Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: pH Dependent Reactivity of Boehmite Surfaces From First Principles Molecular Dynamics

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Prior Experimental Results

Table S1: Prior experimental results of the point of zero change (PZC) of boehmite.

Authors	PZC
Kaledin et al[1]	9.5 ± 0.5
Kaledin et al[1]	11.4 ± 0.2
Parks[2]	7.7-9.4
Chivas-Joly[3]	10.0
Tanaka et al.[4]	8.7-9.2

Classical Molecular Dynamics Simulations

The classical molecular dynamics simulations were performed using the LAMMPS package. Initial equilibration was done using the *NPT* and then the *NVT* ensemble using the Nose-Hoover thermostat and barostat with a relaxation time of 0.1 ps with a time step of 1.0 fs. Each ensemble was ran for a minimum of 6 ns before starting the production run. The production run used the NVE ensemble with the same timestep as equilibration for a total of 15 ns, the atomic coordinates were captured every 200 fs. Three sets of atomic coordinates from the last 5 n of the production run were used as initial coordinates for the AIMD trajectory to ensure the model was not in a local minima on the potential energy surface.

edge	$\hat{x}$ (Å)	$\hat{y}$ (Å)	$\hat{z}$ (Å)	Waters
(100)	95.00	61.20	25.96	2835
(010)	23.01	127.15	29.67	1260
(001)	31.63	61.20	86.00	3150

Table S2: Size of boehmite supercell and corresponding waters at the interface within the classical molecular dynamics simulations.

Table S3: Force field parameters employed for the classical molecular dynamics simulations.

<table>
<tr><td colspan="5">Nonbonded (Coulomb and Lennard-Jones)</td></tr>
<tr><td>Species</td><td>Symbol</td><td>q(e)</td><td>ϵ (kcal/mol)</td><td>σ ($\AA$)</td></tr>
<tr><td>Octahedral</td><td>Al</td><td>1.5750</td><td>1.3298 x 10-6</td><td>4.7943</td></tr>
<tr><td>Bridging O</td><td>Ob</td><td>-1.0500</td><td>0.1554</td><td>3.5532</td></tr>
<tr><td>Hydroxyl O</td><td>Oh</td><td>-0.9500</td><td>0.1554</td><td>3.5532</td></tr>
<tr><td>Hydroxyl H</td><td>Hh</td><td>0.4250</td><td>0</td><td>0</td></tr>
<tr><td>Water O.</td><td>Ow</td><td>-0.8200</td><td>0.1554</td><td>3.5532</td></tr>
<tr><td>Water H</td><td>Hw</td><td>0.4100</td><td>0</td><td>0</td></tr>
<tr><td colspan="5">Morse Bond Potential ($E_{\text{bond}}^{\text{Morse}} = D_0[1 - e^{-\alpha(r-r_0)}]^2$)</td></tr>
<tr><td colspan="2">bond</td><td>D_o</td><td>α</td><td>r_o</td></tr>
<tr><td colspan="2">Oh-Hh</td><td>132.2491</td><td>2.1350</td><td>0.9572</td></tr>
<tr><td colspan="5">Harmonic Bond Potential ($E_{\text{bond}}^{\text{harmonic}} = k(r - r_0)^2$)</td></tr>
<tr><td colspan="2">bond</td><td colspan="2">k (kcal/mol $\AA^2$)</td><td>r_o</td></tr>
<tr><td colspan="2">Ow-Hw</td><td colspan="2">554.1349</td><td>1.00</td></tr>
<tr><td colspan="5">Harmonic Angle Potential ($E_{\text{angle}}^{\text{harmonic}} = k(\theta - \theta_0)^2$)</td></tr>
<tr><td colspan="2">angle</td><td colspan="2">k (kcal/mol rad^2)</td><td>θ (deg)</td></tr>
<tr><td colspan="2">Al-Oh-Hh</td><td colspan="2">45.770</td><td>109.47</td></tr>
</table>

Static DFT and Ab initio Molecular Dynamics

Table S4: Harmonic potential parameters for the removed proton

	Acids	N_d	d_0	k_d	n_α	α_0	α_d
Edge Surface (100)	μ-1	1	1.89	0.1	1	2.0 $(Al-O-H_d)$	0.1
	μ-2	1	1.89	0.1	2	2.0 $(Al-O-H_d)$	0.1
	μ-3	1	1.89	0.1	3	2.0 $(Al-O-H_d)$	0.1
	H_3O^+	3	1.89	1.0	2	1.94 $(H-O-H_d)$	0.1
Basal Surface (010)	μ-2	1	1.89	0.1	2	2.0 $(Al-O-H_d)$	0.1
	H_3O^+	3	1.89	1.0	2	1.94 $(H-O-H_d)$	0.1
Edge Surface (001)	μ-1	1	1.89	0.1	1	2.0 $(Al-O-H_d)$	0.1
	μ-3	1	1.89	0.1	3	2.0 $(Al-O-H_d)$	0.1
	H_3O^+	3	1.89	1.0	2	1.94 $(H-O-H_d)$	0.1
Edge Surface (101)	μ-1	1	1.89	0.1	1	2.0 $(Al-O-H_d)$	0.1
	μ-2	1	1.89	0.1	2	2.0 $(Al-O-H_d)$	0.1
	H_3O^+	3	1.89	1.0	2	1.94 $(H-O-H_d)$	0.1

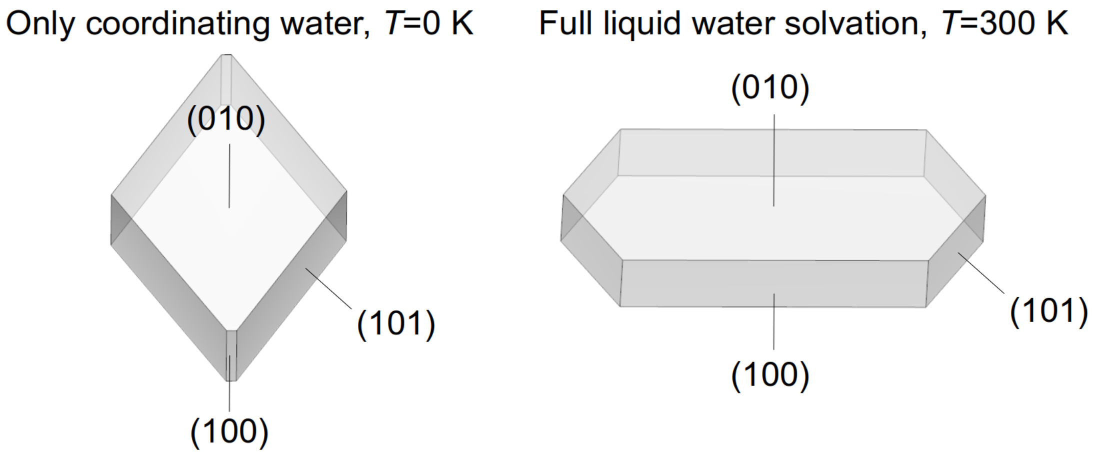

Figure S1: Boehmite equilibrium morphologies with two degrees of hydration

Table S5: Surface aluminum coordination numbers and their density, *d*: density in number per nm^2, and surface energies (γ in kcal/mol/nm^2) under differing solvation models

Surface	$d(CN$ Al-O)	γ
(001) vacuum		
2w	5: 4.29, 6: 4.29	184
2w-μ_3OH[a]	5: 4.29, 6: 4.29	190
4w	6: 8.59	140, *162*
(001) solvated		
2w-DFTMD	6: 8.14; 5: 0.74	91
4w-DFTMD	6: 8.14; 5: 0.74	**79**
(010) vacuum		
0w	6: 9.37	71
1wHB[b]	6	27, *45*
(010) solvated		
0w-DFTMD	6: 9.37	**17**
(100) vacuum		
0w	5: 5.44	170
2w	6: 5.44	154
2w-μ_3OH[a]	6: 5.44	128
2w-2wHB[b]	6: 5.44	78, *111*
(100) solvated		
2w-DFTMD	6: 5.44	**27**
(101) vacuum		
2w[a]	5: 3.59; 6: 3.59	169
4w[a]	6: 7.17	82, *78*
(101) solvated		
4w-DFTMD	6: 7.17	**53**

Current work: all non-DFTMD surface energies from RPBE-D3/DZVP-PW, all DFTMD surface energies are average potential energies with RPBE-D3/DZVP-PW MD. Italics: RPBE-D3/PAW from Prange et al.[5] *d*: density in number per nm^2; w: water; sw: surface water; (*hkl*)-Xw: X H_2O per surface initially coordinated to Al, normalized to the unit cell. For every surface: the lowest γ for surfaces without non-coordinating H_2O are underlined. The μ_3O are bare oxygens unless specified otherwise. [a] Surface selected for the pKa calculations, snapshot in Figure [b] XwHB: X water molecules are not coordinated to the Al but form HBs with the surface.

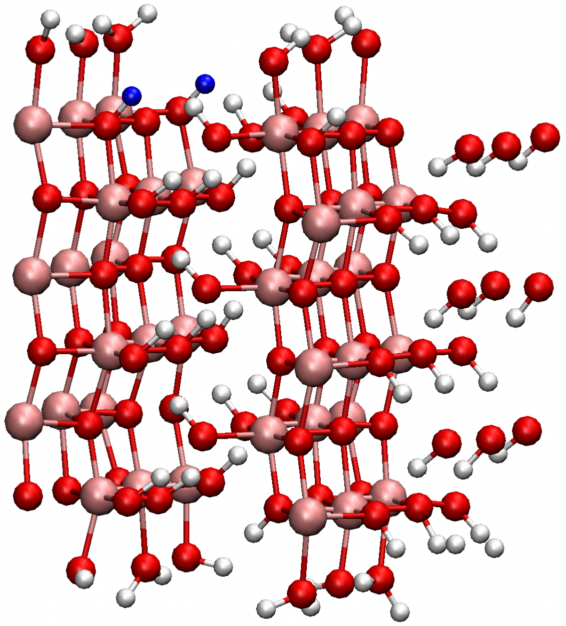

Figure S2: (100) surface used for local enviroment testing. Aluminum, oxygen, and hydrogen atoms are shown in pink, red, and white respectively. The two sites tested for their acidity constant are shown in blue.

Table S6: Block Averaging of the free energies of the deprotonation of singly-protonated surface hydroxides and hydronium

Surface	Protonated species	Block timescale length (ns)	Block 1 ΔA	Block 1 ΔA	Block 3 ΔA	Standard Deviation
(010)	μ_2	2	20.645	20.664	20.648	0.010
	H_3O^+		19.531	19.553	19.512	0.011
(100)	μ_1	2.33	20.290	20.309	20.281	0.014
	μ_2		19.995	19.978	20.031	0.027
	μ_3		19.458	19.424	19.448	0.017
	H_3O^+		18.887	18.904	18.887	0.010
(001)	μ_1	2.33	20.175	20.131	20.137	0.024
	μ_2		19.127	19.010	19.096	0.017
	H_3O^+		18.658	18.602	18.639	0.028
(101)	μ_1	3	20.076	20.048	20.094	0.023
	μ_2		19.874	19.860	19.941	0.043
	H_3O^+		18.662	18.650	18.671	0.010

Table S7: Block Averaging of the free energies of the deprotonation of doubly-protonated surface hydroxides and hydronium

Surface	Protonated species	Block timescale length (ns)	Block 1 ΔA	Block 1 ΔA	Block 3 ΔA	Standard Deviation
(010)	μ_2	2	19.898	19.880	19.911	0.016
(100)	μ_1	2.33	19.640	19.723	19.653	0.045
(001)	μ_1	2.33	19.347	219.384	19.350	0.021
(101)	μ_1	3	19.517	19.470	19.508	0.025

Table S8: Surface Energy Calculations under given pH environments, γ given in kcal/mol/nm^2

Surface	$\gamma_{\text{neutral surface}}$	$\gamma_{pH=3}$	$\gamma_{pH=5}$	$\gamma_{pH=10}$
(001)	79	47.605	77.897	156.655
(010)	17	16.964	20.172	20.172
(100)	27	28.161	31.914	44.017
(101)	53	51.213	51.213	90.181

References

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