

Degradation of toluene gas at the surface of ZnO/SnO₂ photocatalysts in a baffled bed reactor

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Abstract To eliminate volatile organic compounds (VOCs) from contaminated air, a novel medium-scale baffled photocatalytic reactor was designed and fabricated, using immobilized ZnO/SnO₂ coupled oxide photocatalysts. Toluene was chosen as a representative pollutant of VOCs to investigate the degradation mechanism and the parameters affecting photocatalytic degradation efficiency. The preliminary experimental results indicate that the degradation efficiency of toluene increased with the increase of the light irradiation dosage, while it decreased with the increase of concentrations of toluene. The degradation efficiency increased rapidly with the increase of the relative humidity in a low humidity range from 0 to 35%, but decreased gradually in a high relative humidity (i.e., >35%). The optimum experimental conditions for toluene degradation is a toluene concentration of 106 mg m⁻³, a relative humidity of 35%, and an illumination intensity of ca. 6 mW cm⁻² at the surface of ZnO/SnO₂ photocatalysts. The intermediates produced during the gaseous photocatalytic degradation process were identified using the GC–MS technique. Based on these identified intermediates, the photocatalytic mechanism of toluene into ZnO/SnO₂ coupled oxide catalyst was also deduced.

Keywords ZnO/SnO₂ coupled oxide · Toluene · Photocatalytic degradation · Kinetics · Degradation mechanism · Baffled bed reactor

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Introduction

Volatile organic compounds (VOCs), together with nitrogen oxides (NO_x), sulfur oxides, and suspended particulates in air, are important pollutants originating from anthropogenic activities. VOCs are the main components that affect air quality and are detrimental to human health, with, e.g., carcinogenic, mutagenic, and teratogenic effects [1]. VOCs can also lead to sick building syndrome (SBS). Besides these adverse effects on human health and the atmospheric environment, the photodegradation of these compounds in the presence of NO_x can also lead to the formation of photochemical smog, of which toluene is the model component [2]. Toluene is a widely used raw material for producing benzaldehyde, benzyl alcohol, benzoic acid, and its chlorinated derivatives; it is also used as a solvent in the painting industries and in rotogravure factories. Zhao et al. [3] found that toluene was the most abundant aromatic VOC with concentrations ranging from 13.6 to 158.1 $\mu\text{g m}^{-3}$ in Guangzhou City, China, and up to 821 $\mu\text{g m}^{-3}$ in printing factories. Toluene is indeed ubiquitous in the atmospheric environment and can be considered as a typical aromatic pollutant in the atmosphere. Numerous research works have disclosed that the exposure to toluene may cause severe liver damage and reduce cytochrome activity [3–5].

Due to the severe toxicity of toluene and the extensive existence of toluene gas in air, a lot of effort has been devoted to abate its content in air [6–9]. Many methods have been proposed to remove toluene from the atmosphere. Adsorption using activated carbon is often used to transfer pollutants from the gaseous phase to the solid phase; however, this method can only be used in continuous processes and suffers from limited capacity. A photocatalytic degradation process using TiO_2 has been demonstrated as an efficient and promising technology for continuous VOCs abatement and air purification [10]. However, most of the investigations and experimental optimizations were conducted on very small scales, e.g., at a scale of mL of VOCs [1]. This may not reflect the actual situation when the processing scale is significantly enlarged, for example, to a medium scale. Furthermore, before the method can be used practically in the real world, the degradation efficiency still needs to be further improved by modifying TiO_2 photocatalysts such as noble metal deposition, ion doping, and coupled metal dioxide [11–13].

In our previous work, a nano-sized coupled oxide, ZnO/SnO_2 , was prepared and used for the degradation of trichloroethene in the air [10], as well as methyl orange in aqueous solution [14, 15], in small-scale reactors. It was found that both the freestanding nanoparticulate and immobilized ZnO/SnO_2 photocatalysts possessed excellent photocatalytic activity for the abatement of organic pollutants from contaminated air and water. In the present study, this ZnO/SnO_2 photocatalyst is employed to degrade toluene in a medium-scale baffled photocatalytic reactor. The aims of this study consist of three parts: (1) to test the photocatalytic activity of the coupled oxide ZnO/SnO_2 immobilized on the baffled bed reactor; (2) to optimize the kinetic parameters affecting photocatalytic degradation efficiency of toluene in this medium-scale reactor for practical applications; and (3) to investigate the photocatalytic degradation mechanism of toluene by the ZnO/SnO_2 photocatalysts.

Experimental section

Preparation and immobilization of the ZnO/SnO₂ photocatalysts

All the chemicals and reagents used in this experiment, including toluene, ZnSO₄·7H₂O, SnCl₄·5H₂O, HCl, and NH₃·H₂O, were analytical grade without further purification. ZnO/SnO₂ coupled oxide photocatalysts were prepared using a co-precipitation method [15]. Aluminum plates (215 × 250 × 3 mm) were washed 3 times with 0.1 M NaOH and deionized water. The immobilization of the photocatalyst on the aluminum plate was carried out using a dip-coating method. Subsequently, about 0.864 g of photocatalyst was coated onto both sides of each aluminum plate. The detailed procedures were described in our previous work [10].

Experimental setup for photocatalytic degradation

A schematic diagram of the experimental setup is shown in Fig. 1. The experimental apparatus used in this study consisted of an air compressor providing dry air, a 55-L baffled bed photocatalytic reactor, and a 5-L air mixer. The photocatalytic reactor and air mixer were made of stainless steel and connected with stainless steel tubes. Four UV lamps with a maximum emitting radiation peak of 365 nm (GGZ500; Shanghai Yaming Lighting) were installed, and five aluminum plates immobilized with the ZnO/SnO₂ coupled oxide photocatalyst were mounted alternately in the reactor, in order to assure enough residence time of toluene in the reactor and efficient contact between the toluene and the illuminated catalyst. Cooling circulation water was used around the jacket of the photocatalytic reactor to keep the temperature at room temperature.

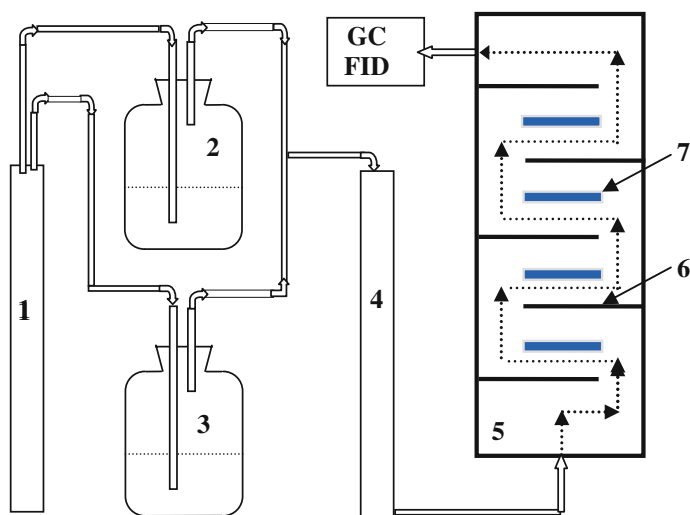


Fig. 1 Schematic diagram of the photocatalytic degradation reactor setup. 1 Air supplier; 2 toluene liquid tank; 3 humidifier; 4 air mixing tank; 5 photocatalytic reactor; 6 ZnO/SnO₂ coated aluminum plates; 7 UV lamp

Photocatalytic reaction

Toluene gas was obtained by pumping dry air through a thermostatic reservoir of toluene liquid, and the humidified air was generated by sparging air through a thermostatic bottle containing deionized water. Thereafter, the toluene gas was mixed and diluted in the air mixer with the humidified air to get the simulated contaminated air with known concentrations of toluene and relative humidity. Then, the mixed polluted air was pumped into the photocatalytic reactor with the flow rate of 400 L h^{-1} with the inlet concentrations varying from 49 to 324 mg m^{-3} , and with the ranges of the relative humidity varying from 0 to 75%.

Analyses

The inlet and outlet concentrations of toluene were measured with HP 5890 chromatography, coupled with a flame ionization detector (FID), and equipped with a DB-5 fused silica capillary column ($30 \text{ m} \times 0.32 \text{ mm I.D} \times 0.25 \mu\text{m}$; Agilent Technologies, USA). The oven temperature was initially set at 40°C (hold for 5 min), then raised with a ramp of 5°C min^{-1} to 100°C , then $25^\circ\text{C min}^{-1}$ to 295°C (hold for 10 min). The injector temperature was set at 230°C , and the temperature of FID was set at 270°C .

The intermediates produced in the photocatalytic reaction were measured by an Entech 7100 Pre-concentrator (Entech Instruments, CA, USA) coupled with a 5973 gas chromatography–mass detector (Agilent Technologies). A HP-1 fused silica capillary column ($60 \text{ m} \times 0.32 \text{ mm I.D} \times 1.0 \mu\text{m}$; Agilent Technologies) was used for separation, and helium was used as carrier gas with a flow rate of 1.2 mL min^{-1} . The column temperature was programmed as follows: 40°C (hold for 2 min), raised at a ramp of 6°C min^{-1} to 230°C (hold for 5 min). A full scan mode (m/z 30–350 amu) of the mass detector was used.

Results and discussion

Kinetics aspect

Two control experiments were carried out to measure the toluene removal efficiencies, by circulating the toluene mixture in the reactor in the presence of the photocatalysts without UV illumination (i.e., dark adsorption) and in the absence of the photocatalysts but under UV irradiation (i.e., pure photolytic reaction). It was found that the removal efficiency of the dark adsorption experiment was less than 5% within 3 h, implying that the adsorption reaction was trivial and not responsible for the removal of toluene. The results of the photolytic reaction showed that the removal efficiency of toluene was ca. 50% for 3 h. This suggests that complete degradation was not achieved by the pure photolytic reaction in 3 h though a portion of toluene was decomposed (Fig. 2), showing that the removal efficiencies of both photolytic and photocatalytic degradation increased very quickly at the first 20 min, and then leveled off as a steady state. In strong contrast with the pure photolytic reaction,

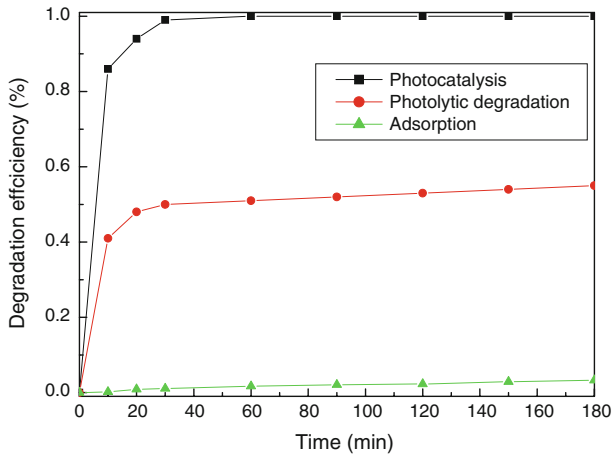


Fig. 2 The comparison of the photocatalytic degradation reaction, the pure photolytic degradation reaction, and the dark adsorption reaction

under the same conditions of initial toluene concentration, relative humidity, and irradiation intensity, the removal efficiency of the photocatalytic degradation was achieved to almost 100%. That is, toluene gas can be completely degraded by photocatalytic process in this reactor under optimal conditions. This conclusion can be confirmed by the results obtained from the GC–MS data (see later).

The effects of initial concentration of toluene on the degradation efficiency

The influences of the initial concentrations on the photocatalytic degradation efficiency of toluene are shown in Fig. 3. It can be seen that, under a specific condition with a relative humidity of 35% and the illumination intensity of about 6 mW cm⁻² at the surface of the immobilized photocatalyst, the photocatalytic degradation efficiency increased rapidly and then achieved 100% within 10 min when the initial concentrations of toluene was at 49 mg m⁻³, and reached 100% within 30 min when the initial concentration was 106 mg m⁻³. However, with the further increase in the initial concentration of toluene, the removal efficiency gradually decreased, and then reached the steady removal efficiency. This is because, at the low toluene concentration, the toluene molecules were not sufficient to fully cover the active reaction sites of the photocatalysts. In contrast, when the toluene was sufficient to mask the active site of the ZnO/SnO₂ coupled oxides photocatalysts at high toluene concentration, this led to a reduction of the reaction sites.

The effect of relative humidity on the degradation efficiencies

In order to study the relationship between the relative humidity and the degradation efficiency, a series of experiments were conducted under the same experimental conditions of initial toluene concentration at 246 mg m⁻³ and illumination intensity at 6 mW cm⁻², and the profiles are shown in Fig. 4. It can be seen from Fig. 4 that

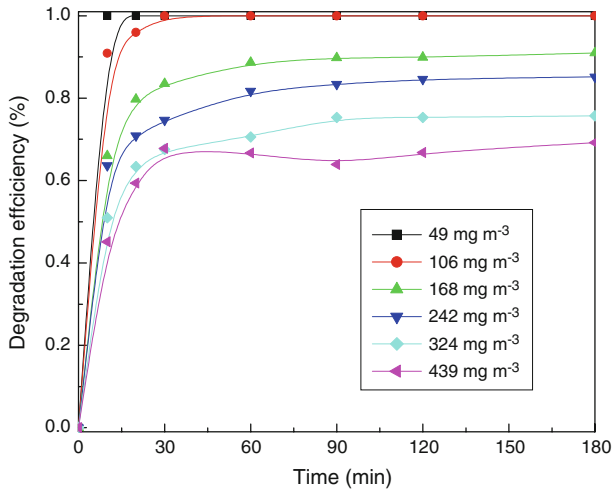


Fig. 3 Effect of initial concentrations of toluene on the photocatalytic degradation efficiency

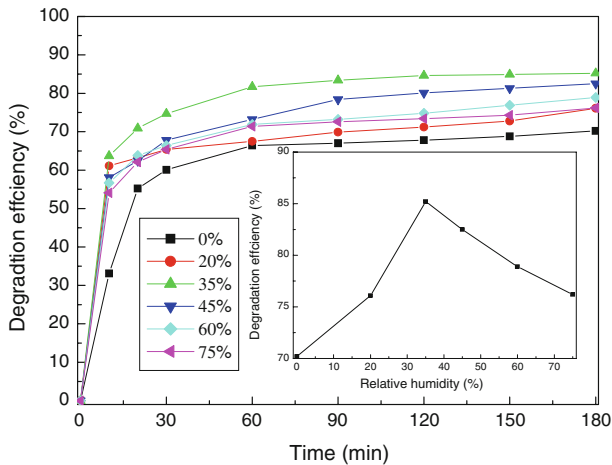


Fig. 4 Effect of relative humidity on the photocatalytic degradation efficiency

the relative humidity has a significant influence on the photocatalytic degradation efficiency of toluene. The degradation efficiency of toluene increased gradually with the increase in the relative humidity from 0 to 35%, and reached the maximum degradation efficiency of 85.2% at a relative humidity of 35%. After that, the degradation efficiency of toluene decreased with the further increase of the relative humidity from 35 to 75%. This indicates that the appropriate content of water, i.e., the relative humidity of $\leq 35\%$, could promote the degradation efficiency of toluene, while excessive water could slow it down. This may be interpreted as indicating that the water molecules adsorbed at the catalyst surface can be oxidized and

transformed to $\bullet\text{OH}$ radical by the holes at the surface of the photocatalysts. In the low water content range (i.e., the relative humidity of $\leq 35\%$), the more the water molecules are adsorbed at the catalyst surface, the more $\bullet\text{OH}$ radicals will be generated; hence, higher photocatalytic degradation efficiencies are achieved. In contrast, excessive water molecules adsorbed at the catalyst surface would compete with the active sites with the reactant, toluene, resulting in lower degradation efficiency [9]. Similar results were also obtained in our previous work [10, 14] and in the literature [8, 16], although a different organic pollutant gas was selected to test the activity of photocatalysts.

The effects of irradiation dosages on the degradation efficiencies

Irradiation dosage is a key factor for the photocatalytic degradation of toluene. To better understand the effects of the illumination dosage on the photocatalytic efficiency, four different experiments were carried out under fixed experimental conditions (i.e., with an initial toluene concentration of 246 mg m^{-3} and a relative humidity of 35%), using 1, 2, 3, and 4 lamps, respectively. The corresponding removal efficiencies were measured and are shown in Fig. 5. When 1 lamp was turned on, the removal efficiency was about 34.0%. When 2 lamps were turned on, the removal efficiency of toluene was obtained as 49.8%. Similarly, when 3 and 4 lamps were turned on, the corresponding removal efficiencies were 71.5 and 85.2%, respectively. The results indicated that the degradation efficiencies increased gradually if the light dosage increased steadily when more lamps were turned on. This is because more photoholes were generated with the higher irradiation dosage, leading to the higher photocatalytic degradation efficiencies of toluene [17, 18].

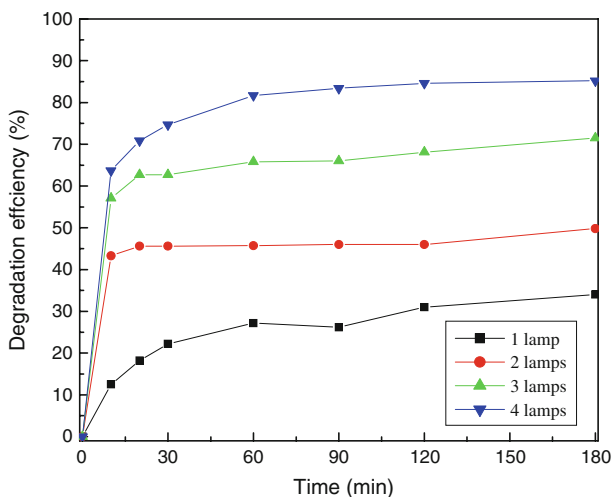


Fig. 5 Effect of irradiation dosage on the photocatalytic degradation efficiency

Effect of O₂ concentrations on the photocatalytic efficiencies

It is well known that dioxygen is a good electron capturer in the photocatalytic oxidation system. Dioxygen can trap the electrons generated at the surface of the photocatalysts under illumination so as to facilitate the separation of electrons and holes. Meanwhile, dioxygen can be reduced to the HO₂[•] radical by these electrons, then be further transformed to the [•]OH radical, which plays an important role in the subsequent photocatalytic reaction [14]. In this study, we have found that the removal efficiency of toluene was lower than 60% in the absence of O₂. But in the similar conditions of the relative humidity of 35% and the initial toluene concentration (168 mg m⁻³), the removal efficiency was up to 100% by using compressed air (21% O₂ concentration) as the carrier gas (Fig. 6). Thus, it can be concluded that O₂ is necessary for photocatalytic degradation of organic compounds. Zhang et al. [14] also found that O₂ can accelerate the catalytic reaction when the concentration was lower than 30%, whereas higher O₂ concentrations in the photocatalytic system had no further positive effect on the progression of the catalytic reaction. Because our reactor was designed at a medium scale, a safety factor was imposed and no further experiment was conducted with higher O₂ concentrations for this reason. Thus, the optimal O₂ concentration was selected as 21% for the rest of this work.

Degradation pathways and reaction mechanism

The TIC diagram of photolytic reaction and photocatalytic degradation is shown in Fig. 7. It is worth noting that, although a portion of the tested toluene was decomposed during the photolytic reaction, many degraded intermediates were still produced, including ring-retained products such as benzene, benzaldehyde, and a

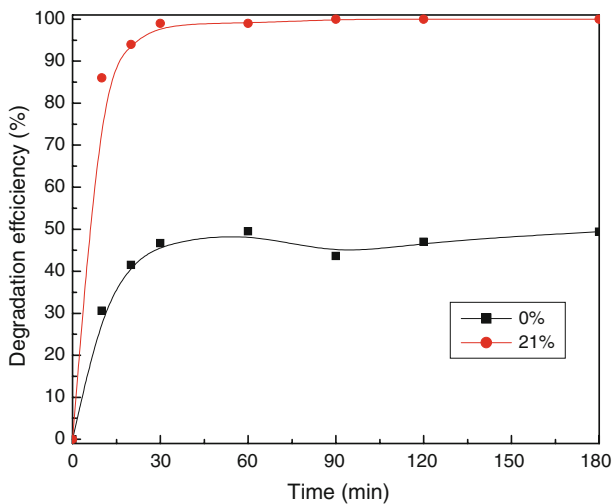


Fig. 6 Effect of dioxygen on the photocatalytic degradation efficiency

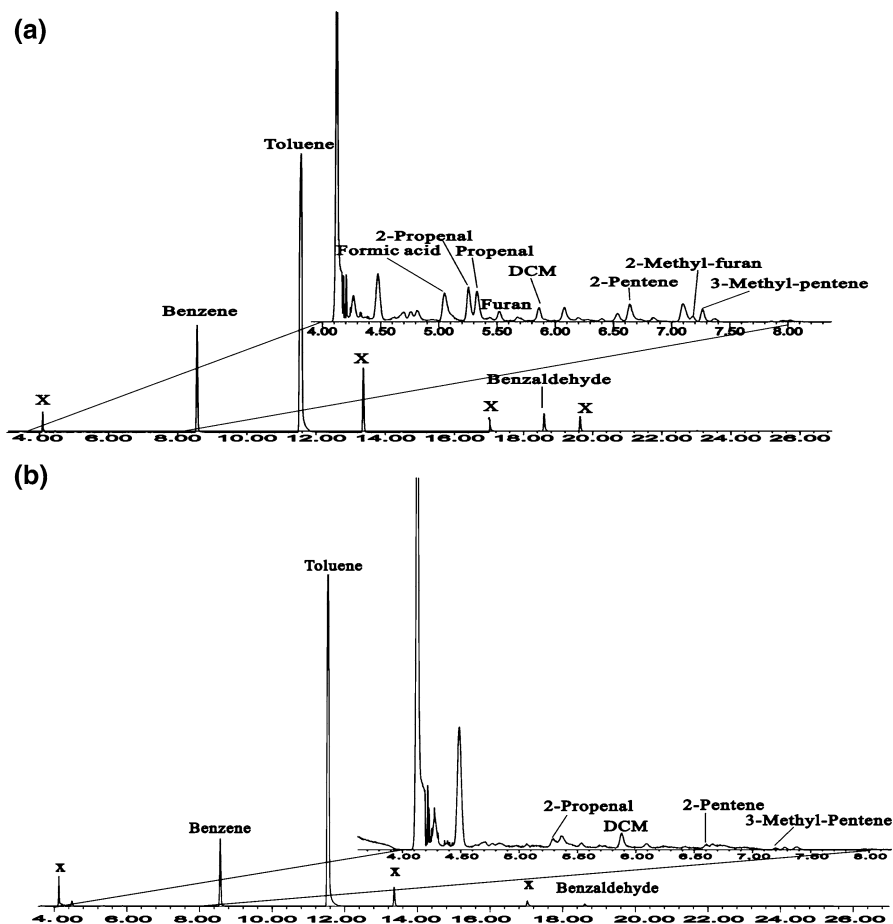
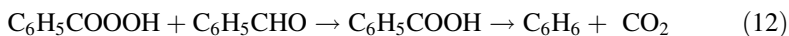
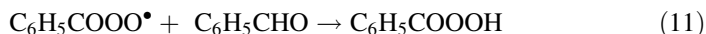
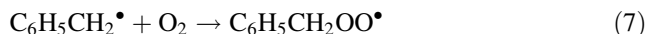
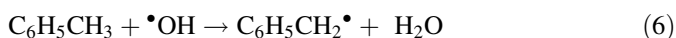
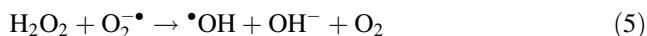
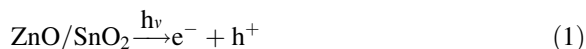


Fig. 7 TIC profiles of GC-MS for the photolytic degradation reaction (a), and the photocatalytic degradation reaction (b) of toluene

series of ring-opened products, such as propenal, 2-methyl-furan, and furan (Fig. 7a). These compounds are important components of photochemical smog and would impose destructive effects on human health and the atmospheric environment [19]. In addition, a large amount of unidentified products were also detected simultaneously during the direct photolytic reaction. However, the photocatalytic degradation of toluene with TiO₂ as photocatalyst was initiated by H-abstraction from the methyl group or $\cdot\text{OH}$ addition reaction to the aromatic ring; the mechanisms of these reactions have been reported by Bloss et al. [20]. However, the photocatalytic degradation mechanism of gaseous organic pollutants by using the ZnO/SnO₂ photocatalyst has still not been attempted. In this work, we mainly focus on the difference between the photolytic degradation and the photocatalytic degradation mechanisms, and try to clarify the difference in intermediates between these two systems.

In the photocatalytic system, highly reactive electron–hole pairs can be excited at the photocatalyst surface under UV irradiation in addition to the photolytic reaction, generating large amounts of active radicals. These active radicals can initiate a series of oxidation degradation of toluene. Compared with the photolytic reaction of toluene, fewer intermediates and smaller amounts of ring-retained products were detected in the photocatalytic system (Fig. 7b). This reveals that the photolytic reaction of toluene proceeds along different pathways. Similar work has been reported in the earlier published reference using TiO_2 as photocatalyst [21]. The enhancement mechanism of photocatalytic degradation of methylene orange in water by using ZnO/SnO_2 as photocatalyst have been summarized in our previous publications [15].

The possible degradation pathways and reaction mechanism were deduced based on identified intermediates during the photocatalytic degradation. H-atom was abstracted from the methyl group by the $\cdot\text{OH}$ radical to form the $\text{C}_6\text{H}_6\text{CH}_2\cdot$ radical, which was further transformed to $\text{C}_6\text{H}_6\text{CH}_2\text{OO}\cdot$ in the presence of O_2 ; then, the peroxy radical $\text{C}_6\text{H}_6\text{CH}_2\text{OO}\cdot$ was transformed to benzaldehyde. The benzaldehyde so obtained was attacked again by $\cdot\text{OH}$ to form the $\text{C}_6\text{H}_5\text{CO}\cdot$ radical, which was oxidized to the $\text{C}_6\text{H}_5\text{COOO}\cdot$ radical by O_2 ; then, the resulting radical abstracted an H-atom from another benzaldehyde molecular to form $\text{C}_6\text{H}_5\text{COOOH}$, followed by a series of chemical reactions until the production of benzene. These reaction procedures were listed as follows:



The other possible pathway is that the $\cdot\text{OH}$ radical was rapidly added to the benzene ring to form a cyclohexadienyl radical, which was then oxidized to a peroxy radical in the presence of O_2 . Subsequently, this peroxy radical was transformed to various ring-opening degraded intermediates, such as 2-propenal, 2-pentene, and 3-methyl-pentene, until complete mineralization to form CO_2 and H_2O [22]. From the above discussion, we can conclude that the proposed method

can completely degrade toluene in contaminated air in very mild conditions, and that the photocatalytic system is much more efficient than the pure photolytic system for elimination of toluene in air.

Conclusions

For the removal of toluene from air, a baffled reactor using nano-sized coupled oxide ZnO/SnO₂ photocatalysts was designed and fabricated. A series of experiments concerning the light dosage, the initial concentrations of toluene, and the relative humidity, as well as the content of dioxygen were carried out to optimize the degradation conditions. The results indicate that light dosage played an important role in photocatalytic decomposition of toluene, and relative humidity also had a significant influence on the photocatalytic degradation efficiency. The photocatalytic degradation method can be used to efficiently remove toluene from air in a medium-scale reactor. The optimum experimental conditions are: a toluene concentration of 106 mg m⁻³, a relative humidity of 35%, and an illumination intensity of 6mW cm⁻². The reaction mechanisms of the photocatalytic degradation of toluene were investigated by comparing them with photolytic degradation.

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