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Advances in Fundamental Materials Research

Complementary In Situ Spectroscopy and Theory for Fundamental Materials Characterization: Case Study of DMMP Decomposition on CuO

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Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic, volatile compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metal oxides, including copper oxide. Despite decades of work to develop highly effective and versatile filtration materials, little is known about the mechanisms of CWA degradation by material surfaces and filter deactivation/poisoning, in part due to the challenges involved with spectroscopic characterization of filtration material surfaces under operating conditions. Enabling the rational design of novel materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present work detailing the mechanism of adsorption and decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant, on polycrystalline copper(II) oxide. Ambient-pressure XPS enables examination of the solid surface and adsorbed species during exposure to DMMP and other common atmospheric gases, such as water vapor and NO_x. Multiple DMMP decomposition products are observed on CuO at room temperature, with evidence of significant P-OCH_3, O-CH_3, and P-CH_3 bond breaking. Complementary density functional theory (DFT) and *in situ* FTIR studies corroborate our XPS experimental findings and are used to propose likely decomposition pathways. Lattice oxygen atoms in CuO play a critical role in the formation of new bonds with decomposition products. Exposure of the CuO surface to water vapor or NO_x prior to introducing DMMP affects the decomposition product distribution, but does not appear to significantly inhibit the initial DMMP adsorption.

This work was supported by the Department of Defense through the Defense Threat Reduction Agency under grant number HDTRA11510005. The ALS and the MES beamline 11.0.2 are supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences and Materials Sciences Division of the US Department of Energy at the Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231.