



Continuous elimination of gaseous dimethyl methylphosphonate by a photocatalytic flow reaction system



Nobuaki Mera^a, Tsutomu Hirakawa^a, Taizo Sano^a, Koji Takeuchi^a, Hiromichi Ichinose^b, Yasuo Seto^c, Nobuaki Negishi^{a,*}

^a Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, Japan

^b Saga Ceramic Research Laboratory (SCRL), 3037-7 Hinoe Kuromuta, Arita-Cho, Saga 844-0022, Japan

^c National Research Institute of Polis Science (NRIPS), 6-3-1 Kashiwanoha, Kashiwa-shi, Chiba 277-0882, Japan

ARTICLE INFO

Article history:

Received 26 September 2012

Received in revised form 18 March 2013

Accepted 4 April 2013

Available online 22 April 2013

Keywords:

TiO₂

Photocatalyst

DMMP

Sarin

Flow type photoreactor

ABSTRACT

Dimethyl methylphosphonate (DMMP) removal by a continuous photocatalytic reaction system at different levels of humidity (RH) was investigated for the purpose of allowing rescue operations at disaster sites over an extended period of time when applied to gas masks or other protective gear. With a high flow rate of air (10 L/min), around 85% of the 0.17 μmol/L DMMP was successfully eliminated by this photocatalytic reaction system regardless of relative humidity. On the other hand, the formation of intermediates on the TiO₂ surface indicated that photocatalytic activity was dependent on relative humidity, and during a 5-h test period, the ratio of photocatalytic DMMP conversion reached 74.5% at 100% RH. DMMP adsorption onto the TiO₂ surface was found to be quite strong; DMMP removal was observed despite low humidity and dark conditions

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Over the last decade, photocatalysis has been studied as one of the most progressive, green and low cost environmental remediation technologies which has been applied to such areas as the removal of automobile exhaust gas on highways and the development of self-cleaning materials. One of the applications for the elimination of gaseous pollutants is the photodecomposition of chemicals used in warfare. Various studies have been carried out on the elimination of gaseous dimethyl methylphosphonate (DMMP), a sarin simulant [1–11]. DMMP has a characteristic strong adsorption onto TiO₂ or other solid surfaces on which methanol is formed continuously by the hydrolysis of DMMP [2–6,8,9,12]. It is well known that, upon UV irradiation, DMMP on TiO₂ is photooxidized to CO, CO₂ and H₂O – the major final products while methanol, formaldehyde, formic acid, methyl formate and dimethyl ether are formed as intermediates in the gas phase [1–6,8,9,11,13–15]. Moss et al. have reported that the adsorption and accumulation of nonvolatile phosphoric compounds, i.e., DMMP, methyl methylphosphonate (MMP), methylphosphonic acid (MPA) and phosphoric acid (PA) on the TiO₂ surface, cause great difficulty in

the removal of chemical agents used in warfare [6]. For its practical application, several investigations have been carried out on the effects of the relative humidity on the photocatalytic elimination of DMMP in batches. Trubitsyn and Vorontsov have examined the photocatalytic oxidation of low (0.9 μmol) and high (45 μmol) coverage of DMMP on TiO₂ at both 1% and 50% relative humidity (RH) [5]. They reported that, with high DMMP coverage quantity, the photocatalytic oxidation rate at 50% RH was slightly less than in the case of 1% RH. In contrast, Besov et al., who investigated the photocatalytic elimination of DMMP by TiO₂ aerosol at 4% and 37% RH, have reported that the rate of the photocatalytic oxidation was significantly increased with the rise in relative humidity [9]. Also, Kiselev et al. have examined the photocatalytic degradation of DMMP on rutile TiO₂ under dry and wet conditions (0% and 7% RH) [7]. They observed that the existence of a few water layers reduced the formation of intermediates on the TiO₂ surface and that the water layers preserved high photocatalytic activity. These results provide important information regarding the effects of relative humidity on gaseous DMMP removal in batches. Studies on DMMP removal under conditions of continuous flow have not yet been fully conducted, although necessary when considering actual situations in which the elimination of chemical warfare agents will be urgently required.

The final goal of our study is to develop a lightweight photocatalytic air-purifier combined with charcoal canister for gas masks

* Corresponding author. Tel.: +81 29 861 8165; fax: +81 29 861 8866.
E-mail address: n-negishi@aist.go.jp (N. Negishi).

designed to allow the extension of time for rescue operations. We have constructed a flow-type photocatalytic reaction system and have succeeded in carrying out the continuous removal of gaseous DMMP using a photocatalytic system. To simulate real-life situations, the concentration of DMMP-contaminated air was adjusted to the same level as that of sarin gas of LD₅₀. The gas was then introduced into the reaction system at a flow rate of 10 L/min, which is higher than normal respiratory minute volume. We investigated DMMP elimination under various relative humidity conditions and identified the photooxidation products on the TiO₂ surface while continuously introducing DMMP-contaminated air into the reaction system.

2. Materials and methods

2.1. Preparation and characterization of the TiO₂-coated silica foams

A commercial peroxy-modified anatase photocatalyst sol (SLEC-PA; Office Takahashi Inc., Saga, Japan) was used in this study [16,17]. SLEC-PA was immobilized onto doughnut-shaped silica foams (10 mm thick, 40 mm in diameter, 20 mm diameter hole, and 84% porosity; Fig. 1A) by a dip-coating method. Photocatalyst-immobilized silica foams were prepared as follows: sixteen pieces of the doughnut-shaped silica foams were dip-coated with SLEC-PA and were withdrawn at a speed of 1.5 mm/s. TiO₂-coated silica foams were obtained after calcination at 450 °C for 1 h. These procedures (coating – calcination) were repeated three times. The total amount of TiO₂ on the 16 pieces of silica foam was 0.56 g, as calculated by subtracting the weight of the raw silica foams from the weight of the TiO₂-coated silica foams. The TiO₂-coated silica foam was characterized by the crystalline structure and SEM image. Rigaku SmartLab carried out observation of crystalline structure of the samples. The surface structure of TiO₂ coated silica foam was observed by Hitachi SEM-4700 field emission scanning electron microscope (FE-SEM). The specific surface area of photocatalyst is one of important factor for photocatalytic activity. However, observation of TiO₂ on the silica foam is difficult. Therefore, the specific surface area of the calcined SLEC-PA gel was measured by Quantachrome AS-1.

Fig. 1B shows the inside structure of the flow-type photoreactor and Fig. 1C shows a picture of the photoreactor. The photoreactor is cylindrical-shaped, 190 mm in length and 40 mm in internal diameter, and a quartz glass tube (19 mm in external diameter) was placed at the center of the reactor. Of the 0.185 L inside volume of the empty reactor, 0.15 L was available as an operational volume for the TiO₂-coated silica foams (16 pieces). A UV lamp with a central wavelength of 352 nm (6 W Black light blue FL6BL-B; Hitachi Lighting Ltd., Tokyo, Japan) was placed inside the glass tube while the TiO₂-coated silica foams were isolated from the UV lamp by the quartz glass tube. The TiO₂-coated silica foams were pre-exposed to UV light for 1 h in order to remove the adhesive organic compounds from the TiO₂ surface. The UV light intensity at the surface of the TiO₂-coated silica foams in this system was measured at 7.2 mW/cm², using a UD-36 UV Radiometer (Topcon Co., Tokyo, Japan). Dimethyl methylphosphonate (DMMP, Tokyo Chemical Industry Co., Tokyo, Japan) was used as the sarin simulant.

2.2. Flow-type photoreactor, continuous photocatalytic reactions, gas and ion chromatographs

The flow-type photocatalytic reaction system is shown in Fig. 2. Air was used as the carrier gas and was dried by passing through a membrane dryer (DM-XB05; Ube Industries, Ltd., Tokyo, Japan) and silica gel. The dried air was separated into the three ways: to

the water bubbler (generation of wet air), DMMP bubbler (generation of gaseous DMMP), and to the mass-flow controller for dry air. DMMP mist generated by bubbling was removed in a mist trap before being mixed with dry air. The concentration of DMMP was controlled at 0.17 μmol/L in the carrier gas. The flow rate of the DMMP-mixed air was adjusted to 10 L/min, which is larger than the respiratory minute volume in normal conditions. The concentration of DMMP was determined to be 0.17 μmol/L (=1.7 μmol/10 L) as it was about the same level as a 50% lethal dose, or LD₅₀, of sarin gas (around 20 ppm). The relative humidity (RH) of the DMMP-mixed air was adjusted to 0%, 50% and 100% by controlling the flow rates of dry and wet air. All of the experiments were carried out at a room temperature of around 25 °C.

A gas chromatograph GC-2014 (GC; Shimadzu Co., Kyoto, Japan) was used to analyze the gas components every 12 min. The outlet gas was automatically injected into the GC through a stainless steel tube that was connected directly to the photocatalytic system. A Rtx-1 capillary column (30 m length × 0.53 mm diameter × 5.0 μm thickness, Shimadzu GLC, Ltd., Kyoto, Japan) was used for temperature-programmed analysis by GC (from 50 °C to 80 °C). The organic compounds (intermediates of DMMP) and phosphoric compounds (DMMP and its intermediates) in the gas phase were detected by FID and FPD, respectively. First, the path of the gas flow was switched from bypass to the photoreactor after confirming the initial concentration of the DMMP gas. The residence time of the gas in the photoreactor was around 0.9 s (as 10 L/min). The path of the gas flow was switched back to bypass after the reaction. After the experiment, the TiO₂-coated silica foams (16 pieces) were removed from the photoreactor, dipped in 400 mL ultra pure water for 30 min, and the washings were analyzed by an ion chromatograph IC-2001 (IC; Tosoh Co., Tokyo, Japan). The concentrations of the intermediates – methylphosphonic acid (MPA) and phosphoric acid (PA) – and the final products were then analyzed by IC.

3. Results and discussion

3.1. Characteristics of photocatalyst

The photocatalyst, SLEC-PA which we used, is a commercialized material. However, this photocatalyst is not yet widely known in the world. We will show the details of the characteristics of this photocatalyst. Fig. 3 shows the surface structure of TiO₂-coated silica foam. As shown in the Fig. 3A, TiO₂ was partially peeled off from the substrate. SiO₂ foam itself is relatively fragile and we predicted that the peeled off was partially occurred. By the high-resolution observation of the TiO₂ silica foam, it is clarified that TiO₂ layer had many nanopores as shown in Fig. 3B. It is expected that the specific surface area of TiO₂ must be large. Consequently, the specific surface area of calcined SLEC-PA was observed, and the result was 99.84 m²/g. This value is twice of P25 (Evonik), and it is considered that the surface area of TiO₂ coated silica foam was enough for photocatalysis. Fig. 4 shows the XRD observation results. As shown in Fig. 4A, silica foam had a quartz structure [18], on the other hand, these quartz structure was hidden by TiO₂ coating as shown in Fig. 4B. The crystalline structure of TiO₂ on the silica foam was mainly anatase phase, however, one sharp peak was found at around 30. It is expected that this 2θ value be attributed to TiO₂ brookite phase [19].

3.2. Removal of DMMP by continuous photocatalytic reactions

For practical applications in such protective equipment as gas masks, guarantees of long life and safety are required for the products as well as allowance for relative humidity. We have, thus, investigated the effect of the relative humidity on the

Download English Version:

<https://daneshyari.com/en/article/45184>

Download Persian Version:

<https://daneshyari.com/article/45184>

[Daneshyari.com](https://daneshyari.com)