

An Atomistic Description of the γ -Alumina/Water Interface Revealed by Ab Initio Molecular Dynamics

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We report ab initio molecular dynamics (AIMD) simulations of the (100) and (110) γ -Al₂O₃/water interfaces at 300 K, using two sets of supercell models for each surface and two time lengths of simulation (10 and 40 ps). We first show that the effect of liquid water on the vibrational frequencies of hydroxyl groups at the interface varies according to the type of surface.

This trend is explained by two key parameters affecting the interaction of both surfaces with water: the nature of the OH groups (i.e., μ_1 -OH, μ_1 -H₂O, μ_2 -OH, and μ_3 -OH) and H-bond network among surface OH groups. The hydroxylated (110) surface favors the local structuration of water at the interface and the solvation of its μ_1 -OH and μ_1 -H₂O groups by water similarly as in bulk liquid water. By contrast, on the (100) surface, a stronger H-bond network among μ_1 -OH and μ_1 -H₂O groups reduces the water/surface interaction. We illustrate also how the interfacial interacting sites are spatially organized on the surfaces by twodimensional maps of O-H distances. On both surfaces, the interfacial water layer orientation is predominantly H_{up}-H_{down}. For long AIMD simulation time, Grotthuss-like mechanisms are identified on the (110) surface.