Photocatalysis of o-, m- and p-Xylene Using Element-Enhanced Visible-Light Driven Titanium Dioxide

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Abstract

Enhancing with non-metallic elemental nitrogen(N) is one of several methods that have been proposed to modify the electronic properties of bulk titanium dioxide(TiO_2), in order to make TiO_2 effective under visible-light irradiation. Accordingly, current study evaluated the feasibility of applying visible-light-induced TiO_2 enhanced with N element to cleanse aromatic compounds, focusing on xylene isomers at indoor air quality(IAQ) levels. The N-enhanced TiO_2 was prepared by applying two popular processes, and they were coated by applying two well-known methods. For three o-, m-, and p-xylene, the two coating methods exhibited different photocatalytic oxidation(PCO) efficiencies. Similarly, the two N-doping processes showed different PCO efficiencies. For all three stream flow rates(SFRs), the degradation efficiencies were similar between o-xylene and m,p-xylene. The degradation efficiencies of all target compounds increased as the SFR decreased. The degradation efficiencies determined via a PCO system with N-enhanced visible-light induced TiO_2 was somewhat lower than that with ultraviolet(UV)-light induced unmodified TiO_2, which was reported by previous studies. Nevertheless, it is noteworthy that PCO efficiencies increased up to 94% for o-xylene and 97% for the m,p-xylene under lower SFR(0.5 L min^{-1}). Consequently, it is suggested that with appropriate SFR conditions, the visible-light-assisted photocatalytic systems could also become important tools for improving IAQ.

Key Words : Xylene photocatalysis, N-Enhanced TiO_2, Degradation efficiency, Doping process, Coating method

1. Introduction

Volatile organic compounds(VOCs) has received a public concern because of their prevalence in various environments and their potential toxicity. Among VOCs, xylene, including o-, m- and p-xylene isomers is included in gasoline and is a powerful solvent employed in printing, rubber, synthetic fiber, and plastics industries[1]. This popular usage of xylene results in inevitably elevating environmental levels of xylene. Moreover, this compound is toxic to the kidneys and liver, and is abused as neuro-stimulant agents[2,3].

Decrease of cell viability also has been documented[4,5]. These characteristics of xylene isomers warrant the development of control means to minimize health risk from environmental exposures.

The most popular traditional technique for the control of gas-phase VOCs has been an adsorption by granular activated carbon. However, by adsorption, the pollutants are not eliminated but only transferred to another phase, and regeneration and additional disposal are subsequently required. The use of heterogeneous PCO technique has recently attracted interest as an alternative technique due to a number of advantages over the traditional activated carbon technique[6~8]. Due to their modular characteristics, low pressure drop across the reactor and room temperature operation, PCO reactors can be incorporated into existing heating, ventilation, and air

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conditioning systems. Rather than transferring pollu-
tants from the gas phase to the solid phase, PCO pro-
vides a reduction of absolute toxicity as the gaseous
products from the complete PCO of toxic hydrocarbons
are carbon dioxide and water. However, heterogeneous
TiO_2 photocatalysis exhibits relatively high activity on-
ly under UV-light irradiation, which exceed the
band-gap energy of 3.0 or 3.2 eV in the rutile or anatase
crystalline phase, respectively[9]. Consequently, the effi-
cient 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 visi-
ble-light irradiation, several methods have been pro-
posed to modify the electronic properties of bulk TiO_2
photocatalysts[9]. These methods include the reductive
hydrogen plasma treatment[10], dye sensitization[11], tran-
sition metals doping[12] and non-metal doping[13,14].
Among these, doping with non-metallic elemental N is
a more recent technique. Several recent studies have
applied N-enhanced TiO_2, upon irradiationof visible
light, for degradation of various environmental
pollutants. These pollutants tested include acetalde-
hyde[13,15,16], benzene[15], 4-chlorophenol[15], methylene
blue[13], toluene[17] and trichloroethylene[16].

Nevertheless, most of these studies were focused on
water applications[9]. Moreover, less-documented air
studies have primarily dealt with a high ppm concen-
trations, which is more typical for chemical process
stream concentrations than IAQ levels. Extrapolation
of oxidation performance data collected at concen-
trations much higher than those in the intended appli-
cation may not be valid. Accordingly, the current study
was conducted to establish the feasibility of applying
visible-light-induced TiO_2 enhanced with N element to
cleanse xylene isomers at 100 ppb commonly asso-
ciated with IAQ issues.

2. Materials and Methods

2.1. Experimental protocol

A schematic diagram of the experimental apparatus
is presented in Fig. 1. The reactor consisted of a Pyrex
tube uncoated or coated on the inner surface with a
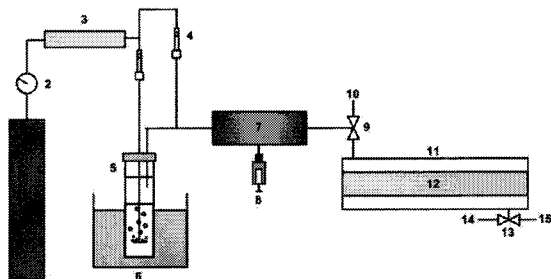thin film of TiO_2 photocatalyst or a thin film of the

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.

N-enhanced TiO_2 photocatalyst. A cylindrical visible-
light source was inserted inside the glass tube and
served as the inner surface of the annular reactor. The
gas flowed through the annular region. This design is
particularly suited for research, because it provides a
well-characterized reactive catalyst surface along the
longitudinal direction of the reactor body and allows
uniform light distribution[6]. The reactor was wrapped
with aluminum foil to minimize the transmission loss
of light from reactor lamp through the glass reactor
surface as well as the transmission gain of light from
laboratory fluorescent lamps. Moreover, the reactor
was designed to direct the flow of incoming air toward
the visible light in order to increase the air turbulence
inside the reactor, thereby enhancing the distribution of
the target compounds onto the inner surface of the
reactor.

A time-series of concentration measurements of
three xylene isomers was conducted at the inlet and
outlet of reactor prior to or after turning on the visi-
ble-light lamp. Prior to turning on the lamp, six 10-min
samples were collected for 4 hrs with an interval of
1 hr at each of the inlet and outlet. Adsorption process
between the titania catalyst and target compounds
reached equilibrium, nominally 2 hrs after the in-
troduction of the target compounds, as indicated by
equality between the inlet and outlet concentrations.
After 4 hrs after the introduction of the target com-
pounds(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 all target compounds, the steady-state results were discussed as regards the destruction efficiency of the target compounds. Each experiment was repeated three times, and the repeated experiments showed very similar patterns. Thus, average values are presented for all experimental conditions.

Five parameters were controlled to their representative values: 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 SFR, visible-light source, and weight of photocatalyst film. 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 W26). 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 100 ppb to represent an indoor air quality level. The desired concentration was achieved through the use of a syringe pump(Model 210, KD Scientific Co.). The representative HD of reactor was 20 mm. The SFR was 0.5 L min^{-1}. Measurements of SFR were carried out using identical rotameters(0-5 L min^{-1}) 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, SFR was further tested for three conditions(0.5, 1.0, and 2.0 L min^{-1}).

2.2. Preparation and coating of N-enhanced TiO₂

The N-enhanced TiO₂ photocatalysts were prepared by applying two popular processes[9,18,19] and coated by applying two well-known methods[20,21]. Two preparation processes included those employed by Bacsa et

al.[18] and Nosaka et al.[19], and two coating methods included those used by Xagas et al.[20] and Nazeeruddin et al.[21]. The method employed by Nosaka et al.[19] was applied for the preparation of N-enhanced TiO₂ powders. Urea was employed as a N-source for mechanical N-doping. 8 g of commercially available TiO₂ powder(Degussa P-25) was added to 20 ml of aqueous solution of the organic nitrogen compounds and stirred at room temperature for 1 hr. The mixture was kept in dark for one day and then dried under reduced pressure. N-enhanced TiO₂ powder was calcined at 500°C for 3 hrs under aerated conditions to obtain yellow powder. The calcined powder was washed with diluted sulfuric acid and then with pure water, and dried by vacuum. The N-enhanced photocatalyst was also prepared by applying Bacsa et al.'s method[18]. Titania colloids were prepared with titanium tetraisoprop-oxide(TTIP) and urea. These were mixed in ethanol in the ratio of 1:4. The consequent slurry was concentrated and poured into a Petri dish. Then, it was inserted into an oven at 450-500°C for 3 hrs . Finally, yellow powders were obtained.

After preparation, the N-enhanced TiO₂ powders were coated on the inner surface of the PCO reactors by applying the method employed by Xagas et al.[20]. Grinding 0.5 g TiO₂ powder(Degussa, P25) with 2 ml of a 0.1 M aqueous ethylenediaminotetraacetic acid(EDTA) solution was grinded to produce a viscous paste. The paste was diluted by slow addition of 1 ml of water. Then, 0.1 ml of Triton X 100 was added and the paste was smeared on a glass substrate immobilized by an adhesive tape strip. After drying at 100℃ for 15 min, the film was calcined in an oven at 500℃ for 30 min.

For the Nazeeruddin et al.'s coating method[21], commercial TiO₂(P25, Degussa AG, Germany) was employed. The commercial TiO₂ was ground in a mortar with a small amount of water containing acetylacetone. The powder was diluted by addition of water under continued grinding. A detergent(Triton X 100, Aldrich) was added to facilitate the spreading of the colloid on the substrate. The other process was same as that for the Xagas et al.'s method[20].

2.3. Sampling and analysis

Target isomers in the air stream were collected by filling an evacuated 5 L Tedlar bag at a constant flow rate. Air from this bag was then drawn through a sorbent trap containing 0.3 g 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). The target compounds collected on the sorbent trap were 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 target compounds 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 limits ranged from 1.2 to 3.3 μg m^{-3}, depending on isomers.

3. Results and Discussion

3.1. Comparison of two coating methods

Two coating methods(Xagas et al.'s[20] and Nazeeruddin et al.'s[21] methods) were compared for photocatalytic degradation efficiencies. The N-enhanced TiO$_2$ prepared on the basis of Nosaka et al's doping process[19] was applied to the inside surface of annular PCO reactor, by employing the two coating methods. Fig. 2 shows the temporal variation of o-xylene concentrations, which was obtained prior to and after visible-light induced PCO by N-enhanced photocatalyst, according to coating methods. The PCO efficiencies were higher for the Nazeeruddin et al.'s[21] coating method than for the Xagas et al.'s coating method[20]. According to the steady-state concentrations of o-xylene prior to and after PCO process, the PCO efficiencies were 95% for the former coating method and 75% for the latter coating method. As shown in
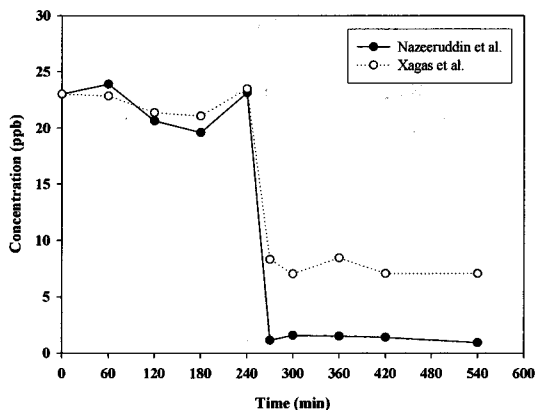

Fig. 2. Concentrations of o-xylene measured prior to and after turning on lamp according to N-coating method(Xagas et al.[20] and Nazeeruddin et al.[21] methods). Visible-light lamp was turned on after 4 hrs.
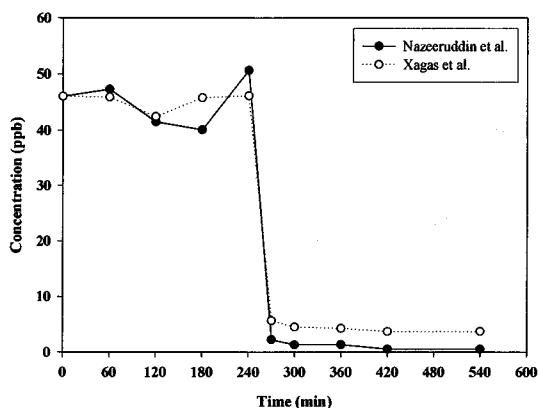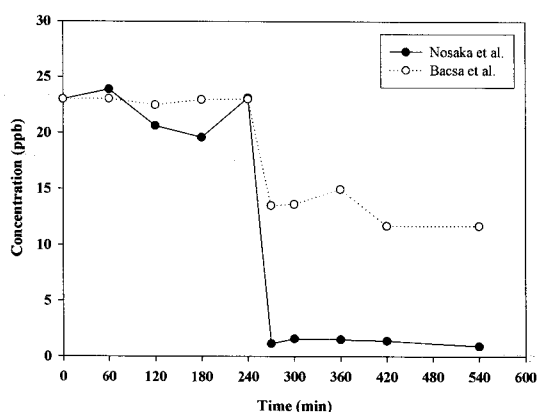

Fig. 3. Concentrations of m,p-xylene measured prior to and after turning on lamp according to N-coating methodXagas et al.[20] and Nazeeruddin et al.[21] methods). Visible-light lamp was turned on after 4 hrs.

Fig. 3, for m,p-xylene the PCO efficiencies were also higher for the Nazeeruddin et al.'s coating method[21] than for the Xagas et al.'s coating method[20]. Thus, Nazeeruddin et al.'s coating method[21] only was employed when coating the inner surface of Pyrex reactor with N-enhanced photocatalyst prepared on the basis of Bacsa et al.'s method[18].

3.2. Photocatalysis efficiencies with two doping processes

The inside wall of annular photocatalytic reactor

was coated with N-enhanced TiO$_2$ prepared on the basis of both the Nosaka et al.'s doping process[19] and Bacsa et al.'s process[18]. Figs. 4 and 5 present the temporal variation of o-xylene and m,p-xylene concentrations, respectively, which were obtained prior to and after PCO by N-enhanced photocatalyst, according to doping processes. For both o-xylene and m,p-xylene, the N-enhanced photocatalyst prepared by applying the Nosaka et al.'s doping method[19] exhibited greater photocatalytic degradation efficiencies as compared to the Bacsa et al.'s method[18]. According to the steady-state

Fig. 4. Concentrations of o-xylene measured prior to and after turning on lamp according to N-doping process(Nosaka et al.[19] and Bacsa et al.[18] processes). Visible-light lamp was turned on after 4 hrs.
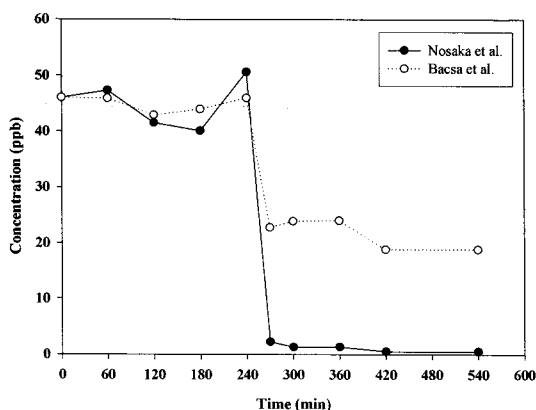
Fig. 5. Concentrations of m,p-xylene measured prior to and after turning on lamp according to N-doping process(Nosaka et al.[19] and Bacsa et al.[18] processes). Visible-light lamp was turned on after 4 hrs.

concentrations obtained prior to and after PCO, the PCO efficiencies for the Nosaka et al.'s doping method[19] were 75% and 80% for o-xylene and m,p-xylene, respectively, while that for the Bacsa et al.'s method[18] was 43% and 53%. Consequently, the PCO reactor prepared on the basis of s Nosaka et al.'s doping method[19] and Nazeeruddin et al.'s coating method[21] was chosen in order to further investigate the effect of SFR on PCO efficiency.

3.3. PCO efficiencies by SFR

Three SFRs(0.5, 1.0, and 2.0 L min^{-1}) were tested for degradation efficiencies of the o-xylene and m,p-xylene, using a 20 mm-HD reactor coated with the N-enhanced TiO$_2$. The residence times, which were calculated by dividing the reactor volume by SFR, were 22.0, 11.0, and 5.5 sec for the SFRs of 0.5, 1.0, and 2.0 L min^{-1}, respectively. In addition, the respective face velocities were 1.1, 2.2, and 4.4 cm s^{-1}. The degradation efficiencies of target compounds determined via photocatalytic reactor with N-enhanced TiO$_2$ according to SFR are shown in Table 1. For all three SFRs, the degradation efficiencies were similar between o-xylene and m,p-xylene. The degradation efficiencies of all target compounds increased as the SFR decreased. The PCO efficiencies were between 65% and 94% for o-xylene and between 70 and 97%, depending upon the SFRs. This trend suggests that SFR is an important parameter for the application of TiO$_2$ photocatalytic technology for cleansing indoor air VOCs. The lower destruction efficiencies for the high SFR could be caused by an insufficient residence time inside the reactor. In addition, bulk mass transport of the target compounds from the gas-phase to the surface of the catalyst particle due to convection and diffusion,

Table 1. Comparison of PCO efficiencies of o,m,p-xylene according to SFR

Compound	PCO efficiency(%)		
	0.5 L min^{-1}	1.0 L min^{-1}	2.0 L min^{-1}
o-Xylene	94	78	65
m,p-Xylene	97	82	70

Notes: N-enhanced photocatalyst prepared by Nosaka et al.'s doping process[19] and Nazeeruddin et al.'s coating method[21] was employed for obtaining these data.

an important heterogeneous catalytic reaction process,[22,23] would be insufficient for a high SFR(high face velocity for the same HD reactor). This assertion is further supported by Obee and Brown's study[24], which reported that face velocity influenced the mass transfer of formaldehyde, toluene and 1,3-butadiene.

The degradation efficiencies determined via a PCO system with N-enhanced visible-light induced TiO_2 were somewhat lower than that with UV-light induced unmodified TiO_2, which was obtained from other studies[6,25]. 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[19,26]. Nevertheless, it is noteworthy that under lower SFR(0.5 L min^{-1}) PCO efficiencies increased up to 94% for o-xylene and 97% for m,p-xylene. Consequently, when combined withthe advantage of visible light use over UV-light use, it is suggested that with appropriate SFR conditions, the visible-light-assisted photocatalytic systems can also become an important tool for improving IAQ.

4. Conclusions

The present study evaluated the degradation efficiencies of o-xylene and m,p-xylene using continuous air-flow photocatalytic systems coated with N-enhanced visible-light-induced TiO_2. Within the conditions of the present study, the results clearly demonstrated that the use of continuous visible-light-driven photocatalytic system coated with N-enhanced TiO_2 can effectively cleanse gaseous o,m,p-xylene, and that the destruction efficiencies were dependent on the SFR. Accordingly, when combined with such operational attributes as a low-pressure drop across the PCO system and ambient temperature operation, a continuous visible-light-driven photocatalytic system is clearly an important cleaning means for making better indoor air quality.

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