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Specific properties on TiO_2 photocatalysis to decompose isopropyl methylphosphonofluoridate and dimethyl methylphosphonate in Gas Phase

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ABSTRACT

The specific differences on TiO_2 photocatalytic decomposition rates of vaporized isopropyl methylphosphonofluoridate, sarin (GB), r_{GB} as a real Chemical Warfare Agent (CWA) and vaporized dimethyl methylphosphonate (DMMP), r_{DMMP} as CWA simulant in gas phase have been investigated by Gas chromatography/mass spectrometry (GC/MS) analysis in ambient. The concentration of GB molecules adsorbed at the surface of TiO_2 in the dark, C_{GB}, was 28 times larger than C_{DMMP} in the dark. The r_{GB} was then 3.3 times faster than the r_{DMMP}. The results were explained by taking into account faster hydrolysis of GB molecules at the surface of TiO_2 and the larger diffusion constant of GB in the gas phase than DMMP molecules. The effect of F^- adsorption at the surface of TiO_2 as fluoridated surface on the TiO_2 photocatalysis was also studied.

1. Introduction

Decontamination of the environmental area contaminated by Chemical Warfare Agents, CWAs, has been studied [1–6]. Since titanium dioxide (TiO_2) has been shown to be an effective photocatalyst for the decomposition of a large number of organic compounds [7–10], a lot of studies on the TiO_2 photocatalytic decomposition of CWA simulants in the gas and liquid phase have been reported [11–26]. In particular, dimethyl methyl phosphonate (DMMP) [11–24] and di-isopropylfluorophosphate (DFP) [25,26] have been known for one of the major CWA simulants as nerve agents, which are isopropyl methylphosphonofluoridate, Sarin (GB) and trimethylpropyl methylphosphonofluoridate, tabun (GA). Complete decomposition of these simulants by TiO_2 photocatalysis and the detailed decomposition mechanism at the surface of TiO_2 photocatalyst are well elucidated and widely known [11–26]. However, a few studies on the photocatalytic decomposition for the real CWA have been reported. Recently, the photocatalytic adsorption and decomposition mechanism of GB has been investigated by ATR-FTIR and complete decomposition of GB in the TiO_2 photocatalysis has also been researched by our research group [27,28]. Although the TiO_2 photocatalytic decontamination mechanism of GB molecules as a real CWA and DMMP as a GB simulant on the TiO_2 photocatalyst have been reported as stated above, the differences on the TiO_2 photocatalysis between GB and DMMP have never been reported yet.

The structural differences between the GB and DMMP molecule are that the GB molecule have an F group as shown in Scheme 1. The E_a of GB as F group at the metal oxide surface is much lower than that of DMMP as O-CH_3 group as listed Table 1, it is expected that quantity of GB molecules chemically adsorbed at the surface of TiO_2 in the dark will be larger than that of DMMP. However, considering the fact that the volatility of DMMP molecule is lower than that of GB, it is expected that the adsorption of the DMMP molecule at the surface of TiO_2 will be larger than that of GB molecule. The actual behavior of them as adsorption quantity is therefore unknown. Besides, the difference of E_a will result in a difference of the TiO_2 photocatalytic decomposition rate r between GB and DMMP molecules. From another perspective of the GB molecular structure, the F group of GB molecule is hydrolyzed by the surface hydroxyl groups or/and decomposed by the TiO_2 photocatalysis and the F^- ion is produced at the surface of TiO_2. The F^- ion adsorption at the TiO_2 surface and Ti-F bond formation can be expected. In our previous study on the ATR-FTIR analysis, the Ti-F bond formation by the TiO_2 photocatalytic decomposition of GB molecule could not be recognized but it has been shown by the study on

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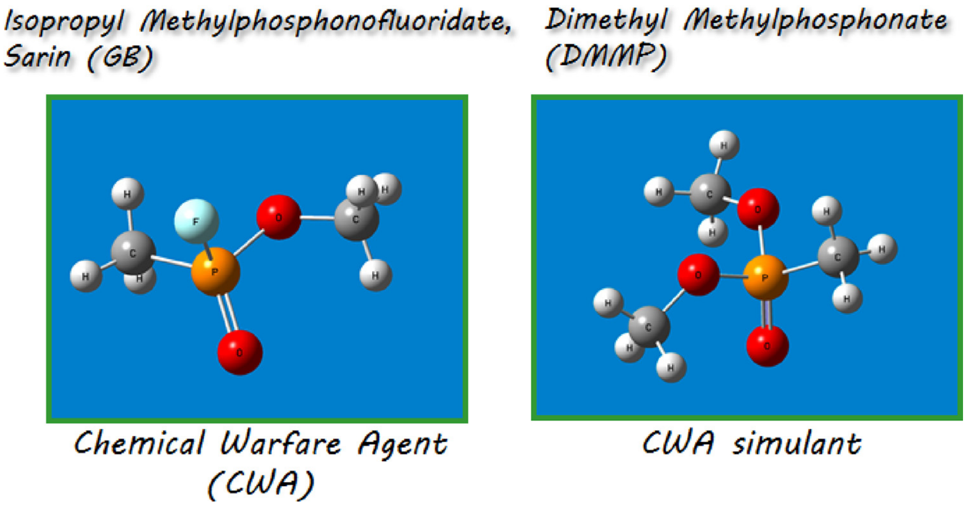

Scheme 1. Molecular structure images of isopropyl methylphosphonofluoridate (GB) as Chemical Warfare Agent (CWA) and Dimethyl methylphosphonate (DMMP) as CWA simulant [29].

DRIFTS analysis of the DFP decomposition in the TiO_2 photocatalysis [27,28]. As has been known well, the formation of Ti—F bond at the surface of TiO_2 selectively accelerates producing the homogeneous OH radical in the TiO_2 photocatalysis [40–42]. However, the effect of Ti—F bond on the TiO_2 photocatalysis to decontaminate CWA has never been studied yet.

Herein, we focus on the comparison of the GB as CWA and of DMMP as the GB stimulant in the TiO_2 photocatalytic decontamination process to know their specific differences as the TiO_2 photocatalytic decomposition rate and an effect of Ti—F bond formation at the surface of TiO_2.

2. Experimental

2.1. Samples

TiO_2 powder (P25, Japan aerojil) was used as a photocatalyst.[43] The primary particle size, BET surface area and crystallinity of the P25 TiO_2 powder are 32 nm, 49 m^2/g and 80% anatase-20% rutile mixture powder, respectively. Isopropyl methylphosphonofluoridate, GB, (the purity was >97% according to the supplier) was obtained from TNO Prince Maurits Laboratory, Rijswijk, the Netherlands and used with the permission of the Ministry of Economy, Trade and Industry of Japan. Dimethyl methylphosphonate (DMMP: Aldrich, >97%), HCl (Wako, 37%) and NaF (>97%, Wako) were used without further purification.

2.2. F/TiO_2 preparation

Two of pH of solution was prepared by injecting 2 M of HCl. Of P25 powder, 3 g was suspended in 500 ml of the solution and agitated by an ultrasound bath for 30 min. After sonication, known concentration of NaF was added into the TiO_2 suspension. The concentration of NaF in the TiO_2 suspension was 10 and 100 mM, respectively. The TiO_2 suspension was then stirred vigorously for 1 h. The precipitation of the TiO_2 powder in the suspension started for 15–30 min in stirring. After 1 h stirring, the supernatant was discarded and the precipitated TiO_2 powder was re-suspended in 500 mL MilliQ-water for 10 min two times. The pH of the suspension was finally 3.5. The TiO_2 powder modified by F^- ion, F/TiO_2, was concentrated by centrifugation and dried for 12 h by lyophilization (FreeZone, LABCONCO). The samples were then named F

Table 1
Characteristic physical and chemical properties of GB and DMMP.

	GB	DMMP
Vapor pressure: log P/Torr	^{a}9.4-2700/T(K)	^{h}16-32.6/{T(K)-51.7}
E_a in alkaline solution/kJ mol^{-1}	^{b}38.1, ^{c}44.4	^{i}52-62
E_a at metal oxide/kJ $mo1^{-1}$	^{d}16.7–29.3 (Al_2O_3), ^{e}18(Al_2O_3), ^{e}17.6(MgO)	^{j}49($Ti0_2$)
Thermal stability	^{f}Decomposed at 433–438 K. ^{f}Decomposed completely at423Kfor2 hrs. ^{g}Fairly stable at 338 K.	^{k}Fairly stable at 373 K
Refractive index		^{l}1.411
Molecular weight	^{a}140.1	^{l}124.08
Melting point/K	^{a}223	^{l}<323
Density: g/ml	^{a}1.09 at 298 K	^{l}1.145 at 293 K

[a] Reference [3].
[b] Reference [30].
[c] Reference [31].
[d] Reference [32].
[e] Reference [33].
[f] Reference [34].
[g] Reference [35].
[h] Reference [36].
[i] Reference [37].
[j] Reference [38].
[k] Reference [23].
[l] Reference [39].