

Comparison of TiO₂ and SnO₂ (100) and (110) hydrated surfaces via molecular modeling

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Periodic density functional theory (DFT) calculations using the programs CASTEP and VASP were carried out to model the H₂O-TiO₂ and the H₂O-SnO₂ (100) and (110) interfaces. These two minerals have the same crystal structures but different unit cell dimensions and dielectric constants. Comparisons of the behavior of H₂O at each surface can be used to test the effects of these two parameters on H₂O dissociation and interfacial structure. Energy minimization and molecular dynamics (MD) simulations were conducted with periodic DFT methods to examine the relative energetic stability of a variety of configurations. In order to more completely sample configuration space, interatomic force fields were developed for the H₂O-TiO₂ and H₂O-SnO₂ interfaces using the program GULP. Thus, classical MD simulations could be carried out over longer time periods than practical with the DFT method. The force field reproduces structures calculated with DFT reasonably well and the relative energies of configurations are similar between the two methods. In addition, the effects of deprotonating the surfaces to mimic the negative surface charge on real surfaces are examined. Differences in H₂O adsorption mechanisms are attributable to unit cell parameters and basicities of surface oxygen atoms. Starting with the associated H₂O molecules we have obtained the mixed associative-dissociated structure in the case of SnO₂. The most interesting observation is that dissociation of H₂O occurred indirectly. In the first stage, the H⁺ bonds to a bridging oxygen from one of nearest H₂O, forming the intermediate OH⁻ state. In the second stage, the terminal H₂O H⁺ transfers to the OH⁻ ion forming the new H₂O molecule and terminal OH⁻. No such process was observed for TiO₂ surface. A stable mixed adsorption structure was obtained by optimization after manual H⁺ transfer on the same path as was spontaneously passed in the case of SnO₂. Analogously, starting with the broken H₂O molecules in the first layer, we have obtained the stable dissociated structures both for TiO₂ and SnO₂ where hydroxyls were attached to 5-fold Me and H⁺ were bonded to the bridging oxygens.

Molecular Simulations User's Guide (1999) CASTEP –
Cambridge Serial Total Energy Package Version 4.2, San
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