

In operando studies of zirconium-based metal organic frameworks as nerve-agent filtration materials

Anna M. Plonka,^{1,*} Qi Wang,¹ Wesley O. Gordon,² Alex Balboa,² Diego Troya,³ Weiwei Guo,⁴ Conor H. Sharp,³ Sanjaya D. Senanayake,⁵ John R. Morris,³ Craig L. Hill,⁴ Anatoly I. Frenkel¹

¹Department of Material Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794, USA

²U.S. Army Edgewood Chemical Biological Center APG, MD 21010, USA

³Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

⁴Department of Chemistry, Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322, USA

⁵Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA

*anna.plonka@stonybrook.edu

New materials for the rapid decomposition of chemical warfare agents (CWAs) are in high demand for protecting military and civilian populations from these weapons of mass destruction. The need for novel sorbents and decontamination catalysts has gained great urgency as terrorists groups demonstrate the ability to synthesize and deploy agents in chemical attacks. Although many new materials, such as metal-organic frameworks (MOFs), have been proposed to use as CWA filtration media, their eventual transition requires a detailed understanding of the atomic-scale reaction mechanisms.

Zr-based MOFs were recently shown to be among the fastest catalysts of nerve-agent hydrolysis reaction in solution. We show the results of a detailed study of the adsorption and decomposition of a nerve-agent simulant, dimethyl methylphosphonate (DMMP), on UiO-66, UiO-67, MOF-808 and NU-1000 MOFs (that have different pore sizes and connectivities) using synchrotron-based X-ray powder diffraction, X-ray absorption and infrared spectroscopies, which reveals key aspects of the reaction mechanism.[1] This study describes the implementation of a newly developed experimental setup for delivering vaporized DMMP to a reaction cell containing a MOF sample.

The diffraction measurements indicate that all four MOFs adsorb DMMP (introduced at atmospheric pressures through a flow of helium or in air) within the pore space. In addition, the combination of X-ray absorption and infrared spectra suggests direct coordination of DMMP to the Zr₆ cores of all MOFs and its subsequent decomposition to phosphonate products. Further, we show that DMMP is actively adsorbed from air with good selectivity, even in the presence of humidity or other ambient gases, demonstrating that Zr₆-based MOFs may serve as effective sorbents for CWAs under ambient conditions. These experimental probes into the mechanism of adsorption and decomposition of chemical warfare agent simulants on Zr-based MOFs open new opportunities for rational design of new and superior decontamination materials.

1. Plonka, A.M., Wang, Q., Gordon, W.O., Balboa, A., Troya, D., Guo, W., Sharp, C.H., Senanayake, S.D., Morris, J.R., Hill, C.L. and Frenkel, A.I., 2017. In Situ Probes of Capture and Decomposition of Chemical Warfare Agent Simulants by Zr-based Metal Organic Frameworks. *J. Am. Chem. Soc.*, **2017**, 139 (2), pp 599–602