Supporting Information:

Structuration and Dynamics of Interfacial Liquid Water at Hydrated γ-Alumina Determined by Ab Initio Molecular Simulations: Implications for Nanoparticle Stability.

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Digne or Wischert's model?

Two models exist – namely Digne's and Wischert's models – for the (110) γ -Al₂O₃ surface. They were showed to have variable relative stability upon surface hydration. They distinguish themselves by the relative number of octahedral and tetrahedral aluminum centers, namely 3:1 and 2:2 for Digne's and Wischert's models respectively.

Even if the energy difference between the two Al surface distributions decreases upon surface hydration, Digne's model remains the most stable up until about 3 H₂O nm⁻². Calculated on the primitive unit cell (ca. $8.30 \times 8.02 \text{ Å}^2$), Wischert's model was however showed to be 53 kJ/mol more stable for 4.5 H₂O nm⁻².¹ To see wether this inversion is maintained with further increase of the water coverage, we compared the two models for different water compositions. The results are given in Table S1. The geometry optimizations were performed with the same electronic set up as described in the main article, using the (2×2) slab, to consider Γ -point only calculations. The energies were divided by 4 to compare with the aforementioned earlier published data. We used Wischert's chemically saturated surface as an energy reference.

Table S1: Relative energies of the Digne's and Wischert's models for various coverages. The energies are not corrected for ZPE and BSSE.

Al surface distribution	$\#H_2O_{(\chi)}$	$\#H_2O_{(\phi)}$	$\# H_2 O_{(g)}$	$\theta_{H_2O} \ (\mathrm{nm}^{-2})$	$\Delta E (kJ/mol)$
Digne	5	0	1	7.5	+42
Wischert	5	0	1	7.5	0
Digne	6	0	0	9.0	-61
Wischert	5	1	0	9.0	-77

At a coverage of 7.5 H₂O nm⁻², namely the saturation of all the Lewis acid sites on Wischert's model surface, Wischert's model surface remains more stable than Digne's, with the range of energy difference as that determined earlier by Wischert *et al.* (42 kJ/mol).¹ However Digne's model surface can chemically adsorb water molecules up until 9.0 H₂O nm⁻². The chemisorption of this extra water molecule in accompanied with an important energetic stabilization of -61 - 42 = -103 kJ/mol. Even if Wischert's model surface does

not have unsaturated Lewis acid sites at the same coverage, it can still physisorb water molecules. The physisorption of this extra water molecule is 77 kJ/mol downhill. All in all, Wischert's model surface still is the more stable for water coverages $\geq 7.5 \text{ H}_2\text{O} \text{ nm}^{-2}$.

Spacial correlation functions: radial distribution function in each layer.

The oxygen-oxygen radial distribution functions (rdf) of unbound water molecules are given in Figure S1. They are averaged over the water molecules that belong to the same layer. The position of the peaks is given in Table S2. As we can see, the closer to the surface, the more shifted to smaller radii the position of the peaks. This suggests that the hydrogen bond network becomes denser. The arise of a new peak in the case of the physisorbed layer even suggests that the hydrogen bond network becomes more complex, likely because of a strong interaction with aluminol groups that have, on the surface, their own spacial surface distribution. Figure S2 focuses on the transition and bulk layers only. They appear to be very similar in terms of rdfs. The higher probability at the minimum near 3.2 Å in the transition layer is also indicative for a stronger interaction between water molecules within the transition layer.

layer	peak positions (Å)		
water/void	2.78	4.44	6.60
bulk	2.73	4.31	6.55
transition layer	2.73	4.28	6.47
physisorbed layer	2.70	3.68(4.24)	6.26

Table S2: Position of the peaks in the oxygen-oxygen rdfs in the different layers.



Figure S1: Radial distribution functions for water oxygen atoms in the different layers defined in the article. For clarity, the curves associated to the transition layer, the bulk layer and the water/void interface are shifted of 0.5, 1.0 and 1.5 respectively.



Figure S2: Comparison between the radial distribution functions of the transition and bulk layers.

Time correlation functions: Mean Square Displacement and Autocorrelation Orientation Function.

To quantitatively assess for the dynamics of water molecules we determined, in each layer, both the Mean Square Displacement MSD(t) of water oxygen atoms on the one hand, and the 2nd order Autocorrelation Orientation Function $C_2(t)$ on the other hand (see Figures S3 and S4). The definition of the latter is given in the main text of the article.

Using Einstein relationship (see Equation 1), we determined the translational diffusivity of water from MSD(t).



$$D = \lim_{t \to \infty} \frac{MSD(t)}{6t} \tag{1}$$

Figure S3: Mean square displacements (MSD) of the oxygen of the water molecules that initially were in the layers defined above. MSDs are normalized for the number of water molecules.

To determine the reorientation relaxation time, we fitted the time evolution of $C_2(t)$ with a two exponential decay function (see Equation 2).^{2,3}

$$C_2(t) = a \exp\left(-\frac{t}{\tau_\ell}\right) + (1-a) \exp\left(-\frac{t}{\tau_2}\right)$$
(2)

 τ_{ℓ} is the sub-picosecond relaxation time due to libration, while τ_2 is the relevant reorientation due to rotational motions. The fits were performed over 10 ps. After 10 ps, the sampling becomes indeed very noisy (at least at in the water/void interface). The results of the fit are given in Table S3.



Figure S4: Second order orientation autocorrelation function $C_2(t)$ of OH bonds in each layer.

Table S3: Optimized parameters obtained from the fitting of $C_2(t)$ with a double exponential decay function. τ_{ℓ} and τ_2 are the libration and angular reorientation relaxation times.

layer	$\tau_{\ell} (ps)$	$\tau_2 (ps)$
water/void	0.170	3.5
bulk	0.125	5.7
transition	0.125	8.0
physisorbed	0.090	35

References

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