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Dehydrochlorination Decomposition Of Sulfur Mustard And 2-cees On Rutile-tio2(110): A Dft Study

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The deployment of chemical warfare agents (CWAs) in a modern conflict poses major risks to humanity and necessitates research into facile decomposition of CWAs under ambient conditions. CWAs were first deployed in World War I. Mustard gas was utilized at the Battle of Ypres in 1917 causing blistering in skin, eyes, and lungs of exposed soldiers as well as long-term development of cancers. This project focuses on neutralization of mustard gas, also known as sulfur mustard, along with its simulant, 2-chloroethyl ethyl sulfide (2-CEES), by new highly efficient catalysts in ambient conditions.

The structure of sulfur mustard, known chemically as bis(2‑chloroethyl) sulfide, allows its two chloroethyl groups to undergo a cyclic first-order reaction, forming an unstable episulfonium intermediate. In biological systems, the episulfonium cation alkylates DNA, driving carcinogenesis. Therefore, a neutralization of mustard should involve β-elimination of the chlorine atoms. Pathways for dehydrochlorination of mustard on various model catalysts are constructed to determine the optimal strategy for neutralization.

The decomposition of sulfur mustard and 2-CEES was explored through ab initio computational analysis of the dehydrochlorination reaction to produce a non-vesicant divinylsulfide (DVS) product. Dehydrochlorination was modelled on Pt single atom catalysts (SACs) supported on rutile-TiO2 (100), as well as on pristine r-TiO2 to determine the optimal catalyst and pathway. Density functional theory (DFT) calculations were used to study the structure and reactivity of highly dispersed metal sites and to screen candidate materials for experimental testing. Calculations were performed with the Vienna Ab Initio Simulation Package (VASP) using the PBE+U functional with dDsC correction. The 2x4 model surface is constructed with 4 O-Ti-O tri-layers with the first tri-layer frozen to mimic the bulk.

The most favorable adsorption configuration of mustard and 2-CEES was calculated on three catalysts, pristine r-TiO2, Ptsub/r-TiO2, and PtO2/r-TiO2. Mustard and 2-CEES adsorbs favorably on all three surfaces. The adsorption energy for mustard was -1.73 eV for pristine r-TiO2, -3.33 eV for PtO2/r-TiO2, and -2.91 eV for Ptsub/r-TiO2. The adsorption energy for 2-CEES was -1.57 eV for pristine TiO2, -3.18 eV for PtO2/r-TiO2, and -2.99 eV for Ptsub/r-TiO2. The adsorption energies of both molecules on PtO2/r-TiO2 and Ptsub/r-TiO2 are considerably stronger than on pristine r-TiO2 because of the Pt-S interaction present in the former two catalysts.

The reaction energy to form DVS from the adsorbed mustard is -0.506 eV for pristine r-TiO2, -0.352 eV for PtO2/r-TiO2, and +0.04 eV for Ptsub/r-TiO2. The dehydrochlorination reaction can be stabilized by the Cl-Ti interaction for all three catalysts. The cleaved Cl prefers to interact with Ti atoms further from the Pt SAC. For the PtO2/r-TiO2, the β-eliminated hydrogens bind more favorably with the oxygens from PtO2 than the bridging oxygen, contributing to the dehydrochlorination being more favorable on PtO2/r-TiO2 than Ptsub/r-TiO2. The strong Pt-S interaction present for the Pt single atom catalysts greatly increased the stability of mustard and 2-CEES adsorption but hinders desorption of the DVS product. On the pristine r-TiO2, DVS readily desorbs due to the weaker Ti-S interaction, contributing to the thermodynamic favorability of dehydrochlorination on this catalyst.