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Fundamental Studies Of Metal-organic Framework-supported Single Metal Atoms For The Capture And Decomposition Of Toxic Compounds: Mechanistic Insight Into Carbon Monoxide Oxidation

Mikaela Boyanich Virginia Tech **Eric Johnson** Virginia Tech **Diego Troya** Virginia Tech **Danya Nahas** Virginia Tech **Amanda Morris** Virginia Tech **John Morris** Virginia Tech

Metal-Organic Frameworks (MOFs) have previously been studied for the capture of hazardous vapor-phase substances, including toxic industrial compounds (TICs) and chemical warfare agents (CWAs). However, catalytic oxidative destruction of target compounds remains challenging. To address this challenge, single-atom sites, which have previously proven to be effective catalysts for oxidative chemistry on metal-oxide supports, have been inserted within high-surface area MOFs. The oxidation of CO was utilized as a model reaction to interrogate activity of the metal@MOF materials for oxygen activation and CO2 production. Mechanistic studies were carried out utilizing a plug-flow reactor coupled to an infrared spectrometer for on-stream identification of reaction products under operationally-relevant conditions. The most promising materials were also investigated via ultra-high vacuum-based surface science methods for directly interrogating surface-bound species and reaction rates. In addition, we employed surface-adsorbed CO as an infrared-light sensitive probe molecule to directly interrogate the oxidation state and coordination of the metals within each MOF. These methods, coupled with density functional theory (DFT), have provided new insight into the reaction mechanism of CO oxidation over these single-atom metal decorated MOFs. These model studies will enable the community to better predict the most promising materials for oxygen activation–one of the key steps in the oxidation of more complex molecules, such as CWAs. Ultimately, we aim to identify the most effective single-atom doped MOF catalysts for application in preexisting equipment for the sorption and oxidative destruction of CWAs to improve protection of the warfighter against such threats.

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