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Gaseous by-products from the TiO_2 Photocatalytic Oxidation of Benzene

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Abstract

Photocatalytic oxidations of benzene gas using the closed system (batch reactor) were induced to determine its by-products and investigate the effect of humidity and oxygen concentration on their generation. The study was able to identify 11 gaseous by-products: 2-methylpropene, acetaldehyde, acetone, pentane, methylcyclobutane, methylcyclopentane, cyclohexane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, and hexane. All the by-products were saturated hydrocarbons, which are less toxic than benzene and were probably formed through hydrogenation reaction on the photocatalytic surface. The photocatalytic oxidation of benzene under higher humidity produced less by-products. However, the amount of acetone released increased with higher humidity and oxygen concentration.

Keywords: Photocatalytic oxidation, Titanium dioxide, Benzene, By-products, Permissible exposure limits

1. Introduction

Various volatile organic compounds (VOCs) are heavily used in many industrial processes. Once released into the environment, they can cause serious water and air pollution. They are also considered as main pollutants of indoor air.[1)] In addition, VOCs are precursors in the production of ozone and peroxyacetyl nitrate (PAN) in the atmosphere through the photo-oxidation with nitrogen oxide, thereby causing smog.[2,3)] Furthermore, some of VOCs are carcinogenic to human and animals, and even small amounts of VOCs can adversely affect people due to their odor.

Many technologies have been applied to reduce VOCs emitted in the working places of industries. In particular, photocatalytic oxidation is being actively studied because of its potential of removing and destroying low-level pollutants in air.[4)] TiO_2 is the most widely used photocatalyst, since it is less expensive and stable under light and in a biological process. Since TiO_2 has the band gap energy of 3.2 eV, absorption of less than 400 nm wavelength of light excites TiO_2 and induces formation of electron-hole pairs. When the excited catalyst reacts with an aqueous solution, the hole generates an OH radical, a powerful oxidant. The produced OH radical, then, participates in oxidation that decomposes organics, and electrons are utilized during reduction.[5,6)] Based on this mechanism, many researchers have studied oxidation, oxidation efficiency, and reaction by-products of a wide variety of VOCs. They were able to prove that photocatalytic oxidation is a very effective in treating air pollutants such as aldehydes, alcohols, light hydrocarbons, aromatics, trichloroethylene, and chlorinated solvents.[4,7-11)]

The photo-oxidation of benzene has been studied using an annular flow reactor to measure the treatment efficiency. However, when the removal efficiency of the system was evaluated, only the increase in carbon dioxide and decrease in benzene in the reactor were considered. In the studies performed by Turchi and Ollis,[12)] Jacoby et al.[4)] and d’Hennezel et al.,[13)] the identification of the by-products from the photo-oxidation of benzene were tried. They tried to detect gaseous by-products on the surface of the catalyst. Using solvent-induced extraction from the surface of the catalyst in photocatalytic reactions, they merely proved the existence of by-products such as phenol, 1,4-benzoquinone, hydroquinone (1,4-dihydroxybenzene), malonic acid, formic acids, and acetic acids. These by-products on the catalytic surface were not in gaseous state, since vapor pressure was very low at room temperatures. These by-products continually participated in photocatalytic reactions before finally being oxidized into CO_2 and H_2O. However, the by-products with high vapor pressure rapidly volatilize into the gas phase from the

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catalyst surface, and did not further participate into photocatalytic reactions.

Previous studies on the photocatalytic reactions of benzene have not identified gaseous by-products, which is probably due to the set-up of a reactor and low concentration of benzene used. Therefore, this study investigated whether harmful and toxic gaseous by-products are generated during the photocatalytic reaction of benzene, by introducing high concentration of benzene into a batch reactor instead of the annular flow reactor to allow gaseous by-products to accumulate. The effects of the change in oxygen concentration and relative humidity in the reactor on the generation of gaseous by-products were also investigated.

2. Materials and Methods

TiO_2 from Pepcon Corp. was used, which was manufactured using a Sol-Gel method and coated on the glass tube (length: 4.5 cm, id: 0.7 cm). The XRD measurement revealed that the TiO_2 photocatalyst mostly had anatase structure. Likewise, the SEM measurement showed that the TiO_2 was coated with a 0.26 ㎛ thick scaffold surface. A 365-nm UV lamp (Sankyo Denki's blacklight blue, Model F15T8BLB) was also used as a light source. The reactor was filled with pure nitrogen, air, and oxygen, respectively. J.T. Baker-made benzene (100%) was used as the target compound of a photocatalytic reaction.

Fig. 1 shows the photo-reactor used in the experiment, which was designed as a closed rectangular parallel-piped polypropylene panel case with 6.7-L volume. A quartz with a diameter of 50 mm was installed in the reactor for the UV lamp, in order to allow closer irradiation to the catalyst. A small fan was installed to completely mix the test gas in the reactor. A sampling port was also set up to enable the easy injection and collection of gas sample. Gas samples were collected from the reactor using a 10 mL gas tight syringe.

A GC/MSD (Agilent, GC6890 & MSD-5973N) equipped with OV-624 (30 m×0.32 mm×1.8 ㎛) and an HP-PLOT/Al_2O_3 (50 m×0.32 mm×8.0 ㎛) column was used to identify the by-products generated in the photocatalytic reaction of benzene. Oxygen was supplied for two hours during the experiment, while about 9,400 ppmv (37.3 mL/m^3) liquid benzene was injected into the reactor using a micro syringe. Water was also injected in order to attain a 100% relative humidity (17.3 mL/m^3) at 20°C. After the two-day photocatalytic reaction, 1-mL gas sample was collected using a gas tight syringe. The gas sample was then injected into the GC/MSD.

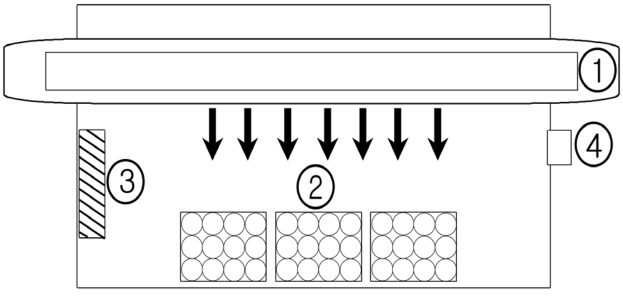

Fig. 1. Schematic diagram of photocatalytic reactor. ①UV light source, ②Photocatalyst, ③Mixing fan, ④Sampling port.

To determine the effects of the change in oxygen concentration and relative humidity on the generation of by-products, the study used a GC/FID (GC5890, Agilent) equipped with a DB-624 (30 m×0.53 mm×3.0 ㎛) column. Three reactors were prepared for the test, using the same procedure of emitting nitrogen, air, and oxygen for two hours in the by-product identification test. The amount of water was also adjusted to a relative humidity of 0%, 40%, and 100% at 20°C. 9,400 ppmv (37.3 mL/m^3) of benzene was then injected into each reactor. For the analysis of the test gas, changes in the by-products were observed with the passage of time after turning on the light source.

For the determination of the by-products using the TiO_2 photocatalyst, blank tests were conducted to determine the compounds generated during chemical reactions aside from photocatalytic reactions, e.g., benzene decomposition through UV, polypropylene decomposition through UV, and chemical reactions between benzene and polypropylene. Two experiments were performed, i.e., one with UV light source, photocatalyst, moisture, and without benzene, and the other with UV light source, benzene, moisture, and without TiO_2.

3. Results and Discussions

Fig. 2 shows the results of the blank experiment of photocatalytic reactors. Fig. 2(a) shows the chromatogram obtained under the blank experiment without benzene. It does not show any peaks except the one for oxygen. Thus, the result confirmed that there were no gaseous by-products from the photocatalytic reactions of polypropylene or other materials. On the other hand, Fig. 2(b) shows the condition with benzene but without TiO_2. The same components verified in the photocatalytic reaction of benzene were detected. However, a very small amount of benzene was decomposed by UV.

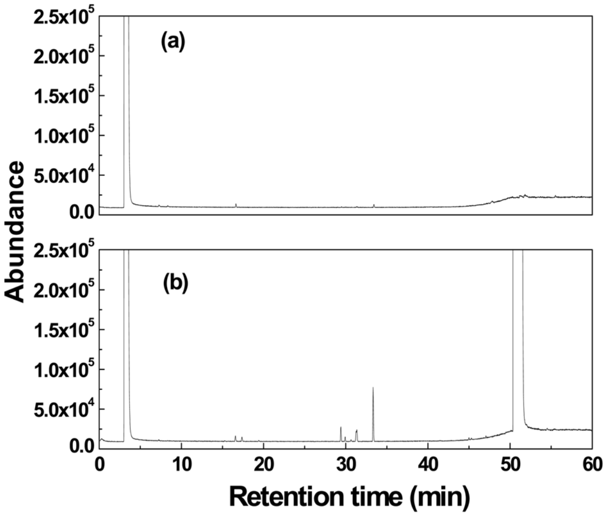

Fig. 2. GC/MSD chromatograms obtained during the photocatalytic reaction. (a) $[C_6H_6]_0$ = 0 mL/m^3 (0 ppmv), $[H_2O]_0$ = 17.3 mL/m^3 (relative humidity 100%), 10 W/m^2, UV lamp, and TiO_2 photocatalytic. (b) $[C_6H_6]_0$ = 37.3 mL/m^3 (9400 ppmv), $[H_2O]_0$ = 17.3 mL/m^3, 10 W/m^2, UV lamp without TiO_2 photocatalytic ; HP- PLOT/Al_2O_3.

Fig. 3(a) and (b) show the GC/MSD chromatogram of the gases generated during the photocatalytic oxidation of benzene. Eleven gaseous by-products were identified from the oxidation of benzene, e.g., 2-methylpropene (C_4H_8), acetaldehyde (C_2H_4O), acetone (C_3H_6O), pentane (C_5H_{12}), methylcyclobutane (C_5H_{10}), methylcyclopentane (C_6H_{12}), cyclohexane (C_6H_{12}), 2,3-dimethylbutane (C_6H_{14}), 2-methylpentane (C_6H_{14}), 3-methylpentane (C_6H_{14}), and hexane (C_6H_{14}).

The effects of the changes in background gases and relative humidity inside the photo-reactor on the generation of gaseous by-products during the photocatalytic oxidation of benzene were investigated. A GC/FID equipped with DB-624 column was used in the analysis, i.e., describing the concentration of the observed gaseous by-products in the benzene-injected reactor up to 100 hr.

Figs 4, 5, and 6 show the time profiles of the gaseous by-products generated in the reactor with different background gases and at relative humidity of 0%, 40%, and 100%. Results show that the amount of by-products generated in the reactor with 0% relative humidity were two times higher than that in the reactor with 40% relative humidity, as well as three times higher than that in the reactor with 100% relative humidity. 2-methylproene (C_4H_8) was identified prevalent in all reactors, showing rapid accumulation inside the reactors as time passed. Under the condition where moisture was present, a relatively higher concentration of acetone (C_3H_6O) was observed in the reactor filled with oxygen and air compared to the reactor with nitrogen.

Except for acetaldehyde and acetone, all by-products (saturated hydrocarbons less than C6) were probably generated through the direct hydrogenation reaction of benzene on the catalytic surface.[6] Through the elution analysis of solvents, Turchi and Ollis[12] and Obee and Brown[7] revealed that malonic acid, acetic acid, phenol, 1,4-benzoquinone, 1,4-dihydroxybenzene, 1,2-benzenediol, and 1,2,3-benzenetriol were generated through the oxidation of benzene on the catalytic surface. However, they could not detect these substances in gas phase, probably due to the thermo-dynamic characteristics of the generated by-products.

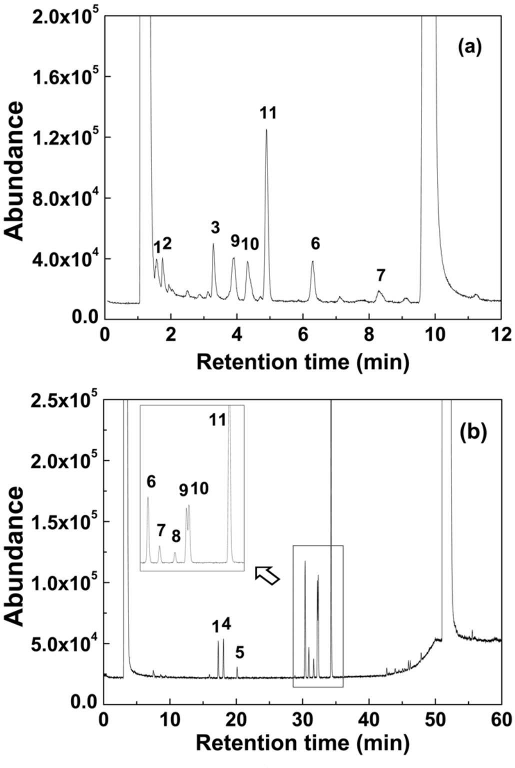

Fig. 3. GC/MSD chromatograms of benzene by-products, 2-methylpropene(1), acetaldehyde(2), acetone(3), pentane(4), methylcyclobutane(5), methylcyclopentane(6), cyclohexane(7), 2.3-dimethylbutane (8), 2-methylpentane(9), 3-methylpentane(10), and hexane(11). $[C_6H_6]_0$ = 37.3 mL/m^3 (9400 ppmv), $[H_2O]_0$ = 17.3 mL/m^3 (relative humidity 100%), 10 W/m^2, UV lamp, and TiO_2 photocatalytic. ; OV-624(a), HP-PLOT/Al_2O_3(b).

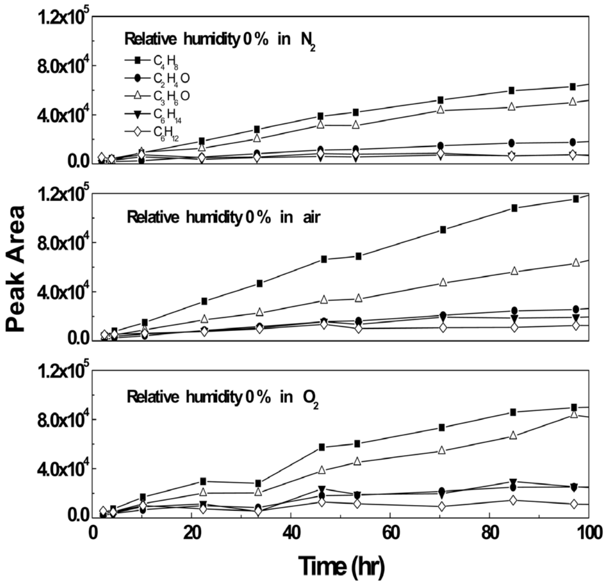

Fig. 4. Time profiles of the by-products in the benzene photocatalytic oxidation. $[C_6H_6]_0$ = 9400 ppmv, relative humidity 0%, 10 W/m^2 UV lamp.

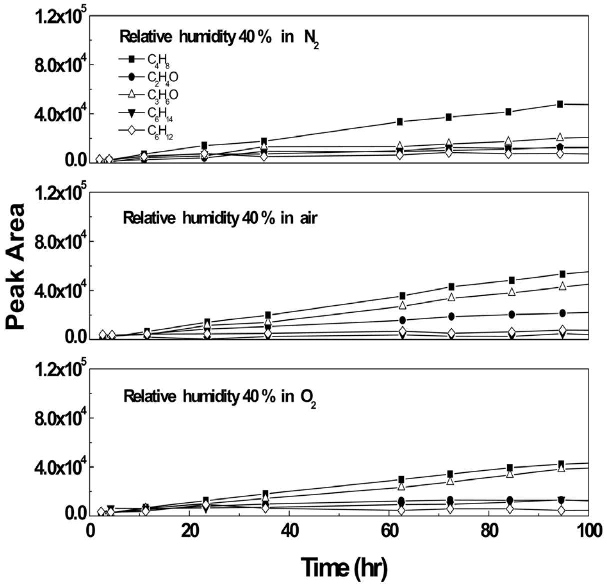

Fig. 5. Time profiles of the by-products in the benzene photocatalytic oxidation. $[C_6H_6]_0$ = 9400 ppmv, relative humidity 40%, 10 W/m^2 UV lamp.

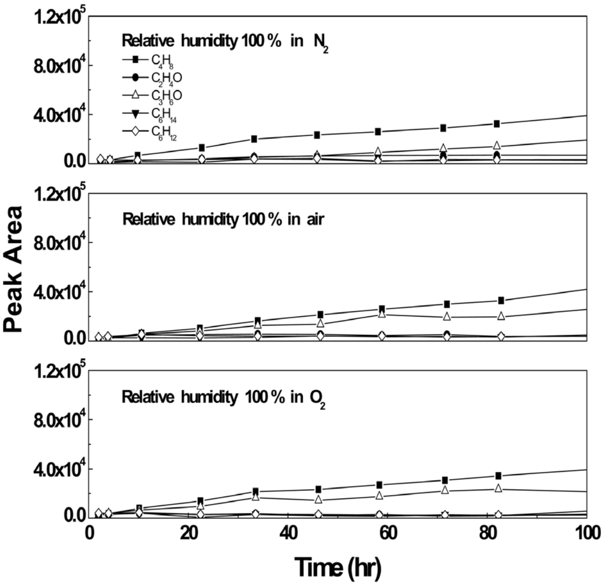

Fig. 6. Time profiles of the by-products in the benzene photocatalytic oxidation. $[C_6H_6]_0$ = 9400 ppmv, relative humidity 100%, 10 W/m^2 UV lamp.

The by-products identified in their studies had lower vapor pressure compared to the gaseous by-products identified in previous studies.[14)] Due to their low vapor pressure, the by-products could not release into gas phase at room temperature, and they were absorbed on the catalytic surface instead. On the other hand, the by-products with high vapor pressure volatilized into gaseous state as soon as they were generated. Consequently, the question of hazardousness was of little significance because the by-products on the surface of TiO_2 had low vapor pressure; thus, they were not emitted in the air. As mentioned earlier, the generated by-products that change into gaseous state due to higher vapor pressures are emitted in the air; thus, they do not participate in photocatalytic reactions. As such, if these substances were more toxic than the target matter (benzene), they would adversely affect humans; hence the need to determine the degree of toxicity and hazardousness of the benzene gaseous by-products found in this study.

Table 1 shows the permissible exposure limits of the hazardous chemicals in the air as set by the Occupational Safety and Health Administration (OSHA) in the United States. The time-weighted average limit (TWA) of gaseous by-products such as acetaldehyde (200 ppm), acetone (1000 ppm), pentane (1000 ppm), cyclohexane (300 ppm), and hexane (500 ppm) is higher compared to benzene (1 ppm, STEL: 5 ppm).

The other identified by-products, e.g., 2-methylpropene, methylcyclobutane, methylcyclopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane do not fall under this standard. This indicates that the gaseous by-products from the photocatalytic reaction of benzene were less toxic and hazardous than benzene.[15)]

4. Conclusion

The study identified 11 gaseous by-products of benzene. Compared to the by-products identified on the catalytic surface, these gaseous by-products had higher vapor pressure at room temperature; thus, they were easily detected in gaseous state. Except for acetaldehyde and acetone, saturated hydrocarbons of less than C6 were generated through the direct hydrogenation reaction of benzene instead of oxidation. They also continuously accumulated in the reactor. The amount of the generated gaseous by-products depended on the concentration of moisture and oxygen in the reactor. As moisture increased, the generation of gaseous by-products generally decreased. On the other hand, the amount of acetone in the reactor filled with oxygen was high.

The by-products identified from the TiO_2 photocatalytic oxidation of benzene were lower permissible exposure limits than benzene.

Table 1. Permissible exposure limits for the by-products in the TiO_2 photocatalytic oxidation of benzene

By product	PELs(ppm)	By product	PELs(ppm)
	U.S.A OSHA		U.S.A OSHA
Acetaldehyde	200 (TWA)	Acetone	1000 (TWA)
2-methylpropene	-	Methylcyclobutane	-
Pentane	1000 (TWA)	Methylcyclopentane	-
Cyclohexane	300 (TWA)	2-methylpentane	-
3-methylpentane	-	2,3-dimethylbutane	-
Hexane	500 (TWA)	Benzene	1 (TWA) 5 (STEL)

PELs : Permissible exposure limits.
TWA : (an 8-hour) time-weighted average limit.
STEL : (15 minutes) short-term exposure limit.

References

1. USEPA, Total Exposure Assessment Methodology (TEAM) study, Report 600/6-87/002a (1987).
2. Sillman, S., "The Relation between Ozone, NOx and Hydrocarbons in urban and polluted rural environments," *Atmos. Environ.*, **33**, 1821-1845 (1999).
3. Placet, M., Mann, C. O., Gilbert, R. O., and Niefer, M. J., "Emissions of Ozone precursors from stationary sources: a critical review," *Atmos. Environ.*, **34**, 2183-2204 (2000).
4. Jacoby, W. A., Blake, D. M., Fennell, J. A., Boulter, J. E., Vargo, L. M., George, M., C., and Dolberg, S. K., "Heterogeneous photocatalysis for control of volatile organic compounds in indoor air," *Air & Waste Manage. Assoc.*, **46**, 891-898 (1996).
5. Hoffmann, M. R., Martin, S. T., Choi, W., and Bahnemann, D. W., "Environmental applications of semiconductor photocatalysis," *Chem. Rev.*, **95**, 69-96 (1995).
6. Sitkiewitz, S., and Heller, A., "Photocatalytic oxidation of benzene and satiric acid on sol-gel derived TiO_2 thin films attached to glass," *New J. Chem.*, **20**, 233-241 (1996).
7. Obee, T. N., and Brown, R. T., "TiO_2 Photocatalysis for indoor air applications: Effects of humidity and trace contaminant levels on the oxidation rates of formaldehyde, toluene, and 1,3-butadiene," *Environ. Sci. Technol.*, **29**, 1223-1231 (1995).

8. Luo, Y., and Ollis, D. F., "Heterogeneous photocatalytic oxidation of trichloroethylene and toluene mixtures in air: kinetic promotion and inhibition, time-dependent catalyst activity," *J., Catal.*, **163**, 1-11 (1996).
9. Sauer, M. L., and Ollis, D. F., "Photocatalyzed oxidation of ethanol and acetaldehyde in humidified air," *J., Catal.*, **158**, 570-582 (1996).
10. Yoon, J. K., Kang, J. W., Lee, T. K., Jeon, M. S., and Joo, H. K., "Photocatalytic degradation of trichloroethylene in gas phase using TiO_2/UV," *J. of Korea Society of Environmental Engineers*, **21**(5), 1003-1011(1999).
11. Vorontsov, A. V., Savinov, E. N., Barannik, G. B., Troitsky, V. N., and Parmon, V. N., "Quantitative studies on the heterogeneous gas-phase photooxidation of CO and simple VOCs by air over TiO_2," *Catal. Today*, **39**, 207-218 (1997).
12. Turchi, C. S., and Ollis, D. F., "Mixed reactant photocatalysis : Intermediates and mutual rate inhibition," *J., Catal.*, **119**, 483-496 (1989).
13. 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., Photochem. Photobiol. A*, **118**, 197-204 (1998).
14. Budavari, S., O'Neil, M., J., Smith, A., and Heckelman, P. E., The Merck Index, Merck & Co., Inc., Rahway (1989).
15. Mackinson, F. W., Occupational Health Guidelines for Chemical Hazards-DHHS (NIOSH) Publication, 1981, 1988, 1992, 1995, R. Scott Stricoff, Lawrence J. Partridge, Jr., and A. D. Little. Inc. (1995).