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Effect of TiO_2/adsorbent hybrid photocatalysts for toluene decomposition in gas phase

Jinhan Mo, Yinping Zhang*, Qiujian Xu, Rui Yang

Department of Building Science, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

12 hybrid photocatalysts consisting of titania (TiO_2) and an adsorbent such as mordenite were investigated for the photocatalytic decomposition of toluene, a major indoor contaminant in indoor air. The highest decomposition rate was obtained with the use of mordenite and silicon dioxide (SiO_2) as additives to TiO_2. The photocatalytic activities of hybrid photocatalysts in decomposing toluene are 1.33 times as high as pure P25 at the net weight loading of 0.49 mg/cm^2 under the test condition. Scanning electron microscopy (SEM) images confirmed that the hybrid photocatalyst films were very porously distributed; TiO_2 was adsorbed on the surface of mordenite and SiO_2, increasing the reaction area of TiO_2. The unimolecular Langmuir–Hishelwood model and mass-transfer-based (MTB) method were used to evaluate the reaction coefficients and adsorption equilibrium coefficients of hybrid photocatalysts. It is evidenced that the reaction areas of two hybrid photocatalysts were 1.52 and 1.64 times larger than that of P25, respectively, which is the major reason to make the high removal efficiency of toluene.

1. Introduction

In the past decades, buildings have been sealed more tightly to reduce the energy consumption. Meanwhile, synthetic building materials and furnishings, which emit volatile organic compounds (VOCs), were widely used in the urban buildings. These situations made the indoor VOC concentrations being higher than the level permitted by the standards (e.g., the Chinese National Standard GB9671 [1]). Those may cause general symptoms, such as headache; eye, nose or throat irritations; dry cough; dizziness and nausea; difficulty in concentrating; and tiredness [2–5]. Those may also do great harm to respiratory system, cardiovascular system and nervous system of human beings [6].

Developing effective technology for a sustainable environment aiming at removing VOCs quickly and economically is now a recognized goal of many governmental and industrial organizations and researchers in the related fields. Photocatalytic oxidation (PCO) by employing UV radiation is an innovative and promising approach that may meet such demand. When a semiconductor material such as nanometer titania (TiO_2) particles is illuminated by photons of greater energy than their band-gap energies, the material absorbs the photons. The electrons in the valence band of the material are excited into the conduction band and leave electron holes in the valence band. The components of this activated pair, when transferred across the interface, are capable of reducing and oxidizing a surface-adsorbed organic compound. Studies have shown that gas–solid photocatalysis may decompose a wide variety of VOCs, including typical indoor contaminant such as acetone, toluene, formaldehyde and benzene [7–9]. TiO_2 is a commonly used photocatalyst because of its high photoactivity and good stability [10]. Titania is normally loaded on the carrier surface as a thin film on which the photocatalytic reaction takes place. However, TiO_2 exhibits low adsorption ability, especially for non-polar substances due to its polar structure [11], which restricts the PCO reaction. Some researchers have found that mixing some adsorbents with nanometer TiO_2 can increase the photocatalytic reaction effectiveness in aqueous system [12–15]. Normally, it was thought that the adsorbents would absorb the compounds on the adsorbent support. Then a high concentration environment of the compounds was formed around the loaded TiO_2, resulting in an increase in the photoreaction rate. However, few have investigated this phenomenon in gas-phase systems. Yoneyama and Torimoto [16] used various adsorbents, such as zeolite, alumina, silica, mordenite, ferrierite, and activated carbon, as the support of TiO_2 and showed that the hybrid photocatalysts were effective in achieving high decomposition rates of propionaldehyde in air. The mordenite was the best among the tested adsorbents. They also found that the best weight fraction of doping mordenite with TiO_2 was 47%. However, they got this result under static experimental condition, which is not similar to normal once-through air cleaning process in indoor environment. Moreover, propionaldehyde is not a typical indoor air contaminant.

* Corresponding author. Tel.: +86 10 6277 2518; fax: +86 10 6277 3461.
E-mail address: zhangyp@mail.tsinghua.edu.cn (Y. Zhang).

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Nomenclature

C_{in}	average inlet concentration (ppm)
C_{out}	average outlet concentration (ppm)
C_s	gas-phase concentration close to the reaction surface (ppm)
r	average decomposition rate (ppm m/s)
k	reaction coefficient (ppm m/s)
K_{ad}	adsorption equilibrium coefficient (ppm^{-1})
A_r	reaction surface area (m^2)
r'	equivalent reaction rate (ppm m/s)
k'	equivalent reaction coefficient (ppm m/s)
A'_r	projection area of reaction surface (m^2)
n	the ratio between reaction surface area and projection area
G	volumetric airflow rate (m^3/s)

In the present study, we used a glass-plate photoreactor to investigate the effect of applying TiO_2/adsorbent hybrid photocatalysts to remove low concentration toluene (ppmv level) which is a major indoor contaminant [17] for common air-conditioned space. Optimal net weight loading and mixing weight ratio of P25 and adsorbents were studied and obtained. The unimolecular Langmuir–Hishelwood (L–H) model and mass-transfer-based (MTB) method were used to evaluate the reaction coefficients and adsorption equilibrium coefficients of two hybrid photocatalysts. The reason why the hybrid photocatalysts had higher performance than pure TiO_2 was discussed.

2. Experimental

2.1. Film preparation

Degussa P25 titania is a kind of widely used nanometer photocatalyst [16,18] with a primary particle diameter of 30 nm, 50 m^2/g specific surface area, a crystal distribution of 70% anatase and 30% rutile. 12 commercial adsorbents (Table 1) were mixed with P25, respectively, at the specific weight ratios. The hybrid photocatalyst film was deposited on the glass plate with dimensions of 90.0 mm in length, 4.0 mm in height and 25.0 mm in width by dipped-coating method [19]. Before the process, the glass plate was washed in 10 wt.% NaOH solution and distilled water by sequence, and then dried in oven at 70 °C until the glass surface was dry. The solution was 1.25 wt.% of the hybrid photocatalyst or pure P25 in absolute ethanol. The film was prepared by dipping the glass plate in the dipped-coating several times, air drying between dipping, and then drying in oven at 70 °C for 2 min. This process was repeated until a specific net weight loading of material (per side) was achieved on the glass plate.

Table 1
Physical parameters of various materials.

Symbol	Material	Particle size	Specific surface (m^2/g)
P25	Degussa P25 titania	30 nm	50
AZ	Artifical zeolite	<4 μm	13
CR	Clinoptilolite (R)	325 mesh	0.65–0.70
CY	Clinoptilolite (Y)	325 mesh	0.65–0.70
CW	Clinoptilolite (W)	280–290 mesh	0.57
M	Mordenite	12–16 μm	250–300
S1	SiO_2 (SD-400L)	1 μm	260–320
S2	SiO_2 (SD-520)	2 μm	300–350
S3	SiO_2 (SD-520L)	2 μm	300–350
A	Alumina	10 μm	250
Z1	ZSM-5-25H molecular sieve		
Z2	ZSM-5-38H molecular sieve	2–4 μm	342–360
Z3	ZSM-5-50H molecular sieve		

2.2. Glass-plate photoreactor

The decomposing effect of toluene was measured in a glass-plate photoreactor (Fig. 1). Two parallel germicidal lamps (254 nm peak intensity, Philips Hg-Lamp, TUV 15W G15T8 UV-C, made in Holland) provided UV light for the photoreactor. Adjusting the distance between the light and the photoreactor varied the light intensity. The light intensity at the reaction surface was measured using a UV power meter (HANDY 00000176, made in China). Synthetic air (mixture of high-purity nitrogen and oxygen with volume ratio 79:21) was supplied from a compressed cylinder. The air passed through a filter and was then divided into two streams. One stream passed through a flow meter while the other passed through a humidifier to control the tested air on the desired humidity level. Toluene was mixed with the synthetic air and then the mixed gas was supplied through a mass flow controller to the reactor. The photocatalyst-coated glass plates were placed in a well (25.0 mm wide, 380.0 mm long and 4.0 mm deep) made of stainless steel and covered with a quartz window (its transmittance at 254 nm wavelength is 0.80). The space between the photocatalyst-coated glass plate and the quartz window was the flow section of 25.0 mm wide and 2.0 mm high.

INNOVA photoacoustic multi-gas monitor 1312 and multipoint sampler and doser 1303 were used to measure the inlet and outlet concentrations of the reactor: water vapor, carbon dioxide, carbon monoxide and toluene. Four copper–constantan thermocouples were installed at the photoreactor inlet, outlet and inside, respectively. A data logger recorded the temperature. Table 2 lists the uncertainly of the measured parameters. All experiments were performed at room temperature of 25.0–27.0 °C. The relative humidity (RH) was set to a common air conditioning level of about 47%. The total air volumetric flow rate was 4.00 L/min, which formed a laminar flow with Reynolds number (based on the 25.0 mm by 2.0 mm flow cross-sectional area) of 330 in the reactor. The UV light intensity at the glass-plate surface was 1.64 mW/cm^2. Three pieces of same-coated glass plates were placed in series in the photoreactor. The other glass plate (90.0 mm long, 25.0 mm wide and 4.0 mm thick) without photocatalyst was placed in front of the coated glass plates to make the reaction part being in the fully developed region of laminar flow. Each experiment was repeated under the same experiment condition.

2.3. Test procedure

The procedure for all the experiments was as follows: (1) airflow was started; (2) after the photoreactor inlet and outlet humidity readings were steady and equal, the toluene was introduced; (3) when the photoreactor inlet and outlet toluene concentrations were approximately equal, the UV lamps were turned on; (4) after the inlet and outlet toluene levels again reached steady state, the UV lamps were turned off and the toluene flow was stopped; and (5) the photoreactor was flushed with the synthetic air for 15 min, and then airflow was stopped. Normally, it took about 3 h to finish the whole procedures.

2.4. Data analysis and characterization

For the data measured by the glass-plate photoreactor, the single-pass removal efficiency, ε was used [20,21]:

$$\varepsilon = \frac{C_{in} - C_{out}}{C_{in}} \quad (1)$$