Trends in Binding Phenomena of Small Organic Molecules and CW Simulants to Selected Materials

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Objective: Over the course of the project, we will conduct a series of atomistic simulations and practical experiments to understand the interactions of CWA molecules with certain surfaces. We have chosen to investigate solid metal oxide surfaces, porous activated carbon, and the external and internal surfaces found in layered double hydroxides (clays), both un-altered and substituted versions. In this poster we present our results on the investigation of the adsorption of small organic molecules, 2-CEES, mustard, and DMMP to the surfaces of alumina, iron oxide hydroxide, and graphite.

Pairing laboratory and computational experiments brings clarity to both sets of results. Simulations will investigate both CW simulants and actual agent molecules; experiments will ground simulations in the real world. Simulations use idealized surfaces, specific crystal faces, pure components – while experimental surfaces are more complex and can include contaminants, packing faults, etc.

The strength of the association of a chemical warfare molecule to a sorbent or catalyst surface is fundamental to all decontamination and remediation efforts. Understanding the adsorption of these compounds and the relative strength of their attraction to surfaces will allow for improved catalyst development, better materials selection for deployed surfaces, and the development of practical decontamination strategies.

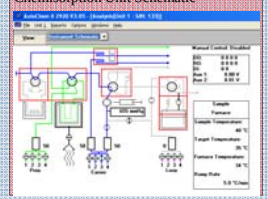
Laboratory Experimental Approach and Results.

Laboratory work has employed a Chemisorption unit (Micromeritics Autochem 2920 – see Fig. 1) to determine a molecule's Heat of Desorption, E_d (kJ/(mol *K)).

The general equation is: $\ln(\beta/T_p^2) = -E_d/RT_p + \ln(E_dA/RC)$

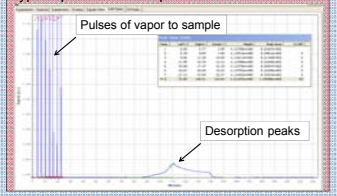
Where:
- β = ramp rate (deg/min)
- T_p = Temperature at peak max (K)
- E_d = Heat of Desorption (kJ/mol K)
- R = gas constant (J/(mol*K))
- A = quantity of gas adsorbed at saturation
- C = desorption rate constant

Chemisorption Unit Schematic

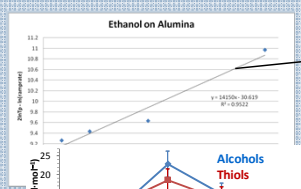


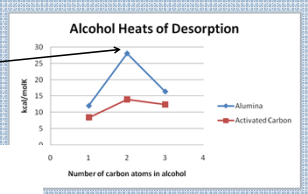
Three desorption experiments are run with different ramp rates. By plotting: $2\ln T_p - \ln \beta$ vs. $1/T_p$, the slope of the line is E_d/R.

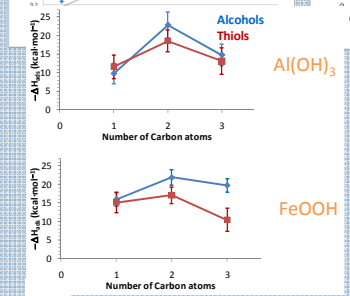
Typical pulse chemisorption runs

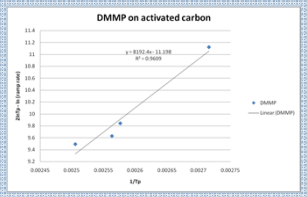


The pulse chemisorption experiment begins with a degas step to 600 ˚C. The sample is cooled to RT, then dosed with adsorbate until saturation, which is determined by a thermal conductivity (TCD) detector. The furnace then heats the sample at a specified ramp rate, and the desorbing gas is monitored. In these experiments, the samples were heated to 600 ˚C between 2 and 15 deg/min.



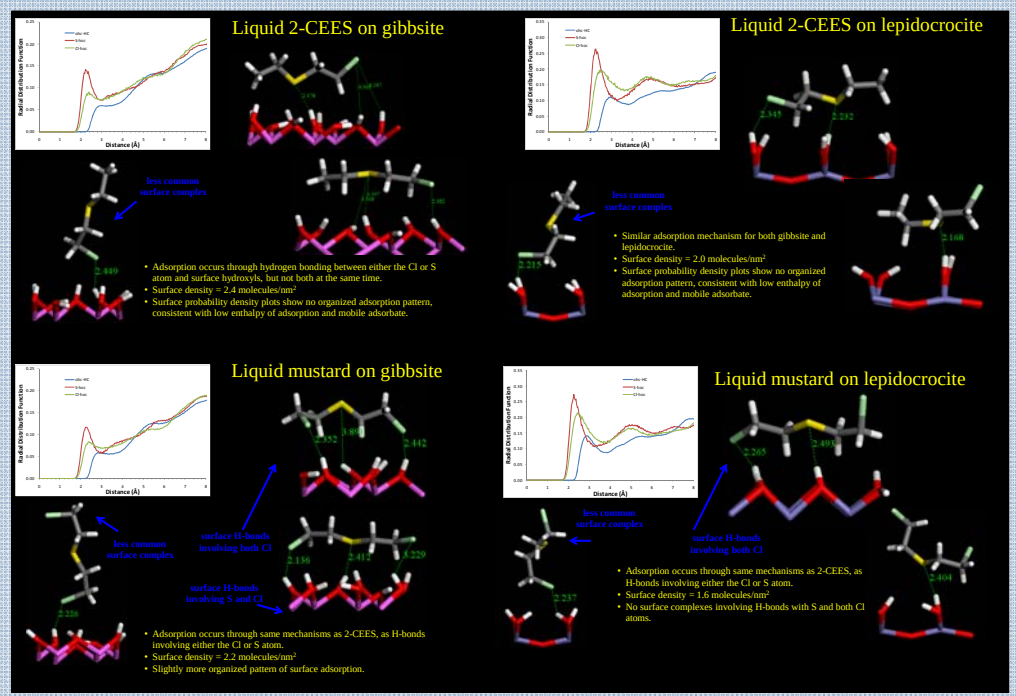




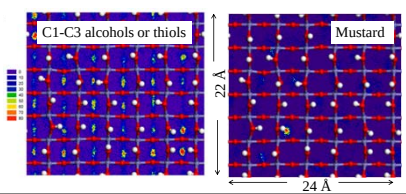


Computational Experimental Approach and Results.

- Initial study of small (C1-C3) alcohol and thiol adsorption on metal oxide surfaces: $Al(OH)_3$, FeOOH, and graphite, expanded to investigate 2-CEES and mustard adsorbates
- Classical molecular dynamics (MD) simulations use the LAMMPS code and involve approximate interaction parameters (force field) optimized for hybrid organic-inorganic systems. CLAYFF parameters used for the surface, OPLS parameters used for all adsorbates.
- Model systems consist of slabs 10-15 Å thick of the corresponding layered mineral, with a vacuum termination. Periodic boundary conditions used to effectively model a macroscopic system.
- Range of adsorbate surface coverage from infinite dilution (0.2 molecules/nm²) to > 1 monolayer (6.9 molecules/nm²).
- Adsorption enthalpies at infinite dilution obtained by simulating one molecule on a surface.
- Molecular flexibility.
  - Adsorbates: fully flexible (bond stretch, angle bend, etc).
  - Oxides: upper metal hydroxide layer allowed to move for infinite dilution simulations. Only hydroxyl H atoms allowed to move for monolayer simulations. Other atoms remain fixed for computational efficiency.
- Production simulations are 0.5-ns in length using a 1.0-fs timestep, at 300 K.



Adsorption probability density on Lepidocrocite (FeOOH)



Comparison between gibbsite and lepidocrocite

Adsorption enthalpies (kcal/mol)

Mineral	2-CEES	Mustard
$Al(OH)_3$	7.2 ± 4	19.6 ± 3
FeOOH	3.2 ± 2	6.6 ± 2
Graphite	3.8 ± 3	7.7 +- 3
Self-energy	3.74	8.98

Surface densities (molecules/nm²)

Mineral	2-CEES	Mustard
$Al(OH)_3$	2.4	2.2
FeOOH	2.0	1.6
Graphite	2.5	2.3

Surface-2CEES radial distribution functions

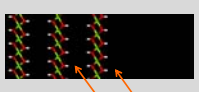
Mineral	S-H	Cl-H
$Al(OH)_3$	2.23	2.37
FeOOH	2.23	2.50

Surface-mustard radial distribution functions

Mineral	S-H	Cl-H
$Al(OH)_3$	2.25	2.40
FeOOH	2.25	2.43

Conclusions

- Modeling and experimental values for the adsorption enthalpies and heats of desorption of C1-C3 alcohols are in good agreement.
- From the computational results, the mustard and the simulant behave similarly towards the three surfaces, adsorbing only moderately onto the $Al(OH)_3$ surface, and weakly to the other surfaces.
- The mustard/2-CEES -surface complexes may form through hydrogen bonding to the Cl or S atoms.
- Experimental results with DMMP indicate a slightly stronger interaction with the activated carbon surface than the alcohols studied.



Future work:

- Complete simulations on DMMP and Sarin on surfaces. Compare to laboratory results.
- Begin simulations of hydrotalcite, Al/Mg$(OH)_2$, comparing adsorption enthalpies on an external surface vs. intercalated between layers.
- Continue laboratory work with 2-CEES on $AlOH_3$ FeOOH, graphite and hydrotalcites. Compare with computational results,
- Begin simulations on substituted hydrotalcites.

National Nuclear Security Administration

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