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Structural Properties of Organically Modified Aluminum Oxyhydroxide Nanomaterials from Molecular Simulation

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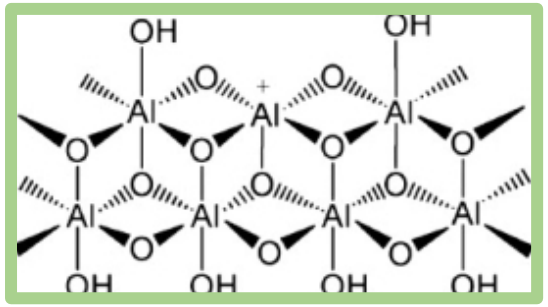
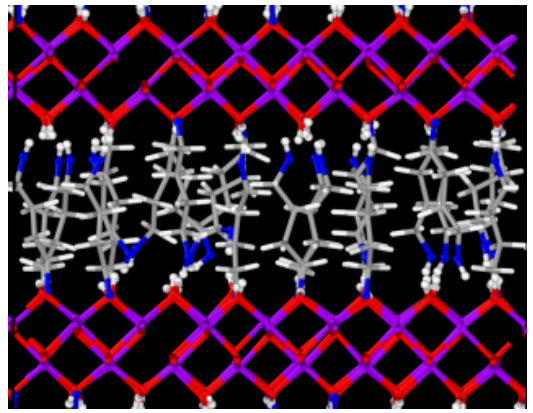
Motivation

Goal. Design anion getter materials for EBS seal systems based on organically modified boehmite (AlOOH)

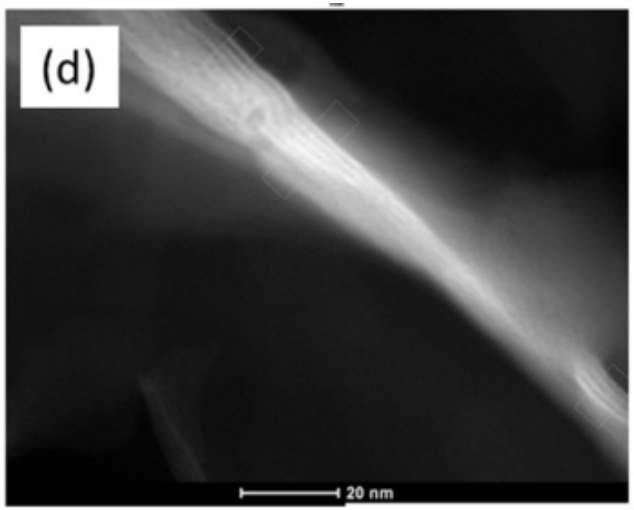


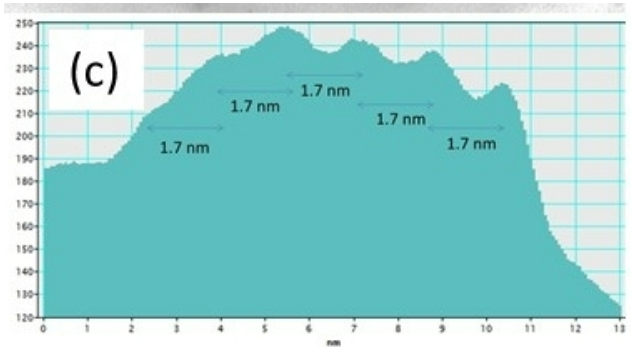
Boehmite

Glycol-based synthesis routes using covalent surface derivation



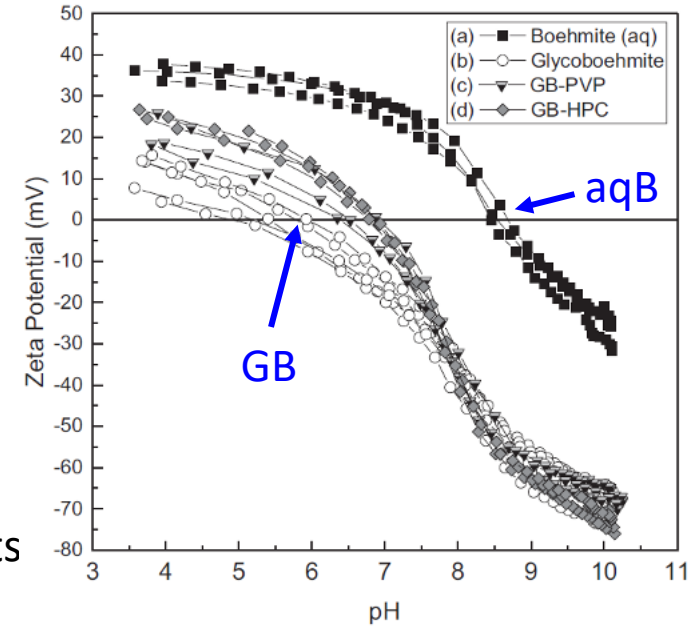
Glycoboehmite (GB)





TEM imaging reveals expanded interlayer in GB.

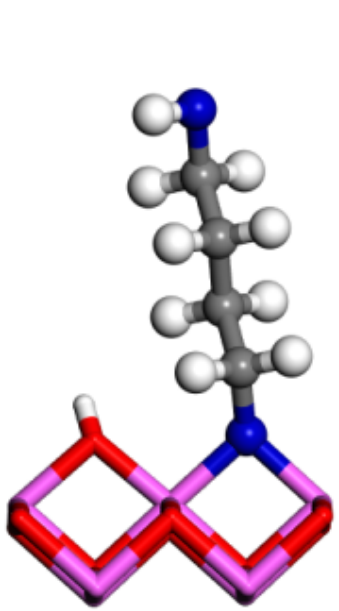
Different isoelectric points



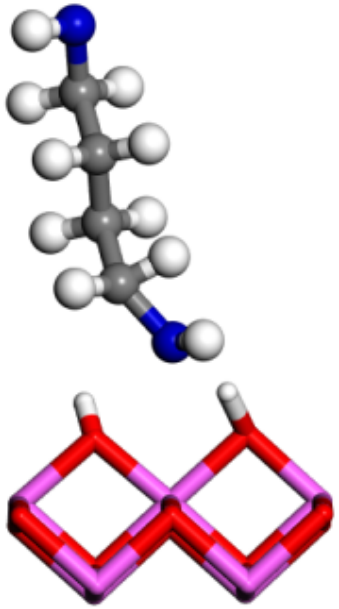
N.S. Bell et al, *Appl. Clay Sci.* **214** (2021) 106273.

Classical Molecular Dynamics (CMD) Simulations of Glycoboehmite

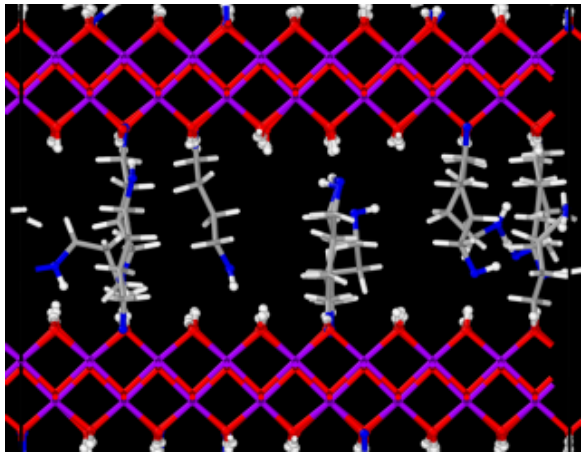
- Diol-boehmite binding models
  - Chemisorbed (Al-O-C bonds)
  - Physisorbed (intercalated)
- Clayff for boehmite, OPLS for butanediol.
- LAMMPS simulation methods
  - Supercells 23.0 Å x 22.5 Å in the lateral (*x*,*z*) dimensions
  - Constant pressure (NPT), 300 K, cell changes in *y*-only.



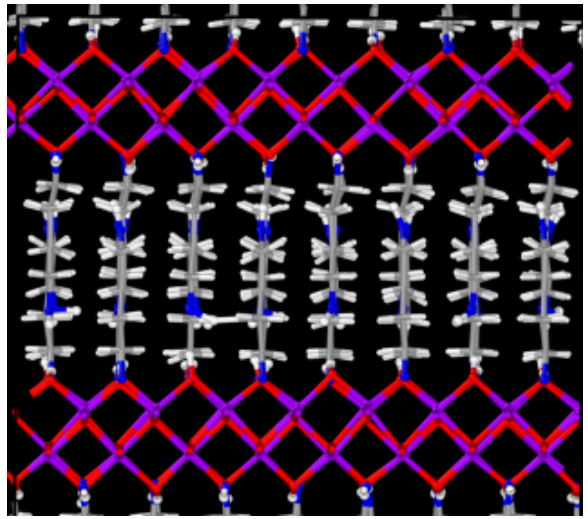
Chemisorbed (GB)



Physisorbed (aqB)



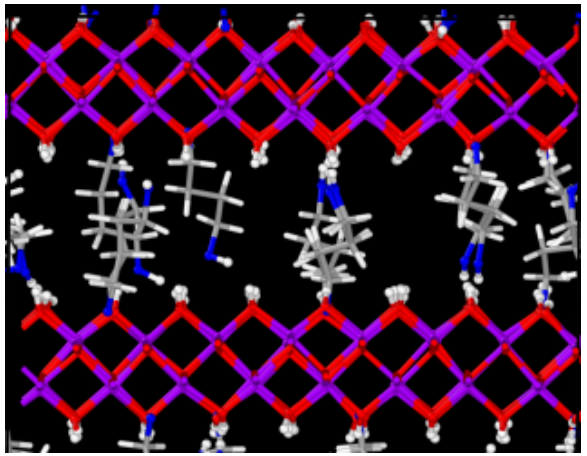
Low diol loading



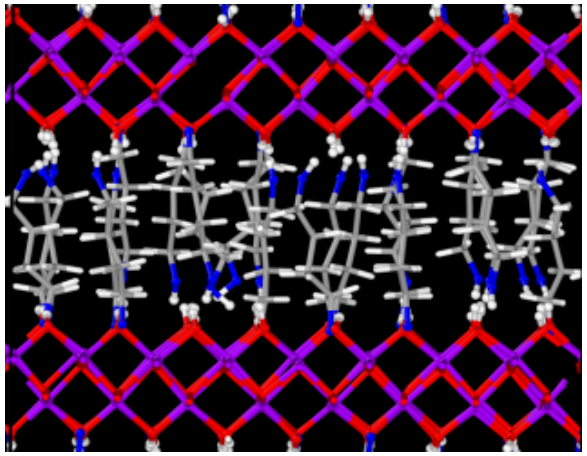
High diol loading

MD Results: Interlayer Expansion with Chemisorbed Butanediol (300 K)

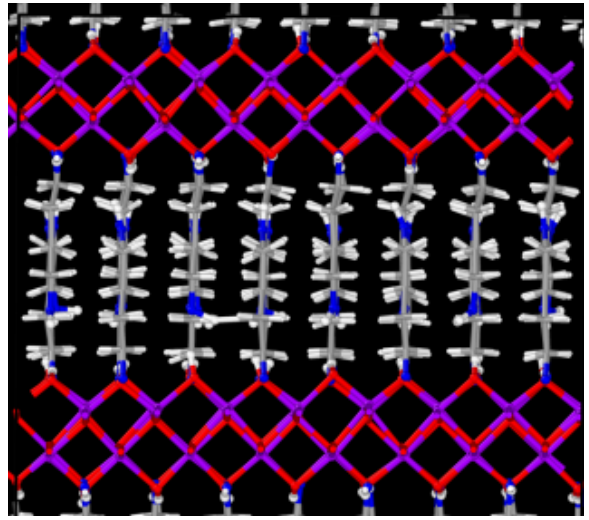
0.5 diol/uc
initial expansion

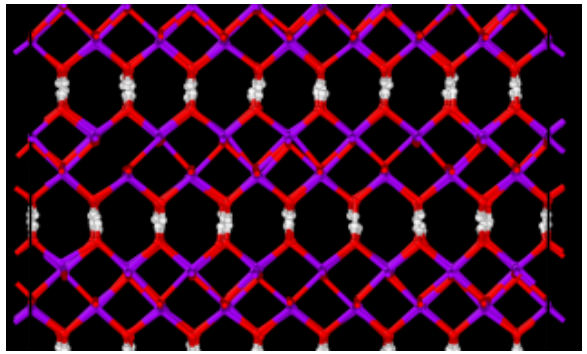


1 diol/uc
partial monolayers

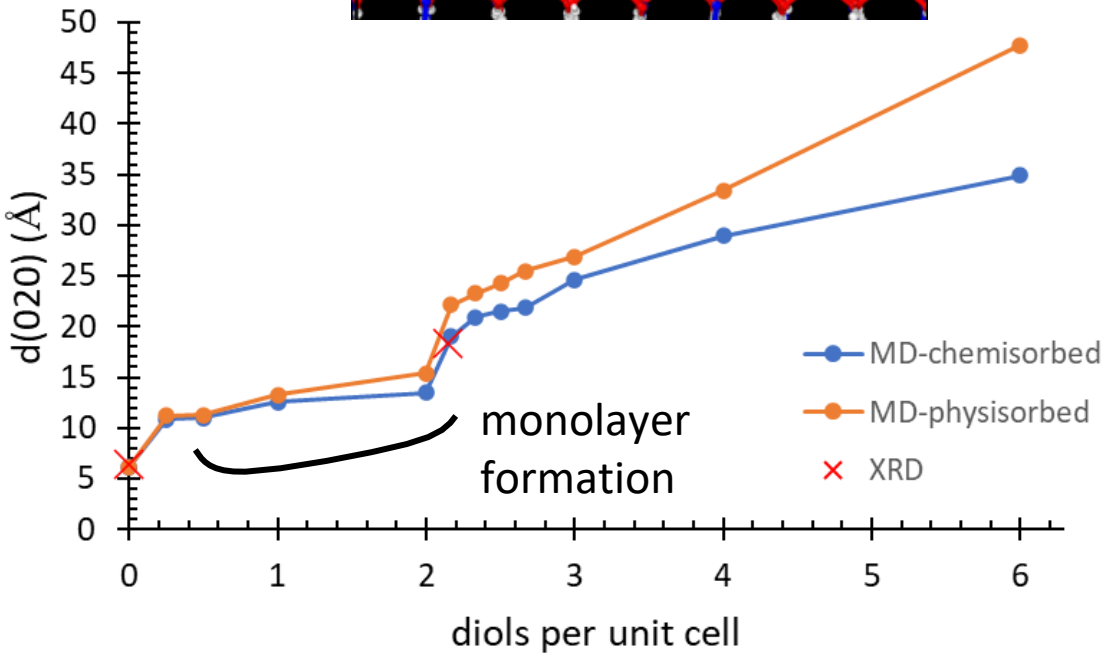


2 diol/uc
monolayers





0 diol/uc
pure boehmite



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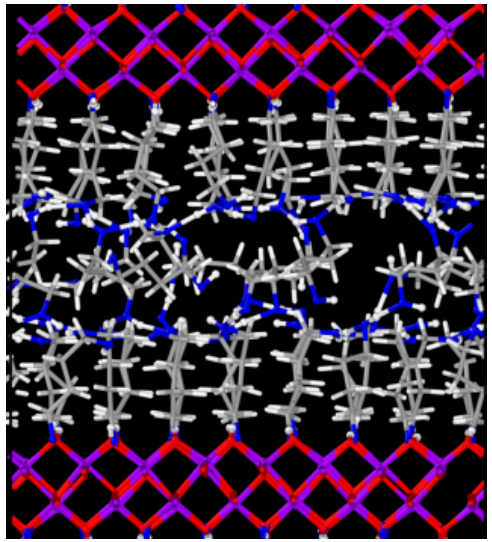
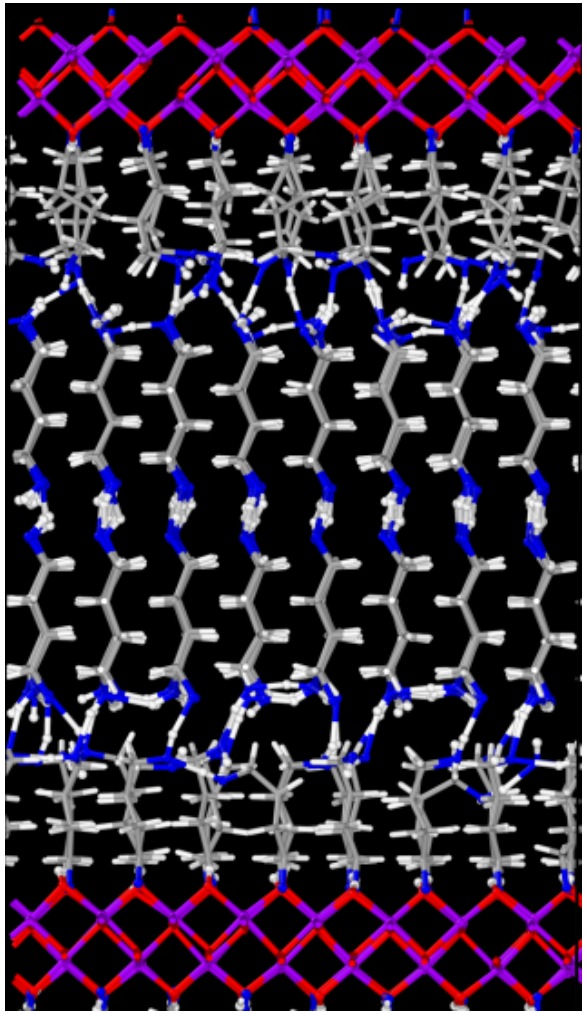
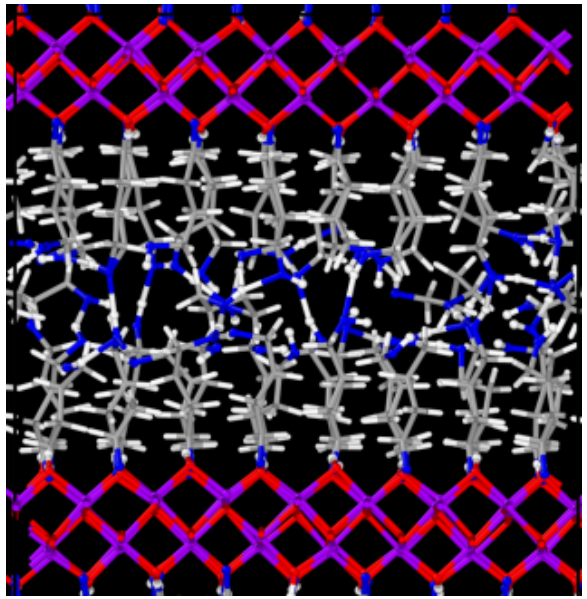
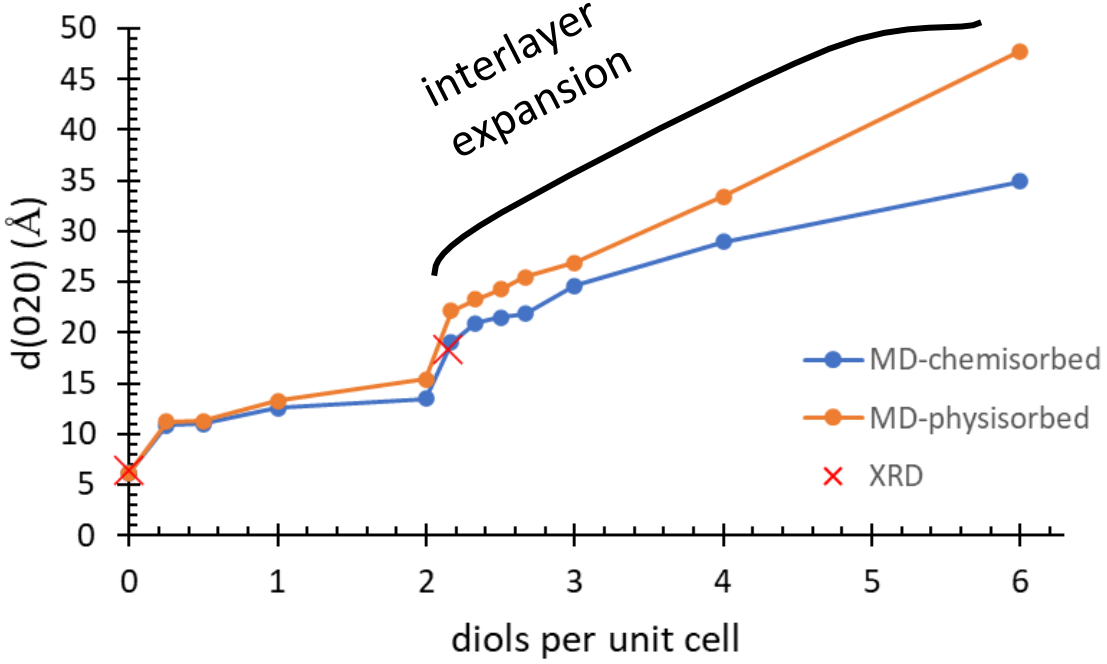


6 diol/uc
bilayers



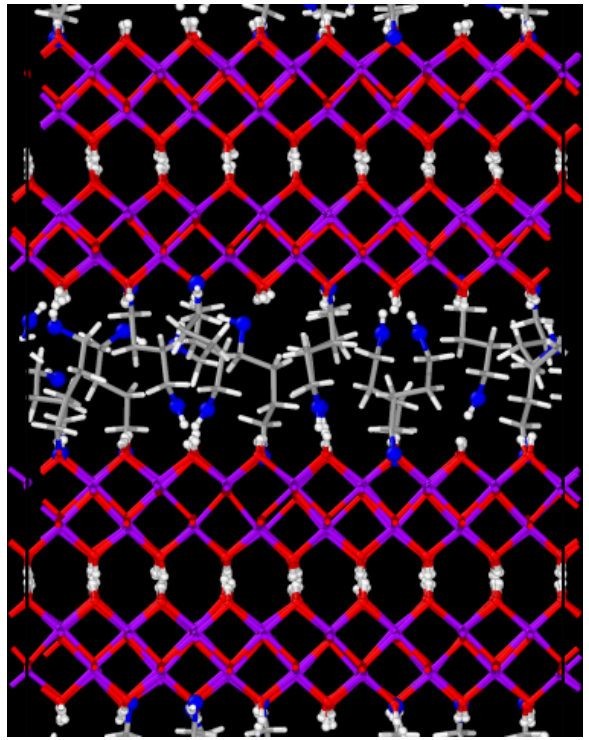


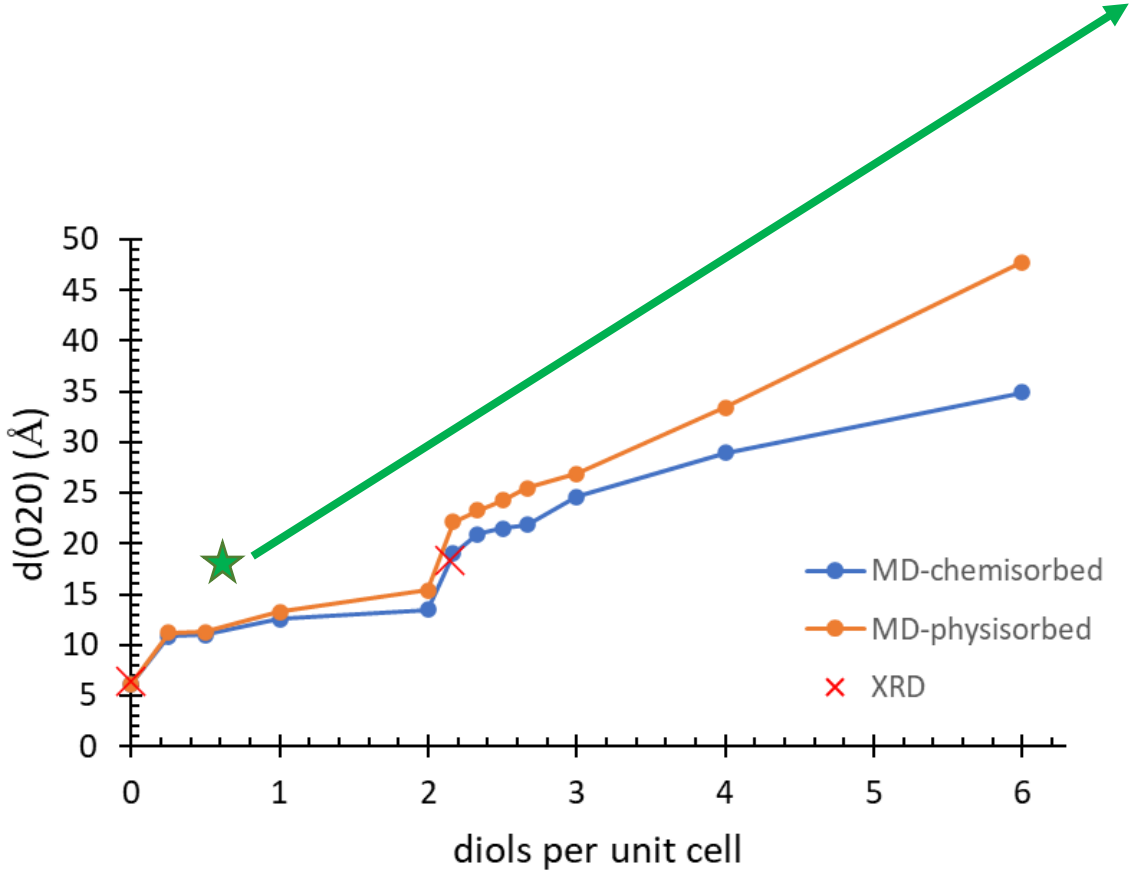
2.2 diol/uc
3rd layer forming



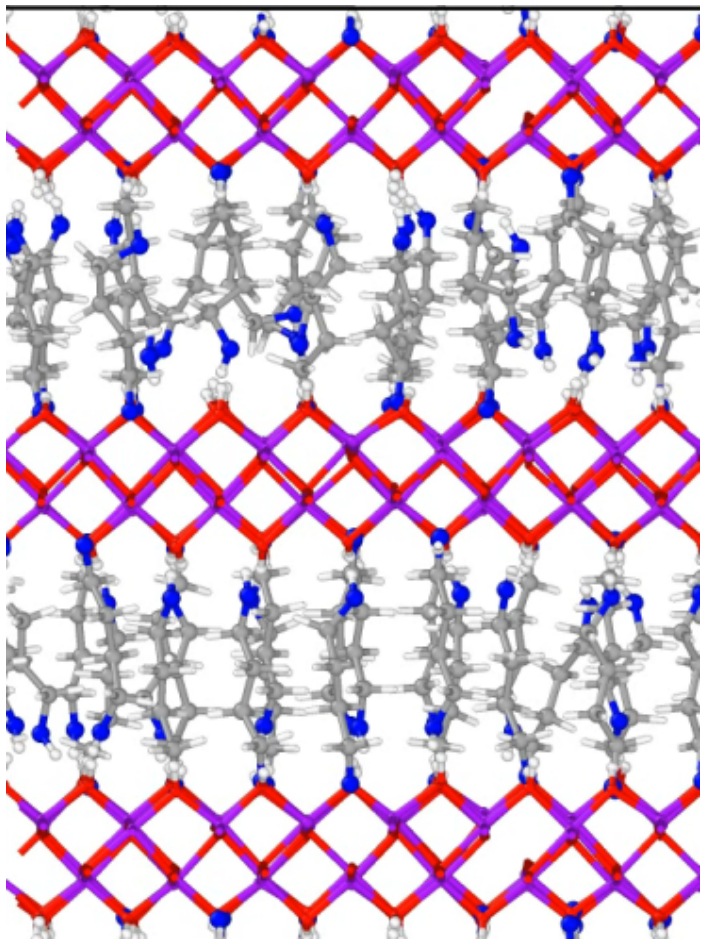
Two Possible Structures for GB

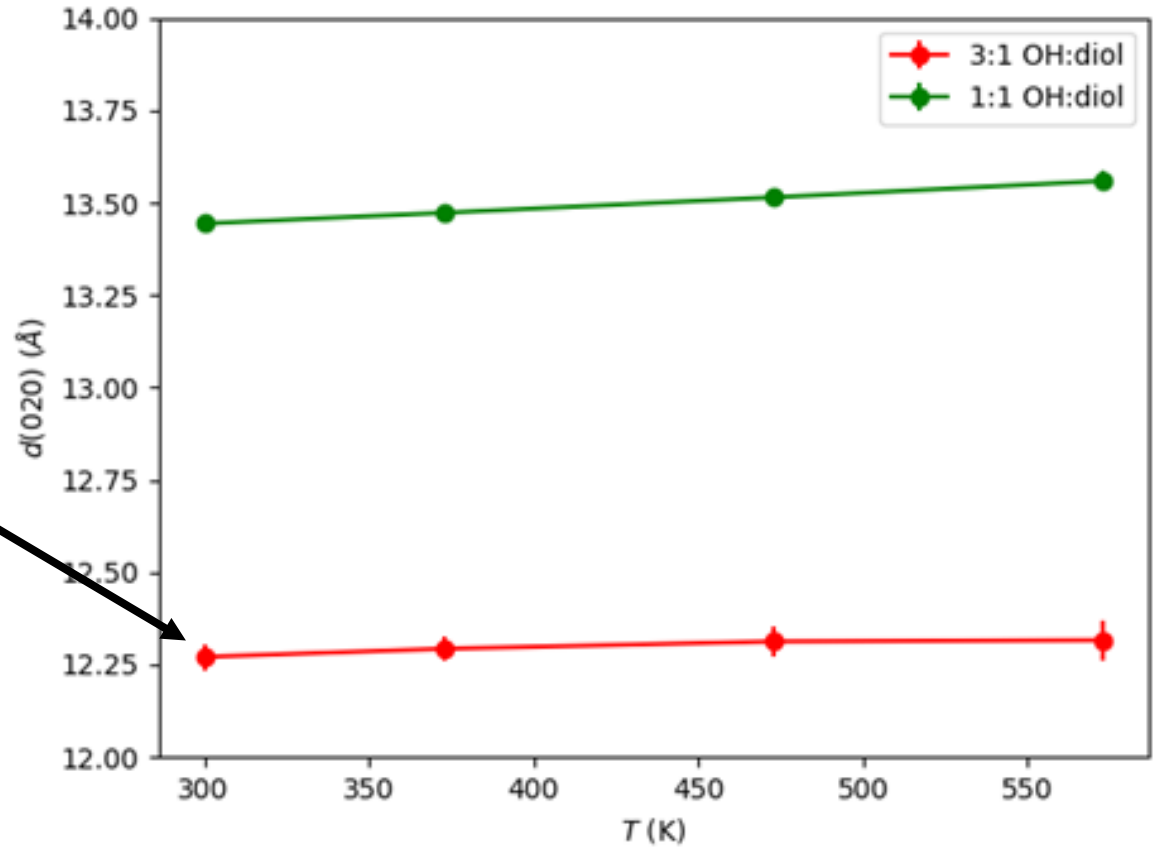
"Secondary Structure": 2:1 boehmite/diol layers
Synthesis at low water content
d(020) = 17.9 Å (MD)
18.4 Å (XRD)
Inoue et al, Chem. Mater. 9 (1997), 1614





Thermally Stable Structures

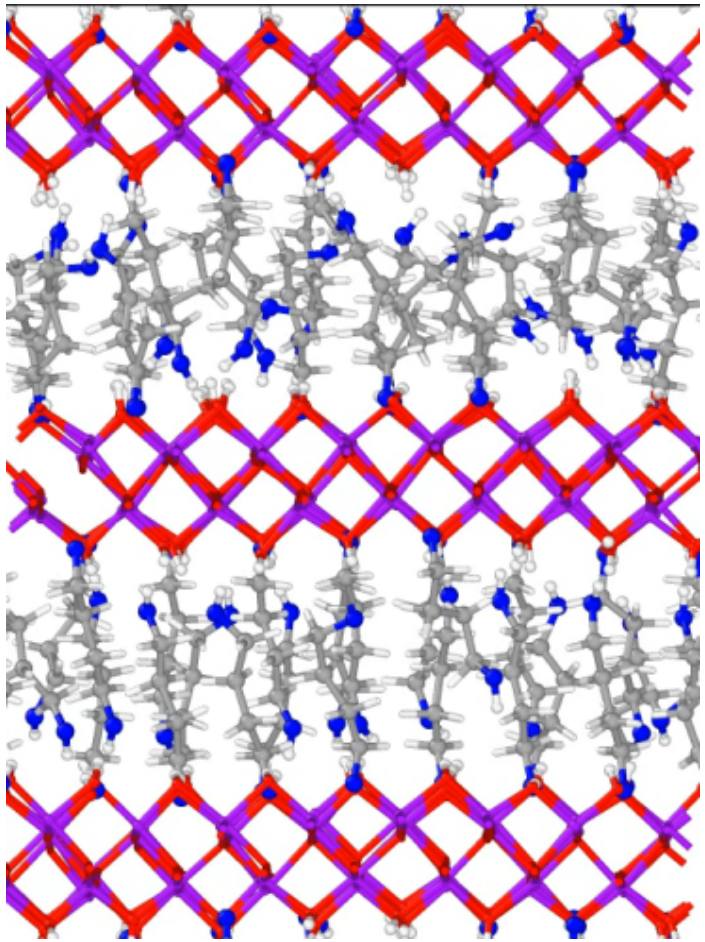


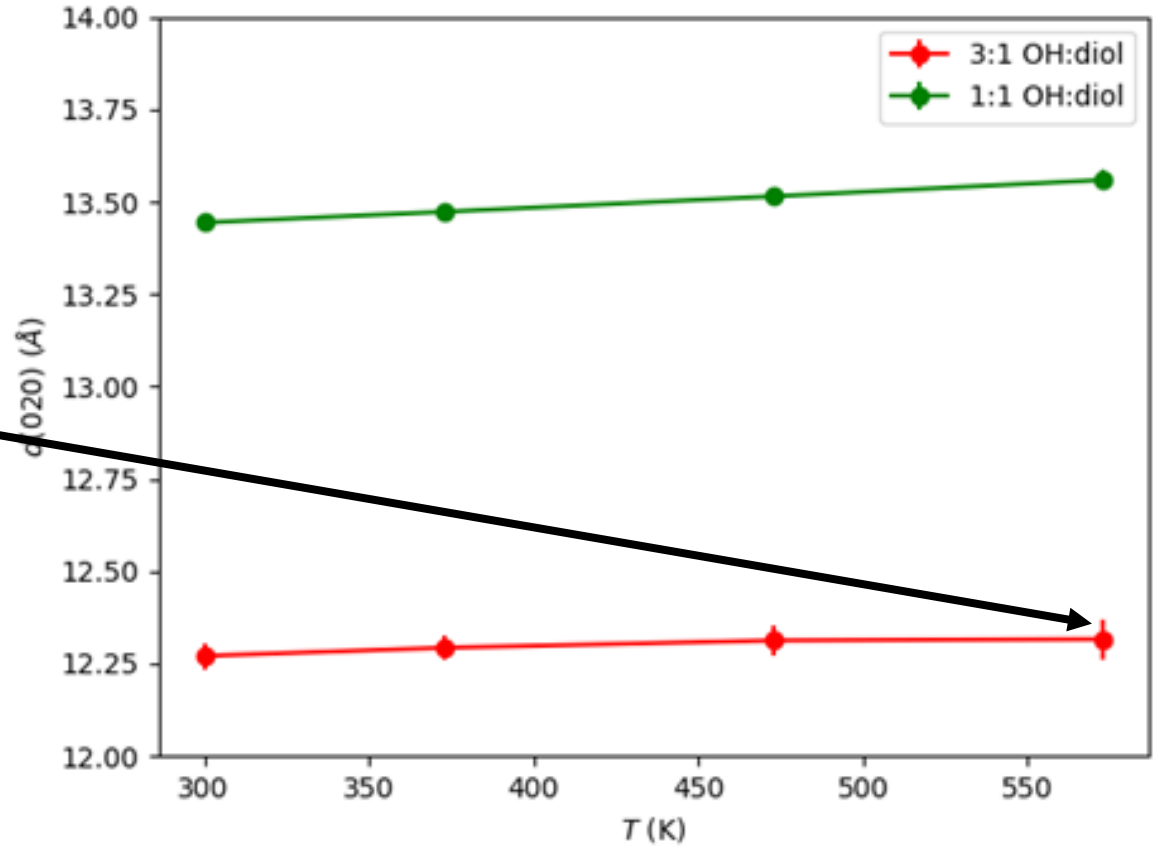


low diol loading (3:1 OH:diol)

300 K

Thermally Stable Structures



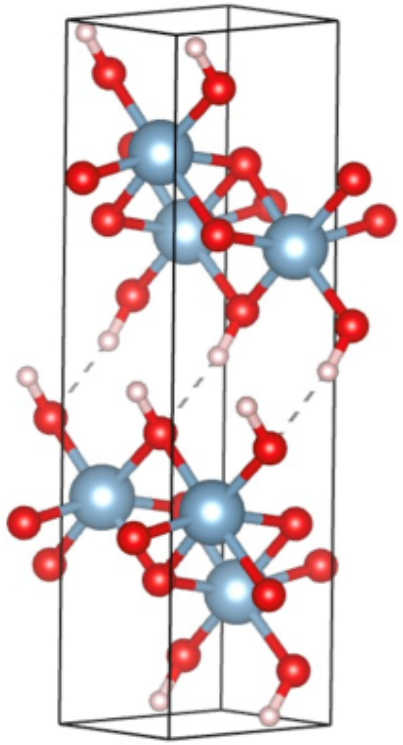


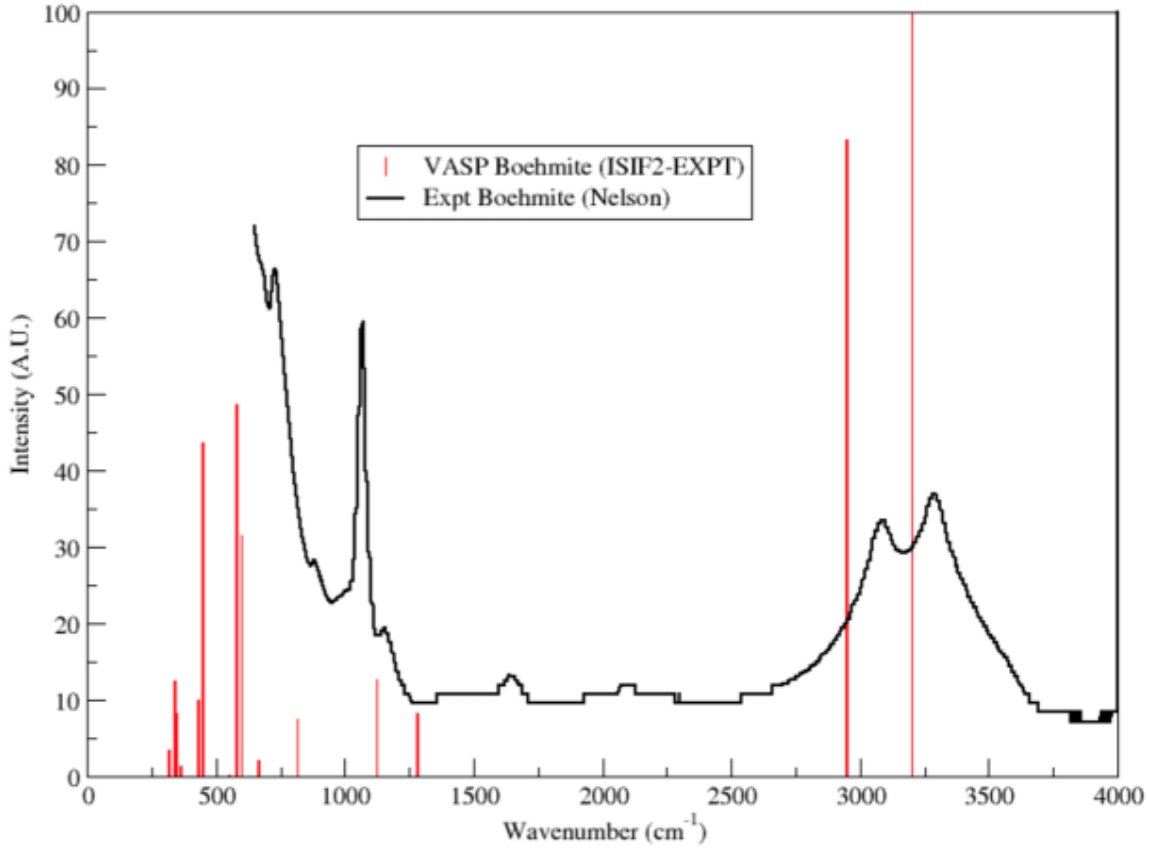
low diol loading (3:1 OH:diol)

573 K (300 °C)

IR Spectra from DFT: Boehmite

- Boehmite and glycoboehmite crystal structures were relaxed using density functional theory (DFT) with the Vienna Ab Initio Simulation Package (VASP).
- PBE parameterization with projector augmented wave (PAW) pseudopotential.
- 2 × 1 ×1 supercell
- Vibrational frequencies were obtained from density functional perturbation theory (DFPT) calculations.

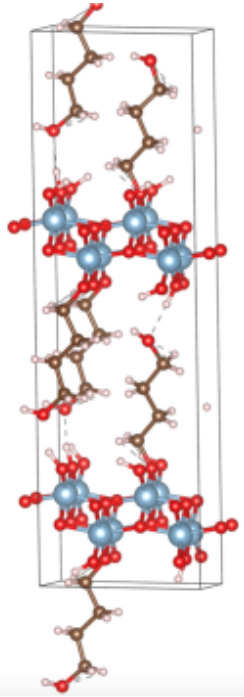


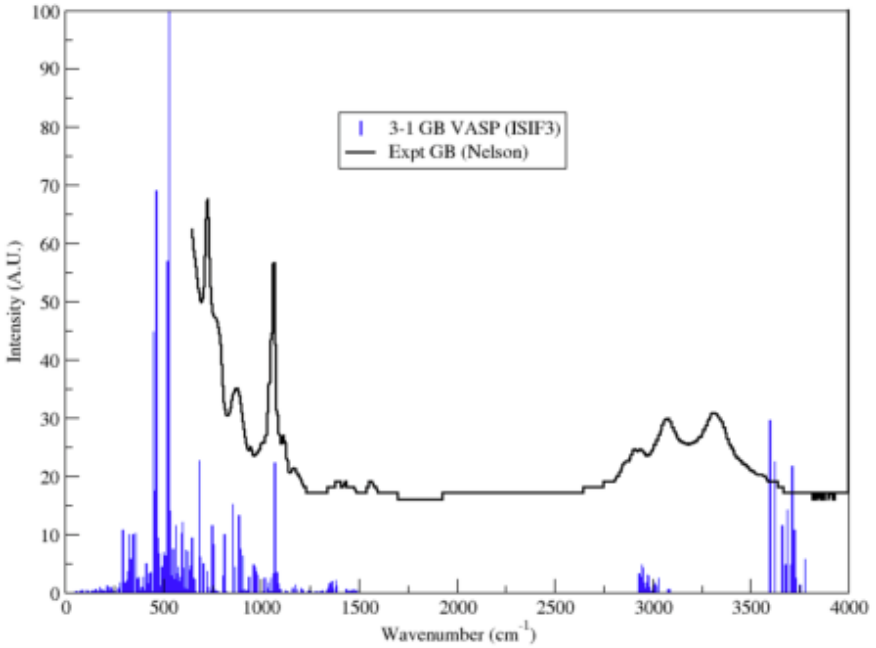


Slight shift in some frequencies, but otherwise good agreement with experimental spectra.

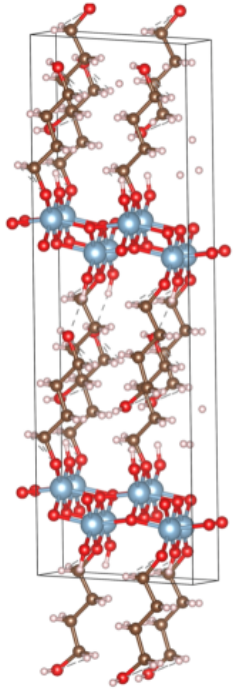
IR Spectra from DFT: Glycoboehmite (GB)

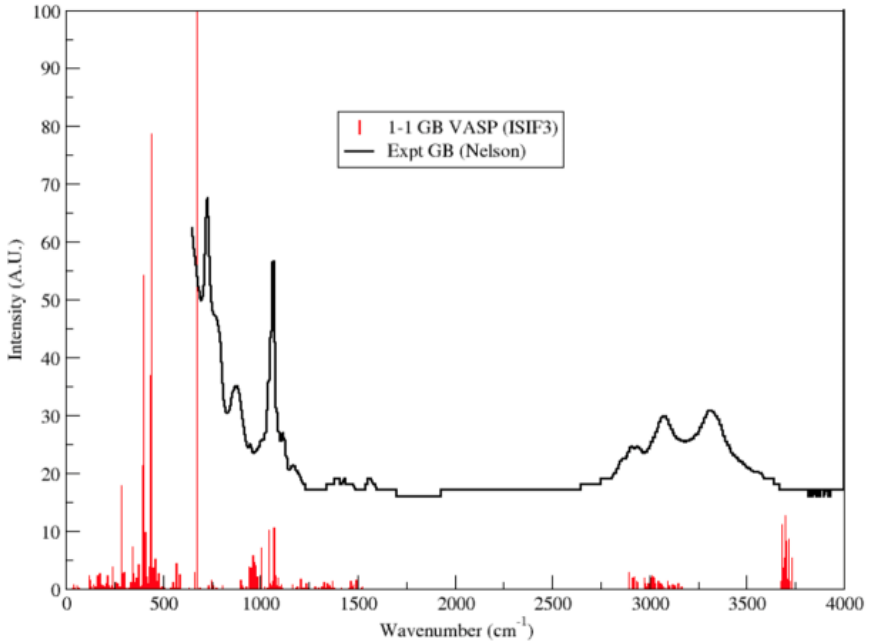
Low diol content





High diol content

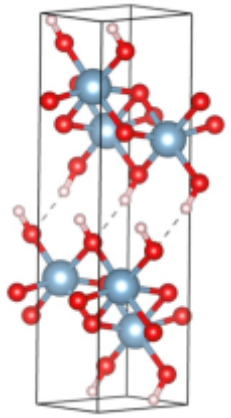




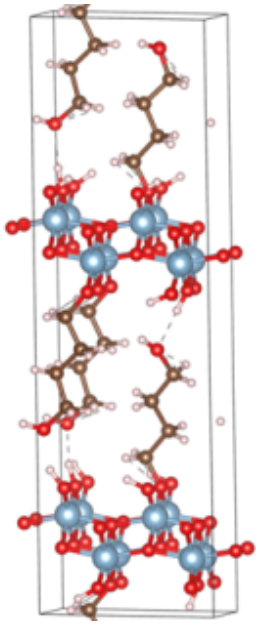
Little or no O-H stretch frequencies (> 3500 cm^{-1}) in the experimental spectrum.
Additional reaction of diols in the interlayer.

IR Spectra from DFT: 1st and 2nd Stage GB Structures

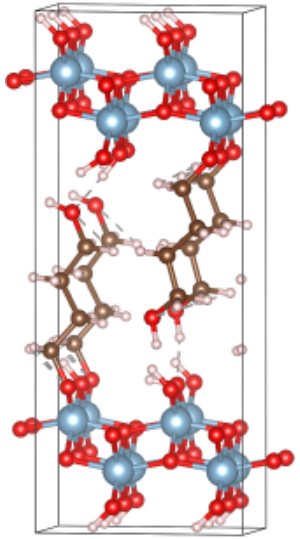
bulk

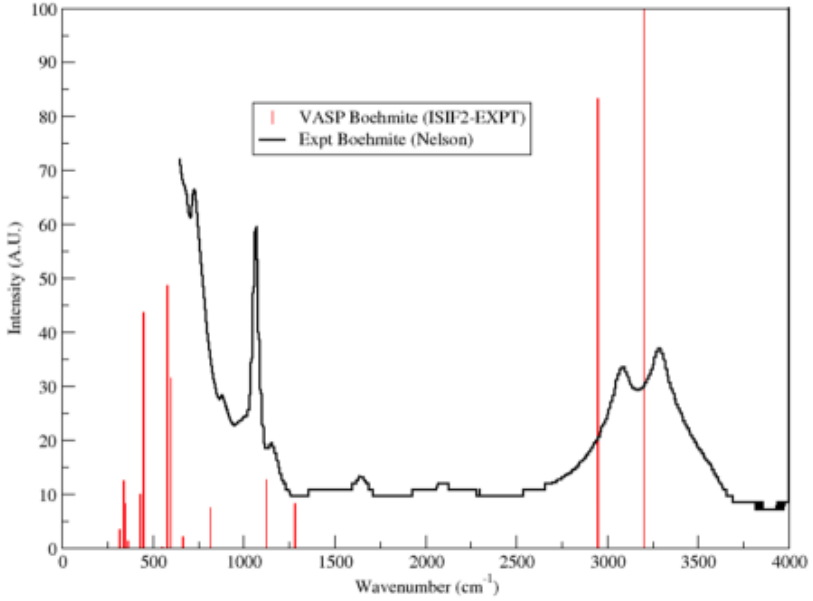


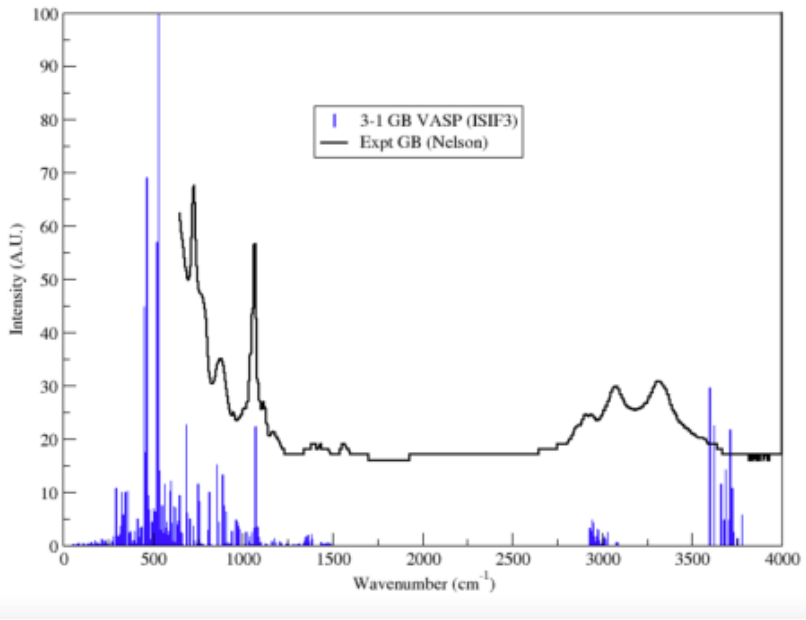
1st Stage GB
1:1 AlOOH:diol

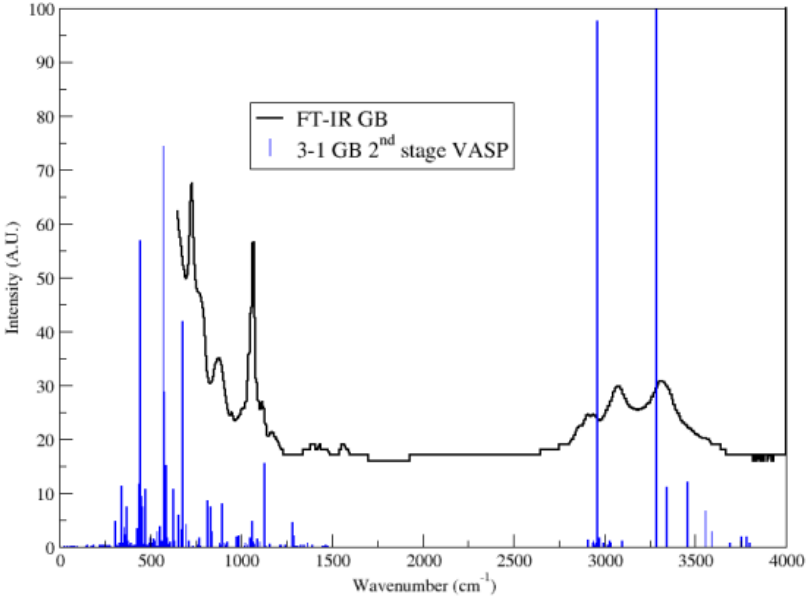


2nd Stage GB
2:1 AlOOH:diol









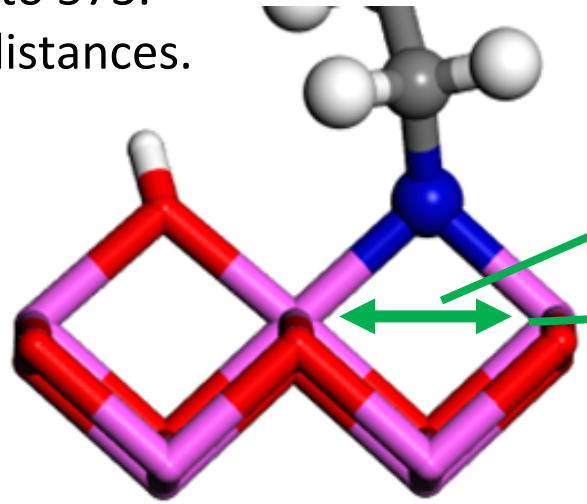
Local Coordination from MD Simulations

ab initio molecular dynamics (AIMD)

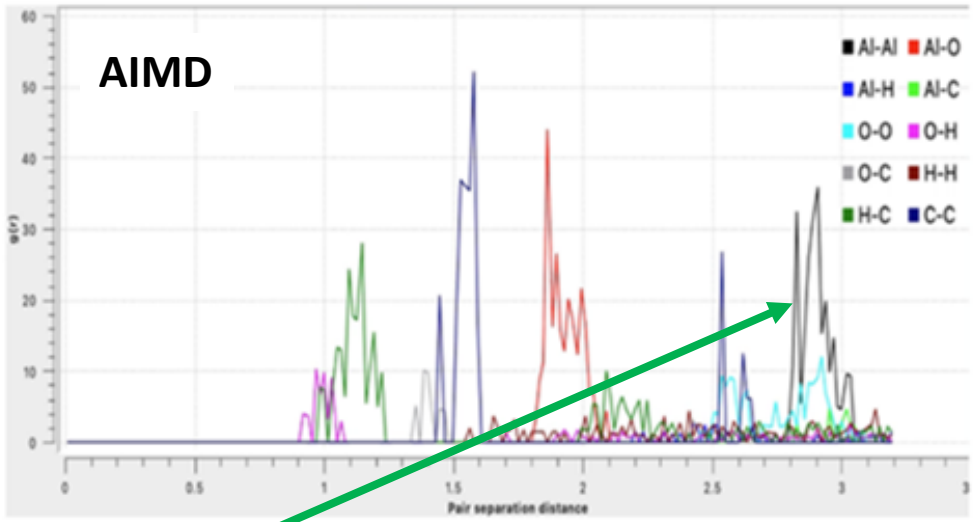
- VASP code.
- Constant volume (NVT), 300 – 573 K.
- 20 ps simulation time.
- Chemisorbed models (GB) at low and high diol loading.

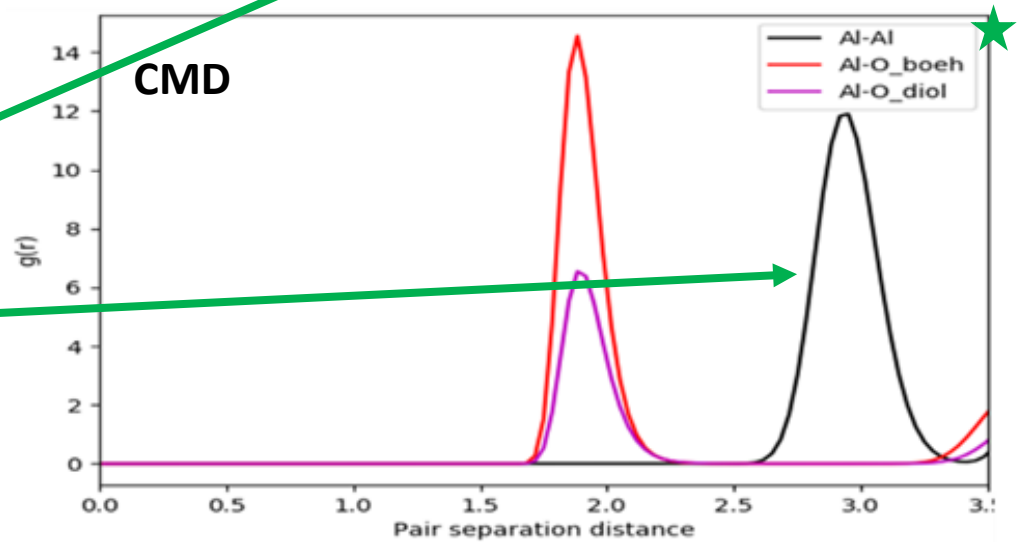
Consistency between AIMD and CMD

- No diol decomposition or OH/CH bond dissociation up to 573.
- Al-Al and Al-O distances.



Radial Distribution Functions





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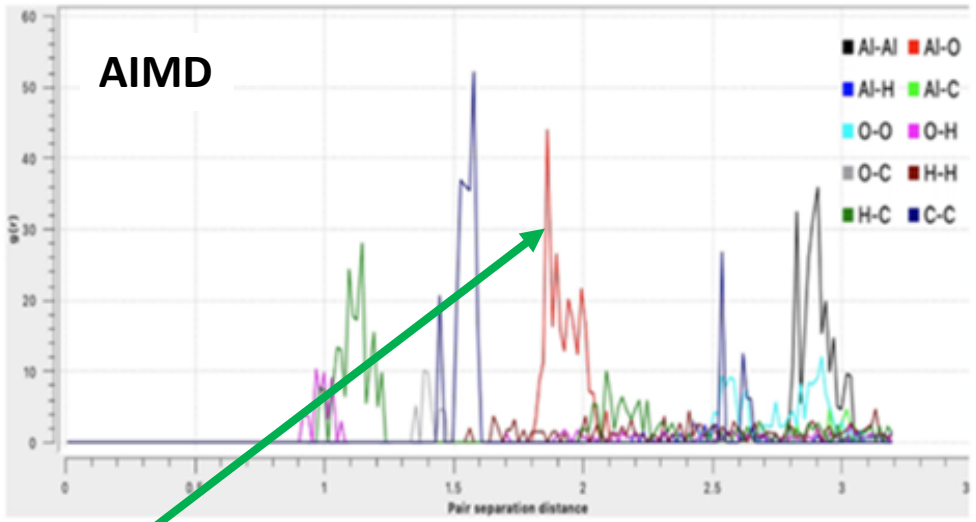

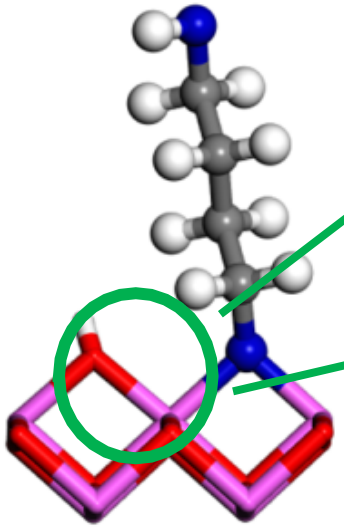

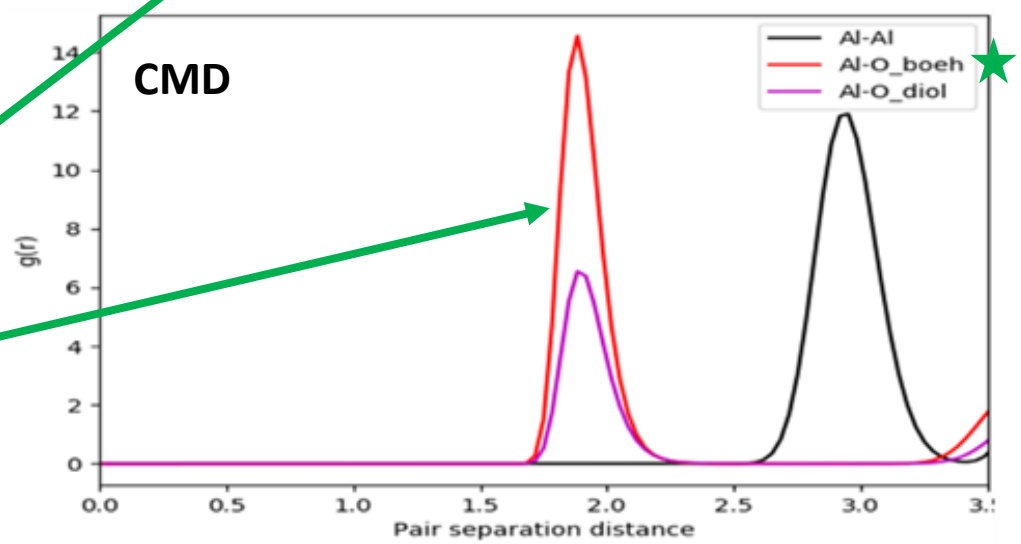

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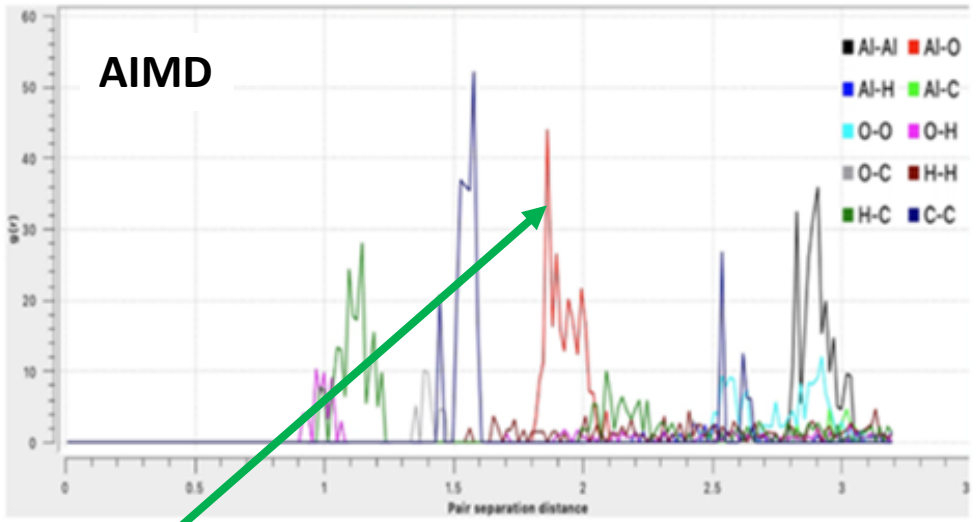
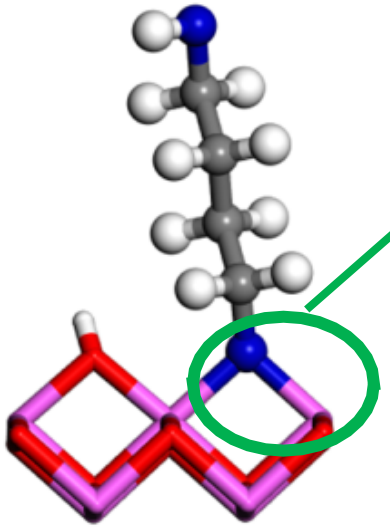
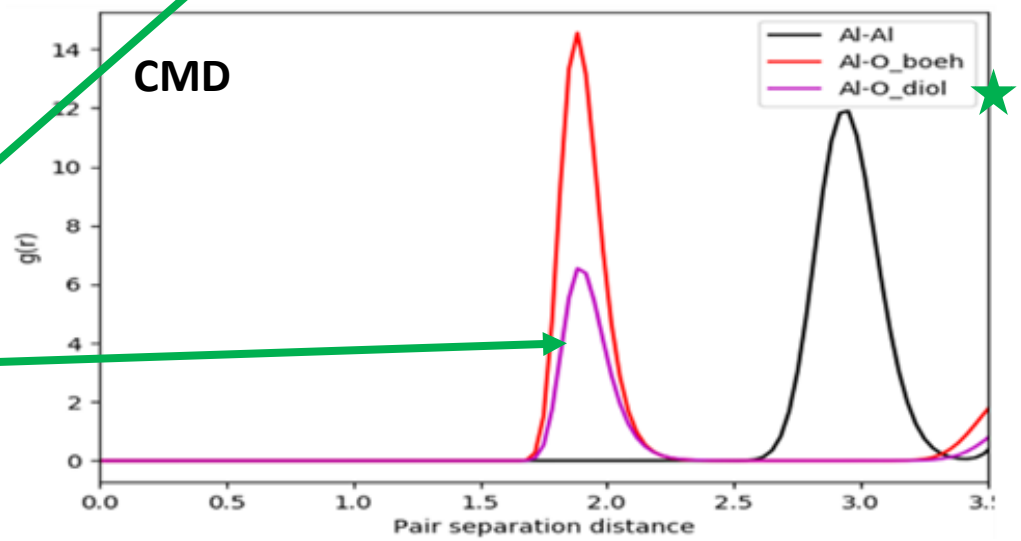
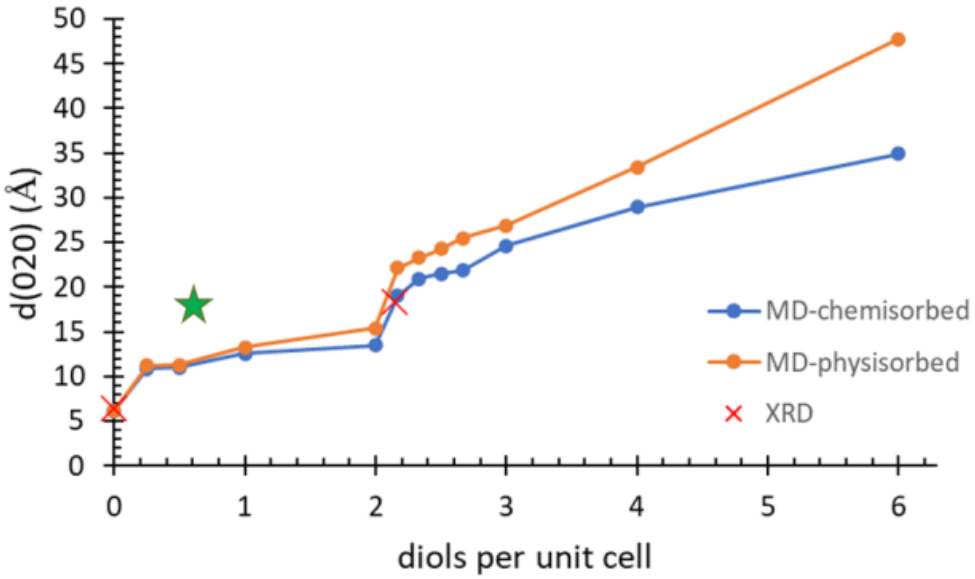


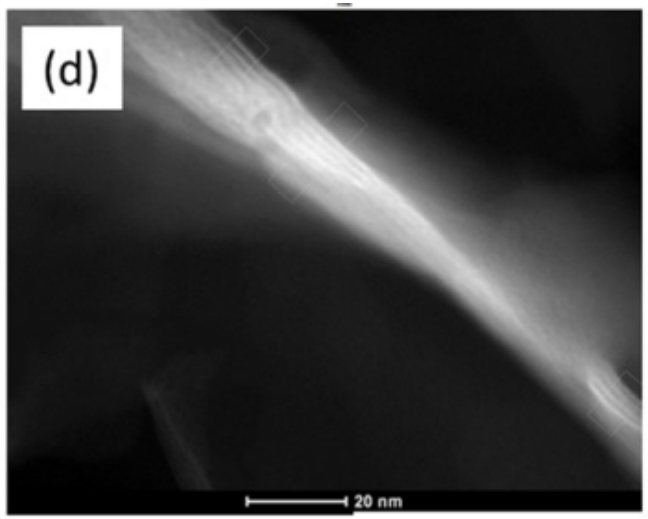




Summary

- Organically modified boehmite exhibits expanded interlayers and enhanced iodide adsorption capability.
- Molecular modeling of structural and spectroscopic properties are good in agreement with experiment.
- Simulated structures are thermally stable up to 300 °C.
- Simulations indicate a stepwise interlayer expansion as organic loading increases, for both chemisorbed and physisorbed diol models.





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Material synthesis and characterization
Nelson Bell
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Mark Rodriguez
Bernadette Hernandez-Sanchez
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Paul Kotula