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Metal–Organic Frameworks

Detoxification of Chemical Warfare Agents Using a Zr_6-Based Metal–Organic Framework/Polymer Mixture

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Abstract: Owing to their high surface area, periodic distribution of metal sites, and water stability, zirconium-based metal–organic frameworks (Zr_6-MOFs) have shown promising activity for the hydrolysis of nerve agents GD and VX, as well as the simulant, dimethyl 4-nitrophenylphosphate (DMNP), in buffered solutions. A hurdle to using MOFs for this application is the current need for a buffer solution. Here the destruction of the simulant DMNP, as well as the chemical warfare agents (GD and VX) through hydrolysis using a MOF catalyst mixed with a non-volatile, water-insoluble, heterogeneous buffer is reported. The hydrolysis of the simulant and nerve agents in the presence of the heterogeneous buffer was fast and effective.

Some organophosphates, such as DNA and RNA, are essential biomolecules, whereas others such as pesticides (parathion and paraoxon) and nerve agents (GD and VX) (Figure 1 c) can be extremely toxic. Although their toxicity (ex. LD_{50}, VX > GD ≫ pesticides) and physical properties such as vapor pressure and boiling point vary, their mechanism of action in the human body is identical.[1] Toxic organophosphates bind irreversibly to the enzyme acetylcholinesterase (AChE), preventing the breakdown of acetylcholine, which leads to sustained muscle contraction, and eventually oxygen deprivation and death.[1,2] Though some organophosphates can be decomposed by hydrolysis in water, reaction rates in the absence of catalysts are typically too slow to be effective. There have been many studies focusing on the detoxification or removal of simulants and nerve agents using catalysts such as metal oxides (TiO_2, $Zr(OH)_4$, and Al_2O_3),[3] activated carbon,[4] mesoporous silica,[5] zeolites,[6] and surfactants/metallosurfactants.[7] However, more highly potent catalytically active materials are needed.

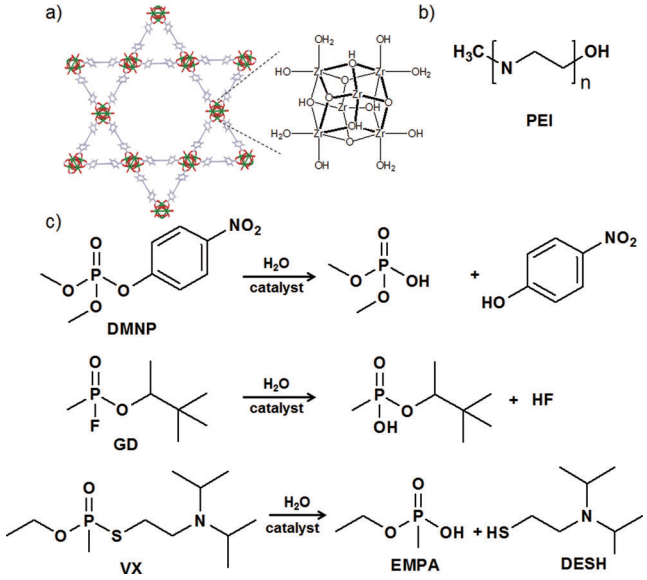

Figure 1. Chemical structures of a) NU-1000 and b) linear-polyethyleneimine (PEI), and c) hydrolysis reaction of phosphonate-based nerve agents (*O*-pinacolyl methylphosphonofluoridate, GD and *O*-ethyl *S*-(2-(diisopropylamino)-ethyl)methylphosphonothioate, VX) and a simulant (dimethyl 4-nitrophenyl phosphonate, DMNP).

Towards the goal of nerve-agent detoxification, some research groups including ours have studied various kinds of catalysts including supramolecular assemblies,[8] porous organic polymers (POPs),[9] and metal–organic frameworks (MOFs).[10] In particular, MOFs have shown great potential as catalysts given the high concentration of well-dispersed and periodic metal-based nodes and organic linkers, combined with exceptionally high surface areas and impressive water stability over a wide pH range.[11] Recently, we have focused on the detoxification of nerve agents and simulants through hydrolysis utilizing MOF catalysts containing Zr_6 clusters in basic aqueous buffer solution (0.45 M *N*-ethylmorpholine solution).[10a–e,g,12] Remarkably, Zr-MOFs show high catalytic activity for the hydrolysis of simulants and real nerve agents in buffer solution. For example, some Zr-MOFs are among the fastest synthetic catalysts reported to date, including UiO-66-NH_2,[10b] NU-1000-dehydrated,[10c] and MOF-808,[10d] and show half-lives of < 2 min for the destruction of the simulant (DMNP) and nerve agents (GD and VX), in buffer solution.

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Although Zr-MOFs show high catalytic activity for the hydrolysis of the organophosphorus simulant and nerve agents, the reaction requires the presence of *N*-ethylmorpholine as a buffer solution. The buffer acts to remove acidic byproducts from the reaction such as HF as well as to deprotonate water molecules and facilitate the reaction. The need for a buffering solution makes it difficult to use these catalysts in applications such as masks and protective suits.[13] To overcome the limitations associated with the use of a homogeneous buffer, we sought to heterogenize the buffer using a basic polymer.

Polyethyleneimine (PEI) is a polymer containing amine groups and aliphatic carbons that can be linear or branched. This polymer is used in detergents, adhesives, cosmetics, water treatment agents, and in CO_2-capture applications.[14] In particular, linear polyethyleneimine (Figure 1 b) consists of a number of secondary amines and is insoluble in water, making it a great candidate for use as a basic heterogeneous buffer for the MOF-catalyzed hydrolysis of nerve agents and simulants. In this study, we demonstrate the hydrolysis of the simulant (DMNP) and nerve agents (GD and VX) with a MOF catalyst/heterogeneous buffer mixture.

To evaluate the heterogeneous buffering ability of the cationic polymer, the hydrolysis of DMNP utilizing the Zr-MOF, NU-1000 (Figure 1 a), and PEI was conducted under conditions similar to those previously reported for NU-1000. Thus, PEI was used in place of a 0.45 M aqueous solution of *N*-ethylmorpholine. NU-1000 was chosen as a test catalyst due to its well-defined pore structure, controllable particle size, and tunable catalytically active sites.[10c] The hydrolysis of DMNP was monitored in situ by ^{31}P NMR spectroscopy, and hydrolysis profiles were plotted as conversion versus time. As shown in Figure 2 a, NU-1000 with PEI buffer (NU-1000/PEI) hydrolyzes DMNP effectively in water. In addition, the rate of hydrolysis is affected by the amount of PEI used (Figure S1 in the Supporting Information). It should be noted that the hydrolysis reaction with NU-1000 or PEI alone in water is negligible (Figure S1). Under optimized conditions, NU-1000/PEI [1.5 μmol of NU-1000 (3.3 mg), 0.003 mmol of PEI (7.5 mg, MW: 2,500), 0.16 mmol of amine] showed an identical hydrolysis rate (8 min half-life) to NU-1000/*N*-ethylmorpholine (0.39 mmol of amine; Figure 2 a and Table 1). That fewer amine groups were required to reach the same reaction rate when using PEI as the buffer versus *N*-ethylmorpholine might indicate that the amines are more effective as buffers in heterogeneous than homogeneous form. The reusability of NU-1000/PEI was also demonstrated after testing the initial catalytic hydrolysis (see the Experimental Section in the Supporting Information). A second cycle using NU-1000/PEI showed 60% conversion of DMNP at 30 min under the same conditions used previously. The decrease in catalytic activity is attributed to residual hydrolysis products on the catalyst causing inhibition and loss of catalyst and/or PEI after washing.

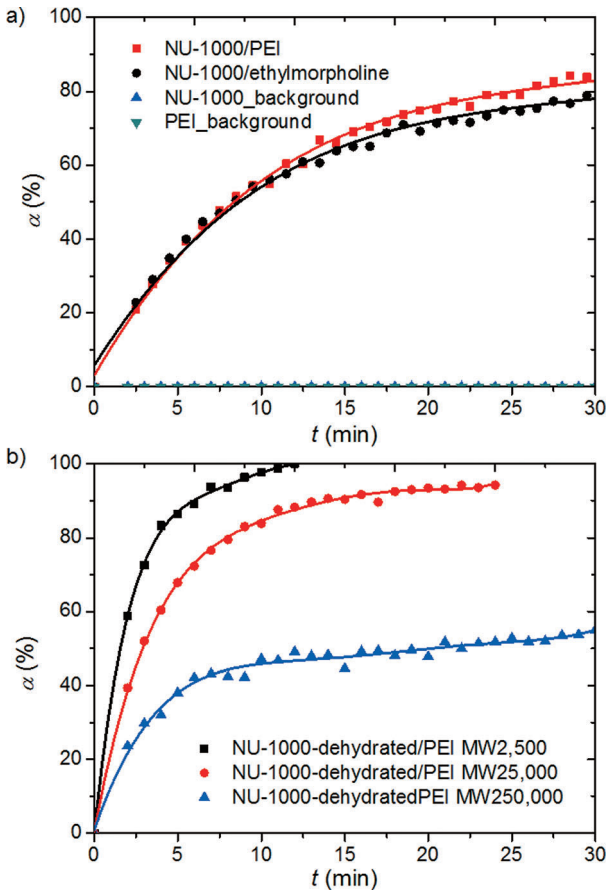

Figure 2. a) Hydrolysis profiles of DMNP using NU-1000 and PEI (MW: 2,500) in water and NU-1000 under 0.45 M *N*-ethylmorpholine buffer solution, b) hydrolysis profiles of DMNP using the NU-1000 previously dehydrated at 300 °C with different molecular weight PEIs in water; the moles of amine for the different molecular weight polymers were kept consistent at 0.31 mmol to facilitate comparisons.

Table 1. Comparison of the hydrolysis rate of a simulant (DMNP) and nerve agents (GD and VX) with MOFs under different buffers.

Substrate	MOF[a]/base	mmol	Molecular weight of base [g mol^{-1}]	Amine [mmol]	Half life [min][e]
DMNP[b] (simulant)	NU-1000/ethylmorpholine	0.39 (50 μL)	115	0.39	8.3 ± 0.2
	NU-1000/PEI	0.003 (7.5 mg)	2,500	0.16	8.4 ± 0.2
	NU-1000-dehydrated/PEI	0.006 (14.5 mg)	2,500	0.31	1.8 ± 0.1
GD[c] (Soman)	NU-1000-dehydrated/PEI	0.006 (14.5 mg)	2,500	0.31	4.8 ± 0.1
VX[d]	NU-1000-dehydrated/PEI	0.0006 (14.5 mg)	25,000	0.31	12.7 ± 0.4

[a] 1.5 μmol of catalyst and [b] 25 μmol of DMNP, [c] 14.6 μmol of GD, [d] 14.7 μmol of VX were used for each reaction. [e] Initial half-lives were calculated by plotting the natural log of conversion versus time; the slope ($m = k$) is related to the half-life by $t_{1/2} = \ln 2/k$ (Figure S3 in the Supporting Information).

In a previous study, the dehydrated form of NU-1000 showed remarkably enhanced catalytic activity for the hydrolysis of DMNP, yielding a half-life of 1.5 min in 0.45 M *N*-ethylmorpholine buffer solution.[10c,15] As a result, we tested if NU-1000-dehydrated/PEI could hydrolyze DMNP in water. Indeed, NU-1000-dehydrated/PEI (MW: 2,500) showed a significantly enhanced reaction rate, half-life of ≈2 min, which is similar to that of NU-1000-dehydrated in the presence of 0.45 M *N*-ethylmorpholine buffer solution (Figure 2b and Table 1). It is also worth noting that the rate of hydrolysis of the simulant significantly decreases as the molecular weight of the polymer increases (as shown in Figure 2b); we attribute this to the relatively low pH of the polymer solution with high molecular weight PEI in water (MW 2,500: pH 9.2, MW 25,000: pH 8.8, and MW 250,000: 7.7). It should be noted that bimodal kinetic behavior was observed for the hydrolysis of DMNP using NU-1000-dehydrated and high-MW PEI. This is attributed to the effects of product inhibition on the catalyst after the fast initial reaction rate.

Inspired by these results, we decided to test the NU-1000-dehydrated/PEI system for the hydrolysis of the chemical warfare agents GD and VX in water. We again used in situ ^{31}P NMR spectroscopy to investigate the decomposition of GD and VX with NU-1000-dehydrated/PEI in water. As shown in Figure 3a, GD is effectively hydrolyzed with a half-life of 3.8 min using NU-1000-dehydrated/PEI (MW: 2500) in water, which is comparable to the half-life of 1.8 min for DMNP hydrolysis with the same mixture. The detoxification of VX is considerably more complicated than that of GD owing to the presence of multiple potential hydrolysis sites. For example P–O cleavage produces the toxic byproduct EA-2192, which is equally as toxic as VX (Figure S2 in the Supporting Information).[10e,16] Importantly, VX is selectively hydrolyzed to non-toxic products, ethylmethylphosphonic acid (EMPA) and 2-(diisopropylamino)ethanethiol (DESH) by cleavage of the P–S bond with a half-life of 12.7 min in the presence of NU-1000-dehydrated/PEI (Figure 3b). Intriguingly, the molecular weight of the polymer has a significant effect on the half-lives of detoxification for GD and VX. For GD, low molecular weight PEI (MW: 2,500) is more effective than high-molecular-weight PEI (MW: 25,000), which is similar to the behavior of the simulant DMNP. In contrast, VX is hydrolyzed more quickly with high-MW PEI.[17] A tentative explanation centers on the observations that the pH of the reaction solution in the presence of MW 2,500 PEI is 9.2 compared to 8.8 for MW 25,000 PEI and that the first step in the hydrolysis of VX entails protonation of the tertiary amine ($pK_a = 8.6$), a step that is thermodynamically more favorable in the pH 8.8 environment engendered by high-MW PEI.[2c,18]

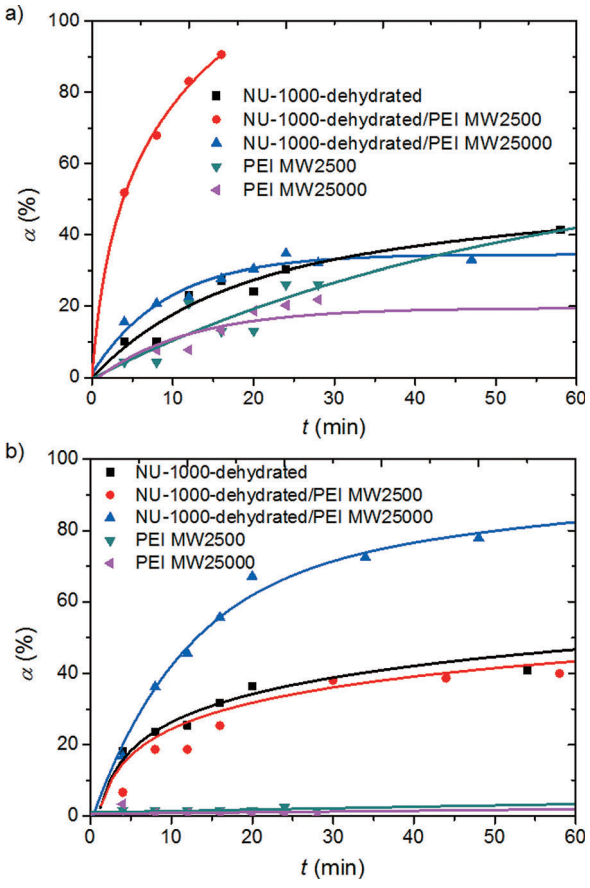

Figure 3. Hydrolysis profiles of a) GD and b) VX in the presence of catalyst and/or different molecular weight PEI. Solid lines are used as a guide.

Given the success of the heterogeneous catalyst and buffer system in water, we prepared a simple solid composite material consisting of a MOF catalyst, polymer buffer, and cellulose as a substrate, which is portable and amenable for use in protective gear such as masks, suits, gloves, and cleaning mats. In addition, cellulose has a highly porous structure that can absorb liquid (water), making it a great candidate as a matrix for the catalytic hydrolysis reaction with MOF/PEI. To prepare the MOF/PEI/cellulose composite, NU-1000-dehydrated and PEI were evenly dispersed in water using sonication, and then cellulose was added to the mixture. The simulant was dropped on a glass slide and then wiped using the cellulose composite (Figure 4, see also the Experimental Section in the Supporting Information). To evaluate the hydrolysis of DMNP, the reaction solution was obtained after sitting in the composite for 30 min by placing the composite inside a centrifuge tube equipped with a filter and then centrifuging and collecting the filtrate. An internal standard (7.5 mg, 0.091 mmol of phosphonic acid) was then added to the solution to allow for quantification of the hydrolysis reaction. The ^{31}P NMR spectrum of the resulting solution showed only a peak for dimethoxy phosphate anion

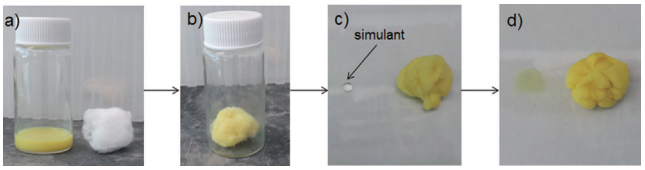

Figure 4. Detoxification of DMNP with MOF/PEI/cellulose composite. a) MOF and PEI were dispersed in water. b) A cotton ball was place into the mixture solution, which absorbed the solution mixture immediately. c) and d) 4 μL DMNP on the glass was wiped using MOF/PEI/cellulose composite and then the composite was squeezed and the solution was transferred to an NMR tube after 30 min.

(DMPA, product) without any evidence of DMNP (Figure S4a in the Supporting Information). In addition, 78% of the maximum expected DMPA product was observed in the initial filtrate collected. To confirm the nature of the residual chemical left in the composite, water (2×2 mL) was added to wash the composite and the filtrate was obtained in the same way as described previously. The ^{31}P NMR spectrum of the wash solutions show only a peak for dimethoxy phosphate anion and nearly all of the product (97% total) was retrieved by the washes (Figure S4b and S4c in the Supporting Information). This proof-of-concept experiment implies that the heterogeneous MOF/polymer can also be easily impregnated/incorporated into fabric, making it amenable for use in a variety of protective or remedial applications.

In conclusion, a heterogeneous system consisting of a Zr-MOF catalyst, NU-1000, and a cationic polymer (PEI) is capable of hydrolyzing the simulant DMNP in water. In particular, NU-1000-dehydrated not only hydrolyzes DMNP, but also the nerve agents in water with remarkable efficiency (initial $t_{1/2}$ of 1.8 min for DMNP, 3.8 min for GD, and 12.7 min for VX). Importantly, this heterogeneous mixture can also be prepared as a composite with a cellulose fiber that is still effective at detoxifying the simulant. Our team is currently exploring the feasibility of conducting these experiments using simulants and agents dispersed in the vapor phase with the aim of completely eliminating condensed-phase water as a reaction medium.

Experimental Section

Monitoring the hydrolysis of DMNP

Hydrolysis profiles were recorded by in situ ^{31}P NMR spectroscopy at room temperature. NU-1000/NU-1000-dehydrated (3.3 mg, 1.5 μmol of Zr_6-based nodes) and PEI (7.5 mg) were loaded into a 1.5 dram vial and 1 mL of 10% D_2O solution (0.9 mL DI water/0.1 mL D_2O) was added and then sonicated for 1 min to disperse homogeneously. DMNP (4 μL, 25 μmol) was added to mixture solution and swirled for 20 s. The reaction mixture was then transferred to an NMR tube and the spectrum was immediately measured. Background reactivity was evaluated under identical conditions, apart from the absence of catalyst or PEI, and monitored by in situ ^{31}P NMR spectroscopy.

Monitoring the hydrolysis of nerve agents GD and VX

NU-1000/NU-1000-dehydrated (3.3 mg, 1.5 μmol of Zr_6-based nodes) and PEI (14.5 mg) were loaded into a 5 mm NMR tube followed by 1 mL of 10% D_2O solution. A nerve agent (GD 2.6 μL, 14.6 μmol or VX 3.9 μL, 14.6 μmol) was then added, the tube capped, and vigorously shaken before placing into the NMR magnet for monitoring by ^{31}P NMR. Caution! Experiments utilizing GD and VX should be run by trained personnel using appropriate safety procedures.

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Keywords: heterogeneous buffer · heterogeneous catalysis · hydrolysis · nerve agents · zirconium MOF

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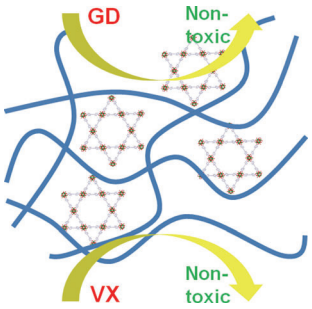

A heterogeneous catalyst system consisting of a Zr-MOF and cationic polymer could effectively detoxify not only a nerve agent simulant, dimethyl 4-nitrophenylphosphate, but also nerve agents, GD and VX, in water. This heterogeneous mixture was prepared as a composite with cellulose fiber, which can be used in protective gear such as masks, suits, gloves, and cleaning mats.