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Availability of Zr-Based MOFs for the degradation of nerve agents in all humidity conditions

Sam Gon Ryu[*], Min-Kun Kim, Myungkyu Park, Seong On Jang, Sung Hun Kim, Hyunsook Jung

Agency for Defense Development, Yuseong P.O. Box 35-5, Daejeon, 34186, Republic of Korea

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ABSTRACT

Organophosphate-based nerve agents are among the most toxic chemical compounds known to mankind. In this report, we studied the degradation of soman (GD) and VX, two of the major nerve agents, by $Zr(OH)_4$ and Zr-based Metal-Organic Frameworks (MOFs) such as MOF-808, UiO-66 and UiO-66-NH_2 in the neat condition and in non-buffered aqueous solution at room temperature. Unlike $Zr(OH)_4$, relatively less hydrophilic Zr-based MOFs were found to maintain excellent nerve agent decomposition ability, even under high relative humidity and in water. This study's results demonstrated that these Zr-based MOFs are all-weather materials that can be used to decompose nerve agents in all humidity conditions and even in water. The enhancement effect by the amine group of UiO-66-NH_2 was not observed for decomposition of nerve agents in the present study, unlike the results obtained in alkaline buffered solution, which were reported previously. It was also demonstrated that MOF-808 with a pore size larger than the UiO-66 series had a better ability to degrade nerve agents.

1. Introduction

Despite being the most inhuman weapon, Chemical Warfare Agents (CWAs) have been used in conflict zones and by terrorist groups around the world due to their mass kill capability and cost-effectiveness, and many countries and groups are still stockpiling CWAs. If toxic CWAs are released to the environment, the means of decontamination of the human body, important facilities and areas must be provided. Therefore, techniques have been developed to decompose CWAs into harmless molecules at a high rate at room temperature [1–4].

Recently, it has been reported that $Zr(OH)_4$ [5,6] and Zr-based Metal-Organic Frameworks (MOFs) [7–16] such as UiO-66, UiO-66-NH_2, MOF-808, NU-1000 and PCN-777, which are reactive materials using zirconium as a central metal, are excellent in the decomposition of CWAs, especially nerve agents. These materials are known to hydrolyze *O*-pinacolyl methylphosphonofluoridate (soman, GD) and *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX), which are the most representative nerve agents, to pinacolyl methylphosphonic acid (PMPA) and ethyl methylphosphonic acid (EMPA), respectively, with little toxicity, as depicted in Scheme 1 [6–8]. However, most studies on these reactive materials have been performed using simulants due to the practical limitation of using live CWAs. Even when live CWAs are used, most degradation experiments have been performed in alkaline buffered solutions, and some studies have recently been reported that did not employ buffer, but they have also been processed in aqueous solution [7,13], which are very different from actual situations of direct contact with the atmosphere.

When reactive MOF particles are used to decontaminate CWAs in a field, they can be exposed to a variety of environments, ranging from low to high humidity, and may even become wet with water. In other words, they can be affected by various humidity conditions, but to date, there have been no results confirming the influence of atmospheric moisture in the decomposition of nerve agents by these MOF materials. Only for GD, the results of degradation by NU-1000 at 50% relative humidity (RH) have been reported [9], but systematic studies on the effect of atmospheric moisture on nerve agent decomposition by MOFs are notably rare.

In the case of $Zr(OH)_4$ particles pretreated at 50% RH, VX was decomposed almost instantaneously and GD was also decomposed at a considerable rate [6]. Recently, it has been reported that decomposition of dimethyl methylphosphonate (DMMP), a simulant of nerve agents by $Zr(OH)_4$, proceeds more rapidly at 50% RH air than dry N_2 due to the positive influence of moisture on the surface [5]. However, to the best of our knowledge, cases of decomposing nerve agents by using $Zr(OH)_4$ particles in a humidity condition higher than 50% RH have not been reported. Moreover, it has been reported that $Zr(OH)_4$ particles in aqueous solution cannot efficiently decompose Dimethyl 4-nitrophenyl phosphate (DMNP), a simulant of nerve agents [9].

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[*] Corresponding author. Agency for Defense Development, Yuseong P.O. Box 35-5, Daejeon 34186, Republic of Korea.
E-mail address: sgryu@add.re.kr (S.G. Ryu).

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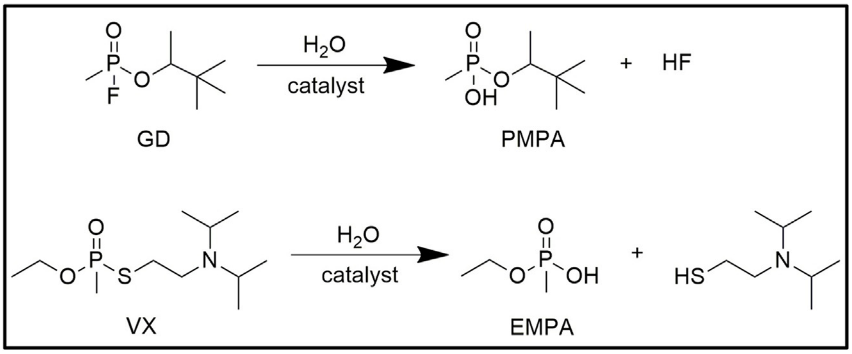

Scheme 1. Hydrolysis reaction of nerve agents GD and VX on Zr-based reactive materials.

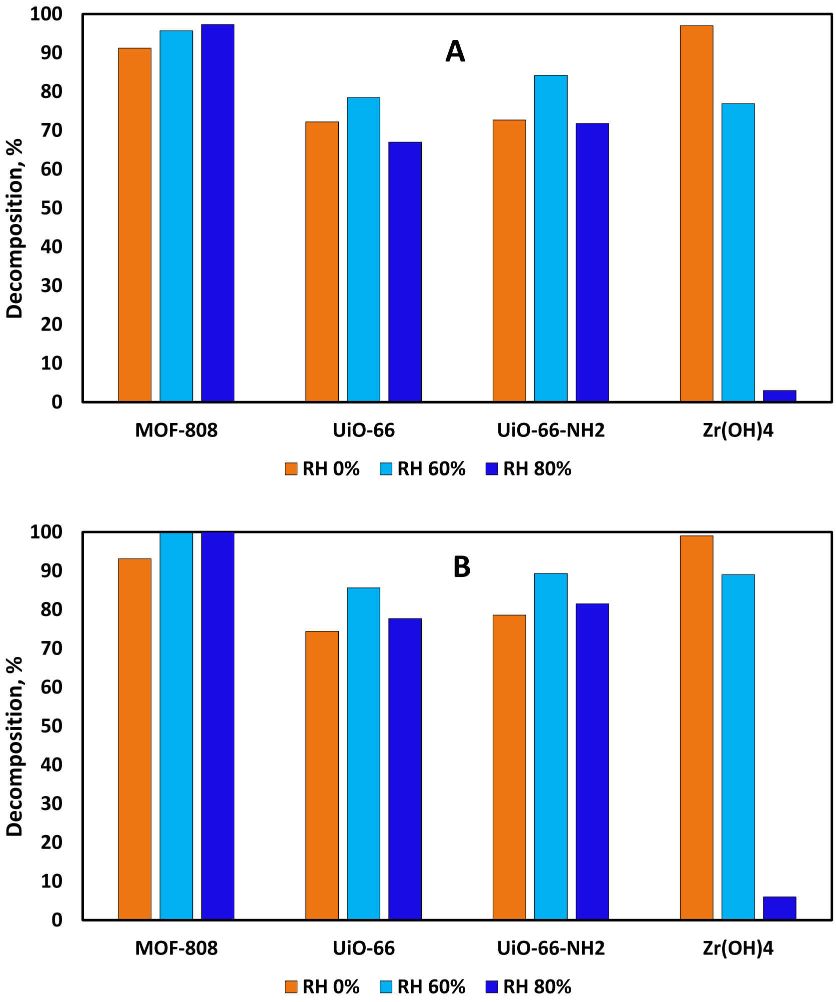

Fig. 1. Comparison of GD degradation rates of Zr-based reactive particles according to pretreatment humidity conditions; A: 5 min reaction, B: 10 min reaction, GD: 0.4 μL (0.0022 mmol), Sample weight: 10 mg.

As described above, there is almost no systematic and detailed study on the decomposition ability of CWAs by Zr-based reactive materials under various humidity conditions in the actual field environment. Therefore, to confirm the practical use of these Zr-based reactive materials, it is necessary to study the decomposition of CWAs under field-like conditions.

In this study, we attempted to identify the GD and VX decomposition abilities of $Zr(OH)_4$, MOF-808, UiO-66 and UiO-66-NH_2 in neat and aqueous solutions at room temperature. In the case of the neat condition, the nerve agent's degradation ability of each materials was tested after pretreatment at 0, 60, and 80% RH. Additionally, with the collected results, we discussed the effects of water on the decomposition of the nerve agents of these materials, differences in the nerve agent degradation ability between MOF-808 and UiO-66 series MOFs, and the contribution of the amine functional group in UiO-66-NH_2 to the degradation reactions.