TODAY'S INNOVATION, TOMORROW'S WARFIGHTER CAPABILITIES

Advances in Fundamental Materials Research

Chemical Warfare Agent Simulant Decontamination on Zr(OH)4 under Operando Conditions

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Much effort has been focused on developing materials and sorbents for decontamination of chemical warfare agents (CWAs); however, CWAs can have different reactivity and decomposition pathways, making it difficult to find an all-in-one decontamination solution. Zirconium hydroxide ($Zr(OH)_4$) has excellent sorption properties and wide-ranging reactivity towards numerous types of CWA and simulants. This reactivity has been attributed to a combination of diverse surface hydroxyl species (terminal, bridging, etc.) and under-coordinated Zr defects. Unfortunately, these promising preliminary results were often obtained under pristine and unrealistic operating conditions in which the potential impact of atmospheric components (e.g. H_2O and CO_2) and trace contaminants (e.g. NO_x, SO_2, H_2S and various hydrocarbons) was not a factor.

A more complete picture of the reactivity under *operando* conditions is necessary to evaluate the potential field use of $Zr(OH)_4$ for CWA decontamination. We couple insights from theory with a suite of *operando* surface analysis techniques, especially attenuated total reflectance infrared spectroscopy (ATR-FTIR), to probe the $Zr(OH)_4$ surface, at ambient pressure, with atmospheric components such as H_2O, CO_2, and SO_2. The structure of the material and the chemical nature of its surface is determined, particularly the presence of reactive coordinatively-unsaturated (cus) Zr sites and the distribution of various hydroxyl groups thought to be involved in DMMP decomposition. Next, the buildup and removal of reaction byproducts such as carbonates and sulfites is monitored as a function of component concentration, RH, and temperature. Contaminated $Zr(OH)_4$ surfaces are then exposed to a sarin simulant, DMMP, to evaluate the impact of the adsorbed surface contaminants on the DMMP decomposition mechanism and performance. These results are interpreted in light of atomic force microscopy (AFM) phase images showing relative humidity (RH)-dependent surface features. We combine surface analysis with mass spectrometry and transmission IR of the head space above the reactants to obtain a holistic understanding of $Zr(OH)_4$ with DMMP in real-world conditions for filtration and decomposition.

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