VUV Photocatalytic Degradation of Toluene in the Gas Phase

Pengyi Zhang,* Juan Liu, and Zhongliang Zhang
Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, P. R. China

(Received July 7, 2004; CL-040801)

The photocatalytic degradation rate of gaseous toluene under irradiation of vacuum ultraviolet (185 nm) was 2–3 times faster than that under irradiation of 254 nm. The 185-nm VUV photolysis was greatly improved by the presence of TiO_2 photocatalyst.

The heterogeneous photocatalysis is considered as one of the most promising methods to decontaminate indoor pollutants such as volatile organic compounds (VOCs), bacteria, and allergen. Photocatalytic degradations of various kinds of VOCs and bacteria in the gas phase have been widely investigated in the past two decades.[1–3] And the commercial air purifiers based on photocatalysis have been on sale. However the deactivation of TiO_2 photocatalyst during VOCs degradation was reported frequently.[4,5] The main reason was the accumulation of intermediate on the surfaces of the photocatalyst because of its slow reaction rate. The combination of photocatalysis with microwave,[6] magnetic field,[7] or ozone[8] was investigated to enhance photocatalysis, which accordingly resulted in extra cost.

Vacuum ultraviolet (VUV) with high-energy photon (185 nm wavelength corresponds to a photon energy 6.7 eV) can break most chemical bonds. Under VUV irradiation, oxygen and water in air are dissociated and accordingly ozone and hydroxyl radical are formed. In the meanwhile, VOCs may also be photolyzed by VUV directly. Though low-pressure mercury lamp emitting 185-nm VUV was evaluated to generate ozone long before,[9] its feasibility for air purification was little investigated probably because of low radiation at 185 nm. We found that toluene, a typical indoor VOC, was effectively degraded by 185-nm VUV, furthermore the presence of TiO_2 greatly increased the degradation rate of toluene by VUV.

Photochemical reactions were conducted in a cylindrical reactor with diameter of 64 mm, length of 530 mm and effective volume 1.44 L, reported elsewhere.[8] A 15-W low-pressure mercury lamp emitting 254 and 185 nm was placed at the center of the reactor, ozone generated by this lamp depended on flow rate and humidity as shown in Figure 1. The same power lamp only emitting 254 nm was used for UV photocatalysis. The TiO_2 coated aluminum sheet (440 mm × 201 mm) was closely attached the interior surface of the reactor. The diluted toluene gas was continuously generated by blowing toluene in a saturator and detected with GC/FID.

Figure 2 clearly shows that toluene was degraded fastest by VUV photocatalysis (TiO_2/VUV) among three processes. The reaction rate by TiO_2/VUV continuously increased with increase of inlet concentration of toluene, which was in good agreement with Langmuir–Hinshelwood (L–H) model as shown in Figure 3 ($k = 51.8\,mg/m^3.min$, $K = 0.49\,m^3/mg$). On the contrary, the reaction rate reached a maximum in the VUV and TiO_2/UV (254 nm) processes and did not agree with L–H model. The reaction rate of TiO_2/VUV at inlet concentration 7 mg/m^3 was more than 20 mg/m^3.min, however it was only 10 mg/m^3.min or less for other two processes.

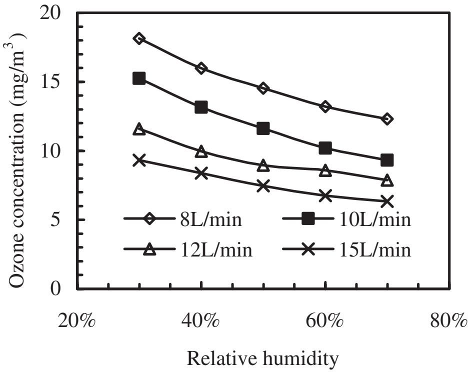

Figure 1. Ozone production by the VUV lamp.

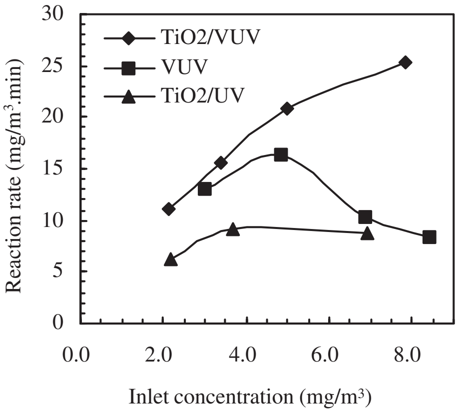

Figure 2. Variation of reaction rate with toluene concentration (Q = 12 L/min, RH = 35%).

In the VUV/TiO_2 process, toluene was degraded via multiple pathways: (1) direct photolysis resulting from 185-nm VUV absorption by toluene; (2) reactions with reactive species like atom oxygen and hydroxyl radical generated from water and oxygen dissociation by 185nm ($H_2O + 185\,nm \rightarrow H + OH$, $O_2 + 185\,nm \rightarrow 2\ O$, $O + H_2O \rightarrow 2\ OH$); (3) photocatalysis on the TiO_2 surface by 254 and 185 nm. Accordingly toluene degraded fastest in VUV/TiO_2 process. It was still not clear why in the VUV process the reaction rate decreased at higher toluene concentration. One possible reason was the competitive absorption of 185-nm light by toluene (ε at 185 nm is about $9000\,cm^{-1}M^{-1}$),[10] which consequently reduced the hydroxyl radical formation from water and oxygen dissociation.

Figure 4 shows the effect of relative humidity (RH) on the removal rate of toluene. VUV and TiO_2/UV were more signifi-

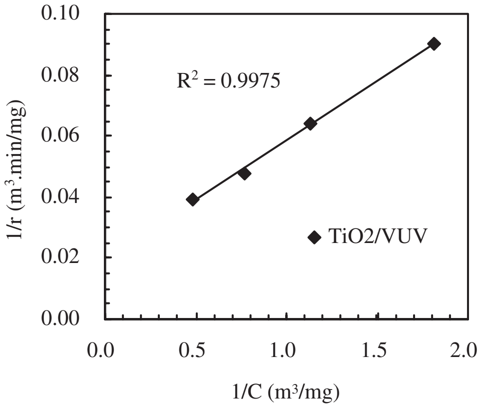

Figure 3. Plot of reciprocal of reaction rate (1/r) vs the reciprocal of toluene concentration (1/C).

cantly influenced than the TiO_2/VUV. It has been well demonstrated that in the TiO_2/UV process reaction rate firstly increased with RH increase and then decreased due to competition adsorption of water molecules with VOC on the TiO_2 surface.[11] The competitive adsorption of water reduced the reaction rate of toluene on TiO_2 surface. For VUV photolysis, though with RH increase less ozone was generated as shown in Figure 1, the removal rate of toluene increased greatly. It is understandable that with increase of humidity, more 185-nm photons were absorbed by water molecule and accordingly more hydroxyl radicals were generated, by which toluene degraded more effectively, and less photon was absorbed by oxygen molecule resulting in reduced ozone generation. In addition, more hydroxyl radicals were generated via reaction between water and atom oxygen resulting from oxygen dissociation by 185-nm light, while the ozone generation was reduced ($O + O_2 \rightarrow O_3$). For the TiO_2/VUV process, the removal rate increased more slowly than in VUV process with RH increase due to water competitive adsorption with toluene on TiO_2 surface.

This work was financially supported by NSFC (50178038, 59908004).

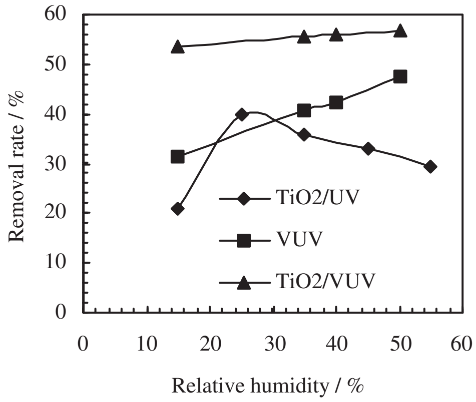

Figure 4. The effect of relative humidity on removal rate ($C_0 = 3.5$–$5.2\,mg/m^3$, $Q = 12\,L/min$).

References

1 W. A. Jacoby, D. M. Blake, J. A. Fennell, J. E. Boulter, L. M. Vargo, M. C. George, and S. K. Dolberg, *J. Air Waste Manage.*, **46**, 891 (1996).
2 J. Peral, X. Domenech, and D. F. Ollis, *J. Chem. Technol. Biotechnol.*, **70**, 117 (1997).
3 W. A. Jacoby, P. C. Maness, E. J. Wolfrum, D. M. Blake, and J. A. Fennell, *Environ. Sci. Technol.*, **32**, 2650 (1998).
4 S. A. Larson and J. L. Falconer, *Catatl. Lett.*, **44**, 57 (1997).
5 L. X. Cao, Z. Gao, S. L. Suib, T. N. Obee, S. O. Hay, and J. D. Freihaut, *J. Catal.*, **196**, 253 (2000).
6 S. Kataoka, D. T. Tompkins, W. A. Zeltner, and M. A. Anderson, *J. Photochem. Photobiol., A*, **148**, 323 (2002).
7 W. Zhang, X. X. Wang, and X. Z. Fu, *Chem. Commun.*, **2003**, 2196.
8 P. Y. Zhang, F. Y. Liang, G. Yu, Q. Chen, and W. P. Zhu, *J. Photochem. Photobiol., A*, **156**, 189 (2003).
9 J. M. Dohan and W. J. Masschelein, *Ozone: Sci. Eng.*, **9**, 315 (1987).
10 A. Bolovinos, J. Philis, E. Pantos, P. Tsekeris, and G. Andritsopoulos, *J. Chem. Phys.*, **75**, 4343 (1981).
11 T. N. Obee and R. T. Brown, *Environ. Sci. Technol.*, **29**, 1223 (1997).

Published on the web (Advance View) August 28, 2004; DOI 10.1246/cl.2004.1242