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by Nano-TiO₂ in a Fluidized Bed

Xiaoping Zhang*

Cong Liao†

*South China University of Technology, xpzhang@scut.edu.cn

†South China University of Technology

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Zhang and Liao: Photocatalytic Degradation of Toluene by Nano-TiO₂

PHOTOCATALYTIC DEGRADATION OF TOLUENE BY NANO-TiO₂ IN A FLUIDIZED BED

Xiaoping Zhang, Cong Liao
College of Environmental Science and Engineering,
South China University of Technology,
Guangzhou 510640, P.R.China

T: +86-020-87110077; F: +86-020-87111378; E: xpzhang@scut.edu.cn

ABSTRACT

A fluidized bed reactor with ultraviolet lamp and TiO₂/silica photo-catalyst prepared in our laboratory was used as a photo-reactor to degrade toluene in a simulated toluene-air mixture. The effects of operating parameters including initial toluene concentration, superficial gas velocity, ultraviolet light intensity and catalyst bed height on degradation rate of toluene have been investigated in this paper. The experimental results showed that degradation rate of toluene was independent of initial toluene concentration in the tested range of 20-55 mg/m³, but decreased with increasing the inlet toluene concentration. The degradation rate of toluene increased with increasing gas velocity at gas velocities below 4.0 cm/s, but decreased with increasing gas velocity at gas velocities higher than 4.0 cm/s. The results also showed that the degradation rate of toluene increased with increasing UV light intensity and catalyst bed height.

INTRODUCTION

Volatile Organic Compounds (VOCs) are organic compounds with a low boiling point between 50 to 260°C (1) and saturated vapor pressure below 10⁻³ mmHg (2), including hydrocarbon, halogenated hydrocarbon, polycyclic aromatic hydrocarbon and fluorocarbons etc. (3). VOCs are the common air pollutants emitted in the chemical and petrochemical industries. VOCs are also the main component of indoor air pollutants in new buildings and decorative materials, house hood scours, pesticides and deodorizers. From an environmental point of view, VOCs generate greenhouse effect and cause ozone depletion. And some VOCs can affect the growth of plants and the health of human beings and animals (4). The traditional controlling methods of VOCs are combustion, adsorption, absorption and condensation (5). But these methods still have many disadvantages. Combustion method must be carried out at high temperatures, so more energy is needed. Adsorption method needs high capital investment, high expenditure of operation and can cause secondary pollution (6). Absorption and condensation methods are limited to the treatment of VOCs with low concentrations (7). Under certain circumstances, the high efficient photo-catalytic technique emerges as a new treatment technique, which not only can improve the decomposition rate of VOCs, but also does not produce secondary pollutants.

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In the past decades, fluidization technology became popular in industrial processes, including environmental treatment process. Satoru et al. (8) investigated ultrafine TiO₂ particle fluidization and its application to photo-catalytic treatment of NO_x, and found that the fluidized bed of 7 nm TiO₂ exhibited high NO_x removal efficiency because of its large specific surface area. Tak et al. (9) reported that two-dimensional fluidized-bed photo-reactor was an effective tool for high NO decomposition with efficient utilization of photon energy. So the design of a suitable fluidized bed is the key to application of the fluidization technique. So far, the performance of photo-catalyst has been studied, but not so much work has been done on photo-catalytic reactors especially using the fluidized bed reactor.

According to the structure, gas-solid photo-catalytic reactors can be divided into two types, fixed bed and fluidized bed. Comparing with fixed bed, fluidized bed has a better mass and heat transfer rate, easier to put in practice and to operate continually. Alexander et al. (10) compared photo-catalytic degradation of acetone in fluidized bed and fixed bed under identical operating conditions, and found that the activity of TiO₂ catalyst increased in the fluidized bed because of the random motion of catalyst and higher absorption of scattered UV light. Tak et al. (9) found that the removal rate of NO was much higher in a modified two-dimensional fluidized-bed reactor than that in a fixed-bed photo-catalytic reactor, and demonstrated that the photo-reactor was better than the flow reactor. However, few investigations have been carried out on the fluidization of nano-TiO₂. The purpose of this paper is to study photo-catalytic decomposition of VOCs by the use of nano-TiO₂ catalyst in a fluidized-bed reactor and to provide the possibility of an economical way to treat organic waste gas.

EXPERIMENTS

Chemicals and Materials

Chemicals that in this study include the following: titanium tetrabutoxide [Ti(OC₄H₉)₄](from Shanghai Xingta Chemical plant), ethanol (C₂H₅OH)(Tianjin first Chemical plant), nitric acid (HNO₃)(Guangzhou Donghong Chemical plant), toluene (CH₃C₆H₅) (Guangzhou Chemicals plant). The water used was double-distilled water prepared in laboratory. The experimental apparatus used in this study include the following: GC900 gas chromatogram, 101-1 galvanothermy blast dryer, 78HW-1 electromagnetic stirrer, KXX-4-13A muffle and UV lights. Porous silica gel particles, with a density of 1400 kg/m³ and a specific surface area of 480 m²/g, were used as carrier for TiO₂ catalyst particles. Preparation of TiO₂/silica gel catalyst was carried out by the sol-gel method. The catalyst loading was 0.19 g TiO₂/g silica gel (11).

Surface Behaviors of TiO₂/Silica Gel Catalysts

The surface atomic compositions of the TiO₂/silica gel catalysts can be determined by X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800pci) using Mg K α lines (1253.6 eV) as an excitation source. After being detected, the TiO₂ on the surface of catalyst was anatase and its granularity was 30-80nm. The TiO₂ loading on the surface of silica gel can be seen from the photos taken by Scanning Electron Microscope (SEM). Fig.1 is an SEM photo of coarse silica gel with TiO₂ loaded on the surface. The bright part in the photo is the TiO₂ film. Because the atomic number

of Ti is bigger than Si, the light grounding in the scanning image formed by secondary electronic emission. Zhang and Liao: Photocatalytic Degradation of Toluene by Nano-TiO₂ TiO₂ on the surface of coarse silica gel is uniform, but crackles can be seen. The crackles may be caused by the stress, which was generated by the vaporization of organic materials when the catalyst was dried and calcined in high temperature. In addition, the surface of coarse silica gel is not covered with TiO₂ completely and some holes and pores can be seen, which would help coarse silica gel maintain the characteristics of adsorption and increase the photo-catalytic reaction surface area.

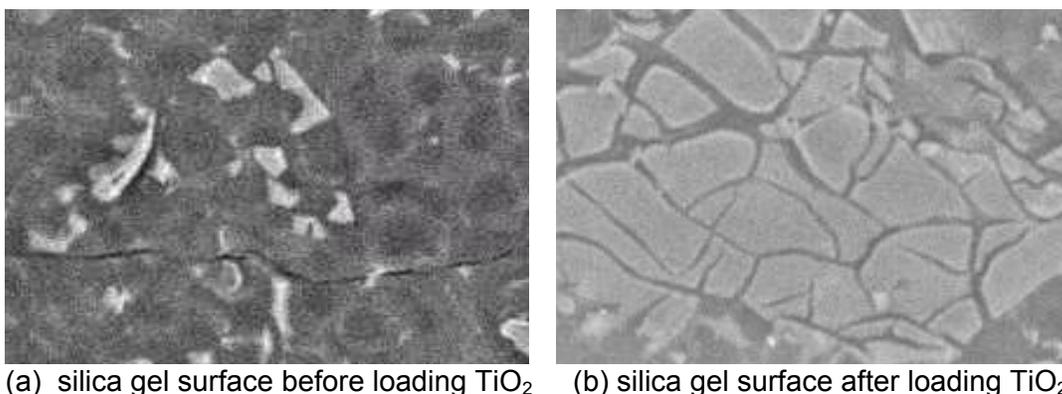


Fig.1 SEM pattern of porous silica.

Photocatalysis in a Fluidized Bed

The schematic diagram of the experimental set-up is shown in Fig.2. Air from a gas cylinder is divided into three streams, one enters the buffer tank directly, one enters the buffer tank with toluene gas, and one enters with the water vapor. The gas flow rate in the pipe is adjusted by a rotameter. The mixed gas containing toluene goes into the fluidized bed photo-reactor from the bottom and leaves the reactor from the top. The fluidized bed photo-reactor was made of quartz glass since it has the property of better light transmission. And the reactor is an annulus shape with a total height of 500mm. UV light is installed in the center of the column, and catalyst particles are placed in the annulus. There are sampling ports in the inlet and outlet of the reactor, respectively.

To determine the gas velocity for the fluidization of TiO₂/silica gel particles in the photo reactor, minimum fluidization velocity were first determined. Mean particle size in bed is around 265 μm and particle size distribution is between 125-425 μm. Gas distributor is made of a G1 grit stone plate with the hole diameter of 200 μm. The total amount of particles used in the reactor is 37g. At a given gas velocity through the reactor, the pressure drop between the inlet and outlet of the reactor was measured with catalyst in the reactor and without catalyst in the reactor, respectively. The minimum fluidization gas velocity was then determined based on the plot of gas velocity versus the pressure difference of the catalyst layer. The minimum fluidization velocity was found to be 1.06 to 1.23 cm/s.

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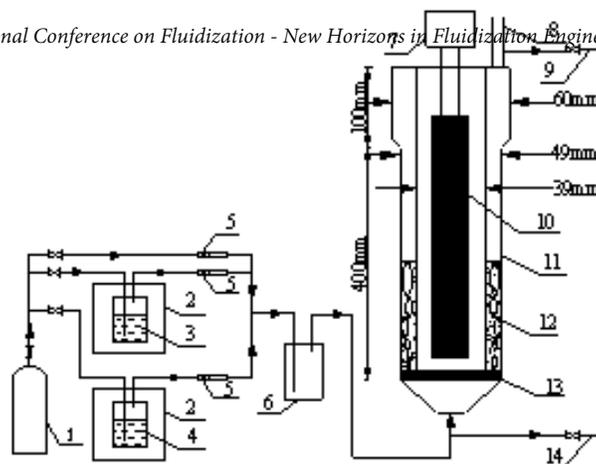


Fig. 2 Experimental set-up

1.Compressed air 2.Attemperator 3.Toluene 4.Water 5.Rotameter 6.Buffer tank 7.Power supply 8.Outlet 9.Sampling line 10.UV light tube 11.Fluidized bed photo reactor 12.TiO₂/silica gel catalyst 13.Gas distribution chamber 14.Sampling line.

Before photo-catalytic experiment started, TiO₂/silica catalyst was placed into the reactor and the gas mixture containing toluene was fed into the reactor to have the catalyst bed fluidized. Taking the gas samples from both the inlet and outlet with sampling probes, the toluene concentration was determined by the use a GC900 gas analyzer. When the concentration of inlet and outlet became approximately the same, the photo-catalytic experiment was started with UV light irradiation turned on. After that, the toluene concentration of inlet and outlet was monitored over 20 minutes intervals, with the decomposition rate of toluene over different irradiation time intervals being obtained.

RESULTS AND DISCUSSIONS

Effect of Initial Concentration on Toluene Decomposition

The photochemical decomposition of toluene under UV light irradiation in the absence and in the presence of TiO₂/silica gel has been studied, respectively. With 15W UV light source, 4.0 cm/s of operating gas velocity and 135 mm of fixed bed height, the result is shown in Fig.3. As can be seen in Fig.3, the decomposition rate is lower by direct UV light irradiation without catalyst. Therefore, it can be claimed that the absence of TiO₂/silica almost cannot bring about the photo-catalytic decomposition of toluene.

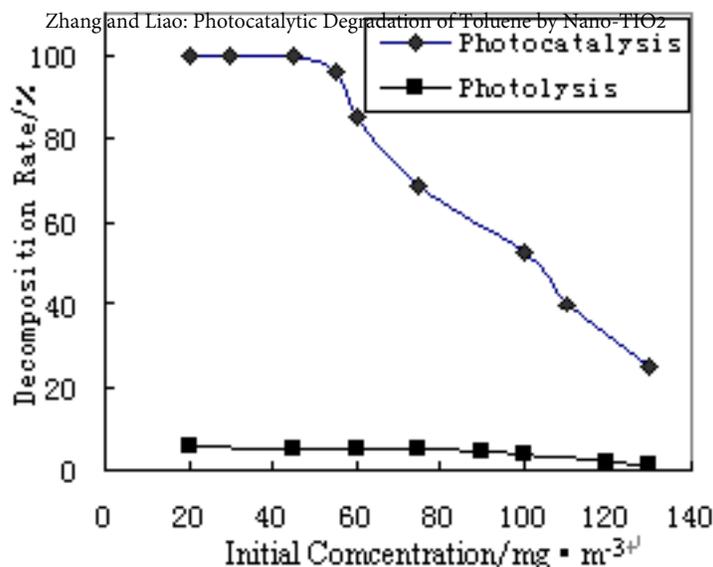


Fig.3 Effect of initial toluene concentration on toluene decomposition both in the presence and absence of photo catalyst.

As TiO₂/silica is added into the reactor, the decomposition rate becomes significant. Almost 100% toluene conversion was achieved at low toluene concentrations between 20~55mg/m³, and the decomposition rate is almost independent of the initial toluene concentration. This shows that fluidization of catalyst increases the transmission rate of UV light and promotes the contact between toluene and catalyst surface, so toluene can be more effectively decomposed in shorter residence time. At higher toluene inlet concentrations, the decomposition rate decreases with increasing initial toluene concentration because of the generation of more and more intermediate, outgrowth and terminating products. Some of the intermediate products are strong adsorptive species. According to Langmuir adsorption equation, the products generated from the reaction could compete with toluene for the active sites on the catalyst surface, resulting in lower photo-catalytic reaction efficiency. On the other hand, part of the products couldn't be removed from the catalyst surface in time and thus interfered with photo-catalytic reactions.

Effect of operational gas velocity on toluene decomposition

Operational gas velocity is another influencing factor on toluene decomposition. With 15W UV light, 60mg/m³ of initial concentration, and 135 mm of catalyst bed height, the result is shown in Fig.4. As can be seen in Fig.4, decomposition rate first increases with an increase of gas velocity. After gas velocity goes above certain value (4.0 cm/s), the decomposition rate of toluene decreases with an increase of gas velocity. In case of low gas velocities, toluene gas stayed longer in the reactor and had longer contact time with catalyst. But the intermediate products, secondary products and final products couldn't be removed from the system in time. These products would interfere the contact or adsorption of toluene to TiO₂/silica gel catalyst surface. Also, fewer bubbles formed at lower gas velocities, and the void fraction is lower in the reactor, leading to lower UV light transmission or penetration through the catalyst layer. At higher gas velocity, the products generated in the photo-catalytic reaction could be removed easily from the system. Furthermore,

vigorous movement of particles and high void fraction increased light transmission in the reactor and thus improved the decomposition rate. As gas velocity further increased, the gas residence time in the reactor would be reduced, and catalyst may be entrained out of the reactor. So the decomposition rate became lower and lower as gas velocity further increased.

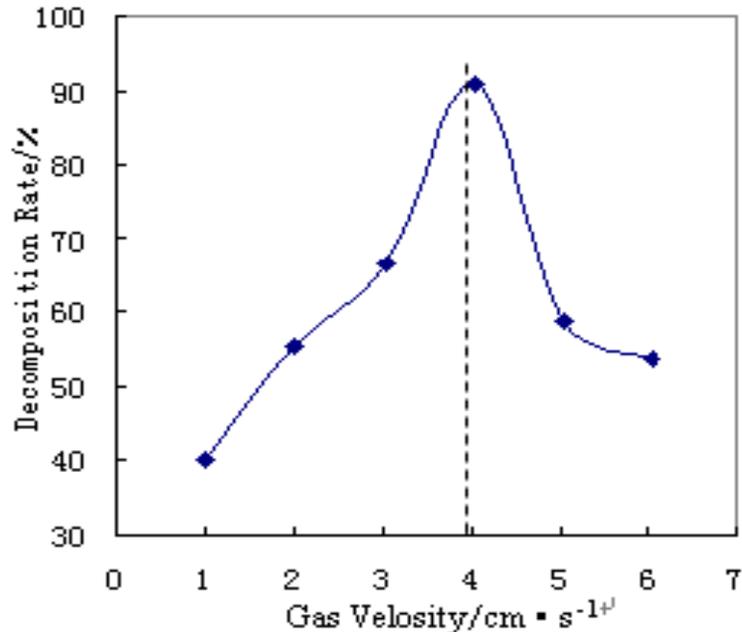


Fig.4 Effect of operational gas velocity on toluene decomposition

Effect of UV intensity on toluene decomposition

At 4.0 cm/s of operating gas velocity and 135mm of bed layer height, UV lights of different intensity were used to decompose toluene. A series of experiments were carried out to examine the influence of irradiation intensity on decomposition rate of toluene and the result is shown in Fig.5. It shows that decomposition rate decreases with an increase of initial concentration, at all UV intensity levels. The result also shows that decomposition rate is higher with UV light of higher intensity under the same initial toluene concentration. That means toluene decomposition increases with increasing UV light intensity, which produces more photons to excite more electron-hole pairs. Series of free-radical reaction taking place in the reactor are (12).



And



So more photons generated from higher UV light intensity, more photons participated in the photo-catalytic reaction. As a result, more OH• radicals with strong oxidizability were generated to decompose more toluene. With the increase in UV light intensity, toluene decomposition rate would also increase.

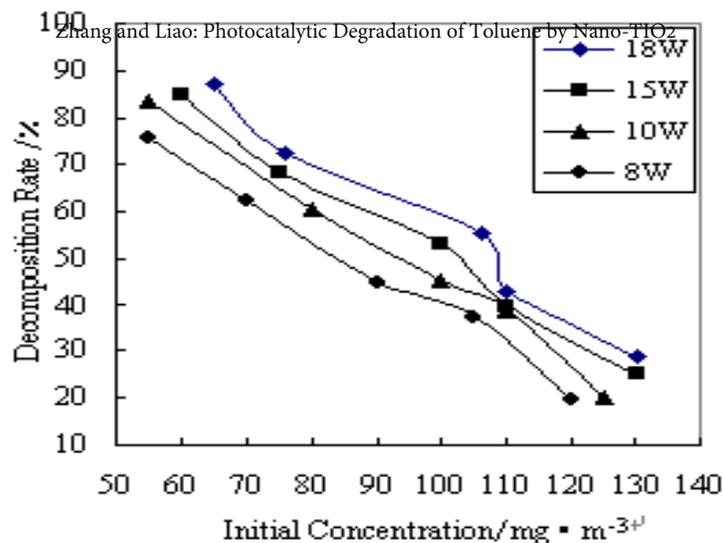


Fig.5 Effect of UV intensity on toluene decomposition

Effect of Catalyst Bed Height on Toluene Decomposition

Effect of catalyst bed height on toluene decomposition under the condition of 15W UV light, 60 mg/m^3 of initial concentration and 4.0 cm/s of operating gas velocity has been studied. The result is shown in Fig.6. As can be seen in Fig.6, decomposition rate increases linearly with increasing catalyst bed height. In fact, the increase of catalyst bed height increases the amount of $\text{TiO}_2/\text{silica gel}$. And it means more catalyst took part in the photo-catalytic reaction. In addition, the increase of catalyst bed height also increased the residence time of toluene in the reactor, which resulted in higher decomposition rate. As toluene decomposition rate is directly proportional to catalyst bed height, we expect that the decomposition rate should be equal to zero when the line is extrapolated to intersect with the y-axis. Because of the existence of some distance between the reactor bottom and the entrance in the photo reactor, some toluene could be decomposed by direct irradiation before entering the reactor. Theoretically, toluene could hardly be decomposed with low catalyst bed height. With the increase of the bed height, higher and higher fluidizing gas velocity will be needed. When gas velocity maintains at the same value, decomposition rate will decrease with an excess increase in the catalyst bed height.

CONCLUSIONS

The toluene in a air-toluene gas mixture was successfully decomposed by the photo-catalytic reaction in a fluidized-bed photo reactor under UV irradiation conditions. Undoubtedly the nano- $\text{TiO}_2/\text{silica gel}$ catalyst prepared in the laboratory showed good photo-catalytic performance. On the other hand, the operating parameters including initial toluene concentration, operating gas velocity, ultraviolet light intensity and catalyst bed height have great effects on toluene decomposition rate. The results showed that degradation rate of toluene was independent of the initial concentration at low toluene concentrations ranging from $20\text{-}55 \text{ mg/m}^3$, but decreased with increasing initial concentration at high initial toluene concentrations. The degradation rate of toluene increased with increasing gas velocity at gas velocities below 4.0 cm/s , but decreased at gas velocities above 4.0 cm/s . The

results also showed that the degradation rate of toluene increased with increasing UV light intensity and the catalyst bed height. Fundamental research on the interaction among fluidization behaviour, light absorption of reactants and reaction kinetics is needed to provide a basis for the modeling of fluidized bed photo-catalytic reactors.

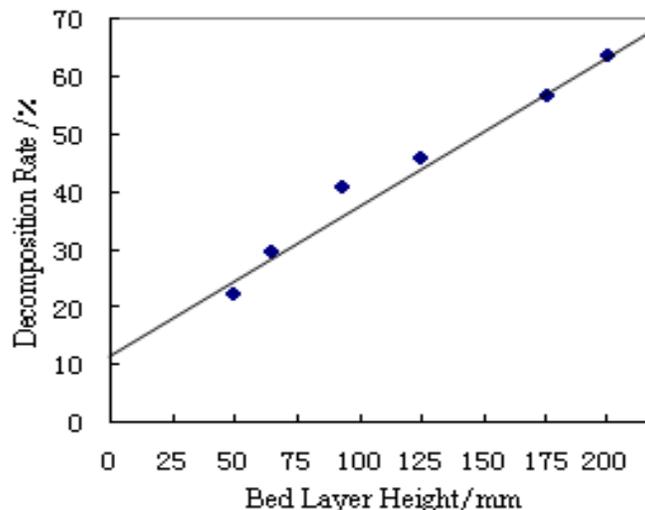


Fig.6 Effect of catalyst bed height on toluene decomposition

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