

Ab Initio Calculations of Chemical Warfare Agent Binding on Oxide Surfaces

Ivan Iordanov¹, Christopher Karwacki²

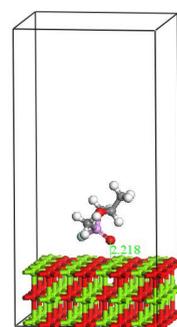
(1) National Research Council Postdoc at U.S. Army Edgewood Chemical Biological Center, (2) U.S. Army Edgewood Chemical Biological Center

Abstract

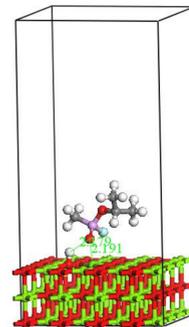
The objective of our research is to provide an in depth investigation of the surface interaction between magnesium oxide and sarin (GB). Density functional theory (DFT) calculations have been used to determine the binding energy, bond type and orientation of GB on bare MgO (1 0 0). Further calculations have been done for cases in which the surface is hydrogenated or contains defects. Molecular dynamics simulations at temperatures varying from 300-2000K are currently in progress. We also expect to confirm some of our computational results through future experimental work. Ultimately, this work will improve our understanding of metal oxide catalysts, and provide a template to extend our approach to other metal oxide surfaces.

Bare Surface

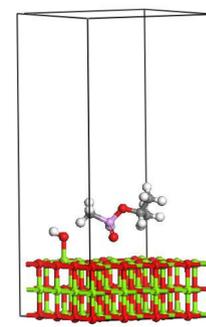
For the bare MgO surface, we find that GB binds through a long range 2.22 Å ionic bond between the outlying GB oxygen and a surface Mg, with a binding energy of 1.36eV (31.4kcal/mol). The Mg atom puckers up slightly from the surface layer, suggesting this is a fairly strong single bond. When the same calculation is done without the van der Waals (vdW) correction, the binding energy drops to 1.005eV, showing that while vdW corrections are certainly important for this case, the majority of the binding energy is due to an ionic interaction which is well characterized through DFT. Furthermore, the energy lost due to the puckered Mg atom is 0.68eV, a significant distortion that further suggests a single strong bond.



Bare surface
BE: 1.38eV



Single H
1.86eV



Single OH
1.67eV

Single OH and H Groups

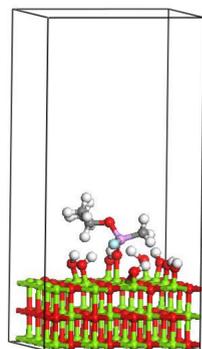
- The simplest cases show the effects of very low density hydrogenation.
- Both increase the binding energy significantly.
- However, character of binding is still same as bare surface, ionic bond to surface Mg.
- Future calculations will focus on other configurations where a single hydrogen atom or OH group could change the character of the binding.

Computational Details

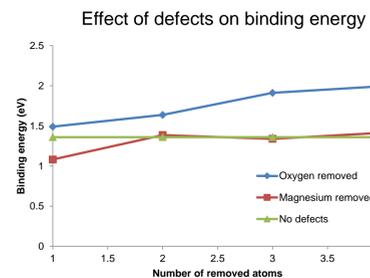
The calculations used a plane-wave implementation of DFT using the Perdew-Burke-Ernzerhof functional and projector-augmented plane-wave pseudopotentials, with an energy cut off of 45 Ry. Van der Waals interactions were included with the semi-empirical Grimme method, and calculations were done with the Quantum Espresso computational package. All reported results are due to fully relaxed calculations (no atoms were fixed or frozen). The surface was simulated as a 3-layer vacuum slab with unit cell dimensions of 11.9x11.9x25.0 Å, with a vacuum region of ~15 Å. The effect on the BE of GB due to larger unit cells, more layers, and a larger vacuum region were all examined, and the current size was chosen as the best compromise of accuracy and computational cost. Relative to the chosen size, a ~20 Å vacuum region changes the energy by just 0.01eV. Increasing the number of layers to 5 increases the binding energy by 0.09eV, while doubling the surface area lowers it by 0.17eV. We plan to increase the surface dimensions further and provide more precise units for the binding to the bare MgO surface in the future; however, the accuracy of the chosen unit cell is sufficient for looking at trends in behavior as the surface is modified.

Large-scale Hydrogenation

- In reality, metal oxide surfaces are often hydrogenated to a significant degree.
- In order to have a controlled examination of larger scale hydrogenation we manually attach hydrogen atoms or hydroxyl groups to the surface.
- In calculations so far, adding hydrogen atoms increases the binding energy (BE), however attaching many hydroxyls lowers the BE.

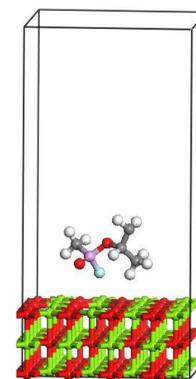


Half Hydroxyl groups

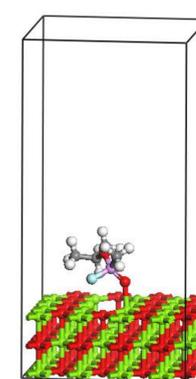


Defects

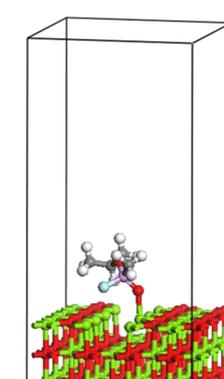
- Defects often play a significant role in binding and catalysis.
- As a starting point, we look at the effects of single vacancies – removing surface O and Mg atoms.
- To check for trends, we remove additional atoms in a line, up to 4, effectively simulating a channel in the surface.
- Results show that removing more oxygen increases the binding fairly linearly, most likely a polarization effect.
- Future work will examine other defects and hydrogenated surfaces with defects.



Removed: Single Mg



Double O

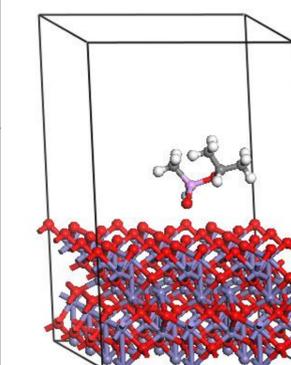


Four O (channel)

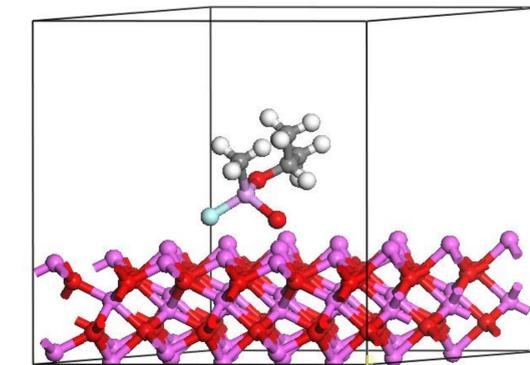
Future Work

In the short run, our goal is to greatly expand the molecular dynamics simulations, with longer runtimes, additional temperatures, and more water molecules, and use the results to expand our other calculations. In conjunction, experimental work at ECBC will be done that could complement and confirm our theoretical results.

Ultimately this work should serve as a template for investigating other CWA/metal oxide interfaces. Metal oxides are used widely both industrially and in decontamination applications. A series of investigations, using the same methods to characterize different CWA/metal oxide interface, could provide valuable insight into trends of behavior across this class of materials. Examples of surfaces we have started to look at are provided.



Fe₂O₃ surface

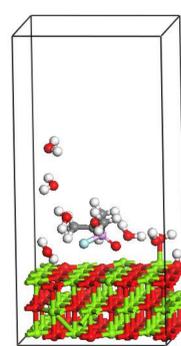


Al₂O₃ surface

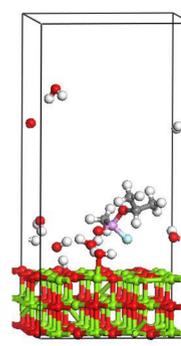
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Molecular Dynamics

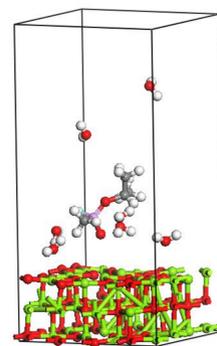
- Molecular dynamics simulations provide us with a more realistic picture of how GB would interact with a hydrogenated and wetted MgO surface.
- Calculations are ongoing, pictures on the left provide the final state of the system after 0.96 picoseconds of simulation at the labeled temperature, starting from the same initial conditions.
- Will provide us with realistic hydrogenated surfaces to use in single point calculations for binding energies for a hydrogenated surface.



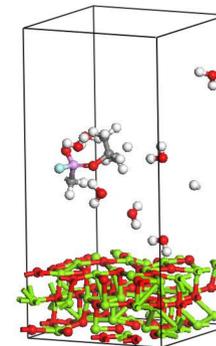
300K



500K

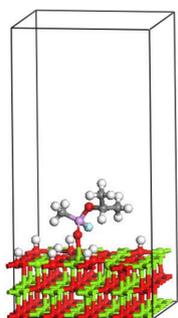


1000K

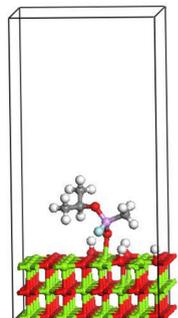


2000K

Half Hydrogen atoms



Quarter Hydrogen atoms



RDECOM

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