Adsorption of Selenium Oxo-anions on [012] Alumina and Hematite Surfaces and Its Dependence on Configuration and Protonation

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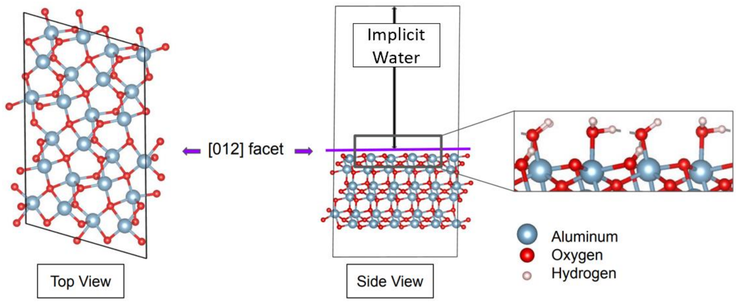
Research Motivation and Background

Selenium oxo-anions are toxic substances present in drinking water. These can be removed by using Hematite and Alumina as the adsorbent materials. The adsorption capacity depends on many factors including configurations of oxo-anions, pH (degrees of protonation), and the adsorbent materials. Alumina and Hematite have the same crystal structure, allowing to probe composition dependent effects. The goal of this research is using first principle calculations to understand these factors, which are important in designing selective models that can improve water resources efficiently using less energy and low cost.

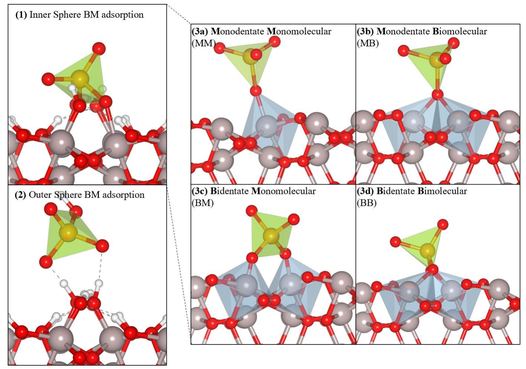
Methods

Perform Density Functional Theory using VASP



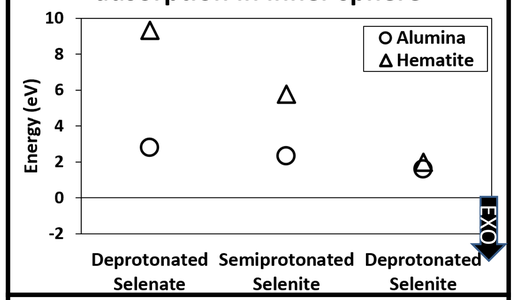
$$Al_2O_3.12OH^-.12H^+ + H_xSeO_4^{2-x} + (2-x)H_3O^+ \rightarrow Al_2O_3.(12-y)OH^-.12H^+.H_xSeO_4^{2-x} + (2-x)H_3O^+ + yOH^-$$

Adsorption of Selenate and Selenite on Alumina and Hematite at Above Point of Zero Charge (PZC)

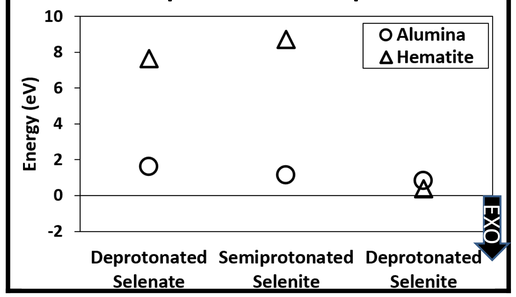


- Oxo-anions are adsorbed in monomolecular complexes or outer sphere complexes

Bidentate monomolecular (BM) adsorption in inner sphere

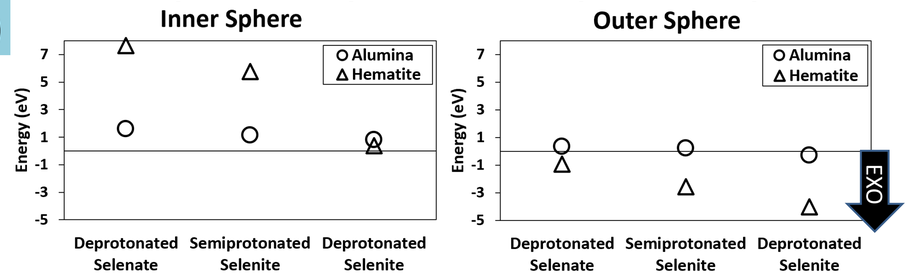


Monodentate monomolecular (MM) adsorption in inner sphere



- Adsorption energies are endothermic in inner sphere configuration
- Deprotonated selenite is more strongly adsorbed in inner sphere configuration
- BM is highly unlikely due to high adsorption energy
- Alumina performs better than Hematite in inner sphere configuration

Outer sphere adsorption vs. Inner sphere adsorption



- Oxo anions are preferentially adsorbed in outer sphere configuration on both Alumina and Hematite at above PZC
- Hematite is better adsorbent than Alumina at above PZC for Selenium oxo-anions
- Both Alumina and Hematite selectively adsorb deprotonated selenite as compared to deprotonated selenate and semiprotonated selenite
- Both Selenium oxo-anions are adsorbed in outer sphere over Alumina and Hematite (012) facet at above PZC

Conclusions

- Both Alumina and Hematite [012] surfaces are more selective towards deprotonated selenite adsorption
- Monodentate configuration is more probable than bidentate configuration
- Hematite performs better than Alumina in outer sphere configuration
- Outer sphere adsorption is more exothermic than inner sphere adsorption
- Outer sphere is the most probable configuration for oxo-anions observed at high pH

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