



The advanced removal of benzene from aerosols by photocatalytic oxidation and adsorption of Cu–TiO₂/PU under visible light irradiation



Thanh-Dong Pham, Byeong-Kyu Lee*, Chi-Hyeon Lee

Department of Civil and Environmental Engineering, University of Ulsan, Daehakro 93, Namgu, Ulsan 680-749, Republic of Korea

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ABSTRACT

In this study, we used Cu(NO₃)₂ as a precursor of Cu dopants, which defected the TiO₂ lattice and copper oxides, which in turn distributed on the TiO₂ surface to enhance the photocatalytic oxidation activity of the TiO₂. Porous polyurethane (PU) was used as a substrate for the immobilization of the enhanced TiO₂, to increase the adsorption capacity of the photocatalyst. Therefore, the synthesized Cu–TiO₂, immobilized on PU (Cu–TiO₂/PU) materials, exhibited both improved photocatalytic oxidation and adsorption activity for the effective removal of benzene from indoor aerosols. The benzene removal, by Cu–TiO₂/PU under visible light conditions, was due to the combination of improved adsorption and photocatalytic oxidation. The removal of benzene from the aerosol was strongly dependent on humid environmental conditions, and the amount of Cu in the Cu/TiO₂. Optimal humidity conditions and the amount of Cu in the Cu/TiO₂, for the photocatalytic oxidation of benzene in the aerosol by the Cu–TiO₂/PU photocatalyst, were 60% RH and 6 wt%, respectively. Under visible light irradiation, and at a relative humidity of 60% RH, the 6% Cu–TiO₂/PU material removed 86% of the benzene in 100 ppm inlet gas, while 91% of the removed amount was mineralized into CO₂ and H₂O.

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1. Introduction

A lot of volatile organic compounds (VOCs), with boiling points from 50 to 250 °C, are emitted from various sources, such as: industrial processes, transport and house-hold activities [1]. In addition, a significant amount of VOCs could be emitted from indoor facilities and wall surfaces. Many VOCs have been reported to have significant adverse impacts to the environment and human health [2]. In particular, some aromatic and chloro chemicals, such as benzene, chloroform and chloroethylene, are regulated as carcinogenic [3]. For the treatment of carcinogenic VOCs emitted from indoor facilities or vehicles, various physical, chemical and biological techniques, including: adsorption, incineration, condensation, wet scrubbing, membrane separation, bioreaction and plasma oxidation, have been employed [4,5]. However, these technologies have still exhibited some disadvantages or limitations, in terms of broader application [6]. For example, the adsorption technology simply transfers organics from the gas phase to the solid phase, and subsequently requires further treatment processes, which means that this method would not be an economical option for the removal of large amounts of VOCs. The incineration and condensation technologies are cost-effective, as they are only used for the

treatment of VOCs in moderate to high concentration. These techniques are limited, in terms of their practicality, as it pertains to controlling indoor carcinogens like benzene; this is because indoor emissions or concentrations are not typically high enough to make the application of these methods practical or economical.

Currently, the use of photocatalysts in photocatalytic oxidation, for the removal of VOCs, has been become a very attractive and promising alternative technology, particularly for indoor air purification [7,8]. It has already been reported that VOCs could be oxidized to carbon dioxide, water and simple mineral acids by TiO₂ photocatalysts, under or near UV irradiation [9]. TiO₂, a semiconductor, is usually used as an ideal photocatalyst since it is relatively cheap, non-toxic, highly stable from a chemical point of view and easily available [10,11]. However, one of the inherent disadvantages of the TiO₂ is that UV light (or near UV light) in the wavelength range ($\lambda < 400$ nm) must be used to initiate for the photocatalytic oxidation process. Thus the limitation of the applications of the photocatalysis, in the practical system, are associated with UV use and accompanied by safety issues and high energy consumption [12]. Therefore, numerous studies have been carried out to extend the absorption of the TiO₂ in the visible light range (400–700 nm) to overcome the disadvantages concerning the use of UV irradiation as an initiation source for photo-oxidation processes [10,12]. One of the most promising techniques for improving the visible light absorption of the TiO₂ photocatalyst is to use metals such as Cu, V, Cr, Mo, Fe, Co and W (as doping agents) to narrow the TiO₂

* Corresponding author. Fax: +82 52 259 2629.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

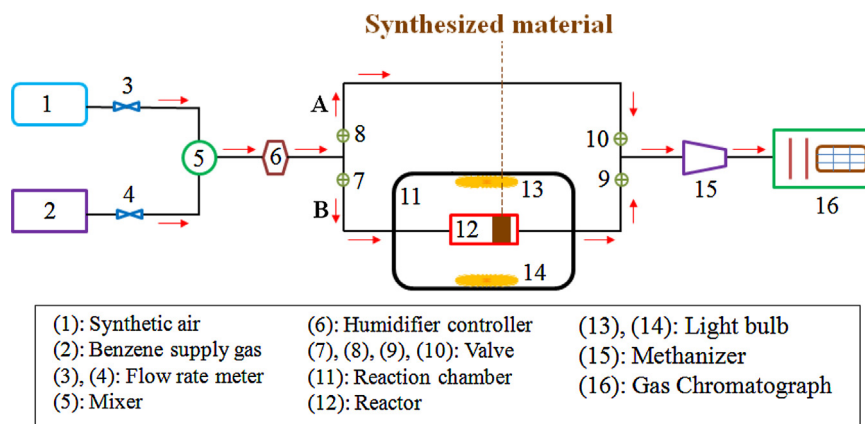


Fig. 1. The schematic diagram of the benzene removal system.

band gap (3.2 eV) [13,14]. This metal doping could also increase the electron–hole generation capacity of TiO_2 , leading to enhancing the photocatalytic activity of the photocatalyst [14]. In our previous study, Cu was used as a doping agent to improve the photocatalytic disinfection activity of TiO_2 , immobilized on glass fiber [15]. The synthesized Cu– TiO_2 /GF exhibited high photocatalytic disinfection activity in the removal bioaerosol, even under visible light.

There are a few reports about the effects of Cu doped TiO_2 on the photocatalytic oxidation of VOCs in aerosols [16]. In our previous study, the synthesized Cu– TiO_2 /GF could exhibit only photocatalytic activity; however, its adsorption ability seemed to be very low; this was because the Cu– TiO_2 /GF used glass fiber, a material with a small specific surface area, which only acted as a substrate for the immobilization of the Cu doped TiO_2 . Therefore, in this study, we used PU – a material with a high specific surface area – as a promising substrate to not only immobilize the Cu doped TiO_2 , but also to increase the adsorption ability of the photocatalyst. Thus, the synthesized Cu doped TiO_2 , immobilized on PU (Cu– TiO_2 /PU), is expected to exhibit both improved adsorption and photocatalytic oxidation activity in the removal of the benzene (classified as class I carcinogenic VOCs by the International Agency for Research on Cancer) from aerosols, even under visible light irradiation [17]. In addition, the removal of the benzene from indoor aerosols is strongly affected by the concentration of water in the air stream [18–21]. The water could be adsorbed on the photocatalyst surface, hindering the further adsorption of the targeted contaminants [20]. The presence of water molecules is also considered to play an important role in the formation of the highly reactive hydroxyl radicals, directly affecting the photocatalytic oxidation process [22]. There are several discrepancies within the previous explanations, with regard to the moisture effect on the photocatalytic activity; therefore, in this study, we extended the previous theories, in an attempt to clarify the effects of humidity on the removal of benzene from indoor aerosols by adsorption and the photocatalytic oxidation of Cu– TiO_2 /PU, under visible light conditions.

2. Materials and methods

2.1. Material synthesis

First, pristine PU was activated using a mixed solution of toluene, toluene-2,4-diisocyanate, and anhydrous triethylamine, to introduce isocyanate groups (NCO) onto its surface [23]. Second, titanium tetrakisopropoxide (TTIP) was reacted with γ -aminopropyl triethoxysilane (APTES) to synthesize amino titanasiloxane, which contains Si–O–Ti bonds and an amine group (NH_2) [23]. Third, the activated PU was immersed into the amino titanasiloxane solution for 1 h, to fix the titanasiloxane on PU; this fixing occurred, based on

the urea bond that forms as a result of the reaction between the isocyanate groups of the isocyanated PU, and the amino group (NH_2) of the amino titanasiloxane [23]. A 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution, which was prepared by the dissolution of $\text{Cu}(\text{NO}_3)_2$ in deionized water at 60 °C, was slowly added (drop-wise) onto the amino titanasiloxane fixed on PU. The obtained material was cleaned using 1 M oxalic acid solution, then was irradiated with a UV light (60 W) for 5 h and then calcined under nitrogen at 200 °C for 5 h to produce Cu-doped TiO_2 fixed on PU (Cu– TiO_2 /PU). The addition volume of $\text{Cu}(\text{NO}_3)_2$ solution was adjusted in order to synthesize 0, 2, 4, 6, 8 and 10% Cu– TiO_2 /PU materials, which the ratios of Cu/ TiO_2 had 0, 2, 4, 6, 8 and 10 wt%, respectively.

2.2. Material characterization

A Thermo Fisher K-Alpha X-ray Photoelectron Spectrometer system was used to obtain the X-ray photoelectron spectroscopy (XPS) spectra of the Cu– TiO_2 /PU materials. The Gaussian multi-peak shapes were applied to fit the Cu $2p_{3/2}$ and Ti $2p_{3/2}$ peaks in the obtained XPS spectra, to determine the elemental state of the copper and titanium in the synthesized materials. X-ray diffraction (XRD) measurements of Cu– TiO_2 /PU were performed, using a Bruker AXN model with a Cu– $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) source, and operated at a scan rate of $0.02^\circ \text{ s}^{-1}$ over a 2θ range of 10–80°. A Hitachi S-4700 scanning electron microscope (SEM) was used to determine the surface morphology of the Cu– TiO_2 /PU, with different ratios of Cu/ TiO_2 . Before the SEM analysis, all the samples were coated with Pt to increase the conductivity of the sample surface. The surface area (S_{BET}) of the synthesized Cu– TiO_2 /PU materials were calculated, based on the Brunauer–Emmett–Teller (BET) isotherm carried out by nitrogen adsorption and desorption at 77 K. An Evolution 300 spectrophotometer (UV-1700 Shimadzu) was used to measure the light absorption spectra of the Cu– TiO_2 /PU in the wavelength range 300–700 nm.

2.3. Experiments for the removal of benzene

A continuous online system for experiments involving the removal of benzene from aerosols, using Cu– TiO_2 /PU materials was shown in Fig. 1. A cylinder containing 1000 ppm benzene in nitrogen gas was used as the benzene supply gas. The benzene gas was mixed with synthetic air, containing 20.5% vol O_2 and 79.5% vol N_2 , to obtain a gas mixture of benzene concentration. Flow rate meters (3) and (4) were controlled to achieve a flow rate of 100 mL/min of 100 ppm benzene in the gas mixture. The humidity controller was employed to control the relative humidity of the gas mixture. Before the benzene removal experiments, valves (7) and (9) were closed, and valves (8) and (10) were opened to ori-

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