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Design of an efficient photocatalytic reactor for the decomposition of gaseous organic contaminants in air

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ABSTRACT

Here, a strategy for decomposing gaseous organic contaminants by photocatalytic reactions is reported. A photocatalytic reactor is designed, based on an open tubular reactor with a UV light source installed at the center of the glass tube to permit the vertical irradiation of light onto the photocatalyst. TiO_2 immobilized on a stainless steel plate and a fiber based material, respectively, are placed on the inner wall of an open tubular reactor. The fibers of felt induce wake and eddy flow near the inner surface of the reactor, resulting in compression of boundary layer. The compressed boundary layer provides a higher probability of contact between organic contaminants and the photocatalyst, consequently resulting in the enhanced photocatalytic oxidative decomposition of organic compounds. The inlet of photoreactor is modified in order to better control the bulk stream to form spiral-like flow. The reactor with a single tangent inlet exhibits the highest photocatalytic performance among the reactors examined, as an evidence of the improved probability of contact. Importantly, the reactor with a single tangent inlet, in which TiO_2 immobilized felt is installed, maintains its photocatalytic activities for as long as twenty days.

1. Introduction

The emission of various organic contaminants, such as odorous gases, volatile organic compounds (VOCs), and related compounds, tends to increase in parallel with increasing industrial development. In particular, indoor air pollution is becoming more and more serious with the increase in the use of man-made building materials, leading to the sick house syndrome [1,2]. Since organic pollutants emitted from building materials can attack human organs for a long period of time, thus causing various diseases, numerous attempts have been made to remove them from the atmosphere using several methods such as adsorption on activated carbon, catalytic oxidation, advanced oxidation techniques, and so on. Among the more recently developed technologies, photocatalytic advanced oxidation using a combination of ultraviolet (UV) radiation and TiO_2 is generally considered to be a promising technique for indoor air purification in the future [3–12]. TiO_2 is one of the representative n-type photocatalytic materials with a wide band gap energy (E_g) of 3.0–3.2 eV [13–16]. TiO_2 generates electron (e^-) and hole (h^+) pairs when it is irradiated with UV light ($\lambda < 380$ nm). The photo-generated excitons mainly produce reactive hydroxyl radicals ($^{\bullet}OH$), which have a high standard reductive potential compared to other oxidants that are in the conventional use. Moreover, TiO_2 is a harmless and inexpensive material and can be used at room temperature with semi-permanent usage.

In spite of the superiorities of UV/TiO_2 systems in environmental applications, photocatalytic air purification has not been developed successfully, due to difficulties with the design of an efficient photocatalytic reaction system. A photocatalytic oxidation system in the gas phase requires that the photocatalyst receive a sufficient amount of irradiation as well as a high probability of contact between the photocatalyst and reactants. Packed-bed reactors, which are generally used for catalytic reactions cannot be expected to be effectively used in photocatalytic systems because the penetration of UV light is restricted by the packed catalyst and also with the high pressure drop [17]. The installation of a honeycomb support in photocatalytic reactor is not preferred because it is not easy to direct the irradiated light vertically onto the photocatalyst. Efficient irradiation of light can be achieved by installing the UV light lamp at the center of the open tubular reaction system. Moreover, the pressure drop is prevented by using the thin photocatalytic support instead of introduction of thick foam-based support. As a result, the catalytic reaction takes place in outer region of an

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annular space. The probability of contact between the photocatalyst and organic contaminants, however, is not better than other well-known reaction systems [18,19].

Accordingly, a strategy for enhancing the probability of their contact in an open tubular photocatalytic reactor is suggested herein to produce a high performance UV/TiO_2 air purification system. Powdered TiO_2 was immobilized on a fiber based material, felt, and then installed it on the inner wall of the reactor. Wake and eddy flow can be formed when fluid flows on a rough surface [20]. Their formation result in the compression of the boundary layer, providing higher probability of contact between the photocatalyst and reactants. Moreover, it has a larger surface area than that of smooth plate, which would be advantageous for a catalytic reaction. In addition, various types of photocatalytic reactors were evaluated in order to investigate the effect of gas stream behavior on photocatalytic performance. The gas, including reactants, needs to flow in close contact with the photocatalyst on the wall in an open tubular reactor to enhance the photocatalytic performance. If the stream flows in an open tubular reactor with having small kinetic energy, a large amount of pollutants can pass through the reactor without any reaction because of the dead volume in the reactor. The probability of contact between the reactants and the photocatalyst can be significantly increased when the wake flow is well-developed near the inner surface of the tubular reactor. To accomplish this, a reactor should be designed to permit contaminated gas to pass along the wall. Inducing a spiral-like flow is a promising technique for achieving this. Herein, several approaches are proposed for controlling the stream, which involve quite simple and straight forward modifications of the reactor. In addition, computational fluid simulations (based on actual reaction conditions) were conducted to understand the behavior of the stream in each tubular reactor. Then, various types of tubular reactors used for the photocatalytic oxidative decomposition of dimethyl sulfide (DMS) were examined. DMS is one of the well known odorous VOCs, which can be produced easily, both indoors and outdoors [21–23]. The decomposition of DMS using the proposed photoreactor was compared with results obtained by computational flow calculations.

2. Experimental

2.1. Experimental set up and photocatalytic reaction

The photocatalytic performance of each reaction system was examined for the oxidative decomposition of dimethyl sulfide (DMS, Aldrich) in the gas phase under irradiation by UV light (Sankyo Denki, G4T5, UV-C, 4 W, length = 134.5 mm). The average wavelength of light irradiated is 254 nm and then the energy of 1 mole of photons is calculated to be 4.71×10^5 J. More details for calculating apparent quantum yield (AQY) are shown in supporting materials. Commercial TiO_2, P25 (Degussa), was used as a photocatalyst in this reaction.

A schematic diagram of the total reaction system is shown in Fig. 1A. Before introduction into the photocatalytic reactor, air containing vapor and DMS was heated at 110 °C to achieve total vaporization. An aqueous solution of DMS was injected via a syringe pump (74900 series, Cole-parmer) at a constant rate. The linear velocity of the vaporized DMS and air mixture was varied from 0.056 m s^{-1} (1 l min^{-1}) to 0.357 m s^{-1} (7 l min^{-1}). The range of linear velocity is considered to be applicable to various fields [24,25]. The linear velocity cannot be controlled higher than 0.357 m s^{-1} due to concerns related to the high pressure breakdown of the photocatalytic reactor. Air flow was fully saturated with water vapor. Relative humidity was measured by a hygrometer (Testo 635, Testo). The concentration of DMS at the inlet of the photocatalytic reactor was maintained at 1 ppm during the reaction. 1.0 ml of the sample from the output of the photocatalytic reactor was collected by means of a syringe, and its concentration was determined by a gas chromatography–mass spectrometry detector (GC-MSD, 7890A GC-5975C MSD, Agilent Technologies) using the selected ion monitoring mode. Moreover, the number of incident photons was measured by a light power meter (Nova II, Ophir) where power fan cooled thermal sensor (FL500A) is equipped to calculate AQY. It is assumed that all incident photons are absorbed by the photocatalyst. Details of the method for calculating the number of incident photons is presented in supplementary material.

2.2. Immobilization of TiO_2

2.2.1. TiO_2 on stainless steel

In this study, two types of supports were used, stainless steel (STS) and felt. Powdered TiO_2 was immobilized on the STS using a doctor blade [26]. A STS plate was prepared as a support. The thickness of the plate is 50 μm. It was washed with ethanol, followed by drying at 80 °C for 10 min before the coating. A TiO_2 paste for the film coating was prepared by the following method. 0.6 g of powdered TiO_2 was mixed with 0.2 g of acetyl acetone (Aldrich). 3.0 ml of deionized water was then introduced into the mixture with adding 0.12 g of polyethylene oxide (M.W. 10,000, Aldrich) and the same amount of polyethylene glycol (M.W. 8000, Aldrich). The viscous paste was vigorously mixed and stirred for 8 h. The prepared paste was layered homogeneously on the STS plate using doctor blade. The TiO_2 coated STS was heat-treated with air at 550 °C for 4 h, and it is referred to herein as PH-S. The PH-S is rolled to form a tube that can be inserted into the tubular reactor.

2.2.2. TiO_2 on felt

TiO_2 was immobilized on the felt by a spraying method. A commercial felt made from cotton was cleaned by placing it in a vacuum oven at 80 °C for 30 min prior to spraying. Glabrous fibers are tangled in felt as shown in Fig. S1. 0.2 g of TiO_2 powder was suspended in 10 ml of deionized water by sonication for 1 h. The suspension was sprayed on the felt using a spraying device, and it is referred to herein as PH-F. The PH-F is also rolled to form a tube that can be inserted into the tubular reactor. The attachment of immobilized photocatalyst of the PH-F will be studied herein as a durability test.

The surface area and surface morphology of P25 coated supports (PH-S and PH-F) were measured by BET (ASAP 2010, Micromeritics) and SEM (JSM-6701F/X-MAX, Jeol), respectively.

2.3. Reactor design

Various types of open tubular reactors (annular type, volume = 42.18 cm^3, pyrex) were designed in this study to investigate how the behavior of the stream affects photocatalytic activity. A lamp protector is to protect lamp by oxidation from water which is made by pyrex. A basis reactor was used as a standard to characterize the developed photocatalytic oxidation system (Fig. S3). Other types of reactors such as a 6-winged baffle reactor, a single-tangent inlet reactor, and a double-tangent inlet reactor were also examined to compare the photocatalytic activities with that of the basis reactor. A 6-winged baffle reactor is similar to a basis reactor. The only difference is that a 6-winged baffle is installed inside the basis reactor to change the behavior of the stream. For a single tangent inlet reactor, a single inlet was installed in the tangential direction into the reactor to cause stream to flow along the wall of the reactor. A double tangent inlet reactor was also proposed, in which two tangential inlets confront each other, splitting the stream into two. The behaviors of the stream induced by each designed reactor were evaluated by computational flow