Supporting Information

Beyond γ -Al₂O₃ Crystallite Surfaces: the Hidden Features of Edges Revealed by Solid-State ¹H

NMR and DFT Calculations

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S1. Alumina samples characterization

X-ray diffraction was performed on a PANalytical X'Pert Pro diffractometer with a copper anode (K α =0.15402 nm) and a X'célérator detector, scanning an angle range of 5 to 72° 2 θ (Figure S1).



Figure S1. XRD diffractrogams of P-egg and T-flat (red-P-egg; black-T-flat; blue- γ -Al₂O₃ reference ICDD n° 00-010-0425).

 N_2 physisorption was done using a Micromeritics ASAP 2420 equipment, samples were pre-treated at 350°C for 3h under vacuum.

Hg porosimetry was done using a Micromeritics Autopore IV equipment, samples were pre-treated at 250°C for 3h. The corresponding results, BET surface, mesoporous volume and mesopore diameter evaluated at half the mesoporous volume, are reported in Table S1.

Table S1. Properties of P-egg and T-flat aluminas given by N₂ physisorption and Hg porosimetry.

	\mathbf{S}_{BET}	D _{Vmeso/2}	V _{meso}
	(m^2g^{-1})	(nm)	(mL/g)
P-egg	183±9	9.8±0.2	0.49±0.02
T-flat	149±7	15.1±0.3	0.60±0.03

High resolution Transmission Electron Microscopy (HR-TEM) images in Bright field mode and nanobeam electron diffraction patterns were acquired on a JEOL JEM 2100F microscope.

For the P-egg sample (Figure S2), the following crystallite dimensions (from about 30 measurements) were measured:

-Length between 4 and 16 nm (average 12.5 nm)

-Width between 4 and 11 nm (average 6 nm)

-Thickness approximately between 4 and 6 nm



Figure S2. a) and b) TEM images of P-egg alumina (scale: 20 nm), c) scheme of possible crystallite morphology.

For the T-flat sample (Figure S3), the following crystallite dimensions (from about 30 measurements)

were measured:

-Length between 7 and 27 nm (average 14.5 nm)

-Width between 5 and 16 nm (average 9 nm)

-Thickness approximately between 3 and 5 nm



Figure S3. TEM images of T-flat alumina (scale: a) 50 nm; b) 20 nm), and c) scheme of possible crystallite morphology.



Figure S4. Plane indexation of the illustrated crystallites (b) and c) performed by a) Fourier transform indexation from a HR-TEM image for P-egg sample (b) and by c) nanobeam electron diffraction pattern indexation for T-flat sample (d).

¹H NMR spectral deconvolution was done using DMFit[1] as illustrated in Figure S4. The results are reported in Table S2.

Samples with $0.5\%_{w/w}$ Cl were subjected to a thermal treatment at 500°C using a humid air flow after calcination to tune the chlorine content. All samples were treated under H₂ for 2h at 500°C prior to NMR acquisition.



Figure S5. Relative peak intensity contributions obtained from fitting the ¹H DEPTH spectra of both alumina samples without chlorine, blue – experimental spectrum, red – best fitted model. Note that for P-egg samples the central signals were fitted using two Gaussians while for T-flat samples only one Gaussian was used.



Figure S6. ¹H MAS NMR spectra (800 MHz, MAS 30 kHz) of a) P-egg, P-egg – 0.5%Cl and P-egg – 1.4%Cl samples and of b) T-flat, T-flat – 0.5%Cl and T-flat – 1.4%Cl samples.

Table S2. Relative peak intensity contributions obtained from fitting the ¹H DEPTH spectra. Note that these values have an estimated uncertainty of 10%; which is largely due to the impact of manual baseline correction. This impact is particularly relevant for signals above 5 ppm. Values below 5% are not precise.

P	-egg	P-egg -	- 0.5%Cl	P-egg	-1.4%Cl	Т	-flat	T-flat	– 0.5%Cl	T-flat	– 1.4%Cl
	Fit								Fit		
δ ¹ H	Int. %	δ ¹ H	Int. %	δ ¹ H	Int. %	δ ¹ H	Int. %	δ ¹ H	Int. %	δ ¹ H	Int. %
-0.1	12	-0.04	3		-	-0.4	4	-0.3	1	-0.3	0.1
1.6	56	1.5	64	1.7	46	1.2	48	1.4	51	1.5	40
2.2	5	2.1	3	2.3	22	3.8	15	3.7	17	3.5	44
3.7	19	3.6	23	3.9	25	5.7	33	6.0	31	6.9	17
6.8	8	6.2	7	7.1	7		•				

For T-flat, the intensity decrease for $\delta > 5$ ppm is caused by the loss of H-bond donor species. This implies that the number of μ_1 -OH edge sites on the T-flat crystallites do not enable the exchange of all Cl atoms at 1.4%Cl, which is supported by the T-flat – 0.5%Cl sample (Table S2). Hence, some (110) surface μ_1 -OH are the next favourable sites to be exchanged (-28 to -16 kJ.mol⁻¹) at 1.4%Cl. With chlorine atoms in place of formally H-bonded hydroxyls, the H-bond network on the T-flat alumina surface is partially broken.[2] Some formally H-bond donor species may become free or H-bond acceptors. This effect is revealed in the increase in intensity of the 3-5 ppm region and of the shoulder at 1.7 ppm. By contrast, the number of edge sites of the P-egg crystallites seems to be high enough to be exchanged with 1.4%Cl since the spectral regions at $\delta > 3$ ppm are weakly disturbed.

Table S3. Total proton signal from spectral integration (range: 12 to -5 ppm), corrected for number of scans, receiver gain and mass and normalized to the highest value of the list (T-flat - 1.4%Cl). An uncertainty of 10%, due to the impact of manual baseline correction, must be considered.

	Spectra integral (normalized)
P-egg	0.6
P-egg - 1.4%Cl	0.5
T-flat	1.0
T-flat - 1.4%Cl	1.0

Table S3 indicates that the total signal for T-flat is double that of P-egg. As the aluminas have distinct morphologies, they also have different proportions of exposed surfaces which have differing hydration degrees at a given T,P condition. Indeed, as the electron diffraction study suggests, TH100 seems to present a larger proportion of (111) surface, which is highly hydrated (see below). It is also observed that there is no impact of chlorine doping on the total signal as the loading used is quite small.

S2. DFT calculations

Structures were re-optimized using PBE-dDsC exchange correlation functional[3,4] and PAW pseudopotentials[5] with an energy cut off of 400 eV using the VASP code[6,7].

S2.1. DFT alumina surface models

The models used were taken from Digne et al.[8] and were re-optimized without major changes (except for the (110) surface, see below). The adsorbed water and the two upper atomic layers of the slab were allowed to relax for the (100) and (110) surface models, the full slab was relaxed for the (111) surface model. without major changes. With the exception of the (111) surface, the "slab" models used correspond to 2x2 supercells with respect to Digne's unit cells (Figure S7). The (100) surface model used in the present study consists of a triperiodic cell, the size of which is $16.8 \times 11.1 \times 28.0$ Å³, occupied by a 6.0 Å wide alumina slab surmounted by a 22 Å wide vacuum slab. The (110) surface model is $16.1 \times 16.8 \times 28.0$ Å³ wide, occupied by a 6.0 Å thick alumina slab, surmounted by a 22 Å wide vacuum slab. The (111) surface model is identical to that of Digne[8] with a 9.7 x 8.4 x 21.5 Å³ wide cell occupied by a symmetric slab (hydroxylated on both sides) with a vacuum thickness of 12Å.



Figure S7. Example of (110) 3.0 OH/nm² surface slab in which Digne's unit is highlighted by the black square and is repeated four times (2 by 2).

(110) surface

The surface reconstruction proposed by Wischert et al.[9] is here present for the surfaces at an OH coverage of 9.0 and 12.0 OH/nm².

Table S4. (110) models used, color coded as red-oxygen; purple-aluminium; white-hydrogen. Blue traced lines indicate hydrogen-bonds (bond length's threshold of 2.5 Å). Hydroxyls and adsorbed water identified by numbers and letters in each model, blue - μ_1 -OH; green - μ_2 -OH; orange - μ_3 -OH; grey - adsorbed water. Black square indicates Digne's surface unit.



12.0 OH/nm²

17.7 OH/nm²



(100) surface

Table S5. (100) models, colour coded as red-oxygen; purple-aluminium; white-hydrogen. Blue traced lines indicate hydrogen-bonds (bond length's threshold of 2.5Å). Hydroxyls and adsorbed water identified by numbers and letters in each model, blue - μ_1 -OH; green - μ_2 -OH; orange - μ_3 -OH; grey - adsorbed water. Black square indicates Digne's surface unit.



(111) surface

Table S6. (111) models, colour coded as red-oxygen; purple-aluminium; white-hydrogen. Blue traced lines indicate hydrogen-bonds (bond length's threshold of 2.5Å). Hydroxyls and adsorbed water identified by numbers and letters in each model, blue - μ_1 -OH; green - μ_2 -OH; orange - μ_3 -OH; grey - adsorbed water. Black square indicates Digne's surface unit.

12.3 OH/nm²



Thermodynamic diagrams

The hydration state of each surface that would most likely correspond to that of our alumina samples after thermal treatment at 773.15 K was estimated thanks to thermodynamic calculations (without vibrational components, similar to ref.[8]. In Figure S8 are represented diagrams of water adsorption energy as a function of hydroxyl coverage and temperature for two given water pressure values (10⁻⁴ and 10⁻⁶ bar) considered representative of experimental conditions (thermal treatment at 500°C). For each surface, the most stable hydrated model in the 700-800 K temperature range was chosen as representative of the hydration state of our samples.



Figure S8. Water adsorption energy as a function of hydroxyl coverage and temperature for $P(H_2O)=10^{-4}$ and 10^{-6} bar for a) (110), b) (100) and c) (111) surface models.

S2.2. DFT alumina edge models

The (110)-(100) edge model was constructed as a nano-rod (Figure S9).



Figure S9. a) Representation of the (110)-(100) nano-rod and b) detailed view of all rod sides: top (110) surface, side (100) surface and view perpendicular to edges.

Table S7. Hydrated (110)-(100) edge model with one water molecule adsorbed colour coded as redoxygen; purple-aluminium; white-hydrogen. Blue traced lines indicate hydrogen-bonds (bond length's threshold of 2.5Å). Hydroxyls and adsorbed water identified by numbers and letters in each model, blue - μ_1 -OH; green - μ_2 -OH; orange - μ_3 -OH; grey - adsorbed water.



Table S8. Hydrated (110)-(100) edge model with six water molecules adsorbed colour coded as redoxygen; purple-aluminium; white-hydrogen. Blue traced lines indicate hydrogen-bonds (bond length's threshold of 2.5Å). Hydroxyls and adsorbed water identified by numbers and letters in each model, blue - μ_1 -OH; green - μ_2 -OH; orange - μ_3 -OH; grey - adsorbed water.

(110)-(100) edge					
6H2O					
View perpendicular to edge					
Top (110) surface view					



Figure S10. Water adsorption energy as a function of adsorbed water molecules per unit cell of simulation and temperature for $P(H_2O)=10^{-4}$ and 10^{-6} bar for the (110)-(100) edge model.

S2.3. Chemical shift calculation results

Chemical shifts were calculated by periodic DFT, with the linear response approach[10,11] as implemented in VASP. The step size for the finite difference k-space derivative was set to 0.003. First order of the finite difference stencil was used to calculate the magnetic susceptibility. The calculations were performed at the gamma point for (110) and (100) models, and the k-points mesh was set to 1x3x3 for (111) models and to 1x2x1 for edge models (tests were performed with denser grids and show no significant deviation with a tolerance of less than 0.1 ppm). Also, the calculations were performed at various energy cutoff (400, 500, 600 and 700 eV), and for hydrogen-bond acceptors and isolated OH groups, the deviation was lower than 0.2 ppm. Finally, we also tested the influence of the exchange correlation functional on some relevant cases and found that with a cutoff of 400 eV, the proton chemical shifts differ by less than 0.3 ppm when using optPBE-vdW (most adapted for [12])with respect to the ones obtained with the PBE dDsC functional.

	(110) surface						
			3.0 OH/nm ²				
		Hydroxyl	δ^{1} H (nnm)				
#	μ _x	HO-Al _n	H-bond type				
1	μ1	Al _{IV}	Donor	1.5			
2	μ ₂	Al _{IV} ; Al _{IV}	Donor	10.7			
		I	6.0 OH/nm ²	I			
1	μ1	Al_{IV}	Donor/acceptor	1.7			
2	μ ₂	Al _{IV} ; Al _V	Donor	15.2			
3	H ₂ Oa	Δ1	Donor	8.0			
4	H ₂ Ob	Aiv	Donor	11.0			
	9.0 OH/nm ²						
1	μ1	Al_{IV}	Donor	2.7			
2	μ1	Al _{IV}	Donor/acceptor	3.4			
3	μ ₂	Al _V ; Al _V	Free	2.1			
4	μ ₂	Al _{VI} ; Al _{VI}	Donor	5.4			
5	μ ₂	Al _{IV} ; Al _V	Donor	11.0			
6	μ ₃	$Al_V; Al_V; Al_{VI}$	Donor	9.6			
	12.0 OH/nm ²						
1	μ1	Al _{IV}	Donor/acceptor	2.8			
2	μ1	Al_{IV}	Donor/acceptor	3.1			
3	μ ₂	Al _v ; Al _{vI}	Free	2.0			
4	μ ₂	$Al_{IV}; Al_{V}$	Donor/acceptor	7.0			
5	μ ₂	Al _{IV} ; Al _V	Donor	9.2			

Table S9. Calculated proton chemical shifts for (110) surface models at five hydration degrees.

6	μ3	$Al_V; Al_{VI}; Al_{VI}$	Donor	7.9				
a	H ₂ Oa	Alvı	Donor	7.5				
b	H ₂ Ob		Donor	9.6				
	17.7 OH/nm ²							
1	μ1	Al _{VI}	Acceptor	0.7				
2	μ_1	Al_{VI}	Acceptor	1.6				
3	μ_1	Al_IV	Donor/acceptor	2.2				
4	μ_1	Al_V	Donor/acceptor	3.0				
5	μ_1	Al_{VI}	Donor/acceptor	3.3				
6	μ ₂	Al _{VI} ; Al _{VI}	Free	1.5				
7	μ ₂	Al _{IV} ; Al _{VI}	Donor/acceptor	7.7				
8	μ ₂	Al _v ; Al _v	Donor/acceptor	7.8				
9	μ ₂	Al _{IV} ; Al _{VI}	Donor	11.8				
10	μ3	$Al_V; Al_{VI}; Al_{VI}$	Donor	9.4				
11	μ3	Al _{VI} ; Al _{VI} ; Al _{VI}	Donor	11.3				
12	μ3	Al _{VI} ; Al _{VI} ; Al _{VI}	Donor	11.7				

	(100) surface						
			4.3 OH/nm ²				
		Hydroxyl	δ ¹ H (nnm)				
#	μ _x	HO-Al _n	H-bond type				
1	μ1	Al _{VI}	Acceptor	0.7			
2	μ ₂	Al _v ;Al _v	Donor	10.7			
			8.6 OH/nm ²				
1	μ1	Al _{VI}	Acceptor	1.2			
2	μ2	Al _v ; Al _{vI}	Donor	5.8			
a	H ₂ Oa	Δ1	Free	0.8			
b	H ₂ Ob	Αιγι	Donor	15.5			
	13.0 OH/nm ²						
1	μ1	Al_V	Acceptor	0.8			
2	μ1	Al_V	Acceptor	1.8			
3	μ2	Al _v ; Al _{vI}	Donor	8.1			
4	μ2	Al _{IV} ; Al _V	Donor	9.9			
a	H ₂ Oa	A.1	Donor	9.5			
b	H ₂ Ob	Αιγι	Donor	11.0			
			17.2 OH/nm ²				
1	μ1	Al_V	Donor/acceptor	1.6			
2	μ1	Al _{VI}	Donor/acceptor	4.2			
3	μ ₂	Al _{IV} ; Al _V	Donor/acceptor	8.6			
4	μ3	Al _{VI} ; Al _{VI} ; Al _V	Donor	6.2			
a	H ₂ Oa	Al_V	Free	2.0			

Table S10. Calculated proton chemical shifts for (100) surface models at four hydration degrees.

b	H ₂ Ob		Donor	12.8
с	H ₂ Oc	Al _{VI}	Free	2.4
d	H ₂ Od		Donor	16.2

Table S11. Calculated proton chemical shifts for (111) surface models at two hydration degrees.

	(111) surface					
			9.8 OH/nm²			
		Hydroxy	δ ¹ μ (nnm)			
#	μ _x	HO-Al _n	H-bond type	o n (ppm)		
1	μ1	Al _V	Donor/acceptor	5.5		
2	μ ₂	Al _{VI} ; Al _{VI}	Acceptor	0.6		
3	μ ₂	Al _V ; Al _{VI}	Acceptor	0.9		
4	μ ₂	Al _{IV} ; Al _{VI}	Free	1.4		
5	μ ₂	Al _{IV} ; Al _{VI}	Free	2.1		
6	μ ₂	Al _V ; Al _{VI}	Donor	6.3		
7	μ ₂	Al _v ; Al _{vI}	Donor	6.5		
8	μ ₂	Al _v ; Al _{vI}	Donor	6.2		
		I	12.3 OH/nm ²			
1	μ_1	Al _{VI}	Acceptor	0.4		
2	μ_1	Al _{IV}	Donor/acceptor	3.6		
3	μ ₂	Al _{VI} ; Al _{VI}	Acceptor	0.5		
4	μ ₂	Al _{VI} ; Al _{VI}	Acceptor	0.5		
5	μ ₂	Al _{IV} ; Al _{VI}	Free	1.6		
6	μ ₂	$Al_{IV}; Al_{VI}$	Donor	10.2		
7	μ ₂	Al _v ; Al _{vI}	Free	2.8		

8	μ ₂	Al _{VI} ; Al _{VI}	Donor	5.4
9	μ ₂	Al _{VI} ; Al _{VI}	Donor	6.3
10	μ ₂	Al _{IV} ; Al _{VI}	Donor	9.1

	(110)-(100) edge							
			1H ₂ O					
		Hydroxy	$\delta^{1}\mathbf{H}(\mathbf{nnm})$					
#	μ _x	HO-Al _n	H-bond type	o II (ppm)				
1	μ1	Al _{IV}	Free	-0.1				
2	μ ₂	$Al_V; Al_V$	Free	2.5				
	6H ₂ O							
1	μ1	Al _{IV}	Free	0.6				
2	μ1	Al _{IV}	Free	0.9				
3	μ1	Al _{IV}	Donor/acceptor	3.1				
4	μ1	Al _{IV}	Donor/acceptor	5.7				
5	μ ₂	$Al_V; Al_V$	Free	2.1				
6	μ ₂	Al _V ; Al _V	Free	2.4				
7	μ ₂	Al _{IV} ; Al _V	Donor	10.0				
8	μ ₂	Al _V ; Al _V	Free	2.3				
9	μ ₂	Al _{IV} ; Al _V	Donor	7.1				
10	μ ₂	Al _{IV} ; Al _V	Donor	8.2				
11	μ ₂	Al _{VI} ; Al _{VI}	Donor	3.3				
12	μ ₃	Al _v ; Al _{vI}	Donor	14.2				

Table S12. Calculated proton chemical shifts for (110)-(100) edge models at two hydration degrees.



Figure S11. Correlation between length of hydroxyl O-H bond and ¹H chemical shift for H-bond donor surface hydroxyls represented as blue- μ_1 -OH, green- μ_2 -OH and orange μ_3 -OH and squares – (110) 3.0 OH/nm²; lozenges – (110) 9.0 OH/nm²; circles – (111) 12.3 OH/nm².



Figure S12. Correlation between H-bond length and ¹H chemical shift for H-bond donor surface hydroxyls blue- μ_1 -OH, green- μ_2 -OH and orange μ_3 -OH and squares – (110) 3.0 OH/nm²; lozenges – (110) 9.0 OH/nm²; circles – (111) 12.3 OH/nm².

S2.5. Substitution of hydroxyl groups by chlorine

In order to find the most stable location of chlorine on each surface or edge model of interest, the exchange energy of each given hydroxyl with a Cl atom (as illustrated in Figure S13) was calculated as Equation S2

Equation S2.
$$\Delta E_{exch} = E(-Al_n(Cl)) + E(H_2O) - E(-Al_n(OH)) - E(HCl)$$

assuming this exchange follows Equation S3

Equation S3. -Al_n(OH)- + HCl
$$\rightarrow$$
 -Al_n'(HCl)- + H₂O

as in Digne et al.[13] For the (110)-(100) edge $6H_2O$ model, both Al-edge μ_1 -OH (#1 and #2) have been simultaneously exchanged with chlorine.



Figure S13. Top view of (110)-(100) edge 6H2O were edge μ_1 -OH (labelled #1) was exchanged with chlorine.

Table S13. Exchange energy of the given indicated hydroxyl with a chlorine atom for surface hydroxyls.

#	μ _x	$\Delta E_{exch} (kJ mol^{-1})$					
(110) 3.0 OH/nm ²							
1	μ_1	-28					
2	μ ₂	77					
(110) 12.0 OH/nm ²							
1	μ_1	-16					
2	μ_1	-2					
3	μ_2	5					
4	μ ₂	50					
5	μ ₂	127					
6	μ3	140					
(111) 12.3 OH/nm ²							
1	μ_1	-3					
2	μ_1	-4					
3	μ ₂	52					
4	μ ₂	21					
5	μ ₂	42					
6	μ_2	99					
7	μ_2	56					
8	μ ₂	66					
9	μ ₂	68					
10	μ_2	46					

Table S14. Exchange energy of the given indicated hydroxyl with a chlorine atom for edge hydroxyls.

#	μ _x	ΔE _{exch} (kJ mol ⁻¹)				
(110)-(100) edge 1H ₂ O						
1	μ_1	-38				
2	μ ₂	19				
(110)-(100) edge 6H ₂ O						
1	μ_1	-31				
2	μ_1	-26				
3	μ1	-9				
4	μ_1	1				
5	μ ₂	12				
6	μ ₂	27				
7	μ ₂	139				
8	μ ₂	23				
9	μ ₂	39				
10	μ ₂	55				
11	μ ₂	26				
12	μ3	149				
1 and 2	both μ_1	-58				

Table S15. Calculated proton chemical shifts for (110) 9.00 H/nm² surface model having exchanged the most favourable μ_1 -OH with Cl and for (110)-(100) edge 6H₂O model having exchanged the two edge μ_1 -OH with Cl.

	(110) surface						
9.0 OH/nm ²							
Hydroxyl		δ^{1} H (ppm)					
#	μ _x	H-bond type	-	With Cl			
1	μ_1	Donor	2.7	-			
2	μ1	Donor/acceptor	3.4	2.3			
3	μ ₂	Free	2.1	2.0			
4	μ2	Donor	5.4	5.3			
5	μ2	Donor	11.0	11.0			
6	μ3	Donor	9.6	9.6			
	(110)-(100) edge						
		6	H ₂ O				
	Hydroxyl		δ ¹ H (ppm)				
#	μ _x	H-bond type	-	With Cl			
1	μ_1	Free	0.6	-			
2	μ_1	Free	0.9	-			
3	μ_1	Donor/acceptor	3.1	3.1			
4	μ1	Donor/acceptor	5.7	5.9			
5	μ ₂	Free	2.1	2.1			
6	μ ₂	Free	2.4	2.4			
7	μ2	Donor	10.0	10.0			
8	μ ₂	Free	2.3	2.2			

9	μ ₂	Donor	7.1	7.2
10	μ ₂	Donor	8.2	8.1
11	μ ₂	Donor	3.3	3.1
12	μ ₃	Donor	14.2	14.8

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