

Photocatalytic Degradation of Toluene with Ozone Addition

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Abstract—The main goal of this study is to analyze the characteristics of photodegradation and photocatalytic activation experimentally with the major parameters such as air flow rate, inlet toluene concentration, ozone concentration, UV light and bead material, etc.. In particular, the effects of transmissivity of UV radiation with TiO₂ coated supporter (bead material) and void fraction (bead size) on the photocatalytic degradation are estimated for TiO₂/UV and O₃/TiO₂/UV process. In results, the experiment shows that the UV light transmissivity of 5 mm glass bead becomes much higher than that of 6.5 mm alumina bead in spite of lower void fraction inducing the higher photoactivation. The conversion of toluene represents about 96% during reaction time 420 min at the toluene concentration of 100 ppm and ozone concentration of 2.5 ppm, showing a conversion rate of ozone of 95% for O₃/TiO₂/UV process.

Key words: Photodegradation, Photoactivation, Transmissivity, Bead Material, Regeneration

INTRODUCTION

The control of indoor and industrial air pollutants—volatile organic compounds (VOCs)—has been strongly tightened due to the significant hazards they pose. Conventional purification methods such as filtration, activated carbon adsorption, plasma process, and catalytic oxidation are widely proposed for removing these compounds. Recently, a photocatalytic technique as an advanced oxidation process (AOP) is increasingly concerned in removing VOCs, since the AOP is effective for the treatment of gaseous pollutants, waste water treatment and purification by generating OH radical for a strong oxidation reaction. However, the application of photocatalyst has been limited with the problem of photocatalyst deactivation during a photocatalytic degradation process. The photocatalyst deactivation is caused by a yellowish discoloration of TiO₂ due to the build-up (formation) of polymeric species on the catalyst surface [Shen and Ku, 2002; Wonyong, 2001; Zhang, 2003; d'Hennezel et al., 1998].

Thus, it is very important to recover the activity of the used deactivated photocatalyst by addition of ozone and nitric acid, etc. Many studies on the effect of oxidant addition have been carried out for photocatalytic treatment of aqueous pollutants, but those of gas phase pollutants, VOCs, are rarely studied [Mizuno et al., 1992; Kang et al., 2001]. In this study, characteristics of the photocatalytic degradation and photoactivation with ozone addition to a photooxidation system for the treatment of toluene as a gaseous pollutant are investigated more quantitatively with the major experimental variables such as air flow rate, ozone instillation concentration, inlet toluene concentration, bead material (glass, alumina bead), bead size (or reactor's void fraction), and UV light, etc. The UV light intensity and transmissivity which reciprocally depends upon the phys-

ical property of TiO₂ film supporter (i.e., bead material such as glass and alumina) and reactor void fraction with bead size are closely related to the effect of photocatalytic degradation. Thus, the effects of UV light transmissivity with both bead material (glass, alumina bead) and void fraction by bead size in a reaction system are specifically analyzed for a conversion rate of toluene and intermediate products such as benzaldehyde, benzoic acid and benzyl alcohol in this experiment. The above parameters are to be considered as other major factors for the design of a photocatalytic oxidation system and process analysis. Therefore, the main purpose of this study is to analyze quantitatively the characteristics of the photocatalytic oxidation process and photocatalytic activation with the pre-mentioned experimental parameters.

EXPERIMENTAL

TiO₂ photocatalyst as the product of E. company is prepared by a sol-gel method. The characteristics of TiO₂ sol are presented in Table 1. The SEM photograph and X-ray diffraction pattern are shown in Fig. 1. A thin TiO₂ photocatalyst film is coated on the surface of alumina and glass bead as a photocatalyst supporter by dip-coating method.

The experimental design of a photoreactor system to investigate the characteristics of photocatalyst degradation of toluene is presented in Fig. 2. The experimental system consists of VOCs generator, air supplier, ozone generator, photoreactor, and measurement system, etc. in this study. The toluene gas is bubbled by passing the compressed air into a bottle containing liquid toluene. The humidity

Table 1. Physical and chemical properties of TiO₂ solution

Crystal structure	Anatase
Solvent	Water
Particle size	30-40 nm
pH	9-10
Particle shape	Spherical type

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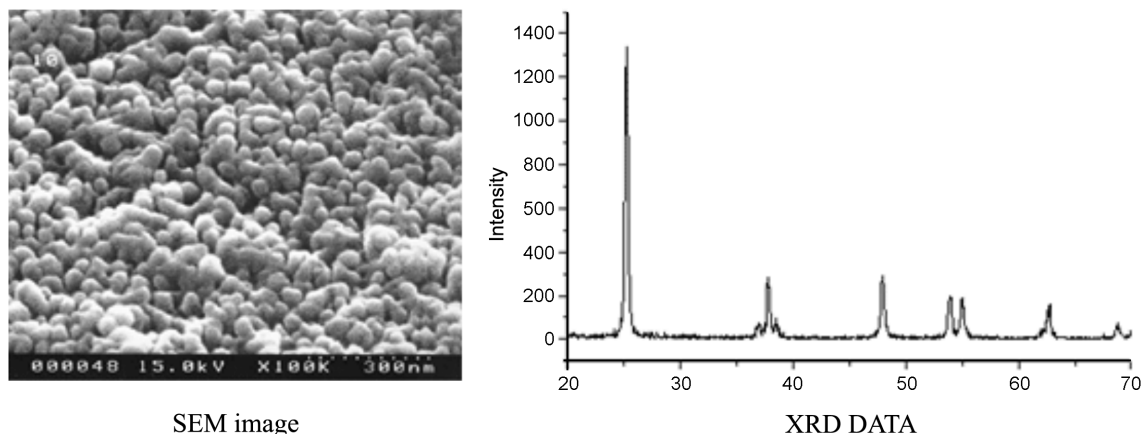


Fig. 1. SEM photograph and X-ray diffraction pattern of TiO_2 sol.

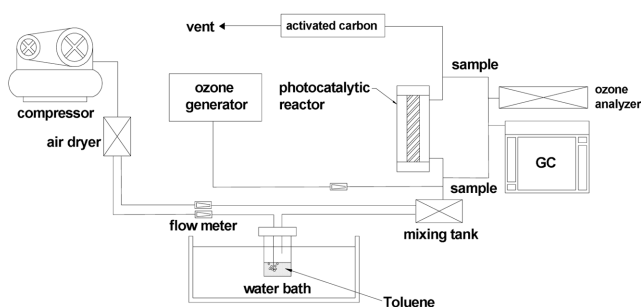


Fig. 2. Schematic diagram of the photocatalytic reactor system.

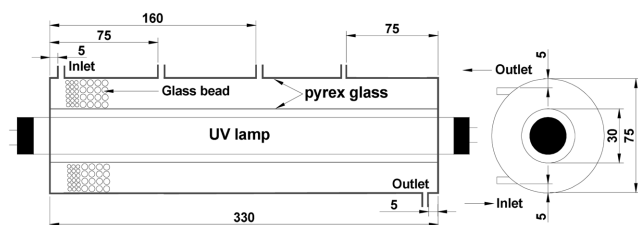


Fig. 3. Schematic diagram of photoreactor designed for this application.

fied air stream (relative humidity $25 \pm 5\%$) is mixed with bubbling toluene gas in a mixing tank.

The photoreactor is designed as an annular tube type of pyrex material with UV source inside the center area of an annular tube. The UV lamp used in this experiment, is specified as wavelength range 300–400 nm (UV-A), lamp length 436 mm and diameter 25.5 mm of Sankyo Denki company. The physical dimensions and configuration of photoreactor are specifically described in Fig. 3.

The toluene concentration is estimated by gas chromatography (HP 5890II) with FID (Flame Ionization Detector). The measurement system includes highly purified N_2 as a carrier gas and HP-20M ($25 \text{ m} \times 0.32 \text{ mm} \times 0.3 \mu\text{m}$) column. The operational conditions of the GC are presented in Table 2. Additionally, GC-MS (Shimadzu GC(FID)/MS QP-5050A, Tekmar autoscan System) is used to analyze the intermediate products during photocatalyst oxidation process, specifically. The concentrations of ozone at inlet and exit of photoreactor are measured by ozone analyzer (Ozomat GM, Ger-

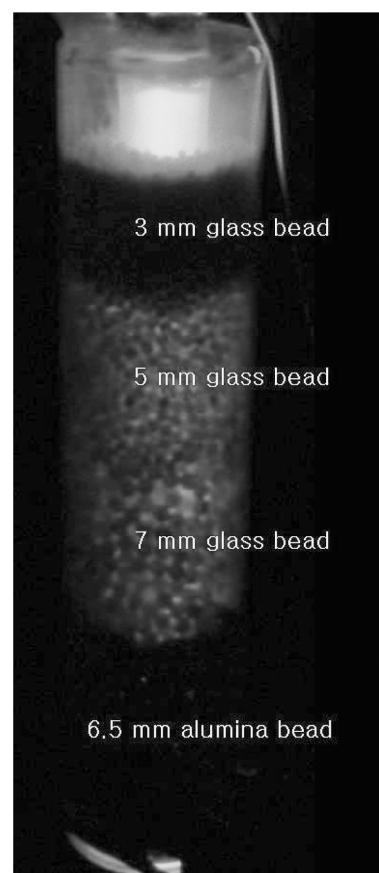


Fig. 4. Transmissivity of UV radiation with bead material and bead size (glass bead : 3, 5, 7 mm, alumina bead : 6.5 mm).

many, accuracy ± 0.1 ppm).

RESULTS AND DISCUSSION

1. Transmissivity of UV Radiation and Photoactivation

Fig. 4 shows the characteristics of UV radiation transmissivity closely related to a photocatalyst activation with bead material (opaque alumina bead, transparent glass bead) and bead size (i.e., void fraction). It turns out that the radiation transmissivity of 5 mm glass bead

(void fraction 44%) becomes much higher than that of 6.5 mm alumina bead (void fraction 46%) despite lower void fraction by the brightness of a packed bed, and also than that of 3 mm glass bead (void fraction 40%) due to higher void fraction.

Fig. 5 represents the conversion of toluene with bead material

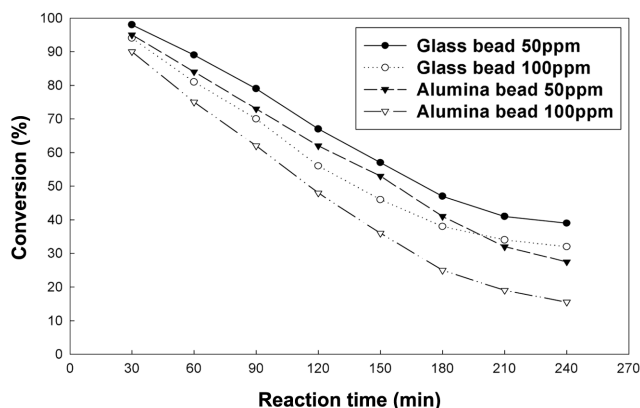
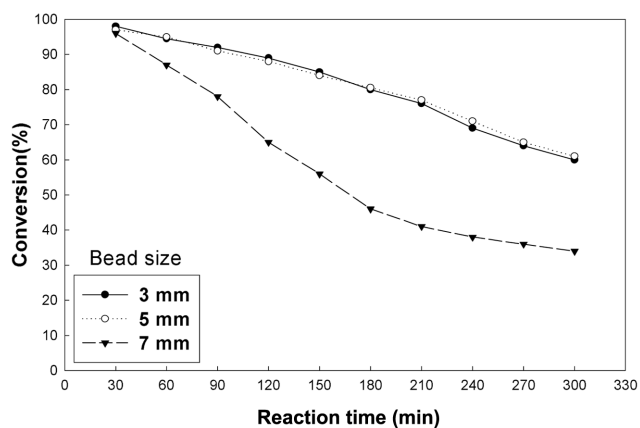
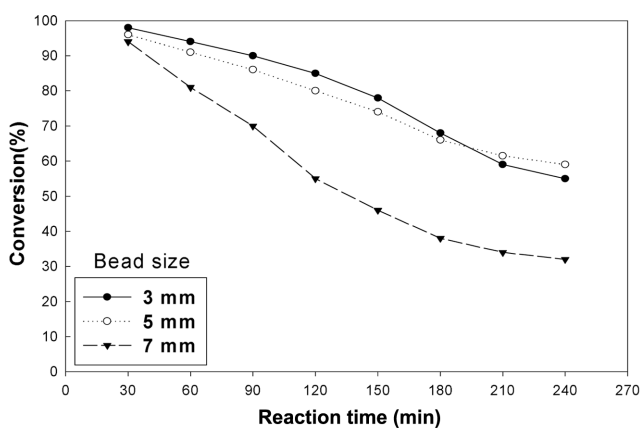


Fig. 5. Effect of bead material on the conversion of toluene for TiO_2/UV process (flow rate 250 mL/min, RH 25%, 7 mm glass bead/6.5 mm alumina bead).



(a) Toluene 50 ppm



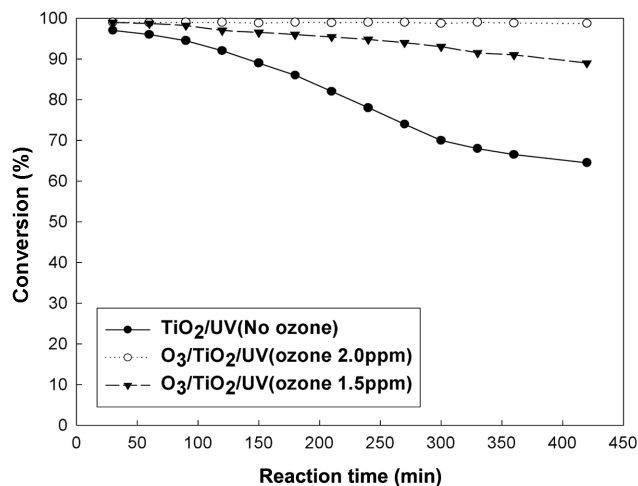
(b) Toluene 100 ppm

Fig. 6. Conversion of toluene with bead size and inlet toluene concentration for TiO_2/UV process (flow rate 250 mL/min, RH 25%, glass bead).

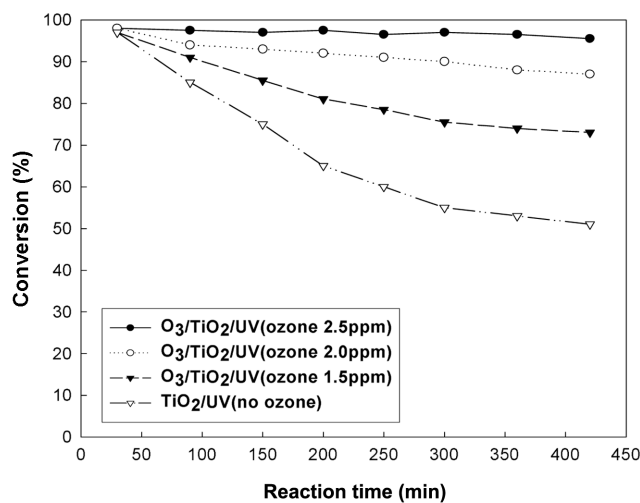
and size (7 mm glass bead, 6.5 mm alumina bead) at inlet toluene concentration 50, 100 ppm for TiO_2/UV process. As expected in Fig. 4, at the same toluene concentration, the effect of photodegradation of glass bead is to be higher than that of alumina bead and the difference of conversion rate with bead material becomes larger with increase of reaction time and inlet toluene concentration from 50 to 100 ppm.

2. Photocatalytic Degradation for TiO_2/UV and $\text{O}_3/\text{TiO}_2/\text{UV}$ Process

The photocatalytic degradation of toluene is considered with the size range (3, 5, 7 mm) of glass bead as a TiO_2 film supporter and inlet toluene concentration. Fig. 6(a), (b) represents the conversion rate of toluene with reaction time (30–300 min) at inlet toluene concentration of 50, 100 ppm and flow rate, 250 mL/min for TiO_2/UV process. The photodegradation of toluene decreases rapidly with increase of reaction time and bead size showing that of a similar trend for the bead diameter 3, 5 mm, and lower conversion rate for 7 mm bead. The photocatalyst of 5 mm bead maintains a little higher removal efficiency of toluene than that of 3 mm bead after reaction



(a) Toluene 50 ppm

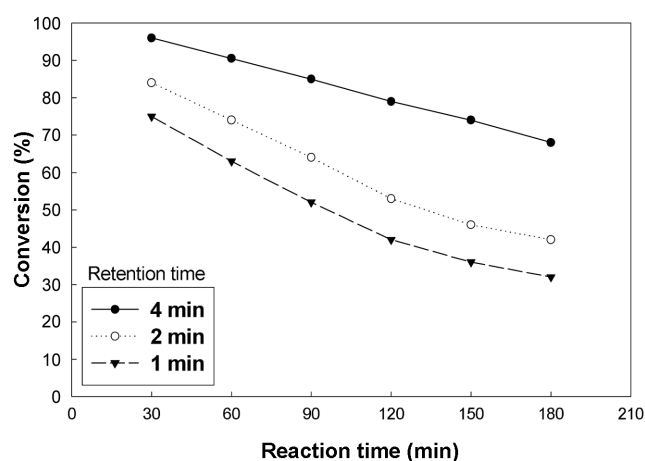


(b) Toluene 100 ppm

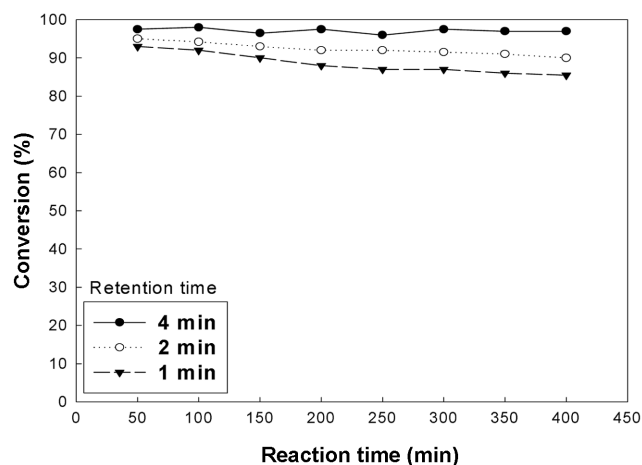
Fig. 7. Effect of ozone on the conversion of toluene for $\text{O}_3/\text{TiO}_2/\text{UV}$ process (flow rate 250 mL/min, RH 25%, 5 mm glass bead).

time 180 min despite of larger specific surface area of 3 mm bead comparing to that of 5 mm bead. At the end of the experiment, discoloration of photocatalyst is found on the surface of glass bead at the outer region of annular type reactor as well as that at inner region in case of 5 mm bead size as the result of photodegradation by the effect of UV light [Luo et al., 1996; Vincenzo et al., 1999; Lixin, 2000], while the discoloration is not found at the outer region by non-photodegradation effect in case of 5 mm bead size. It is due to the photocatalyst activation generated by UV radiation passing through larger void space between 5 mm glass beads compared to that of 3 mm bead by the far reaching nature of radiation.

As shown in Fig. 7, at inlet toluene concentration of 50 ppm, the conversion rates of toluene maintain 99% during reaction time 50 min, and 89% after oxidation reaction time of 420 min for the inlet ozone concentration 1.5 ppm, showing slight discoloration on the surface of photocatalyst for $O_3/TiO_2/UV$ process. In case of ozone concentration 2.0 ppm, the non-discoloration of photocatalyst surface is found showing a high conversion rate of 99% during reaction time of 420 min by the maintenance of high activation of photocatalyst. The conversion rate of toluene decreases with increment of inlet toluene concentration from 50 to 100 ppm showing a simi-



(a) TiO_2/UV process



(b) $O_3/TiO_2/UV$ process

Fig. 8. Effect of retention time on the conversion of toluene (toluene 100 ppm, RH 25%, 5 mm glass bead).

lar trend of photodegradation. Specifically, in case of ozone concentration 2.5 ppm, the conversion rate of toluene is represented as about 96% during 420 min at the toluene concentration 100 ppm without the discoloration of photocatalyst. From Fig. 7, with increase of toluene concentration, the ozone addition must be required to sustain almost the same removal efficiency of toluene (i.e., ozone concentration 2.0, 2.5 ppm for toluene concentration 50, 100 ppm, respectively). These results are similarly accepted in many VOCs treatment processes by photocatalytic oxidation and ozone addition process. The surface of TiO_2 coated glass bead in $O_3/TiO_2/UV$ process maintains the slight presence and absence of discoloration since the intermediate products are oxidized before being sorbed on the bead surface by ozone addition [Shen and Ku, 2002].

The residual ozone concentration after oxidation reaction is seriously treated since ozone itself is harmful to human health. It is found that the outlet ozone concentration from $O_3/TiO_2/UV$ process is slightly 0.1 ppm or not detected in the present experimental conditions because most of ozone added to the present oxidation system is conserved to OH radical (the conversion rate of ozone is measured as 95%).

Fig. 8(a), (b) represents the conversion rate of toluene with the retention time (air flow rate) for the TiO_2/UV and $O_3/TiO_2/UV$ process. The experiment is executed under the conditions of retention time 4, 2, 1 min (flow rate 0.25, 0.5, 1.0 L/min), inlet toluene concentration 100 ppm, and ozone concentration 2.5 ppm. The conversion rates of the TiO_2/UV process abruptly decrease with reaction time as the retention time decreases in comparison with those of the $O_3/TiO_2/UV$ process. Moreover, it is found that the difference of conversion rate between the different retention time for $O_3/TiO_2/UV$ process becomes much lower than that of TiO_2/UV process with increase of reaction time.

3. Regeneration of Photocatalyst and Intermediate Products

The deactivation of TiO_2 photocatalyst occurs by the strong adsorption of intermediate products on TiO_2 surface. Many studies on regeneration of deactivated catalyst have been performed using pure air and UV radiation without air contaminant. In this study, the effects on regeneration of photocatalyst deactivation are to be comparatively considered by air flow/UV radiation and ozone.

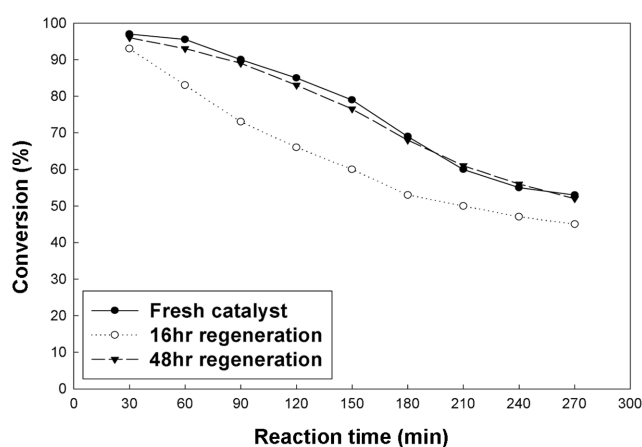


Fig. 9. Conversion of toluene for regeneration catalyst by air flow/UV for TiO_2/UV process (flow rate 250 mL/min, toluene 100 ppm, RH 25%).

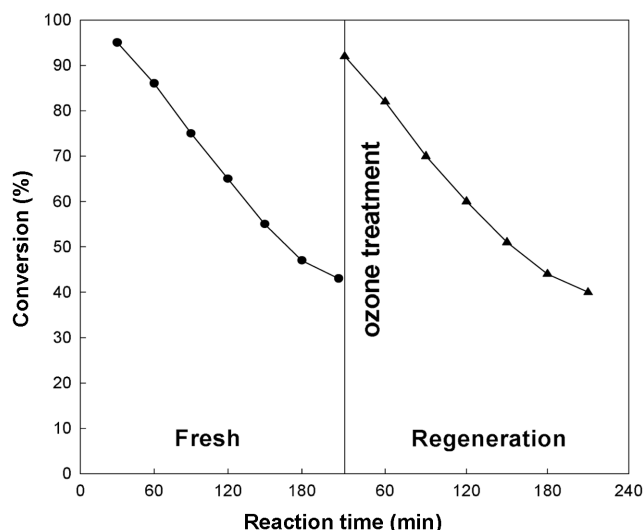


Fig. 10. Conversion of toluene for regeneration catalyst by ozone addition for TiO_2/UV process (ozone 2.5 ppm, flow rate 250 mL/min, toluene 150 ppm, RH 30%).

Fig. 9 represents the conversion rate of fresh and regenerated photocatalyst under air flow and UV irradiation. For the comparison of photocatalyst activity with regeneration time, the photocatalysts regenerated during 16 hr and 48 hr are employed under the conditions of air flow (2 L/min) and UV light (365 nm).

In case of a regeneration time of 16 hrs, the color of the bead surface is not completely recovered to the original white color, representing an insufficient regeneration, so that the conversion rate of toluene becomes lower than that of fresh catalyst.

However, in the case of 48 hrs, the used TiO_2 photocatalyst is fully regenerated, showing almost the same conversion rate of toluene as that of fresh catalyst. It means that a long time regeneration is required to come back to similar photoactivity with that of fresh catalyst.

Fig. 10 shows the comparison of photoactivity for the fresh photocatalyst and used photocatalyst regenerated by adding 2.5 ppm ozone to air flow and UV irradiation. The surface color of the regenerated bead turns to the original white color of fresh catalyst, showing similar photoactivity with that of fresh catalyst. It is found that the addition of ozone can significantly shorten the regeneration time 1 hr compared to the regeneration system by air flow/UV radiation.

The photocatalyst deactivation is caused by the strong adsorption on the bead surface of intermediate products generated during photodegradation process for the treatment of air contaminants. The photodegradation of gas-phase toluene produces benzaldehyde, benzoic acid and benzyl alcohol, etc. as the intermediate products. Among them, the major intermediate product is benzaldehyde which is oxidized to benzoic acid by oxygen. The benzaldehyde and benzoic acid are known as the major substances inducing the discoloration on the TiO_2 bead surface. Benzoic acid is strongly adsorbed on the surface of photocatalyst, and the accumulation of benzoic acid on the surface appears to be responsible for the photocatalyst deactivation.

Figs. 11 and 12 represent the intermediate products for TiO_2/UV and $\text{O}_3/\text{TiO}_2/\text{UV}$ process (inlet toluene concentration 100 ppm) in

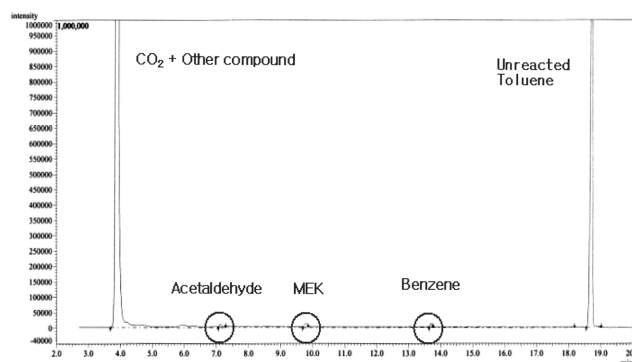


Fig. 11. GC/MS analysis of main products by the photooxidation of toluene.

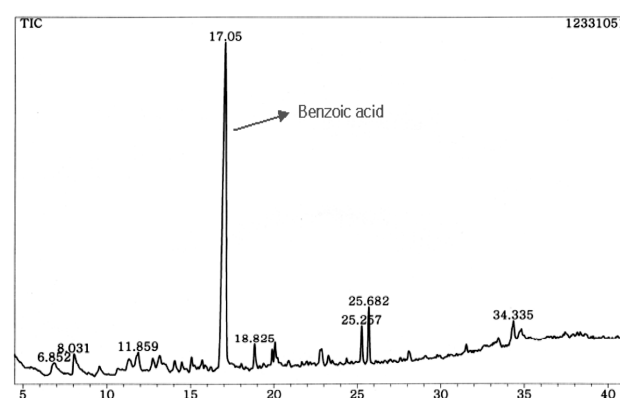


Fig. 12. GC/MS (scan mode, TIC) analysis of intermediate products by the methanol extraction.

the case of removal efficiency of 89%. In these two processes, the main products such as non-reaction toluene, CO_2 and small quantities of benzene are detected showing the peak of benzene, acetaldehyde, and MEK in gaseous phase. Non-gaseous phase intermediate products are also detected by GC/MS analysis. The benzoic acid of highest peak and small amounts of benzyl alcohol are found by analyzing the intermediate species adsorbed on the photocatalyst dissolved in methanol.

CONCLUSION

The main objective of this study was to investigate quantitatively the characteristics of photodegradation of gas-phase toluene with the major experimental parameters such as air flow rate, inlet toluene concentration, ozone concentration and TiO_2 coated supporter, etc. Specifically, the experiments were executed to analyze the effect of photodegradation by the addition of ozone and transmissivity of UV radiation with bead material and bead size for TiO_2/UV and $\text{O}_3/\text{UV}/\text{TiO}_2$ process. As the results of this experiment, the following conclusions are made.

1. The transmissivity of UV radiation related to photocatalyst activation significantly depends upon the TiO_2 coated bead material (opaque or transparent bead) and bead size (void fraction). The transmissivity of UV light of 5 mm glass beads becomes much higher

than that of 6.5 mm alumina beads despite of lower void fraction.

2. The difference of conversion rate with bead material (glass, alumina bead) is to be larger with increase of reaction time and inlet toluene concentration from 50 to 100 ppm, maintaining higher conversion for glass beads in comparison with that for alumina beads.

3. For O_3 /UV/ TiO_2 process, the conversion of toluene is maintained at about 96% during reaction time 420 min at the inlet toluene concentration 100 ppm and ozone 2.5 ppm without discoloration of photocatalyst, showing a conversion rate of ozone of 95%.

4. The regeneration of deactivated photocatalyst by ozone addition to air flow/UV radiation is much more effective than that by only air flow/UV radiation system requiring a long time regeneration (about 48 hrs). Specifically, the surface of discolored photocatalyst turns to the original white color, recovering a complete regeneration within 1 hr in case of 2.5 ppm ozone dosage.

5. For TiO_2 /UV and O_3 / TiO_2 /UV process, the intermediate products such as benzoic acid of highest peak and small amounts of benzyl alcohol are detected by GC/MS analysis. The accumulation of benzoic acid strongly adsorbed on the catalyst surface appears to be responsible for the photocatalyst deactivation.

REFERENCES

- d'Hennezel, O., Pichat, P. and Ollis, D. F., "Benzene and Toluene Gas-phase Photocatalytic Degradation over H_2O and HCL Pretreated TiO_2 : By-products and Mechanisms," *J. Photochemistry and Photobiology A : Chemistry*, **118**, 197 (1998).
- Kang, J. W., Lee, K. H., Koh, C. I. and Nam, S. N., "The Kinetics of the Sonochemical Process for the Destruction of Aliphatic and Aromatic Hydrocarbons," *Korean J. Chem. Eng.*, **18**(3), 336 (2001).
- Lee, H. J., Kang, D. W. and Chi, J., "Degradation Kinetics of Recalcitrant Organic Compounds in a Decontamination Process with UV/ H_2O_2 and UV/ H_2O_2 / TiO_2 Processes," *Korean J. Chem. Eng.*, **20**(3), 503 (2003).
- Lixin, C., "Photocatalytic Oxidation of Toluene on Nanoscale TiO_2 Catalysts : Studies of Deactivation and Regeneration," *J. Catalysts*, **196**, 253 (2000).
- Luo, Y. and Ollis, D. F., "Heterogeneous Photocatalytic Oxidation of TCE and Toluene Mixture in air : Kinetic Promotion and Inhibition, Time-Dependent Catalyst Activity," *J. Catalysis*, **163**, 1 (1996).
- Mizuno, A., Yamazaki, Y., Ito, H. and Yoshida, H., "AC Energized Ferroelectric Pellet Bed Gas Cleaner," *IEEE Transactions on Industry Applications*, **28**, 535 (1992).
- Park, D. R., Ahn, B. J., Park, H. S., Yamashita, H. and Masakazu, A., "Photocatalytic Oxidation of Ethylene to CO_2 and H_2O on Ultrafine Powered TiO_2 Photocatalysts: Effects of the Presence of O_2 and H_2O and the Addition of Pt," *Korean J. Chem. Eng.*, **18**, 930 (2001).
- Shen, Y. S. and Ku, Y., "Decomposition of Gas-phase TCE by the UV/ TiO_2 Process in the Presence of Ozone," *Chemosphere*, **46**, 101 (2002).
- Vincenzo, A., Coluccia, S. and Loddo, V., "Photocatalytic Oxidation of Gaseous Toluene on Anatase TiO_2 Catalyst : Mechanistic Aspects and FT-IR Investigation," *Applied Catalysis B : Environmental*, **20**, 15 (1999).
- Wonyong, C., "Investigation on TiO_2 -coated Optical Fibers for Gas-phase Photocatalytic Oxidation of Acetone," *Applied Catalysis B : Environmental*, **31**, 209 (2001).
- Xianyu, W. X., Park, M. K. and Lee, W. I., "Thickness Effect in the Photocatalytic Activity of TiO_2 Thin Films Derived from Sol-Gel Process," *Korean J. Chem. Eng.*, **18**(6), 903 (2001).
- Xiaoli, Y., Huixiang, S. and Dahui, W., "Photoelectrocatalytic Degradation of Phenol Using a TiO_2 /Ni Thin-film Electrode," *Korean J. Chem. Eng.*, **20**(4), 679 (2003).
- You, Y. S., Chung, K. H., Kim, J. H. and Seo, G., "Photocatalytic Oxidation of Toluene over TiO_2 Catalysts Supported on Glass Fiber," *Korean J. Chem. Eng.*, **18**, 924 (2001).
- Zhang, Pengyi, "A Comparative Study on Decomposition of Gaseous Toluene by O_3 /UV, TiO_2 /UV and O_3 / TiO_2 /UV," *Journal of Photochemistry and Photobiology A : Chemistry*, **6219**, 1 (2003).