Photocatalysis of Low Concentration of Gaseous-Phase Benzene Using Visible-Light Irradiated N-doped and S-doped Titanium Dioxide

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Abstract

Studies on visible-light-driven photocatalysis of air pollutants at indoor air quality (IAQ) levels have been limited. Current study investigated visible-light derived photocatalysis with N-doped and S-doped titanium dioxide (TiO$_2$) for the control of benzene at indoor levels. Two preparation processes were employed for each of the two types of photocatalyst: urea-Degussa P-25 TiO$_2$ and titania-colloid methods for the N-doped TiO$_2$; and titanium isopropoxid- and tetraisopropoxide-thiourea methods for the S-doped TiO$_2$. Furthermore, two coating methods (EDTA- and acetylacetone-dissolving methods) were tested for both the N-doped and S-doped TiO$_2$. The two coating methods exhibited different photocatalytic degradation efficiency for the N-doped photocatalysts, whereas they did not exhibit any difference for the S-doped photocatalysts. In addition, the two doping processes showed different photocatalytic degradation efficiency for both the S-doped and N-doped photocatalysts. For both the N-doped and S-doped TiO$_2$, the photocatalytic oxidation (PCO) efficiency increased as the hydraulic diameter (HD) decreased. The degradation efficiency determined via a PCO system with visible-light induced TiO$_2$ was lower than that with UV-light induced unmodified TiO$_2$, which was obtained from previous studies. Nevertheless, it is noteworthy that for the photocatalytic annular reactor with the HD of 0.5 cm, PCO efficiency increased up to 52% for the N-doped TiO$_2$ and 60% for the S-doped TiO$_2$. Consequently, when combined with the advantage of visible light use over UV light use, it is suggested that with appropriate HD conditions, the visible-light-assisted photocatalytic systems can also become an important tool for improving IAQ.

Keywords: Photocatalytic oxidation, TiO$_2$, Coating method, Doping process

1. Introduction

Indoor air quality (IAQ) has become an important community concern due to the increased amount of personal time spent in indoor environments.[1] For those compounds with indoor sources, indoor exposure can be high. In particular, volatile organic compounds (VOCs) including benzene have well known indoor sources, including cigarette smoke, building materials, furnishings, cleaning compounds, dry cleaning agents, paints, glues, cosmetics, textiles, and combustion sources.[1-3] Furthermore, VOCs in urban atmosphere, mainly as a result of human activities such as motor vehicle exhausts and other combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes,[4-6] can penetrate indoors, thereby elevating the indoor concentration levels.[7] Benzene, which is one of most toxic VOCs, is a known carcinogen such as leukemia.[8] These characteristics of benzene warrant the development of control means to minimize health risk from environmental exposures.

Heterogeneous photocatalytic oxidation (PCO) typically coated with titanium dioxide (TiO$_2$) mediated has become an attractive technique for environmental VOC remediation, due to a number of advantages over the traditional techniques.[9-13] Due to their modular characteristics, low pressure drop across PCO system and room temperature operation, PCO systems can be incorporated into existing heating, ventilation, and air conditioning systems. Rather than transferring pollutants from the gas phase to the solid phase, PCO provides a reduction of absolute toxicity as the gaseous products from the complete PCO of toxic hydrocarbons are carbon dioxide and water. However, TiO$_2$ photocatalysis shows relatively high activity only under ultraviolet (UV) light, which exceed the band-gap energy of 3.0 or 3.2 eV in the rutile or anatase crystalline phase, respectively. Consequently, the efficient use of sunlight, indoor light, or other rays from artificial sources has been an appealing challenge for extending the utilization of TiO$_2$ photocatalytic techniques.

In order to make TiO$_2$ effective under visible light, several

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methods have been proposed to modify the electronic properties of bulk TiO_2 photocatalysts.[14] These methods include the reductive hydrogen plasma treatment,[15] dye sensitization,[16] transition metals doping,[17] and non-metal doping.[18,19] Among these, doping with non-metallic elements like N, C and S doping is a more recent technique.[14] Several studies have applied N-doped TiO_2, upon irradiation of visible light, for degradation of various environmental pollutants. These pollutants tested include acetaldhyde,[18,20,21] benzene,[20] 4-chlorophenol,[20] toluene,[22] and trichloroethylene.[23] Similarly, the applications of S-doped TiO_2 were less documented.[19,24,25] However, most of these N- or S-doped techniques were focused on liquid phase applications.[14] Moreover, the limited gas-phase studies have primarily dealt with a high ppm concentrations of trichloroethylene and dimethyl sulfide,[25] which is more typical for chemical process stream concentrations than IAQ levels. Extrapolation of oxidation performance data collected at concentrations much higher than those in the intended application may not be valid. Accordingly, the present study was conducted to establish the feasibility of applying visible-light-induced TiO_2 doped with N and S elements to cleanse VOCs at IAQ levels. A special attention was paid to the preparation and coating methods of the N- and S-doped photocatalysts. In addition, various photocatalytic conditions were considered in regards to the degradation efficiencies of target compounds.

2. Methods

2.1. Construction of Photocatalytic Reactor

In order to evaluate visible-light-induced photocatalysts for the removal efficiency of benzene, each of N- and S-doped TiO_2 photocatalysts was prepared by applying two popular processes,[18,19,24-26] and both photocatalysts were coated by applying two well-known methods.[27,28] Two preparation processes included urea-Degussa P-25 TiO_2[24] and titania-colloid[24] methods for the N-doped photocatalysts, and included titanium isopropoxid-[17] and tetraisopropoxide-thiourea[24] methods for the S-doped photocatalysts. Furthermore, two coating methods included a EDTA-[27] and a acetylacetone-dissolving[28] methods for both the N- and S-doped photocatalysts.

The PCO reactors used in this investigation had annular geometries. The inner surface of *Pyrex* reactor was coated with N- or S-doped photocatalysts. A cylindrical visible-light source was inserted inside the *Pyrex* tube and served as the inner surface of the annular reactor. The application of a thin, uniform coating on the inside of the glass reactor tubes was essential. The coated reactor was dried for an hour at room temperature and then baked for 30 mins at 450°C. The gas was flowed through the annular region. This design is well adapted to the research environment because it provides a well-characterized reactive catalyst surface along the length of the reactor body and allows uniform light distribution.[29] Moreover, the reactor was designed to direct the flow of incoming air normally to the visible light to increase air turbulence inside the reactor, thus enhancing distribution of target compounds onto the catalytic surface of the reactor.

2.2. Experimental Parameters

Main parameters controlled for this experiment included relative humidity (RH), initial concentration, hydraulic diameter (HD, defined as the inside diameter of the annular reactor tube minus the outside diameter of the lamp), fixed stream flow rate (SFR), visible-light source, and weight of photocatalyst film. These parameters were fixed to their representative values. RH was fixed to between 50 and 60%, which was adjusted by passing zero-grade air through a humidification device in a water bath (Cole-Parmer HAAKE W.[26] The RH was measured just prior to the photocatalytic reactor inlet using a humidity meter (Thermo Recorder TR-72S, T & D Co.). The initial concentration surveyed was 31 ppb, which was within typical IAQ levels. The desired concentration was achieved through the use of a syringe pump (KdScientific Model 210), and was confirmed by measuring the air samples collected at the inlet of the reactor, with a deviation of less than 10%. The representative HD of reactor was 2.0 cm. The SFR was 0.5 L/min. Measurements of SFR were carried out using identical rotameters (0 - 5 L/min) calibrated against a dry test meter (URG 3000-020C). Visible radiation was supplied by an 8-W fluorescent daylight lamp (F8T5DL, Youngwha Lamp Co.). The visible radiation intensity measured at a distance from the visible-light lamp equal to half the hydraulic diameter of the reactor using a Digital Lux Meter (INS Model DX-100) was 1.9 mW/cm^2. The weight of photocatalyst coated inside the reactor were 2.8 mg/cm^2. Meanwhile, an important experimental parameter, HD was further tested for three conditions (0.5, 2.0, and 4.0 cm).

2.3. Procedures

A time-series of concentration measurements of benzene was performed at the inlet and outlet of reactor prior to or after turning on the visible-light lamp (Fig. 1). Prior to turning on the lamp, six 10-min samples were collected for 4 or 5 hrs with an interval of 1 hr at each of the inlet and outlet. Adsorption process between the titania catalyst and target compound reached equilibrium, nominally 2 hrs after the introduction of the target compound, as indicated by equality between the inlet and outlet concentrations. After 4 hrs the introduction of the target compound (adsorption equilibrium), the lamp was turned on. Then, another six 10-min samples were collected for 5 hrs with an interval of 1 hr at each of the inlet and outlet. Since the outlet concentrations of the reactor reached a steady state within 1 hr after the lamp was turned on for the target compound, the steady-state results were discussed as regards the destruction efficiency of the target compound. Each experiment was repeated three times, and the repeated experiments showed very similar patterns. Thus, average values are presented for all experimental conditions.

2.4. Sampling and Analysis

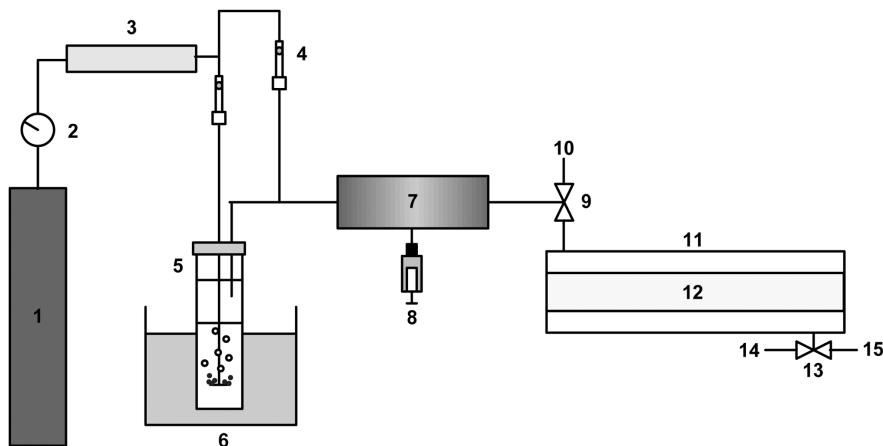Samples from the air stream were collected by filling an eva-

Fig. 1. Schematic diagram of experimental set-up: 1, zero-grade air ; 2, regulator ; 3, charcoal filter ; 4, flowmeter ; 5, water column ; 6, water bath ; 7, mixing chamber ; 8, syringe pump ; 9, 3-way valve ; 10, sampling port or vent system ; 11, PCO reactor ; 12, lamp ; 13, 3-way valve ; 14, sampling port ; and 15, vent system.

cuated 5 L Tedlar bag at a constant flow rate. Air from this bag was then drawn through a sorbent trap containing 0.3 grams of Tenax TA using a constant flow-sampling pump (A.P. Buck Inc. Model I.H). All samples were taken at ambient room temperature (19-25°C). Benzene collected on the sorbent trap was analyzed by coupling a thermal desorption system (Tekmar Model Aerotrap 6000) to a gas chromatograph (Varian 3400CX) with a flame ionization detector using a 0.32-mm-i.d. by 60-m-length fused silica column (Supelco Co. SPB-5).

The quality assurance /quality control program for the measurements of benzene included laboratory blank traps and spiked samples. At the beginning of the day, a laboratory blank trap was analyzed to check for any trap contamination; however, no trap contamination was identified. An external standard was analyzed daily to check the quantitative response. When the quantitative response differed more than ±20% from that predicted by the specified calibration equation, a new calibration equation was determined. The method detection limit was 4.7 μ g/m^3.

3. Results and Discussion

3.1. PCO Efficiency with Two Coating Methods

The inner surface of Pyrex reactor was coated with N-doped TiO$_2$ prepared on the basis of Nosaka et al's doping process[26] or S-doped TiO$_2$ of Ohno et al.'s doping process,[19] by employing two coating methods. Fig. 2 presents the variation of benzene concentrations with time, which was obtained prior to and after PCO by S-doped photocatalyst, according to coating methods. Although at an early stage of PCO process (360 min after turning lamp on) the trend was deviated from an over-all trend, the S-doped photocatalyst prepared by applying Nazeeruddin et al.'s coating method[28] exhibited similar efficiency of photocatalytic degradation to Xagas et al.'s coating method.[27] As shown in Fig. 3, however, the N-doped photocatalyst prepared by applying Nazeeruddin et al.'s coating method[28] exhibited a greater photocatalytic degradation efficiency as compared to
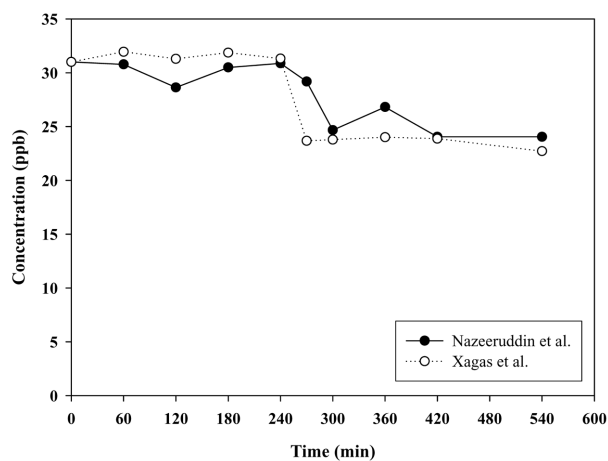

Fig. 2. Concentrations of benzene measured prior to and after turning on lamp according to S-coating method. Visible-light lamp was turned on after 181 min.
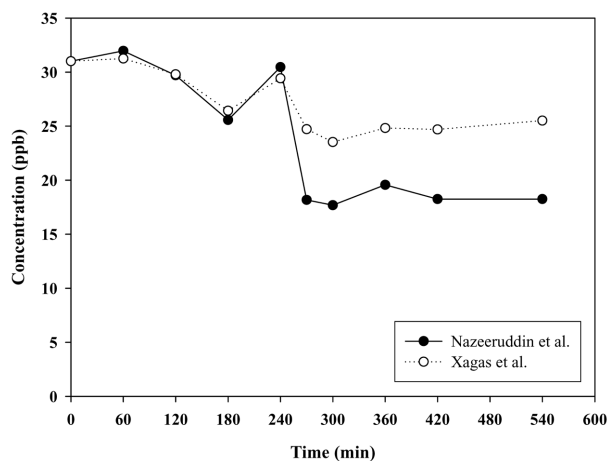

Fig. 3. Concentrations of benzene measured prior to and after turning on lamp according to N-coating method. Visible-light lamp was turned on after 181 min.

Xagas et al.'s method.[27] This difference is likely due to the enhanced colloidal effect of acetylacetone compared to EDTA.[28]

As such, Nazeeruddin et al.'s coating method[28] only was employed when coating the inner surface of Pyrex reactor with S-doped or N-doped photocatalyst prepared on the basis of Bacsa et al.'s method.[24]

3.2. PCO Efficiency with Two N-Doping or S-Doping Processes

The inner surface of Pyrex reactor was coated with S-doped TiO_2 prepared on the basis of Ohno et al.'s doping process[19] and Bacsa et al.'s process.[24] Fig. 4 exhibits the variation of benzene concentrations with time, which was obtained prior to and after PCO by S-doped photocatalyst, according to doping processes. The S-doped photocatalyst prepared by applying the Ohno et al.'s doping method[19] exhibited just a slightly greater photocatalytic degradation efficiency as compared to the Bacsa et al.'s method.[24] According to the steady-state concentrations obtained prior to and after PCO, the PCO efficiency for the Ohno et al.'s doping method[19] was 24%, while that for the Bacsa et al.'s method[24] was 17%. The higher PCO efficiency for the Ohno et al.'s doping method appears to be due to the superior solubility of thiourea with titanium isopropoxid than with tetraisopropoxide.[17]
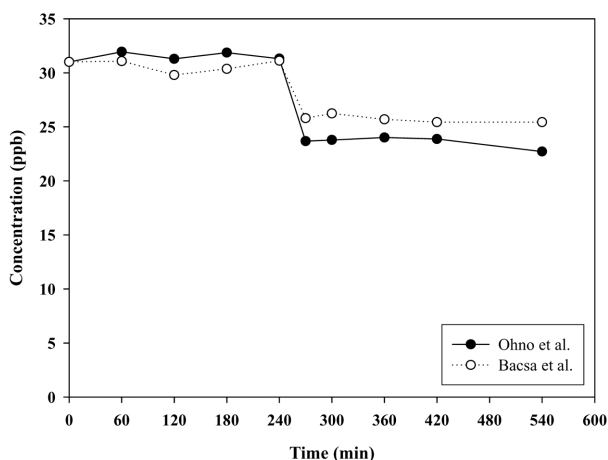

Fig. 4. Concentrations of benzene measured prior to and after turning on lamp according to S-doping process. Visible-light lamp was turned on after 181 min.

Meanwhile, the variation of benzene concentrations with time, which was obtained prior to and after PCO by N-doped photocatalyst, was presented in Fig. 5, according to doping processes. The N-doped photocatalyst prepared by applying the Nosaka et al.'s doping method[26] exhibited a greater photocatalytic degradation efficiency as compared to the Bacsa et al.'s method.[24] According to the steady-state concentrations obtained prior to and after PCO, the PCO efficiency for the Nosaka et al.'s doping method[26] was 41%, while that for the Bacsa et al.'s
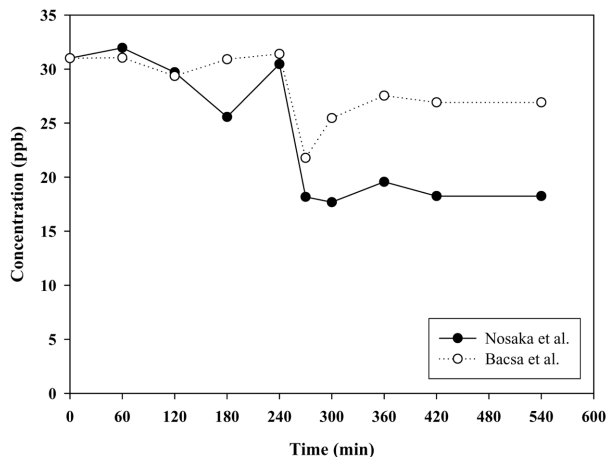

Fig. 5. Concentrations of benzene measured prior to and after turning on lamp according to N-doping process. Visible-light lamp was turned on after 181 min.

method[24] was 18%. Furthermore, Table 1 allows the comparison of PCO efficiency between N-doped TiO_2 and S-doped TiO_2. The N-doped TiO_2 prepared on the basis of Nosaka et al.'s doping method[26] showed a greater PCO efficiency than the S-doped TiO_2 prepared on the basis of Ohno et al.'s doping method[19] or Bacsa et al.'s method.[24] This difference is seemingly due to lower N-TiO_2 combination energy of the urea-Degussa P-25 TiO_2 compared to that of the titania- colloid.[24]

3.3. PCO Efficiency by HDs

Table 2 presents the PCO efficiency of benzene determined via PCO systems with S-doped and doped TiO_2 according to HD. The N-doped photocatalyst prepared by applying the Nosaka et al.'s doping method[26] and the S-doped TiO_2 by Ohno et al.'s doping method[19] were chosen for this survey. The PCO efficiency was obtained using the same reactor residence time (5 s) based on adjusting SFRs. For both the N-doped and S-doped TiO_2, the PCO efficiency increased as the HD decreased. To be activated, photocatalyst should absorb the light enough to provide the energy to overcome band gap between valance band and conduction bands.[14,25] The energy is provided by photons, and more photons are produced as light intensity increases. As such, since the distance of the catalyst from the light source increases when increasing the HD, the decrease in the light intensity in the reactor with a higher HD would seem to be the most obvious reason for the drop in the PCO of the target compounds. This light-intensity effect is also supported by previous studies,[30,31] which found that the oxidation rate of BTEX or trichloroethylene increased with an increase in the UV intensity.

Table 1. Comparison of PCO efficiency (%) of benzene between N-doped TiO_2 and S-doped TiO_2 according to doping processes

Coating method	N-doped TiO_2		S-doped TiO_2	
	Nosaka et al.	Bacsa et al.	Ohno et al.	Bacsa et al.
Nazeeruddin et al.	41	18	24	17

Nosaka et al.[24] ; Bacsa et al.[22] ; Ohno et al.[17] ; and Nazeeruddin et al.[26]

Table 2. Comparison of PCO efficiency (%) of benzene according to HDs

Photocatalyst type	PCO efficiency (%)		
	0.5 cm	2.0 cm	4.0 cm
N-doped	60	41	18
S-doped	52	24	15

Meanwhile, the degradation efficiency determined via a PCO system with S-doped visible-light induced TiO_2 was lower than that with UV-light induced unmodified TiO_2, which was obtained from other studies (nearly 100%).[32] The superior characteristic of the UV-light-induced unmodified TiO_2 is likely due to the enhanced light absorption and photocatalytic activity of the unmodified TiO_2 under UV-light irradiation.[19,25,26] Nevertheless, it is noteworthy that PCO efficiency increased up to 52% for the N-doped TiO_2 and 60% for the S-doped TiO_2. When combined with the advantage of visible light use over UV light use, it is suggested that with appropriate HD conditions, the visible-light-assisted photocatalytic systems can also become an important tool for improving IAQ. Furthermore, considering such operational attributes as a low-pressure drop across the PCO system and ambient temperature operation,[14,29] a continuous visible-light-driven photocatalytic system can easily be incorporated into any existing or other air cleaning devices. For example, a back-up device such as adsorbent will help removing of VOCs that exit from PCO systems without being decomposed and of potential byproducts that can be generated during PCO processes.[33,34] Consequently, this kind of back-up device will extend the application of the visible-light induced photocatalytic systems to the control of IAQ levels of benzene.

4. Conclusions

The present study evaluated the degradation efficiency of benzene using continuous air-flow photocatalytic systems coated with S-doped and N-doped visible-light-induced TiO_2. A special attention was paid to the preparation and coating methods of the N- and S-doped photocatalysts. It was found that the photocatalytic efficiency varied with the preparation methods and coating methods as regards both N- and S-doped photocatalysts. Furthermore, within the conditions of the present study, the results clearly demonstrated that the use of continuous visible-light-driven photocatalytic systems can effectively cleanse gaseous benzene, and that the destruction efficiency was dependent on the HD.

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