS/GF catalyst.

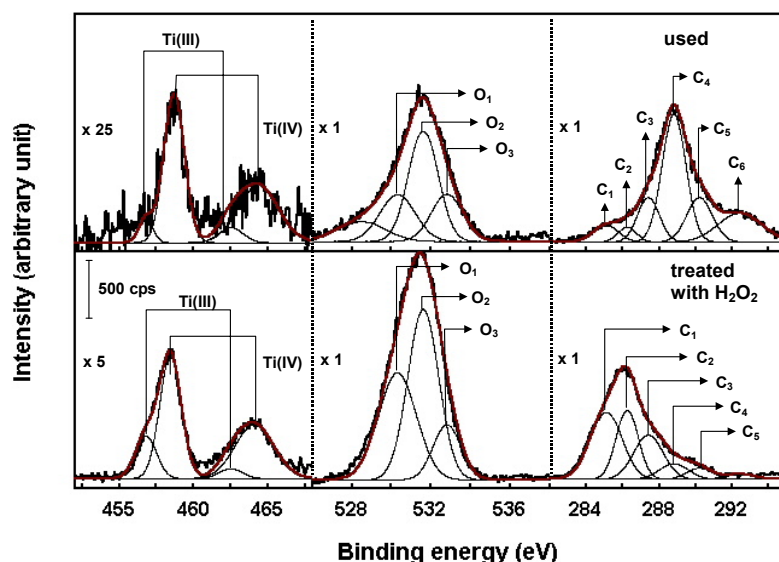


Fig. 4. XPS spectra of the DTS/GF catalysts: used and treated with hydrogen peroxide.

Conclusion

Titania can be dispersed on glass fiber by impregnation of anatase-type powder and by direct hydrolysis of dilute titanium isopropoxide solution. Both the DTS/GF and P25/GF catalysts are active in the photocatalytic degradation of toluene, while their activities become lower due to accumulation of reactant or carbonaceous material on the catalyst surface. Hydrogen peroxide not only regenerates completely 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.

References

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