Study on photocatalytic degradation of several volatile organic compounds

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Abstract

The gas-phase photolytic and photocatalytic reactions of several aromatics and chlorohydrocarbons were investigated. The experimental results revealed that chlorohydrocarbons like trichloroethylene, dichloromethane and chloroform could be degraded through either photolysis or photocatalysis under irradiation of germicidal lamp, and the elimination rate of chlorohydrocarbons through photolysis was quicker than that through photocatalysis. UV light from a germicidal lamp could directly lead to degradation of toluene but could hardly act on benzene. The photodegradation rate for these volatile organic compounds (VOCs) through photolysis followed an order: trichloroethylene > chloroform > dichloromethane > toluene > benzene > carbon tetrachloride, and through photocatalysis followed: trichloroethylene > chloroform > toluene > dichloromethane > benzene > carbon tetrachloride. Besides, a series of modified TiO_2 photocatalysts were prepared by depositing noble metal, doping with transition metal ion, recombining with metal oxides and modifying with super strong acid. Activity of these catalysts was examined upon photocatalytic degradation of benzene as a typical compound that was hard to be degraded. It indicated that these modification methods could promote the activity of TiO_2 catalyst to different extent. The apparent zero-order reaction rate constant for degrading benzene over SnO_2/TiO_2 catalyst had the highest value, which was nearly three times as that over P25 TiO_2. But it simultaneously had the lowest rate for mineralizing the objective compound. In spite that Fe^{3+}/TiO_2 catalyst behaved slightly less active than SnO_2/TiO_2 for degradation of benzene, the mineralization rate over Fe^{3+}/TiO_2 was the highest one among the prepared catalysts.
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1. Introduction

A great deal of attention has been given to air quality. The use of photochemical conversion and photocatalytic oxidation technology to eliminate organic hazardous chemicals has attracted considerable interests in recent years [1–3]. Photolytic degradation of a variety of VOCs has been well studied, and it was demonstrated to be a simple and efficient technique to purify the polluted air [4–8]. Nevertheless, only some particular molecules with photochemical activity could be degraded through photolysis, and a large number of VOCs were still hard to be processed. It has been accepted that the photocatalytic processes has a potential ability to degrade most of organic compounds. Studies on photocatalytic degradation of a variety of volatile organic compounds (VOCs) were frequently documented. Alberici and Jardim [9] investigated the photocatalysis of 17 VOCs and compared their reactivity on the basis of conversion efficiency and kinetics parameters. Photocatalytic oxidation of chlorohydrocarbons has become an active field, mainly focused on the preparation of catalytic materials, reaction mechanisms and kinetic discussions [10–13]. Besides, it was demonstrated that aromatics like benzene and toluene were hard to be degraded through photocatalysis. Many efforts had been made on photocatalytic degradation of these compounds [14–18]. However, it was still impracticable to compare the results obtained from different literatures because of the large variety of photoreactor concepts, lamps, experimental conditions and analytical methods used.

For the photocatalyst, TiO_2 was widely used due to its high activity. It was shown that the activity of TiO_2 could be enhanced through series of methods. Benefits of modifications to a photocatalyst can be summarized as follows:

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(1) inhibiting electron–hole recombination by increasing the charge separation, (2) increasing the wavelength response range and (3) changing the selectivity or yield of a particular product. The most typical modification methods involve depositing noble metals, doping transition metal ions, combining with semiconductors and modifying with other substances [19–24]. But comparison of these modification methods was rarely done for one certain reaction. In this work, gas-phase photolytic and photocatalytic reactions of several chlorohydrocarbons and aromatics were examined for comparing their reactivity. Subsequently, benzene was chosen as a typical compound to evaluate the catalysts modified via varied methods.

2. Experimental

2.1. Photocatalyst preparation

All photocatalysts used in this work were based on TiO_2. Commercially available TiO_2 powder (Degussa P25) was used as a referenced catalyst. Ag and Pt as noble metal was deposited on P25 TiO_2 with a proportion of 0.5 wt% using a photo-reduction method described by Siemon et al. [19] and Sung-Suh et al. [20]. Firstly, 5 g P25 TiO_2 was suspended in distilled water, and a calculated volume of 2.0 mM H_2PtCl_6 solution (or $AgNO_3$ solution) was added. The suspension was irradiated with a 250 W high-pressure mercury lamp for 6 h under vigorous stirring. Then, the samples were washed twice with distilled water, centrifuged, dried at 120 °C.

TiO_2 series catalysts were also prepared by sol–gel method using $Ti(OC_4H_9)_4$ as precursor in ethanol. Hydrolysis of the $Ti(OC_4H_9)_4$ solution was achieved by adding certain volume of distilled water. The proportion (v/v) of the raw materials followed: $Ti(OC_4H_9)_4:C_2H_5OH:H_2O = 3:24:1$. A light yellow sol was obtained, aging for 24 h at room temperature, and dried at 80 °C for 48 h. TiO_2 powder was then obtained by calcinating the dried gel. Doped TiO_2 were synthesized using almost the same method. Fe^{3+} and Pb^{2+} were doped into TiO_2 catalyst with a proportion of 0.5% by adding a certain amount of $Fe(NO_3)_3$ or $Pb(NO_3)_2$ in the water prior to hydrolysis of $Ti(OC_4H_9)$ [21]. Sulphation of TiO_2 was performed by impregnating the dried gel (pretreated at 200 °C for 2 h) in 1 M H_2SO_4 (50 mL/g) for 6 h, the suspension was then centrifuged and dried at 120 °C [22]. For the synthesis of WO_3/TiO_2 a modification method described by Li et al. [23] was applied. After the TiO_2 sol was synthesized as described above, a calculated volume of ammonium tungstate $(NH_4)_{10}H_2W_{12}O_{42}\cdot4H_2O$ solution was added drop-wise to the sol under vigorous stirring for 2 h, WO_3/TiO_2 sample was obtained in a coupling level of 2.0% after aged for 3 days. The SnO_2/TiO_2 coupled catalyst was prepared according to Liu et al. [24]. Firstly, proper proportion of $SnCl_4\cdot5H_2O$ was added into isopropanol and reflux at 60–100 °C for 1 h to get stannic isopropoxide, and it subsequently hydrolyzed by adding certain volume of water, the SnO_2 sol was obtained
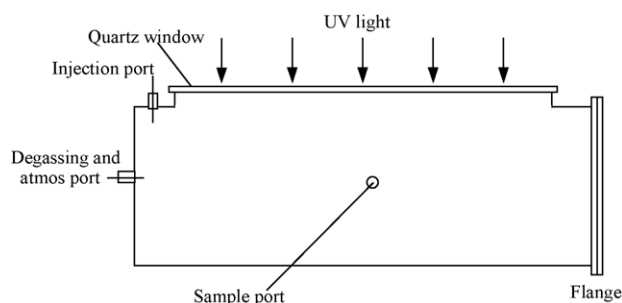

Fig. 1. Schematic drawing of photoreactor.

after stirring for 72 h and ageing for a week. Then, a mixture of SnO_2 sol and TiO_2 sol was obtained with a proportion of Sn:Ti = 1:9, and dried at 120 °C. The above catalysts based on sol–gel method were calcined at 500 °C for 3 h to obtain TiO_2 of anatase.

2.2. Photolytic reaction

The gas-phase photolytic and photocatalytic reactions of VOCs were carried out in a self-designed batch photoreactor, as illustrated in Fig. 1. It was composed of a quartz light window of approximately $100 \, cm^2$ and a columnar stainless steel chamber with 10 cm diameter and 25 cm length, both of which were adhered together with thermomelting adhesive to form a space of approximately 3.3 L. VOCs vapors were generated by a method of static vacuum, i.e. to degas the reactor, to inject VOC liquid into the chamber with a syringe and then introduce air upon complete vaporization. UV light from germicidal lamp of 8 W (253.7 nm peak density) was introduced into the reactor through a quartz light window. The UV light irradiation intensity into the reactor was measured with a UV-B-254 nm ultraviolet irradiator (Photoelectric Instrument Factory of Beijing Normal University) close up to the inner surface of light window.

Vapor and gas concentrations in reactor were qualitatively and quantitatively analyzed by a Mass-spectrometer (Balzers OmniStar[TM]) in a manner of consecutive sampling. For qualitative measurement, standard concentration of CO_2 and VOCs vapors should be prepared for calibration.

2.3. Photocatalytic reaction

For photocatalytic reactions of VOCs vapors, one could blend 0.3 g P25 TiO_2 powder with small amount of distilled water and make a uniform coating onto inner surface of the light window upon air-drying. When UV light irradiated the light window, the coating of catalyst would be activated farthest upon absorbing UV light, and it simultaneously weaken the irradiation intensity into the chamber, this could greatly avoid a direct photodegradation of target compounds. It was experimentally observed that quartz light window caused only 10% loss of UV light irradiation intensity. However, the irradiation intensity would decrease from

$0.60 \, mW/cm^2$ to $0.025 \, mW/cm^2$ when a germicidal lamp of 8 W irradiated through the light window coated with TiO_2 layer. This implied that most of the UV light was absorbed or reflected by TiO_2 coating.

Photocatalytic reactions of benzene for evaluating the prepared catalysts were performed using almost the same method, but the catalyst (0.3 g) was placed at bottom of the reactor and received an irradiation intensity of $0.36 \, mW/cm^2$ from germicidal lamp. The vapor concentration of benzene was initially generated as 380 ppm.

3. Results and discussion

3.1. Photolytic and photocatalytic degradation of several VOCs

Photolytic and photocatalytic reactions of two aromatics and four chlorohydrocarbons were performed under the same irradiation intensity of germicidal lamp. The results were shown in Fig. 2. When UV light from germicidal lamp directly irradiated benzene vapor, degradation did not evidently occur. However, the degradation would be observed when P25 TiO_2 catalyst was coated onto the backface of light window. The elimination rate of benzene was not very fast and would gradually slow down along with the reaction process. Only about 25% of benzene was eliminated upon 2 h-on-irradiation, and 40% of which could be completely mineralized into CO_2. This suggested that benzene was of those compounds that were difficult to be degraded through photocatalysis. Except for CO_2, no product and intermediate was detected in the gas phase using a direct sampling mass spectrometer. This was in accordance with the results obtained by Hennezel et al. [15], but who further identified phenol, hydroquinone and 1,4-benzoquinone as major intermediates adsorbed on the surface of photocatalyst. To toluene vapor, it behaved unstable under irradiation of germicidal lamp. Concentration of toluene gradually
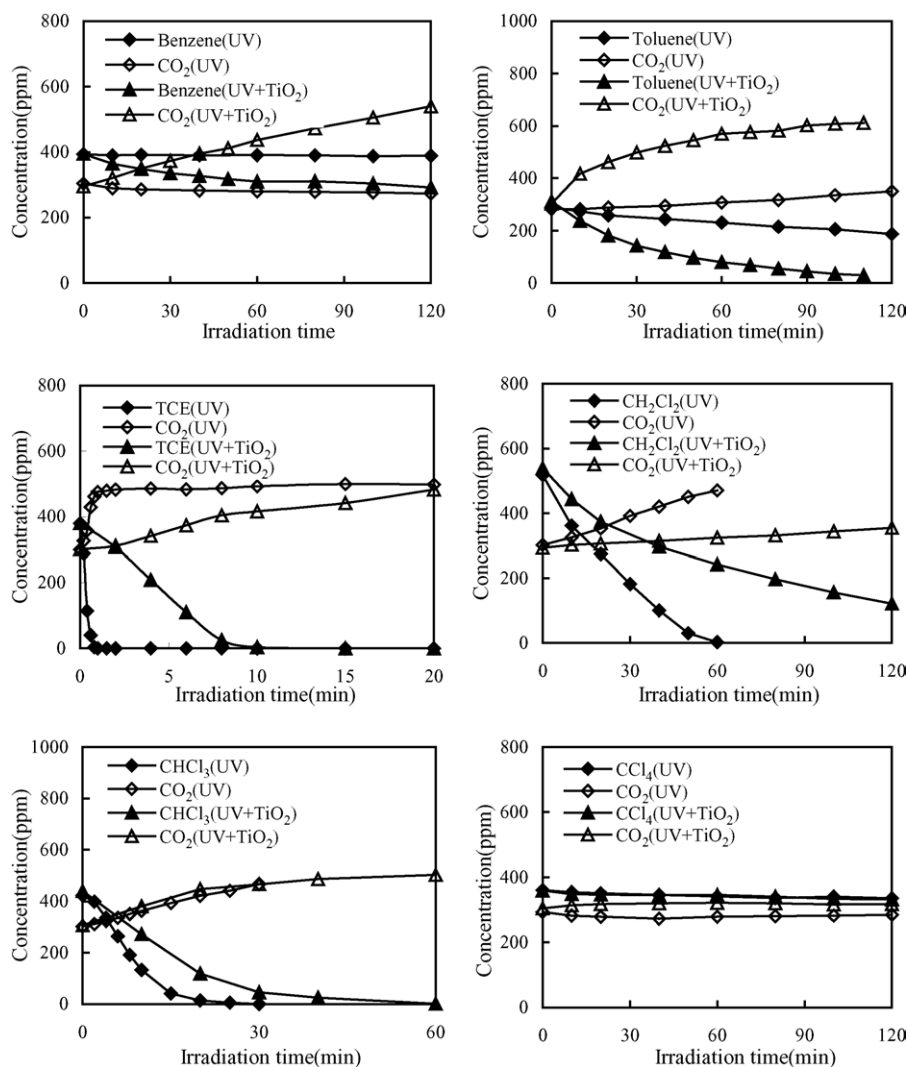

Fig. 2. Photolysis and photocatalysis of several VOCs in air.

decreased, and little amount of CO_2 was generated during the reaction. And that, the addition of photocatalyst could remarkably accelerate the elimination rate, more than 90% of toluene vapor was eliminated upon 2 h-on-irradiation, but only 16% of which was mineralized into CO_2. As compared with benzene, in spite that the elimination rate of toluene was much quicker, the mineralization rate (or CO_2 generation rate) was not significantly quicker than that of benzene. It has been shown that benzylalcohol, benzaldehyde and benzoic acid were formed on the surface of catalyst during photocatalytic degradation of toluene [14,15]. Thus, it can be seen, $-CH_3$ group enhanced the reactivity of toluene molecule, and it may be easily destroyed through photocatalytic oxidation, but the aromatic cycle was still hard to be destroyed.

For reactions of chlorohydrocarbons, it was observed that all the studied compounds except for CCl_4 can be easily degraded through both photolysis and photocatalysis under irradiation of germicidal lamp, and the reaction rate of photolysis was much quicker than that of photocatalysis under these conditions. In several, when UV light started to irradiate through the light window, trichloroethylene (TCE) concentration would sharply decrease down and 99.9% of TCE vapor was eliminated within 1 min for the vapor of 380 ppm, and CO_2 concentration quickly increased to a maximum value around 500 ppm. However, once the inner surface of light window was coated with TiO_2 film, the degradation rate of TCE would slow down, and it needs nearly 10 min to degrade 99% of TCE. The similar phenomena were also observed during photolytic and photocatalytic degradation of dichloromethane and chloroform, but the elimination rates of these two compounds were not so fast as that of TCE. Alberici and Jardim [9] also obtained similar results, and made the degradation of CCl_4 possible through photocatalytic reduction by introducing methanol as electron donor. Choi and Hoffmann [12,13] reported that degradation of CCl_4 could achieve in aqueous solution through photocatalytic reduction, and H_2O acted as an electron donor to capture the photo-generated hole. On the other hand, the photodegradation pathways of chlorohydrocarbons could mainly contributed to a direct photolysis and $^\bullet Cl$ radical initiated/sensitized oxidation reactions [6]. This implied that C–Cl bond in chlorohydrocarbon molecules might be cleaved upon adsorption of UV light irradiation, and the generated $^\bullet Cl$ free radial may subsequently offence the molecule to accelerate the degradation rate.

In order to have a kinetic comparison of the photolytic and photocatalytic degradation of these vapors, the apparent zero-order reaction rate constants were calculated and presented in Table 1. It can be seen that the photodegradation rate for the VOCs studied through photolysis followed an order: TCE > chloroform > dichloromethane > toluene > benzene > carbon tetrachloride, and through photocatalysis followed an order: TCE > chloroform > toluene > dichloromethane > benzene > carbon tetrachloride.

Table 1
The zero-order reaction rate constants for the photolysis and photocatalysis of several VOCs

VOCs	Initial concentration (ppm)	k (μmol L^{-1} min^{-1})	
		Photolysis	Photocatalysis
Trichloroethylene	380	26.6	2.03
Chloroform	420	1.14	0.56
Dichloromethane	520	0.45	0.17
Toluene	290	0.033	0.22
Benzene	400	0.002	0.066
Carbon tetrachloride	360	0.0	0.0

3.2. Photocatalytic degradation of benzene over several catalysts

It has been experimentally testified that benzene could not be degraded through photolysis but could be done, despite slowly, through photocatalysis under irradiation of germicidal lamp. Thus, photocatalytic degradation of benzene as a typical compound was performed to evaluate the prepared catalysts. An apparent zero-order kinetic equation was applied to extract the reaction rate constants.

As shown in Fig. 3, one could observe that the activity P25 TiO_2 was enhanced by depositing 0.5 wt% of Ag, but Pt deposited catalyst was not superior to P25 TiO_2. Theoretically, the addition of noble metals to TiO_2 can accelerate electrons flowing to the metal from TiO_2, and lead to a decreasing of electron density within TiO_2. Accordingly, it will increase the amount of hydroxyl group and finally result in enhancing the photocatalytic oxidation activity of the catalyst.

Under these experimental conditions, the pure TiO_2 catalyst prepared via sol–gel method behaved less active than the commercialized P25 TiO_2. However, the catalysts based
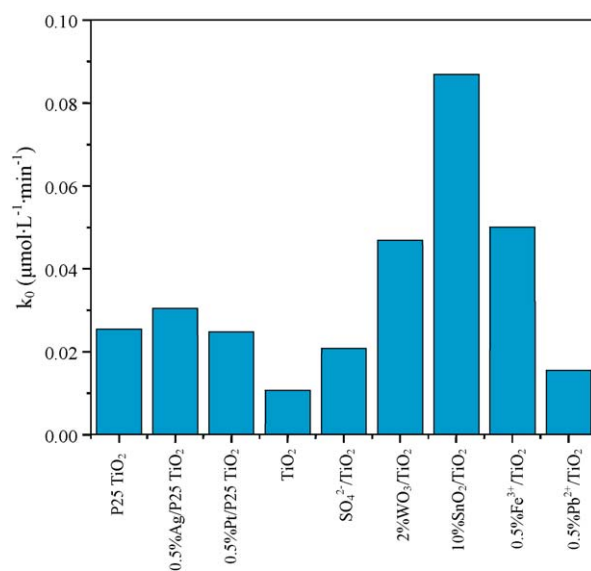

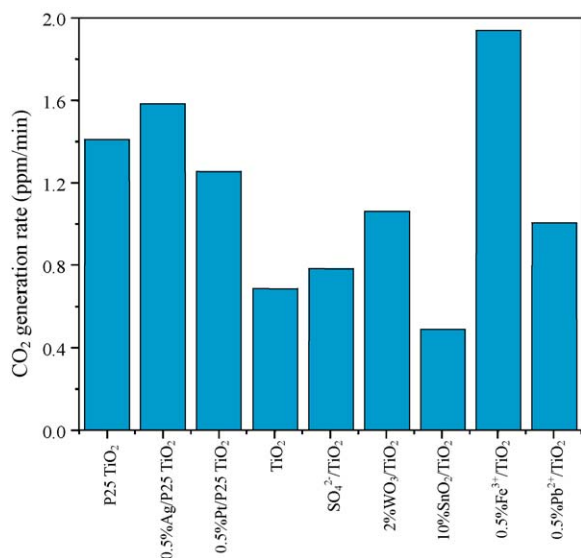Fig. 3. The zero-order reaction rate constants for photocatalysis of benzene on several catalysts.

Fig. 4. CO_2 generation rate for photocatalytic degradation of benzene on several catalysts.

on sol–gel method with doping Fe^{3+} and Pb^{2+} could remarkably enhance the activity, and the Fe^{3+}/TiO_2 catalyst was even more active than P25 TiO_2. It was believed that the benefit of transition metal doping was the improved trapping of electrons to inhibit electron–hole recombination during illumination [1]. Besides, the activity of TiO_2 catalyst could also be promoted by sulphation modification, as shown in Fig. 3. Since the acid sites was charged ions over TiO_2, which can accelerate the migration rate of the photo-generated electron to inhibit electron–hole recombination, and therefore increase the efficiency of photocatalytic process. The recombined semiconductor catalysts prepared in this work SnO_2/TiO_2 and WO_3/TiO_2 also showed a high activity upon photocatalytic degradation of benzene. The apparent zero-order reaction rate constant of SnO_2/TiO_2 was nearly three times as that of P25 TiO_2.

For photocatalytic degradation of benzene over a certain catalyst, it was found that the increasing rate of CO_2 concentration kept constant during the experiment course for 3 h. Then, the mineralization rate of benzene over a photocatalyst can be evaluated by calculating the CO_2 generation rate, and this could also represent the oxidation ability of a catalyst. The obtained results were shown in Fig. 4. It can be seen that CO_2 generation rate over P25 TiO_2 was basically higher than over those prepared with sol–gel method, except for Fe^{3+}/TiO_2 that had the highest value. The SnO_2/TiO_2 catalyst has a very low CO_2 generation rate in spite of its highest activity for photodegradation of benzene. Generally, the coupling effect might lead to increasing the charge separation and extending the energy range of photo-excitation, this would finally result in a increasing of the amount of the oxidation species over the catalyst to enhance its activity. On the other hand, coupling of the semiconductors may virtually narrow the band gap of the catalyst, this may possibly lower

the oxidation ability of the generated oxidation species, and this will go against deep oxidizing a compound like benzene.

Thus, it can be seen, the modification methods via depositing noble metal, doping with transition metal ion, recombining with semiconductors and modifying with super strong acid could promote the activity of TiO_2 to different extent. It seemed that modification of TiO_2 catalyst via doping 0.5% of Fe^{3+} was the most significant method for photocatalytic degradation of benzene in both elimination and mineralization rate.

4. Conclusions

In conclusion, chlorohydrocarbons except for CCl_4 could be degraded through either photolysis or photocatalysis under irradiation of germicidal lamp, and the elimination rate of chlorohydrocarbons through photolysis was quicker than that through photocatalysis. To aromatics, UV light from germicidal lamp could directly lead to degradation of toluene but could hardly act on benzene, the degradation rate could significantly accelerated by adding TiO_2 catalyst to the reaction system. Modification of TiO_2 catalyst via different methods was demonstrated to be effective for photocatalytic degradation of benzene. And the Fe^{3+}/TiO_2 catalyst behaved relatively excellent in both elimination and mineralization rate.

References

[1] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, Chem. Rev. 95 (1995) 735–758.
[2] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.
[3] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.
[4] J.H. Wang, M.B. Ray, Application of ultraviolet photooxidation to remove organic pollutants in the gas phase, Sep. Purif. Technol. 19 (2000) 11–20.
[5] Y.-S. Shen, Y. Ku, Decomposition of gas-phase chloroethylenes by UV/O_3 process, Water Res. 32 (1998) 2669–2679.
[6] F. Chen, S.O. Pehkonen, M.B. Ray, Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase, Water Res. 36 (2002) 4203–4214.
[7] F. Chen, Q. Yang, S.O. Pehkonen, M.B. Ray, Modeling of gas phase photodegradation of chlorinated VOCs, J. Air Waste Manage. Assoc. 54 (2004) 1281–1292.
[8] M. Bhowmick, M.J. Semmens, Ultraviolet photooxidation for the destruction of VOCs in air, Water Res. 28 (1994) 2407–2415.
[9] R.M. Alberici, W.F. Jardim, Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide, Appl. Catal. B: Environ. 14 (1997) 55–68.
[10] L.A. Phillips, G.B. Raupp, Infrared spectroscopic investigation of gas–solid heterogeneous photocatalytic oxidation of trichloroethylene, J. Mol. Catal. 77 (1992) 297–311.
[11] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, Direct mass spectrometric studies of the destruction of hazardous wastes. 2. Gas-phase photocatalytic oxidation of trichloroethylene over TiO_2: products and mechanisms, Environ. Sci. Technol. 27 (1993) 732–740.

[12] W. Choi, M.R. Hoffmann, Photoreductive, mechanism of CCl_4 degradation on TiO_2 particles and effects of electron donors, Environ. Sci. Technol. 29 (1995) 1646–1654.

[13] W. Choi, M.R. Hoffmann, Kinetics and mechanism of CCl_4 photoreductive degradation on TiO_2: the role of trichloromethyl radical and dichlorocarbene, J. Phys. Chem. 100 (1996) 2161–2169.

[14] X.Z. Fu, W.A. Zeltner, M.A. Anderson, The gas-phase photocatalytic mineralization of benzene on porous titania-based catalysts, Appl. Catal. B: Environ. 6 (1995) 209–224.

[15] O. Hennezel, P. Pichat, D.F. Ollis, Benzene and toluene gas-phase photocatalytic degradation over H_2O and HCl pretreated TiO_2: by-products and mechanisms, J. Photochem. Photobiol. A: Chem. 118 (1998) 197–204.

[16] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra1, L. Palmisano, M. Schiavello, Photocatalytic oxidation of gaseous toluene on anatase TiO_2 catalyst: mechanistic aspects and FT-IR investigation, Appl. Catal. B: Environ. 20 (1999) 15–27.

[17] H. Einaga, S. Futamura, T. Ibusuki, Heterogeneous photocatalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition behavior on photoirradiated TiO_2 catalyst, Appl. Catal. B: Environ. 38 (2002) 215–225.

[18] A. Bouzaza, A. Laplanche, Photocatalytic degradation of toluene in the gas phase: comparative study of some TiO_2 supports, J. Photochem. Photobiol. A: Chem. 150 (2002) 207–212.

[19] U. Siemon, D. Bahnemann, J.J. Testa, D. Rodriguez, M.I. Litter, N. Bruno, Heterogeneous photocatalytic reactions comparing TiO_2 and Pt/TiO_2, J. Photochem. Photobiol. A: Chem. 148 (2002) 247–255.

[20] H.M. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO_2 under visible and UV light irradiation, J. Photochem. Photobiol. A: Chem. 163 (2004) 37–44.

[21] P. Yang, C. Lu, N. Hua, Y. Du, Titanium dioxide nanoparticles Co-doped with Fe^{3+} and Eu^{3+} ions for photocatalysis, Mater. Lett. 57 (2002) 794–801.

[22] S. Liao, H. Donggen, D. Yu, Y. Su, G. Yuan, Preparation and characterization of ZnO/TiO_2, $SO_4^{2-}/ZnO/TiO_2$ photocatalyst and their photocatalysis, J. Photochem. Photobiol. A: Chem. 168 (2004) 7–13.

[23] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, Photocatalytic activity of WO_x-TiO_2 under visible light irradiation, J. Photochem. Photobiol. A: Chem. 141 (2001) 209–217.

[24] P. Liu, T.Y. Zhou, H.X. Lin, X.Z. Fu, Coupling effect for SnO_2/TiO_2 compound semiconductor photocatalyst, Acta Phys. Chim. Sin. 17 (2001) 265–269.