Supporting Information

Revisiting γ–alumina surface models through the topotactic transformation of boehmite surfaces

Thomas Pigeon,^{1,2} Céline Chizallet,^{1,2} Pascal Raybaud^{1,2,*}

¹IFP Energies Nouvelles, Rond-Point de l'Echangeur de Solaize,

BP 3, 69360 Solaize, France

²Univ Lyon, ENS de Lyon, CNRS UMR 5182, Laboratoire de Chimie,

F69342 Lyon, France

Email: pascal.raybaud@ifpen.fr

SI.1 Comparison between surface energies computed with and without the vibrational components of enthalpy and entropy.

In **Figure S1** we present the evolution of the surface energy of the $(1 \ 1 \ 0)_b$ surface model built by dehydration of a $(0 \ 1 \ 0)$ boehmite slab in the case where the vibrational parts of free energy were included (red curves) and in the case where they were not (blue curves).



Figure S1: Evolution of the surface energy (mJ nm⁻²) as a function of temperature (K). The water pressure if fixed a $P(H_2O) = 10^{-6}$ bar. Red curves: without vibrational contributions; Blue curves: including vibrational contributions.

We observe that the temperature at which the hydrations or dehydrations are not much impacted by the fact that we did not include the vibrational parts. We assume for the rest of our study that the other surfaces studied would behave similarly and thus to be able to consider more possibilities we did not included vibrational components in free energies.

SI.2. Dehydration of the interlayers and surface of (0 1 0) slab of boehmite

The initial structure of the boehmite surface is presented in **Figure S2a**. The first question is whether the dehydration of the surface occurs before or after the dehydration of the interlayers. To address this, we performed different optimizations after removing one water molecule either on the surface, or in the first interlayer, or in the second one. We considered each possible way for removing a water molecule in each case. The dehydration energies of all the possible cases are given in **Table S1**.



Figure S2: a) Side view of a Boehmite (0 1 0) slab, b) same boehmite slab dehydrated on the surface 'along X', as the two removed protons were located on a line parallel to X axis (the axis references are defined from the boehmite cell). Color legend: Red: Oxygen, Grey: Aluminum, White: Hydrogen. The circle highlights the surface atoms in a) to be removed to form the structure b).

We observe that in all cases, this dehydration would require some extreme conditions (vacuum and/or very high temperature) because the energy required is higher than 330 kJ.mol⁻¹ at 0 K. The removal of one water molecule is less favorable in the bulk (interlayers) than on the surface. This is induced by the interlayer hydrogen bonds stabilizing the OH groups in bulk.

Structure	Dehydration energy (at 0 K) (kJ mol ⁻¹)
Surface – Along X	369
Surface – Along Z	331
First interlayer – Along X	397
First interlayer – Along Y	366
First interlayer – Along Z	434
Second interlayer – Along X	398
Second interlayer – Along Y	366
Second interlayer – Along Z	434
S _{50,0}	139
S _{0,0}	134

Table S1: Dehydration energies of the different cases considered. In the structure column, "along X, Y or Z" means that the proton has been removed from the nearest hydroxyl along in the direction X, Y or Z from the removed hydroxyl. An example is given in **Figure S2b**.

However, a strong stabilizing factor of the interlayer dehydration is the bulk reconstruction involving contraction and shearing with formation of new Al-O-Al bonds bridging each layer. This leads to the dehydrated initial structure " $S_{0,0}$ " defined by Krokidis as the alumina "matrix" before any Al diffusions.^[9] The interlayer dehydration energy should be influenced by this bulk transformation. We thus re-optimized the $S_{50,0}$ and $S_{0,0}$ structures at the same level of theory and determined the corresponding water dehydration energy. As shown in Table S1, these dehydration energies are strongly reduced to ~130 kJ mol⁻¹ and the interlayer dehydration becomes strongly favored with

respect to the surface dehydration (by about 200 kJ.mol⁻¹). This means that the calcination process involves a collective removal of interlayer water molecules directly combined with bulk reconstruction. We conclude that during the first step of the bulk transformation from boehmite to gamma alumina, the (0 1 0) surface remains hydrated while the bulk is already dehydrated. The overall process will lead to the $(1 1 0)_b$ surface. Thus, we built such a model where the core of the slab has been the object of the Krokidis et al.[1] mechanism whereas the surface layer remains hydroxylated in the same way as on the boehmite (1 0 0) surface.

SI.3 Optimization of the fully hydrated (1 1 0)_b surface and (P,T) thermodynamic diagram

Figure S3 reveals the difference between migrations 1 and 2 described in the main text, resulting from the coordination of sub-layer oxygen atoms. Moreover, the orientation of the bridging hydroxyls has an impact on the total energy, so finally four cases for each type of migration have been considered (**Table S2** and **Figure S4**). The most stable surface corresponds to orientation 3 as defined in **Figure S4**.



Figure S3: Side views of the slabs generated after bulk plus surface migrations at the $(1\ 1\ 0)_b$ alumina surface depicting the subsurface differences between the two types of migration: (a) migration 1 and (b) migration 2, as defined in the main text figure 3a. Hydroxyls orientation 3 (as defined in Figure S4) have been chosen for both a) and b). Circled in light green: oxygen atoms linked to 5 octahedral aluminum, named $O(AI_{VI})_5$; in darker green: $O(AI_{IV})_2(AI_{VI})$; in blue: $O(AI_{IV})(AI_{VI})_3$. The cell vectors correspond to boehmite orientation. Color legend: Red: Oxygen, Grey: Aluminum, White: Hydrogen.



Figure S4: Hydroxyls orientations of the $(1 \ 1 \ 0)_b$ surface: a) Orientation 1; b) Orientation 2; c) Orientation 3; d) Orientation 4; Circled in green: μ_2 -OH, circled in blue: μ_1 -OH (kept fixed). The cell vectors correspond to boehmite. Color legend: Red: Oxygen, Grey: Aluminum, White: Hydrogen.

Structure	Surface energy at 0 K with respect to γ-alumina bulk at 0 K (mJ m ⁻²)	Energy difference with respect to migration 2 at 0 K (kJ mol ⁻¹ of migrated Al)	Energy difference with respect to OH orientation 3 at 0 K (kJ mol ⁻¹ of µ ₂ -OH)
Migration 1 - orientation 1	185	20.2	8.4
Migration 1 - orientation 2	185	20.2	8.4
Migration 1 - orientation 3	122	20.5	0.0
Migration 1 - orientation 4	173	19.7	6.8
Migration 2 - orientation 1	34	0.0	8.8
Migration 2 - orientation 2	34	0.0	8.7
Migration 2 - orientation 3	-32	0.0	0.0
Migration 2 - orientation 4	26	0.0	7.7

Table S2 : Surface energy and relative energy of the 8 different structures of the (1 1 0)_b surface

We finally conclude that the most stable structure corresponds to migration 2 with OH orientation 3.



Figure S5. Stable hydroxyl coverages domain as a function of $P(H_2O)$ and temperature for the $(1\ 1\ 0)_b$ surface built from the boehmite (0 1 0) slab. The colored lines represent the solid/vapor, liquid/vapor and solid/liquid equilibria of water. The diagram is only valid on the right-hand side of the violet and green lines where vapor exists.

SI.4. Construction of the $(1\ 1\ 0)_b$ surface model by the bulk alumina cleavage and (P,T) thermodynamic diagrams



Figure S6: a) Position of the cleavage plane of bulk alumina leading to a symmetric (1 1 0) slab model in the direction corresponding to the (0 1 0) boehmite plane. b), d): Side and c), e) top views of b), c) dehydrated (1 1 0) surface, d), e) fully hydrated (1 1 0) surface (18.0 OH nm⁻²). The axes are those of the boehmite, so the normal of the surface is given by y. Color legend: red balls: oxygen, grey balls: aluminum, white balls: hydrogen. The black frames represent the periodic cell boundaries.



Figure S7. a) Stable hydroxyl coverages domain as a function of $P(H_2O)$ and Temperature for the (1 1 0)_b surface built from bulk alumina. b) Stability domains of the two types of (1 1 0)_b surfaces as a function of $P(H_2O)$ and Temperature. The colored lines represent the solid/vapor, liquid/vapor and solid/liquid equilibria of water. The diagram is only valid on the right-hand side of the violet and green lines where vapor exists.

SI.5. Construction and thermodynamic diagrams of (1 1 0)₁ surface models.

5.1 Construction using the topotactic transformation of the (1 0 0) slab of boehmite

Starting from the slab generated at the 3rd step of **Figure 5** in main text, Al migrations (toward tetrahedral or octahedral sites) must occur during the 4th step to generate the lateral alumina (1 1 0)₁ slab. With such a method, one possible alumina surface is the same as the one proposed by Digne et al.[2, 3] However, as represented in **Figure S8b**, not only the Digne's surface can be formed. The difference occurs after doing half the migrations in the first former interlayer. The choices made for Al bulk migrations depend on: first selecting the pair of migrating Al atoms to migrate (2 possible pairs are illustrated by the two pairs of Al atoms circled in dark blue and dark green in **Figure S8b**), second transferring octahedral Al atoms either in tetrahedral sites in 'canal' 1 or 2 of the second interlayer (labelled 1 and 2 in **Figure S8b**). Overall, 4 different surfaces can be obtained. To generate the surface proposed by Digne, the migration must involve the Al pair circled in dark green which migrate to the tetrahedral sites located in canal 2 as shown in **Figure 8b**. Only the first two layers are represented, the other migrations are deduced from the two first paired migrations and the non-spinel bulk structure of Krokidis.[1] Depending on the thickness on the initial slab, the surface model will be symmetric or not. Two surfaces require a 4n layers slab while the two others with a 4n+2 layers slab to be symmetric.



Figure S8: Top views of the intermediate hydroxylated alumina surfaces built in the lateral (1 1 0) direction. Balls and sticks: surface layer; line: first sublayer. Non optimized structures of **a**) slab obtained before Al migrations (3^{rd} step of **Figure 5** in main text), **b**) migrations of Al leading to 13% Al_{Td} located in the first interlayer only **c**) migrations of Al leading to 25% Al_{Td} located in the second interlayer with Al_{Td} located in canal 2 after migration from the Al_{Oh} site within dark green circle in **b**). The cell vectors correspond to boehmite orientation so the normal to the surface is given by x. Color legend: red balls: oxygen, grey balls: aluminum, white balls: hydrogen. The black lines represent the periodic cell boundaries.

5.2 Construction by cleavage of alumina bulk

Four different $(1\ 1\ 0)_I$ surfaces can be built by cleavage of the gamma alumina bulk as shown in **Figure 6** of the main text. **Figure S9** illustrates the top views of these four non-hydrated models. We can show that these four models are identical to those constructed by the dehydration of boehmite surface models.

5.3 Analysis of (1 1 0) surface models and thermodynamic diagrams

A first observation, only based on the surface layer, is that there are two types of surfaces model: the models labelled "L" for which the surface AI_{IV-Ss} are aligned in the y direction, and the models "A" for which they are alternated. In addition, two Al distributions in subsurface may exist for each model type ("L_x" and "A_x"). As mentioned, the 4 surfaces represented in **Figure S9** are fully equivalent to the one expected from the previous method.



Figure S9: Top view of the four different possible terminations of the (1 1 0) lateral surface with the adopted denominations, top layer: ball and sticks, first sublayer: thinner sticks, second sublayer: line. The terminations are named after a recurring AI_{IV} pattern of lines, Lx, or alternating, Ax, surface aluminum atoms, with enumeration by x (depending on the subsurface arrangement). The vectors correspond to boehmite orientation. Color legend: red balls: oxygen, grey balls: aluminum. The blue circles highlight the AI_{IV-Ss} sites.

The next logical step is to identify the most stable model among these four possible ones. The criterion chosen in the initial study by Digne et al. ^[24] was based on the value of 0 K surface energy for a dehydrated state. Doing so, we confirm that the dehydrated A1 surface exhibits the lowest 0K surface energy which corresponds well to the model chosen by Digne.^[24] A complementary criterion can be to consider surface energy at given experimental conditions such as used for the calcination of boehmite into γ -Al₂O₃ (temperatures around 800 K and non-zero water pressure). In such conditions, the hydroxyl coverage may not be equal to zero. To address this question, it is needed to screen the different hydration states and compare their stability as a function of temperature and water pressure. The corresponding thermodynamic diagrams are presented in **Figure S10**.



Figure S10. a), c), e) and g) Evolution of the surface energy and hydroxyl coverages as a function of temperature for a water pressure is fixed a $P(H_2O) = 10^{-6}$ bar. b), d), f) and h) (P, T) thermodynamic diagram of hydroxyl coverages for the 4 different $(1\ 1\ 0)_1$ surface models. The colored lines represent the solid/vapor, liquid/vapor and solid/liquid equilibria of water. The diagram is only valid on the right-hand side of the violet and green lines where vapor exists.

SI.6 Structure and thermodynamic diagrams of (1 1 1) surface models.

6.1 Slab models



Figure S11: Representation of the six possible slab models of (1 1 1) surfaces for 14.8 OH.nm⁻² after geometry optimization. Color legend: red balls: oxygen, grey balls: aluminum, white balls: hydrogen. The black lines represent the periodic cell boundaries. The dashed line represents the separation between the systems of axes.

6.2 Thermodynamic diagrams





Figure S52: a), c), e), g), i) and k) Evolution of the surface energy and hydroxyl coverages as a function of temperature for a water pressure is fixed a $P(H_2O) = 10^{-6}$ bar. b), d), f), h), j) and l) (P, T) thermodynamic diagrams of hydroxyl coverages for the 6 different (1 1 1) surface models. The colored lines represent the solid/vapor, liquid/vapor and solid/liquid equilibria of water. The diagram is only valid on the right-hand side of the violet and green lines where vapor exists.

SI.7 Dehydrated slab models for the (0 0 1) orientation

Two of the slabs (10_1 and 8_1, **Figure S13**) can be found by cleaving the bulk γ -alumina structure (top path of **Scheme 1**) while the other two (10_2 and 8_2) cannot be directly obtained by cleavage as the corresponding slabs are not stoichiometric and they need thus to be modify in the proper way to become stoichiometric. The most stable 8_1 model corresponds to Digne's model as shown by **Table S3**.[2, 3]



Figure S13: Four different slabs structures considered to model the (0 0 1) surface. Names correspond to the number of oxygen layers. Color legend: red balls: oxygen, grey balls: aluminum, white balls: hydrogen. Axis are taken from boehmite *Cmcm* representation.

Model label	Surface energy at 0 K and 0 OH nm ⁻² (mJ nm ⁻²)
10_1	1782
10_2	1487
8_1	1231
8_2	1882

Table S3: Surface energy at 0 K of each considered model for the (0 0 1) orientation.

SI.8 Complementary morphology analysis

	Surfaces - Multiplicity	350 K	550 K	750 K
	(1 1 0) _b - 2	36	36	32
Topotactic transformation	(0 0 1) - 2	5	26	37
of boehmite	(1 1 0)-2	17	20	19
	(1 1 1) - 4	42	18	12
	(1 1 0) _b - 2	~0	5	4
Alumina bulk*	(0 0 1) - 6	0	31	93
	$(1\ 1\ 0)_{I} - 10$	76	53	0.0
	(1 1 1) - 8	25	11	3
	(1 1 0) - 12	98	63	0
Spinel bulk**	(0 0 1) - 6	0	33	99
	(1 1 1) - 8	2	4	1

Table S4. Proportion (%) of each facet as a function of synthesis pathway and temperature at $P=10^{-6}$ bar.

* The bulk and surface structures used are those defined in [1] and in the present work, while the multiplicities of the $(1\ 1\ 0)_b+(1\ 1\ 0)_l$ and $(1\ 1\ 1)$ facets correspond to the multiplicity found in spinel symmetry, although some of these facets are not equivalent.

**For the spinel reference system, the bulk structure is the one of a spinel while surface energies are approximated by those calculated in the present work with the γ -alumina bulk [1].

	Surfaces - Multiplicity	550 K	750 K		
	(1 1 0) _b – 2	36.0	37.3		
Topotactic transformation	(0 0 1) - 2	4.9	21.0		
of boehmite	(1 1 0) ₁ – 2	18.7	20.1		
	(1 1 1) - 4	40.4	21.6		
	(1 1 0) _b -2	0.5	4.6		
Alumina bulk*	(0 0 1) - 6	0.0	10.8		
	$(1\ 1\ 0)_{I} - 10$	77.8	69.9		
	(1 1 1) - 8	21.7	14.7		

Table S5. Proportion (%) of each facet as a function of synthesis pathway and temperature at P=1 bar.

* The bulk and surface structures used are those defined in [1] and in the present work, while the multiplicities of the (1 1 0) and (1 1 1) facets are given by a spinel symmetry, although some of these facets are not equivalent.

If we consider a non-topotactic synthesis path where the morphology can be deduced from surface energies calculated from the γ -alumina bulk (without considering the boehmite history),[1] different facets are likely to appear at the particle surface. In this case, we used the surface energy obtained from γ -alumina bulk cleavage for the basal $(1 \ 1 \ 0)_b$ surface as defined in **Figure 4 b** (and not the one inherited from boehmite). Moreover, we assumed that the multiplicities of the $(1 \ 1 \ 1)$ and $(1 \ 1 \ 0)_l + (1 \ 1 \ 0)_b$ facets correspond to the multiplicity found in spinel symmetry, although some of these facets are not equivalent since our γ -alumina bulk[1] differs from a spinel one. However, it is beyond the scope of the present work to evaluate the surface energies of all these complementary facets. As a consequence, the proportion of the $(1 \ 1 \ 0)_b$ surface drops significantly to less than 5% whatever the temperature and pressure (**Figure S14 d**, **e**, **e'**, **f** and **f'**). As for the topotactic model, the proportion of the $(0 \ 0 \ 1)$ surface varies in an opposite direction to $(1 \ 1 \ 1)$ and $(1 \ 1 \ 0)_l$ facets is always larger than the one of $(1 \ 1 \ 1)$. This trend is rather similar for the spinel bulk system illustrated in **Figure S14 a**), **b**) and **c**) excepting that the $(1 \ 1 \ 1)$ facets are less present in the spinel bulk system according to our assumptions made on surface energies.



Figure S14. γ -alumina crystallite morphologies deduced from DFT surface energies for three temperatures (350, 550 and 750 K) and two pressures (P=10⁻⁶ and 1 bar) and by using two methods: a), b) and c) using spinel bulk symmetry and surface energies calculated in the present work; d), e), e'), f) and f') using γ -alumina bulk defined in [1] and surface energies calculated in the present work (hypothesis on facets multiplicity as reported in **Tables S4** and **S5**). The numerical proportions of facets are reported in **Tables S4** and **S5**.

SI.9 Inventory of surface Bronsted and Lewis acid sites.

(1 1 0) _b				
T = 400K	T = 700	T = 700K	T = 800K	T = 800K
Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁶ bar
$\theta = 9.0 \text{ OH nm}^{-2}$	θ = 9.0 OH nm ⁻²	θ = 9.0 OH nm ⁻	$\theta = 9.0 \text{ OH nm}^{-2}$	θ = 4.5 OH nm
2 OH-µ1-(Al _{IV})	2 OH-µ1-(AlIV)	2 OH-µ1-(Al _{IV})	2 OH-μ ₁ -(Al _{IV})	2 OH-µ2-(Al _{VI} -Al _{VI})
2 OH-µ2-(Alvi-Alvi)	2 OH-µ2-(Alvi-Alvi)	2 OH-µ2-(Alvi-Alvi)	2 OH-µ2-(Alvi-Alvi)	
2 Alvi-oh	2 Alvi-oh	2 Alvi-on	2 Alvi-oh	2 Alvi-oh
2 Aliv-Td	2 Aliv-Td	2 Aliv-td	2 Aliv-td	2 Aliv-td
	ł	(1 1 0) _I A1		
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K
Р _{н20} = 10 ⁻² bar;	Р _{н20} = 10 ⁻² bar;	Р _{н20} = 10 ⁻⁴ bar;	Р _{н20} = 10 ⁻⁴ bar;	P _{H20} = 10 ⁻⁶ bar;
$\theta = 15.0 \text{ OH nm}^{-2}$	$\theta = 9.0 \text{ OH nm}^{-2}$	$\theta = 9.0 \text{ OH nm}^{-2}$	$\theta = 3.0 \text{ OH nm}^{-2}$	$\theta = 3.0 \text{ OH nm}^{-2}$
2 OH-µ1-(Al _{IV})	2 OH-µ1-(Al _{IV})	2 OH-µ1-(Al _{IV})	$2 \text{ OH-}\mu_2 - (\text{Al}_{V} - \text{Al}_{V})$	2 OH-µ ₂ -(Al _{IV} -Al _{IV})
1 OH-μ ₂ -(Al _{IV} -Al _{VI})	1 OH-μ ₂ -(Al _{IV} -Al _V)	1 OH-μ ₂ -(Al _{IV} -Al _V)	1-1	,
2 OH-µ2-(Al _{VI} -Al _{VI})	1 OH-µ2-(Alv-Alv)	1 OH-μ ₂ -(Al _V -Al _V)		
1 OH-µ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	1 OH-μ ₂ -(Al _{VI} -Al _{VI})	1 OH-μ ₂ -(Al _{VI} -Al _{VI})		
2 H ₂ O-μ ₁ -(Al _{VI})	1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})		
2 Alvi-oh	2 Alv-sp	2 Alv-sp	3 Aliv-ss	3 Aliv-ss
2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}
		(1 1 0) _I A2		
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K
$P_{H20} = 10^{-2} \text{ bar}$:	$P_{H20} = 10^{-2} \text{ bar}$	$P_{H20} = 10^{-4} \text{ bar}$:	$P_{H20} = 10^{-4} \text{ bar}$:	$P_{\rm H2O} = 10^{-6} \text{ bar}$:
$\theta = 18.0 \text{ OH nm}^{-2}$	$\theta = 9.0 \text{ OH nm}^{-2}$	$\theta = 9.0 \text{ OH nm}^{-2}$	$\theta = 6.0 \text{ OH nm}^{-2}$	$\theta = 6.0 \text{ OH nm}^{-2}$
1 OH-u1-(Aliv)	2 OH-u1-(Aliv)	1 OH-u1-(Aliv)	$2 \text{ OH-} \mu_2 - (\text{Aliv}-\text{Aliv})$	2 OH-u2-(Aliv-Aliv)
3 OH-u2-(Alvi-Alvi)	1 OH-u2-(Alv-Alv)	1 OH-u2-(Alv-Alv)	= 0.1 p.2 (- •··· µ2 (/ //)
4 H ₂ O-μ ₁ -(Al _{VI})	2 OH-112-(Alv-Alv)	2 OH-112-(Alv-Alvi)		
	1 H ₂ O-μ ₁ -(Al _{VI} -Al _{VI})	1 H ₂ O-μ ₁ -(Al _V)		
3 Alvi-oh	2 Alv-sp	2 Alv-sp	3 Aliv-ss	3 Aliv-ss
1 Alıv-td	2 Aliv-Td	2 Al _{IV-Td}	2 Alıv-Td	2 Aliv-Td
		(1 1 0) _I L1		
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K
Р _{н20} = 10 ⁻² bar;	Р _{н20} = 10 ⁻² bar;	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁴ bar;	Р _{н20} = 10 ⁻⁶ bar
$\theta = 12.0 \text{ OH nm}^{-2}$	$\theta = 12.0 \text{ OH nm}^{-2}$	$\theta = 12.0 \text{ OH nm}^{-2}$	$\theta = 12.0 \text{ OH nm}^{-2}$	$\theta = 3.0 \text{ OH nm}^{-2}$
1 OH-μ ₁ -(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	2 OH-μ ₂ -(Al _{IV} -Al _{IV})	2 OH-μ ₂ -(Al _{IV} -Al _{IV})
1 OH-μ ₂ -(Al _{IV} -Al _{VI})	1 OH-μ ₂ -(Al _{IV} -Al _{VI})	1 OH-μ ₂ -(Al _{IV} -Al _{VI})		
5 OH-μ ₂ -(Al _{vi} -Al _{vi})	5 OH-μ ₂ -(Al _{vi} -Al _{vi})	5 OH-μ ₂ -(Al _{vi} -Al _{vi})		
1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})		
3 Alvi-Oh	3 Alvi-Oh	3 Alvi-oh	3 Alvi-Oh	3 Al _{IV-Ss}
1 Al _{IV-Td}	1 Al _{IV-Td}	1 Al _{IV-Td}	1 Al _{IV-Td}	2 Al _{IV-Td}
		(1 1 0) _I L2		
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K
P _{H2O} = 10 ⁻² bar;	Р _{н20} = 10 ⁻² bar;	Р _{н20} = 10 ⁻⁴ bar	Р _{H2O} = 10 ⁻⁴ bar;	Р _{н20} = 10 ⁻⁶ bar
θ = 12.0 OH nm ⁻²	θ = 12.0 OH nm ⁻²	θ = 12.0 OH nm ⁻²	θ = 12.0 OH nm ⁻²	θ = 3.0 OH nm ⁻²
1 OH-μ ₁ -(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	2 OH-µ2-(Al _{IV} -Al _{IV})	2 OH-µ ₂ -(Al _{IV} -Al _{IV})
3 OH-μ ₂ -(Al _{IV} -Al _{VI})	3 OH-μ₂-(Al _{IV} -Al _{VI})	3 OH-μ ₂ -(Al _{IV} -Al _{VI})		
3 OH-μ ₂ -(Al _{VI} -Al _{VI})	$3 \text{ OH}-\mu_2-(\text{Al}_{VI}-\text{Al}_{VI})$	3 OH-μ ₂ -(Al _{vi} -Al _{vi})		
$1 \text{ OH-}\mu_3 - (\text{Al}_{VI} - \text{Al}_{VI} - \text{Al}_{VI})$	$1 \text{ OH-}\mu_3 \text{-}(\text{Al}_{VI}\text{-}\text{Al}_{VI}\text{-}\text{Al}_{VI})$	$1 \text{ OH-}\mu_3$ -(Al _{VI} -Al _{VI} -Al _{VI})	2.41	2.41
3 Alvi-oh	3 Alvi-oh	3 Alvi-oh	3 Aliv-Ss	3 Aliv-ss
T AIIV-Td	T MIN-IQ		Z AIIV-Td	Z AIIV-Td
T - 100K	T – 7004		T - 2004	T - 2004
$P_{\rm H20} = 10^{-2} har$	$P_{\mu a \sigma} = 10^{-2} har$	P _{upo} = 10 ⁻⁴ har	$P_{\text{upo}} = 10^{-4} \text{har}$	$P_{\text{upo}} = 10^{-6} \text{har}$
$F_{H20} = 10$ Udi $A = 1/20 \mu m^{-2}$	$F_{H20} = 10$ Jdl $A = 12.2 \ OU \ nm^{-2}$	$F_{H20} = 10$ Ddi A = 0 0 AL Am ⁻²	$F_{H2O} = 10$ Dd rm^{-2}	$P = Q \circ O U \circ m^{-2}$
0 – 14.0 UH IIII -	0 – 12.2 UH IIII -	0 – 9.0 UH IIIII -	0 – 9.0 UH IIII -	0 – 9.0 UH IIII -

1 OH-μ ₁ -(Al _{IV})	1 OH-µ ₁ -(Al _{IV})	1 OH-µ1-(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	
2 OH-μ ₁ -(Al _{VI})	1 OH-μ1-(Al _{VI})	1 OH-μ2-(Al _{IV} -Al _V)	1 OH-μ2-(Al _{IV} -Al _V)	1 OH-μ ₂ -(Al _{IV} -Al _V)	
3 OH-μ ₂ -(Al _{IV} -Al _{VI})	3 OH-μ₂-(Al _{IV} -Al _{VI})	2 OH-μ ₂ -(Al _V -Al _{VI})	2 OH-μ ₂ -(Al _V -Al _{VI})	2 OH-μ ₂ -(Al _v -Al _{vi})	
5 OH-μ ₂ -(Al _{vi} -Al _{vi})	1 OH-μ ₂ -(Al _v -Al _{vι})	3 OH-μ ₂ -(Al _{vi} -Al _{vi})	3 OH-μ ₂ -(Al _{vi} -Al _{vi})	3 OH-μ ₂ -(Al _{vi} -Al _{vi})	
1 OH-µ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	4 OH-μ ₂ -(Al _{vi} -Al _{vi})				
6 Alvi-oh	5 Alvi-oh	4 Al _{VI-Oh}	4 Alvı-oh	4 Al _{VI-Oh}	
2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}	2 Al _{IV-Td}	
	1 Alv-SBP	2 Alv-SP	2 Alv-SP	2 Alv-SP	
		(1 1 1)D2			
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K	
Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁶ bar	
θ = 14.8 OH nm ⁻²	θ = 12.2 OH nm ⁻²	θ = 9.8 OH nm ⁻²	θ = 7.3 OH nm ⁻²	θ = 7.3 OH nm ⁻²	
1 OH-μ1-(Al _{IV})	1 OH-μ ₁ -(Al _{IV})	1 OH-μ1-(Al _{IV})	1 OH-μ1-(Al _{IV})	1 OH-μ1-(Al _{IV})	
2 OH-μ ₁ -(Al _{vi})	1 OH-μ ₁ -(Al _{vi})	1 OH-μ ₂ -(Al _{ιv} -Al _v)	2 OH-μ ₂ -(Al _{IV} -Al _{VI})	2 OH-μ ₂ -(Al _{IV} -Al _{VI})	
3 OH-μ ₂ -(Al _{IV} -Al _{VI})	2 OH-µ2-(Al _{IV} -Al _{VI})	2 OH-μ ₂ -(Al _v -Al _{vI})	4 OH-μ ₂ -(Al _v -Al _{vI})	4 OH-μ ₂ -(Al _V -Al _{VI})	
5 OH-μ2-(Al _{VI} -Al _{VI})	1 OH-μ2-(Al _{IV} -Al _V)	3 OH-μ2-(Al _{VI} -Al _{VI})			
1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	5 OH-μ ₂ -(Al _{vi} -Al _{vi})				
6 Al _{VI-Oh}	5 Al _{VI-Oh}	4 Al _{VI-Oh}	4 Al _{VI-Oh}	2 Al _{VI-Oh}	
2 Alıv-Td	2 Al _{IV-Td}	2 Aliv-Td	2 Alıv-td	2 Alıv-Td	
	1 Alv-sp	2 Alv-SP	2 Alv-SP	4 Alv-sp	
		(1 1 1)P1_2			
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K	
P _{H2O} = 10 ⁻² bar	P _{H2O} = 10 ⁻² bar	Р _{н20} = 10 ⁻⁴ bar	P _{H2O} = 10 ⁻⁴ bar	P _{H2O} = 10 ⁻⁶ bar	
$\theta = 14.8 \text{ OH nm}^{-2}$	θ = 9.8 OH nm ⁻²	θ = 9.8 OH nm ⁻²	θ = 7.3 OH nm ⁻²	θ = 7.3 OH nm ⁻²	
9 OH-μ ₂ -(Al _{VI} -Al _{VI})	6 OH-μ ₂ -(Al _v -Al _{vi})	6 OH-μ ₂ -(Al _v -Al _{vι})	2 OH-µ2-(Alv-Alv)	2 OH-µ2-(Al _V -Al _V)	
3 OH-μ ₃ -(Al _{vi} -Al _{vi} -Al _{vi})	1 OH-μ2-(Al _{VI} -Al _{VI})	1 OH-μ2-(Al _{VI} -Al _{VI})	4 OH-μ2-(Al _V -Al _{VI})	4 OH-μ ₂ -(Al _V -Al _{VI})	
	1 OH-µ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})	1 OH-μ ₃ -(Al _{VI} -Al _{VI} -Al _{VI})			
9 Al _{VI-Oh}	5 Al _{VI-Oh}	5 Al _{VI-Oh}	3 Al _{VI-Oh}	3 Al _{VI-Oh}	
	4 Alv-sp	4 Alv-sp	6 Alv-sp	6 Alv-sp	
(0 0 1)					
T = 400K	T = 700K	T = 700K	T = 800K	T = 800K	
Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻² bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁴ bar	Р _{н20} = 10 ⁻⁶ bar	
$\theta = 13.0 \text{ OH nm}^{-2}$	$\theta = 0 \text{ OH nm}^{-2}$	$\theta = 0 \text{ OH nm}^{-2}$	$\theta = 0 \text{ OH nm}^{-2}$	$\theta = 0 \text{ OH nm}^{-2}$	
2 OH-u1-(Alvi)					
1 OH-µ ₂ -(Al _{IV} -Al _V)					
1 OH-µ2-(Al _V -Al _{VI})					
1 OH ₂ -μ ₁ -(Al _{VI})					
3 Alvi-Oh	4 Alv-sp	4 Alv-sp	4 Al _{V-SP}	4 Alv-sp	
1 Al _{V-SBBP}					

Table S6: Inventory of the Lewis and Bronsted acid sites present on the most stable surface models. Note: The first index after an AI atom is its coordination number and the second its VSEPR geometry (Oh: Octahedral, Td: Tetrahedral, Ss: Seesaw, SP: Square pyramidal)

References

- X. Krokidis, P. Raybaud, A.E. Gobichon, B. Rebours, P. Euzen, H. Toulhoat, J. Phys. Chem. B 105 (2001) 5121.
 M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 211 (2002) 1.
- [3] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 226 (2004) 54.