SUPPORTING INFORMATION

Structural Characterization of Phosphate Species Adsorbed on γ-Alumina by Combining DNP Surface Enhanced NMR Spectroscopy and DFT Calculations

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1. Materials and Experimental Methods

1.1. Sample Preparation

 γ -Al₂O₃ samples were prepared from commercial powdered Pural SB3 (Sasol). Pural SB3 powders were shaped as extrudates, calcined at 450°C for 4 hours and crushed to reach particle sizes between 400 and 800 µm. The support has a surface area of 209 m² g⁻¹ and a pore volume of 0.88 cm³ g⁻¹. The different samples were impregnated with phosphoric acid by the aqueous incipient wetness impregnation technique. A solution of diluted phosphoric acid was prepared from a commercial solution (85 %, Alfa Aesar) in different concentrations impregnated on the support. The precise phosphate content in the samples was then determined by X-ray fluorescence spectroscopy to 0.39, 1.06, 2.06, 2.89 and 4.25 wt.%. This corresponds to 0.4, 1.0, 2.0, 2.8 and 4.1 P atoms nm⁻², assuming that the specific surface area does not change by phosphate addition. Then, the impregnated solids were placed in a watersaturated atmosphere overnight and then dried at 120°C for 6 hours. We will use the term phosphate, which shall include here all protonation states of the acid.

1.2. Solid-state NMR

1.2.1. Room temperature Magic Angle Spinning NMR

Magic Angle Spinning (MAS) solid-state NMR experiments were performed on a Bruker Avance III 400 wide bore spectrometer equipped with triple resonance 2.5 mm MAS probe. Dried samples were prepared for analysis at ambient conditions and packed into 2.5 mm zirconia rotors under ambient conditions. One-dimensional ³¹P spectra were recorded with a $\pi/2$ pulse of 2.5 µs on ¹H, followed by a cross-polarization (CP) step with a 4 ms contact time, an RF field of 83 kHz on ³¹P and a linear ramp from 108 to 129 kHz RF field on ¹H. Recycle delays were set to 1.3**T*₁(¹H). Experiments were performed at a MAS rate of 30 kHz. ³¹P spectra were referenced to a 85 % solution of H₃PO₄. The number of scans for each sample in indicated in **table S1**.

1.2.2. MAS NMR under DNP conditions

Dynamic Nuclear Polarization (DNP) MAS NMR experiments were performed on Bruker Avance III 400 wide bore spectrometer (9.4 T, 400 MHz ¹H Larmor frequency) equipped with triple resonance 3.2 mm low-temperature DNP MAS probe and at a sample temperature of approx. 110 K. The samples were irradiated with continuous wave high-power microwaves at a frequency of 263 GHz. The samples were impregnated using the incipient wetness impregnation method with approx. 40 mg of a 16 mM TEKPol solution in degassed and dried 1,1,2,2-tetrachloroethane (TCE) for 20 mg of the dry sample. TCE (purity \geq 98 %) was purchased from Sigma Aldrich and used as received. TEKPol was kindly donated by Olivier Ouari (Aix-Marseille University). The wetted powder was packed in a 3.2 mm zirconia rotor under inert atmosphere.

The enhancement factors were determined by the intensity ratio between the microwave (MW) on and microwave off signal. Solvent enhancement factors were recorded by comparing ¹H spectra with MW on and off. A ¹H DEPTH pulse sequence was used, consisting of a $\pi/2$ pulse followed by two π pulses phase cycled according to a combined "EXORCYCLE" and "CYCLOPS" scheme. $\pi/2$ pulses of 2.5 µs (100 kHz RF field) were used. Overall, surface enhancement factors between 67 and 130 were obtained (**Table S1**).

1D ³¹P Incredible Natural Abundance DoublE QUAntum Transfer Experiment (INADEQUATE) and 1D ³¹P triple-quantum filtered spectra under DNP conditions were recorded starting with a $\pi/2$ pulse of 2.5 µs on ¹H, followed by a CP step, with a 3 ms contact

time, an RF field of 85 kHz on ³¹P and a linear ramp from 100 to 120 kHz RF field on ¹H. The double quantum evolution and reconversion delays were set to 4 or 8 ms. Recycle delays were set to 2 s. ³¹P $\pi/2$ pulses were set to 3.75 μ s. 100 kHz spinal-64 ¹H decoupling was applied during the whole sequence. Experiments were performed at a MAS rate of 8 kHz. The number of scans for each sample is indicated in **table S1.** DNP enhancement factors can be found in **Table S2**. Spectra were referenced to ammonium dihydrogen phosphate for ³¹P.

Two-dimensional ³¹P-²⁷Al through-bond INEPT spectra were recorded starting with a $\pi/2$ pulse of 2.5 µs on ¹H, followed by a CP step with a 3 ms contact, an RF field of 85 kHz on ³¹P and a linear ramp from 100 to 120 kHz RF field on ¹H. ³¹P $\pi/2$ pulses were set to 3.75 µs and ²⁷Al $\pi/2$ pulses to 10.5 µs. Evolution times were set to 48 times the rotor period. A total of 64 t₁ increments were recorded. The number of scans for each sample is indicated in **table S1**. DNP enhancement factors can be found in **Table S2**.

Two-dimensional ³¹P-²⁷Al dipolar INEPT spectra were recorded starting with a $\pi/2$ pulse of 2.5 µs on ¹H, followed by a CP step with 3 ms contact time, an RF field of 85 kHz on ³¹P and a linear ramp from 100 to 120 kHz RF field on ¹H. ³¹P $\pi/2$ pulses were set to 3.75 µs and ²⁷Al $\pi/2$ pulses to 10.5 µs. Evolution times under SR421 recoupling ¹ were set to 12 times the rotor period, with a RF field of 2 times the spinning frequency. A total of 64 t₁ increments were recorded. The number of scans for each sample is indicated in **table S1**. Experiments were performed at a MAS rate of 12 kHz for samples with 0.5, 1 and 2 wt% P, and at 8 kHz for samples with 3 and 4.5 wt% P. DNP enhancement factors can be found in **Table S2**. Spectra were referenced to ammonium dihydrogen phosphate for ³¹P and a 1 M solution of aluminium nitrate for ²⁷Al.

CP	exp.
sample	Number of scans
0.4 P nm ⁻²	12288
1.0 P nm ⁻²	4096
2.0 P nm ⁻²	2048
2.8 P nm ⁻²	1024
4.1 P nm ⁻²	4096
DQ INADE	QUATE exp.
sample	Number of scans
1.0 P nm ⁻²	1280
2.0 P nm ⁻²	1024
2.8 P nm ⁻²	1024
4.1 P nm ⁻²	1024
TQ-filt	ered exp.
sample	Number of scans
2.0 P nm ⁻²	864
2.8 P nm ⁻²	1152
4.1 P nm ⁻²	288
Dipolar I	NEPT exp.
sample	Number of scans
0.4 P nm ⁻²	64
1.0 P nm ⁻²	64
2.0 P nm ⁻²	32
2.8 P nm ⁻²	64
4.1 P nm ⁻²	32
J-based I	NEPT exp.
sample	Number of scans
0.4 P nm ⁻²	288
1.0 P nm ⁻²	128
2.0 P nm ⁻²	128
2.8 P nm ⁻²	512
4.1 P nm ⁻²	64

Table S1: Number of scans for the room temperature and DNP MAS NMR experiments.

Table S2: ¹H and ³¹P DNP enhancement factors of samples impregnated with 16 mm TEKPol in TCE, determined by comparison of experiments recorded with microwaves on and off. Different samples were prepared for the 2Q and 3Q filtered experiments on one hand and for the dipolar-based and J-based INEPT experiments on the other hand, leading to slightly differing enhancement factors.

2Q- and 3Q-filtered experiments							
sample	ε (¹ H)	ε (³¹ P CP)					
1.0 P nm ⁻²	104	102					
2.0 P nm ⁻²	95	98					
2.8 P nm ⁻²	129	107					
4.1 P nm ⁻²	132	113					
Dipolar-based and J-based INEPT							
Dipolar-Da	iseu anu J-Das	sed INEP I					
Dipolar-Da	experiments	sed INEP I					
sample	experiments ε(¹ H)	ε (³¹ P CP)					
sample 0.4 P nm ⁻²	experiments ε(¹ H) 107	ε (³¹ P CP) 92					
sample 0.4 P nm ⁻² 1.0 P nm ⁻²	experiments ε(¹ H) 107 50	ε (³¹ Ρ CP) 92 57					
sample 0.4 P nm ⁻² 1.0 P nm ⁻² 2.0 P nm ⁻²	experiments ε (¹ H) 107 50 110	ε (³¹ P CP) 92 57 96					
sample 0.4 P nm ⁻² 1.0 P nm ⁻² 2.0 P nm ⁻² 2.8 P nm ⁻²	experiments ε(¹ H) 107 50 110 129	ε (³¹ P CP) 92 57 96 130					



1.2.3. Estimation of the fraction of P-O-P species from INADEQUATE experiments

Figure S1: Relative fraction α of P-O-P species, as estimated from the INADEQUATE spectra and normalized to the fraction of P-O-P at 1 Pnm⁻².

The values were calculated from the ratio of the signal-to-noise ratio (S) per unit of time measured in 1D ³¹P INADEQUATE and CP spectra. These ratios were then corrected to take into account differences in the length of the excitation and reconversion periods in INADEQUATE data as well as differences in T_2 ' values.

More specifically, the fractions α were calculated from equation (1) and (2):

$$a_{P-O-P} = \frac{S_{inadequate}}{S_{CP}} \cdot \frac{I_0}{I_{DQ}} \quad (1)$$

$$\frac{I_{DQ}}{I_0} = \sin^2(2\pi J_{P-O-P}t) \cdot \exp\left(\frac{-2t}{T_2'}\right) \quad (2)$$

$$\alpha = \frac{a(x Pnm^{-2})}{a(1.0 Pnm^{-2})} \quad (3)$$

where $S_{\text{inadequate}}$ is the signal-to-noise ratio per unit of time of the ³¹P INADEQUATE spectra, S_{CP} the signal-to-noise ratio per unit of time of the ³¹P CP spectra, acquired under the same conditions, T_2 ' the refocused transverse dephasing time, determined experimentally by Hahn echo experiments, J_{P-O-P} the two-bond ³¹P-³¹P coupling constant (estimated here to 16 Hz) and τ the experimental values used in the $\tau - \pi - \tau$ periods of the INADEQUATE experiments (either 2 or 4 ms). The fractions were then scaled to the value calculated for the 1 P/nm² sample.



Figure S2. Two-dimensional DNP enhanced dipolar- (a) and scalar- (b) based ${}^{27}\text{Al}{-}^{31}\text{P}$ INEPT correlation experiments recorded (9.4 T, 400 MHz ¹H resonance frequency, 263 GHz microwave frequency, approx. 110 K). The MAS frequency was 12 kHz for the 0.4, 1 and 2 P nm⁻² loading, and 8 kHz for the others. The chemical shifts of some correlation signals are highlighted for clarity. The 1D ³¹P CP MAS spectra are reported on the left of the 2D maps. The 1D ²⁷Al CP MAS spectrum of γ -Al₂O₃ (pure Pural SB3) is shown above the plots for comparison.

1.2.4. One-dimensional projections extracted from 2D through-space and through-bond correlation experiments.



Figure S3. Projections along the ²⁷Al dimension extracted from dipolar (left) and *J*-based (right) ²⁷Al-³¹P INEPT spectra.



Figure S4. Quadrupolar coupling constants and relative peak intensity of ²⁷Al signals in Jbased INEPT spectra. The fit was carried out using DMFit with the Czjzek Simple model. ²

0.4 P nm ⁻²									
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	51.8	36	19.3	2207					
Al V	29.4	17	17.0	1904					
Al VI	-3.3	47	12.6	3036					
		1.0 P nm ⁻²							
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	51.1	25	19.2	1994					
Al V	29.6	24	30.8	1768					
Al VI	-5.9	51	10.0	3257					
2.0 P nm ⁻²									
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	45.7	42	22.3	2186					
Al V	19.9	11	10.8	2693					
Al VI	-7.2	47	9.5	3132					
		2.8 P nm-2							
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	45.6	43	20.5	2031					
Al V	19.1	19	8	2924					
Al VI	-7.7	38	10.3	2644					
		4.1 P nm-2							
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	44.8	40	5.4	3352					
Al V	17.6	7	12.3	2196					
Al VI	-8.5	53	7.9	2883					

Table S3. Peak positions, signal intensities, peakwidths and quadrupolar coupling constants of ²⁷Al signals in J-based INEPT spectra. The fit was carried out using DMFit with the Czjzek Simple model.



Figure S5. Quadrupolar coupling constants and relative peak intensity of ²⁷Al signals in dipolar-based INEPT spectra. The fit was carried out using DMFit with the Czjzek Simple model.

0.4 P nm ⁻²									
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	48.0	22	25.2	1910					
Al V	26.1	14	21.1	1670					
Al VI	2.4	64	14.5	3092					
		1.0 P nm	- ²						
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	48.8	21	22.3	2631					
Al V	25.1	17	24.4	1768					
Al VI	0.1	62	14.0	3155					
2.0 P nm ⁻²									
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	45.5	19	22.6	2019					
Al V	22.6	21	25.6	1783					
Al VI	-2.3	60	14.3	3131					
		2.8 P nm	l ⁻²						
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
Al IV	40.4	17	15.8	1993					
Al V	19.9	37	29.7	1806					
Al VI	-3.4	46	16.2	2653					
		4.1 P nm	-2						
Species	Position / ppm	Intensity / %	Peakwidth / ppm	C _Q / kHz					
AI IV	39.6	10	12.4	1627					
Al V	19.4	42	33.3	1868					
Al VI	-5.4	48	12.4	2769					

Table S4. Peak positions, signal intensities, peakwidths and quadrupolar coupling constants of ²⁷Al signals in dipolar-based INEPT spectra. The fit was carried out using DMFit with the Czjzek Simple model.



Figure S6. Overlay of 1D spectra and of 2D projections for the alumina sample with a coverage of 4.1 P nm^{-2} .

2. Computational details

The following should give an elaborate picture in which way the vast configuration space of phosphate adsorption on γ -alumina. After giving details on our computational parameters, we introduce the general framework and explain surface properties, like symmetry and adsorption sites as well as the included adsorption modes in detail.

2.1. Total energy calculations

Density functional theory (DFT) calculations were undertaken by using PBE-D3, a standard GGA functional with additional dispersion correction ^{3–5}.

The electronic structure was approximated within the PAW formalism with valence states spanned in a projected plane wave basis up to 500 eV kinetic energy and with Projector Augmented-Wave method pseudopotentials as implemented in VASP v5.4.⁶ The Brillouin zone was sampled by Monkhorst-Pack *k*-point meshes with 0.06 Å⁻¹ spacing.⁷ Self-consistent field convergences were fixed to energy differences smaller than 0.001 meV, and geometry relaxation was continued until the forces on all atoms were smaller than 10 meV Å⁻¹.

We tested these computational parameters on the γ -alumina bulk model by Krokidis et al.⁸ and three aluminium phosphate structures: berlinite, variscite and wavellite.^{9–12} To avoid noise during optimization of the lattice parameters, we used a finer *k*-point mesh of around 0.03 Å⁻¹ during bulk optimization. For all surface models, asymmetric 8-layers surface slabs (or 2 unit cells respectively) were used. Two topmost layers were relaxed, while the remaining atoms were kept fixed in bulk geometry. To minimize perpendicular interaction between the slabs, a minimum inter-slab distance (vacuum thickness) of 20 Å and dipole corrections on forces and energies were used.

Geometry relaxations until 10 meV $Å^{-1}$ were necessary to fully relax X-OH surface rotamers in the vast majority of systems. The structures were also tested by determining second energy derivatives numerically and diagonalizing the symmetrized Hessian matrix. If any of the resulting normal modes were imaginary, the systems were reoptimized with tighter force criteria until no imaginary mode was detected.

2.1.1. Free enthalpy calculations

Finite temperature and pressure calculations were done within the harmonic approximation (see ¹³ a full description of statistical mechanics formulae and ¹⁴ for their application in slab model calculations). Enthalpy, entropy and Gibbs free energy estimates for our systems were done for experimental drying conditions: 120 °C and 2kPa vapour pressure (assuming that samples were initially exposed in an atmosphere with 60 % relative humidity at 25 °C).

Since the surface models are partially constraint systems by construction, the calculated Hessian matrix is a *partial* Hessian matrix. We chose to add only the topmost atom layer of the alumina network, as defined in fig.S8. As such its derived normal modes contain three physically meaningless frustrated translation, which can create additional noise in the modes with the lowest frequencies. These modes are well defined by their components (all atoms move in x, y or z direction). We remove them by projection from the Hessian matrix.

Note that the choice of the *partial* Hessian matrix is arbitrary and the resulting absolute values depend on this choice. However, the calculated energy differences in the adsorption reaction energies only depend on a consistent choice. The differences converge rapidly with increasing size of the partial Hessian.

For molecular references, that are in our case H_2O and H_3PO_4 , we determine the full Hessian matrix numerically using the same procedure as for the surfaces, and project out translational and rotational components from the normal modes before determining the vibrational components.

As discussed in the main text, the adsorption free enthalpies of all presented systems can be expressed by the chemical equations eq. 2, 3 and 5 in the main manuscript. We can generalize the reaction by only considering the number of added phosphates, m and exchanged water molecules, n. The free enthalpy of adsorption is then given as:

$$\Delta G_{ads} = \frac{1}{m} [G(\text{Surf} - mH_3PO_4) - G(\text{Surf} - nH_2O)] + \frac{n}{m} G(H_2O_{(g)}) - G(H_3PO_{4(g)})$$
(4)

To allow direct comparison between all systems, we normalized this quantity per mole of phosphate (m). The corresponding reaction enthalpy and entropy are written as follows:

$$\Delta H_{ads} = \frac{1}{m} [H(\text{Surf} - mH_3PO_4) - H(\text{Surf} - nH_2O)] + \frac{n}{m} H(H_2O_{(g)}) - H(H_3PO_{4(g)})$$
(5)

$$\Delta H_{ads} = \frac{1}{m} \Delta H_{vib} + \frac{n}{m} H_{rot+trans} (H_2 O_{(g)}) - H_{rot+trans} (H_3 P O_{4(g)})$$
(6)

$$\Delta H_{vib} = \frac{1}{m} [H_{vib} (\text{Surf} - mH_3 P O_4) - H_{vib} (\text{Surf} - nH_2 O)] + \frac{n}{m} H_{vib} (H_2 O_{(g)}) - H_{vib} (H_3 P O_{4(g)})$$
(7)

$$\Delta S_{ads} = \frac{1}{m} [S (\text{Surf} - mH_3 P O_4) - S (\text{Surf} - nH_2 O)] + \frac{n}{m} S (H_2 O_{(g)}) - S (H_3 P O_{4(g)})$$
(8)

$$\Delta S_{ads} = \frac{1}{m} \Delta S_{vib} + \frac{n}{m} S_{rot+trans} (H_2 O_{(g)}) - S_{rot+trans} (H_3 P O_{4(g)})$$
(9)

$$\Delta S_{vib} = \frac{1}{m} [S_{vib} (\text{Surf} - mH_3 P O_4) - S_{vib} (\text{Surf} - nH_2 O)] + \frac{n}{m} S_{vib} (H_2 O_{(g)}) - S_{vib} (H_3 P O_{4(g)})$$
(10)

Note: The applied approximations are acceptable for the simulated conditions, however, there is no easily accessible reservoir for phosphoric acid, to define absolute adsorption energies. For sake of simplicity, we defined the same conditions for H₃PO₄ as for water, knowing that this reference is arbitrary.

2.1.2. Chemical shift calculations

To calculate ³¹P chemical shift on our periodic slab models, we applied the GIPAW method¹⁵ using the same computational parameters as aforementioned for total energy calculations, with a slightly denser *k*-point mesh (0.04 Å⁻¹ spacing) for the surface model (corresponding to 3x5x1 for (100) and (3x3x1) for (110)). To compare the calculated ³¹P-NMR isotropic chemical shift with the experimental data, we need to use a reference compound analogous to the experimental reference 85 % phosphoric acid. The theoretical reference can be different as long as experimental ³¹P-NMR shift data is available. NMR parameters, σ , given by DFT can be then easily connected to ³¹P-NMR shifts (δ_x) by using a DFT calculated reference σ_{ref} :

$$\delta_x - \delta_{\text{ref}} = \sigma_{\text{ref}} - \sigma_x \tag{4}$$

where σ_{ref} , represents the chemical shift computed for the DFT reference and σ_x a DFT shift in each tested system, and δ_{ref} represents the experimental ³¹P-NMR shifts. Since the calculated σ_{ref} is by itself prone to a systematic DFT error, slight differences are expected depending on the chosen reference. In order to minimize this error, we used a set of three well characterized aluminum phosphates solids, Berlinite, Variscite and Wavellite.^{9–12}

	Lattice	e paramet	ers (Å)	k-noints	S S.	Gud	σ_{x}	
	а	b	c	R-points	$O_X = O_{\text{ref}}$	Orei		
Berlinite	4.96	4.96	11.01	(9x9x4)	-25.3	-322.7	-297.4	
Variscite	5.16	9.70	9.73	(9x5x5)	-19.2	-313.7	-294.5	
Wavellite	7.00	17.04	9.70	(5x2x4)	-11.2	-305.3	-294.1	

Table S5. Lattice parameters, applied k-point meshed for bulk structures, experimental and theoretical chemical shift values for the tested aluminum phosphates.

Therefore, the averaged constant shift σ_x to connect computation and experiment (or in other words: the DFT extrapolated chemical shift of 85% phosphoric acid) is -295.3.

We apply a similar approach to determine the 27Al-NMR shifts by using the experimental data available on γ -alumina, Berlinite and Variscite.^{16,17} For calculation on γ -alumina, the DFT bulk model of Krokidis et al. was used as reference.⁸

	$\delta_x - \delta_{ref}$	σ_{ref}	σ_{x}
Berlinite	42.7	-519.0	-561.7
γ–alumina (Oh)	14.2	-544.4	-564.3
γ–alumina (Td)	74.0	-490.3	-558.6

The averaged constant shift σ_x to connect computation and experiment (DFT extrapolated chemical shift with respect to experimental reference) is -561.5.

2.2. Framework to sample the adsorption modes of phosphate on y-alumina

The tested systems are described as follows:

1.	Structural reference	(surface facets, reconstruction)
2.	Phosphate type, coverage	(coadsorption, oligomerization)
3.	Adsorption mode, surface hydrat	on (surface dentates)
4.	Adsorption sites	(competing sites for same adsorption mode)
5.	Hydrogen bond network	(different H-bonds with OH and H ₂ O)

Note that this hierarchy is designed to organize static calculations like our geometry optimizations. **Figure S7** shows a tiny excerpt from the whole data tree. Our study is based on

the non-spinel model γ -alumina developed by Krokidis et al.⁸ and its derived hydrated model surfaces by Digne et al.^{18,19} Microscopic studies suggest that the most exposed facets on the γ -alumina surface are (1 0 0) and (1 1 0).¹⁸ Thus, we focused on these two facets. Within early test calculations, we noticed the importance of the surface reconstruction on the (1 1 0) facet. ²⁰ This reconstruction is stabilized at high temperature after partial hydration, but it is metastable at our considered drying conditions (393 K, 2 kPa H₂O pressure). In our calculations the most favorable systems are mostly the on R(1 1 0). This leads to a total of three structural models for two facets, the unreconstructed, "normal" n(1 1 0) surface, the reconstructed R(1 1 0), and the (1 0 0) surface.

For those structural models, we sampled a configuration space consistent surface coverages in experimental samples. For the adsorption of single H₃PO₄, a single 'P' on the three model surfaces required >300 test calculations. Coadsorption, '2 P', and diphosphates, H₄P₂O₇, 'P₂', can be constructed by combining from results of single phosphate adsorption modes. However, since testing all possible configurations for 2P and P₂ atoms becomes unfeasible, we only used the most favourable results of the single phosphate set to construct coadsorption and diphosphate structures.

By applying this restriction we could reduce the total number of test configurations to ~1000 systems. Note that while we restricted ourselves to these three groups, P, 2 P and P₂, one can continue to construct more complex patterns and extend the framework to oligomers like P₃, P_2+P , 3 P, P_2+2P , etc.



Figure S7: Excerpt from the full screening tree of all tested structures throughout this study. Dentation modes are symbolized by v_x , where x is the number of phosphate bonds with the surface. Surface sites are symbolized with letters (see below for a description). For a given surface, dentation mode and adsorption site, two test structures are symbolized by numbers (1, 2) on the right. The full tree comprises ~1000 tests. To derive a single adsorbed phosphate, P, we need to pick a reference structure, i.e. (1 0 0), and adsorb it, i.e. by substituting hydroxyl or water from site b. Since the H-bond network is sensitive to this change, H⁺ are empirically reshuffled across sites. Our naming scheme just follows the tree, i.e. (1 0 0)v₁[a2] or R(1 1 0)v₃₁. The latter described an oligomer, which is indicated by the two digits 3 and 1. Missing brackets refer to the best structure (by energy) of a given pattern.

2.3. Identification of adsorption sites on y-alumina surface models

Figure S8 illustrates complementary top views of the alumina surface models as discussed in the main text.



Figure S8. Schematic perspective views and their corresponding top views of the hydrated γ -Al₂O₃ reference surface structures. In top views, the frame indicates the cell unit used for the simulation. Oxygen atoms originating from water adsorbed molecules are shown in red, the ones from the bulk γ -Al₂O₃ are shown in blue. Surface aluminum atoms are shown in black, the subsurface ones in grey. (a) (1 0 0) facet has 4 inequivalent octahedral Alv₁ exposed for adsorption, which can accept one H₂O molecule each; (b) the n(1 1 0) facet exposes 3 inequivalent octahedral Alv₁ and 1 tetrahedral Al₁v site: Al₁v binds one µ₁-OH, the two neighboring Alv₁ bind to µ₁-OH, µ₁-OH₂ and µ₂-OH and the further Alv₁ presents two adsorption sites and binds to µ₁-OH and µ₁-OH₂; (c) the reconstructed R(1 1 0) facet results from the migration of one Alv₁ to an Al₁v site (represented by the dotted arrows), which induces the loss of one chemisorbed water, the transformation of a µ₃-OH into a µ₂-OH, and some proton rearrangements.

Figure S8 presents the three surface models including notations for adsorption sites used in this work. The symmetry of the surface models of γ -alumina is inherited from its bulk non-spinel model. Its space group, P21/m, is characterized by its C₂-rotational axes perpendicular

to its mirror planes. The surface slabs, $(1\ 0\ 0)$ and $(1\ 1\ 0)$ are both cut along the rotational axis, hence only the mirror plane remains. In terms mathematical terms of group theory, both facets belong to the *pm* wallpaper group, where *p* indicates a primitive cell, and *m* the mirror plane. **Figure S9** provides labels and symmetry planes of the studied γ -alumina references. On the reconstructed R(1 1 0) facet the *pm* symmetry is lost when the octahedral Al atom at **E-e-B-e'** is moved to a tetrahedral gap at **E-D-e**. Despite losing 1 available adsorption site, the former **e'**-site, the total number of *inequivalent* sites is increased by 3 with new sites **c**, **C**, and **F**. As a consequence, the R(1 1 0) surface is the most complicated case.



Figure S9: Three reference surfaces, a): $(1\ 0\ 0)$, b): $n(1\ 1\ 0)$ and c): $R(1\ 1\ 0)$. Al atoms are in the center of their coordination octahedra (blue) and tetrahedra (green). O sites from adsorbed water are labelled with red lowercase while alumina O sites are labelled with blue uppercase letters. Mirror planes are shown as thick black lines in a) and b). For any site that is not part of the mirror plane there is a symmetry-equivalent site, i. e. sites **b** and **b**' on $n(1\ 1\ 0)$. Since $R(1\ 1\ 0)$ has no mirror planes, the number of distinct sites increases, i. e. site **b**' in $n(1\ 1\ 0)$ becomes **c** in $R(1\ 1\ 0)$.

2.4. Phosphate adsorption: modes and sites

To screen through the configuration space we have, rigorously 3N degrees of freedom where N represents all relaxed atoms per structure. Though this is unfeasible and arguably irrational, we do not know a different, general, approach. In our study this problem was solved by systematic exploration of adsorption patterns using the labelled sited pictured in Figure S9. We produced a grid over the two structural models of the (1 1 0) facet and included two phosphate orientations per grid point. On the (100) facet we find a surface cavity located over the Al-tetrahedron (green). In this area H-bond interactions are maximized; hence the screening was focused on this location. Monodentate adsorption involves substitution of one H₂O molecule from the surface. As a first constraint, we exclusively exchanged H₂O and OH from chemisordbed water molecules on alumina (red labels in fig. S8). The topmost alumina oxygen (blue labels) are μ_2 -O, μ_3 -O and μ_4 -O sites, cannot compete with the μ_1 -OH and μ_2 -OH and μ_3 -OH and μ_4 -OH a H₂O sites of the chemisorbed water monolayer, and are also encumbered by steric constraints. This leads, after taking into account symmetry equivalent sites, to three different sites on $(1\ 0\ 0)$, four on $n(1\ 1\ 0)$ and five different on $R(1\ 1\ 0)$. For bidentates we involve pairs of neighboring O that define bidentate sites together. On the (1 0 0) surface, four sites can be defined: aa', ab, bc and c-. The latter two differ by the binding sites visible in the center of fig. S8a (defined as **bc**), and **cb** being the site connecting **c** with site **b** in its right neighbour periodic image. On n(1 1 0) and on R(1 1 0) we find four sites named **ab**, **bb**', **de** and **ee'** and **ab**, **bc**, **ca** and **de**, respectively. It shall be noted here that the O-O distance in phosphates is slightly shorter than the average O-O distance in alumina. Bidentates on $n/R(1 \ 1 \ 0)$ ad or bd are thus ruled out by distance mismatch. Tridentates based on substitution of preadsorbed water are only possible on $(1 \ 0 \ 0)$ utilizing **a**, **b** and **c** sites. This system is affected by significant strain due to mismatch between surface and phosphate patterns. As an alternative approach, the topmost alumina oxygen sites were included. Oxygen atoms like abD (any

reference structure in fig. S8), are arranged as almost regular triangles, which allow them to be matched with a face of the phosphate tetrahedra. Extension to other sites increases the number of possibilities to 8 cases in each surface model: on (1 0 0) abc, acb, aa'B, aa'C, abA, abD, bcD and cbA; on n(1 1 0) abA, abD, bb'B, bb'E, deA, deD, ee'B and ee'E; on R(1 1 0) abA, abD, bcB, bcE, caC, caF, deA, deD. We started to explore these 24 tridentate structures systematically and found structures within a broad energy range of approximately 400 kJ mol⁻¹. The vast majority of structures can be ruled out by Pauling's third rule for structure determination in ionic crystals (i.e.: the anion polyhedral should bind to each other with the least possible number atoms). According to this rule, one atom (corners) is more stable than two atoms (edges) or three (faces). Our initial tests showed that phosphate can only share corners with aluminium octahedra and tetrahedra. To our knowledge, this is consistent observations in crystalline aluminium phosphates. By these considerations, the number of tridentates is vastly reduced to 8 sites. On (100) it only leaves abc and acb, on n(1 1 0) **bb'B**, **bb'E**, **deA**, and on R(1 1 0) **bcB**, **bcE**, **deA**. Using Pauling's third rule, several bidentates could be ruled out as well: The OH on **a** in $n/R(1 \ 1 \ 0)$ cannot be part in bidentate sites; ee' is 20 kJ mol⁻¹ less stable than the favoured de site.

Throughout the screening we discovered one notable exception: a stable bidentate e-B on R(1 1 0). While being no part of the screening set, it occurs by reconstruction of n(1 1 0)ee'B, where the octahedral aluminium atom under e, B, e' and E flips over to a tetrahedral gap, binding to oxygen at D. This opens the question about screening a multitude of other combinations, including more bidentates involving alumina oxygen or tridentates involving at least two alumina oxygen. Most of these cases can be excluded since they do not follow Pauling's third rule and others are sterically hindered, i.e. R(1 1 0)eAB, abides the former, but is in too close proximity to OH on site b. In fact, the only additional combinations are R(1 1 0)dC, BC, and EF.

2.5. Interplay between Phosphate adsorption and Hydrogen bond network

In the full model, H₂O molecules form an H-bond network, while some even dissociate and protonate neighbouring alumina O sites. Since this optimization needs to be done for the reference state of the surface before impregnation, and repeated for every adsorption case, it is crucial to gather as much information about the protonation network as possible.. The two most vital questions are:

- 1) What qualifies the most stable protonation states?
- 2) Have we found the most stable configuration?

On the initial alumina slab models, the preadsorbed water fragments bind to the alumina as μ_1 -OH_x adsorbates, which allows all of them to rotate freely during structural relaxation. Since the all Alv₁-OH bond axes on the (1 1 0) are tilted by 45° (54° for Al₁v), as a consequence of the fundamental fcc oxygen lattice of γ -alumina. This also leads to strong H-bonds between alumina oxygen and adsorbates. For instance the reference n(1 1 0) contains 6 H₂O adsorbed to the surface, 3-4 of them dissociated producing 3-4 OH adsorbates and another 3-4 OH with alumina oxygen. The μ_1 -OH are stabilized by H-bonds from the sites below, while μ_1 -H₂O form H-bonds with μ_3 -O. If all protons are distributed over all sites (that means all 6 H₂O are dissociated and 12 OH are constructed over all sites **a** to **e**' and **A** to **E**') then we are close to a state where all μ_1 -OH (**b** to **e**') are stabilized by H-bonds from μ_2 -OH and μ_3 -OH (**A** to **E**'). The extent to which this degree of water dissociation is stable depends on the structural relaxation. On the n(1 1 0) structure surface relaxation compensates water dissociation, as 12 protons from 6 H₂O can distributed in only one way on 12 sites. For the R(1 1 0) structure we need to distribute 10 protons on 11 sites leading to 11 calculations in general but, by removing a proton from one out of the two available μ_3 -O sites within the topmost alumina oxygen, one

achieves the best result. Hence, only two tests are needed in this case, keeping in mind, that we do not need to manually test all degrees of protonation as they are automatically rectified during structural relaxation.

Unfortunately, the same method does not apply on the (1 0 0) facet. Here, the Al-O bond axes of the adsorbed H₂O and OH are perpendicular to the surface plane which also hinders strong interaction with surface oxygen sites. However, the smaller (1 0 0) unit cell gives less room for variation: the two μ 4-O sites (**D** and **D**') are never protonated, leaving alumina oxygen for protonation (**A**, **A'**, **B** and **C**). Of the different combined protonation states only **A**+**C** is stable. Additional protons preferably bind to μ 1-OH, forming μ 1-H₂O rather than to alumina oxygen. Overall about 6 different protonation states were tested for each system.

Upon phosphate adsorption, the total number of protons in the system changes dramatically due to water substitution. Especially for co-adsorption we model systems from 18 protons in $n(1 \ 1 \ 0)v_0+v_0$ to only 4 protons in $R(1 \ 1 \ 0)v_3+v_3$. Clearly, we cannot just resort to the H-bond network found in the structural references.

The first question ultimately asks for the oxygen site basicity and involves ordering different sites by their proton affinity. We were guided by the expected intrinsic acid strength of OH species depending primarily on its coordination to Al atoms ²¹:

$$Al_{VI}OH \sim Al_{IV}OH \ll (Al_{VI})_2OH \ll (Al_{VI})_3OH \ll (Al_{VI})_4OH$$
(S1)

that means while Alv_IOH is too basic to be deprotonated, (Alv_I)₄O is never protonated and the range in between depends on the total number of surface protons. The latter trend is consistent with qualitative trend from computational results obtained from the screening procedure:

$$\mu_1 \text{-}O \gg \mu_2 \text{-}O > P \text{-}O \approx (Al_{VI})\mu_1 \text{-}OH \approx \mu_3 \text{-}O > (Al_{IV})\mu_1 \text{-}OH \gg \mu_4 \text{-}O$$
(S2)

Using this, we can predict the protonation state on most sites. Instead of oxygen atoms at the surface, only P-O, μ_3 -O and $(Al_{VI})\mu_1$ -OH, need to be considered after protonating all μ_1 -O and μ_2 -O. In general systems with a regular proton distribution are favored.

3. Complementary Results

3.1. Most stable sites for each dentation mode

The system stability depends with similar weights on two factors: adsorption site and H-bond network. Direct adsorption of a single phosphate occurs without water substitution. However, H₃PO₄ protonates the surface once or twice, and the best candidate structure maximizes the number of H-bonds. For proton affinity, we defined a stability order in eq. S2: the P-O, (Alv₁)µ₁-OH and µ₃-O species have similar proton affinities but if any of these groups are *not* protonated in a given system, then in *all* stable candidates, P-O is stabilized by H-bonds, while it does not seem to be strictly necessary for the latter two. For example, (Alv₁)µ₁-OH can form H-bonds to P-O in close proximity. The first substitution occurs with preference on sites with the highest OH basicity, and can then always form favorable bidentates and tridentates involving the same sites. For (1 0 0) v₁, v₂ and v₃, are **a**, **ab** and **abc**. At first glance it might surprise that on (1 0 0) the **ab** bidentate is preferred over **aa'**, however, while the latter stabilization is limited to the formation of Al-O-P bonds, **ab** can in addition form H-bonds with the adsorbed H₂O at **c**. For coadsorption, (1 0 0) is much more constrained. Indeed, it can fit two bidentates (v₂+v₂), but only by arranging them on **aa'** and **bc**, which, due to the lack of free rotations around the Al-O-P bonds, cannot be stabilized by H-bonds.

On the $n(1\ 1\ 0)$ the favored candidates for v_1 , v_2 and v_3 are **e**, **de**, **deA**. In this cell, a set of different species might form at **b**, **bb'**, **bb'B**. For R(1 1 0) there is an equivalent set **b**, **bc**, **bcB**; with the exception here that **bc** is slightly less stable than the most favored adsorbate, **eB**. This is likely a consequence of the n->R surface reconstruction as at **B** one Al-O bond was split, hence the oxygen atom at **B** is more available for bonding to the phosphate. On both (1 1 0) facets competing sites for tridentates are available and in therefore both can carry two phosphates as v_3+v_3 .

Table S6. Free enthalpy of adsorption in kJ mol⁻¹ (of phosphate) and ³¹P-NMR shift in ppm rel to 85% H_3PO_4 for the (at 393 K) most stable system of every tested single adsorption site, labeled according to **fig. S8.** The most stable site for each adsorption mode is highlighted in bold.

		ΔG_{ads}			31	P-NMR
facet	298 K	393 K	573 K		site	
(100)	-152	-126	-78	Vo		7.1
(100)	-128	-121	-108	V1	a	6.3
(100)	-87	-83	-75	V1	b	13.5
(100)	-95	-88	-74	V1	c	13.5
(100)	-99	-113	-138	V2	aa'	5.7
(100)	-144	-156	-178	V 2	ab	4.2
(100)	-126	-140	-166	V2	bc	6.3
(100)	-97	-111	-136	V2	cb	13.0
(100)	-41	-72	-129	V3	aa'B	5.4
(100)	-76	-107	-165	V3	aa'C	5.7
(100)	-81	-112	-170	V3	abA	8.2
(100)	-91	-122	-181	V 3	abc	11.7
(100)	-31	-63	-123	V3	acb	13.3
n(110)	-78	-56	-15	Vo		11.9
n(110)	-81	-76	-67	V1	а	5.6
n(110)	-103	-100	-95	V1	b	1.5
n(110)	-91	-85	-75	V1	d	8.6
n(110)	-109	-105	-98	V1	e	2.6
n(110)	-60	-74	-100	V2	ab	1.9
n(110)	-118	-132	-158	V2	bb'	-8.6
n(110)	-119	-132	-159	V 2	de	-15.0
n(110)	-98	-112	-138	V2	ee'	10.9
n(110)	-90	-122	-182	V3	bb'B	-4.9
n(110)	-106	-137	-195	V3	bb'E	-6.5
n(110)	-119	-150	-209	<u>V</u> 3	deA	-11.0
R(110)	-69	-66	-59	Vo		1.3
R(110)	-72	-85	-111	V1	а	4.1
R(110)	-96	-112	-143	V1	b	-1.0
R(110)	-106	-120	-147	V1	c	-4.1
R(110)	-72	-86	-112	V1	d	-3.6
R(110)	-83	-98	-125	V1	e	3.7
R(110)	-75	-108	-170	V2	ab	-0.1
R(110)	-79	-113	-177	V2	bc	-5.4
R(110)	-72	-103	-159	V2	cB	-0.6
R(110)	-30	-63	-126	V2	ca	-1.7
R(110)	-63	-97	-161	V2	de	-1.1
R(110)	-129	-160	-219	V 2	eB	-4.4
R(110)	4	-46	-139	V3	abA	-5.5
R(110)	-118	-168	-263	V 3	bcB	-1.7
R(110)	-54	-106	-203	V3	bcE	-13.6
R(110)	6	-45	-141	V3	cEF	-11.4
R(110)	-85	-134	-227	V3	deA	-7.2
R(110)	0	-50	-144	V3	deD	1.9

Table S7: Free enthalpy of adsorption in kJ mol⁻¹ (of phosphate) and ³¹P-NMR shift in ppm relative to 85% H_3PO_4 for the (at 393 K) most stable system of every tested coadsorption case by combining single adsorption results. For labelling compare with **fig. S8.** The most stable site for each adsorption mode is highlighted in bold.

		ΔG_{ads}			3	¹ P-NMR		31	P-NMR
facet	298 K	393 K	573 K	1 st	site		2^{nd}	site	
(100)	-98	-74	-27	Vo		2.1	Vo		1.3
(100)	-93	-77	-47	V1	а	-3.2	V0		5.5
(100)	-105	-91	-64	V1	b	-2.0	Vo		4.1
(100)	-84	-69	-41	V1	c	-8.8	ν0		9.0
(100)	-82	-75	-62	V1	а	5.5	ν_1	а	-6.2
(100)	-102	-97	-86	V1	a	11.6	V 1	b	-5.3
(100)	-90	-85	-75	V 1	а	-11.1	V1	c	4.9
(100)	-107	-101	-88	V2	ab	1.6	V0		-6.0
(100)	-119	-114	-102	V2	bc	1.5	Vo		12.1
(100)	-116	-119	-126	V2	ab	12.7	V 1	a	-6.0
(100)	-91	-95	-101	V2	ab	8.8	ν_1	c	0.4
(100)	-105	-110	-118	V2	bc	-2.6	V 1	а	-0.6
(100)	-102	-116	-141	V2	aa	1.7	V 2	bc	8.3
(100)	-66	-80	-106	V2	aa	8.8	V2	cb	12.4
(100)	-77	-80	-85	V3	abc	9.6	Vo		-4.7
(100)	-91	-105	-132	V 3	abc	-0.8	V 1	a	-4.9
(100)	-84	-106	-148	V3	aaC	9.4	V 2	bc	6.4
(100)	-76	-98	-139	V3	aaC	1.0	V2	cb	7.7
n(110)	-101	-77	-33	Vo		47	Vo		0.1
n(110)	-112	-99	-72	V0 V1	b	10.6	Vo		8.1
n(110) n(110)	-89	-75	-48	VI VI	e	-10.7	V0		0.3
n(110)	-111	-106	-96	V1 V1	b	-8.3	V1	e'	3.4
n(110)	-83	-78	-69	V1 V1	e	12.3	V1	e'	9.6
n(110)	-102	-97	-88	V2	de	-15.0	Vo		13.4
n(110)	-89	-92	-99	V2	bb'	-13.7	V1	e	9.3
n(110)	-101	-106	-115	V2	de	-14.2	V1	b	-0.2
n(110)	-114	-127	-153	V2	bb'	-13.2	V 2	de	-10.9
n(110)	-89	-93	-101	V3	deA	-9.4	Vo		13.3
n(110)	-76	-90	-116	V3	bb'E	-6.4	V1	d	0.0
n(110)	-90	-103	-126	V3	bb'E	-9.2	ν_1	e	5.2
n(110)	-101	-114	-138	V3	deA	-17.6	V 1	b	7.7
n(110)	-97	-110	-134	V3	deA	-11.7	V1	b'	5.9
n(110)	-95	-108	-132	V3	deA	-7.2	V1	f	0.8
n(110)	-106	-128	-169	V3	bb'E	-11.3	V 2	de	-9.4
n(110)	-105	-127	-169	V3	deA	-13.9	V2	bb'	-7.9
n(110)	-68	-100	-159	V3	deA	-10.8	V 3	bb'E	-20.2
R(110)	-76	-61	_34	Vo		39	Vo		87
R(110)	_,0 _81	-68	-41	vu Vo		2.8	Vo		12.5
R(110)	-102	_97	-85	V0 V1	с	-2.0	Vo		-2.5
R(110)	-71	-75	-83	V1 V1	b	10.3	V1	с	-7.5
R(110)	-97	-101	-109	ν ₁ ν ₁	c	16.5	V1	d	-6.6
R(110)	-105	-110	-120	V1	c	5.0	V1	e	-3.0
R(110)	-75	-81	-91	V2	bc	-16.8	V0		7.2

R(110)	-95	-99	-105	V 2	eB	-4.0	Vo		1.1
R(110)	-93	-108	-136	V2	bc	-15.2	V1	d	-9.7
R(110)	-95	-108	-133	V2	bc	-26.5	V1	e	4.2
R(110)	-83	-96	-121	V2	eB	-9.8	V1	b	8.3
R(110)	-100	-113	-139	V2	eB	-8.3	V1	с	-4.7
R(110)	-120	-132	-155	V 2	eB	-5.1	V1	d	2.2
R(110)	-56	-79	-121	V 2	bc	-24.9	V 2	eB	-9.4
R(110)	-89	-102	-126	V 3	bcB	1.1	Vo		3.6
R(110)	-96	-119	-161	V3	bcB	0.8	ν_1	а	3.3
R(110)	-99	-121	-164	V3	bcB	-3.1	V1	d	-1.9
R(110)	-87	-109	-152	V3	bcB	-2.7	ν_1	e	8.5
R(110)	-36	-68	-127	V3	bcE	-8.7	V2	eB	-15.4
R(110)	-66	-98	-157	V3	deA	-14.9	V 2	eB	-12.3
R(110)	-73	-113	-188	V 3	bcB	-11.7	V3	deA	-6.8
R(110)	-36	-76	-153	V3	bcE	-20.5	V3	deA	-16.5

Table S8: Free enthalpy of adsorption of $H_4P_2O_7$ in kJ mol⁻¹ (given per phosphate) and ³¹P-NMR isoshift in ppm rel to 85% H_3PO_4 for the (at 393 K) most stable system of every tested case. For labelling compare with **fig. S8.** The most stable site for each adsorption mode is highlighted in bold.

		ΔG_{ads}			3	³¹ P-NMR		3	¹ P-NMR
facet	298 K	393 K	573 K	1 st	site		2^{nd}	site	;
(100)	-49	-35	-8	Vo		-7.9	Vo		1.7
(100)	-96	-89	-76	V1	a	-19.2	Vo		-23.8
(100)	-95	-99	-107	V1	a	-18.0	V1	a	-10.2
(100)	-74	-78	-86	ν_1	а	-13.9	ν_1	b	-10.7
(100)	-79	-82	-87	ν_1	а	-22.3	ν_1	c	-10.7
(100)	-94	-97	-104	V 2	ab	-9.7	Vo		-8.5
(100)	-93	-106	-130	V 2	bc	-11.0	V1	a	-10.4
(100)	-84	-97	-122	V2	cb	-4.0	ν_1	а	-12.7
(100)	-49	-62	-88	V 3	abc	-3.0	Vo		-16.4
n(110)	-66	-52	-26	Vo		-5.8	Vo		-7.6
n(110)	-63	-58	-49	V1	а	-18.7	Vo		-11.1
n(110)	-83	-78	-70	V1	b	-8.7	Vo		-7.0
n(110)	-78	-73	-62	V1	d	-16.7	Vo		-1.8
n(110)	-86	-81	-71	V1	e	-10.3	Vo		-5.5
n(110)	-81	-85	-92	V1	а	-10.4	ν_1	d	-8.9
n(110)	-94	-99	-109	v_1	b	-17.3	ν_1	b'	-21.2
n(110)	-51	-56	-64	ν_1	b	-17.2	ν_1	d	-11.5
n(110)	-69	-72	-79	ν_1	b'	-17.5	ν_1	а	-14.6
n(110)	-83	-87	-95	ν_1	d	-12.9	ν_1	e	-18.4
n(110)	-97	-100	-106	V1	e	-5.7	V1	b	-13.5
n(110)	-89	-94	-102	ν_1	e	-13.6	ν_1	e'	-15.4
n(110)	-48	-51	-58	V2	ab	-6.7	V 0		-9.4
n(110)	-63	-68	-79	V2	bb'	-23.6	V 0		-8.8
n(110)	-82	-85	-92	V 2	de	-26.3	Vo		-9.0
n(110)	-75	-88	-113	V2	bb'	-32.6	ν_1	e	-4.8

n(110)	-69	-81	-105	V2	de	-33.0	V 1	a	-14.0
n(110)	-84	-97	-122	V 2	de	-25.2	V 1	b	-10.5
n(110)	-46	-69	-112	V2	bb'	2.7	V2	ee'	-34.3
n(110)	-51	-74	-117	V 2	de	-25.9	V 2	ab	-35.9
n(110)	-35	-59	-103	V2	ee'	-32.6	V2	bc	4.7
n(110)	-20	-34	-59	V3	bb'E	-16.1	V0		-5.0
n(110)	-43	-56	-83	V 3	deA	-27.0	Vo		-5.6
n(110)	-61	-84	-125	V 3	bb'E	-21.6	V 1	e	-13.8
n(110)	-57	-79	-121	V3	deA	-25.2	V1	b	-8.6
n(110)	-35	-67	-127	V 3	bb'B	-18.3	V 2	ee'	8.3
n(110)	4	-28	-89	V3	bb'E	-14.1	V2	ee'	12.0
n(110)	-16	-47	-107	V3	deA	-21.7	V2	ab	-13.7
R(110)	-84	-79	-69	Vo	c	-6.3	Vo		-13.6
R(110)	-81	-85	-94	V1	c	-14.0	Vo		-15.1
R(110)	-82	-96	-123	V1	b	-15.8	V1	c	-25.6
R(110)	-68	-82	-107	V 1	с	-30.0	V1	d	-21.0
R(110)	-54	-67	-92	ν_1	c	-17.4	V1	e	-21.4
R(110)	-72	-86	-112	V2	bc	-35.3	V0		-16.2
R(110)	-86	-99	-123	V2	eB	-10.6	Vo		-13.5
R(110)	-9	-31	-72	V2	bc	-27.8	V1	В	-1.3
R(110)	19	-3	-44	V2	bc	-19.7	V1	Е	-14.3
R(110)	-11	-33	-75	V2	bc	-20.5	V1	F	-6.2
R(110)	-64	-87	-131	V2	bc	-30.4	V1	e	-12.2
R(110)	-54	-77	-122	V2	bc	-35.5	V1	e	-23.2
R(110)	-83	-105	-147	V 2	eB	-19.3	V 1	b	-12.5
R(110)	-70	-92	-134	V2	eB	-13.7	V1	c	-10.4
R(110)	-78	-100	-142	V2	eB	-17.8	V1	d	-19.0
R(110)	-84	-116	-175	V 2	eB	-27.4	V 2	bc	-15.9
R(110)	-66	-87	-127	V 3	bcB	-17.2	Vo		-16.0
R(110)	-58	-79	-119	V3	bcE	-20.4	٧٥		-10.4
R (110)	-85	-117	-176	V 3	bcB	-19.7	V 1	e	-18.7
R(110)	-38	-70	-130	V3	bcE	-22.3	V1	e	-21.3
R(110)	55	13	-66	V3	deA	-17.4	V2	ab	-15.6

3.2. Coverage effect on ³¹P-NMR iso-shift

Here, the change of chemical shift with coverage is referred to as "coverage effect". This effect can be the consequence of direct or indirect phosphate–phosphate interactions. Here we attempt to reproduce this effect focusing on the 6 most stable single phosphate adsorption cases (fig. 6 right in the main text). We keep the dentation as well as the site constant and cover three coverage values per surface. Moreover, we reproduced the structures of monophosphates in larger unit cells to reach lower coverage values : 1.1 P nm⁻² on the (100) surface and 0.7 P nm⁻² on the (110) surfaces. The results are shown in **fig. S9.** In this plot we can see the ³¹P-NMR shift of the same phosphate group under changing coverage conditions. The data strongly overlap with the results in fig. 6 left in the main text and are also those given in **tab. S6 and S7.** We observe that the chemical shift can decrease as P coverage increases for any given site, but the downwards shift is quite small and, in the high coverage regime, we observe signal broadening due to additional upwards shifts.

These results support our previous analysis, as we see that we need to invoke different adsorption modes and sites to rationalize the experimental ³¹P-NMR chemical shift. Only by taking into account oligomers we can rationalize the experiments. Although the upper range of the overall chemical shift range is dominated by phosphate monomers on the (1 1 0) facet, the lower range of the spectra suggests diphosphate formation in competition with coadsorption between -15 and -20 ppm.



Figure S10: Computed ³¹P-NMR shifts of phosphates, H₃PO₄, adsorption involving v_2 - or v_3 -dentation on either phosphate terminus on the n(1 1 0) (green symbols), R(1 1 0) (deep red symbols) and (1 0 0) (blue symbols) facets.

3.3. Calculation of ²⁷Al chemical shifts

Figure S11 illustrates that the calculated ²⁷Al chemical shifts, ²⁷Al δ_{iso} , are quantitatively consistent with previous calculated and experimental data reported by Wischert et al. ²² As shown previously, the DFT calculation is able to distinguish the two main families of chemical isoshifts corresponding to Alv₁ and Al₁v sites present on the hydroxylated surface in absence and in presence of adsorbed phosphate. A comparison of absolute calculated values obtained with INEPT experiments is not straightforward, however we expect that the trend could be semi-quantitatively interpreted. If we consider first the average values for Al octahedral and tetrahedral sites, the presence of adsorbed phosphates and polyphosphates obviously implies an upfield shift of ²⁷Al δ_{iso} . This effect is generally more pronounced at higher P coverage. In addition, we observe that all Al sites (covalently bonded to P through

Al-O-P bridge and non covalently bonded) exhibit upfield shifts, even if covalently bonded sites are slightly more impacted.



Figure S11. ²⁷Al chemical shift calculated for the various surfaces with and without phosphorus species in the most relevant adsorption modes: a) Al octahedral sites of the (100) surface; b) Al octahedral sites of the (110) surface; c) Al tetrahedral sites of the (110) surface; d) Al octahedral sites of the R(110) surface; e) Al tetrahedral sites of the R(110) surface. The average values of chemical shift are calculated for all Al sites, Al covalently bonded to P, and Al non-covalently bonded to P (when one bar is not represented, this means that the site does not exist).



3.4. H₃PO₄ adsorption energy trends under drying conditions

Figure S10: Enthalpy ΔH_{ads} and entropy ($-T\Delta S_{ads}$) components, (a) and (b), given for drying conditions, 393 K and 2 kPa.

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