Electronic Supplementary Information

Structure of Clean and Hydrated α-Al_2O_3 $(1\bar{1}02)$ Surfaces: Implication on Surface Charge.

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Surface free energy calculation for a clean (bare) surface with an asymmetrical slab

Some of the slabs considered during this work for building the α-Al_2O_3 structure in the $[1\bar{1}02]$ direction are asymmetric. In that case, in order to determine the surface free energy of the upper surface (respectively bottom surface), we must first be able to calculate the contribution of the bottom surface (respectively upper surface). This is achieved by building a non-stoichiometric system in equilibrium with O_2 molecules. **Fig S1** shows an example of the surface free energy calculation for a non- stoichiometric slab exposing surface B2 from a stoichiometric slab exposing surface A on both sides. The symmetrical slab, with the A termination, has the stoichiometric formula $Al_{12}O_{18}$ and Γ_A can easily be calculated (see details below). The surface free energy of surface B2 is then obtained by constructing a non-stoichiometric slab having a formula $Al_{12}O_{18}O_2$. This slab has a B2 termination for the upper surface and a A termination for the lower surface. The details of the calculation of the surface free energy of surface B2 are detailed below.

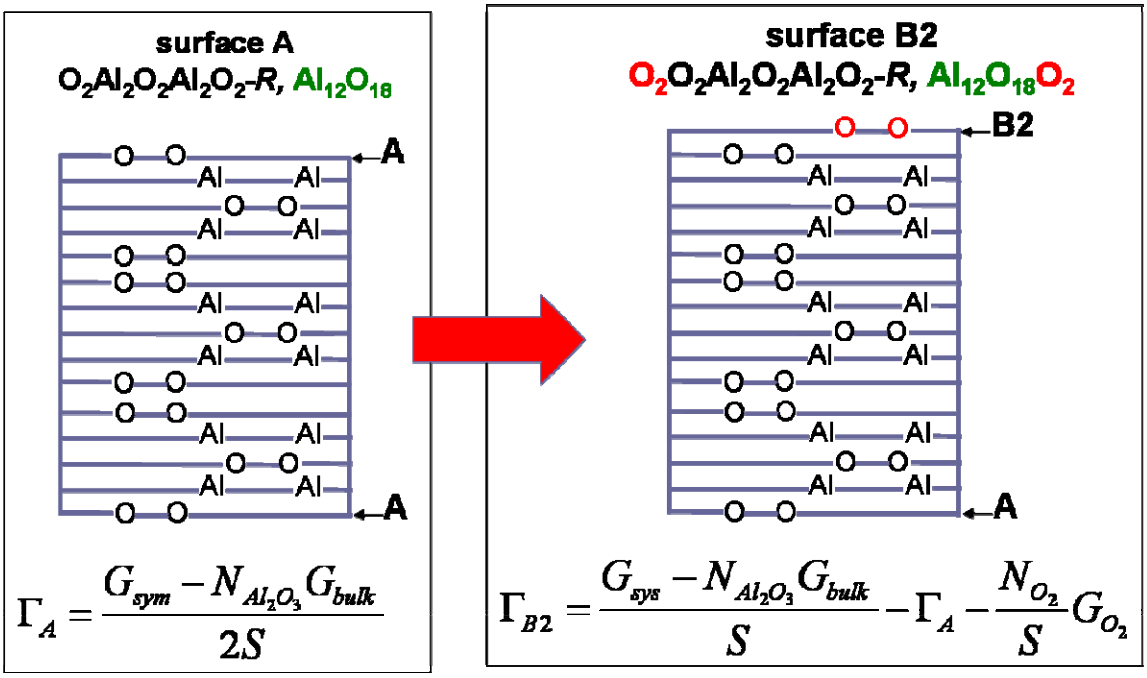

Fig. S1: Graphical representation for surface free energy calculation for stoichiometric (left, Γ_A) and non- stoichiometric (left, Γ_{B2}) slabs.

The Gibbs free energy of the system (G_{sys}) is defined as:

$$G_{sys} = N_{relax}G_{bulk} + S\Gamma^{0}_{hkl} + S\Gamma^{sym}_{hkl} + N_{O_2}G_{O_2} \qquad (1)$$

Where S is the surface area, G_{bulk} the Gibbs free energy of bulk Al_2O_3 per Al_2O_3 unit, G_{O_2} the Gibbs free energy of dioxygen, N_{relax} and N_{O_2} respectively the number of Al_2O_3 unit of the system and the number of O_2 molecules per unit cell adsorbed at the upper surface, Γ^{0}_{hkl} and Γ^{sym}_{hkl} are respectively the surface energy (per surface area) of the upper layer and of the lower layer (per surface area) taken from a symmetric slab.

Γ^{sym}_{hkl} is obtained by calculating the total energy of the symmetric slab (termination A, left hand-side in **Fig S1**). In that case, $\Gamma^{0}_{hkl} = \Gamma^{sym}_{hkl}$. By analogy with equation (1), the Gibbs free energy of the stoichiometric system can then be expressed as:

$$G_{sym} = N_{relax}G_{bulk} + 2S\Gamma^{sym}_{hkl} \qquad (2)$$

The term referring to the adsorption of O_2 molecules ($N_{O_2}G_{O_2}$) is gone since no excess O_2 molecules are considered for the A surface.

Hence, the surface free energy normalized by surface area for the relaxed symmetric system is (with $N_{relax} = N_{Al_2O_3}$):

$$\Gamma^{sym}_{hkl} = \Gamma_{A} = \frac{G_{sym} - N_{Al_2O_3}G_{bulk}}{2S} \qquad (3)$$

By combining equations (1) and (3), the surface energy of the upper surface Γ^{0}_{hkl} is then calculated:

$$\Gamma^{0}_{hkl} = \frac{G_{sys} - N_{Al_2O_3}G_{bulk}}{S} - \Gamma_{A} - N_{O_2}G_{O_2} \qquad (4)$$

Numerical validation of equation 10

Vibrational contributions can only be significant for hydrated surfaces since both vibrational and entropic contributions from the bulk and from non-hydrated surfaces are the same and will cancel out. Conversely, for hydrated surfaces, the vibrational entropy contribution of adsorbed hydroxyl species has no equivalent in the bulk. As demonstrated in the text (see section 2.2 Thermodynamic description) the term corresponding to the vibrational contribution to the hydrated surface free energy is $\theta_{H_2O}[U_{hyd,vib}(T) - TS_{hyd}(T)]$. In order to check that the contribution of this last term can be neglected, we have calculated this contribution for one of the surfaces of interest at 298.5 K.

The vibrational partition functions (z) of dehydrated surface A and of the corresponding hydrated surface (surface obtained by dissociative adsorption of two water molecules on dehydrated surface A) has the following expression:

$$z = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \qquad (5)$$

Where *h* is the Planck's constant (6,62.10^{-34} J.s), *k* the Boltzmann constant (1,38.10^{-23} J.K^{-1}), *ν* the vibration frequency and *T* the temperature.

The vibrational internal energy and entropy are related to z by equation (6) and (7) respectively.

$$U_{vib} = \frac{N.h\nu}{e^{\frac{h\nu}{kT}} - 1} \qquad (6)$$

$$S = k.\ln z + \frac{U_{vib}}{T} \qquad (7)$$

The vibrational frequencies of the dehydrated and hydrated surface A were obtained with the same calculation parameters than those used previously for optimization of the different systems. Vibrational frequencies are automatically calculated by VASP with two displacements of 0.005 Å around the equilibrium position. Results are given in table S1.

ν (cm^{-1}) for Dehydrated surface A	ν (cm^{-1}) for Hydrated surface A, 1 ML (2H_2O)
229.708379	158.407071
229.708379	160.468819
229.708379	180.716527
290.61394	193.700569
290.61394	210.558956
360.870097	264.65718
371.208564	274.925976
401.90279	326.631008
443.781145	336.246099
482.264744	353.288682
485.156514	357.888543
526.419533	404.518398
535.293988	421.96644
587.39413	427.164638
605.023558	455.437822
693.560469	491.76056
721.226952	512.653753
755.149261	523.065639
	536.844303
	568.471046
	609.208614
	631.784687
	688.540643
	707.003547
	719.860911
	758.637278
	918.445443
	941.21606
	953.766835
	1030.429738
	1108.28739
	1153.218237
	3114.127056
	3184.07804
	3561.270402
	3621.495822

Table S1 : Calculated vibrational frequencies related to the hydrated (1 ML) and dry surface A.

Using equations (5), (6), (7) and vibrational frequencies reported in table S1, it is now possible to evaluate the contribution $\theta_{H_2O}[U_{hyd,vib}(T) - TS_{hyd}(T)]$ at T = 298 K by subtracting the results for the bare surface from those of the hydrated surface.

The results show that the $\theta_{H_2O}[U_{hyd,vib}(T) - TS_{hyd}(T)]$ contribution amounts to 0.0427 J.m^{-2} while the contribution of $\Gamma_{hkl}^{hyd}(0K) + \theta_{H_2O}[-U_{H_2O}(298K) - R \times 298K + TS_{H_2O}(298K) + U_{H_2O}(0K)]$ is 1.43 J.m^{-2}. Hence, the contribution of $\theta_{H_2O}[U_{hyd,vib}(T) - TS_{hyd}(T)]$ to the total surface energy is lower than 3 %. We can thus safely conclude that this last term can be neglected which means that the approximation used in this work (variations of volume, entropy and internal energy with temperature are negligible for the condensed phase) is correct.

Test calculations of k-point grid for the Brillouin integration, number of alumina layers and vacuum thickness.

k-point grid for the Brillouin integration. The following figure (S2) shows the calculation test performed for optimizing the k-point grid for the Brillouin integration for a slab containing 12 Al and 18 O ($Al_{12}O_{18}$). The calculation convergence is reached for a distance between k-points in the reciprocal space of 20 $Å^{-1}$.

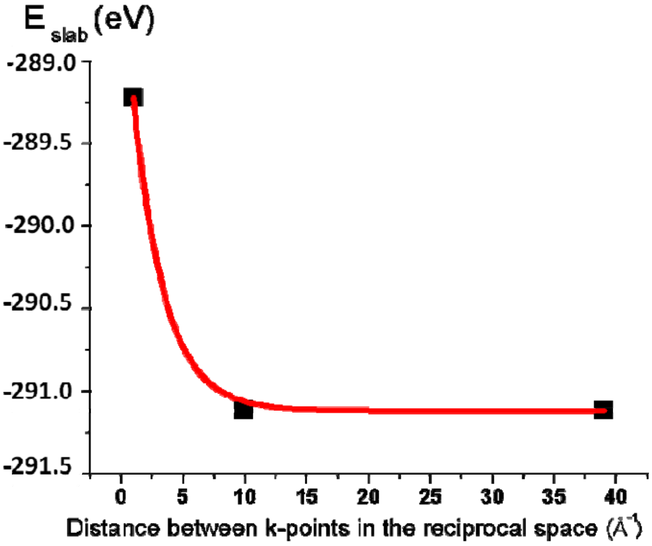

Fig. S2 : Variation of the slab energy as a function of the distance between k-points in the reciprocal space ($Å^{-1}$).

Number of alumina layers. The following figure (S3) shows the calculation test performed for optimizing the number of alumina layers needed to reach the energy convergence. The test has been carried out for three different slabs: Al_8O_{12}, $Al_{12}O_{18}$ and $Al_{16}O_{24}$. The calculation convergence is reached for the slab containing 12 Al and 18 O ($Al_{12}O_{18}$).

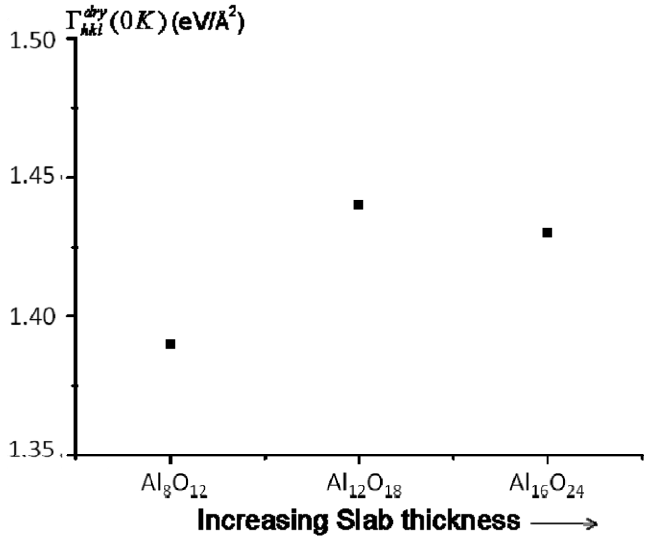

Fig. S3 : Variation of the relaxed surface energy as a function of slab thickness

Vacuum thickness. The following figure (S4) shows the calculation test performed for optimizing the vacuum thickness between successive slabs. The variation of the unrelaxed surface energy as a function of the vacuum thickness between successive slabs is shown. The calculation convergence is reached for a vacuum of 15 Å.

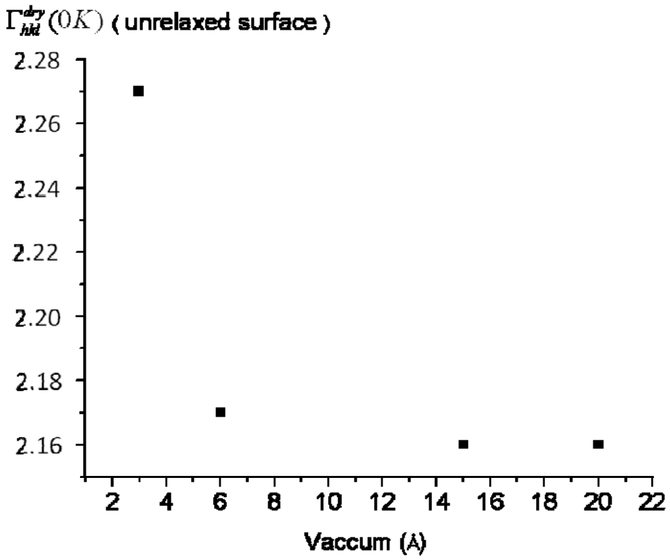

Fig. S4 : Variation of the unrelaxed surface energy as a function of the vacuum thickness between successive slabs