REMOVAL OF VOC BY PHOTOCATALYTIC DEGRADATION INVOLVING PHOTOCHEMICAL REACTION WITH O₃ UNDER SHORT-WAVELENGTH UV IRRADIATION

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ABSTRACT

Photocatalytic degradation of volatile organic compounds (VOC) with short-wavelength UV light (254 nm) is an attractive technique in the view of perfect mineralization to CO₂. In this study, shorter wavelength of UV light involving 185 nm which generates O₃ was used as a light source, and as a photocatalyst, titanium dioxide (TiO₂) and its mixture with ozone decomposition catalyst (ODC) was tested to improve photocatalytic activity. Their validity was evaluated from the removal ratio of toluene by photocatalysis and the size distribution of generated particles by gas-to-particle conversion. Using short-wavelength UV-light with 185 nm and O₃, both photocatalytic degradation and photochemical reaction (gas-to-particle conversion) via labile species (i.e. O₃, O⁺, OH⁻ etc.) caused simultaneously VOC destruction.

INTRODUCTION

Gaseous contamination of volatile organic compounds (VOC) in indoor spaces [1] now is well-known to be a troublesome problem from the leading industries to general living environments because of its damage to wafer surface and health effects on humans. The latter is the so-called sick building syndrome (SBS) [2] which has received with considerable attention. Trace gaseous contamination in indoor air is caused by outdoor air and outgases from working people, equipments and building materials. Though photocatalytic oxidation is very effective in destruction of the VOC, it is still difficult to completely remove it without formation of by-products, such as aldehydes. Especially, formaldehyde could bring about chronic damage for respiratory organs of the human body at levels of several ten ppb [3]. Therefore, various approach to the progress in photocatalytic activity has been carried out, for instance, addition of metal oxides [4,5], adsorbents [6,7] or positive ions [8] to titania photocatalyst (TiO₂). While, it was reported that photocatalytic degradation efficiency of VOC and perfect mineralization ratio to CO₂ were increased by short wavelength of 254 nm UV-light as a light source in comparison with 365 nm UV-light [9].

In this study, fundamental investigations of the destruction of toluene as a representative of VOC by photocatalytic and photochemical reaction with different wavelength of UV light, above 254 nm UV-irradiation and shorter 185 nm UV-irradiation which generate O₃, were achieved at several conditions using an annular denuder type cylindrical flow reactor [10]. Furthermore, in order to enhance photocatalytic performance, TiO₂ was mixed with ODC which functions as an adsorbent and destroys partly VOC by the reaction with labile species formed from O₃ even at dark condition [11].

METHODS

As shown in Figure 1, the experimental apparatus used in this investigation consists of three
blocks, a preparation unit for experimental gases, an evaluation unit for the validity of photocatalyst and photochemical reactivity, and a measurement unit for particles and gases. Characteristic values for two types of UV-lamps (Sankyo Denki, Co., Ltd.) used in this investigation, lamp A and lamp B, are indicated in Table 1. The annular denuder type cylindrical flow reactor [10] is illustrated in Figure 2 in detail. It consists of Pyrex glass sheath cylinder, five short inner cylinders to coat photocatalyst, and UV-lamp settled in the middle of the inner cylinders. The reactor volume was ca. 0.55 L. Supplied experimental gas was flowed through the inner cylinders coated with different types of catalysts, ODC, ODC + TiO₂ (1:1 w/w) or TiO₂ on inside wall in the central three cylinders. ODC and TiO₂ (P25) were purchased from Nippon Syokubai Kagaku Kougyo, Co., Ltd. and Nippon Earosiru Co., Ltd., respectively. The cylinders coated each of them were prepared with wash-coat dip method by dipping the cylinders into their suspension (1.5 g in 100 mL of pure water), and then dried for a day at 150 °C. The each amount of ODC, ODC + TiO₂ and TiO₂ deposited onto the inner cylinders was 84.9 mg, 60.3 mg and 16.1 mg, respectively.

Typical VOC gas in atmosphere, toluene was chosen as an experimental gas to evaluate the validity of photocatalyst and photochemical reactivity under short-wavelength UV irradiation, the former was investigated by removal ratio of toluene and the latter was characterized by tendencies of particle formation based on the size distributions measured with scanning electrical mobility spectrometer (SEMS, SMPS-Model-3934, TSI Co., Ltd.). High
concentration of O₃ generated by 185 nm UV-irradiation was diluted and measured at the outlet of the reactor with UV detector (UV-D) O₃ analyzer (Model-UVAD-1000, Shimadzu Co., Ltd.). O₃ generation was not recognized under 254 nm UV-irradiation. Therefore, in the reactor, O₃ is only formed by 185 nm UV-irradiation. Toluene concentration was monitored at inlet and outlet of the reactor by a gas chromatograph with a flame ionization detector (FID) (GC-15A, Shimadzu Co., Ltd.). When the sampling gas contained O₃, it was selectively removed with KI (potassium iodide)-coated annular denuder [12] to protect GC-column. All experiments were carried out in room temperature controlled at 25 ± 2 °C, and the removal ratio of toluene, R, is defined by the Equation (1).

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R (%) = 100 \left( \frac{C_{in} - \alpha C_{out}}{C_{in}} \right) \quad \cdots (1)
\]

where:
- \(C_{in}\): Initial concentration of toluene supplied to the reactor (ppb)
- \(C_{out}\): Concentration of residual toluene monitored at outlet of the reactor (ppb)
- \(\alpha\): Correction coefficient of \(C_{out}\) reduced by adsorption onto denuder surface (-)

RESULTS AND DISCUSSION

Interaction between O₃ and three types of catalysts

In order to investigate the removal efficiency of O₃, It was supplied to the reactor at the concentration of sub-ppm to ppm level. The results of O₃ destruction by interaction with ODC, ODC+TiO₂, or TiO₂ catalyst under UV irradiation of 254 nm (lamp A) are shown in Figure 3. At dark condition, O₃ was not removed unless the catalyst include ODC. However, when 254 nm UV-light was irradiated, more than 90% of O₃ was destroyed when using the all types of catalysts. From these results, at UV irradiated condition, O₃ destruction was promoted at not only ODC but also at the TiO₂ surface. While, in other experiments of O₃ generation, lamp B (254+185 nm) was used as a light source, and its UV light was irradiated to purified air. Their results are shown in Figure 4. When the catalysts was placed in the reactor, only half or less of O₃ formed in comparison with the no catalyst condition, about 40 ppm at 1.0 L/min. In this experiment, interaction between O₃ and the catalysts was also recognized.

![Figure 3. Removal efficiencies of O₃ by catalysts with or without UV irradiation.](image-url)
Through the experiments in toluene destruction using the cylindrical flow reactor, the effects of ODC, TiO$_2$, O$_3$, H$_2$O and 185 nm UV irradiation were investigated. In case of O$_3$ addition, about 40 ppm of O$_3$ formed by UV irradiation with lamp B (cf. in Figure 4) was supplied to the reactor. Their results are shown in Figure 5. Toluene is mainly decomposed via photochemical reaction with OH radicals, therefore not only photocatalytic surface reaction but also homogeneous photochemical reaction under UV irradiation was discussed here. Formation processes of OH radicals on the photocatalyst surface [13,14] and by photochemical reaction [15] were shown in Scheme 1 and 2, respectively.

As shown in Figure 5, under the UV irradiation with lamp A, photocatalytic activity was normally observed with the catalysts including TiO$_2$. This destruction mechanism is concerned with OH radicals formed in the following Equations (2) ~ (8) (Scheme 1). While, when O$_3$ was added to the reactor, the catalysts including ODC indicated high removal efficiency of toluene even at dark condition. From this result, it was thought that the labile species were formed from O$_3$ at ODC surface by similar reaction of the Equation (iv) (Scheme 2), and then OH radicals were formed through the Equation (v) to destroy toluene effectively. Furthermore, by coexisting O$_3$ with short-wavelength UV irradiation (O$_3$ + lamp A and lamp B in Figure 5), 254 nm and 185 nm UV-light promotes the Equations (iv),

**Scheme 1. Formation process of OH radicals on the photocatalyst (TiO$_2$) surface.**

- TiO$_2$ + hv ($\lambda < 400$ nm) $\rightarrow$ \textit{e} (electron) + \textit{p} (positive hole) \\
- \textit{e} + O$_2$ $\rightarrow$ ·O$_2$ $\cdot$ \\
- O$_2$ + H$^+$ $\rightarrow$ H$^+ +$ OH$^-$ $\cdot$ \\
- 2H$_2$O $\rightarrow$ O$_2$ + H$_2$O$_2$ \\
- H$_2$O$_2$ + ·O$_2$ $\rightarrow$ OH + HO$_2$ $\cdot$ \\
- \textit{p} + 2H$_2$O $\rightarrow$ OH + H$_2$O$^*$ $\cdot$ \\
- \textit{p} + OH$^-$ $\rightarrow$ OH $\cdot$

**Scheme 2. Formation process of OH radicals by photochemical reaction.**

- H$_2$O + hv ($\lambda < 242$ nm) $\rightarrow$ H + ·OH
- O$_3$ + hv ($\lambda < 243$ nm) $\rightarrow$ O + O
- O + O$_2$ + M $\rightarrow$ O$_3$ + M (M = O$_2$ or N$_2$) \\
- O$_3$ + hv ($\lambda < 320$ nm) $\rightarrow$ O$_2$ + O($^1$D) \\
- H$_2$O + O($^1$D) $\rightarrow$ 2·OH
(v) and (i) ~ (v), respectively. Especially, at wet condition (H₂O + lamp B), the highest removal efficiency of all experiments was obtained. This result was caused by remarkable photochemical reaction via OH radicals formed by the Equation (i), rather than photocatalytic reaction. Because, close removal efficiency to the value with TiO₂ was obtained at no catalyst condition as shown in Figure 5. In order to investigate the photocatalytic surface reaction in addition of H₂O with the catalyst including ODC, other experiment on toluene destruction was done by changing relative humidity (R.H.) under 254 nm (lamp A) UV-irradiation. This result is shown in Figure 6. Using the catalyst including ODC, photocatalytic surface reaction was strongly disturbed by H₂O because of its adsorptive property.

In these circumstances, photocatalytic activity could be improved by mixing ODC with TiO₂ photocatalyst under O₃ existing condition. While, in the case of H₂O addition, photochemical reactivity was improved. However, it acted disadvantageously for photocatalysis on surface. On the basis of these results, we are now looking for the optimal combination of these techniques while considering the conversion ratio of toluene to CO₂.

**Size distribution of fine particles formed by photochemical reaction**

In order to evaluate the photochemical reactivity, size distributions of fine particles generated by UV irradiation and reaction with O₃ were measured at dry (R.H.: < 10 %) and wet conditions (R.H.: 40 %) with SEMS under the various conditions corresponding in Figure 5. As particle generation was not detected under 254 nm UV-irradiation (lamp A), toluene destruction was mainly performed on catalyst surface. When O₃ was added to the reactor, particle formation by gas phase reaction was recognized, and their measured size distributions were almost the same because of equal gas phase reactivity. Therefore, it was thought that the difference in removal ratio of toluene by O₃ addition was due to the reaction with labile species from O₃ on the ODC surface. The size distributions of fine particles generated by UV (lamp B) irradiation are shown in Figure 7. The particle formation was promoted at wet condition by the supply of OH radicals through the Equation (i) (Scheme 2). Therefore, as mentioned above, not only photocatalytic degradation but also photochemical reaction (gas-to-particle conversion) could be effectively acted on toluene destruction by adding H₂O under 185 nm UV-irradiation. The utilization of photocatalyst under short-wavelength UV light could be expected as a new air cleaning technique.
CONCLUSIONS

Toluene removal of photocatalysis and size distribution of generated particles by gas-to-particle conversion under UV irradiation were investigated to evaluate the validity of short-wavelength of UV light, O₃ and ODC mixed with TiO₂. When O₃ was added to the experimental gas directly under the coexisting with ODC, high removal ratio of toluene was obtained with or without UV irradiation because of labile species formed from O₃ on the ODC surface. While, removal ratio of toluene by photocatalysis under 185 nm UV-irradiation was higher than that of 254 nm UV-irradiation, especially in wet condition. Because, both photocatalytic degradation and photochemical reaction associated with gas-to-particle conversion via labile species caused simultaneously VOC destruction. Although there is currently concern about health effects of fine particles and O₃ generated by 185 nm UV-irradiation, they could be easily removed in combination with other removal methods. Therefore, it was thought that utilization of labile species formed from HZO or OS by short-wavelength UV irradiation and ODC was very effective for VOC destruction and could be a new air cleaning technique. In order to evaluate this techniques comprehensively, more research on conversion ratio of toluene to CO₂ is now in progress.

REFERENCES