

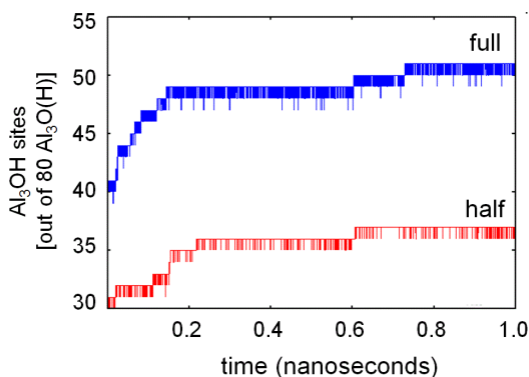
Water dissociation on two terminations of the Al_2O_3 R-plane surface with reactive force fields

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There are two proposed terminations of the R-plane of Al_2O_3 : one stoichiometric (or “full-layer”) termination and one non-stoichiometric (or “half-layer”) termination. The two proposed terminations have the same number of singly-coordinated $\text{AlOH}_{(2)}$ and triply-coordinated $\text{Al}_3\text{O}(\text{H})$ groups, but the arrangements of these groups are quite different on the two surfaces. In the half-layer termination, the Al_3OH sites sit directly underneath the $\text{AlOH}_{(2)}$ sites and are more deeply buried; in the full-layer termination, the Al_3OH sites are immediately adjacent to the $\text{AlOH}_{(2)}$ groups and participate in hydrogen bonding with solvating water molecules. Because of these structural differences, the extent of protonation of the $\text{Al}_3\text{O}(\text{H})$ sites (and therefore also the $\text{AlOH}_{(2)}$ sites) would be expected to differ on the two surfaces. A reactive force field, allowing for spontaneous surface hydrolysis reactions, was used to simulate the populations of functional groups in the two proposed terminations.

The calculations indicate that the proton affinities of the Al_3O groups on the half-layer surface are much lower than in the full-layer termination, as shown in the Figure.



This is not simply due to kinetics, as the populations can be reversed through titration with hydroxide ions. The calculations therefore indicate that “secondary” structure has a strong effect on the pK_a s of surface functional groups on oxide surfaces.