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Removal of Air Pollutants by Photocatalysis with Ozone in a Continuous-Flow Reactor

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Abstract

Photocatalysis was combined with O_3 (O_3-PCO) for better destruction performance of formaldehyde and toluene. It is of significance to study the stability of O_3-PCO process since it is essential to the application of O_3-PCO technology. The present work investigated the mechanism of enhanced performance and improved stability in the O_3-PCO process under different operating conditions (e.g., humidity and initial O_3 concentration). Results indicated that O_3 improved remarkably the removal efficiency of formaldehyde and toluene with increased photocatalyst durability. The O_3-PCO process exhibited excellent stability during the variation of humidity and initial O_3 concentration. O_3-PCO process has enhanced performance because it comprises more sub-processes (e.g., UV/O_3 and O_3/TiO_2) for destroying pollutants than the PCO process alone does.

Key words: ozone; photocatalysis; air pollution; toluene destruction; stability

Introduction

Indoor air pollution causes great harm to both the environment and human health. It may be responsible for up to 2.4 million premature deaths a year (UNEP, 2006). People spend 80%–90% of their time in the indoor environment. Thus, indoor environment quality may impose important effects on human health and work efficiency. Indoor air pollution is serious in public places such as hospitals, supermarkets, waiting halls, and underground parking. Conventional purification methods for air pollution, such as chemical oxidation and adsorption, have been applied to reduce the pollution. These methods, however, have different kinds of drawbacks (Qi *et al*., 2007). For example, liquid absorption and activated carbon adsorption have secondary pollution, while incineration and catalytic oxidation is expensive and consumes more energy.

Photocatalytic oxidation (PCO), one of the most promising ways to eliminate indoor air pollutants, has been widely studied in the past few decades (Alberici and Jardim, 1997; Zuo *et al*., 2006; Puma *et al*., 2009; Vincent *et al*., 2009). However, its application is greatly limited by low efficiency (Ao *et al*., 2004; Huang *et al*., 2009), electron–hole recombination (Rideh *et al*., 1997; Peng *et al*., 2004), and photocatalyst deactivation (Cao *et al*., 2000; Belver *et al*., 2003; Huang *et al*., 2009). In addition, the PCO performance is greatly affected by the operating parameters such as humidity (Puma *et al*., 2009; Sleiman *et al*., 2009). Many efforts have been made to improve its performance (Belver *et al*., 2003; Luo *et al*., 2006). The combination of O_3 with PCO (O_3-PCO) has been proven to be an efficient way to enhance the PCO performance (Yu and Lee, 2007; Huang *et al*., 2009). However, the previous study mainly focused on the improvement of efficiency and paid little attention to the stability and durability in the O_3-PCO process. Apart from efficiency, the stability is also essential to the application of O_3-PCO technology. Therefore, it is of practical significance to study the stability of O_3-PCO process.

The reactor configuration has much influence on the PCO performance and industrial application. The commonly used PCO reactors are annular or packed-bed reactors (Bouzaza *et al*., 2006; Kuo *et al*., 2009; Vincent *et al*., 2009). Photocatalysts used are generally unsupported powder or supported on the wall of reactors. These reactors have disadvantages such as low convective mass transfer and reaction rate (Mo *et al*., 2009a), and difficulty in photocatalyst coating and reactor making.

Toluene and formaldehyde are chosen as the target pollutants because they are the major indoor air contaminants and widely exist in modern building materials and household products (Ichiura *et al*., 2003). The present work studied the enhanced destruction of toluene and formaldehyde by the O_3-PCO process in a continuous-flow reactor. The stability during the variation of humidity and initial O_3 concentration was investigated. The mechanism on enhanced stability was also studied. The present study is helpful for better understanding and application of the O_3-PCO technology.

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Experimental Methods

Experimental setup

The experimental setup and PCO reactor are shown in Fig. 1. A continuous-flow reactor with TiO_2 catalyst supported on porous nickel foam was used (Fig. 1). It is a cubic container made of acryl glass with size of 30×15×10 cm (length× width×height). The photocatalyst mesh was fixed in the center of the reactor. UV irradiation was provided by two low-pressure mercury UV lamps (254 nm; Philips) with maximum output of ~4 W. This reactor has advantages such as high reaction area and mass transfer rate (Mo *et al.*, 2009a), and low pressure drop, and is capable of commercial application.

Toluene and formaldehyde in the effluent was analyzed online by a gas chromatograph (GC) equipped with a flame ionization detector (FID) (Shimadzu; GC-2010). The capillary column was a fused-silica column (30 m×0.53 mm i.d.) coated with a 0.25 μm film of the chemically bonded phase RTX-5. O_3 was analyzed by iodimetry method (CJ/T3028.2-94). The humidity ratio and airflow rate were 1% and 2 L/min, respectively. The initial toluene and O_3 concentration was 45 and 370 ppm in the toluene destruction process, and the initial formaldehyde and O_3 concentration was 20 and 180 ppm in the formaldehyde destruction process, respectively.

Removal efficiency of toluene (TRE) and formaldehyde was defined as follow:

$$\text{Conversion } (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%, \quad (1)$$

where C_{in} and C_{out} represent the concentration of toluene or formaldehyde at the inlet and outlet of reactor, respectively.

Catalyst preparation

Nano-TiO_2 (P-25; Degussa) was dispersedly immobilized on the γ-Al_2O_3/nickel foam by impregnation method. Briefly, the 10×10×0.2 cm (length×width×thickness) commercial nickel foam support (110 PPI, 320 g/m^2; LiYuan Ltd.) was impregnated in the sol solution of $Al_2O_3 \cdot nH_2O$, dried at 373 K for 2 h, and calcined at 850 K for 4 h to get the γ-Al_2O_3/nickel foam support. TiO_2 was put into distilled water and dispersed fully in an ultrasonic cleaner bath to get 8% wt. TiO_2 slurry. The γ-Al_2O_3/nickel foam support was dipped into the TiO_2 slurry, impregnated for 30 min and, then dried at 100°C for 2 h. The loaded TiO_2 was 1.0 g.

Results and Discussion

Photocatalyst characterization

The degradation efficiency may be very low inside a thick and solid catalyst due to the UV light intensity attenuation by the catalyst. There are not enough volatile organic compound (VOC) molecules available for degradation inside the catalyst because the molecules' diffusion in the catalyst can be very slow (Yu *et al.*, 2007). However, TiO_2/γ-Al_2O_3/nickel foam in this study had a pentagonal framework with a lot of small holes. The photocatalyst was characterized with field emission scanning electron microscopy (S-4800; Hitachi). Figure 2 presents scanning electron microscopy images of the photocatalyst at various magnification times (400 and 100k). It also allows the light to penetrate easily into the inner body of the catalyst to enhance the utilization efficiency of light in the photocatalytic reaction. TiO_2/γ-Al_2O_3/nickel foam has advantages such as low pressure drop and high surface-area-to-volume ratio. Such a three-dimensional structure can improve the molecular transport of reactants and products. The air pollutants were adsorbed and enriched on the photocatalyst, leading to increased PCO rate.

Destruction of formaldehyde and toluene

Toluene and formaldehyde were destroyed in the PCO and O_3-PCO processes. The removal efficiency was compared, as

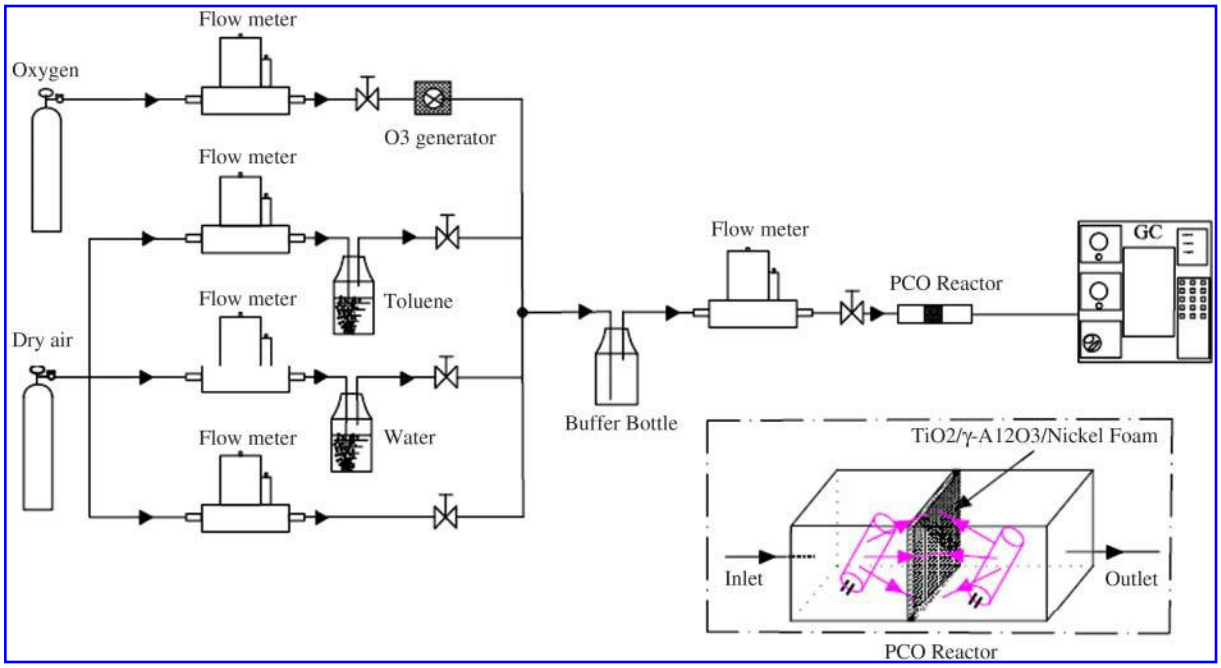

FIG. 1. Schematic diagram of experimental setup.

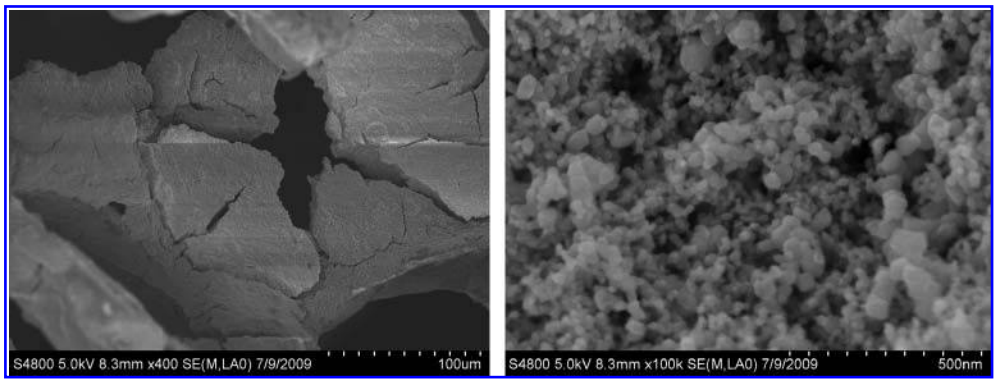

FIG. 2. Scanning electron microscopy graphs of γ-Al_2O_3/nickel foam-supported TiO_2.

shown in Figs. 3 and 4, respectively. The addition of O_3 to the PCO significantly enhanced the destruction of toluene and formaldehyde. The toluene conversion increased from 12% to 96% and the formaldehyde conversion increased from 64% to 97.5% in the O_3-PCO process, respectively, compared with that in the PCO process.

There were multiple processes, including PCO, ozone photolysis (UV/O_3), and catalytic ozonation (O_3/TiO_2). In the O_3-PCO process, toluene oxidation happened not only on the surface of photocatalyst (e.g., in the PCO and O_3/TiO_2 sub-process) but also in the gas phase (e.g., UV/O_3). Toluene destruction is mainly attributed to the UV/TiO_2 and UV/O_3 sub-processes of the O_3-PCO process in previous studies (Zhang *et al*., 2003; Yu and Lee, 2007; Huang *et al*., 2009). However, the role of O_3/TiO_2 sub-process was not properly addressed. As shown in Fig. 4, the TRE is 83.5% in the O_3/TiO_2 sub-process. O_3/TiO_2 sub-process played an important role in toluene oxidation in the O_3-PCO process. In the PCO process, OH• is generally considered as the dominant strong oxidant (Augugliaro *et al*., 1999; Yu and Lee, 2007; Mo *et al*., 2009b), and the pathway of OH• formation is described in Equation 2. The contribution of PCO, <12%, is not significant in the O_3-PCO process. However, there were more processes besides PCO process in the O_3-PCO process. More oxidants (e.g., O•) were generated besides OH•, as described in Equation 3, resulting in the enhanced toluene destruction in the O_3-PCO process. In addition, there are more pathways for OH• formation besides Equation 2, as described in Equation 4 in the O_3-PCO process. O_3 can react with H_2O to generate OH• by electron–hole pair, UV irradiation, or active sites of TiO_2.

$$3e^- + 3h^+ + 2H_2O + O_2 \rightarrow 4OH\bullet \quad (2)$$

$$O_3 \xrightarrow{h\upsilon \text{ or } TiO_2} O\bullet + O_2 \quad (3)$$

$$O_3 + H_2O \xrightarrow{(e^- + h^+) \text{ or } h\upsilon \text{ or } TiO_2} 2OH\bullet + O_2 \quad (4)$$

Comparing Fig. 3 with Fig. 4 reveals that the TRE (12%) is much lower than the removal efficiency of formaldehyde (64%) in the PCO process. It is mainly attributed to three facts: (1) toluene is more difficult to be destroyed due to the low reactivity of aromatic ring; (2) photocatalysts were deactivated during toluene oxidation; (3) toluene oxidation needs higher stoichiometry of oxidants than formaldehyde oxidation. The complete oxidation of a HCHO molecule needs 4 OH• molecules or 2 O• molecules, whereas the amounts of

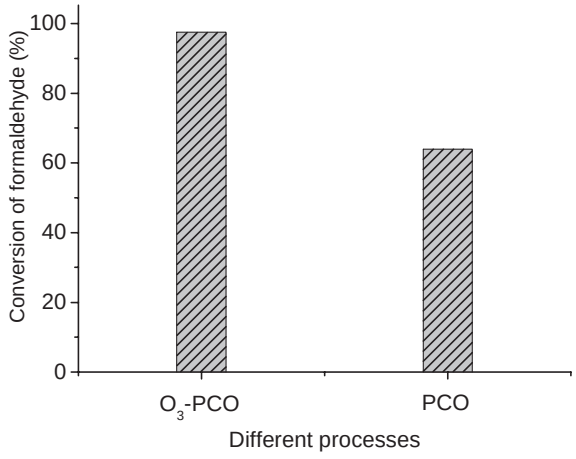

FIG. 3. Conversion of formaldehyde under the same conditions in the PCO and O_3-PCO processes. O_3-PCO, combination of O_3 with photocatalysis.

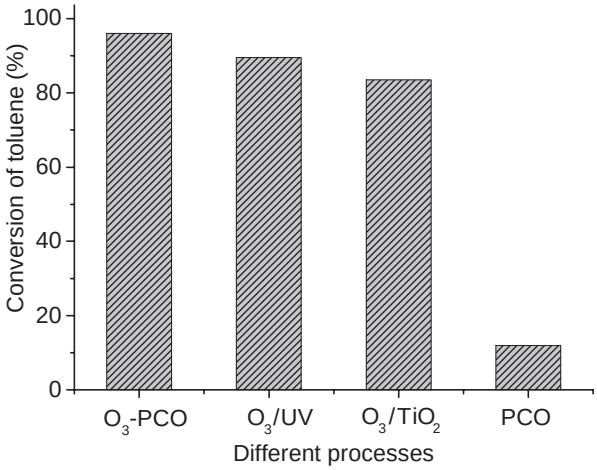

FIG. 4. Destruction of toluene conversion under the same conditions in different processes.

OH• and O• are increased to 36 and 18 for the complete oxidation of a toluene molecule, respectively, as described in Equations 5–8:

$$4OH\bullet + HCHO \rightarrow \bullet\bullet\bullet\bullet\bullet\bullet \rightarrow CO_2 + 3H_2O \quad (5)$$

$$2O\bullet + HCHO \rightarrow \bullet\bullet\bullet\bullet\bullet\bullet \rightarrow CO_2 + H_2O \quad (6)$$

$$36OH\bullet + C_7H_8 \rightarrow \bullet\bullet\bullet\bullet\bullet\bullet \rightarrow 7CO_2 + 22H_2O \quad (7)$$

$$18O\bullet + C_7H_8 \rightarrow \bullet\bullet\bullet\bullet\bullet\bullet \rightarrow 7CO_2 + 4H_2O \quad (8)$$

The detailed destruction processes of toluene and formaldehyde by OH• and O• need further study.

The TRE of PCO starts dropping quickly after the reaction, indicating that the photocatalyst tends to be deactivated in the PCO process. The color of TiO_2 changed from white to yellow in the PCO process after operation for about 1 h. However, such phenomenon was not observed in the O_3-PCO process. The addition of O_3 also remarkably enhanced the durability of photocatalyst. The enhancement of durability mainly attributed to the formation of more oxidants, resulting in the complete oxidation of toluene and formation of less byproduct in the O_3-PCO process. It has been reported that the accumulation of intermediates on the surface of photocatalyst would block the active sites of photocatalyst and lead to the deactivation of photocatalysts (Cao *et al.*, 2000; Huang *et al.*, 2009).

Benzaldehyde, formic acid, and acetic acid were identified by gas chromatograph-mass spectrometer (GC-MS) in the toluene PCO. These byproducts were also found in the previous studies (Mo *et al.*, 2009b; Sleiman *et al.*, 2009). However, only benzaldehyde and benzoic acid were found in the O_3-PCO process. Therefore, the addition of ozone to the PCO process can effectively inhibit the formation of byproducts and remarkably enhance the photocatalyst's durability.

Influencing factors

Toluene was selected to study for its stability due to its refractory nature and low removal efficiency.

Effect of humidity. Humidity imposes a great effect on the PCO efficiency (Qi *et al.*, 2007; Guo *et al.*, 2008; Puma *et al.*, 2009; Sleiman *et al.*, 2009). Its effect on the TRE in different processes is shown in Fig. 5. The humidity ratio greatly affects the TRE in the PCO process. The increase in humidity ratio was beneficial to toluene removal with the humidity ratio lower than 0.5%, but showed adverse effects with the humidity ratio higher than 0.75%. Water was essential for the generation of OH•. In dry air, little OH• can be generated and toluene oxidation tended to form intermediates (e.g., benzaldehyde) on the surface of the photocatalyst, leading to the deactivation of photocatalysts. However, excessive water would depress toluene decomposition because water prevents toluene adsorption on the photocatalyst (Huang and Ye, 2009; Mo *et al.*, 2009b). If more pollutant molecules are adsorbed on the surface of the catalyst, then more pollutant molecules are available for the photocatalytic degradation (Yu *et al.*, 2007). In the O_3-PCO process, the TRE increased from 97.5% to 99.9% with increased humidity ratio from 0% to 2%. The TRE was not significantly affected by humidity ratio in the O_3-PCO process, which was in agreement with previous studies (Zhang *et al.*, 2003; Yu and Lee, 2007). Water vapor can affect the formation of OH• in the PCO and UV/O_3 process and thus has impact on the removal efficiency (Zhang *et al.*, 2003; Yu and Lee, 2007). However, its influence on the formation of OH• and O• in the O_3/TiO_2 process was not well addressed in previous studies. As mentioned above, O_3/TiO_2 sub-process also played an important role in the toluene oxidation in the O_3-PCO process. Therefore, the effect of humidity on the O_3/TiO_2 sub-process should not be excluded.

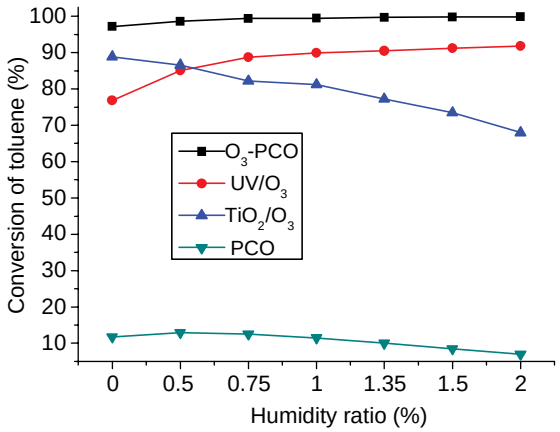

FIG. 5. Effect of humidity ratio on the toluene conversion in different processes.

Water vapor plays a dual role due to its different impact on different sub-processes in the O_3-PCO process. As shown in Fig. 5, the TRE increased from 76.8% to 91.8% in UV/O_3 process, whereas it decreased from 89.1% to 68% in the O_3/TiO_2 process, as the humidity ratio ranged from 0% to 2%. The increase in humidity revealed a positive effect on the TRE in the UV/O_3 process (see Fig. 5). Water molecules play an important role in the initial step of the UV/O_3 chain reaction ($O_3 + H_2O \xrightarrow{h\nu} 2OH\bullet + O_2$). Therefore, OH• formation was favored under high humidity in the UV/O_3 reaction (Yu and Lee, 2007). However, water has negative effect in the O_3/TiO_2 process due to the competitive adsorption of toluene with water (Huang and Ye, 2009). In addition, excessive water also would block the active sites of photocatalysts for the O_3 decomposition and toluene oxidation. As mentioned above, the contribution of PCO was not significant in the O_3-PCO process. Therefore, the humidity had little impact on TRE due to the coexisting of positive and negative effects in the O_3-PCO process. The addition of O_3 could enhance stability of PCO during the variation of humidity.

Effect of initial O_3 concentration. Ozone was the main oxidant instead of oxygen due to its strong oxidation ability in the O_3-PCO process. Figure 6 reveals that when the initial ozone concentration decreased from 370 to 270 ppm, the TRE decreased from 89.5% to 72.9% and from 83.6% to 71.4% in the O_3/UV and O_3/TiO_2 processes, respectively. However, the TRE of O_3-PCO was stable when the initial ozone dropped. This result indicates that O_3 variation had less effect on the TRE of O_3-PCO than on that of O_3/UV and O_3/TiO_2 processes.

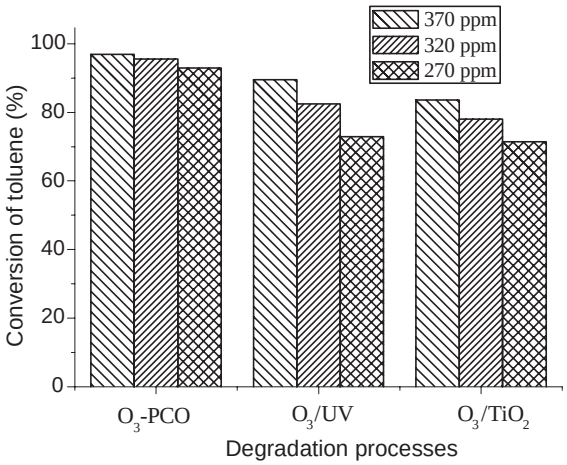

FIG. 6. Effect of initial O_3 concentration on the toluene conversion in different processes.

Conclusion

The removal efficiency of formaldehyde and toluene in the O_3-PCO process was increased from 64% to 97.5% and from 12% to 96%, respectively, compared with that of PCO. By-products from toluene oxidation were reduced with increased durability of photocatalyst. The O_3-PCO process showed excellent stability during the variation of the humidity and initial O_3 concentration. Water plays a dual role in toluene destruction in the O_3-PCO process. Increased humidity is beneficial to toluene destruction in the UV/O_3 process, whereas it is harmful in the O_3/TiO_2 process. The more pathways to generate more reactive oxidants led to the enhanced stability and increased removal efficiency in the O_3-PCO process. O_3-PCO is an efficient way to improve the PCO efficiency.

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Author Disclosure Statement

No competing financial interests exist.

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