

DESTRUCTION OF VOC USING PHOTOCATALYST UNDER UV-LIGHT IRRADIATION -THE INFLUENCE OF UV WAVELENGTH ON MINERALIZATION-

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ABSTRACT

A variety of gaseous pollutants in indoor air now are becoming an object to control. Thus, we studied a removal technique using TiO₂ photocatalyst under 365 nm or 254 nm UV-light irradiation for toluene, benzene, formaldehyde and acetaldehyde as examples of hazardous volatile organic compounds (VOCs), in order to get detailed analytical data for products derived from these contaminants. Although these compounds were effectively destructed, not only CO₂ but also high concentration of toxic compounds, such as aldehydes were formed in the case of under 365 nm UV-light irradiation. However, TiO₂ photocatalysis under 254 nm UV-light irradiation made possible to achieve high removal ratio of VOCs. In addition, a high conversion ratio to CO₂ was obtained. The purification technique using TiO₂ photocatalyst under 254 nm UV-light irradiation is more effective than that under 365 nm UV-light irradiation.

INTRODUCTION

Various particulate and gaseous contaminants exist universally in outdoor and indoor air. Especially, it is well-known that sick building syndrome (SBS) can be caused by VOCs [1]. In order to remove a variety of gaseous contaminants in indoor air, various removing techniques such as filtration and/or adsorption using chemical filters and adsorbents are widely utilized in several industrial fields. However, their techniques are pointed out several faults, such as their large pressure drag, short-lives and outgas from adsorbent, because their techniques use adsorption methods. Thus, we recently proposed removing techniques using chemical reaction [2-4] to solve these problems. They were purification methods using photochemical [2] and photocatalytic reactions [3,4] under UV-light irradiation. Although a large number of studies have been made on photocatalytic destruction of VOC, detailed-analysis of by-products have not been reported in spite of their toxicity. Thus, we investigated the removal ratio of VOC (toluene, benzene, formaldehyde and acetaldehyde) using photocatalytic reaction under UV-light irradiation and analyzes of products generated in there.

EXPERIMENTAL METHOD

The experimental apparatus for photocatalytic reactions is shown in Figure 1. The cylindrical flow reactor consists of a PYREX glass cylinder (170 mm diameter, 500 mm length and *ca.* 10 L inner volume) and two TEFLON plates at the end of the cylinder. Two types of UV-

lamps (6 W, 5 tubes of main wavelength 254 nm or 5 tubes of main wavelength 365 nm) for photocatalytic reaction are placed in the reactor. Sub-ppm level of VOCs, toluene, benzene, formaldehyde, and acetaldehyde were generated from the corresponding compressed gas cylinders as representative VOC of hazardous air pollutants. In order to prepare humid air, synthetic air from a compressed gas cylinder passes through a water bubbler. In these experiments, the flow rate of the experimental gas was 3.0 L/min and the residence time in the reactor was *ca.* 3 min. Titanium dioxide (Degussa Titania P25 purchased from Nippon Earogiru Co., Ltd.) was used as a photocatalyst. About 0.06 g of catalyst powder was coated onto twelve glass rods and they were dried during overnight at 150 °C under air. UV-lamps and TiO₂-coated glass rods were fixed in the outlet-side chamber of the reactor. The photocatalytic reactions for the above VOCs were accomplished with TiO₂ under black light (365 nm) or sterilization lamps (254 nm) irradiation at the following experimental conditions; *ca.* 40 % of relative humidity (R.H.), five UV-lamps, and *ca.* 600 ppb of VOC concentration at the inlet of the reactor.

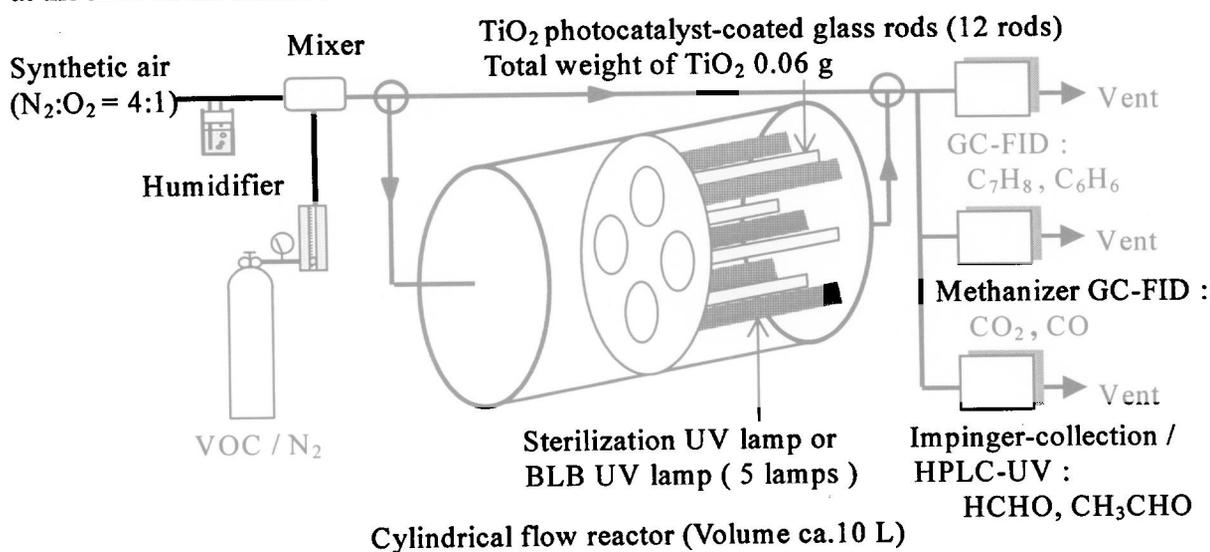


Figure 1. Schematic diagram of the experimental apparatus for destruction of VOC under UV-light irradiation.

Toluene and benzene concentration were monitored by GC-FID (GC-14A, Shimadzu Co., Ltd.). The concentration of produced CO₂ and CO were measured by GC-FID (GC-15A, Shimadzu Co., Ltd.) equipped with methanizer. Formaldehyde and acetaldehyde were collected into a solution of 2,4-dinitrophenylhydrazine (DNPH) using two tandem impingers and their concentration were measured by HPLC-UV (LC-9A, Shimadzu Co., Ltd.).

RESULTS AND DISCUSSION

Photocatalytic reaction under 365 nm UV-light irradiation

Figure 2 shows removal ratio of photocatalytic destruction of toluene and benzene under 365 nm UV-light irradiation. The UV-light irradiation was started at the time of 0 min, then UV-light was turned off after 120 min of irradiation. The above operations were repeated. As shown in Figure 2, about 80 % and 40 % destruction of toluene and benzene were accomplished, respectively. In the dark condition, no destruction of toluene and benzene were observed. In the next irradiation, about 80 % and 40 % destruction of toluene and benzene were maintained successively. From the calculation of carbon balance and the product

analysis for photocatalytic destructions of toluene and benzene, we obtained the results as shown in Figure 3. By-products except CO₂ (64 %) in destruction of toluene were formaldehyde, acetaldehyde and carbon monoxide (CO). Formaldehyde and CO were identified with 66 % CO₂ in the destruction of benzene. The production ratio of CO₂ by destruction of toluene and benzene were both about 65 %. Acetaldehyde was not detected in destructed products of benzene. Furthermore, a very small quantity of the unknown by-product was detected from HPLC-UV in the destruction of toluene and benzene.

Figure 4 shows removal ratio of formaldehyde and acetaldehyde with photocatalytic reaction under 365 nm UV-light irradiation. About 75 % and 80 % of formaldehyde and acetaldehyde were destroyed, respectively. We calculated carbon balance using these results.

Figure 5 shows carbon balances estimated using ratio of various products to formaldehyde and acetaldehyde removed with

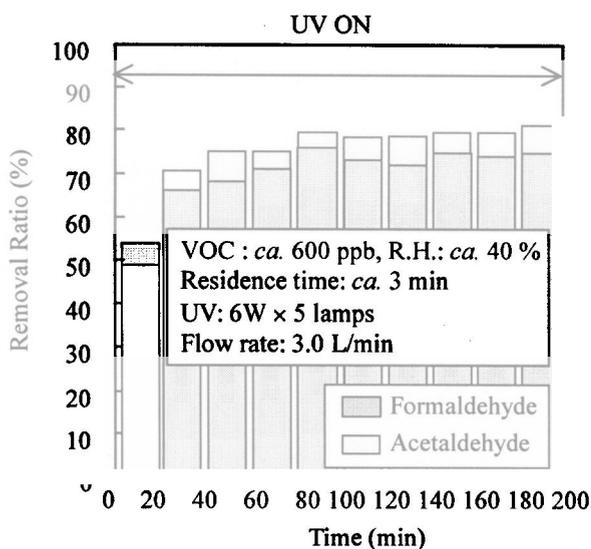


Figure 4. Removal ratio of formaldehyde and acetaldehyde with photocatalytic reaction under 365 nm UV-light irradiation.

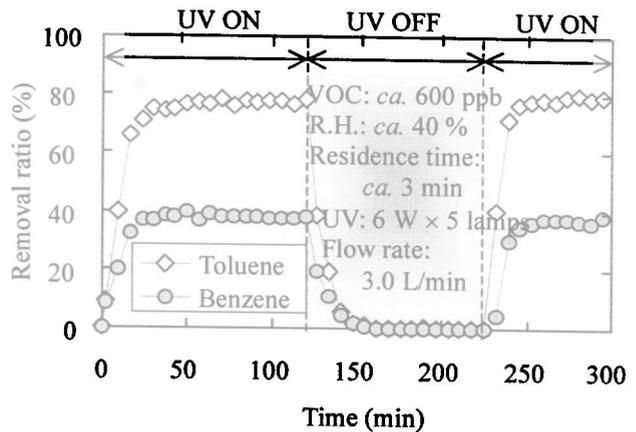


Figure 2. Removal ratio of toluene and benzene with photocatalytic reaction under 365 nm UV-light irradiation.

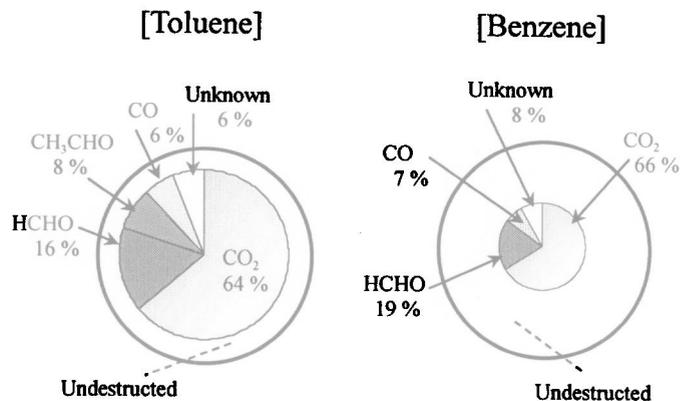


Figure 3. Ratio of various products to toluene and benzene removed with photocatalytic reaction under 365 nm UV-light irradiation.

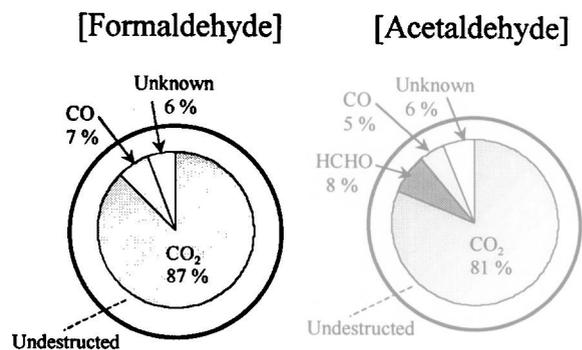


Figure 5. Ratio of various products to formaldehyde and acetaldehyde removed with photocatalytic reaction under 365 nm UV-light irradiation.

photocatalytic reaction. The amount of CO₂ generated by destruction of formaldehyde and acetaldehyde reached to about 90 % and 80 %, respectively. As shown in Figure 5, another by-product from formaldehyde was CO. Formaldehyde and CO were identified as decomposition products of acetaldehyde as well as major product CO₂, and a very small quantity of the unknown by-product was detected from HPLC-UV in the destruction of formaldehyde and acetaldehyde.

Photocatalytic reaction under 254 nm UV-light irradiation

Figure 6 shows removal ratio of toluene (*ca.* 90 %) and benzene (*ca.* 80 %) with photocatalytic reaction under 254 nm UV-light irradiation. These results were used to calculate carbon balance. The ratio of produced CO₂ relative to destructed toluene and benzene were about 88 % and 85 %, respectively. As shown in Figure 7, by-products from toluene by photocatalytic destruction were formaldehyde, acetaldehyde and CO. It was similar to the results of

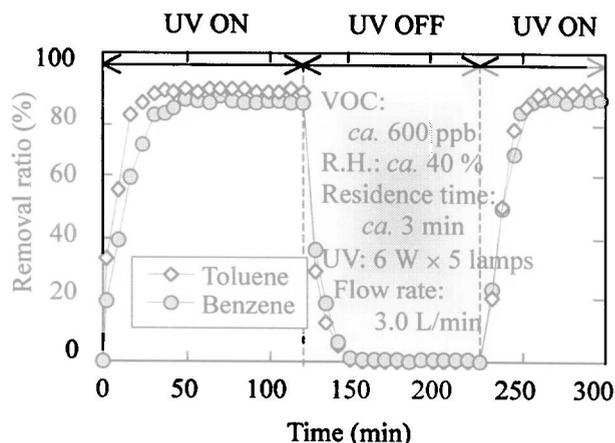


Figure 6. Removal ratio of toluene and benzene with photocatalytic reaction under 254 nm UV-light irradiation.

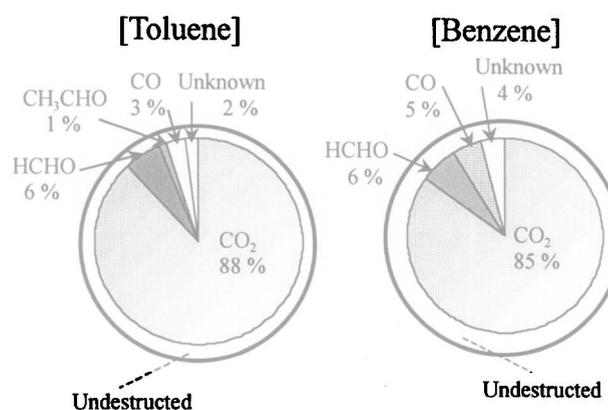


Figure 7. Ratio of various products to toluene and benzene removed with photocatalytic reaction under 254 nm UV-light irradiation.

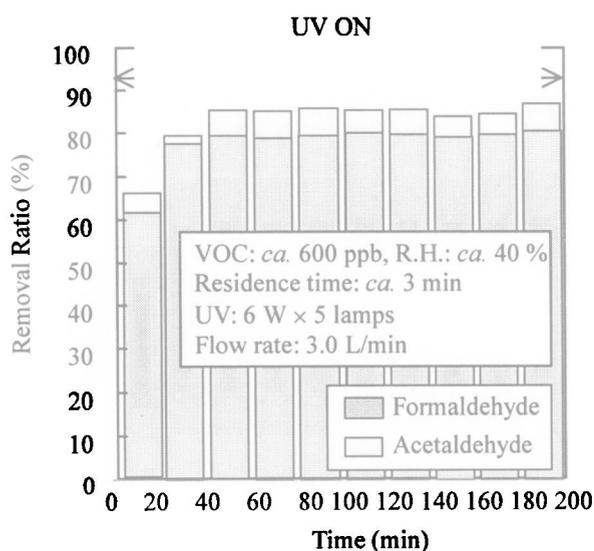


Figure 8. Removal ratio of formaldehyde and acetaldehyde with photocatalytic reaction under 254 nm UV-light irradiation.

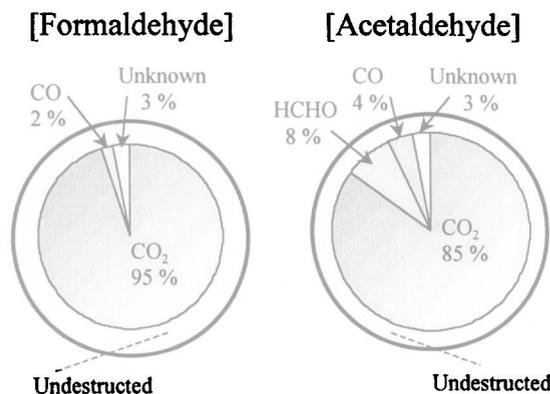


Figure 9. Ratio of various products to formaldehyde and acetaldehyde removed with photocatalytic reaction under 254 nm UV-light irradiation.

photocatalytic destruction under 365 nm UV-light irradiation. These results with photocatalytic destruction of toluene and benzene under 254 nm UV-light irradiation indicated that it is possible to achieve a higher VOC removal ratio than at 365 nm. Furthermore, higher conversion ratio to CO₂ of destructed VOC was obtained under 254 nm UV-light irradiation than at 365 nm UV-light irradiation. In addition, a very small quantity of the unknown by-product was detected from HPLC-UV in the destruction of toluene and benzene. Figure 8 shows removal ratio of formaldehyde and acetaldehyde with photocatalytic destruction under 254 nm UV-light irradiation. About 80 % and 85 % destruction of formaldehyde and acetaldehyde were accomplished under the irradiation, respectively. The conversion ratios to CO₂ of destructed formaldehyde and acetaldehyde were about 95 % and 80 %, respectively. Figure 9 shows carbon balances for formaldehyde and acetaldehyde. The components of these decomposition products were similar to the results of their photocatalytic destruction under 365 nm UV-light irradiation.

Comparison of VOC destruction in photocatalytic reaction using 365 nm UV or 254 nm UV-light irradiation

The difference between 365 nm and 254 nm UV-light irradiation in removal efficiencies of toluene, formaldehyde was not large. However, generally speaking, removal and mineralization efficiencies in photochemical destructions of toluene, formaldehyde and acetaldehyde using shorter-wavelength UV-light were to a small extent higher than that using longer-wavelength UV-light. On the other hand, in the case of photochemical destruction of benzene, photochemical destruction using 254 nm UV-light irradiation gave much higher removal and mineralization efficiencies than that using 365 nm UV-light irradiation. The reason for the results is not clear. It may be that adsorption and photochemical reaction pathways using 254 nm UV-light irradiation are different from the case using 365 nm UV-light irradiation.

Reaction pathway

The reaction pathway based on our photocatalytic destruction of VOC experiments and on previous studies of many researchers [5-9] is shown in Fig. 10. At first, when the TiO₂ semiconductor is irradiated with UV light of wavelength shorter than 400 nm, highly mobile electron-hole pairs can be created (Eq. (a)), and the positive holes react with H₂O contained in the experimental gases (Eq. (b)). Secondary, toluene and benzene react with OH radicals, and aldehydes are formed (Eqs. (c)-(e)). Leone and Seinfeld [5] have proposed that mechanism for the atmospheric photooxidation pathway of toluene producing carbon dioxide, acetaldehyde, and formaldehyde. Bandow et al [6] also have reported that photooxidation of toluene and benzene gave formaldehyde in the NO_x-air system. Recently, Lichtin and Sadeghi [7] reported that carbon dioxide was found in vapor over TiO₂ in photocatalytic oxidation of benzene. Nimlos et al. [8] reported that products from the photocatalytic oxidation of acetaldehyde were carbon dioxide, formaldehyde and acetic acid, the primary product from formaldehyde was carbon dioxide, though at higher concentrations they identified formic acid, and the

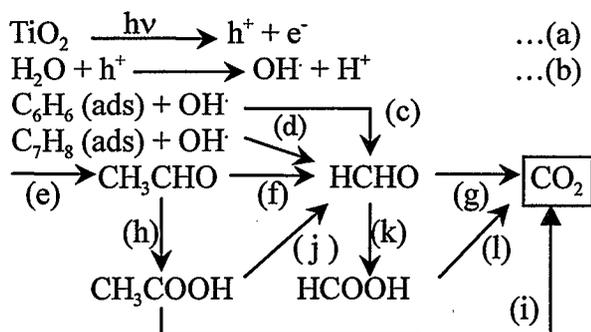


Figure 10. Reaction pathway of the photocatalytic degradation of toluene and benzene.

products from acetic acid were carbon dioxide and formaldehyde in the gas-phase using TiO₂ (Eqs. (f)-(k)). Muggli et al. [9] proposed a formation mechanism for carbon dioxide in the photocatalytic oxidation of formic acid (Eq. (l)). In this pathway, we suggest that toluene and benzene are converted to CO₂ via aldehydes by photocatalytic destructions.

CONCLUSION

(1) In this experimental condition, removal efficiencies of VOCs (toluene, benzene, formaldehyde, and acetaldehyde) using TiO₂ photocatalyst under 365 nm UV-light irradiation were ca. 80 %, ca. 40 %, ca. 75 % and ca. 80 %, respectively. While, removal efficiencies over 80 % for each of VOCs were observed under 254 nm UV-light irradiation.

(2) Conversion ratios to CO₂ (mineralization efficiencies) to initial concentration of VOCs using TiO₂ photocatalyst under 254 nm UV-light irradiation were much higher than that under 365 nm UV-light irradiation.

(3) As these results, it was suggested that the purification technique using TiO₂ photocatalyst under 254 nm UV-light irradiation was more effective than that under 365 nm UV-light irradiation.

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