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Computational determination of pKa values of surface sites on periclase (MgO) in water

SAI K R ADAPA, KE YUAN, JULIANE WEBER, STEPHAN IRLE, LAWRENCE M ANOVITZ AND ANDREW G. STACK

Oak Ridge National Laboratory

Presenting Author: sr4@ornl.gov

Periclase (MgO) are of great interest because their potential utilizations in direct air capture of CO_2 by formation of carbonate minerals. Periclase (MgO) transforms into brucite ($Mg(OH)_2$) when exposed in humid air. It is challenging to capture the atomic scale surface hydration and transformation mechanism using experimental techniques. In this work, we investigated MgO (both (001) and (110))-water interface using the density-functional tight-binding (DFTB) method in conjunction with the 3obw water parameterization. Dftb method enables the reactions like ab initio molecular dynamics (AIMD) and is order of magnitude faster with same accuracy. We observe that protons (H^+) from dissociated water molecules hydroxylated ~25%-66% of the MgO surfaces. A significantly ordered water layer (L1) formed on both the MgO (001) and (110) faces, where the (110) face has 66% O site been hydroxylated comparing to 25% protonation on the (001) surface. Water molecules in the L1 layers of (110) interface are exclusively hydrating the surface Mg-ions however at (001) interface some the water molecules are in direct association with surface. We further simulated the deprotonation reaction of aqueous Mg-ion and applied metadynamics with the multi-walker technique to calculate pKa value and compared that with experimental results. We extended the pKa calculations to MgO (001) - water interface and compared the results with aqueous Mg^{2+} system. Our results are consistent with the concept that transformation of periclase to brucite is facile, as assumed in the direct air capture (and other) literature.