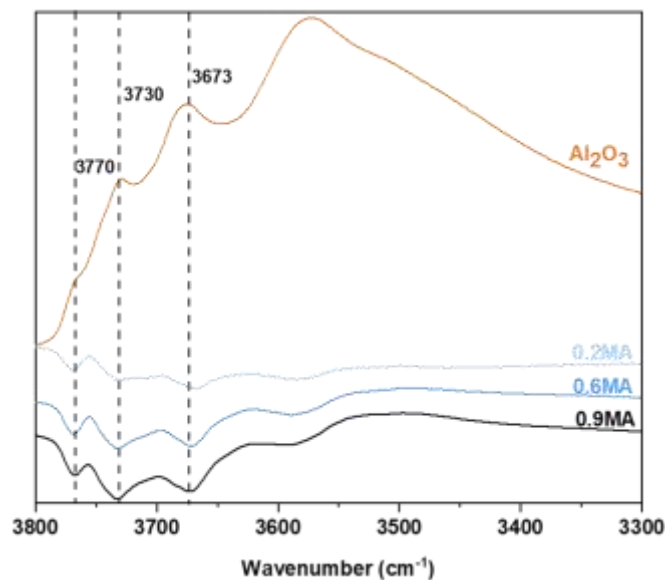


1 **Malonate speciation at γ -alumina surface using surface complex**
 2 **modelling based on a multi-technique characterization approach**
 3 Teddy Roy, Manuel Corral Valero, Thibaut Corre, Olivier Delpoux, Gerhard Pirngruber, Grégory Lefèvre

4 **SUPPORTING INFORMATION**
 5
 6



7
 8 **Figure S1 : Transmission FT-IR difference spectra between γ -Al₂O₃ and alumina impregnated with malonic acid at different**
 9 **content (from 0.2 to 0.9 at/nm²) after activation at 120°C under vacuum (10⁻⁵ mbar), OH stretching region.**

10
 11
 12
 13 **Table S1: Characteristics of γ -Al₂O₃ Surface -OH groups at water coverage of 0.17 and 0.18 OH/nm² for the (100) and (110)**
 14 **orientations¹**

OH site	Al involved	Surface density (nm ⁻²)	
		(100)	(110)
H ₂ O	Al _{VI}	2.17	4.48
μ_1	Al _{VI}	2.17	1.49
μ_1	Al _{IV}	0	1.49
μ_2	Al _{VI} and Al _{IV}	1.09	2.98
μ_2	Only Al _{VI}	0	1.49
μ_3	Only Al _{VI}	1.09	1.49

15

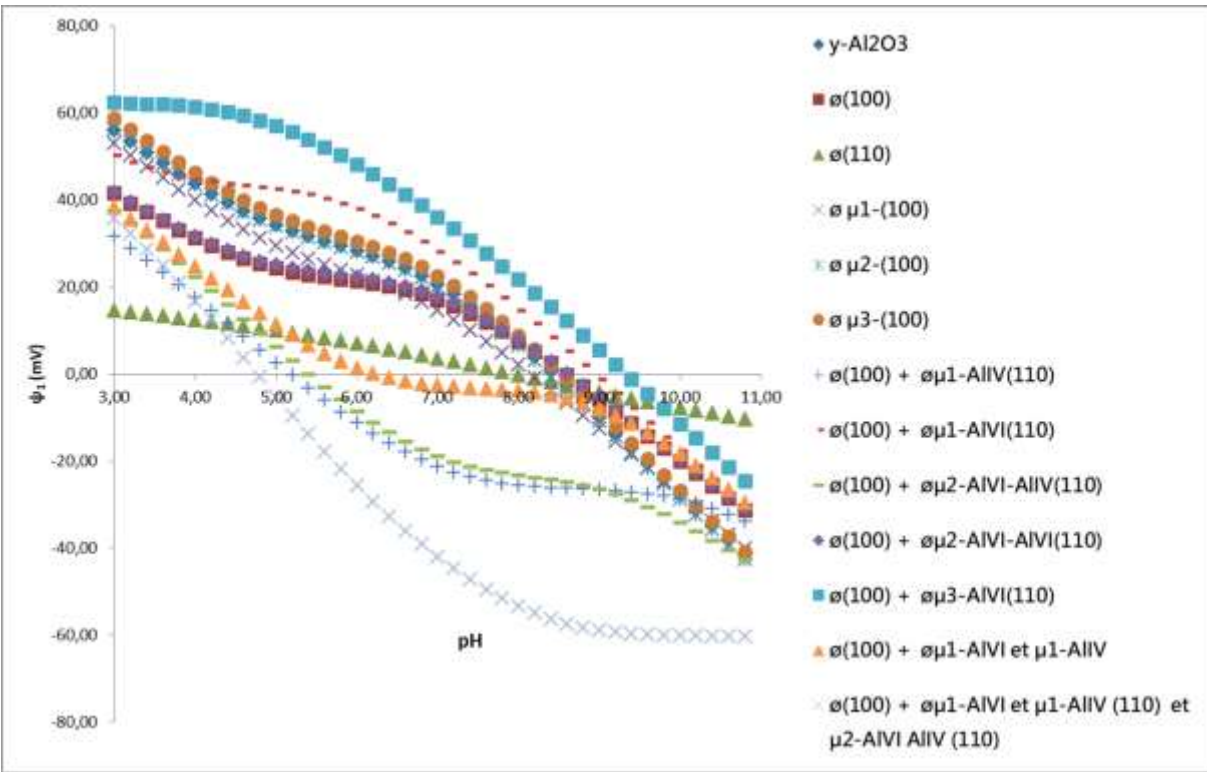
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18 **Table S2: Calculation of Protonation Constants Using AIMD Simulations To Determine the Number of H Bonds around**
 19 **Oxygen Atoms in Hydroxyl Groups (a + d) and the number of H bonds around their respective protons (p)¹**

OH site	Al involved	Protonation reaction	Log K	Nb of H bonds with the proton
Surface (100)				
μ_1	Al _{VI}	$\mu_1\text{OH}^{-0.5} + \text{H}^+ \rightleftharpoons \mu_1\text{OH}_2^{+0.5}$	8.16	0.86
μ_2	Al _{VI} - Al _{IV}	$\mu_2\text{O}^{-0.75} + \text{H}^+ \rightleftharpoons \mu_2\text{OH}^{+0.25}$	10.32	n.a.
μ_3	Al _{VI}	$\mu_3\text{O}^{-0.5} + \text{H}^+ \rightleftharpoons \mu_3\text{OH}^{+0.5}$	5.94	n.a.
Surface (110)				
μ_1	Al _{IV}	$\mu_1\text{OH}^{-0.25} + \text{H}^+ \rightleftharpoons \mu_1\text{OH}_2^{+0.75}$	0.12	0.75
μ_1	Al _{IV}	$\mu_1\text{O}^{-1.25} + \text{H}^+ \rightleftharpoons \mu_1\text{OH}^{-0.25}$	12.97	n.a.
μ_1	Al _{VI}	$\mu_1\text{OH}^{-0.5} + \text{H}^+ \rightleftharpoons \mu_1\text{OH}_2^{+0.5}$	9.16	0.95
μ_2	Al _{VI} - Al _{IV}	$\mu_2\text{O}^{-0.75} + \text{H}^+ \rightleftharpoons \mu_2\text{OH}^{+0.25}$	10.45	n.a.
μ_2	Al _{VI} - Al _{VI}	$\mu_2\text{OH}^0 + \text{H}^+ \rightleftharpoons \mu_2\text{OH}_2^{+1}$	0.29	0.57
μ_2	Al _{VI} - Al _{VI}	$\mu_2\text{O}^{-1} + \text{H}^+ \rightleftharpoons \mu_2\text{OH}^0$	13.86	n.a.
μ_3	Al _{VI}	$\mu_3\text{O}^{-0.5} + \text{H}^+ \rightleftharpoons \mu_3\text{OH}^{+0.5}$	4.75	n.a.

20



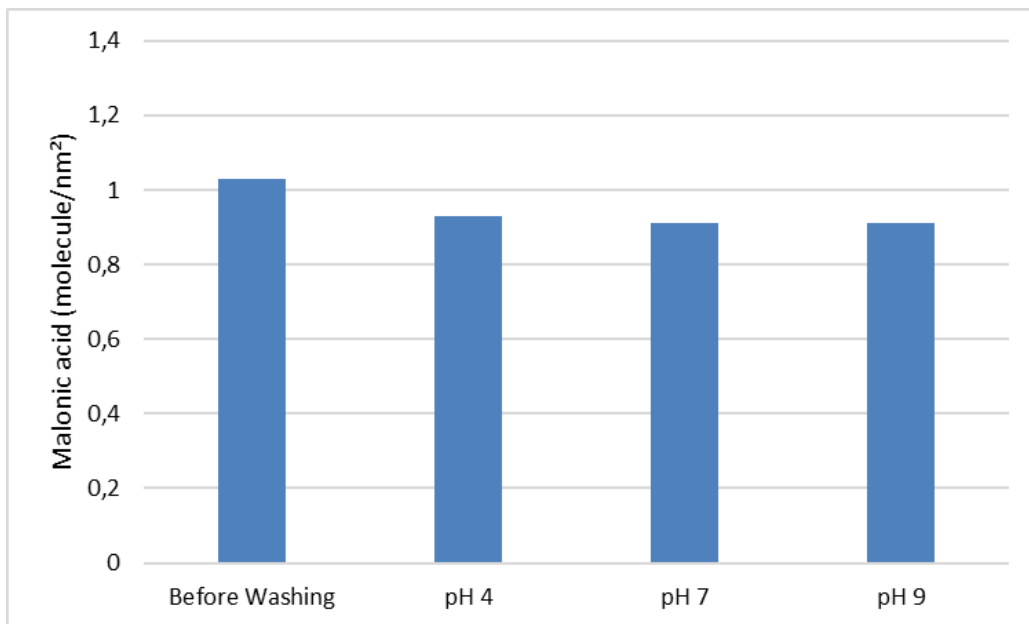
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Figure S2: PHREEQC simulations of the ψ_1 evolution as a function of pH for different scenarios after surface sites removal of the $\gamma\text{-Al}_2\text{O}_3$ model (\emptyset = removal of sites of this face)

24



25

26

Figure S31 : Malonic acid content (molecule/nm²) obtained after a washing stage at different pH

27

28 PHREEQC Script

```

29
30 TITLE CD-MUSIC alumina_Malonic_acid
31
32 PHASES
33 Fix_H+
34     H+ = H+
35     log_k    0
36 SURFACE_MASTER_SPECIES
37 Alo_b Alo_bO-1.5
38 Alo_c Alo_cO-0.75
39 Alo_e Alo_eO-0.5
40
41 Alp_a Alp_aO-1.25
42 Alp_b Alp_bO-1.5
43 Alp_c Alp_cO-0.75
44 Alp_d Alp_dO-1
45 Alp_e Alp_eO-0.5
46
47 SURFACE_SPECIES
48     # face (100)
49
50 Alo_bO-1.5 = Alo_bO-1.5
51 log_k 0
52 -cd_music 0 0 0
53
54 Alo_bO-1.5 + Na+ = Alo_bONa-0.5
55 log_k -0.096
56 -cd_music 0 0 1
57
58 Alo_bO-1.5 + H+ = Alo_bOH-0.5
59 -cd_music 1 0 0
60 log_k 20.6
61
62 Alo_bOH-0.5 + Na+ = Alo_bOHNa+0.5
63 log_k -0.096
64 -cd_music 0 0 1
65
66 Alo_bOH-0.5 + H+ = Alo_bOH2+0.5
67 -cd_music 1 0 0
68 log_k 8.16 #8.72
69
70 Alo_bOH2+0.5 + Cl- = Alo_bOH2Cl-0.5
71 log_k -0.176
72 -cd_music 0 0 -1
73
74 Alo_cO-0.75 = Alo_cO-0.75
75 log_k 0
76 -cd_music 0 0 0
77
78 Alo_cO-0.75 + Na+ = Alo_cONa+0.25
79 log_k -0.096
80 -cd_music 0 0 1

```

```
81
82 Alo_cO-0.75 + H+ = Alo_cOH+0.25
83 -cd_music 1 0 0
84 log_k 10.32
85
86 Alo_cOH+0.25 + Cl- = Alo_cOHCl-0.75
87 log_k -0.176
88 -cd_music 0 0 -1
89
90 Alo_cOH+0.25 + H+ = Alo_cOH2+1.25
91 -cd_music 1 0 0
92 log_k -2.64 #-1.56
93
94
95 Alo_cOH2+1.25 + Cl- = Alo_cOH2Cl+0.25
96 log_k -0.176
97 -cd_music 0 0 -1
98
99 Alo_eO-0.5 = Alo_eO-0.5
100 log_k 0
101 -cd_music 0 0 0
102
103 Alo_eO-0.5 + Na+ = Alo_eONa+0.5
104 log_k -0.096
105 -cd_music 0 0 1
106
107 Alo_eO-0.5 + H+ = Alo_eOH+0.5
108 -cd_music 1 0 0
109 log_k 5.94
110
111 Alo_eOH+0.5 + Cl- = Alo_eOHCl-0.5
112 log_k -0.176
113 -cd_music 0 0 -1
114
115 Alo_eOH+0.5 + H+ = Alo_eOH2+1.5
116 -cd_music 1 0 0
117 log_k -9.84 #-5.94
118
119 Alo_eOH2+1.5 + Cl- = Alo_eOH2Cl+0.5
120 log_k -0.176
121 -cd_music 0 0 -1
122
123 # face (110)
124
125
126 Alp_aO-1.25 = Alp_aO-1.25
127 log_k 0
128 -cd_music 0 0 0
129
130 Alp_aO-1.25 + Na+ = Alp_aONa-0.25
131 log_k -0.096
132 -cd_music 0 0 1
133
134 Alp_aO-1.25 + H+ = Alp_aOH-0.25
```

135 -cd_music 1 0 0
136 log_k 12.97
137
138 $\text{Alp_aOH-0.25} + \text{Na}^+ = \text{Alp_aOHNa+0.75}$
139 log_k -0.096
140 -cd_music 0 0 1
141
142 $\text{Alp_aOH-0.25} + \text{H}^+ = \text{Alp_aOH2+0.75}$
143 -cd_music 1 0 0
144 log_k 0.12 #1.09
145
146 $\text{Alp_aOH2+0.75} + \text{Cl}^- = \text{Alp_aOH2Cl-0.25}$
147 log_k -0.176
148 -cd_music 0 0 -1
149
150 $\text{Alp_bO-1.5} = \text{Alp_bO-1.5}$
151 log_k 0
152 -cd_music 0 0 0
153
154 $\text{Alp_bO-1.5} + \text{Na}^+ = \text{Alp_bONa-0.5}$
155 log_k -0.096
156 -cd_music 0 0 1
157
158 $\text{Alp_bO-1.5} + \text{H}^+ = \text{Alp_bOH-0.5}$
159 -cd_music 1 0 0
160 log_k 21.22
161
162 $\text{Alp_bOH-0.5} + \text{Na}^+ = \text{Alp_bOHNa+0.5}$
163 log_k -0.096
164 -cd_music 0 0 1
165
166 $\text{Alp_bOH-0.5} + \text{H}^+ = \text{Alp_bOH2+0.5}$
167 -cd_music 1 0 0
168 log_k 9.16 #9.34
169
170 $\text{Alp_bOH2+0.5} + \text{Cl}^- = \text{Alp_bOH2Cl-0.5}$
171 log_k -0.176
172 -cd_music 0 0 -1
173
174 $\text{Alp_cO-0.75} = \text{Alp_cO-0.75}$
175 log_k 0
176 -cd_music 0 0 0
177
178 $\text{Alp_cO-0.75} + \text{Na}^+ = \text{Alp_cONa+0.25}$
179 log_k -0.096
180 -cd_music 0 0 1
181
182 $\text{Alp_cO-0.75} + \text{H}^+ = \text{Alp_cOH+0.25}$
183 -cd_music 1 0 0
184 log_k 10.45
185
186 $\text{Alp_cOH+0.25} + \text{Cl}^- = \text{Alp_cOHCl-0.75}$
187 log_k -0.176
188 -cd_music 0 0 -1

189
190 $\text{Alp_cOH}+0.25 + \text{H}^+ = \text{Alp_cOH}_2+1.25$
191 $-\text{cd_music } 1 \ 0 \ 0$
192 $\log_k -1.90 \ \#-1.43$
193
194 $\text{Alp_cOH}+0.25 + \text{Cl}^- = \text{Alp_cOHCl}-0.75$
195 $\log_k -0.176$
196 $-\text{cd_music } 0 \ 0 \ -1$
197
198 $\text{Alp_dO}-1 = \text{Alp_dO}-1$
199 $\log_k 0$
200 $-\text{cd_music } 0 \ 0 \ 0$
201
202 $\text{Alp_dO}-1 + \text{Na}^+ = \text{Alp_dONa}$
203 $\log_k -0.096$
204 $-\text{cd_music } 0 \ 0 \ 1$
205
206 $\text{Alp_dO}-1 + \text{H}^+ = \text{Alp_dOH}$
207 $-\text{cd_music } 1 \ 0 \ 0$
208 $\log_k 13.86$
209
210 $\text{Alp_dOH} + \text{H}^+ = \text{Alp_dOH}_2+1$
211 $-\text{cd_music } 1 \ 0 \ 0$
212 $\log_k 0.29 \ \#1.98$
213
214 $\text{Alp_dOH}_2+1 + \text{Cl}^- = \text{Alp_dOH}_2\text{Cl}$
215 $\log_k -0.176$
216 $-\text{cd_music } 0 \ 0 \ -1$
217
218 $\text{Alp_eO}-0.5 = \text{Alp_eO}-0.5$
219 $\log_k 0$
220 $-\text{cd_music } 0 \ 0 \ 0$
221
222 $\text{Alp_eO}-0.5 + \text{Na}^+ = \text{Alp_eONa}+0.5$
223 $\log_k -0.096$
224 $-\text{cd_music } 0 \ 0 \ 1$
225
226 $\text{Alp_eO}-0.5 + \text{H}^+ = \text{Alp_eOH}+0.5$
227 $-\text{cd_music } 1 \ 0 \ 0$
228 $\log_k 4.75$
229
230 $\text{Alp_eOH}+0.5 + \text{Cl}^- = \text{Alp_eOHCl}-0.5$
231 $\log_k -0.176$
232 $-\text{cd_music } 0 \ 0 \ -1$
233
234 $\text{Alp_eOH}+0.5 + \text{H}^+ = \text{Alp_eOH}_2+1.5$
235 $-\text{cd_music } 1 \ 0 \ 0$
236 $\log_k -8.60 \ \#-7.13$
237
238 $\text{Alp_eOH}_2+1.5 + \text{Cl}^- = \text{Alp_eOH}_2\text{Cl}+0.5$
239 $\log_k -0.176$
240 $-\text{cd_music } 0 \ 0 \ -1$
241
242

```

243 USER_GRAPH
244 chart_title "charge de surface de l'alumine"
245   -headings pH Alo_bOH-0.5 Alo_bOH2+0.5 Alo_cO-0.75 Alo_cOH+0.25 Alo_eO-
246   0.5 Alo_eOH+0.5 charge_Alo Alp_aOH-0.25 Alp_aOH2+0.75 Alp_bOH-0.5
247   Alp_bOH2+0.5 Alp_cO-0.75 Alp_cOH+0.25 Alp_dOH Alp_eO-0.5 Alp_eOH+0.5
248   charge_Alp psil Na_ads Cl_ads Alo_pO-1.5 Alo_pOH-0.5
249   -connect_simulations true
250   -initial_solutions false
251   -axis_titles pH sigma
252   -axis_scale x_axis 2 12 2 1 # minimum 0, maximum 350, major tics at 50,
253   minor tics at 25
254   #   -axis_scale y_axis -8 -3 1
255   -start
256   10 graph_x -la("H+")
257   30 graph_sy mol("Alo_bOH-0.5"), mol("Alo_bOH2+0.5")
258   40 graph_sy mol("Alo_cO-0.75"), mol("Alo_cOH+0.25")
259   60 graph_sy mol("Alo_eO-0.5"), mol("Alo_eOH+0.5")
260   70 graph_y EDL("Sigma","Alo")
261   120 graph_sy mol("Alp_aOH-0.25"), mol("Alp_aOH2+0.75")
262   130 graph_sy mol("Alp_bOH-0.5"), mol("Alp_bOH2+0.5")
263   140 graph_sy mol("Alp_cO-0.75"), mol("Alp_cOH+0.25")
264   150 graph_sy mol("Alp_dOH")
265   160 graph_sy mol("Alp_eO-0.5"), mol("Alp_eOH+0.5")
266   170 graph_y EDL("Sigma","Alp")
267   200 graph_y 0.32*EDL("psil","Alp")+0.08*EDL("psil","Alo")
268   +0.6*EDL("psil","Alpo")
269   210 graph_y 0.8*surf("Na","Alp")+0.2*surf("Na","Alo")
270   220 graph_y 0.8*surf("Cl","Alp")+0.2*surf("Cl","Alo")
271   230 graph_y EDL("psil","Alpo")
272   240 graph_sy mol("Alo_pO-1.5"), mol("Alo_pOH-0.5")
273   -end
274
275 SOLUTION 1
276   Na 100 charge; Cl 100
277 SURFACE 1
278   -sites_units density # site concentration in sites/nm^2
279   Alo_b 0 40 1.0 # 2.17 40 2.0
280   Alo_c 0 # 1.09
281   Alo_e 0 # 1.09
282
283   Alp_a 0 160 1.0 #1.49
284   Alp_b 0 #1.49
285   Alp_c 2.99 # 2.99
286   Alp_d 0.25 # 1.49
287   Alp_e 1.49 # 1.49
288
289 # Alo_b moyen sur la particule : 2 site/nm2
290
291   -capacitance 1.39 5
292   -equilibrate 1
293   -cd_music
294
295
296 EQUILIBRIUM_PHASES;Fix_H+ -2.8 HCl1 END

```


298

299 **References**

300

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