

SUPPORTING INFORMATION

Phosphate Adsorption on γ -Alumina: a Surface Complex Model based on Surface Characterization and Zeta Potential Measurements

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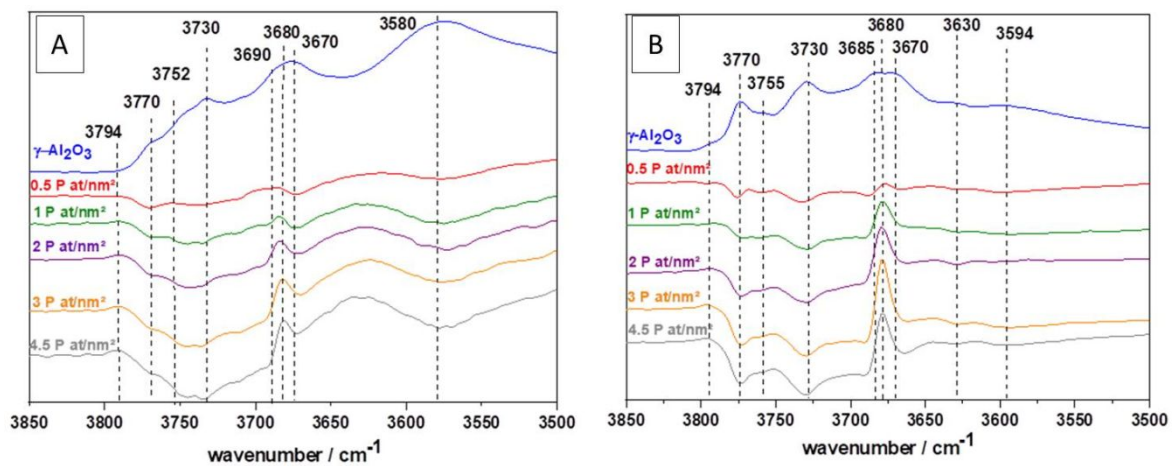


Figure S1 : Transmission FT-IR difference spectra between $\gamma\text{-Al}_2\text{O}_3$ and phosphated alumina at different phosphorus content (from 0.5 to 4.5 at/nm²) after activation (A) at room temperature or (B) 450°C under vacuum (10⁻⁵ mbar), OH stretching region.

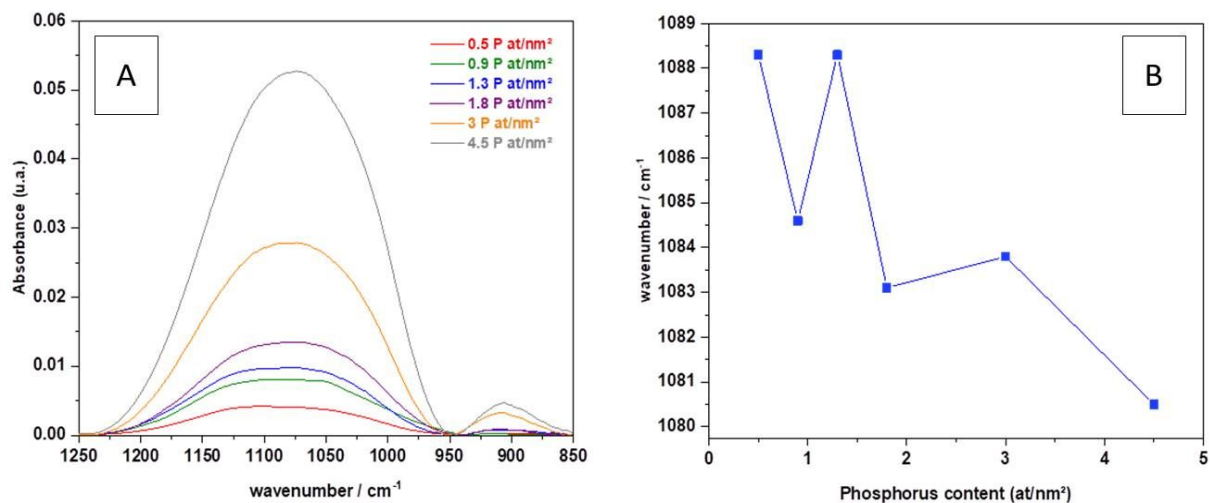


Figure S2 : (A) ATR-IR spectra of dried phosphated alumina at different coverage (from 0.5 to 4.5 at/nm²) subtracted by γ -Al₂O₃ spectra (B) Average location of the ATR-IR band at the different phosphorus coverage ((from 0.5 to 4.5 at/nm²) (line is used as guidance for the reader).

The average location of the band (FigureS2.B) has been calculated using the following formula :

$$\bar{n} = \frac{\sum_{n_i} n_i A(n_i)}{\sum_{n_i} A(n_i)}$$

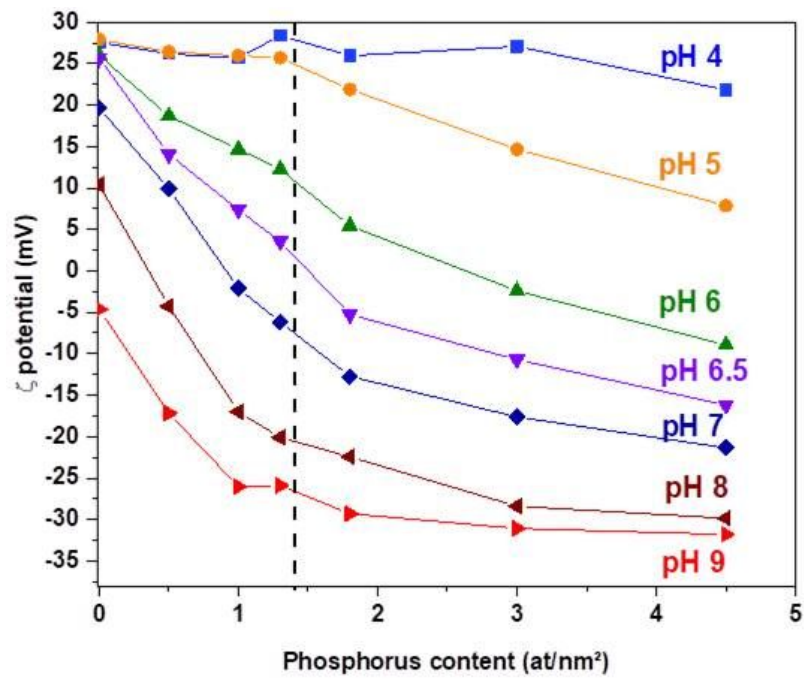


Figure S3 : Evolution of the ζ potential as function of the phosphorus coverage at different pH (from 4 to 9) (lines are used as guidance for the reader).

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) 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

Table S2 : Calculation of Protonation Constants Using AIMD Simulations To Determine the Number of H Bonds around 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}	$\mu_1OH^{-0.5} + H^+ \rightleftharpoons \mu_1OH_2^{+0.5}$	8.16	0.86
μ_2	$Al_{VI} - Al_{IV}$	$\mu_2O^{-0.75} + H^+ \rightleftharpoons \mu_2OH^{+0.25}$	10.32	n.a.
μ_3	Al_{VI}	$\mu_3O^{-0.5} + H^+ \rightleftharpoons \mu_3OH^{+0.5}$	5.94	n.a.
Surface (110)				
μ_1	Al_{IV}	$\mu_1OH^{-0.25} + H^+ \rightleftharpoons \mu_1OH_2^{+0.75}$	0.12	0.75
μ_1	Al_{IV}	$\mu_1O^{-1.25} + H^+ \rightleftharpoons \mu_1OH_2^{-0.25}$	12.97	n.a.
μ_1	Al_{VI}	$\mu_1OH^{-0.5} + H^+ \rightleftharpoons \mu_1OH_2^{+0.5}$	9.16	0.95
μ_2	$Al_{VI} - Al_{IV}$	$\mu_2O^{-1} + H^+ \rightleftharpoons \mu_2OH^0$	10.45	n.a.
μ_2	$Al_{VI} - Al_{VI}$	$\mu_2OH^0 + H^+ \rightleftharpoons \mu_2OH^{+1}$	0.29	0.57
μ_2	$Al_{VI} - Al_{VI}$	$\mu_2O^{-0.75} + H^+ \rightleftharpoons \mu_2OH^{+0.25}$	13.86	n.a.
μ_3	Al_{VI}	$\mu_3O^{-0.5} + H^+ \rightleftharpoons \mu_3OH^{+0.5}$	4.75	n.a.

Supporting Reference

- (1) Corral Valero, M.; Prelot, B.; Lefèvre, G. MUSIC Speciation of γ -Al₂O₃ at the Solid Liquid Interface: How DFT Calculations Can Help with Amorphous and Poorly Crystalline Materials. *Langmuir* **2019**, *35*, 12986–12992.