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Removal of Gaseous Benzene by Photocatalytic Oxidation Process Using TiO_2 Film Coated on Glass Sheets under UVC Irradiation

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Abstract

Benzene is well known as a toxic and carcinogenic air pollutant, which is mainly emitted from industrial processes, vehicles, and residential activities. TiO_2-based photocatalysis is becoming one of the most promising solutions for the treatment of benzene in the ambient air. The present study aims to investigate the photocatalytic activity of TiO_2 film coated on glass sheets for the degradation of gaseous benzene under ultraviolet C (UVC) irradiation. TiO_2 thin film coated glass sheets were prepared through polyvinylpyrrolidone (PVP)-modified sol-gel method coupled with the doctor blade coating technique. It was found that the obtained TiO_2 film consisted of well-shaped TiO_2 particles with good adherents on a glass surface. There was no crack formation found in the film. The average film thickness was 1.187 µm. The maximum removal efficiency of benzene in the photocatalysis test was 4.5 and 6.4 times higher than that of the adsorption and direct photolytic tests, respectively, within 12 h. Moreover, the higher numbers of TiO_2 coated sheets, the higher photocatalytic benzene degradation, was obtained.

Keywords : air pollutant; benzene; photocatalysis; titanium dioxide; ultraviolet C

Introduction

Nowadays, air pollution is increasingly concerned as an important environmental issue. In this sense, volatile organic compounds (VOCs) emitted from industrial and residential activities are considered as one of a major group of air pollutants [1]. Among various VOCs, benzene has been recognized as one of the most dangerous carcinogenic substances, which can pose the highest cancer risk in human [2].

Gaseous benzene can be emitted from three main sources, including the residential activities (e.g. cooking, cleaning, and cigarette smoke), the chemical production processes (e.g. detergents, paints, glues, gasoline, coal, and heating oil production) and the vehicular emission especially in the high traffic areas [3, 4]. Most people can begin to detect the benzene odor at 61 ppm in the air and can identify it as benzene at 97 ppm in the air [5].

Short-term inhalation exposure to benzene can lead to negative effects on human bodies such as anesthesia, headache, tremors, and temporary loss of consciousness. Long-term inhalation exposure to benzene can lead to cancer and aplastic anemia in humans because red and white blood cell productions are inhibited [6]. Consequently, it is necessary to develop an effective solution for the treatment of benzene in the ambient air.

Based on the previous researches, gas-phase heterogeneous photocatalysis has been proven as a promising technology for benzene removal because of its distinguished properties over the conventional techniques such as cost-effectiveness, easy for operation, environmental protection, and applicable measurements [7, 8].

Over the last few decades, titanium dioxide (TiO_2) has attracted significant attention as a semiconductor photocatalyst for air purification from many researchers, scientists, and engineers. This is due to its appropriate band position, simple preparation, commercial availability, inexpensive, and high oxidizing power [9]. TiO_2-based photocatalysis is initiated by irradiation of light (wavelength < 388 nm) over the TiO_2 photocatalyst. UV light is a common source for UV irradiation. After irradiating of UV light, the electrons-hole pairs are generated results in formation of hydroxyl radicals ($^{\bullet}OH$) on the TiO_2 surface. $^{\bullet}OH$ are powerful and non-selective species, which can degrade the organic pollutants to obtain more readily biodegradable intermediate species and final harmless products [10].

There are several reports about the degradation of gaseous benzene by the TiO_2-based photocatalytic oxidation process under UV irradiation. TiO_2 film coated on supporting materials is more suitable for large scale applications than TiO_2 powder because they can be easily reused and separated from the treatment system. For example, Ku et al. (2007) reported that the photocatalytic degradation of gaseous benzene by using TiO_2 coated on glass exhibited higher performance than TiO_2 coated on stainless steel because glass is a nonconductive material. It does not affect the electron flow in TiO_2 molecules. On the other hand, stainless steel is a conductive material. The cations (e.g. Cr^{3+} and Fe^{3+}) can be transferred to the interface of TiO_2 and stainless steel, which lead to electron-hole recombination, and decrease the photocatalytic activity [11]

Xie et al. (2016) reported photocatalytic degradation of benzene by using TiO_2 thin film coated on soda-lime glass. PVP with molecular weight of 58,000 was used as a binder in sol-gel method. TiO_2 was coated on glass by dip coating technique. It was found that the optimal PVP content was 6% by weight. Photocatalytic activity of 6%-PVP TiO_2 film was 4.62 times higher than that of TiO_2 film without PVP [12]. The use of PVP as the binder of TiO_2 in the work of Xie et al. (2016) is interesting, but with dip coating, the thickness of TiO_2 is not easy to control and it is not suitable to the actual applications on the existing window glass or building.

This study focuses on the removal of benzene in the air by TiO_2-based photocatalytic oxidation process. TiO_2 photocatalyst was prepared by PVP-modified sol-gel method and fabricated on soda-lime glass sheets by the doctor blade technique, a process that can be adopted to mass production. The properties of TiO_2 film were characterized by scanning electron microscope (SEM) and energy-dispersive X-Ray spectroscopy (EDS). The comparative study of benzene removal in different reaction conditions (e.g. adsorption, direct photolysis, photocatalysis) and different numbers of TiO_2 coated glasses were performed under UVC irradiation.

Materials and Methods

Chemicals and Materials

Titanium butoxide (Sigma-Aldrich, 97% purity), PVP powder (Sigma-Aldrich, average M_w of 1,300,000), acetylacetone (Carlo Erba Reagents, 99.5% purity), and methanol (RCI Labscan) were used as Ti precursor, binder, stabilizing agent, and solvent for synthesis of TiO_2, respectively. The transparent glass sheets (2 mm thickness) were cut into 5 cm × 15 cm and used as a material for TiO_2 coating. A solvent (2-propanol) from RCI Labscan was used for washing of glass sheets before coating with TiO_2. Benzene (PanReac Quimica SAU, C_6H_6, 99.8% purity) was used to prepare the benzene vapor as a target compound in all experiments.

Preparation of Sol-Gel TiO_2 Film

TiO_2 films were prepared by PVP-modified sol-gel method [13]. PVP (0.8 g) and methanol (20 ml) were mixed until a homogeneous solution was obtained. Titanium butoxide (4 g) and acetylacetone (1.175 g) were added dropwise into the obtained solution and stirred for 30 min. After that the solution was mixed in the ultrasonic mixer (50 Hz) to ensure that the mixture was homogeneous. The glass sheets were washed by 2-propanol and then dried in the oven (105 °C) for 1 h. The obtained TiO_2 sol was coated on both side of glass surface by doctor blade technique. The adhesive tape strip was used to control the film thickness. A glass rod was used to spread the TiO_2 solution on glass surface. The coated glasses were placed in an oven (105 °C) for 1 h. The dried films were then calcined at 500 °C for 2 h. Morphological appearances and elementary components of TiO_2 coated glass were characterized by a JSM-6610 LV scanning electron microscope (SEM) coupled with an oxford INCA EDS.

Experimental Setup

The experiments were conducted in a batch reactor, as shown in Figure 1. A batch reactor is an acrylic rectangular chamber with volume of 14.9 L. A rubber septa was established on the top of the chamber as an injection port and gas sampling port. A small electrical blower was turned on during experiment to ensure the well mixing in the chamber.

All of the experiments were performed at initial concentration of gaseous benzene of 100 ppm which was prepared by injection of liquid benzene with amount of 5.4 μL into the chamber. Effect of reaction conditions which were studied in this work including adsorption, direct photolysis, and photocatalysis. All of the experiments in this study were investigated with

16 glass sheets, excepted the experiment of effect of number of TiO_2 coated glass sheets.

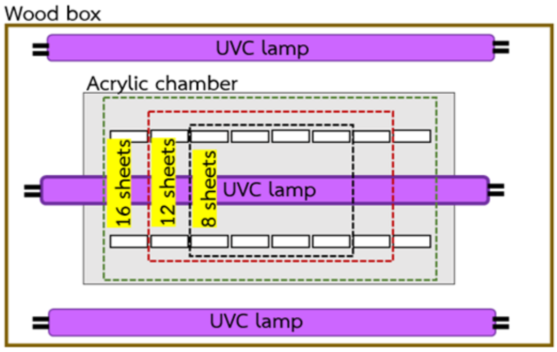

Figure 1 Top view of the experimental setup.

For adsorption test, the TiO_2 coated glass sheets were placed in the chamber. The chamber was kept in the wood box without UV irradiation (dark condition) for a period of time of 12 h. For photolysis test, the uncoated glass sheets were placed in the chamber. The chamber was kept in the dark condition until equilibrium adsorption. After that, three UV lamps (Philips, TUV F17T8, 18W, light intensity = 27 μW/cm^2) with wavelength of 253.7 nm (data provided by the supplier) were turned on for a period time of 7 h.

For photocatalysis test, the TiO_2 coated glass sheets were placed in the chamber, and the experiment was carried out as the same method as photolysis test. In case of effect of number of TiO_2 coated glass sheets, the uses of 8, 12, and 16 TiO_2 coated glass sheets in photocatalysis test were carried out and compared.

Sampling and Analysis of Benzene

A gas sample (1 ml) was withdrawn from the rubber septa by a gas syringe at every time interval of 30 min. A gas chromatograph instrument (Shimadzu, GC-14B) equipped with a capillary column (RTX-502.2, 0.53 mm inner diameter, 105 m length, 3 μm film thickness) and a flame ionization detector (FID) was used for measurement of benzene concentration. Nitrogen gas was used to carry samples through a column. The temperatures of injection port, column, and detector were set up at 100 °C, 100 °C, and 150 °C, respectively.

Results and Discussion

Characterizations of TiO_2 Film

Figure 2 shows the cross-sectional-view images of glass sheets before and after coating. TiO_2 film showed good adherence on the surface of a glass sheet. There was no TiO_2 powder fell out of the film. The color of a thin film was milky white. The coated surface area of TiO_2 film on each side of a glass sheet was 52.0±0.5 cm^2, which was successfully controlled by the adhesive tape strip.

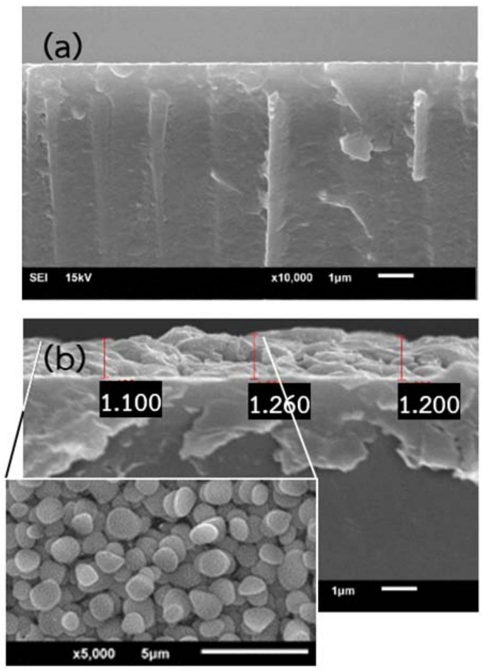

Figure 2 SEM cross-sectional-view images of (a) bare glass sheet and (b) TiO_2 coated glass sheet (inset is a top-view image of TiO_2).

For the bare glass sheet, the surface was smooth without an impurity layer covered on it. For TiO_2 coated glass sheet, the glass surface was covered thoroughly by the well-shaped TiO_2 particles without crack existing, because the influence of PVP in the preparation of TiO_2 sol could be slow down the evaporation of methanol, leading to the prevention of cracking [12]. The average thickness estimated from three different sites on the surface of TiO_2 film was 1.187±0.081 μm.

XRD pattern of the fabricated TiO_2 film shows crystalline phase of anatase (Figure 3). Sirirerkratana et al. (2019) also reported that TiO_2 thin film prepared by sol-gel method and coated on glass substrate were composed of anatase phase [13].

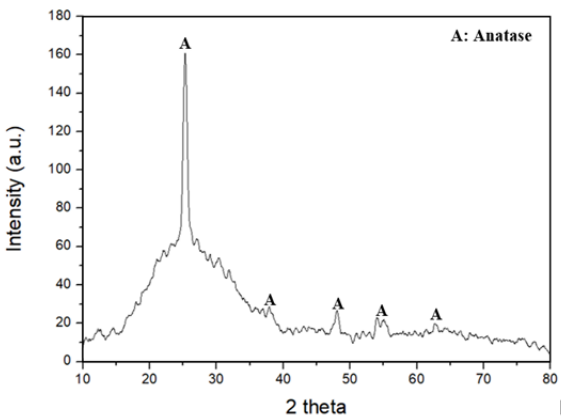

Figure 3 XRD pattern of fabricated TiO_2 film.

The elemental compositions were obtained by EDS of three different points on the surface of a bare glass and TiO_2 coated glass sheets (Table 1). For the bare glass sheet, the elemental composition is in agreement with the typical composition of soda-lime glass, which composed of SiO_2, Na_2O, CaO, MgO, Al_2O_3 and the smaller amount of other compounds [14]. For the TiO_2 coated glass sheet, the elemental composition mainly composed of Ti and O.

Effects of Reaction Conditions on Benzene Removal

From the leakage test by addition of carbon dioxide into the reactor, no leakage was found in the reactor. The removal efficiencies of gaseous benzene under different reaction conditions were compared and presented in Figure 4.

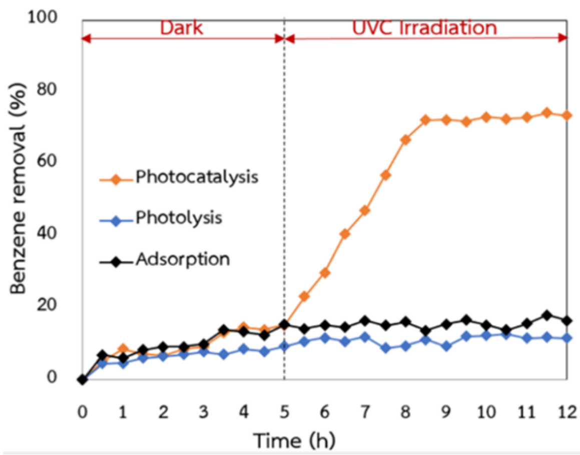

Figure 4 Removal efficiencies of benzene in different reaction conditions.

From the adsorption experiment, the removal efficiencies slightly increased up to 15.4% during 5 h. After that, the efficiencies were not significantly changed. It could be noted that the adsorption of benzene onto the acrylic reactor wall and the TiO_2 film had reached equilibrium at 5 h. For the photolysis experiment (bare glass sheets), benzene was adsorbed onto the acrylic reactor wall and the removal efficiency was stable at 3.5 h (dark condition). The reactor was kept in the dark condition until 5 h to ensure that the adsorption had reached equilibrium. After that, the UVC irradiation was performed for 7 h. It was observed that the efficiency was not significantly changed.

Table 1 Elemental compositions of bare glass sheet and TiO_2 coated glass sheet.

Sample	%Weight									
	Ti	O	Na	Mg	Si	Cl	Ca	C	Sn	Al
Bare glass sheet	0.00	44.02	8.21	2.23	33.10	0.00	5.70	3.25	3.16	0.34
TiO_2 coated glass sheet	40.01	46.73	2.10	0.25	5.56	0.42	1.34	3.57	0.00	0.00

In case of the photocatalysis experiment (TiO_2 coated glass sheets), the reactor was kept in the dark condition until 5 h for adsorption. The remaining benzene concentration was 85.97 ppm. After that, the reactor was irradiated by UVC for another 7 h. During the irradiation of UVC, the removal efficiencies of benzene in the photocatalysis experiment were higher than those of the photolysis experiment because the irradiation of UVC over the TiO_2 photocatalyst could generate the free radicals, resulting in the degradation of benzene molecules through oxidation process. The maximum efficiencies of 75% was observed at 3.5 h of UVC irradiation in the photocatalysis experiment.

Chang and Seo (2014) also reported the same results that the decomposition rate of benzene vapor in UVC-TiO_2 photocatalytic system (wavelength of 254 nm) was much higher than that of UVC direct photolysis [15]. He et al. (2014) reported that the reaction pathways for degradation of benzene by hydroxyl radical ($^{\bullet}OH$) involve three main steps. In the first step, benzene molecules in the air are adsorbed onto the TiO_2 surface and then react with •OH to generate phenol as the first intermediate species. Phenol molecules can also react with $^{\bullet}OH$ to form the subsequent intermediate species. In the second step, oxidation reaction of the intermediates can generate the ring-opened compounds with higher carbon numbers. These species can be subsequently degraded into the smaller aliphatic compounds. In the final step, the remaining species can be mineralized to be CO_2 and H_2O [10].

Effects of Number of TiO_2 Coated Glass Sheets on Benzene Removal

The relationship between removal efficiencies of gaseous benzene by using 8, 12, and 16 TiO_2 coated glass sheets and irradiation time is revealed in Figure 5.

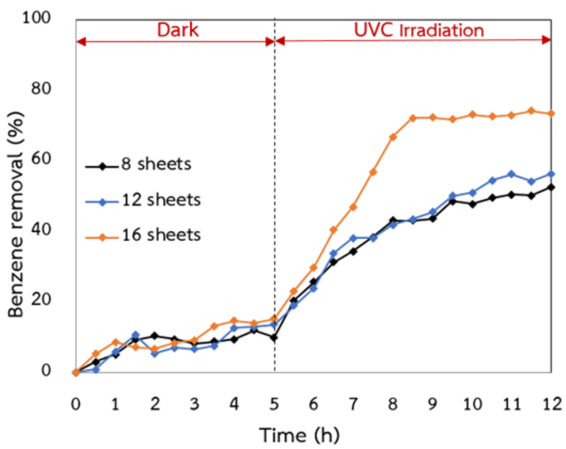

Figure 5 Removal efficiencies of benzene by using different numbers of TiO_2 coated glass sheets.

Conclusions

TiO_2 sols prepared through the PVP-modified sol-gel method can be coated as a thin film on the surface of glass sheets. Doctor blade coating followed by calcination is a promising technique to control the uniform thickness of TiO_2 film. The maximum efficiency for degradation of gaseous benzene was 75%, which was observed in the presence of TiO_2 and UVC irradiation. The benzene removal efficiency can be enhanced by increasing number of the TiO_2 coated sheets which is related to the surface area on supporting materials.

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