

Abstract

One of the major goals of Science Driver 2, Focus 3 of LA-SiGMA is to construct reactive force fields for studying Fischer-Tropsch reactions on metal oxide catalysts and force fields for energy storage applications. We report on preliminary calculations undertaken in Year 1 to begin the construction of metal oxide force fields. Three metal oxides, Al₂O₃, FeO, and Fe₂O₃ are being studied at present. The current objective is to identify and develop confidence in computational protocols that can be used both for force field construction of the oxides mentioned above, and also be adapted to the development of force fields for other metal oxides of interest in the future.

Introduction

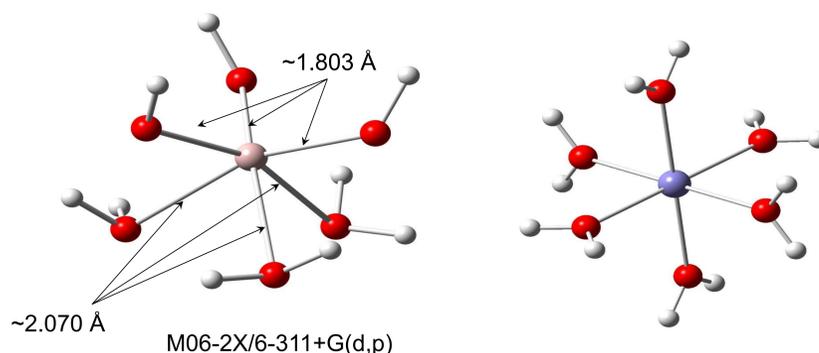
Fischer-Tropsch reactions convert low molecular weight components of natural gas, or biomass into useable petroleum-like liquid hydrocarbons. Catalysts based on oxides of transition metals such as Fe, Co, and Ni play a major role in these reactions. In addition to being a catalyst, alumina is also one of the most common catalytic supports. To understand the catalytic process for these materials, and specifically for the case of alumina, how it behaves as a support, requires their simulation at multiple time and length scales. The most catalytically active sites are often material defects, in which their structures are not well understood or predictable. Due to the fact that *ab initio* calculations investigate only a few atoms over a relatively short period of time, the likelihood of observing these defects is vanishingly small. Because of this, larger scale simulations (10,000s of atoms) that can run over much longer timescales (100s of nanoseconds) would be of significant benefit for the investigation of catalysis. These simulations can be used to efficiently identify potential defect sites, which can be further investigated via more expensive *ab initio* calculations, building a truly multiscale approach to the computational investigation of catalysis.

Context

For alumina, many force fields have already been developed,¹⁻⁶ some of which are quite complicated. However, these have been developed to reproduce the bulk solid structure of alumina, and are mostly based on pair-wise interactions of Al with O. Very few force fields exist for iron oxides, and these have been parameterized to reproduce small iron oxide structures^{7,8} for Fe(III) compounds. We are developing a new strategy to develop oxide force fields that rely on reproducing small cluster structures utilizing new state of the art density functional theory (DFT) functional, and we will also accurately describe different solid phases, and physical interactions with molecules at the surface of these. Furthermore, bonded interactions, such as bond stretching interactions between adjacent atoms and bond bending between three atoms in the solid structure, will be used.

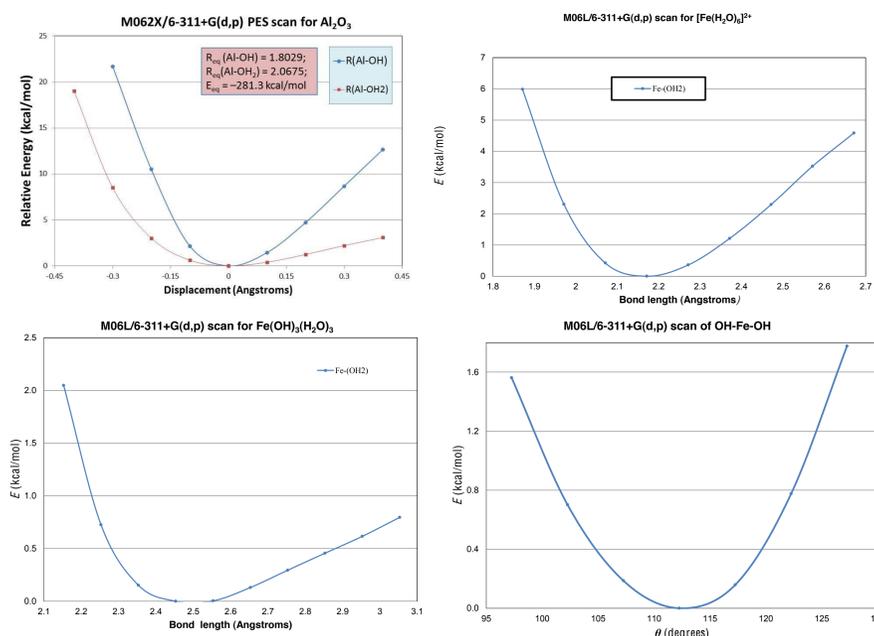
Calculations

Crystal structures of Al₂O₃ and Fe₂O₃ show that the metal atoms are in a distorted octahedral environment of 6 oxygen atoms. The bond lengths and bond angles around the metal atoms fall into two groups. To reproduce this through DFT calculations, we used M(OH)₃(H₂O)₃, M = Al, Fe as models. FeO is a face-centered cube in which the Fe atom is in a perfect octahedral environment of 6 oxygen atoms. [Fe(H₂O)₆]²⁺ was found to reproduce this fairly well.



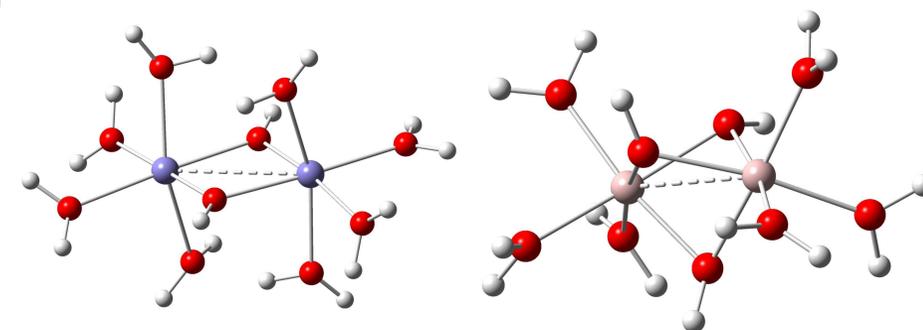
Relaxed PES scans

Relaxed PES scans of the bond lengths and bond angles were done to obtain the force constants for the bonded interactions. The graphs below show the behavior obtained by DFT calculations for structures of the type shown above.



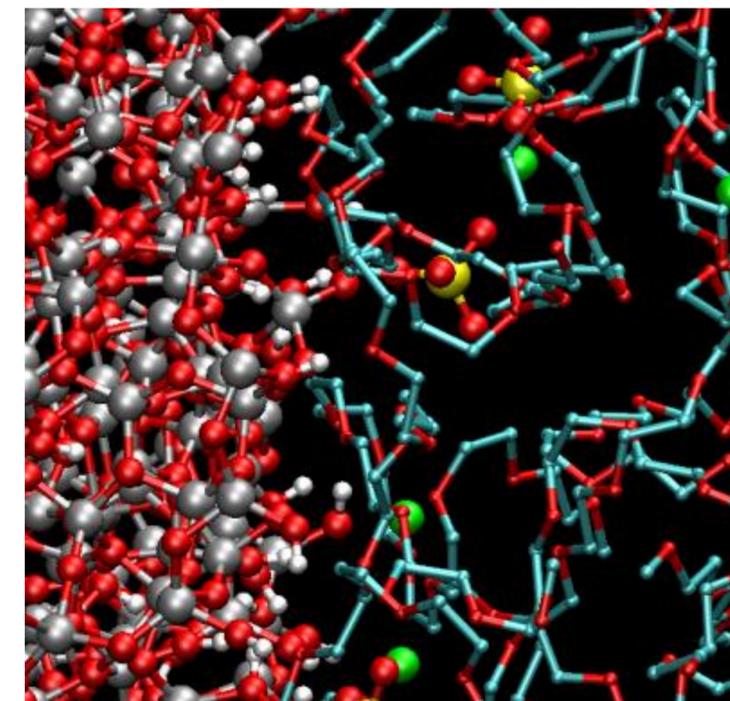
Calculations in Progress

Nonbonded metal-metal interactions are being studied using the dimeric structures [M₂(OH)₃(H₂O)₆]³⁺, M = Al, Fe and [Fe₂(OH)₂(H₂O)₆]²⁺ as shown below. Relaxed potential energy scans will be performed on the equilibrium structures by changing the metal-metal distance indicated by the dashed line.



Alumina in Lithium Ion Batteries

We also parameterized intermolecular interactions for alumina with lithium ions and ether groups. Alumina serves as potential fillers for rechargeable lithium battery polymer electrolytes that promote greater lithium ion mobility and greater electrolyte stability and safety.



Acknowledgements

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