Journal of Photochemistry and Photobiology A: Chemistry 156 (2003) 189–194

www.elsevier.com/locate/jphotochem

A comparative study on decomposition of gaseous toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV

Zhang Pengyi*, Liang Fuyan, Yu Gang, Chen Qing, Zhu Wanpeng

Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Received 13 September 2002; received in revised form 22 November 2002; accepted 4 December 2002

Abstract

The degradations of trace toluene (1.0–20 ppmv) in the gas-phase by O_3/UV, TiO_2/UV and O_3/TiO_2/UV were studied. The effects of the inlet concentration of toluene, flow rate (retention time), relative humidity and ultraviolet (UV) light wavelength on the conversion of toluene in the three processes were examined, respectively. The experimental results showed that the addition of ozone to the photocatalysis process could greatly increase the conversion of toluene. In particular, the deactivation of the photocatalyst at high inlet concentration of toluene was avoided in the presence of ozone. The O_3/TiO_2/UV process was more efficient than the O_3/UV in decomposing toluene in most cases. And the residual ozone concentration in the O_3/TiO_2/UV process was much lower than that in the O_3/UV process. Among them, combined photocatalysis and ozonation (O_3/TiO_2/UV) was the most prospective process for removing trace volatile organic compounds (VOCs) such as in indoor air.

Keywords: Photocatalysis; Ozonation; Toluene; Titanium dioxide; Ozone; Catalyst deactivation; Indoor air

1. Introduction

The pollution of indoor volatile organic compounds (VOCs) has been increasingly concerned in recent years. Conventional indoor air purification methods such as filtration, activated carbon adsorption and ionize show their drawbacks in removing indoor VOCs. Heterogeneous photocatalysis is regarded as a promising technique for purifying indoor VOCs. A large quantity of work has been devoted in this field in the past decade [1–12]. It seems that many kinds of air contaminants, such as alkanes, alkenes, alcohols, ketones, chlorinated hydrocarbons, aromatics, etc. could be successfully degraded in the photocatalysis process. However, the application of this method has been limited with the problem of deactivation of photocatalyst and refractory reaction intermediates [13–21]. For example, in the study of photocatalytic oxidation of heteroatom organics, Peral and Ollis [13,14] found irreversible catalyst deactivation in the case of decamethyltetrasiloxane, pyrrole and indole. Larson and Falconer [15] observed that during trichloroethylene (TCE) photo-oxidation dichloroacetyl chloride (DCAC) formed and strongly adsorbed to TiO_2, which resultantly reduced TCE adsorption. Alberici and Jardim [16] also detected several by-products like phosgene, DCAC and trichloroacetyl chloride while photocatalytically oxidizing tetrachloroethylene, TCE, chloroform and dichloromethane using on-line mass spectrometry and MS^2. Similarly, during gas-phase photocatalytic oxidation of toluene, benzoic acid accumulated on catalyst and catalyst deactivation occurred [17–20]. The buildup of *o*-toluic acid on the catalyst surface may also be responsible for the apparent loss of catalyst activity during the photocatalytic oxidation of dilute *o*-xylene in air [21].

At present, although there are many studies on the influence of addition of inorganic oxidant on photocatalytic oxidation of aqueous contaminants [22–30], the studies in gas-phase is rare [31]. It was demonstrated that the photocatalytic oxidation rate of aqueous contaminants and TOC reduction rate were greatly increased with addition of oxidants including ozone [22–27]. Shen and Ku [31] studied the decomposition of gas-phase TCE by the TiO_2/UV process in the presence of ozone. They found the addition of ozone into the TiO_2/UV/TCE system with 254 or 365 nm UV lamp reduced the removal of TCE, possibly because excessive ozone molecules could scavenge hydroxyl radicals produced from the excitation of TiO_2 by UV radiation.

Toluene is a major indoor and industrial air pollutant, and it was recommended as one of eight representative indoor VOCs by a proposed ASHRAE test method for determining

---

* Corresponding author. Tel.: +86-10-6278-4527; fax: +86-10-6279-4006.
E-mail address: zpy@mail.tsinghua.edu.cn (Z. Pengyi).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1010-6030(02)00432-X

the effectiveness and capacity of gas-phase air filtration equipment for indoor air applications [32]. In addition, catalyst deactivation usually occurred during photocatalytic oxidation of gaseous toluene [17–20]. Thus, in the present paper, toluene was chosen as the model VOC to investigate the effect of added ozone on its photocatalytic oxidation. The degradation efficiency of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV under various conditions was examined and compared. Considering its application in indoor air purification, low initial concentration of toluene (as low as 1.0 ppmv) was adopted in this work.

2. Experimental

2.1. Photocatalyst preparation

The TiO_2 photocatalyst film used in this study was prepared by a modified sol–gel method. The yellowish titanium dioxide sol was prepared by mixing tetrabutylorthotitanate ($Ti(OC_4H_9)_4$, C.P.), acetyl acetone (C_5H_8O, A.R.), deionized water and *n*-propanol (C_3H_8O, A.R.) with a volumetric ratio of 1:0.3:0.4:7 at room temperature. Here acetyl acetone was a chelating agent and was used to control the hydrolysis of tetrabutylorthotitanate. Then the nanometer carbon black powder (Degussa Printex L6, the primary particle size 18 nm and BET surface 265 m^2/g) was added in the sol at the ratio of 1 ml $Ti(OC_4H_9)_4$:2.35 mg carbon black. The prepared mixture could remain stable for months at ambient temperature. While used for coating, the mixture was blend uniformly by ultrasonic for 10 min. Then the polished aluminum sheet was dipped in the mixture. After immersion, the coated aluminum sheet was dried at room temperature and then baked at 500 °C for 2 h. After the aluminum sheet was coated seven times (which was previously optimized), a thin TiO_2 photocatalyst film was coated. The TiO_2 film was very stable and durable without any loss during application.

2.2. Experimental set-up

A schematic diagram of the experimental system for photo-oxidation is shown in Fig. 1(a). The saturated toluene gas was prepared by passing air through a thermostated saturator containing liquid toluene. The humidified air stream was generated by bubbling air through a thermostated glass bottle containing deionized water. Then the saturated toluene gas was mixed and diluted with humidified air stream at the gas mixer. The obtained toluene gas stream entered the photoreactor at flow rates between 1.0 and 5.0 l/min, inlet toluene concentrations between 1.0 and 20 ppmv and relative humidity (RH) in the range of 20–60%. Feed toluene concentrations and relative humidity were set by varying the ratio of gas flow rates and/or varying the saturator temperature. The ozone air stream (50 ml/min) from ozone generator was directed into the photoreactor with the specified production of 10 mg/h.

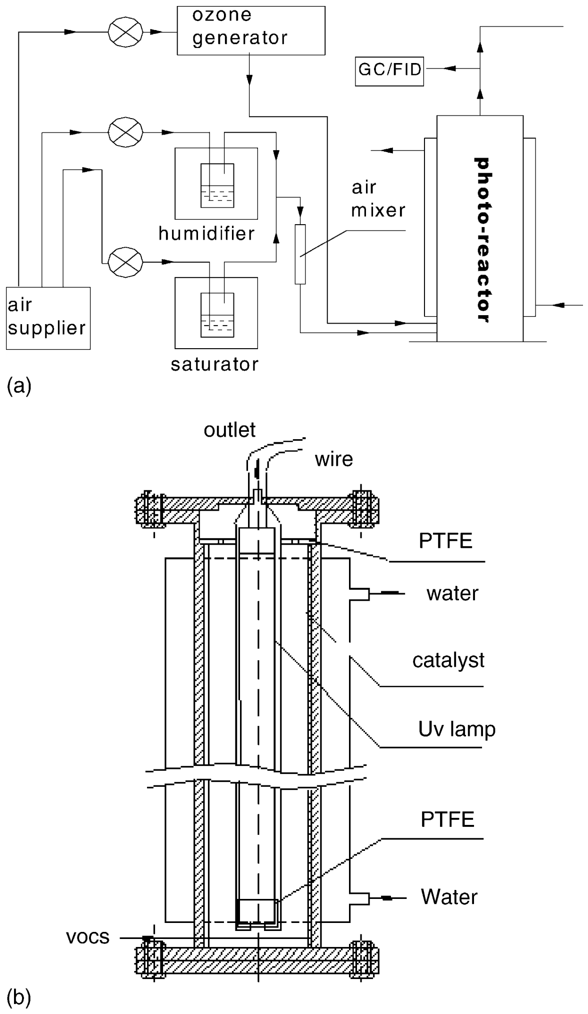

Fig. 1. (a) Schematic diagram of experimental system for photo-oxidation. (b) Schematic diagram of photoreactor designed for this application.

The cylindrical photoreactor shown in Fig. 1(b) was made of stainless steel with a diameter of 64 mm and a length of 530 mm, with effective volume 1.44 l. The outside of the photoreactor was a cooling water sleeve to maintain stable reaction temperature (20–22 °C). Illumination was generally provided by a 15 W germicidal lamp with maximum light intensity output at 254 nm. Only for comparing the effect of different UV wavelengths, a 15 W black light lamp with a maximum at 365 nm was used for replacing the germicidal lamp. The lamp was fixed at the center of the photoreactor without any quartz tube protection. The TiO_2 coated aluminum sheet (length 440 mm, height 201 mm and thickness 0.18 mm) closely attached the interior surface of the photoreactor. For O_3/UV process, no catalyst or aluminum sheet was used.

2.3. Analyses and procedures

The concentration of toluene was analyzed on-line by a HP5890II model gas chromatograph with a flame ionization detector (FID). The gas samples were collected periodically using a six-way valve with a gas sampling loop (500 μl) and transferred into a packed column (AT OV101) with a diameter of 3 mm and a column length of 2 m. The gas chromatograph oven temperature was held at 105 °C and the detector temperature maintained constant at 250 °C. In this work, no intermediates from the degradation of toluene were identified by the gas chromatograph probably due to its detection limit. The concentrations of ozone in influent and effluent streams were determined by iodometry method. The humidity analyzer was used to monitor relative humidity of the mixed air stream.

After the reactor outlet concentration equaled the reactor inlet concentration, the lamp was turned on. And after the photocatalytic (TiO_2/UV) or photolytic (UV) steady state reached, it was kept lasting for at least 150 min. Then the ozone generator was turned on and ozone air stream entered the photoreactor. The ozone enhanced photo-oxidation (O_3/TiO_2/UV or O_3/UV) steady state was reached usually after a few minutes. Similarly, it also lasted at least 150 min.

The conversion C (%) of toluene or ozone was calculated as follows:

$$C = (C_{\mathrm{i}} - C_{\mathrm{o}}) \times \frac{100}{C_{\mathrm{i}}}$$

where C_{i} is the inlet concentration, and C_{o} the outlet concentration at steady state.

3. Results and discussion

In the blank tests, the photolysis of toluene by 254 or 365 nm UV irradiation alone was found to be trivial. The conversion of toluene by ozone alone or combined with TiO_2 without irradiation was less than 5% under the experimental condition studied in this work. Thus, the conversion of toluene contributed by O_3, O_3/TiO_2, and 254 or 365 nm direct photolysis during the TiO_2/UV, O_3/UV, O_3/TiO_2/UV processes can be neglected.

3.1. Effect of inlet concentration of toluene

The effect of inlet concentrations of toluene on its decomposition is shown in Fig. 2(a). The results correspond to the flow rate of 3 l/min (retention time 28.8 s) and relative humidity of 35%. It was found that all the conversions of toluene in the O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes were decreased when the inlet concentration of toluene increased. However, there are big differences among them. As for the O_3/UV process, the conversion of toluene almost decreased linearly in the range of 5–20 ppmv. The conversion of toluene in the O_3/UV process decreased so fast that it was much lower than that in the O_3/TiO_2/UV process when the inlet concentration was larger than 5 ppmv. It demonstrated that the presence of TiO_2 catalyst could greatly enhance the O_3/UV process. As for TiO_2/UV process, the conversion of toluene decreased very slowly when the inlet concentration was raised from 1.0 to 10 ppmv. And at higher inlet concentrations the conversion first dropped quickly with reaction time and then maintained at low level stably within experimental time. The conversion by TiO_2/UV dropped rapidly at high concentrations is due to the deactivation of TiO_2 photocatalyst, which turned from white to brown. Though in the O_3/TiO_2/UV process the conversion of toluene also decreased with increase of inlet concentration, it was generally 10% higher than that in the TiO_2/UV process at lower concentrations and deactivation of photocatalyst did not occur at higher concentrations. Actually as shown in Fig. 2(b), the addition of ozone could reactivate the photocatalyst, which was deactivated in the TiO_2/UV process at higher concentrations. The results indicate the addition of ozone strongly improve TiO_2/UV and avoid the photocatalyst deactivation at higher concentration.

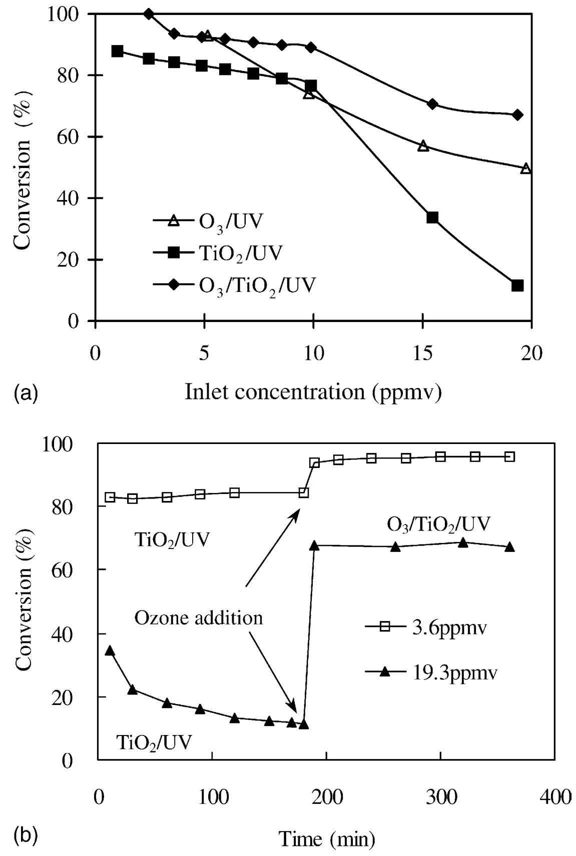

Fig. 2. (a) Effect of inlet concentration on the conversion of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes. Experimental conditions: 254 nm, flow rate 3 l/min, RH 35%. (b) Effect of ozone addition on the conversion of toluene by TiO_2/UV. Experimental conditions: 254 nm, flow rate 3 l/min, RH 35%.

3.2. Effect of flow rate

Fig. 3 shows the effect of flow rate on the decomposition of toluene conducted at the inlet concentration of 4.7–5.2 ppmv and relative humidity of 35%. It was found that

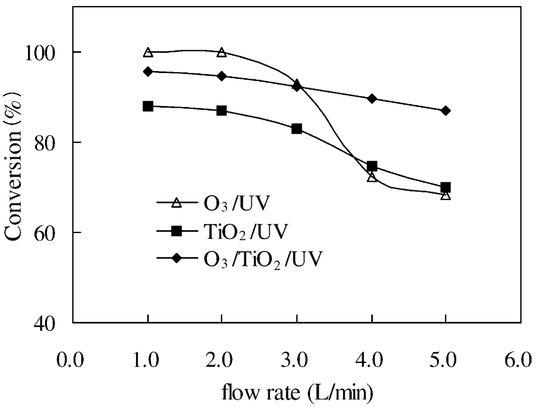

Fig. 3. Effect of flow rate on the conversion of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes. Experimental conditions: 254 nm, inlet concentration 4.7–5.2 ppmv, RH 35%.

the conversions of toluene decreased in all processes with the flow rate increasing from 1.0 to 5.0 l/min corresponding to the retention time decreasing from 86.4 to 17.3 s. However, though at low flow rate ($\leq$3 l/min) the conversion rate in the O_3/UV process was the highest, it dropped dramatically and became the lowest at the higher flow rate. The conversion rate decreased more slowly in O_3/TiO_2/UV than that in TiO_2/UV with increase of flow rate. The reason of dramatic drop of conversion in O_3/UV was that the retention time and the concentration of ozone were greatly reduced when the flow rate increased. For the TiO_2/UV process, the overcast of reaction intermediates decomposed incompletely led to the decrease of efficiency. Compared with the other two processes, O_3/TiO_2/UV was more efficient in decomposing toluene at high flow rate.

3.3. Effect of relative humidity of air stream

As previously reported [4,18], the relative humidity could significantly affect TiO_2/UV process. Considering the typical and comfortable humidity in indoor air, this work studied the effects of humidity in the range of 20–60% on the decompositions of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV. The results are shown in Fig. 4. It was found that the O_3/UV process was most affected by the change of relative humidity. The conversion of toluene by O_3/UV first increased greatly with increase of humidity up to 40% and then slightly decreased at higher humidity, which meant that 40% was the optimal humidity for O_3/UV process under the experimental conditions. As for the processes of TiO_2/UV and O_3/TiO_2/UV, the effect of humidity is similar to that on O_3/UV, and the optimal humidity is about 35%. However, TiO_2/UV and O_3/TiO_2/UV were not so significantly affected by change of relative humidity as O_3/UV. In the range studied in this work, the conversions of toluene were between 78 and 83% for TiO_2/UV and between 90 and 93% for O_3/TiO_2/UV. These results indicated that O_3/TiO_2/UV process was most slightly affected by change of relative humidity.

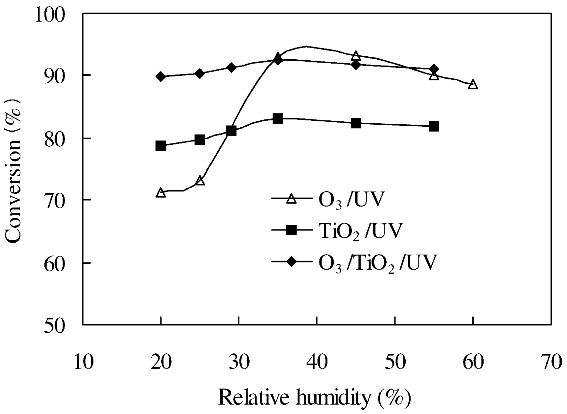

Fig. 4. Effect of the RH on the conversion of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes. Experimental conditions: 254 nm, inlet concentration 4.9–5.4 ppmv, flow rate 3 l/min.

The effect of humidity on the decomposition of toluene was complex. From the experiment results, it was found that the effect of humidity on the decomposition of toluene by the TiO_2/UV, O_3/UV and O_3/TiO_2/UV processes was two-sided: a little humidity can improve the decomposition of toluene while too much humidity will depress the decomposition. It can be explained that humidity can enhance the generation of hydroxyl radicals to decompose more contaminant and at the same time it will impede the contact of toluene with photocatalyst and ozone to decrease the decomposition consequently.

3.4. Effect of UV light wavelength

In this work, a 15 W 254 nm germicidal lamp and a 15 W 365 nm black light lamp were used as the UV irradiation source, respectively. The effect of UV light wavelength on the decomposition of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes is shown in Fig. 5. It was found that in all these three processes the conversion irradiated with 254 nm UV lamp was much higher than that with

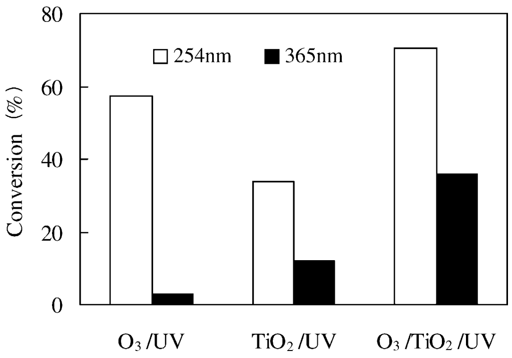

Fig. 5. Effect of UV wavelength on the conversion of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes. Experimental conditions: inlet concentration 15–15.3 ppmv, flow rate 3 l/min, RH 35%.

365 nm. In the $O_3/TiO_2/UV$ process, 92.5% of toluene was decomposed when irradiated with 254 nm UV lamp, while only 63.5% was decomposed when irradiated with 365 nm UV lamp. In O_3/UV and TiO_2/UV processes, the differences of degradation efficiency between 254 nm UV lamp and 365 nm UV lamp were much greater, reaching 51 and 82%, respectively. It was also found that the conversion of toluene by $O_3/TiO_2/UV$ was higher than the sum of conversion by O_3/UV and TiO_2/UV when irradiated with 365 nm UV lamp, however it was not the case when irradiated with 254 nm.

The significant differences resulted from 254 and 365 nm UV lamps are mainly due to two reasons. The first one is that the 254 nm lamp irradiated stronger UV intensity (about 58 W/m^2 on its surface) than that by 365 nm (30 W/m^2 on its surface). Thus, much more photons with higher energy were irradiated by the 254 nm UV lamp, which can basically explain why the TiO_2/UV was much more efficient with 254 nm UV lamp than with 365 nm lamp. The second one is their different abilities in decomposing ozone. Ozone strongly adsorbs 254 nm light and decompose to form hydroxyl radical accordingly, while the 365 nm light cannot efficiently decompose ozone so that no reaction between ozone and 365 nm light. Thus, the O_3/UV is more efficient while irradiated with 254 nm UV lamp.

As for the ozone enhanced photocatalysis ($O_3/TiO_2/UV$), the generation of hydroxyl radical can be generally described as follows:

$$\mathrm{TiO_2} + h\nu \rightarrow \mathrm{h^+} + \mathrm{e^-} \qquad \text{(R1)}$$

$$\mathrm{h^+} + \mathrm{OH^-} \rightarrow \mathrm{OH^\bullet} \qquad \text{(R2)}$$

$$\mathrm{h^+} + \mathrm{H_2O} \rightarrow \mathrm{OH^\bullet} + \mathrm{H^+} \qquad \text{(R3)}$$

$$\mathrm{O_3} + \mathrm{e^-} \rightarrow \mathrm{O_3}^{\bullet -} \qquad \text{(R4)}$$

$$\mathrm{H^+} + \mathrm{O_3}^{\bullet -} \rightarrow \mathrm{HO_3}^\bullet \qquad \text{(R5)}$$

$$\mathrm{HO_3}^\bullet \rightarrow \mathrm{O_2} + \mathrm{OH^\bullet} \qquad \text{(R6)}$$

$$\mathrm{O_3} + h\nu\,(\lambda < 310\,\mathrm{nm}) \rightarrow \mathrm{O^\bullet} + \mathrm{O_2} \qquad \text{(R7)}$$

$$\mathrm{O^\bullet} + \mathrm{H_2O} \rightarrow 2\mathrm{OH^\bullet} \qquad \text{(R8)}$$

If the irradiation is provided by 254 nm light, ozone acts not only as electron acceptor but also as a source to generate hydroxyl radical. However, as Shen and Ku [31] quoted that ozone could also be a scavenger to hydroxyl radical [33] expressed as reaction (9), it is reasonable that the conversion by $O_3/TiO_2/UV$ irradiated with 254 nm lamp was smaller than the sum of TiO_2/UV and O_3/UV:

$$\mathrm{O_3} + \mathrm{OH^\bullet} \rightarrow \mathrm{HO_2}^\bullet + \mathrm{O_2} \qquad \text{(R9)}$$

If irradiated with 365 nm light, ozone will only act as electron acceptor, reaction (7) will not occur. And maybe only a very limited hydroxyl radical was produced and reaction (9) was not important under experimental condition, so the conversion by $O_3/TiO_2/UV$ irradiated with 365 nm light was much larger than the sum of TiO_2/UV and O_3/UV.

In addition to above mentioned two reasons, the different effects of 254 and 365 nm light on photolysis of toluene were also considered. However, unlike under lower flow rate and longer retention time, at experimental conditions in this study the photolysis of toluene was trivial whatever under 254 or 365 nm illumination. Thus, the excitation of toluene under 254 nm was thought to be a minor contribution.

3.5. *Comparison of outlet concentration of ozone*

Ozone itself is harmful to human health. The WHO recommended ozone limit in indoor air is as low as 0.05 ppmv. The residual ozone concentrations from the O_3/UV and $O_3/TiO_2/UV$ processes under different conditions are compared in Table 1. It was found that the outlet concentration of ozone from the $O_3/TiO_2/UV$ process was only about 40% of that from the O_3/UV process in most cases, which demonstrated that the $O_3/TiO_2/UV$ process not only improved the capabilities of O_3/UV and TiO_2/UV processes for decomposing air contaminants but also reduced the hazardousness of O_3/UV process by lowering the residual ozone concentration. The lower residual ozone from $O_3/TiO_2/UV$ is understandable, because in this process ozone is consumed through three reactions: decamped by UV light, acting as scavenger to hydroxyl radical and as electron acceptor, while in the O_3/UV process the last reaction does not happen. As seen from Table 1, the residual ozone is little affected by the relative humidity and inlet concentration, while it is greatly affected by the flow rate. The simple reason is that the ozone is diluted. Much lower ozone concentration could be expected at larger flow rate than that conducted in this work.

Table 1
Outlet concentrations of ozone in O_3/UV and $O_3/TiO_2/UV$ processes

Inlet concentration of toluene (ppmv)	Flow rate (l/min)	RH (%)	Inlet concentration of ozone (ppmv)	Outlet concentration of ozone (ppmv)		Conversion of ozone (%)		Conversion of toluene (%)	
				O_3/UV	$O_3/TiO_2/UV$	O_3/UV	$O_3/TiO_2/UV$	O_3/UV	$O_3/TiO_2/UV$
4.7–5.2	1.0	35	71.0	6.27	1.60	91.2	97.8	100	95.7
4.7–5.2	3.0	35	23.6	2.00	0.81	91.5	96.6	93.0	92.5
4.7–5.2	5.0	35	14.2	1.03	0.43	92.7	97.0	68.2	87.1
4.7–5.2	3.0	20	23.6	2.84	0.74	88.0	96.9	71.2	89.9
4.7–5.2	3.0	55	23.6	2.19	0.83	90.7	96.5	90.1	91.1
19–20	3.0	35	23.6	1.41	0.81	94.1	96.6	49.7	67.1

4. Conclusion

The decompositions of low-level gaseous toluene in the O_3/UV, TiO_2/UV and O_3/TiO_2/UV processes have been studied and compared. The O_3/UV process was most affected by inlet concentration, flow rate and humidity. The conversion of toluene at low level slowly decreased with increase of inlet concentration in the TiO_2/UV and O_3/TiO_2/UV processes, not obeying the first order kinetics. Ozone addition greatly enhanced the capability of TiO_2/UV for decomposing toluene especially at high inlet concentration and large flow rate, at the same time it avoided the deactivation of photocatalyst. The TiO_2/UV and O_3/TiO_2/UV processes were slightly affected by the relative humidity in the range of 20–55%, the optimal humidity was around 35% under experimental conditions. Due to difference in decomposing ozone, O_3/TiO_2/UV irradiated with 254 nm light was more efficient than irradiated with 365 nm light. Ozone would scavenge hydroxyl radical so that the conversion by O_3/TiO_2/UV irradiated with 254 nm was less than the sum of TiO_2/UV and O_3/UV. The results obtained have shown that the O_3/TiO_2/UV process was more efficient than the O_3/UV and TiO_2/UV processes and was the most steady and applicable technology among them, avoiding photocatalyst deactivation and reducing residual ozone concentration.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grant Nos. 59908004 and 50178038), to whom we are grateful.

References

[1] L.A. Dibble, G.B. Raupp, Catal. Lett. 4 (1990) 345.
[2] J. Peral, D.F. Ollis, J. Catal. 136 (1992) 554.
[3] D.F. Ollis, H. Al-Ekabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[4] T.N. Obee, R.T. Brown, Environ. Sci. Technol. 29 (1995) 1223.
[5] W.A. Jacoby, D.M. Blake, J.A. Fennell, J.E. Boulter, L.M. Vargo, M.C. George, S.K. Dolberg, J. Air Waste Manage. 46 (1996) 891.
[6] R.M. Alberici, W.E. Jardim, Appl. Catal. B: Envrion. 14 (1997) 55.
[7] J. Peral, X. Domènech, D.F. Ollis, J. Chem. Technol. Biotechnol. 70 (1997) 117.
[8] M.C. Canela, R.M. Alberici, R.C.R. Sofia, M.N. Eberlin, W.F. Jardim, Environ. Sci. Technol. 33 (1999) 2788.
[9] T. Noguchi, A. Fujishima, Environ. Sci. Technol. 32 (1998) 3831.
[10] A.V. Vorontsov, I.V. Stoyanova, D.V. Kozlov, V.I. Simagina, E.N. Savinov, J. Catal. 189 (2000) 360.
[11] A.J. Maira, K.L. Yeung, J. Soria, J.M. Coronado, C. Belver, C.Y. Lee, V. Augugliaro, Appl. Catal. B: Envrion. 29 (2001) 327.
[12] J. Shang, Y. Du, Z. Xu, Chemosphere 46 (2002) 93.
[13] J. Peral, D.F. Ollis, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 741.
[14] J. Peral, D.F. Ollis, J. Mol. Catal. A: Chem. 115 (1997) 347.
[15] S.A. Larson, J.L. Falconer, Appl. Catal. B: Environ. 4 (1994) 325.
[16] R.M. Alberici, M.A. Mendes, W.F. Jardim, M.N. Eberlin, J. Am. Soc. Mass Spectrosc. 9 (1998) 1321.
[17] R. Mendez-Roman, N. Cardona-Martinez, Catal. Today 40 (1998) 353.
[18] Y. Luo, D.F. Ollis, J. Catal. 163 (1996) 1.
[19] L.X. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, J. Catal. 196 (2000) 253.
[20] S.A. Larson, J.L. Falconer, Catal. Lett. 44 (1997) 57.
[21] M.M. Ameen, G.B. Raupp, J. Catal. 184 (1999) 112.
[22] L. Sanchez, J. Peral, X. Domènech, Appl. Catal. B: Environ. 19 (1998) 59–65.
[23] M. Klare, G. Waldner, R. Bauer, H. Jacobs, Chemosphere 38 (1999) 2013.
[24] E. Piera, C.J. Calpe, E. Brillas, X. Domènech, J. Peral, Appl. Catal. B: Environ. 27 (2000) 169.
[25] P. Kopf, E. Gilbert, S.H. Eberle, J. Photochem. Photobiol. A: Chem. 136 (2000) 163.
[26] G.M. Sandra, S.F. Renato, D. Nelson, Chemosphere 40 (2000) 369.
[27] I.A. Balcioglu, N. Getoff, M. Bekbölet, J. Photochem. Photobiol. A: Chem. 135 (2000) 229.
[28] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Appl. Catal. B: Environ. 17 (1998) 347.
[29] Y. Wang, C.-S. Hong, Water Res. 33 (1999) 2031.
[30] B.J.P.A. Cornish, L.A. Lawton, P.K.J. Robertson, Appl. Catal. B: Environ. 25 (2000) 59.
[31] Y.S. Shen, Y. Ku, Chemosphere 46 (2002) 101.
[32] D.W. VanOsdell, ASHRAE Trans. 100 (1994) 511.
[33] P.T. Buckley, J.W. Birks, Atmos. Environ. 29 (1995) 2409.