

Advances in Fundamental Materials Research

---

## **Solvolysis of Organophosphates via a Multifunctional, Tunable Metal-Organic Framework Materials Platform**

Dorina Sava Gallis, Sandia National Laboratories

Charles Pearce, Sandia National Laboratories

Mark Kinnan, Sandia National Laboratories

Jacob Harvey, Sandia National Laboratories

Jeffery Greathouse, Sandia National Laboratories

New technologies amenable to support damage-free decontamination of sensitive electronics are needed. Owing their highly tunable and modular structures, metal-organic framework materials (MOFs) are unique candidates to offer new solutions to bridge the gap in this important application space via rational materials design.

Herein we detail our recent findings on the solvolysis of organophosphates using MOFs, in a combined experimental-molecular modeling study. The focus has been placed on interrogating the effect played by the metal identity, functionality of the organic linker, and particle size in the solvolysis of organophosphates. In particular, we investigated two isostructural materials systems constructed from metal clusters (hexa- and nonanuclear) with catalytically active Lewis acid centers. Our findings indicate that reaction kinetics are mainly dependent on the metal identity. Optimized performances were achieved with homogeneous dispersions, highlighting that particle size is a very important parameter to control.

Molecular modeling methods were employed as complementary tools to both validate the experimental results and help elucidate the reaction pathways for the decomposition of organophosphates in these systems. Periodic density functional theory (DFT) calculations were used to calculate structural properties of the as-made materials, which were found to be in excellent agreement with the X-ray single crystal structures. Next, density functional perturbation theory was used to calculate infrared frequencies and intensities, in order to probe subtle structural changes that occur as function of metal and functional groups on the organic linker. These were found to agree well with the experimental spectra. Lastly, gas-phase models of representative clusters were extracted from the periodic structures and used to study the adsorption properties and reaction pathways for the decomposition of organophosphates. Solvent effects were included both explicitly and implicitly.

The findings of this study highlight the importance of metal selection and ligand functionalization, to afford faster kinetics in the aqueous-free degradation of organophosphates.

*This work is supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.*