

The Complex Role of Ion Interactions in the Interfacial Reactivity of Gibbsite

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Many predictive models of geochemical processes (e.g., fate and transport of metals) and industrial utilization of minerals, rely upon a detailed understanding of mineral dissolution that is highly influenced by solution pH and interfacial sorbates. Atomistic details are rarely known due to this complex mineral/fluid interfacial environment. An excellent example is the dissolution behavior of gibbsite, a primary source of Al in soils and in ores for the industrial processing of Al metal. Building upon our recent work using classical molecular dynamics to study sorption behavior and speciation of ions from 0.5–10 M NaOH,¹ we now consider

ab initio molecular dynamics simulations with enhanced sampling to explore the detailed process of the detachment of an aluminate monomer to the solution. A realistic surface model is employed that considers two main types of step edges bounding pits on the basal surface in conjunction with changes to solution composition that mimic pH effects. The results indicate two potential pathways for detachment that are differentiated based upon the extent of water hydration at the detaching Al site. The energy profiles of the elementary bond-breaking events indicate the scission of the first or the second hydroxo bridge is the rate-limiting step for the monomer dissociation. The heights of the energy barriers depend upon the local morphology which influence the number of bridges (quasi-)simultaneously broken (1 or 2) or the Al-O coordination of the neighboring aluminum atoms (5 or 6) at the armchair edge. The findings help provide a molecular-level basis for predicting gibbsite dissolution kinetics observable at the mesoscale.

- Liu, W.; Pouvreau, M.; Stack, A.; X.; Clark, A. E. Concentration Dependent Interfacial Chemistry of the NaOH(aq):Gibbsite Interface. *Physical Chemistry Chemical Physics*, **2022**, *24*, 20998 – 21008, DOI: 10.1039/D2CP01997C