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Removal of high concentration dimethyl methylphosphonate in the gas phase by repeated-batch reactions using TiO_2

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ABSTRACT

The aim of our study is to develop apparatuses that use TiO_2 for effective decontamination of air contaminated by Sarin gas. We performed photocatalytic decomposition of gaseous dimethyl methylphosphonate (DMMP) by TiO_2 and identified the oxidization products. The high activity of TiO_2 (0.01 g) was observed under UV-light irradiation and high concentration DMMP (33.5 μM) was removed rapidly. On the other hand, DMMP was not decreased under UV-light irradiation without TiO_2. This indicates that photocatalytic treatment is very effective for the removal of DMMP. Methanol, formaldehyde, formic acid, methyl formate, CO, CO_2 and H_2O were detected as the primary products. In the gas phase, no highly poisonous substances were detected. In order to examine the performance of photocatalytic activity during long-term reactions, we performed photocatalytic decomposition by repeated-batch reactions using TiO_2. High photocatalytic activities decreased gradually. Meanwhile, the strong adsorption of TiO_2 against DMMP was observed as photocatalytic activities decreased. During the repeated-batch reactions with the sample scaled up (TiO_2: 0.1 g), the total amount of removed DMMP reached 968.5 μM by both photocatalytic decomposition and the strong adsorption of TiO_2. These results suggest the possibility of removing large amounts of DMMP.

1. Introduction

In 1994, the first Sarin gas terrorist attack by a cult occurred in Matsumoto, Japan. About 600 people were injured either slightly or seriously and seven were killed [1]. Then, in 1995, the same cult committed a further terrorist attack in the Tokyo subway Sarin incident, in which 12 were killed and about 5500 were injured [2]. At this time, as a consequence of washing of contaminated parts with copious amounts of running water, poisonous gas and contaminated waste water spread through this treatment causing serious secondary damages.

In recent years, photocatalysis has attracted attention as a low cost, environmentally benign method, and detoxification for chemical warfare agents has been studied using this high technology. The following studies report on the decontamination of DMMP (Sarin simulant) in the gas phase: photocatalytic decomposition on TiO_2-coated glass support [3], photooxidation on powdered TiO_2 surface [4], the adsorption and photocatalytic degradation on TiO_2 powders and thin films [5], the effect of air humidity and DMMP quantity on hydrolysis and photocatalytic oxidation over TiO_2 [6] and adsorption and photocatalytic degradation over dry and humidified TiO_2 [7]. The primary products generated by DMMP photooxidation were shown to be CO, CO_2, and H_2O as final products, and methanol, formaldehyde, and formic acid as intermediates in the gas phase, and phosphoric acid and phosphorus-containing products as nonvolatile compounds on TiO_2. However, the strong adsorption and accumulation of nonvolatile compounds on the TiO_2 surface caused deactivation of its photocatalytic reaction [3–7]. Moss et al. [5] reported that the $PO_4{}^{3-}$ and methylphosphonic acid products remaining bound to surface adsorption sites block further adsorption of DMMP vapor, and this leads to an inhibition of photooxidation. In their study to resolve this problem, Obee and Satyapal [3] reported that washing of deactivated catalyst with water is sufficient for complete regeneration of the catalyst, and that the solubility of methyl phosphonic acid and phosphates in water aids in removing these species from catalytically active sites. Kiselev et al. [7] reported that on a wet surface that contains only a few monolayers of water the concentration of intermediate surface species is reduced, and that it is possible to optimize the sustained photocatalytic degradation of organic phosphorous compounds by controlled humidification of the reaction gas. On the other hand, in the negative effect of air humidity, Trubitsyn and Vorontsov [6] examined the adsorption, natural hydrolysis and photocatalytic oxidation at high DMMP surface coverage on TiO_2 under both

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1% and 50% relative humidity, and reported that under 50% relative humidity, while both adsorption and natural hydrolysis were enhanced, the gas-phase product concentrations observed in photocatalytic oxidation were a little smaller than that of 1% relative humidity. Furthermore, Chen et al. [8] reported on photocatalytic degradation of DMMP in the presence of low-frequency ultrasound in the liquid phase and showed that sonication increases the apparent rate constants of DMMP photocatalytic oxidation without releasing intermediate products, and these phenomena were attributed to increased mass transport of DMMP into pores and to the surface of TiO_2. These methods have proved to be excellent measures for the regeneration or maintenance of photocatalytic activity for a relatively short time or for a single batch reaction. However, the effects of photocatalytic activity on gaseous DMMP during long-term reactions have not been fully examined. In a real setting, swift and effective decontamination are required for large contaminated areas or multiple subway cars that are exposed to Sarin gas with high concentration. Thus, it is very important that the performance of TiO_2 in its photocatalytic activity and the possibility of success in removing large amounts of Sarin gas under long-term continuous reactions are tested.

The aim of our study is to develop apparatuses that use TiO_2 for effective decontamination of air contaminated by Sarin gas. In this study, using a batch type photocatalytic-reactor system that was constructed for DMMP analysis in the gas phase (i) we carried out photocatalytic decomposition of gaseous DMMP with TiO_2 and confirmed the identity of the photooxidation products in the gas phase. Furthermore (ii) we performed the repeated-batch photocatalytic reactions using TiO_2 in order to examine the performance of photocatalytic activity during long-term reactions, and to remove large amounts of gaseous DMMP by repeated-batch reactions on a practical scale.

2. Materials and methods

2.1. TiO_2-plate, reagents and lighting

Commercial TiO_2 powder (photocatalyst P-25; Nippon Aerosil Co., Ltd., Tokyo, Japan) was used in this study. TiO_2-plate was prepared as follows: TiO_2 (0.01 g) was dispersed in 3.0 mL of distilled water and spread on a glass-plate (5 cm × 5 cm), which was heated on a hot plate (about 80 °C). Distilled water was evaporated and thus TiO_2 was immobilized on a glass-plate. Sarin simulant used was DMMP (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and a UV lamp with a center wavelength of 357 nm (Black Light EFD15BlB-T; Toshiba Lighting and Technology Co., Tokyo, Japan) as lighting was used. TiO_2-plate was pre-exposed to UV light for 1 h to remove organic compounds adsorbed on the TiO_2-plate. Then, the TiO_2-plate was placed in the photocatalytic-reaction system. UV-light intensity on the TiO_2-plate surface in this system was measured to be 6.3 mW/cm^2, using 51002 Digital Illuminance Meter (Yokogawa Co., Tokyo, Japan).

2.2. Photocatalytic-reaction system, photocatalytic decomposition and repeated-batch reactions

Fig. 1 shows a schematic diagram of the photocatalytic-reaction system for DMMP analysis in the gas phase. Air supplied by the compressor was dried with silica gel, let through a soda lime container to remove CO_2, and bubbled into 97% DMMP undiluted solution. The vaporized DMMP was passed through mist trap to remove aerosol and introduced into a 200-mL PYREX-glass reactor, where a TiO_2-plate was placed. The following were the reactor optimization process employed in order to prevent its inner wall from adsorbing DMMP: the use of a Teflon O-ring as sealing material, by silane application to the interior wall, and the temperature control with ribbon heater. Silane application using 5% (w/v) dichlorodimethylsilane toluene solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was performed following the instruction manual [9] and the procedure described by Näykki [10]. After DMMP concentration in the reactor became stable, valves were closed on both sides to obtain batch condition and DMMP was photocatalytically decomposed with UV irradiation above upside under high temperature (100 °C) and room temperature (27 °C) conditions. Gas chromatograph GC-2014 (GC; Shimadzu Co., Kyoto, Japan) was used to analyze DMMP decrease in the reactor every 12 min. Sample gas in the reactor was injected automatically through the stainless steel pipe connected directly with the reactor. For GC, Rtx-1 capillary column [30 m length × 0.53 mm diameter × 5.0 μm thickness] (Shimadzu GLC Ltd., Kyoto, Japan) and temperature-programmed chromatography (from 50 °C to 80 °C) were used. Organic compounds and phosphoric compounds were detected by FID and FPD, respectively. The gaseous products generated by DMMP photooxidation were analyzed by gas-chromatography–mass spectrometry GC–MS-QP2010 (GC–MS; Shimadzu Co.). Sample gas in the reactor was injected manually using warmed syringe. For GC–MS, Rtx-1 capillary column (above mentioned) and InertCap for amines capillary column [30 m length × 0.32 mm diameter × 0.5 μm thickness] (GL sciences Inc., Tokyo, Japan), and temperature-programmed chromatography (from 50 °C to 80 °C) were used. Products in the gas phase were identified using GC–MS Postrum Analysis software.

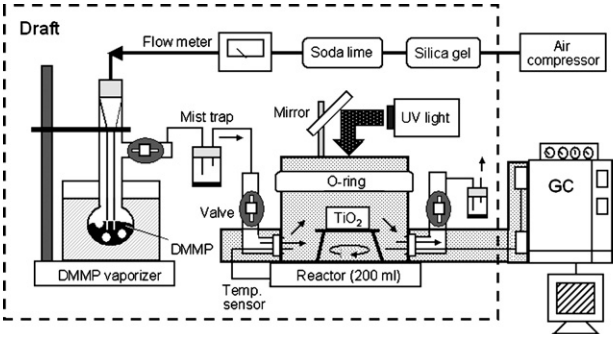

Fig. 1. Diagram of DMMP photocatalytic-reaction and analysis system.

Repeated-batch reactions using TiO_2-plate were carried out by introducing vaporized DMMP repeatedly until photocatalytic activity and/or adsorption of TiO_2-plate against DMMP were lost. Photocatalytic decompositions by repeated-batch reactions were performed under intermittent irradiation of UV light for a long-term period.

Concentration of DMMP in the reactor was obtained from the standard analytical curve. The photocatalytic decomposition rate of DMMP was obtained by subtracting the decrease ratio of DMMP before UV irradiation under the dark condition (sum up the adsorption and the thermal decomposition of DMMP) from the found value of photocatalytic decomposition rate. Net photocatalytic decomposition rates of TiO_2-plate were calculated by deducting adsorption rates (before UV irradiation) from photocatalytic decomposition rates (under UV irradiation).

3. Results and discussion

3.1. Photocatalytic decomposition of gaseous DMMP by TiO_2

Fig. 2 shows the photocatalytic decomposition of DMMP by TiO_2 (0.01 g) in photocatalytic-reaction system. Under high temperature conditions of 100 °C, in the presence of TiO_2 (Fig. 2A; closed circles), DMMP concentration in the reactor became stable at about 33.7 μM