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Molecular Dynamics Simulation of Alcohol and Thiol Adsorption on (Oxy)hydroxide and Graphite Surfaces

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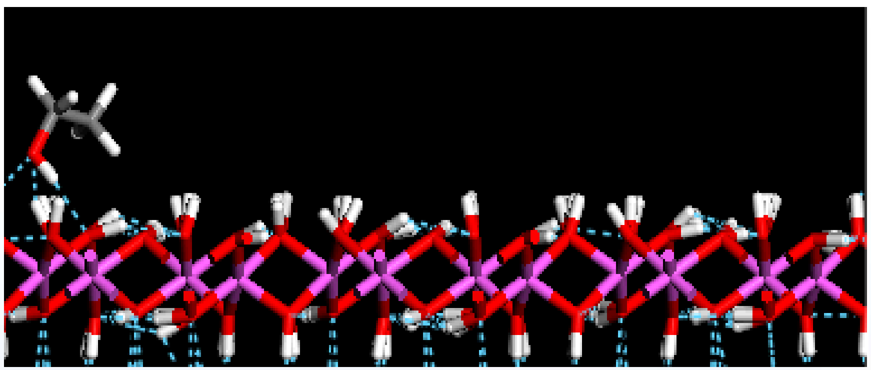
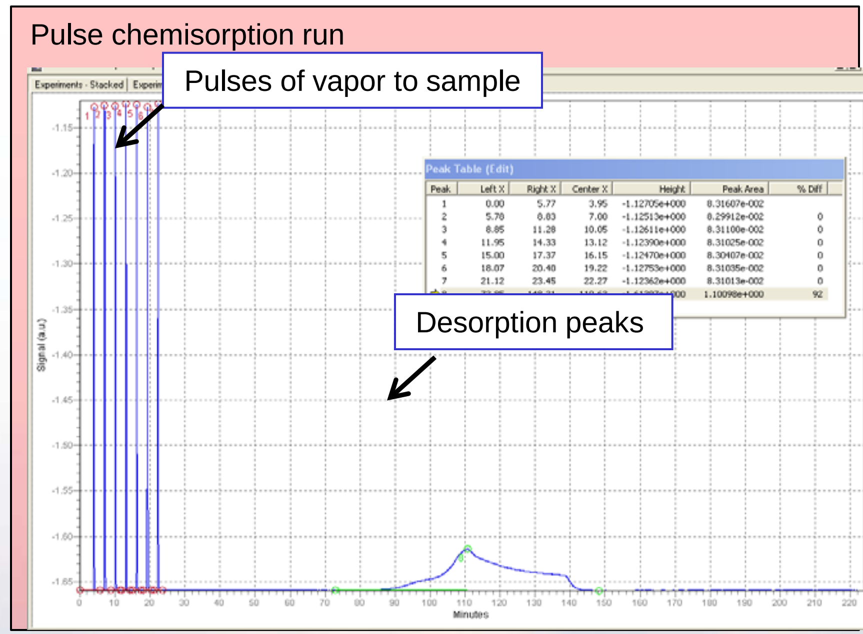
Objective

- **Investigate and compare the interaction of small organic molecules with external surfaces of layered double hydroxides (LDHs) and graphite (activated carbon).**
- **Extend this knowledge to intercalation of organics in LDHs.**

Simulation + Experiment



ethanol adsorbed on gibbsite, $Al(OH)_3$

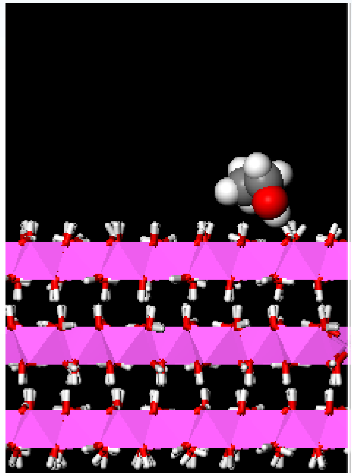


<u>For directed and improved:</u>

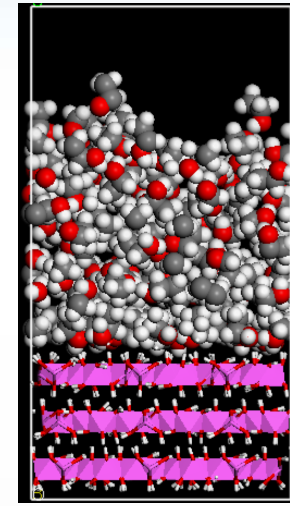
- General mechanistic understanding of adsorbate-surface interactions
- Catalysis research
- Materials formulations (coatings, etc.)

Modeling Methods

Infinite dilution
- adsorption enthalpy
- surface complex geometry



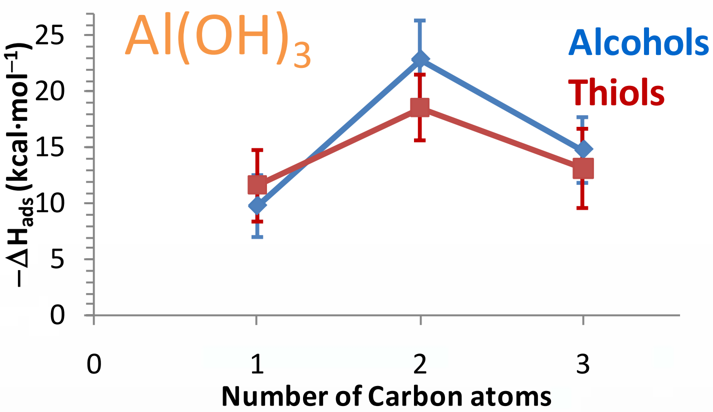
Liquid
- monolayer surface density
- RDFs

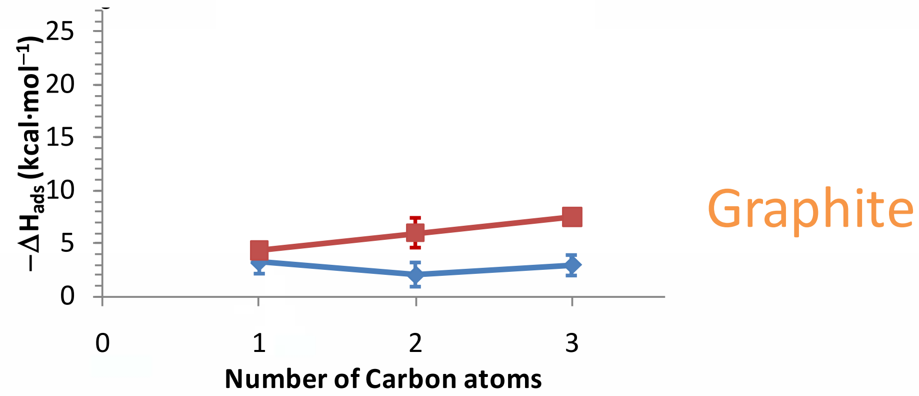


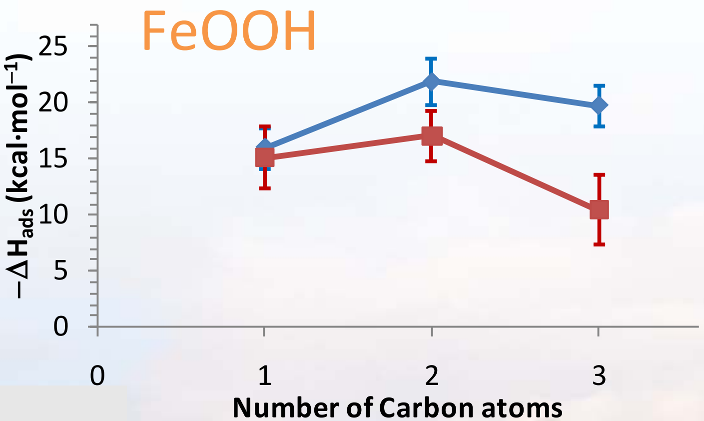
- Surfaces: $Al(OH)_3$ (gibbsite), FeOOH (lepidocrocite), C (graphite), 10-15 Å thickness .
- Molecular dynamics (MD) simulations: LAMMPS code with ClayFF[1] parameters for $Al(OH)_3$ and FeOOH, OPLS[2] parameters for organics, and published parameters for graphite.[3]
- Periodic/slab boundary conditions, includes long-range electrostatic and short-range (van der Waals) interactions.
- Organic adsorbates are fully flexible. Only H atoms in the mineral phases are allowed to move for computational efficiency.
- Production simulations are 1.0-ns in length using a 1.0-fs timestep, at 300 K.

[1]Cygan et al, J*. Phys. Chem B* **2004**, *108*, 1255.
[2]Jorgensen et al, *J. Am. Chem. Soc.* **1996**, *118*, 11255.
[3]Shevade et al, *J. Chem. Phys*. **2000**, *113*, 6933.

Alcohol/Thiol Adsorption Enthalpies

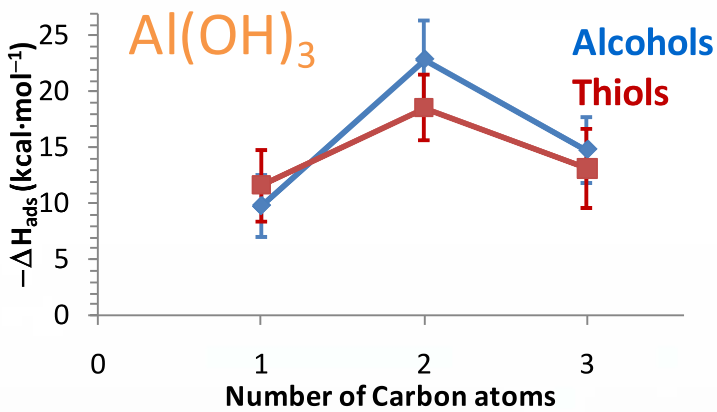


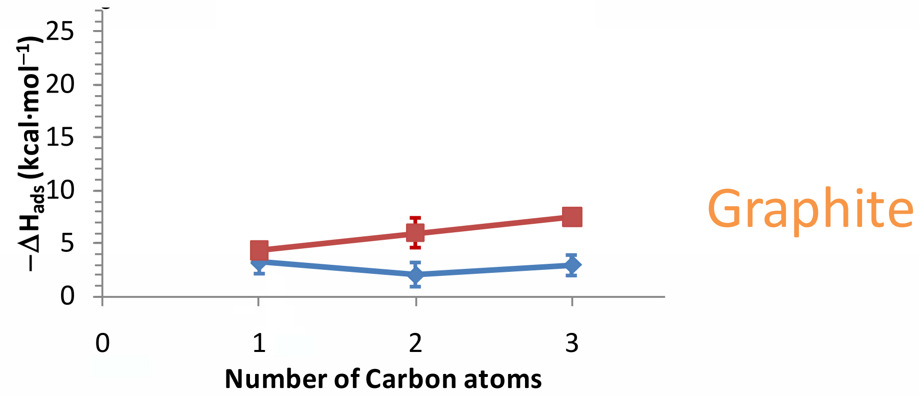


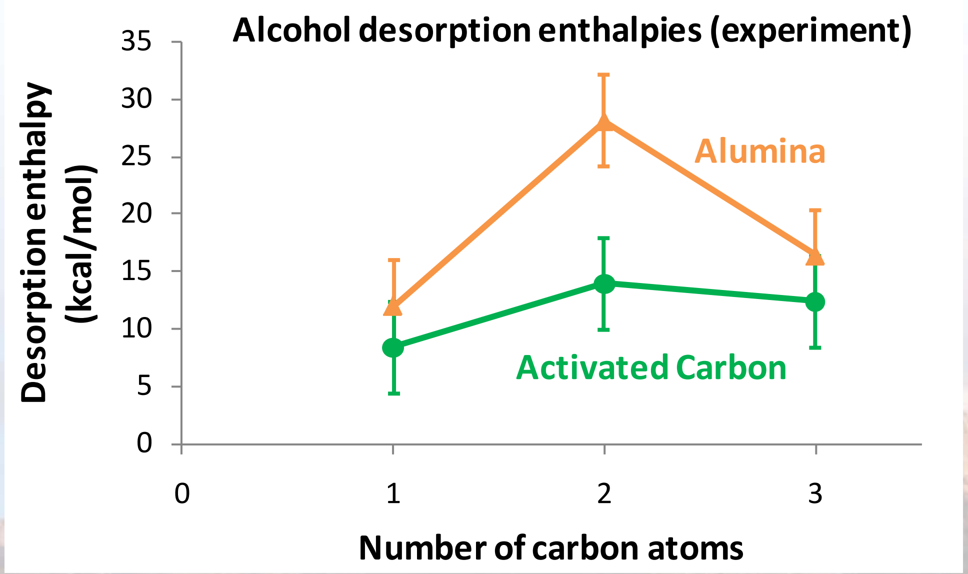


- Ethanol has the largest adsorption enthalpy on each LDH surface.
- Alcohols adsorb more strongly on LDH surfaces than thiols, but the reverse is true on graphite due to enhanced van der Waals interactions.
- Stronger adsorption on the LDH surfaces than the graphite surface, due to H-bonding.

Alcohol/Thiol Adsorption Enthalpies



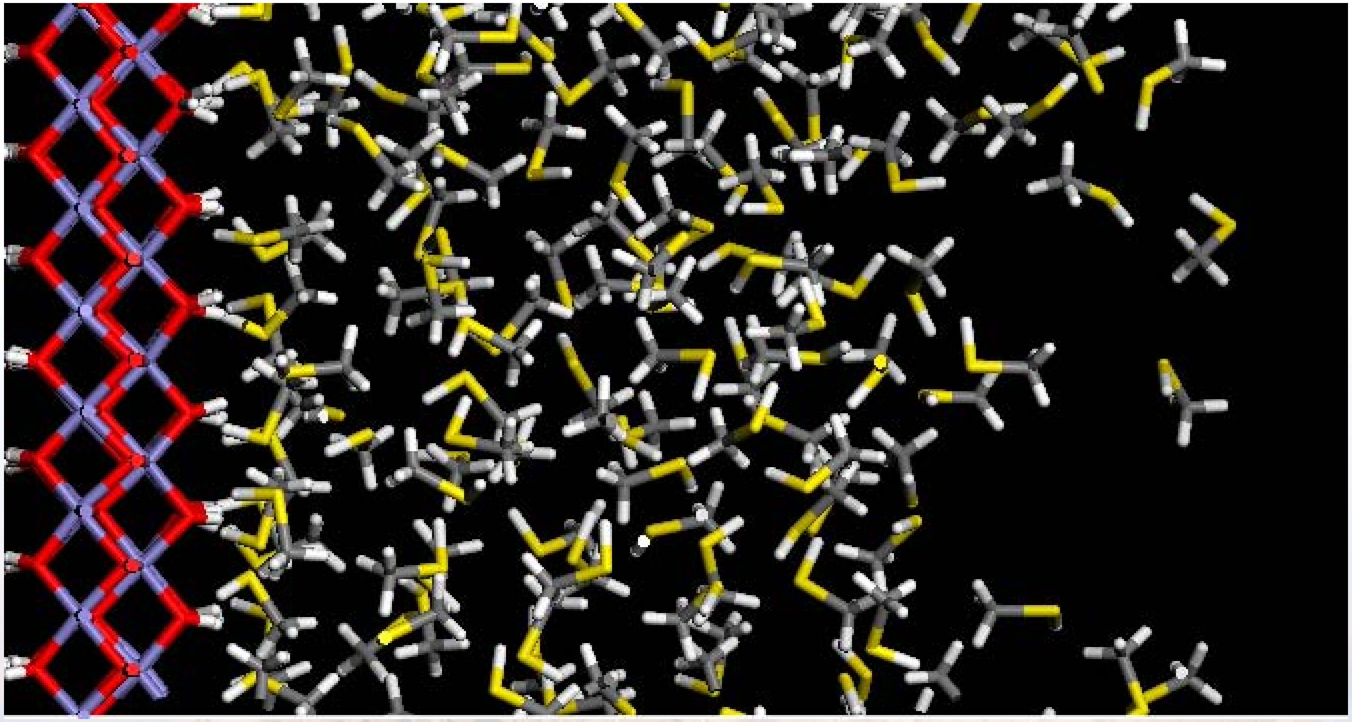




Good agreement between simulation and experiment for ethanol adsorption/ desorption.

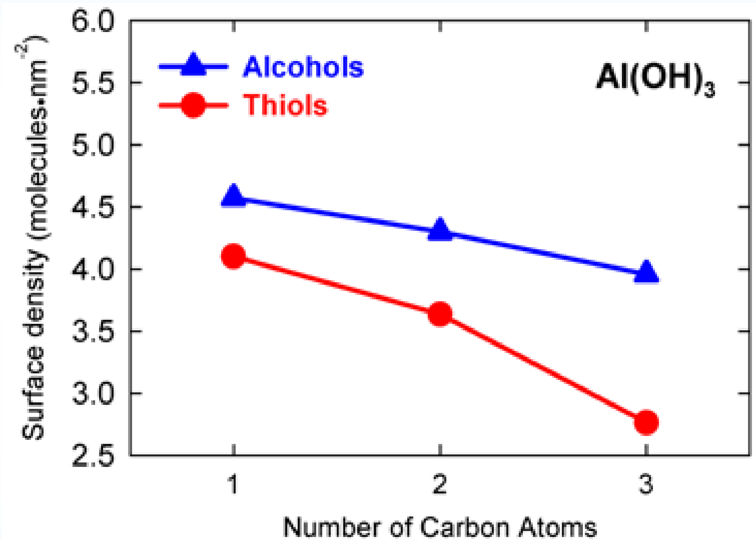
Determination of Monolayer Surface Density

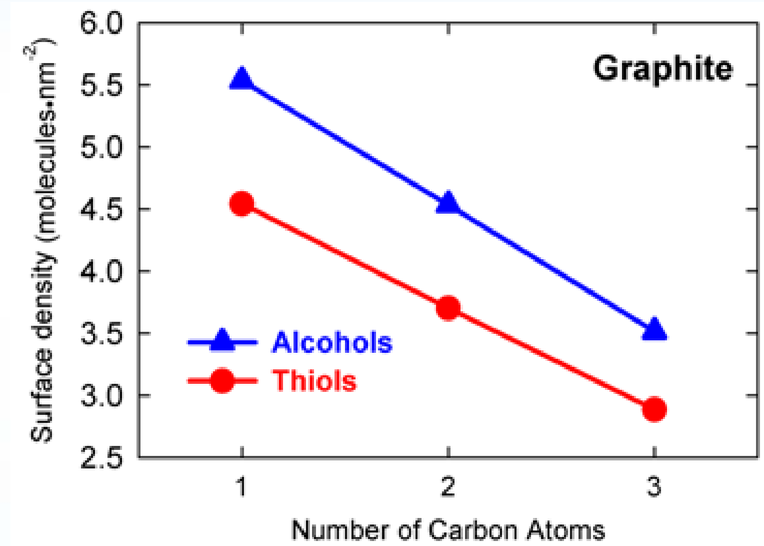
Liquid methanethiol on FeOOH

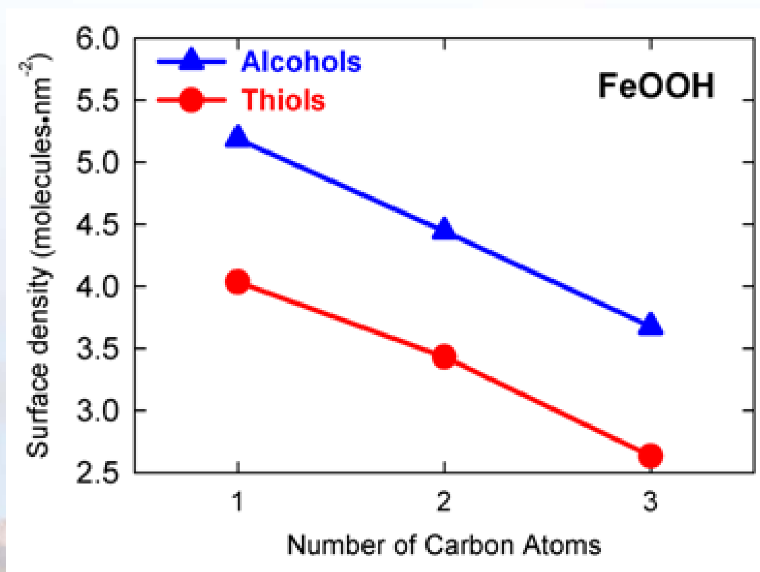


Monolayer surface density determined from atomic density profiles.

Monolayer Surface Densities







Trend in surface densities:

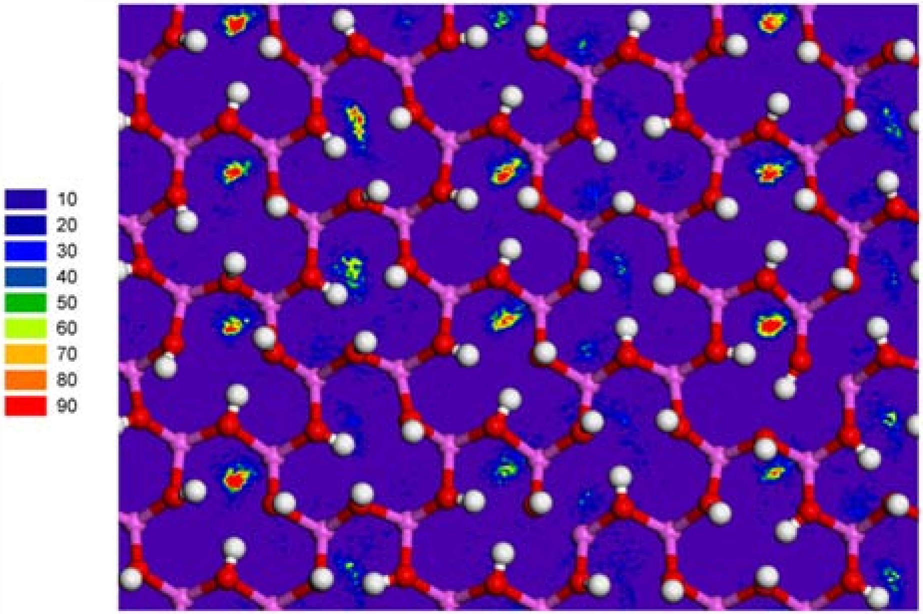
$$C \geq Al(OH)_3 \geq FeOOH$$

The LDH surfaces have a limited number of adsorption sites that facilitate H-bonding with guests, which reduces surface density.

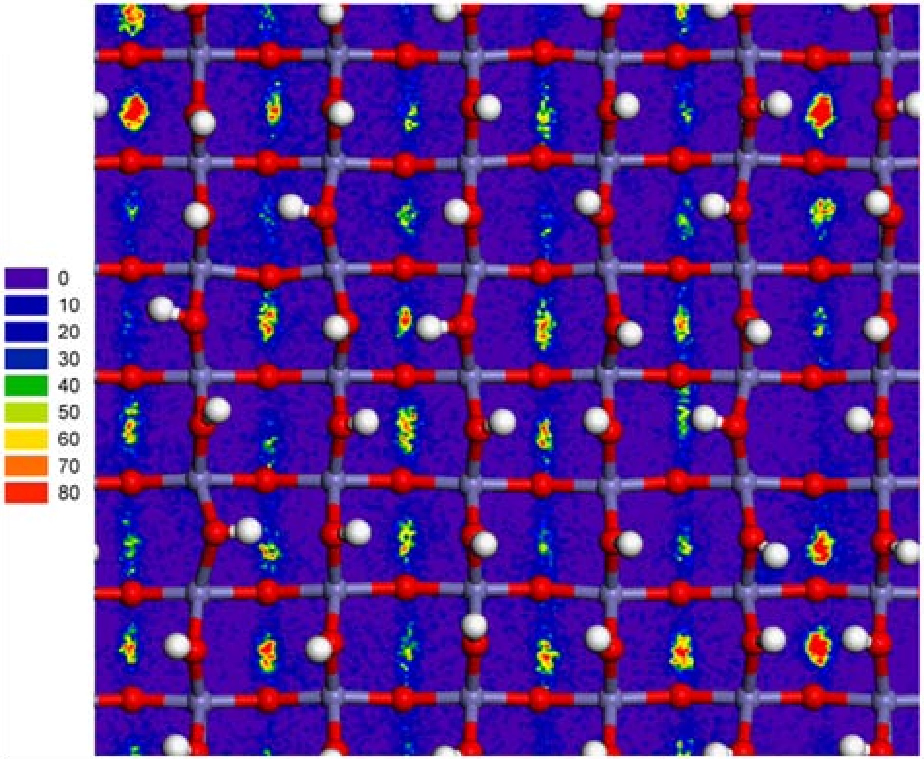
Surface Adsorption Sites

2D density plots of adsorbed ethanol

$Al(OH)_3$



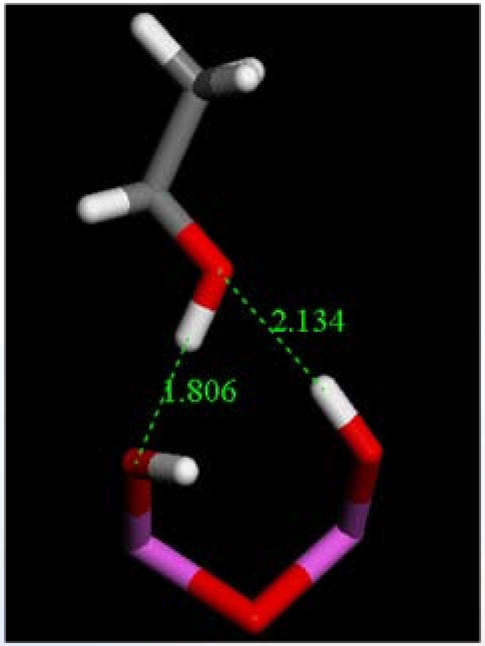
FeOOH



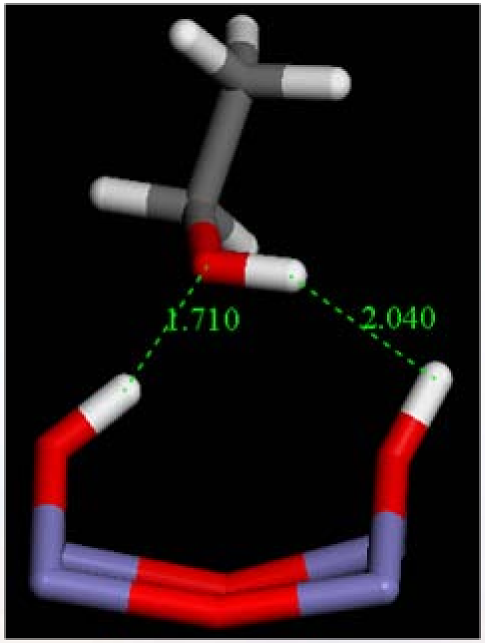
Surface adsorption sites maximize H-bonding between O(S)H groups and surface hydroxyl groups.

Ethanol surface complexes

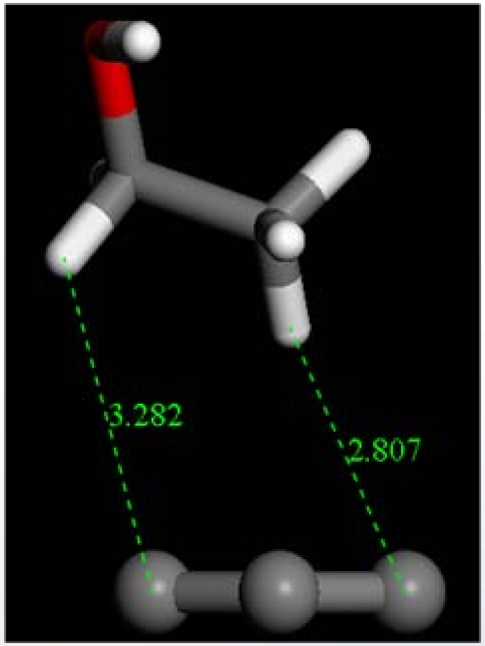
Al(OH)$_3$



FeOOH



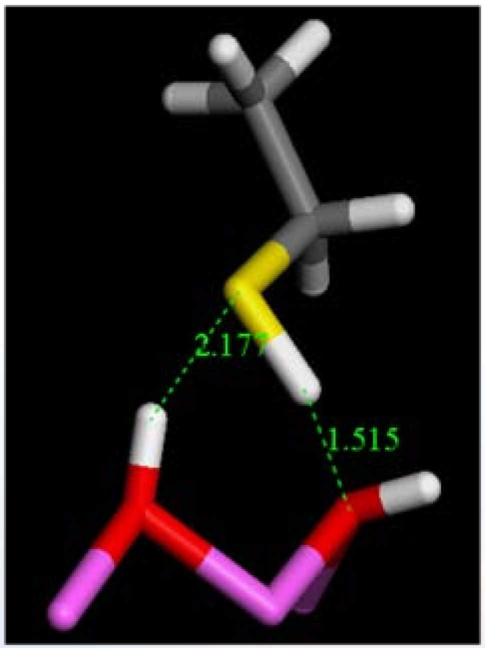
graphite

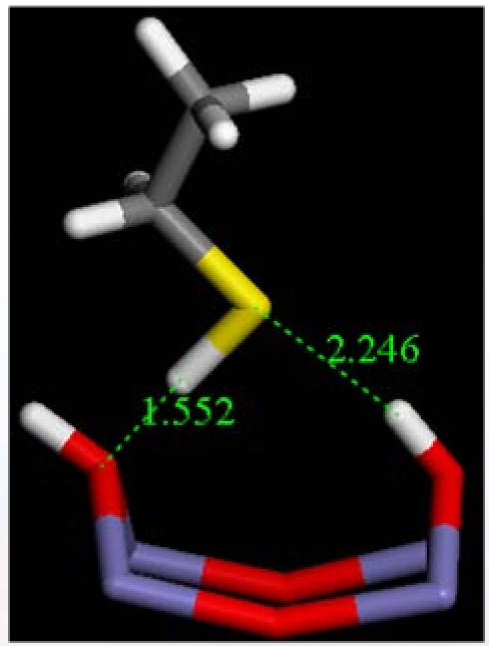


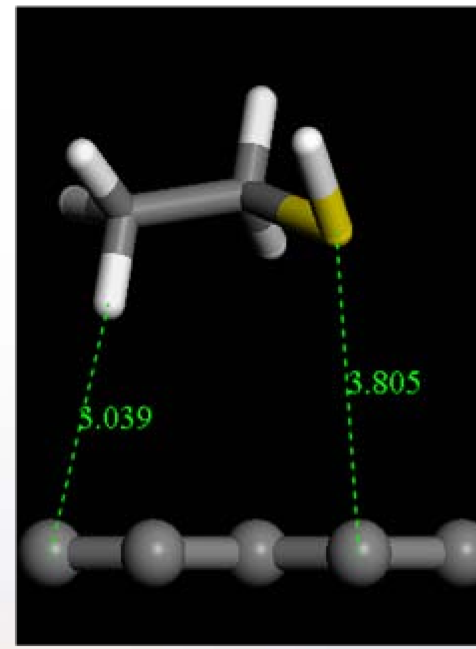
Bifurcated H-bonding with LDH surfaces, while longer adsorbate-surface distances are seen with graphite.

Ethanethiol surface complexes

$Al(OH)_3$ | FeOOH | graphite







Stronger van der Waals interactions involving S atoms results in shorter SH···O_{surf} distances.

Interfacial H-bonding structure

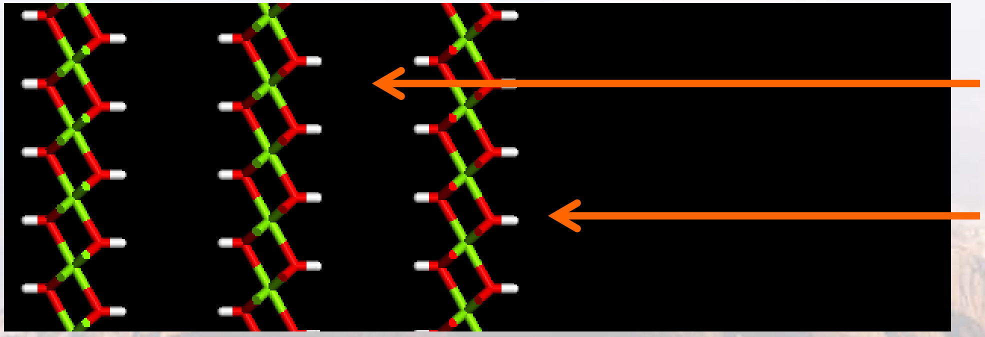
H-bond distances (Å) from radial distribution functions

Surface	Adsorbate	O_{surf}-H_{ads}	O/S_{ads}-H_{surf}
$Al(OH)_3$	MeOH	1.78	1.85
	MeSH	1.61	2.38
	EtOH	1.77	1.86
	EtSH	1.62	2.36
	PrOH	1.77	1.89
	PrSH	1.64	2.36
FeOOH	MeOH	1.79	1.74
	MeSH	1.62	2.23
	EtOH	1.77	1.76
	EtSH	1.61	2.28
	PrOH	1.77	1.77
	PrSH	1.60	2.28

- Little difference in H-bonding distances between $Al(OH)_3$ and FeOOH.
- Thiols have slightly shorter O_{surf}-H_{ads} distances compared to alcohols.
- Alcohols have significantly shorter O_{ads}-H_{surf} distances (≈ 1.8 Å) than the thiol S_{ads}-H_{surf} distances (≈ 2.3 Å)

Conclusions and future work

- Initial simulation results suggest that adsorbate interactions with LDH surfaces are fairly weak, despite the presence of H-bonding between adsorbate and surface.
- Alcohols and thiols are hydrogen bond donors acceptors at LDH surfaces, with C2 adsorbates showing the strongest adsorption.
- Future work:
  - Simulations of hydrotalcite, $[Mg_2Al(OH)_6]Cl$, comparing adsorption enthalpies on an external surface vs. intercalated between layers.
  - Compare adsorption trends between pure hydrotalcite and pillared hydrotalcite.



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