

Computational Chemistry Illuminates Atomistic Processes at Complex Interfaces

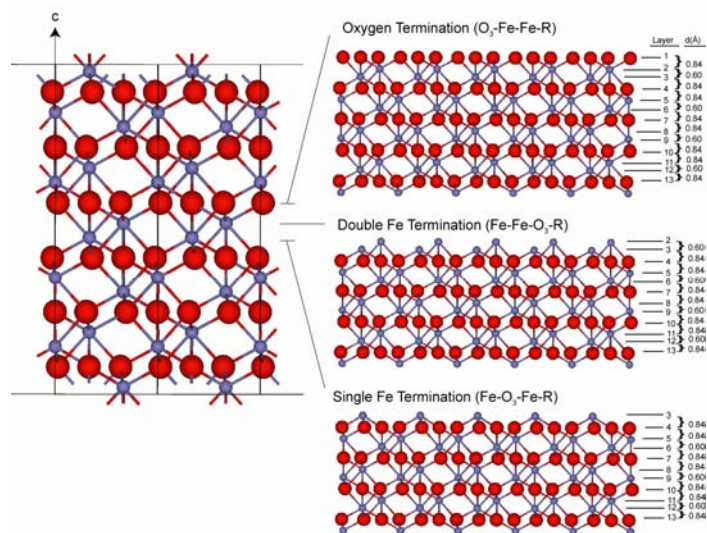
A.M. Chaka (838)

The chemistry of interfaces is of fundamental importance for a wide variety of environmental, industrial, and biological processes such as migration of pollutants in groundwater, catalysis, microelectronics, corrosion, and sensors. Progress in understanding these processes has been limited because the traditional techniques of surface science require ultrahigh vacuum (UHV) and clean, ideal crystalline surfaces, which may have little resemblance to real surfaces in complex environments. Recent advances in experimental surface science, however, have made it possible to conduct experiments on surfaces exposed to high concentrations of chemical species. These new instrument capabilities have revealed dramatic changes in surface chemistry upon exposure to high concentrations of reactants, as indicated by surface structural relaxations and Scanning Tunneling Microscope currents (which measure electronic energy levels), but are incapable of identifying the chemical structures or processes responsible.

NIST partners with key experimental groups to illuminate the chemistry occurring at complex metal oxide surfaces and to extend and validate the theoretical methods developed to predict and understand the surface chemistry for “real” systems.

The situation in quantum theory for surfaces was similar to that in experimental, for example, electronic structure calculation by Density Functional Theory (DFT) is well established for calculating surface structure and energy only at 0 K under vacuum. We have collaborated in the development of new theoretical methods to extend DFT quantum mechanics to capture the thermodynamics and structure of real surfaces in equilibrium with multiple species in the environment at finite temperatures and pressures.

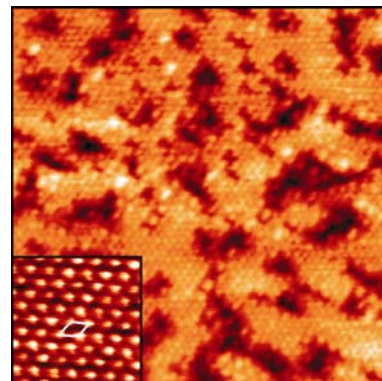
The hematite (0001) surface, $\alpha\text{-Fe}_2\text{O}_3$, is important for many reasons. It is the catalytic surface used commercially to convert ethyl benzene to styrene, the most prevalent mineral surface exposed to ground and surface water, and is a model surface to study corrosion for ferrous-based metals. The first high-oxygen-pressure STM work on the hematite (0001) surface indicated the presence of two distinct chemical domains. These were first interpreted as distinct iron- and oxygen-terminated regions with the $\text{Fe-O}_3\text{-Fe-R}$ and $\text{O}_3\text{-Fe-Fe-R}$ structures, indicated by cleavage planes shown in the figure.



$\alpha\text{-Fe}_2\text{O}_3$ bulk unit cell and surface models for the three possible “clean” terminations that can result from cleavage. Large spheres are O and small spheres are Fe. The surface models are annotated with the labeling scheme used to identify the various atomic layers and the layer spacings for ideal (unrelaxed) atomic positions.

More recent experimental work and our theoretical surface energy calculations indicated that the lowest energy surface that would be formed under the experimental conditions was not the O₃-structure but was a O=Fe (ferryl) structure that resulted from dissociation of oxygen on the Fe-terminated surface.

High resolution STM image of the α -Fe₂O₃ (0001) film prepared at the FHI in 10 Pa (10⁻² mbar) of O₂ at 1020 K (size 30 x 30 nm², Vt = 1.4 V, I = 1 nA) showing the multiple domains of iron- and oxygen-termination. The lattice of protrusions with approximately 5 Å periodicity is clearly seen in the inset (size 3 nm² x 3 nm²). The unit cell is indicated.



The predicted threshold pressure and temperature for the formation of Fe=O was in quantitative agreement with experiment, further validating the first-principles methods used in the model. Theoretical calculations also obtained a Fe=O vibrational stretching frequency of 981 cm⁻¹ in excellent agreement with the 989 cm⁻¹ band observed by infrared reflection absorption spectroscopy (IRAS). The power of computational chemistry has provided great insight and discovery in surface chemistry that had not been previously observed on an iron oxide surface, and a manuscript describing this work has been submitted to *Physical Review Letters*.

In another example of the value of our methodology for calculating surface chemistry, we addressed the reactivity of water at surfaces. Recently, scientists at Stanford University, University of Chicago, Lawrence Berkeley National Lab, and University of Alaska Fairbanks, made the puzzling observation that hematite is much more reactive towards trace amounts of water than the isostructural α -Al₂O₃ (corundum, sapphire), yet is more stable to weathering in nature. Washing the cleaved native hematite mineral surface with dilute acid and immersing it in water resulted in formation of two distinct (one dominant and one minor) domains of unknown chemical structure but with significantly different surface structure relaxations.

To identify these structures and understand the differences in reactivity between iron and aluminum oxide, over thirty model surface structures were examined that might result from water physisorption and dissociation by both heterolytic and homolytic mechanisms. The surface energy phase diagrams for α -Fe₂O₃ and α -Al₂O₃ (0001) indicated that the reaction of iron atoms on the surface to form a fully hydroxylated (HO)₃Fe-O₃-R structure occurs at a water vapor pressure threshold many orders of magnitude lower than for aluminum, consistent with experimental observations. Calculations on the model systems also indicated that this hydroxylated surface iron atom can be readily hydrolyzed and solvated when exposed to an aqueous environment. The underlying oxygen layer becomes hydroxylated in this process to form a very stable structure that is resistant to subsequent hydrolysis. The relaxations calculated for this stable hydroxylated oxygen layer were consistent with the dominant domain observed in the experiments. The minor domain is consistent with residual hydroxylated surface iron atoms.

T.P. Trainor, A.M. Chaka, P.J. Eng, M. Newville, G.A. Waychunas, J.G. Catalano, G. E. Brown, Jr, "Structure and Reactivity of the Hydrated Hematite (0001) Surface," *Surface Science*, 573, (2004).

Hence with the integration of experiment and theory we have successfully identified the surface chemistry that characterizes the fundamental interactions of iron and aluminum oxides with oxygen and water, two of the most prevalent and reactive species in the environment. This knowledge of surface structure and reactivity provides a foundation for subsequent investigations into the molecular mechanisms of catalysis, corrosion, and adsorption and transformation of pollutants in groundwater.