Decomposition of gas-phase toluene by the combination of ozone and photocatalytic oxidation process (TiO₂/UV, TiO₂/UV/O₃, and UV/O₃)

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Abstract

The gas-phase toluene removal efficiencies by photocatalytic oxidation (TiO₂/UV), the combination of ozone and photocatalytic oxidation (TiO₂/UV/O₃), and the UV/O₃ reaction were tested using a quartz tube photoreactor. The experiments were conducted under various ozone concentrations (3.3–15 ppm), toluene concentrations (1–9 ppm), relative humidity (5–80%), and gas flow rates (200–1200 mL/min). The toluene oxidation rates (TORs) of TiO₂/UV/O₃, and UV/O₃ reactions were proportional to the ozone concentrations. The TORs of TiO₂/UV, TiO₂/UV/O₃, and UV/O₃ reactions increased with toluene concentration. However, there were negative correlations between the toluene removal efficiencies of these three kinds of reactions and the toluene concentrations. The order of the TORs and the CO₂ yield rates of these three reactions were TiO₂/UV/O₃ > TiO₂/UV > UV/O₃. The kinetics of TiO₂/UV, and TiO₂/UV/O₃ reactions fit the Langmuir–Hinshelwood rate form. The rate constants (*k*) and Langmuir adsorption constants (*K*) are as follows: TiO₂/UV: *k* = 0.0102 ppm m/s, *K* = 0.146 ppm^{−1}; TiO₂/UV/O₃: *k* = 0.0268 ppm m/s, *K* = 0.0796 ppm^{−1}. The reciprocal of UV/O₃ reaction rate showed a positive linear relationship with the reciprocals of humidity and of toluene concentration. Ozone, also an air pollutant, was removed in the TiO₂/UV/O₃, and UV/O₃ reactions. The ozone removal efficiency of TiO₂/UV/O₃ reaction in the presence and absence of toluene ranged from 61.1 to 99.5% and 38.1 to 95.1%, respectively.

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1. Introduction

Volatile organic compounds (VOCs) are common air pollutants and can be found in both outdoor and indoor settings. VOCs can react with NO_x to form tropospheric O₃ which results in smog in urban air [1]. Exposure to VOCs might cause toxic effects to central nervous system and internal organs, and might cause symptoms, such as headache, respiratory tract irritation, dizziness and nausea, known as the sick building syndrome (SBS) [2,3].

For VOCs emission sources of high concentrations, catalytic treatments, such as catalytic incineration and catalytic combustion, have been well developed. However, these treatments require high temperatures (200–900 °C) and high

concentrations (several hundred of ppm) of oxidizable compounds for successful operation, and are not cost-effective for low pollutant concentrations [4]. Among those available potential air-cleaning technologies for contamination of lower VOCs concentrations and indoor applications, photocatalytic oxidation (PCO) causes extensive concern recently. PCO can oxidize VOCs to carbon dioxide (CO₂) and water (H₂O) under ambient temperature [5–7], and is capable of controlling microbial contaminations which are one of the sources of indoor VOCs.

Although PCO seems to be a promising technology for controlling VOCs contaminations of low concentrations, however, there are still some problems with this technology. For example, many irritative reaction intermediates, such as aldehydes and carboxylic acids, were found in PCO reactions [12,13]. Some of these intermediates may result in photocatalyst deactivation [8–11]. Illuminating the deactivated photocatalyst with ultraviolet (UV) light under high relative humidity in the absence of VOCs can regenerate the activity of

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photocatalyst [14,15], but this method needs a spare unit for replacement during the regeneration. Wang et al. [16] found that ozone (O_3) added into the PCO reaction system had a positive effect on the regeneration of the photocatalyst. Jeong et al. [17] demonstrated that the VOCs removal efficiency and the CO_2 selectivity of PCO when using a UV lamp of short wavelength (185 + 254 nm) was better than that when using a UV lamp of long wavelengths (254 and 365 nm). Many reactive oxidants, including O_3 , $O(^1D)$, and $O(^3P)$, were formed when O_2 was illuminated with a UV lamp of short wavelength. These added reactive oxidants can enhance the effectiveness of PCO.

In this study, we investigated the decomposition of gas-phase toluene by the combination of ozone (a reactive oxidant) and PCO. There were three reactions— TiO_2/UV , $TiO_2/UV/O_3$, and UV/O_3 reactions taking place in the experimental system. The experiments were conducted under different toluene concentrations (1–9 ppm), gas flow rates (200–1200 mL/min), relative humidity (5–80%), and O_3 concentrations (3.3–15 ppm) to investigate the effect of these factors on the toluene oxidation rates (TORs) and the CO_2 yield rates.

Toluene was chosen as the target compound because it is one of the frequently encountered organic compounds in indoor environments [19]. Furthermore, toluene is listed as one of the surrogates for the six major classes of indoor VOCs (aromatic, aldehyde, alkane, ketone, alcohol, and chlorocarbon) by the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) [20]. The major use of toluene is as a mixture additive to improve the octane number of gasoline. Toluene is also used as a solvent in paints, coatings, adhesives, inks, and cleaning agents and is also used in the production of plastic polymers [18]. Exposure to toluene may cause the eye, nasal, mucous membrane, and respiratory tract irritation [21–23].

2. Methodology

2.1. Oxidation reaction system

The schematic diagram of the experimental system is shown in Fig. 1(a). A 45-cm-long and 2.5-cm-interior-diameter quartz tube was used as the photoreactor. We set a 107.5-cm²-glass plate coated with Degussa P25 titania photocatalyst

Fig. 1. Schematic diagram of (a) experimental system and (b) photoreactor.

(0.0818 mg/cm²) in the middle of the quartz tube. To make the gas pass only through the upper part of the tube, the lower half part of the quartz tube was filled with Teflon, as shown in Fig. 1(b). The UV lamp used to illuminate the photocatalyst was a 15-W, UV-C (the central wavelength is 254 nm), long-life strip light bulb (Philips). The gas of the reaction system was supplied by a compressed gas cylinder of air (21% O₂ and 79% N₂) and the gas flow rates were controlled by mass flow controllers (Sierra Instruments Inc.). Toluene (Assay 99.7%, Riedel-deHaën) was selected as the tested VOC. The toluene vapor was generated from the diffusion vials (VICI Metronics) and the toluene concentration was depended on the temperature of the diffusion vial and the flow rate of dilution air. The relative humidity of the experimental system was controlled by the ratio of the dry and saturated air flow rate. The temperature of the reaction system was controlled at 25 ± 0.5 °C by a thermostatic chamber (DENG TNG Instruments Co., Ltd.). We used a Hygromer A2 & 100A to monitor the temperature and relative humidity of the inlet gas. The ozone generator used was an OZONAIR model RXO-5 ozone generator. Ozone Analyzer Model 400A (API Inc.) was used to monitor the ozone concentration at the outlet of the photoreactor. The Q-Trak 8551 (TSI.) was used to monitor the CO₂ and CO concentrations. Gas samples were taken at the inlet and the outlet of the photoreactor with a 125-mL gas sampling bulk (SUPELCO) and a SKC personal sampling pump. Then, the gas sample in the gas sampling bulk was purged by compressed air with a flow rate of 25 mL/min for 10 min and the eluate was sampled on Tenax TA (60/80 mesh) cartridges (SUPELCO). After sampling, the Tenax TA cartridges were thermal desorbed and cryofocussed by TEKMAR 6000 Aero trap Desorber and then analyzed by GC-FID (HP5890 series II) to determine the toluene concentration of the gas sample. Because Tenax TA was found to react with ozone, the calibration curve of toluene was created under different background O₃ concentrations to eliminate the impact of O₃–Tenax reaction.

2.2. Experimental setup

There were three experimental sets (TiO₂/UV, TiO₂/UV/O₃, and UV/O₃) conducted in this study. The TiO₂/UV/O₃ and TiO₂/UV experiments were conducted with and without the ozone generator operating, respectively. During the UV/O₃ experiments, we used a glass plate without coated TiO₂ instead of the original TiO₂-coated one (see Fig. 1(b)). The experimental data were collected under steady states. It took 30 min to 1 h for the experimental system to reach a steady state after the experiment started. The experiments were conducted under different gas flow rates (200–1200 mL/min), toluene concentrations (1–9 ppm), relative humidity (5–80%), and ozone concentrations (3500–15,000 ppb).

The toluene oxidation rates (TORs) of TiO₂/UV/O₃ and TiO₂/UV reactions are calculated by Eq. (1), and the TORs of UV/O₃ reaction by Eq. (2):

$$\text{TOR} = \frac{(C_{\text{in}} - C_{\text{out}})Q}{F \times A} \quad (1)$$

$$\text{TOR} = \frac{(C_{\text{in}} - C_{\text{out}})Q}{F \times V} \quad (2)$$

where C_{in} and C_{out} (ppm) are the inlet and outlet toluene concentrations, respectively; Q (m³/s) is the gas flow rate; F is the conversion factor (=24,500 ppm m³/mol; this is derived from the fact that 1 ppm = 4.09 × 10^{−5} mol/m³); A (m²) is the TiO₂ coating area; V (m³) is the volume of the photoreactor.

The CO₂ yield rate is calculated by the following equation:

$$\text{CO}_2 \text{ yield rate} = \frac{C_{\text{CO}_2}(\text{on}) - C_{\text{CO}_2}(\text{off})}{V/Q} \quad (3)$$

where $C_{\text{CO}_2}(\text{on})$ and $C_{\text{CO}_2}(\text{off})$ (ppm) are the CO₂ concentrations observed at the outlet of the photoreactor by the Q-Trak, when the UV lamp was on and off, respectively; V (m³) is the volume of the photoreactor; Q (m³/s) is the gas flow rate; V/Q (s) is the gas retention time of the photoreactor, which represents the average time for a gas molecule to pass through the photoreactor.

The CO yield rate is calculated by Eq. (4):

$$\text{CO yield rate} = \frac{C_{\text{CO}}(\text{on}) - C_{\text{CO}}(\text{off})}{V/Q} \quad (4)$$

in which $C_{\text{CO}}(\text{on})$ and $C_{\text{CO}}(\text{off})$ (ppm) are the CO₂ concentrations observed at the outlet of the photoreactor by the Q-Trak, when the UV lamp was on and off, respectively; V (m³) is the volume of the photoreactor; Q (m³/s) is the gas flow rate; V/Q (s) is the gas retention time of the photoreactor.

3. Results and discussions

3.1. Effect of toluene concentration

Fig. 2(a) represents the effects of toluene concentration on the TiO₂/UV, TiO₂/UV/O₃, and UV/O₃ reactions. The TORs of TiO₂/UV, TiO₂/UV/O₃, and UV/O₃ reactions increased with the toluene concentrations, but the toluene removal efficiency decreased when the toluene concentrations increased. The CO₂ yield rates of TiO₂/UV and TiO₂/UV/O₃ reactions increased with the toluene concentrations, however, the gap between the TORs and CO₂ yield rates rose with the toluene concentrations, as shown in Fig. 2(a). It indicates that some partial oxidized compounds (intermediates) were not mineralized to CO₂ and H₂O in the TiO₂/UV and TiO₂/UV/O₃ reactions. The intermediates yield rate (IYR) based on carbon balance can be calculated by the following equation:

$$\text{IYR} = \text{TOR} \times 84 - \text{CYR} \times \frac{V \times 12}{F \times A} \quad (5)$$

where TOR is the toluene oxidation rate; 84 is the weight of carbon per molecule of toluene; CYR is the CO₂ yield rate; V (m³) is the volume of the photoreactor; F is the conversion factor (=24,500 ppm m³/mol); A (m²) is the TiO₂ coating area. As shown in Fig. 2(a), the IYRs of TiO₂/UV, and TiO₂/UV/O₃ reactions both rose with the toluene concentrations. The IYRs of TiO₂/UV reaction were smaller than those of TiO₂/UV/O₃ reaction when the toluene concentration ≥ 5 ppm. The IYRs of

Fig. 2. Effect of toluene concentration on (a) toluene oxidation rates (TORs), CO₂ yield rates, CO yield rates, and intermediates yield rates (IYRs) based on carbon balance (b) ozone removal efficiency (ORE) of the TiO₂/UV, TiO₂/UV/O₃, and UV/O₃ reactions (TiO₂/UV/O₃ and UV/O₃: O₃ = 10 ppm, relative humidity = 50%, gas flow rate = 1200 mL/min, retention time: 5.3 s, TiO₂/UV: relative humidity = 50%, gas flow rate = 1200 mL/min, retention time: 5.3 s).

TiO₂/UV/O₃ reaction were very small ($\leq 0.046 \mu\text{g/m}^2\text{-s}$) and had no obvious variation when the toluene concentration ≤ 2 ppm, and increased with the toluene concentrations when the toluene concentration > 2 ppm. This result denotes that when the inlet toluene concentration was below 2 ppm, the partial oxidized compounds were almost totally mineralized to CO₂ and H₂O. However, as the inlet toluene concentration was higher than 2 ppm, the amount of partial oxidized compounds increased with the toluene concentration. According to the previous study, the partial oxidized compounds of gas-phase photocatalytic oxidation of toluene consisted of benzaldehyde, benzoic acid, and benzyl alcohol [12,13]. Some carbon deposits may be formed on the surface of TiO₂ through the polymerization of intermediate radicals [24]. The accumulation of benzoic acid and carbon deposits on the surface of photocatalyst can inhibit the catalytic activity of photocatalyst [13,24]. CO was also considered as an intermediate here. The CO yield rates of TiO₂/UV and TiO₂/UV/O₃ reactions increased from 0.06 to 0.19 and from 0 to 0.32 ppm/s as the toluene concentrations increased from 1 to 9 ppm.

The ozone removal efficiency (ORE) of TiO₂/UV/O₃ reaction increased from 45.2 to 72% when the toluene concentration increased from 0 to 9 ppm, and there was a turning point of the slope at around 3-ppm toluene concentration (the slope before and after 3 ppm were 7.93 and 0.6% ORE/ppm of toluene, respectively). The turning point of the slope of ORE was near the point where the IYRs started to increase,

indicating that the accumulation of the partial oxidized compounds on the surface of photocatalyst might inhibit the ozone decomposition by PCO.

The ORE of UV/O₃ reaction increased slightly from 11.1 to 13.8% when the toluene concentration rose from 1 to 9 ppm, thus, the effect of toluene concentration on the ORE of UV/O₃ reaction was insignificant.

3.1.1. Kinetics of TiO₂/UV and TiO₂/UV/O₃ reactions

We assumed that the TiO₂/UV and TiO₂/UV/O₃ reactions were not gas-phase-mass-transfer limiting at 1200 mL/min gas flow rate discussed in Section 3.2, and the kinetics of TiO₂/UV and TiO₂/UV/O₃ reactions can be described by the Langmuir–Hinshelwood (L–H) rate form:

$$r = \frac{Q}{W} \times \frac{dC_{\text{toluene}}}{dL} = -\frac{kKC_{\text{toluene}}}{1 + KC_{\text{toluene}}} \quad (6)$$

where r is the toluene oxidation rate; Q is the gas flow rate; W is the width of the TiO₂-coated glass plate; C_{toluene} is the toluene concentration; L is the length of the photoreactor; k is the L–H rate coefficient of TiO₂/UV and TiO₂/UV/O₃ reactions; K is the Langmuir adsorption constant.

Integrating both sides of Eq. (6), we have:

$$\frac{A/Q}{(C_{\text{in}} - C_{\text{out}})} = \frac{1}{kK} \times \frac{\ln(C_{\text{in}}/C_{\text{out}})}{(C_{\text{in}} - C_{\text{out}})} + \frac{1}{k} \quad (7)$$

Fig. 3. Plot of $A/Q/(C_{in} - C_{out})$ vs. $\ln(C_{in}/C_{out})/(C_{in} - C_{out})$ (TiO_2/UV : toluene = 1–9 ppm, relative humidity = 50%, gas flow rate = 1200 mL/min, $\text{TiO}_2/\text{UV}/\text{O}_3$: toluene = 1–9 ppm, O_3 = 10 ppm, relative humidity = 50%, gas flow rate = 1200 mL/min, retention time: 5.3 s).

in which C_{in} and C_{out} (ppm) are the inlet and outlet toluene concentrations, respectively; A (m^2) is the TiO_2 coating area.

The assumption that the kinetics of TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$ reactions fits the L–H rate form was authenticated by the experiments, since the plots of $\ln(C_{in}/C_{out})/(C_{in} - C_{out})$ versus $A/Q/(C_{in} - C_{out})$ are linear with a positive intercept of $1/k$ as shown in Fig. 3, and the correlation coefficients (R) of the regression lines of the TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$ experimental data are 0.9997 and 0.9996, respectively. The values of k and K are shown in Fig. 3.

3.2. Effect of gas flow rate

The TORs and CO_2 yield rates of $\text{TiO}_2/\text{UV}/\text{O}_3$, and TiO_2/UV reactions increased with the gas flow rates increasing from

200 to 800 mL/min and achieved a plateau when the gas flow rate ≥ 1000 mL/min, as shown in Fig. 4. In the heterogeneous PCO system ($\text{TiO}_2/\text{UV}/\text{O}_3$ and TiO_2/UV reactions), the rate-determining step was the gas-phase mass transfer, or surface reaction, or both of them, and there was no limited pore diffusion. In the region of lower gas flow rate (200–800 mL/min), the apparent toluene oxidation rate was dependant upon the gas-phase mass transfer rate which increased with the gas flow rate. When the gas flow rate was higher than 1000 mL/min, the rate-determining step became the surface reaction. The mass transfer of toluene to the wall of the straight tube can be described by the semiempirical Lvque equation:

$$Sh = 1.615 \left(Re \times Sch \times \frac{d}{L} \right)^{1/3} = \frac{k_{g\text{-toluene}} \times d}{D_{\text{toluene}}} \quad (8)$$

in which Sh is the Sherwood number; Re is the Reynolds number; Sch is the Schmidt number; d is the hydraulic diameter; L is the length of the photoreactor; $k_{g\text{-toluene}}$ is the mass transfer coefficient of toluene; D_{toluene} is the diffusivity of toluene in the air [15,25]. At 1200-mL/min gas flow rate, the mass transfer coefficient of toluene ($k_{g\text{-toluene}}$) equaled to 1.58×10^{-3} m/s, which was larger than the product of the Langmuir adsorption constant (K) and the L–H rate coefficient (k) of TiO_2/UV reaction ($kK = 1.49 \times 10^{-3}$ m/s) and smaller than that of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction ($kK = 2.13 \times 10^{-3}$ m/s). Therefore, the rate-determining steps of TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$ reactions should be the surface reaction and gas-phase mass transfer, respectively. The experimental result presented in Fig. 4 supported this inferential expectation.

The IYRs of $\text{TiO}_2/\text{UV}/\text{O}_3$ and TiO_2/UV reactions increased from 1.01 to 3.63 $\mu\text{g-carbon}/\text{m}^2\text{-s}$ and from 0.97 to 2.35 $\mu\text{g carbon}/\text{m}^2\text{-s}$, respectively, when the gas flow rate increased from 200 to 1200 mL/min. The CO yield rate of TiO_2/UV

Fig. 4. Effect of gas flow rate on toluene oxidation rates (TORs), CO_2 yield rates, CO yield rates, and intermediates yield rates (IYRs) based on carbon balance (TiO_2/UV : toluene = 5 ppm, relative humidity = 50%, $\text{TiO}_2/\text{UV}/\text{O}_3$ and UV/O_3 : O_3 = 10 ppm, toluene = 5 ppm, relative humidity = 50%).

Fig. 5. Plot of retention time vs. $\ln(C_{O_3in}/C_{O_3out})$ (C_{O_3in} and C_{O_3out} are the inlet and outlet concentration of ozone, respectively) and effect of retention time on ozone removal efficiency ($O_3 = 10$ ppm, relative humidity = 50%, gas flow rate = 200–1200 mL/min).

reaction increased from 0.09 to 0.32 ppm/s as the gas flow rate increased from 200 to 1000 mL/min, and then it decreased to 0.18 ppm/s when the gas flow rate increased from 1000 to 1200 mL/min. The decrease of the CO yield rate may result from the decrease of retention time. The CO yield rate of $TiO_2/UV/O_3$ reaction increased from 0.06 to 0.35 ppm/s when the gas flow rate increased from 200 to 1200 mL/min.

The TORs of UV/O_3 reactions increased when the gas flow rate increased from 200 to 800 mL/min and did not vary with the

gas flow rate thereafter. The UV/O_3 reaction is a homogeneous reaction, thus, there was no gas-phase mass transfer effect in this reaction. However, the gas retention time is inversely proportional to the gas flow rate. At lower gas flow rate (longer gas retention time), the toluene conversion was higher and the average toluene concentration in the photoreactor was relatively low. Since the TOR increased with the toluene concentration, lower TOR was expected at lower gas flow rate. This effect became insignificant when the gas flow rate was higher than 1000 mL/min, because the difference in the average toluene concentration between the 1000- and 1200-mL/min gas flow rates was smaller than 0.2 ppm. This effect also existed in the TiO_2/UV and $TiO_2/UV/O_3$ reactions and it became insignificant when the gas flow rate was above 1000 mL/min.

The ORE of $TiO_2/UV/O_3$ and UV/O_3 reactions increased with the gas retention time, as shown in Fig. 5. For the UV/O_3 reaction, the gas retention time is linear to the $\ln(C_{O_3in}/C_{O_3out})$, in which C_{O_3in} and C_{O_3out} are the inlet and outlet ozone concentrations, respectively. Therefore, the O_3 removal of UV/O_3 reaction was first-order rate form. The rate constants calculated from the regression are shown in Fig. 5(a).

3.3. Effect of humidity

The effect of humidity on the $TiO_2/UV/O_3$, TiO_2/UV , and UV/O_3 reactions are shown in Fig. 6(a). The TORs of TiO_2/UV reaction increased from 0.068 to 0.15 $\mu\text{-mol}/\text{m}^2\text{-s}$ when the

Fig. 6. Effect of humidity on (a) toluene oxidation rates (TORs), CO_2 yield rates, CO yield rates, and intermediates yield rates (IYRs) based on carbon balance (b) ozone removal efficiency ($O_3 = 10$ ppm, toluene = 5 ppm, flow rate = 1200 mL/min, retention time: 5.3 s).

humidity increased from 1517 to 6070 ppm (relative humidity from 5 to 20%), but the TORs dropped from 0.15 to 0.112 $\mu\text{-mol/m}^2\text{-s}$ when the humidity went up from 6070 to 24,270 ppm (relative humidity from 20 to 80%). This result revealed the dual effect of humidity on the TiO_2/UV reaction. In the TiO_2/UV reaction, H_2O molecules were essential for the generation of hydroxyl radicals. No CO_2 evolution in the photocatalytic degradation of toluene was found in the absence of humidity [6,26]. However, the toluene molecules confronted the competition from H_2O molecules for the adsorption sites on the surface of TiO_2 [27]. Therefore, the increase of humidity showed a positive effect when the humidity was smaller than 6070 ppm and showed a negative effect when the humidity was higher than 6070 ppm on the TORs of TiO_2/UV reaction. A competitive L–H model can be used to describe the effects of relative humidity on the TiO_2/UV reaction [27]:

$$r = \frac{k_{\text{competitive}} K_1 C_{\text{toluene}} K_2 C_w}{(1 + K_1 C_{\text{toluene}} + K_2 C_w)^2} \quad (9)$$

where r ($\mu\text{-mol m}^{-2} \text{s}^{-1}$) is the toluene oxidation rate; $k_{\text{competitive}}$ ($\mu\text{-mol m}^{-2} \text{s}^{-1}$) is the rate coefficient of competitive L–H model; K_1 and K_2 (ppm^{-1}) are the competitive Langmuir adsorption constants for toluene and H_2O , respectively; C_{toluene} (ppm) is the toluene concentration; C_w (ppm) is the humidity. The best-fit curve of Eq. (9) to experimental data is shown in Fig. 6(a). According to the curve-fitting result, the values of $k_{\text{competitive}}$, K_1 , and K_2 are 11.7 $\mu\text{-mol m}^{-2} \text{s}^{-1}$, 0.016 ppm^{-1} , and $1 \times 10^{-1} \text{ppm}^{-1}$, respectively.

As shown in Fig. 6(a), the IYRs and CO yield rates of TiO_2/UV reaction had a minimum value at 6070-ppm humidity, indicating this point that should be the optimum operation condition for the TiO_2/UV reaction.

The TORs and CO_2 yield rates of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction decreased from 0.24 to 0.213 $\mu\text{-mol/m}^2\text{-s}$ and from 3.6 to 2.9 ppm/s, respectively, when the humidity increased from 6070 to 24,270 ppm, as shown in Fig. 6(a). Unlike the TiO_2/UV reaction, when the humidity decreased from 6070 to 1517 ppm,

the TORs and CO_2 yield rates of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction dropped slightly from 0.24 to 0.236 $\mu\text{-mol/m}^2\text{-s}$ and 3.6 to 3.5 ppm/s, respectively. Under low humidity or in the absence of humidity, the dominant reaction pathway of the $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction might be the generation of $\bullet\text{O}^-$ radical, as shown in the second column of Table 1. Through this pathway, one O_3 molecule and one electron could generate one $\bullet\text{O}^-$ radical without the involvement of H_2O . The formed $\bullet\text{O}^-$ radical could oxidize toluene and the partial oxidized compounds continuously.

When the humidity was between 1517 and 24,270 ppm, the IYRs and the CO yield rates of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction ranged from 0.28 to 0.42 $\mu\text{g carbon/m}^2\text{-s}$ and 0.19 to 0.37 ppm/s, respectively. However, the correlations between humidity and each of the IYR and the CO yield rate were not very obvious.

The increase of humidity revealed a positive effect on the TORs of UV/O_3 reaction, as shown in Fig. 6(a), owing to that water molecule played an important role in the initial step of the UV/O_3 chain reaction ($\text{O}_3 + \text{H}_2\text{O} \xrightarrow{h\nu} 2\text{OH}\bullet + \text{O}_2$). Therefore, in the UV/O_3 reaction, formation of hydroxyl radicals, the major oxidizer of the UV/O_3 reaction, was favored under high humidity.

The ORE of UV/O_3 reaction increased from 5.3 to 20.4% (with 5-ppm toluene) and from 4.3 to 11.6% (without toluene) when the humidity increased from 1517 to 24,270 ppm, as shown in Fig. 6(b). This was also relevant to the enhancement effect of humidity on the formation of hydroxyl radicals ($\text{OH}\bullet$) in the UV/O_3 chain reaction. The hydroxyl radicals would react with O_3 to generate $\text{HO}_2\bullet$ radicals and O_2 , and then the $\text{HO}_2\bullet$ radicals would react with O_3 to form hydroxyl radical and O_2 [1]:

In the $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction, the increase of humidity was unfavorable for the O_3 removal. As shown in Fig. 6(b), when the humidity increased from 1517 to 24,270 ppm, the ORE of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction decreased from 77.9 to 61.1% and from 65.1 to

Table 1
Possible reaction mechanisms of the TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$ reactions [28,29]

Reaction type	Reaction steps	Stoichiometry
TiO_2/UV	$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + e^- + h^+$ $h^+ + \text{H}_2\text{O} \rightarrow \text{OH}\bullet + \text{H}^+$ $h^+ + \text{OH}^- \rightarrow \text{OH}\bullet$ $e^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-}$ $2\text{O}_2^{\bullet-} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- + \text{O}_2$ $\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}\bullet$	$3e^- + 3h^+ + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{OH}\bullet$
$\text{TiO}_2/\text{UV}/\text{O}_3$	Formation of $\text{OH}\bullet$ radical $\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + e^- + h^+$ $e^- + \text{O}_2 \rightarrow \bullet\text{O}_2^-$ $\bullet\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_2 + \bullet\text{O}_3^-$ $\bullet\text{O}_3^- + \text{H}_2\text{O} \xrightarrow{\text{TiO}_2} \text{OH}\bullet + \text{OH}^- + \text{O}_2$ $\text{OH}^- + h^+ \rightarrow \text{OH}\bullet$ Formation of $\bullet\text{O}^-$ radical $e^- + \text{O}_2 \rightarrow \bullet\text{O}_2^-$ $\bullet\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_2 + \bullet\text{O}_3^-$ $\bullet\text{O}_3^- \xrightarrow{\text{TiO}_2} \bullet\text{O}^- + \text{O}_2$	$e^- + h^+ + \text{H}_2\text{O} + \text{O}_3 \rightarrow 2\text{OH}\bullet + \text{O}_2$ $e^- + \text{O}_3 \rightarrow \bullet\text{O}^- + \text{O}_2$

Fig. 7. Effect of ozone concentrations on (a) toluene oxidation rates (TORs), CO_2 yield rates, CO yield rates, and intermediates yield rates (IYRs) based on carbon balance (b) ozone removal efficiency (toluene = 5 ppm, relative humidity = 50%, flow rate = 1200 mL/min, retention time: 5.3 s).

38.1% in the presence and absence of 5-ppm toluene, respectively. This might result from the competitive adsorption between O_3 molecules and H_2O molecules for the adsorption sites on the surface of TiO_2 .

3.4. Effect of ozone concentration

Fig. 7(a) shows the positive effect of ozone on the TORs of $\text{TiO}_2/\text{UV}/\text{O}_3$ and UV/O_3 reactions. The TORs of $\text{TiO}_2/\text{UV}/\text{O}_3$ and UV/O_3 reactions were proportional to the ozone concentrations. The slope of the linear regression line in Fig. 7(a) was defined as the enhancement index of ozone. The enhancement index of ozone of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction was $7.49 \times 10^{-6} \mu\text{-mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}/\text{ppb}\cdot\text{O}_3$.

The IYRs and CO yield rates of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction had minimum values (IYR = $0.23 \mu\text{g carbon}/\text{m}^2\cdot\text{s}$ and CO yield rate = $0.04 \text{ ppm}/\text{s}$) at 3.9-ppm ozone concentration.

As shown in Fig. 7(b), the ORE of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction ranged from 41.2 to 57.7% in the absence of toluene and ranged from 69.8 to 79.1% in the presence of 5-ppm toluene. The ORE decreased when the ozone concentration increased. The kinetics of ozone removal fits the L–H rate form as described in Eq. (6) in which the inlet and outlet toluene concentrations replaced by the inlet and outlet ozone concentrations, respectively. The regression line of $\ln(C_{\text{O}_3\text{in}}/C_{\text{O}_3\text{out}})/(C_{\text{O}_3\text{in}} - C_{\text{O}_3\text{out}})$ versus $A/Q/(C_{\text{O}_3\text{in}} - C_{\text{O}_3\text{out}})$ is shown in Fig. 8 and the correlation coefficients (R) of the regression lines with 5-ppm toluene and without toluene were 0.9979 and 0.9967, respectively. The L–H rate coefficient of ozone (k_{O_3}) with and

without 5-ppm toluene were 38.9 and 19.7 ppb-m/s, respectively. And the Langmuir adsorption constant of ozone (K_{O_3}) with and without 5-ppm toluene were 8.9×10^{-5} and $1.03 \times 10^{-4} \text{ ppb}^{-1}$, respectively. The values of k_{O_3} and K_{O_3} were calculated on the basis of the regression results.

The enhancement index of ozone of UV/O_3 reaction was $5.82 \times 10^{-4} \mu\text{-mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}/\text{ppb}\cdot\text{O}_3$ ($=5.71 \times 10^{-6} \mu\text{-mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}/\text{ppb}\cdot\text{O}_3$), which was smaller than that of $\text{TiO}_2/\text{UV}/\text{O}_3$ reaction. The OREs of UV/O_3 reaction ranged from 15.3 to 19.5% in the presence of 5-ppm toluene and ranged from 9.2 to

Fig. 8. Plot of $A/Q/(C_{\text{O}_3\text{in}} - C_{\text{O}_3\text{out}})$ vs. $\ln(C_{\text{O}_3\text{in}}/C_{\text{O}_3\text{out}})/(C_{\text{O}_3\text{in}} - C_{\text{O}_3\text{out}})$. The data points were obtained under gas flow rate of 1000–1200 mL/min, where the effect of mass transfer was relatively low (relative humidity = 50%, O_3 = 4060–14,200 ppb, retention time: 5.3–6.33 s).

11.1% in the absence of toluene. The variation of ORE under different ozone concentrations was within 4.2%. This result was consistent with the result in Section 3.2 that the O_3 removal of UV/ O_3 reaction was first-order rate form.

3.5. Comparison between TiO_2 /UV and TiO_2 /UV/ O_3 reactions

The TORs and CO_2 yield rates of TiO_2 /UV/ O_3 reaction were higher than those of TiO_2 /UV reaction, as shown in Figs. 2(a), 4 and 6(a). The gas-phase UV/ O_3 reaction was one of the possible explanations for this result. However, the gap between the TORs of TiO_2 /UV/ O_3 reaction and TiO_2 /UV reaction was larger than that of UV/ O_3 reaction when the toluene concentration was higher than 5 ppm. Furthermore, the CO_2 evolution of UV/ O_3 reaction was lower than the detection limit of the Q-Trak, indicating that the CO_2 yield rate of UV/ O_3 reaction was much lower than the gap between the CO_2 yield rates of TiO_2 /UV/ O_3 reaction and TiO_2 /UV reaction. The possible reasons for this experimental result were that the ratio of ($OH^\bullet$ product)/(electron-hole pairs consumption) of O_3 pathway was higher than that of O_2 pathway, and the electron affinity of O_3 was relatively high (2.1 eV) compared with that of O_2 (0.44 eV) [28]. The hydroxyl radicals acted as the primary oxidizer for organic compounds oxidation in the PCO reaction [29–31]. The possible reaction mechanisms of TiO_2 /UV reaction for the hydroxyl radical formation are shown in Table 1. When an electron on the valence band (VB) of semiconductor absorbed a photon with energy higher than the band gap between the VB and the conduction band (CB), it would be promoted to the CB and thus an electron-hole pair was formed. The holes would oxidize either H_2O or OH^- anions dissociated from water to form hydroxyl radicals. The electrons on the CB reacted with O_2 to generate superoxide ions ($O_2^{\bullet-}$). Then, the superoxide ions would react with H_2O to produce added $OH^\bullet$, OH^- , and O_2 . Combining all the reaction steps and equilibrating all elements, we had the stoichiometry of TiO_2 /UV reaction for hydroxyl radical, as shown in the third column of Table 1. According to this stoichiometry, in the presence of humidity, one oxygen molecule and three electron-hole pairs could generate four hydroxyl radicals.

Owing to the higher electron affinity of O_3 , the excited electrons on the CB of TiO_2 were captured by O_3 more easily than by O_2 . After capturing the electrons, the O_3 became $O_3^{\bullet-}$ anion radical. Then, the $O_3^{\bullet-}$ anion radicals rapidly split into $O^{\bullet-}$ radicals and O_2 molecules or reacted with H_2O to generate $OH^\bullet$ radicals, OH^- ions, and O_2 molecules. These reaction steps are shown in Table 1, and the stoichiometry of TiO_2 /UV/ O_3 reaction for hydroxyl radical was shown in the third column. In accordance with this stoichiometry, one O_3 molecule and one electron-hole pair could generate two hydroxyl radicals and one O_2 molecule. The ratio of “($OH^\bullet$ product)/(electron-hole pairs consumption)” of O_3 pathway (equal to 2) was higher than that of O_2 pathway (equal to 4/3). Therefore, in the presence of ozone, the photocatalytic reaction could generate more hydroxyl radicals via the TiO_2 /UV/ O_3 reaction. And these added hydroxyl radicals could enhance the toluene oxidation rates and the CO_2 -yield rates.

3.6. Reaction mechanisms and kinetics of UV/ O_3 reaction

The possible reaction mechanisms of gas-phase UV/ O_3 chain reactions are shown as the following equations [1,32]:

where RH represents toluene; M is the background molecule (O_2 and N_2). Using the pseudo-steady state approximation (PSSA) to deal with the free radical intermediates ($O(^1D)$, and $OH^\bullet$), we have:

$$\begin{aligned} \frac{dC_{\text{toluene}}}{dt} &= r_{UV/O_3} \\ &= 2k_1 \times \frac{[(k_3 + k_4)/k_8]C_{\text{toluene}}}{1 + [(k_3 + k_4)/k_8]C_{\text{toluene}}} \\ &\quad \times \frac{[k_2/(k_9C_M)]C_w}{1 + [k_2/(k_9C_M)]C_w} \times C_{O_3} \\ &= 2k_1 \times \frac{k'_2C_{\text{toluene}}}{1 + k'_2C_{\text{toluene}}} \times \frac{k'_3C_w}{1 + k'_3C_w} \times C_{O_3} \end{aligned} \quad (13)$$

where C_{toluene} is the toluene concentration; r_{UV/O_3} is the toluene oxidation rate of UV/ O_3 reaction; k_1 – k_4 , k_8 , and k_9 are the rate constants of equations (12.1)–(12.4) and (12.8)–(12.9); C_w is the humidity; C_M is the concentration of the background molecule; $k'_3 = k_2/(k_9C_M)$; $k'_2 = (k_3 + k_4)/k_8$; $k_4 = (0.1/0.9) \times k_3$.

According to Eq. (13), the TOR of UV/ O_3 reaction was proportional to ozone concentration, which was consistent with the result in Fig. 7. Rearranging Eq. (13), we have:

$$\frac{1}{r_{UV/O_3}} = \frac{1}{2k_1C_{O_3}} \times \left(\frac{1}{k'_2C_{\text{toluene}}} + 1 \right) \times \left(\frac{1}{k'_3C_w} + 1 \right) \quad (14)$$

In accordance with Eq. (14), the plots of $1/r_{UV/O_3}$ versus each of $1/C_{\text{toluene}}$ and $1/C_w$ were linear with positive slopes and intercepts. The fitness of experimental data in Eqs. (13) and (14) is shown in Figs. 7 and 9, respectively, yields the values of $k_1 = 8.14 \times 10^{-4} \mu\text{-mol-m}^{-3}\text{-s}^{-1}/\text{ppb-O}_3$, $k'_2 = 0.252 \text{ ppm}^{-1}$,

Fig. 9. Relation between $1/r_{\text{UV/O}_3}$ and $1/C_{\text{toluene}}$, and $1/C_w$.

and $k'_3 = 1.178 \times 10^{-4} \text{ ppm}^{-1}$. Therefore, the rate equation of UV/O₃ reaction can be expressed as the following equation:

$$r_{\text{UV/O}_3} = 1.628 \times 10^{-3} \times \frac{0.252 C_{\text{toluene}}}{1 + 0.252 C_{\text{toluene}}} \times \frac{1.178 \times 10^{-4} C_w}{1 + 1.178 \times 10^{-4} C_w} \times C_{\text{O}_3} \quad (15)$$

4. Conclusions

The TORs of TiO₂/UV/O₃, TiO₂/UV, and UV/O₃ reactions showed positive correlation with toluene concentration and gas flow rate. Similarly, the CO₂ yield rates and IYRs of TiO₂/UV and TiO₂/UV/O₃ reactions increased with toluene concentration and gas flow rate. However, the toluene conversion decreased when the toluene concentration increased. This designates that the TiO₂/UV/O₃, TiO₂/UV, and UV/O₃ reactions may be more suitable for treating VOCs contaminations of low concentration than for that of high concentration. The TORs and CO₂ yield rates of TiO₂/UV/O₃ reaction were higher than those of TiO₂/UV reaction. This fact indicates that the TiO₂/UV/O₃ reaction was more efficient than the TiO₂/UV reaction for removing VOCs pollutants, particularly for treating those of lower concentration, since the IYRs of TiO₂/UV/O₃ reaction was $\leq 0.23 \mu\text{g}/\text{m}^2\text{-s}$ when toluene $\leq 2 \text{ ppm}$. The experimental result showed that the kinetics of TiO₂/UV/O₃ and TiO₂/UV reactions fits the L–H rate form.

Because water molecule was involved in the formation of hydroxyl radical and the competitive adsorption, humidity has a dual effect on the TOR and CO₂ yield rate of TiO₂/UV reaction. Increase of humidity had a negative effect on the ORE of TiO₂/UV/O₃ reaction. The TORs of TiO₂/UV/O₃ and UV/O₃ reactions were proportional to ozone concentrations, and the enhancement index of O₃ of TiO₂/UV/O₃ and UV/O₃ reactions were 7.49×10^{-6} and $5.71 \times 10^{-6} \mu\text{-mol-m}^{-2}\text{-s}^{-1}/\text{ppb-O}_3$, respectively. The ORE of TiO₂/UV/O₃ reaction ranged from 38.1 to 99.5%, and showed positive correlations with toluene concentration and retention time, and showed negative

correlations with humidity and O₃ concentration. The kinetic of ozone removals of TiO₂/UV/O₃ reaction fits the L–H rate form. The ORE of UV/O₃ reaction increased with retention time and humidity. The ozone removals of UV/O₃ reaction were first order regarding ozone concentration.

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References

- [1] H.J. Seinfeld, S.N. Pandis, *Atmospheric Chemistry and Physics*, John Wiley & Sons Inc., New York, 1998.
- [2] Y.M. Kim, S. Harrad, R.M. Harrison, *Environ. Sci. Technol.* 35 (2001) 97.
- [3] J.L. Repace, *Environ. Int.* 8 (1982) 21.
- [4] J. Peral, X. Domènech, D.F. Ollis, *J. Chem. Technol. Biotechnol.* 70 (1997) 117.
- [5] L.M. Sattler, H.M. Liljestrand, *J. Air Waste Manage. Assoc.* 53 (2003) 3.
- [6] J. Zhao, X. Yang, *Build. Environ.* 30 (2003) 645.
- [7] A.J. Maira, K.L. Yeung, J. Soria, J.M. Coenado, C. Belver, C.Y. Lee, V. Augugliaro, *Appl. Catal. B: Environ.* 29 (2001) 327.
- [8] M. Lewandowski, D.F. Ollis, *Appl. Catal. B: Environ.* 43 (2003) 309.
- [9] E. Piera, J.A. Ayllón, X. Domènech, J. Peral, *Catal. Today* 76 (2002) 259.
- [10] L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, *J. Catal.* 196 (2000) 253.
- [11] M.L. Sauer, D.F. Ollis, *J. Catal.* 163 (1996) 215.
- [12] M.C. Blount, J.L. Falconer, *Appl. Catal. B: Environ.* 39 (2002) 39.
- [13] R. Méndez-Román, N. Cardona-Matínez, *Catal. Today* 40 (1998) 353.
- [14] S.B. Kim, C.H. Sung, *Appl. Catal. B: Environ.* 35 (2002) 305.
- [15] R.M. Alberici, W.F. Jardim, *Appl. Catal. B: Environ.* 14 (1997) 58.
- [16] W. Wang, L.-W. Chiang, Y. Ku, *J. Hazard. Mater. B* 101 (2003) 133.
- [17] J. Jeong, K. Sekiguchi, K. Sakamoto, *Chemosphere* 57 (2004) 663.
- [18] Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Toluene (Update)*, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA, 1994.
- [19] A.P. Jones, *Atmos. Environ.* 33 (1999) 4535.
- [20] D.W. VanOsdell, *ASHRAE Trans.* 100 (1994) 511.
- [21] I. Andersen, G.R. Lundqvist, L. Molhave, *Scand. J. Work Environ. Health* 9 (1983) 405.
- [22] J. Baelum, I. Andersen, G.R. Lundqvist, *Scand. J. Work Environ. Health* 11 (1985) 271.
- [23] D. Echeverria, L. Fine, G. Langolf, A. Schork, C. Sampaio, *Br. J. Ind. Med.* 46 (1989) 483.
- [24] H. Einaga, S. Futamura, T. Ibusuki, *Appl. Catal. B: Environ.* 38 (2002) 215.
- [25] R.H. Perry, D.W. Green, J.O. Maloney, *Perry's Chemical Engineers' Handbook*, seventh ed., McGraw-Hill, New York, 1997.
- [26] Y. Luo, D.F. Ollis, *J. Catal.* 163 (1996) 1.
- [27] T. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223.
- [28] P. Pichat, J. Disdier, C. Hoang-Van, D. Mas, G. Goutailler, C. Gaysse, *Catal. Today* 63 (2000) 363.
- [29] H. Al-Ekabi, B. Butters, D. Delany, W. Holden, T. Powell, J. Story, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier Science Publishers B.V., Amsterdam, 1993, pp. 719–725.
- [30] A.W. Adamson, *Physical Chemistry of Surfaces*, fourth ed., John Wiley & Sons, New York, 1982.
- [31] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B: Environ.* 20 (1999) 15.
- [32] M. Bhowmick, M.J. Semmens, *Wat. Res.* 28 (1994) 2407.