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$_2$O 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$_2$O 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

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. TiO₂-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
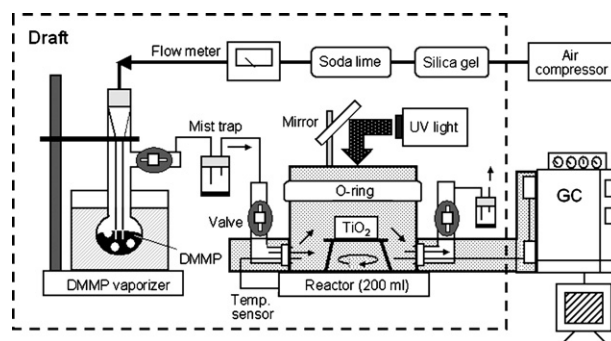

Fig. 1. Diagram of DMMP photocatalytic-reaction and analysis system.

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.

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 TiO₂

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
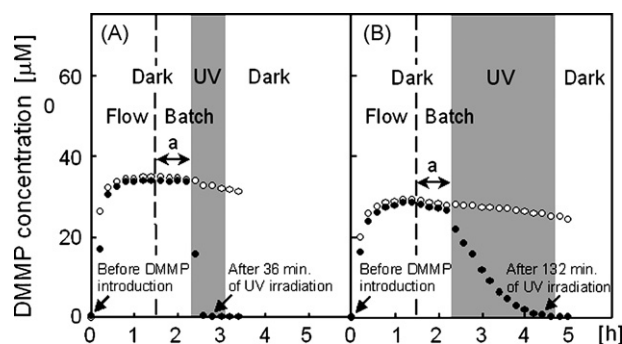
Fig. 2. Photocatalytic decomposition of DMMP in the gas phase under (A) high temperature conditions at 100 °C and (B) room temperature conditions at 27 °C. Closed circles: with TiO_2, open circles: without TiO_2 and (a) before UV.

Fig. 3. Detection of primary products generated by DMMP photooxidation in the gas phase under (A) high temperature conditions at 100 °C and (B) room temperature conditions at 27 °C.

84 min after the introduction of DMMP during the flow condition. Then, photocatalytic decomposition was carried out for DMMP under UV irradiation during the batch condition. Excellent photocatalytic activity was observed and high concentration DMMP in the gas phase decreased rapidly to the measuring limit (0.40 μM) within 24 min under UV irradiation. DMMP decomposition rate observed before UV irradiation due to adsorption and/or thermal reaction was 0.25 μM/h, which is the sum of the adsorption rate and thermal decomposition rate. This rate – we call the "adsorption rate" in this paper – was subtracted from the total DMMP decomposition rate to obtain the net photocatalytic decomposition rate, which was shown to be 76.5 μM/h. Another experiment of DMMP decomposition without TiO_2 was performed in order to examine the photolysis reaction by UV irradiation alone (open circles). The concentration of introduced DMMP became stable at around 34.9 μM during the flow condition, and the concentration remained at about the same level under UV irradiation during the batch condition. Therefore, it was shown that gaseous DMMP was not decomposed by photolysis reaction with UV irradiation alone.

Photooxidation of DMMP in the gas phase by TiO_2 was carried out at room temperature (27 °C)—the temperature close to natural conditions (Fig. 2B; closed circles). Introduced DMMP concentration in the reactor became stable at about 28.5 μM during the flow condition, and DMMP concentration was decreased gradually by photocatalytic decomposition to the measuring limit within 144 min under UV irradiation during the batch condition (0.30 μM). Adsorption rate before UV irradiation and net photocatalytic decomposition rate were 2.65 μM/h and 3.65 μM/h, respectively. On the other hand, in the experiment without TiO_2 (open circles), the concentration of introduced DMMP became stable at about 29.2 μM during the flow condition, and DMMP concentration remained constant under UV irradiation during the batch condition, also.

Several studies have been conducted in order to investigate the effects of temperature conditions on adsorption and decomposition of DMMP on TiO_2 surface [11–16]. Rusu and Yates [15] reported that at the temperature lower than −113 °C, DMMP condenses as an ice layer on the outer surface of TiO_2. In the temperature range from −113 °C to −73 °C, DMMP diffuses into the TiO_2 interior and chemisorbs on TiO_2 through the phosphoryl oxygen to the surface hydroxyl groups and to surface Lewis acid sites. Above −59 °C (from −59 °C to 213 °C), cleavage of P–OCH₃ groups takes place, with the production of Ti–OCH₃ species, and the dissociation of chemisorbed DMMP is seen. Sheinker and Mitchell [16] reported on the thermal decomposition of DMMP on γ-Al_2O_3 at temperatures from 25 °C to 400 °C and showed that the DMMP that is adsorbed is decomposed at 25 °C and increasing temperature brings about an increase in the decomposition activity of the surface. In our study, the temperature of the interior reactor was controlled as one of the optimization
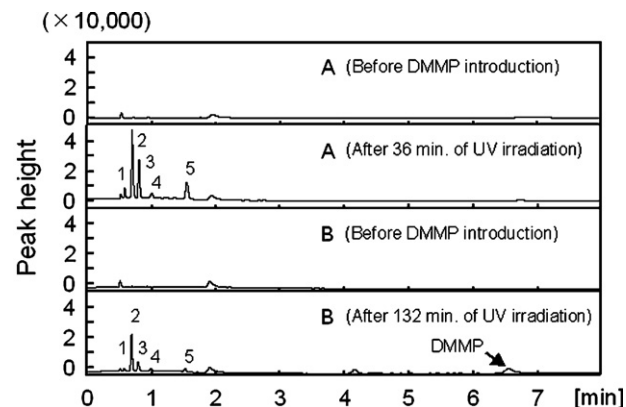
processes, in order to prevent DMMP adsorption as far as possible. Under both high temperature and room temperature conditions with TiO_2 (Fig. 2; closed circles), although the DMMP concentrations in the gas phase before UV irradiation were almost constant, we consider that the adsorbed DMMP on the TiO_2 surfaces was decomposed by thermal decomposition of TiO_2 in both cases. Most studies on the photocatalytic decomposition have been carried out at room temperature [3–7]. Segal and Suib [14] reported that the advantages of photocatalysis are that benign products such as CO_2 and H_2O can be produced, high temperatures can be avoided, and that it may be possible to utilize solar energy for reactions. Furthermore, photoassisted decomposition and thermal decomposition of DMMP over amorphous manganese oxide catalysts were carried out at low temperature (70 °C). They reported that during thermal reactions, significantly less product was formed than during the photocatalysis experiment and no CO_2 was observed. In this study, photocatalytic decompositions of gaseous DMMP by TiO_2 were carried out at both high temperature (100 °C) and room temperature (27 °C). Initial concentration of DMMP (28.5 μM) at 27 °C was slightly lower than that of 33.7 μM at 100 °C. This result suggested the increasing adsorption of DMMP to the inner wall of reactor at 27 °C. It was considered that the amounts of products generated by thermal decompositions were small (this is shown in Section 3.2 in detail) and most DMMP was photocatalytically decomposed under UV irradiation under both temperature conditions. Furthermore, the net photocatalytic decomposition rate at a high temperature was 20.9-fold higher than that at room temperature. No decreases of DMMP were observed under UV irradiation alone without TiO_2 in both cases (open circles). The results proved that photocatalytic treatment is an effective method for decomposition of DMMP in the gas phase, and that photocatalytic decomposition was especially promoted at high temperature.

3.2. Identification of primary products

After photocatalytic decomposition, DMMP decomposition products in the gas phase were examined in order to clarify whether highly poisonous products were generated as volatile compounds. Fig. 3 shows gas chromatograms at a few points both before DMMP introduction (corresponding to Fig. 2A and B before DMMP introduction) and after photocatalytic decompositions (corresponding to Fig. 2A after 36 min of UV irradiation and Fig. 2B after 132 min of UV irradiation). Chromatograms of "after photocatalytic decompositions" at both temperatures showed similar patterns and have five distinctive peaks in common, which represent the main decomposition products. The peak heights were outstanding at high temperature. Thus, we focused on photocatalytic decomposition
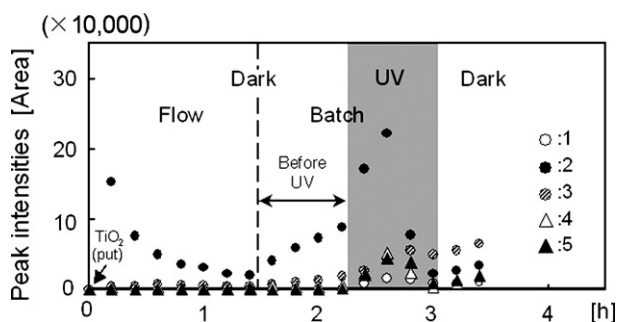
Fig. 4. Time courses of area values of primary products in the gas phase during photocatalytic decomposition at high temperature (100 °C). Fig. 4 corresponds to the time course of Fig. 2(A). TiO$_2$ (put): TiO$_2$ placed in the reactor.

at high temperature condition to proceed with effective investigation in a short period. Fig. 4 shows the time courses of area values of products in the gas phase that correspond to photocatalytic decomposition at high temperature in Fig. 2A. The intensities of Product 2 (closed circles) were the largest of all products and increased especially under UV irradiation. However, Product 2 dramatically decreased at 36 min of the UV irradiation. Because this intensity was also increased before UV irradiation, it was suggested that Product 2 was generated from gaseous DMMP by both photocatalytic decomposition and thermal decomposition. Other Products (1, 3, 4 and 5) were also increased when TiO$_2$ was irradiated with UV light. However, these intensities decreased as the UV irradiation continued, except Product 3 (diagonal circles). It was shown that these products were intermediates of DMMP photocatalytic decomposition. As for Product 3, it was indicated that this product was one of the final products of DMMP photooxidation because its intensity remained relatively stable under the UV irradiation.

The gas-phase products from DMMP decomposition were identified by GC–MS analysis. Three inorganic compounds—CO, CO$_2$ and H$_2$O, and four organic compounds—methanol, formaldehyde, formic acid, and methyl formate were detected. Based on retention time by GC analysis using standard reagents, we examined which organic compound corresponds to which peak in Fig. 3. We found that methanol was Product 2 (easily generated compound), methyl formate was Product 3 (one of the final products), formic acid was Product 5 (intermediate). Product 1 and 4 (intermediates) were yet to be identified. Table 1 shows the increase rates, net photocatalytic decomposition rates, photocatalytic decomposition rates, maximum concentrations and minimum concentrations of methanol, methyl formate and formic acid after photocatalytic decomposition of gaseous DMMP. In the case of methanol, increase rates before UV irradiation (thermal decomposition) and net photocatalytic decomposition (under UV irradiation) were 3.35 μM/h and 9.65 μM/h, respectively. The decrease rate that was observed after 24 min of UV irradiation was 19.5 μM/h. Methanol reached maximum concentration under UV irradiation within 24 min (8.65 μM) and decreased rapidly to 0.85 μM. As for methyl formate, increase rates were 0.55 μM/h (before UV irradiation) and 1.25 μM/h (net photo-

catalytic decomposition), respectively. However, the decrease rate was very low (1.00 μM/h). Maximum concentration under UV irradiation was 1.65 μM, and only a slight decrease was observed (to 1.45 μM). For formic acid, increase rates were 0.10 μM/h (before UV irradiation) and 5.25 μM/h (net photocatalytic decomposition), respectively. The decrease rate was 4.50 μM/h after 24 min of UV irradiation. Maximum concentration under UV irradiation was 2.25 μM and decreased to 0.45 μM.

Studies have been conducted regarding the primary products generated by DMMP photooxidation, and CO, CO$_2$, H$_2$O have been identified as final products and methanol, formaldehyde, formic acid as intermediates in the gas phase [3–7]. Obee and Satyapal [3] reported that complete conversion of any methanol or formaldehyde to produce CO$_2$ and CO appears to be the dominant reaction and that phosphate remains on the surface along with methyl phosphonic acid, which retains a portion of the carbon content of DMMP, thereby explaining the mass balance discrepancy based on gas-phase CO$_2$/CO alone. Furthermore they showed the possibility of methyl formate formation from methanol and formic acid with readiness, and reported that methyl formate was observed only by injecting a mixed gas-phase sample of formic acid and methanol into the GC–MS. In our study, methyl formate (Product 3 in Fig. 4) was detected in the gas-phase products. It was indicated that methyl formate was one of the final products of DMMP photooxidation because its peak intensity remained relatively stable under UV irradiation (Fig. 4). Furthermore, we reconfirmed the stability of methyl formate against photooxidation by carrying out photocatalytic decomposition of methyl formate standard reagent by TiO$_2$. While 33.5 μM of DMMP were photocatalytically decomposed (Fig. 2A), the final concentration of methyl formate was very low (1.45 μM). Thus, it was shown that most DMMP was mineralized (into CO, CO$_2$, H$_2$O) by photooxidation. However, the analysis of the formation of these kinds of products that show stability against photocatalytic decomposition would be an important aspect in this field of study. As for the formaldehyde was detected by GC–MS analysis, it could not be identified with the peak in Fig. 3 because the retention time of formaldehyde was not clear using GC analysis with FID detector. Sheinker and Mitchell [16] reported that dimethyl ether and methanol were produced as volatile products by thermal decomposition of DMMP with γ-alumina at both 25 °C and 100 °C. Knagge et al. [17] reported that thermal reaction of DMMP and O$_2$ on nanocrystalline NaY at 200 °C yielded several gas-phase products including dimethyl ether, formaldehyde, CO, CO$_2$. Therefore, we assumed that unidentified Products 1 and 4 (or in reverse order) in Fig. 4 were dimethyl ether and formaldehyde. We will examine them further. These results show that no highly poisonous substances were produced in the gas phase.

3.3. Decomposition of gaseous DMMP by repeated-batch reactions

In considering the possibility of long-term reaction of TiO$_2$, we performed photocatalytic decomposition of DMMP by repeated-batch reactions under intermittent irradiation of UV light in order

Table 1
Increasse rates, net photocatalytic decomposition rates, photocatalytic decomposition rates, maximum concentrations and minimum concentrations of methanol, methyl formate and formic acid after photocatalytic decomposition of gaseous DMMP.

Product no.	Organic compound*	Rate (μM/h)			Concentration (μM)	
		Before UV	Under UV irradiation			
		Increase	Net photocatalytic decomposition	Photocatalytic decomposition	Maximum	Minimum
2	Methanol	3.35	9.65	13.0	8.65	0.85
3	Methyl formate	0.55	1.25	1.80	1.65	1.45
5	Formic acid	0.10	5.25	5.35	2.25	0.45

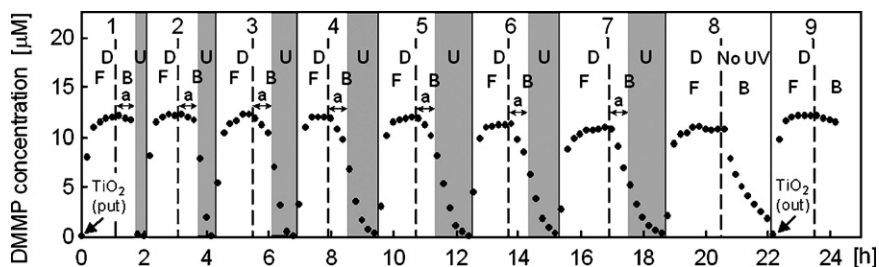Asterisk (*) organic compounds correspond to gaseous products in Fig. 4.

Fig. 5. Photocatalytic decomposition of gaseous DMMP by repeated-batch reactions using TiO_2. The number is the number of the times of repeated-batches. D and U are dark and UV irradiation period, respectively. F and B are flow and batch period, respectively. (a) before UV. TiO_2 (put): TiO_2 placed in the reactor. TiO_2 (out): TiO_2 taken out of the reactor. No UV: without UV irradiation.

to examine the performance of photocatalytic activity of TiO_2 over a long time. Fig. 5 shows the results of eight repeated-batch reactions with TiO_2 (0.01 g) for 22 h and the ninth batch without TiO_2 at high temperature. In each batch, introduced DMMP in the gas phase became stable at about the same concentration (11.6 μM on average). In the first batch reaction, excellent photocatalytic activity was observed under UV irradiation. For the second and the third batches, the performances of photocatalytic activities were still very high. Yet, after that, it decreased gradually with repeated-batch reactions and in the seventh batch, no photocatalytic activity was observed. Instead, we found that the strong adsorption performance of TiO_2 against DMMP appeared as photocatalytic activities decreased. The amount of DMMP decreased by adsorption before UV irradiation while the first and the second batches were very small. This rate increased gradually with repeated-batch reactions thereafter. The strong adsorption was observed in the seventh batch and the concentration of introduced DMMP was decreased by 35.6% due to the adsorption on TiO_2 before UV irradiation. During the eighth batch, even though the reaction was carried out without UV light, most DMMP in the gas phase was removed by adsorption alone (82.5%). When we took TiO_2 out of the reactor for the ninth batch, DMMP concentration in the gas phase was not decreased.

Fig. 6 shows the net photocatalytic decomposition rate and adsorption rate before UV irradiation for each batch. The net photocatalytic decomposition rate was as high as 55.8 μM/h in the first batch. However, the net photocatalytic decomposition rates for the second batch (18.4 μM/h) and the third batch (12.6 μM/h) were 0.33-fold and 0.23-fold lower than that of the first batch, respectively. The rate was only 2.70 μM/h for the sixth batch (0.05-fold of first batch), and during the seventh batch, no net photocatalytic decomposition was observed. On the other hand, adsorption rates before UV irradiation were gradually increased as the repeated-batch reactions proceeded. Although the adsorp-
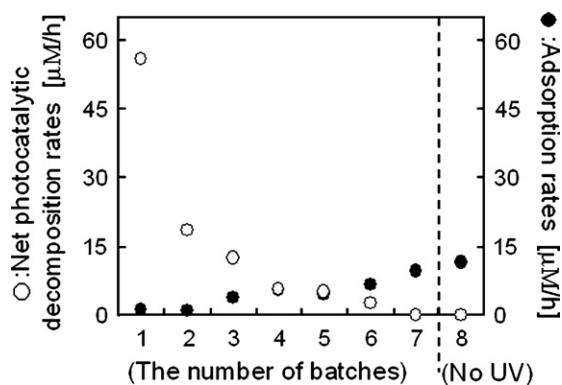
tion rates for the first and the second batch were only 1.20 μM/h and 1.10 μM/h, it was increased to 3.80 μM/h for the third batch. The adsorption rates at in the sixth batch (6.80 μM/h) and the seventh batch (9.65 μM/h) were 5.66-fold and 8.04-fold higher than that of the first batch, respectively. It was increased to 11.5 μM/h (9.58-fold of the first batch) in the eighth batch. Fig. 7 shows the amount of gaseous DMMP removed by repeated-batch reactions (the amount of net photocatalytically decomposed DMMP plus adsorbed DMMP). Most of the DMMP that was introduced for each batch was removed by TiO_2 and the average amount of removed DMMP in each batch was 11.2 μM. The percentages of net photocatalytic decomposition were more than 90% of removed DMMP in the first two batches. Yet, the percentages of net photocatalytic decompositions decreased gradually to 63.3% in the third batch and 15.6% in the sixth batch. Instead, amounts of adsorbed DMMP were increased. Although the percentage of adsorption in the first batch was very low (7.4%), these percentages increased to 36.7% in the third batch and 84.3% in the sixth batch. In the seventh batch where TiO_2 lost the performance of photocatalytic activity and in the eight batch without UV irradiation, the whole DMMP were removed only by adsorption performance.

Methyl methylphosphonate (MMP), methylphosphonic acid (MPA) and phosphoric acid are nonvolatile compounds that are adsorbed on the TiO_2 surface. In the photooxidation of adsorbed DMMP, Moss et al. [5] reported the loss of methoxy groups, to form MMP and MPA, then the loss of the P-bound methyl group to leave a surface-bound PO_4^{3-} species, and showed that the formation of the complete mineralization product PO_4^{3-} is slow, and a high surface concentration of bound MPA remains even after long irradiation times. Furthermore, several studies have investigated the photocatalytic decomposition of DMMP in the liquid phase [18–22]. Vorontsov et al. [19] reported that some other nonvolatile products that appeared in smaller quantities,
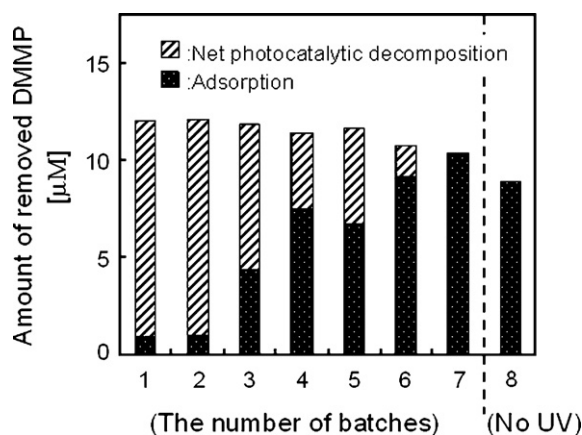

Fig. 6. Net photocatalytic decomposition rates and adsorption rates in the repeated-batch reactions. Net photocatalytic decomposition rates were calculated by subtracting adsorption rates (before UV irradiation) from photocatalytic decomposition rates (under UV irradiation).

Fig. 7. The amounts of removed gaseous DMMP by net photocatalytic decompositions and adsorptions of TiO_2 in repeated-batch reactions.

which are not included among the above-mentioned major products: dimethylphosphoric acid, methylphosphoric acid, dimethyl hydroxymethylphosphonic acid, methyl hydroxymethylphosphonic acid and hydroxymethylphosphonic acid. The deactivation of photocatalytic activity by nonvolatile compounds that are adsorbed on TiO_2 is a serious obstacle for DMMP decomposition. 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 resolving this problem, Obee and Satyapal [3] reported that the water wash strategy (deactivated catalyst sequentially dipped in four fresh cylinders of distilled water and dried at approximately 35 °C for roughly 10 min) was found to completely rejuvenate the catalyst with respect to both DMMP and butene reactivity. Kiselev et al. [7] reported on the adsorption and photocatalytic degradation of DMMP over dry and humidified TiO_2 at room temperature (relative humidity was 7%), and showed that on a wet surface that contains only a few monolayers of water, the concentration of intermediate surface species is reduced, while the rate of decomposition is approximately the same. They showed that it is possible to maintain a high photocatalytic degradation rate of organic phosphorous pollutants. On the other hand, in a negative effect of air humidity, Trubitsyn and Vorontsov [6] examined the adsorption, hydrolysis and photocatalytic oxidation at high DMMP surface coverage on TiO_2 under both 1% and 50% relative humidity at room temperature, and showed that although the 50% relative humidity enhanced both adsorption and hydrolysis processes, the gas-phase product concentrations that were observed in photocatalytic oxidation were a little smaller than that in the case of 1% relative humidity. In this study, dried air was bubbled into 97% DMMP undiluted solution to generate a gaseous DMMP, and photocatalytic decomposition for DMMP by repeated-batch reactions were carried out at high temperature (100 °C). In the second batch (Fig. 6), the net photocatalytic decomposition rate was inhibited significantly and the adsorption rate was slightly decreased compared to the first batch. Thus, the deactivation of TiO_2 was indicated. Through this experiment, however, we found out that through long-term reactions, although the performance of photocatalytic activity was lost gradually, TiO_2 started showing strong adsorptive performance against gaseous DMMP. It was shown that during the eighth batch, most DMMP was removed by adsorption alone without UV irradiation. Moreover, these results suggested that even after the eight batches, a large amount of DMMP could be removed by adsorption (Fig. 7). In our experiment, the relative humidity of the reaction gas was low (dried air was introduced, and the temperature was 100 °C in the reactor). The H_2O in the gas phase that was generated by DMMP photooxidation in each batch was exhausted from the reactor when gaseous DMMP was re-introduced during the flow condition for next repeated-batch reaction. Thus, the effects of relative humidity on the strong adsorption of TiO_2 against DMMP were assumed to be small in our case. Furthermore, we expect that the higher relative humidity of the reaction gas would contribute to the maintenance of photocatalytic activity and enhance the adsorption of TiO_2 against gaseous DMMP. Since the mechanisms of the strong adsorption performance of TiO_2 are as yet unknown, detailed studies are currently underway.

3.4. Removal of a large amount of gaseous DMMP by repeated-batch reactions

In order to remove a large amount of DMMP on a practical scale by both photocatalytic decomposition and the strong adsorption of TiO_2, we performed repeated-batch reactions using TiO_2 scaled up by a factor of 10 (0.1 g). The repeated-batch reaction was extended to 38 batches for 119 h. Photocatalytic activities were observed in the first 19 batches under intermittent irradiation of UV
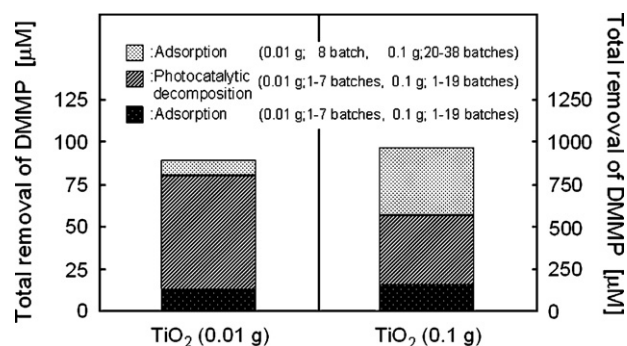
Fig. 8. Total amounts of removed gaseous DMMP by repeated-batch reactions using TiO_2.

light, and large amount of DMMP was removed only by adsorption without UV irradiation from the 20th to the 38th batches. When we took TiO_2 out of the reactor for the 39th batch, DMMP concentration in the gas phase was not decreased. Fig. 8 shows the total amount of removed DMMP by repeated-batch reactions using TiO_2 (0.01 g and 0.1 g). During the repeated-batch reactions with 0.01 g of TiO_2 (Fig. 5), in the first seven batches, the amount of DMMP removed by adsorptions (before UV irradiation) and photocatalytic decompositions (under UV irradiation) were 13.0 μM and 67.5 μM, respectively. In the eighth batch, the removed DMMP by adsorption alone was 8.95 μM without UV irradiation. Total removal of DMMP in eight-batch reactions reached 89.5 μM while the total amount of introduced DMMP was 93.0 μM (The removal rate: 96.2%). During the reactions with 0.1 g of TiO_2, for the first 19 batches, the amount of DMMP removed by adsorptions (before UV irradiation) and photocatalytic decompositions (under UV irradiation) were 157.5 μM and 412.0 μM, respectively. From the 20th to 38th batches, the DMMP removed by adsorption alone was 399.0 μM without UV irradiation. Total removal of DMMP in the 38th batch reactions reached 968.5 μM when the total amount of introduced DMMP was 1131.5 μM of gaseous DMMP (The removal rate: 85.6%).

Regarding the adsorption characteristics of TiO_2 in the liquid phase, Matsuda et al. [23] conducted the adsorption test of TiO_2 for organic phosphates, sugars, carboxylic acids and other compounds, and found that organic phosphates are selectively adsorbed by TiO_2. Furthermore, Sano and Nakamura [24], who belong to this same research group, reported that they developed the column-switching HPLC system for the determination of phosphopeptides on the basis of chemo-affinity of TiO_2. In our experiment with 0.01 g of TiO_2 (Fig. 5), although photocatalytic activity was lost gradually with repeated-batch reactions, we found that the strong adsorption of TiO_2 against gaseous DMMP appeared as a new performance while photocatalytic activities decreased. We did not carry out further investigation for adsorption of TiO_2, but it is expected that the amount of removed DMMP would be increased by adsorptions of TiO_2 with repeated-batch reactions if continued. With 0.1 g of TiO_2 (Fig. 8), we performed the removal of DMMP on a practical scale by both photocatalytic activities and the strong adsorption of TiO_2. The percentage of adsorption accounted for 57.4% of total removal of DMMP. This rate was higher than that of the reactions with 0.01 g of TiO_2 (24.4%). We expect that, for a reaction with 0.01 g of TiO_2 also, the percentage of adsorption would increase if we continued to carry out repeated-batch reactions. These results indicate the possibility of removing large amounts of DMMP on a practical scale, and this may be possible under natural conditions by taking advantage of both photocatalytic activity and the strong adsorption of TiO_2. Currently, with the flow type photocatalytic-reactor system we have constructed, through which the air contaminated with gaseous DMMP flows, we have been performing the photocatalytic

decomposition of DMMP under long-term continuous treatments. These results will be reported later.

4. Conclusions

With the aim of developing an effective decontamination system that uses TiO$_2$ for the purification of air contaminated with Sarin gas (chemical warfare agents). We performed photocatalytic decomposition of gaseous DMMP and identified oxidation products in the gas phase. On the basis of these results, we carried out repeated-batch reactions for a long time period. In the photocatalytic decomposition, high concentration of DMMP in the gas phase decreased rapidly with the presence of TiO$_2$, and no decrease of DMMP was observed under UV irradiation alone. It was shown that photocatalytic treatment was very effective for removal of gaseous DMMP. Three inorganic compounds (CO, CO$_2$, H$_2$O) and four organic compounds (methanol, formaldehyde, formic acid, methyl formate) were detected as the primary products in the gas phase. No highly poisonous substances were generated. In the repeated-batch reactions, photocatalytic activities decreased gradually with repeated-batch reactions due to the accumulation of nonvolatile compounds on the TiO$_2$ surface. Meanwhile, the strong adsorption of TiO$_2$ against gaseous DMMP was found as photocatalytic activities decreased, leading to decrease of a large amount of DMMP. During the repeated-batch reactions using TiO$_2$ scaled up by a factor of 10, the total removal of DMMP reached 968.5 μM due to both activities of TiO$_2$ (photocatalytic activity and the strong adsorption), while the total amount of introduced DMMP was 1131.5 μM. These results suggest the possibility of removing large amounts of DMMP (Sarin simulant) on a practical scale, as well as continuous removal of DMMP under natural conditions by taking full advantage of photocatalytic and adsorptive performances of TiO$_2$.

Acknowledgment

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