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Tuning the electronic properties of the γ - Al_2O_3 surface by phosphorus doping†

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Tuning the electronic properties of oxide surfaces is of pivotal importance, because they find applicability in a variety of industrial processes, including catalysis. Currently, the industrial protocols for synthesizing oxide surfaces are limited to only partial control of the oxide's properties. This is because the ceramic processes result in complex morphologies and *a priori* unpredictable behavior of the products. While the bulk doping of alumina surfaces has been demonstrated to enhance their catalytic applications (*i.e.* hydrodesulphurization (HDS)), the fundamental understanding of this phenomenon and its effect at an atomic level remain unexplored. In our joint experimental and computational study, simulations based on Density Functional Theory (DFT), synthesis, and a variety of surface characterization techniques are exploited for the specific goal of understanding the structure–function relationship of phosphorus-doped γ - Al_2O_3 surfaces. Our theoretical calculations and experimental results agree in finding that P doping of γ - Al_2O_3 leads to a significant decrease in its work function. Our computational models show that this decrease is due to the formation of a new surface dipole, providing a clear picture of the effect of P doping at the surface of γ - Al_2O_3 . In this study, we uncover a general paradigm for tuning support–catalyst interactions that involves electrostatic properties of doped γ - Al_2O_3 surface, specifically the surface dipole. Our findings open a new pathway for engineering the electronic properties of metal oxides' surfaces.

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Introduction

Metal oxides and their surfaces find extensive use in numerous fields of materials science, such as chemical catalysis, photocatalysis, and photovoltaics, among others.^{1,2} Thus, engineering the electronic properties of the oxide surfaces is crucial for a broad application of materials, as well as for the improvement of their current applications.^{1,3} As of today, however, serious limitations affect the extent of this control, mainly for two reasons. First, most synthetic methods yielding well defined doped surfaces are limited to academic use (small scale) – which are not cost effective for industrial applications – or the products are not stable under the operational conditions of most industrial processes.⁴ Secondly, the ceramic processes typically employed in industry to engineer oxide-containing materials result in complex morphologies⁵ and *a priori* unpredictable behavior of the generated materials.

In this work, our primary goal is to generate phosphorous doped alumina surfaces, by employing simple ceramic processes and characterizing their electronic properties. We aim at shedding light on three major points: (1) a theory–experiment correlation to inspect the average or the most likely surface morphology (we consider an array of possible locations of P on γ - Al_2O_3 surfaces); (2) finding a structure–function relationship between the electronic properties and surface morphology. This can be exploited when metal oxides are engineered; and (3) determining the degree of thermodynamic stability for various possible surface terminations, as well as P locations on the P-doped γ - Al_2O_3 (P- γ - Al_2O_3).

Our study focuses on an atomic-level understanding of the morphology and the structure–property relationships of realistic (hydroxylated) surfaces of P- γ - Al_2O_3 nanoparticles. γ - Al_2O_3 has been widely used as an adsorbent and a catalyst,⁶ and also it is perhaps the most important nanomaterial used as a support for metal catalysts.⁷ The properties of Al_2O_3 can change during chemical operations, which include chemical contamination, thermal stress leading to loss of surface area, pore blockage, and undesired crystal phases.^{8–10} It has been empirically observed that dopants improve the overall performance of catalysts acting as crystal phases and/or surface area stabilizers.^{11–13} For example, studies on the fact that treating the surface of γ - Al_2O_3 with phosphates could

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largely promote the performance of the catalysts in hydrodesulphurization (HDS) have been reported.^{13–15} Also, doping of γ -Al₂O₃ is commonly used for tuning its mechanical^{16,17} and optical properties.^{18,19} Many dopants such as metal, silica, and heteroatoms have been used to modify the γ -Al₂O₃ surface or its bulk during fabrication.^{20–23} Phosphorus is our choice of dopant, because it has a variety of atomic coordinations and multiple electronic states. Also, it is known that phosphorus can covalently bind to Al₂O₃, thus making a stable catalyst support.^{24,25}

Experimentally, we characterized the structural and chemical properties of both P-doped and non-doped γ -Al₂O₃ nanoparticles by utilizing Fourier transform infrared (FT-IR) spectroscopy, solid-state magic-angle spinning nuclear magnetic resonance (MAS-NMR), energy-dispersive X-ray spectroscopy (EDS), and PeakForce Kelvin probe force microscopy (PF-KPFM) techniques. On the theoretical side, we carried out several DFT simulations accounting for an array of surface and doping morphological models. Electronic properties were characterized by computing the density of Kohn–Sham states (DOS), surface work function and surface dipole moment, as well as IR and NMR of P-doped and non-doped γ -Al₂O₃.

Results and discussion

To investigate the P content in the doped γ -Al₂O₃ structure, EDS was conducted, using EDAX coupled with FE-SEM Hitachi S-4800. As EDAX microprobe analysis is semi-quantitative, analysis of several samples was carried out and the averaged values are presented in Table 1.

We perform DFT calculations (see the computational details section) where γ -Al₂O₃ and P- γ -Al₂O₃ surfaces are presented for two different essential surface models, namely oxygen terminated and 100% hydroxylated (OH terminated). We considered single-atom doping and two-atom doping (*i.e.*, two interacting and independent P atoms in the simulation cell). Each structure underwent geometry optimization. Although we carried out the simulations on cells of two sizes (a small bulk unit containing 40 atoms and a bulk supercell containing 160 atoms) the presented results are based on the simulations of the larger, more realistic cell, unless otherwise stated. Both slab models consist of five cation layers (tetrahedrally and octahedrally coordinated Al atoms). A vacuum thickness of 15 Å above the surface was added between two periodically repeated slabs. We placed P on one surface of the slab. The bottom 40% of atoms in each slab was kept fixed at their optimized positions throughout the simulations. We consider four different positions for the P atoms in two categories:

- models **sub/surf**: P is located on a subsurface/surface site substituting an Al atom;

- models **md/bd**: P is in a phosphate-type ligand with mono/bidentate complexation to a surface Al atom.

Throughout the manuscript, we use abbreviations to identify each surface model of the relevant termination (*e.g.*, **O-sub** and **OH-sub** are for subsurface locations of P on O-terminated and OH-terminated surfaces, respectively).

In the simulation, we choose the (001) surface of γ -Al₂O₃ in the spinel-like bulk morphology proposed by Gutiérrez *et al.*,²⁶ Pinto *et al.*,²⁷ and Taniike *et al.*²⁸ This structure compares favorably to known crystallographic and physical properties of γ -Al₂O₃.²⁹ In Fig. 1 we depict the computed morphology (a and b) for the O-terminated γ -Al₂O₃ model as well as its associated DOS plot (c). Not surprisingly, this surface termination activates the material. Although it is known that this termination is only detectable at very high temperatures, we present it here as a model for oxygen-rich surface islands.

As our picture of γ -Al₂O₃ is that of a heterogeneous material with OH-rich and O-rich domains, we also present a depiction of the 100% hydroxylated surface termination of the supercell in Fig. 1(d and e) alongside the associated DOS plot (f). From the mentioned figure, it is clear that, as expected, hydroxylated γ -Al₂O₃ is an insulator and electronically stable.

Experimentally, the P- γ -Al₂O₃ was synthesized by impregnation of phosphoric acid and commercially available γ -Al₂O₃, followed by a simple and commonly applied ceramic process, *i.e.* a high temperature annealing process in air (see the experimental details section). By optimizing the ratio of γ -Al₂O₃ and the molarity of H₃PO₄, we are able to tune the doping level of P. In Fig. 2 we show the atomic-level surface morphologies, resulting from the DFT simulations and the corresponding PDOS. When considering phosphate chemisorption, it can be realized through a monodentate or bidentate ligand configuration. Additionally, here we consider two types of slabs: one that is stoichiometric with a P(5+) oxidation state, and one that is consistent with a P(3+) oxidation state. This was accomplished by the addition of an electron donor to the bottom of the slab. The relevant computed morphologies and associated PDOSs can be seen in S1 and S2 (ESI†) for both O-terminated and OH-terminated surface models, where it can be seen that the phosphorous coordination and overall local geometry and surface PDOS are slightly affected by the overall stoichiometry of the slab. This indicates that the chosen slab model is sufficiently thick that the surface properties are resilient to the chemistry occurring at the other end of the slab.

In the models **O-sub/O-surf** and **OH-sub/OH-surf**, the P atom was introduced at a tetrahedral Al site. The theoretical prediction delivers a clear picture for **O-sub**: a planar configuration is assumed for P, consistent with an effective double oxidation (3+ oxidation state). For this model, we also explore the O terminated subsurface doped with two P atoms at the three tetrahedral doping sites (Fig. S3 and S4, ESI†). The three resulting models show how the location of the second P atom introduces significant changes to the shape of the conduction band (CB). As there are unoccupied orbitals with P character, similarly to the previous O terminated P-doped model (**O-sub**) one or both subsurface P atoms have 3+ oxidation state character.

Table 1 The results of EDS analysis for the P- γ -Al₂O₃ samples

Element	Weight (%)	Atomic (%)
O	42.8	56.2
Al	48.7	38.0
P	8.5	5.8

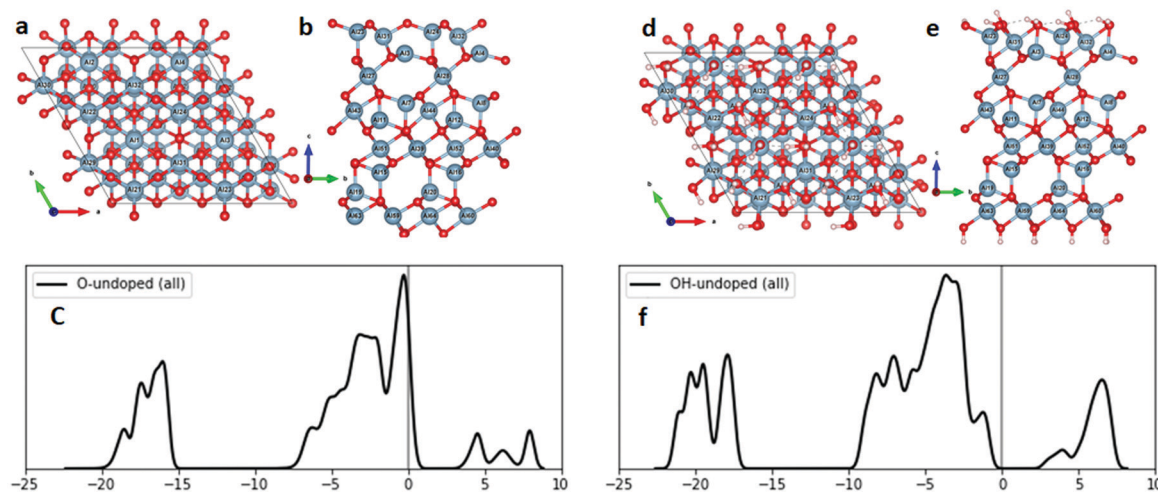


Fig. 1 Computed morphology, both top view (a) and side view (b), and associated DOS (c) of a non-doped O terminated γ - Al_2O_3 surface. Those of the 100% hydroxylated γ - Al_2O_3 surfaces are given in (d), (e), and (f), respectively. Fermi energy placed at zero for DOSs.

When the P atom is located on the surface (model **O-surf**), it causes surface reorganization and distortions across the surface O atoms to form an O-dimer (see the relevant structure in Fig. 2a). The computed PDOS of this model has a band gap of 4 eV and it is shown that the Fermi level lies at the top of the valence band. The computed PDOS plots display no significant changes either in monodentate (**O-md**) or bidentate (**O-bd**) configuration models, even though the surface morphology in **O-bd** was affected by several distortions of surface O atoms.

When doping the OH terminated surface, we obtain the morphology/DOS depicted in Fig. 2. In model **OH-sub**, the P atom is now non-planar, maintaining the lone pair as a partially filled state. At the same time, the P atom is sheltered in a sub-surface site. The surface P atom doping (**OH-surf** model) at the tetrahedral Al site causes the neighboring octahedral Al site to become five coordinated. In this situation, the surface P atom becomes three coordinated (see Fig. S5, ESI†). When considering the phosphate models (**OH-md** and **OH-bd**), we notice that the surface largely maintains its non-doped surface morphology (low reorganization), but the DOS profile changes, displaying clear gaps with no P states on the band edges.

We further investigate the subsurface P doping and also consider higher concentration doping (*i.e.*, two independent P atoms in the same simulation cell). The idea behind this set of simulations is to inspect the extent of nonadditivity/cooperation in the electronic behavior of the surfaces after P-doping. We achieved this by replacing another tetrahedral Al with P. The second P was inserted at three of the different, available and inequivalent tetrahedral Al locations and considered both the OH and O terminated surfaces. For the OH terminated surface, we found two local minima of the potential energy surface. The first structure features one P atom four-coordinated with three subsurface oxygen atoms and one surface hydroxyl group. The second P location is 3 coordinated with its lone pair still on P and points in the direction of the spinel defect site (Fig. S6a, ESI†). In the second local minimum structure, the P closer to the surface moved toward the bulk expelling a water molecule

(Fig. S6b, ESI†). When the O-terminated surface is considered, the two P atoms achieve a planar tri-coordinated geometry. Conceivably, this is an indication that the oxidation state of P atoms is now 3+.

The PDOS of these surfaces showed largely the same trend as for singly doped surfaces. For the O-terminated surfaces, P doping induces narrowing of the gap and the appearance of states with P character at the band edges. The OH-terminated surfaces are more resilient to the doping and maintain a large gap. However, as in the case of the singly doped surface, the valence band (VB) edge has a strong P character (Fig. S7, ESI†). Thus, we do not find a significant cooperative effect between P sites.

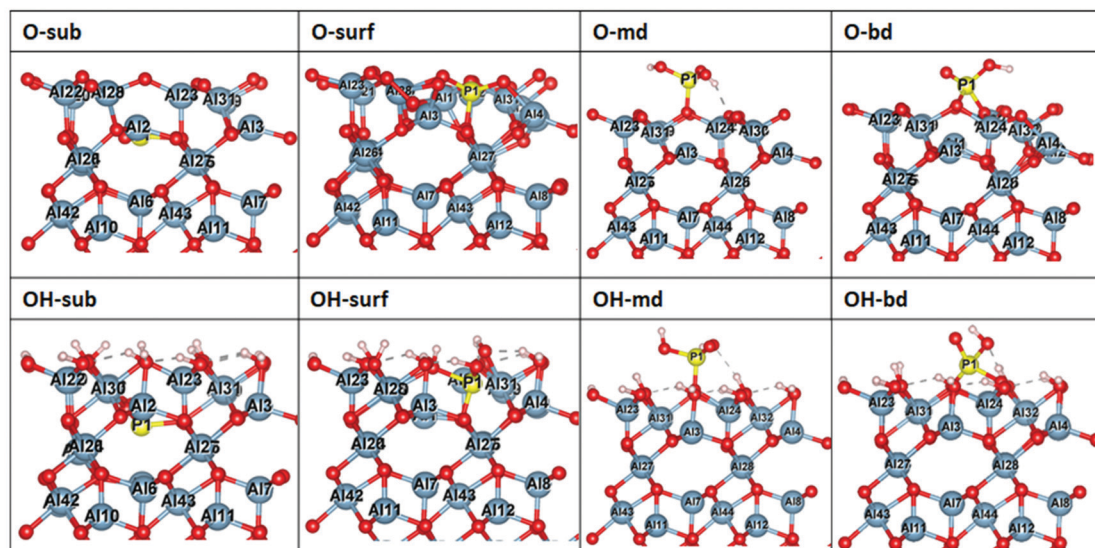
Our next set of investigations is regarding the simulations and measurement of the work function (WF or ϕ) of P doped and non-doped γ - Al_2O_3 nanoparticles. To understand the influence of P doping on the work function of γ - Al_2O_3 nanoparticles, PeakForce Kelvin probe force microscopy (PF-KPFM™) in an argon-filled glovebox is conducted for both doped and non-doped γ - Al_2O_3 nanoparticles (see S8 for more details, ESI†). PF-KPFM measurement is carried out on several nanoparticles with similar dimensions for each sample (Fig. 3).

The average measured WF of γ - Al_2O_3 is 4.88 ± 0.04 eV, while the average measured WF of P- γ - Al_2O_3 is 4.16 ± 0.06 eV. Our results show that doping of γ - Al_2O_3 by phosphorus has lowered its WF by almost 15% (Fig. 4a).

We employ and compare GGA with GGA+*U* for the calculation of the WFs of all surface models. When performing GGA+*U* we derive suitable *U* values for O (1.11 eV) and P (1.77 eV) by employing the Cococcioni-de Gironcoli linear response method³⁰ to the small surface structures (40 atoms). DFT+*U* is chosen here to remove the spurious self-interaction present in semilocal (GGA) exchange–correlation functionals³¹ and is particularly suited to improve the *ab initio* description of surfaces and interfaces.

The corresponding surface-averaged electrostatic potential of each model is plotted as a function of distance from the surface (Fig. in S9, ESI†). The values of WFs and the corresponding

A



b

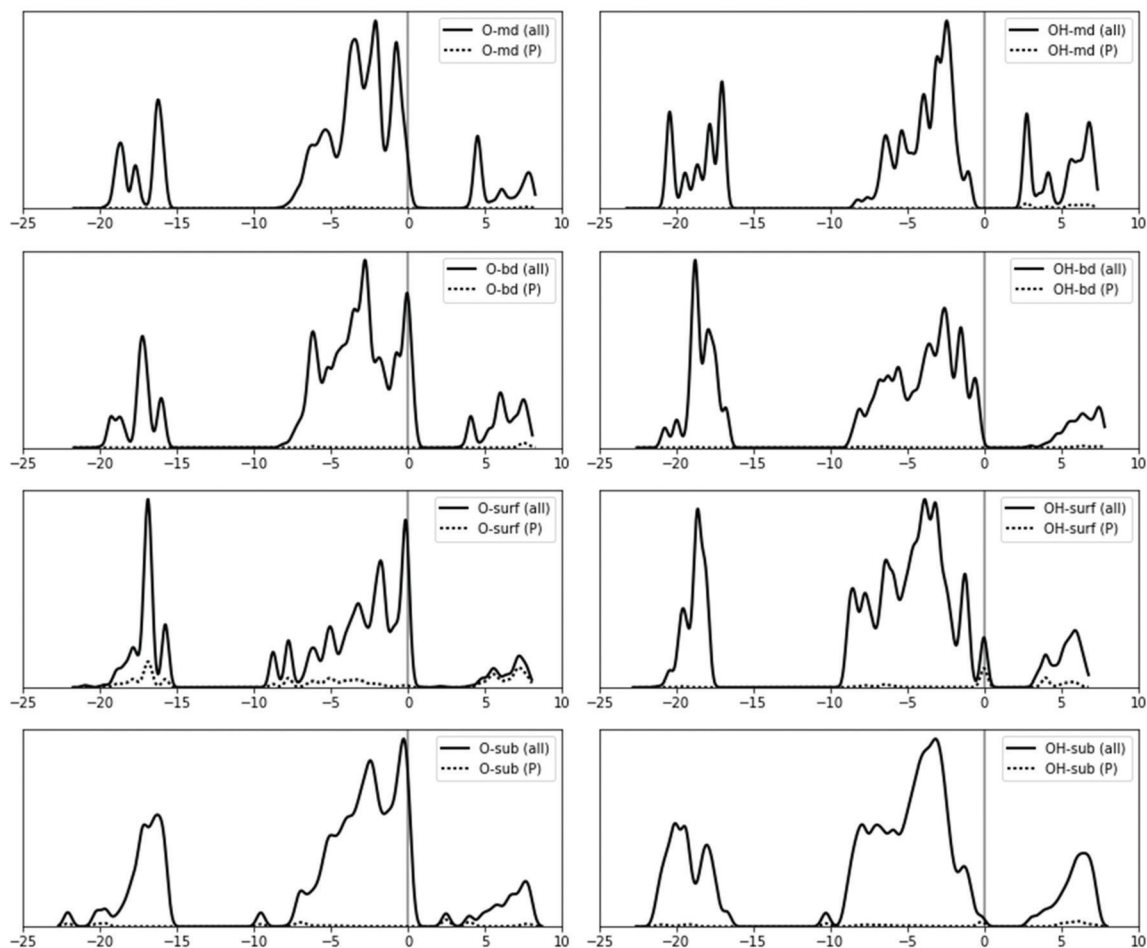


Fig. 2 Models of O terminated and OH terminated $P\text{-}\gamma\text{-Al}_2\text{O}_3$ surfaces (a) and their associated surface PDOSs (b). The P atom is placed at various positions as defined before, particularly at the spinel defect site for **O-sub** and **OH-sub** models. In the PDOSs, the Fermi energy is set to zero. A clearer depiction of the tri-coordinated P atom in **O-surf** of inset (a) is found in Fig. S6 (ESI†).

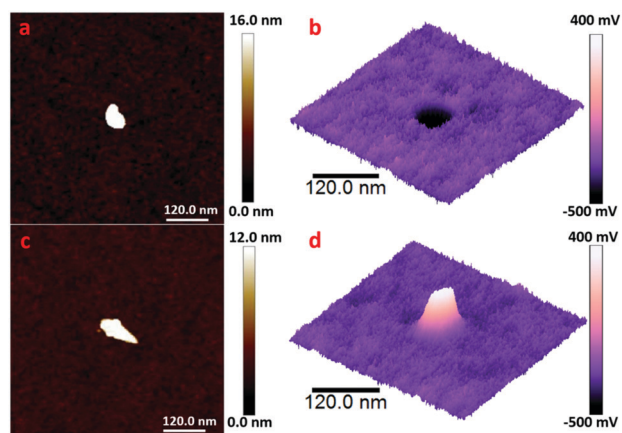


Fig. 3 (A and C) Topography and (B and D) potential mapping images of γ - Al_2O_3 and P- γ - Al_2O_3 nanoparticles, respectively.

surface dipole contributions (ϕ_d) are presented and compared with GGA quantities (see Table S1 for the entire set of calculated values, ESI†).

It is seen that for all surface models except **OH-md** and **OH-bd**, the computed WFs agree with the experiment in that WF is reduced as a result of P-doping. The reason for the fact that **OH-md** and **OH-bd** models stand out is complex and it involves two observations: (1) the surfaces do not rearrange significantly from the non-doped case and (2) the P-OH contribution to the surface dipole is to increase it. Specifically, comparing the P-OH angle and OH direction in **O-md** and **O-bd** with the

OH-counterparts from Fig. 2, we notice that the hydroxylated surfaces have a P-OH pointing upward, while the O-terminated surfaces have a P-OH pointing downward. Thus, when the phosphates are added to the surface, the dipole is depleted for the O-terminated surfaces and enhanced for the OH-terminated ones. This observation is especially important for the **OH-bd** system. When we inspect the effect of doping by two independent P atoms (higher concentration) on the WF for the various structures of subsurface (**O-sub** and **OH-sub**) models (see the Chart in S10a, ESI†), we notice that the addition of the second P atom further decreases the WF. Thus, theory and experiment semiquantitatively agree that on average P- γ - Al_2O_3 has a lower WF than non-doped γ - Al_2O_3 , with the chemisorbed phosphate models going against the trend and increasing the WF values when the OH-terminated surfaces are considered.

To understand the reasons for the WF reduction by P doping we present in Fig. 4b the WF differences ($\Delta\phi$) between the non-doped and P-doped surfaces of each structural model, providing us with a comparison of theory and experimental results. It shows that all the O-terminated surfaces are in accordance with the experiment by yielding lower WF after P-doping (Fig. 4b). However, the dentate models (**OH-md** and **OH-bd**) increase the WF values.

The size of the surface dipole contribution to ϕ (ϕ_d) estimated by computing the difference between the left and right vacuum levels³² exhibits a clear trend that ϕ_d reduces linearly with the increase in the number of P dopants for the O-terminated surfaces whereas it conversely rises for the OH-terminated surfaces (see Fig. S10b, ESI†).

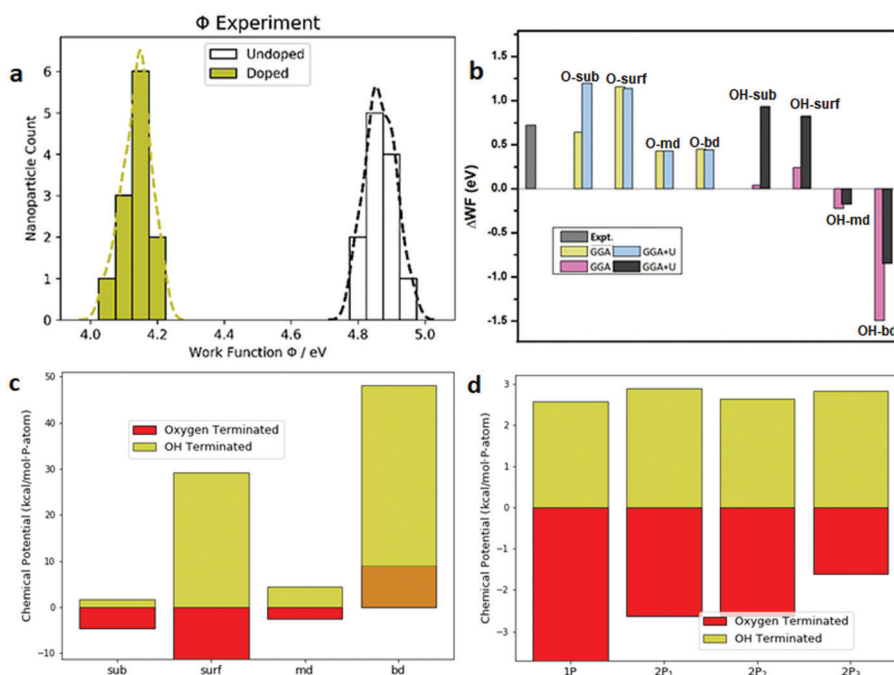


Fig. 4 (a) Experimentally determined WFs for non-doped and P-doped γ - Al_2O_3 . (b) Comparison of the experimentally and theoretically determined WF differences (ΔWF) between non-doped and P-doped structures for supercell models of O-terminated and OH-terminated surfaces. Here, the negative ΔWF denotes the increase in WF after P-doping as opposed to experimental results. (c) Surface stability diagram of P doping in terms of the chemical potential for both O-terminated and OH-terminated surfaces. (d) Surface stability diagram of P doping (**O-sub** and **OH-sub** models) in terms of the chemical potential. 2P₁, 2P₂, and 2P₃ are for three different available tetrahedral Al sites.

Our analysis is substantiated by characterizing the energetic stability of the O-/OH-terminated surfaces in terms of chemical potentials, μ (see Fig. 4c), revealing that dentate attachment models on both O- and OH-terminated surfaces (**O-md/OH-md** and **O-bd/OH-bd**) are less stable compared to other surface models (**O-sub/OH-sub** and **O-surf/OH-surf**). Also, O-terminated surfaces are more stable than OH-terminated ones by providing **O-sub** models as the most stable ones among all possible configurations (Fig. 4d).

Furthermore, to get a structure–function relationship among various surface models of P- γ -Al₂O₃ discussed here, we plot a correlation between the WF and ϕ_d (Fig. S11, ESI[†]), which demonstrate the behavior of the electronic structure against the various P locations on γ -Al₂O₃ surfaces. Fig. S11a (ESI[†]) shows that there exists a clear linear correlation between ϕ and ϕ_d for the models of O-terminated surfaces, whereas a less correlation for $\phi - \phi_d$ occurs for OH-terminated surfaces of supercells (Fig. S11b, ESI[†]). However, the similar plots for the small cell models (**O-** and **OH-**) (see Fig. S11c and d, ESI[†]) display a less linear correlation for O-terminated surfaces but a relatively good correlation for OH-terminated ones. This shows the importance of sizable finite size effects and surface relaxation effects on modeling of γ -Al₂O₃ surfaces.³³ Upon inspection of the Bader charges of the P atom in O-terminated and OH-terminated surfaces, all varying between 0.14 and 0.17, we further confirm that the reduction in the WF witnessed in our simulations is due to a change in the dipole moment orientation rather than to charge transfer.

In order to obtain more detailed information about the structure and change in the chemical environment after P doping, the Al-NMR spectra were obtained for three samples; the as

received γ -Al₂O₃, P doped γ -Al₂O₃ and heated γ -Al₂O₃, which were obtained by annealing γ -Al₂O₃ at the same temperature as that applied for P doped γ -Al₂O₃, just without the H₃PO₄ source (Fig. 5a). The spectrum of the as-received γ -Al₂O₃ sample (in black) shows two peaks which correspond to AlO₄ at around 70 ppm and to AlO₆ at around 12 ppm with about 1 : 2 integration ratio, which is consistent with the values reported in the literature.^{11,34,35} In the case of P- γ -Al₂O₃, the peak positions for AlO₆ and AlO₄ remain unchanged. While a new sharp peak appeared at 42.3 ppm and a shoulder to the octahedral Al peak appeared at around 4 ppm. The peak at 42.3 ppm has been assigned to AlO₅ bonding. It is worth mentioning that the AlO₅ surface units have been considered as selective anchoring sites for Pt catalysts.³⁴ The upshift of the shoulder is possibly caused by the coupling of P with the AlO₆ units to form Al–O–P in the local environment of the surface AlO₆ units.¹¹

To assure that these structural changes are not due to a simple high temperature annealing effect, a control experiment was conducted, where the as-received γ -Al₂O₃ was heated to 550 °C for 4.5 h (the same heating conditions as in the case of the P-doping process, without the phosphorus source). As shown in Fig. 5a, the heated γ -Al₂O₃ shows a similar NMR spectrum to the as-received one,³⁴ suggesting that the P-doping process promoted the structural rearrangement for the formation of so-called pentahedral coordination units (AlO₅) and possible Al–O–P structures.

Additional evidence supporting the experimental measurements for Al-NMR is provided by the theoretical calculations. Computations of bulk γ -Al₂O₃ (carried out with GIPAW³⁶ on bulk γ -Al₂O₃) reproduce the experimental spectrum of the clean

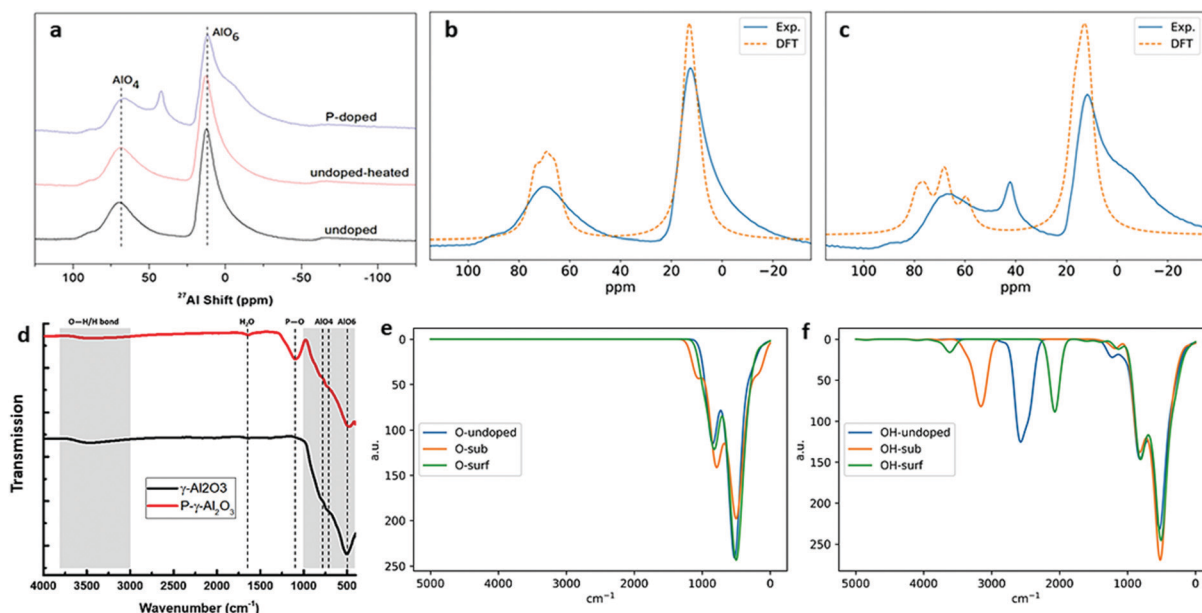


Fig. 5 (a) ²⁷Al magic-angle spinning (MAS) NMR spectra of P- γ -Al₂O₃ (top), heated γ -Al₂O₃ (middle), and as received γ -Al₂O₃ (bottom). Theoretical predictions of solid-state Al-NMR spectra computed on a bulk model supercell including 40 independent atoms and plotted with dashed lines; (b) non-doped γ -Al₂O₃ and (c) P-doped γ -Al₂O₃. (d) Experimental IR spectra of the non-doped and P-doped γ -Al₂O₃ nanoparticles. Calculated IR spectra (e) of subsurface (**O-sub**) and surface (**O-surf**) P-doped O-terminated surface models and (f) of subsurface (**OH-sub**) and surface (**OH-surf**) P-doped OH-terminated surface models.

non-doped γ - Al_2O_3 nanoparticles with remarkable accuracy (Fig. 5b). The computational spectra (Fig. 5c) assign the peak at 42.3 ppm to either distorted tetrahedral or distorted octahedral-coordinated Al atoms. Our work, thus, improves upon recent theoretical results³⁷ which could only tentatively assign the 42.3 ppm peak to pentacoordinated Al atoms. We further find that the pentacoordinated Al atoms, depending on the nature of the bonding (lengths and angles), give rise to NMR peak upfield (not shown) compared to the octahedral Al atoms explaining the presence of the shoulder peak. It should be noted that our DFT calculations for the NMR computation of the P-doped surface structures did not converge. Our works on a comprehensive NMR computation of P-doped γ - Al_2O_3 surface structures to accurately understand the shoulder at 0 ppm and the additional sharp peak at 42.3 ppm are in progress and will be published elsewhere.

To gain more information about the chemical bonds, both non-doped and P-doped γ - Al_2O_3 nanoparticles were characterized with FT-IR spectroscopy (Fig. 5d). Also, we computed the vibrational frequencies for the models of O-terminated (Fig. 5e) and OH-terminated (Fig. 5f) γ - Al_2O_3 surfaces. The experimental spectrum of γ - Al_2O_3 shows a wide peak between 3000 and 3800 cm^{-1} , which is assigned to O–H stretching and the hydrogen bond between the OH groups existing on the surface of Al_2O_3 .^{38,39} The computational spectra of all OH-terminated surface models and dentate models of O-terminated surfaces (**O-md** and **O-bd**) confirmed that the peaks in this region are due to the asymmetric stretching mode of O–H (see Fig. 5f and Fig. S12a, b, ESI†). The EDAX measurement indicated that the P loading in P- γ - Al_2O_3 was around wt 8.5% (atomic 5.6%), which is much higher than those required to react all the surface hydroxy groups on the surface of γ - Al_2O_3 .^{40,41} However, this peak still exists, even though it is weakened in P- γ - Al_2O_3 . At the same time, the peak intensity is increased in P- γ - Al_2O_3 at 1639 cm^{-1} , which has been assigned to the bending moment of adsorbed water molecules.⁴² The remaining weak peak is assigned to the hydroxy group stretching from surface phosphate groups formed upon P doping and/or from water molecules adsorbed on P- γ - Al_2O_3 .⁴⁰ On the other hand, the weak peak with a high P doping level also suggested that either some of the phosphate groups were dehydrated and/or some of the phosphorus was incorporated into the lattice of Al_2O_3 (and not on the surface of the alumina). In the spectra of the **OH-surf** model, similar peaks, an intense peak at around 2000 cm^{-1} and a relatively very small peak at around 1650 cm^{-1} are reproduced due to the asymmetric stretching mode and inplane bending moments of O–H, respectively. A similar O–H bending mode is seen at around 2200 cm^{-1} for the **OH-md** model (see Fig. S12b, ESI†).

Indeed, a significant peak at 1100 cm^{-1} appeared for P- γ - Al_2O_3 , which was considered as the identification of different P–O stretching, especially for ideal tetrahedron $[\text{PO}_4]^{3-}$ groups.^{12,43} However, our computational analysis shows that the **OH-non-doped** model also indicates such a peak and the peaks in this region result from the O–H bending mode for OH-terminated surface models of P- γ - Al_2O_3 . Only the **O-sub** model has a peak due to P–O stretching in this region. For the other models, the

vibrational modes of P appear between 800 and 1000 cm^{-1} as P–O bending mostly. This finding, in combination with the unexpected small peak of the hydroxy group of phosphate in the range of 3000–3800 cm^{-1} , supports our hypothesis that P is either in the form of surface phosphate groups, which did not carry hydrogen atoms, and/or some of the P dopants incorporated inside the lattice or network of Al_2O_3 .

It was reported that absorption in the range of 400–900 cm^{-1} corresponds to the Al–O stretching related to the octahedral (AlO_6) and tetrahedral (AlO_4) units in the network of γ - Al_2O_3 .⁴⁴ The FT-IR spectra of both γ - Al_2O_3 and P- γ - Al_2O_3 show absorptions in this range. More specifically, they all show peaks at 500 cm^{-1} and two shoulders at 720 and 776 cm^{-1} . The intensity of the peaks significantly decreases in P- γ - Al_2O_3 , while the peak positions do not change very much. It was reported that Al–O stretching in AlO_6 and AlO_4 units was around 500–750 cm^{-1} and 750–850 cm^{-1} , respectively. The peak position may change significantly depending on the fabrication methods and existence of defects and dopants in the lattice of γ - Al_2O_3 .⁴⁵ On the other hand, Du *et al.* reported that the bands at 523 and 570 cm^{-1} are related to the stretching mode of Al–O in AlO_6 and AlO_4 , respectively. The bands at 734 and 774 cm^{-1} are related to the symmetric stretching vibration of the AlO_4 tetrahedron.⁴⁴ Boumaza *et al.* reported that Al–O stretching in AlO_6 was 491 cm^{-1} .⁴⁶ Based on these literature reports, the peak at 500 cm^{-1} is assigned to Al–O stretching in the octahedral units (AlO_6)^{46,47} and the shoulders at 720 cm^{-1} and 776 cm^{-1} are related to the symmetric stretching vibration of the AlO_4 tetrahedron.^{44,48} The relative decrease in these peaks upon P doping in this range might be due to the decrease of their population upon introducing phosphorus into the Al_2O_3 lattice or due to the formed PO_4 species covered on the surface, which decreases the detectable absorption of these bands. These results are confirmed by the presence of some P related vibrational modes seen at around 700 cm^{-1} and 500 cm^{-1} in both O/OH-terminated surface models. Overall, our computational approach is able to reproduce the main features of the experimental spectra, especially for **OH-sub** and **OH-surf** models.

Conclusions

In conclusion, employing experimental and computational methods, we have shown that the electronic properties of metal oxide surfaces can be manipulated *via* group 5A doping (P atoms in this work). The surfaces can be made electron-rich in the sense that they have a lower work function than the undoped ones. The main reason for the lowering of the work function is the introduction of a surface dipole after doping. Interestingly, we find that the OH groups of thermodynamically stable mono- and bi-dentate phosphate surface ligands cooperate with the surface by damping its dipole thereby decreasing the work function. Substitutional P-doping leads to nonsymmetric arrangements of P (tri- and four-coordinated) with an added dipole that once again dampens the work functions. The reduced coordination of the P atom correlates with the reported higher catalytic activity

of P-doped alumina surfaces. With this study, we paved the way to use group 5A doping as a tuning knob for engineering the electrostatic properties of metal oxide surfaces with catalytic applications.

Materials and methods

Preparation of samples

Doping γ -Al₂O₃ (Sigma Aldrich, gamma phase aluminum oxide nanopowder) with P was achieved by impregnation of γ -Al₂O₃ with phosphoric acid (with a ratio of 14 g of γ -Al₂O₃ per 100 mL of 1.0 M phosphoric acid, Sigma Aldrich, 85 wt% in H₂O) for 7 h while stirring to reach equilibrium adsorption.⁴⁹ After impregnation, the sample was dried at 100 °C overnight, and then was placed in an oven at 550 °C for 4.5 h. The product was then sonicated and dispersed in ultrapure water and centrifuged 5 times at 5000 rpm for 8 min, to make sure that there is no free phosphoric acid in the sample. The final product was then dried at 100 °C overnight.

Characterization

PF-KPFM measurements on the alumina samples were conducted with a Dimension ICON AFM setup inside an argon-filled glove box where both H₂O and O₂ levels were below 0.1 ppm. The probes used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. The highly inert environment helped us to conduct more accurate measurements. P- γ -Al₂O₃ and γ -Al₂O₃ particles were first dispersed into ethanol, using bath sonication for 3 minutes. Then the samples were prepared by drop casting the dispersion of P- γ -Al₂O₃ and γ -Al₂O₃ particles onto a boron-doped silicon substrate. Solid state ²⁷Al (130.2 MHz) magic-angle spinning (MAS) NMR spectra were acquired at a magnetic field of 11.74T with a Bruker Avance III HD spectrometer equipped with a 4 mm solid-state broadband probe (Bruker Biospin, Billerica, MA). One-pulse spectra were recorded with 45 deg pulse of 1 μ s and 0.4 s relaxation delay, collecting 1 K data points over 104 kHz with the sample spinning at 10 kHz in a 4 mm zirconia rotor, in which the finely powdered samples were packed. The FT-IR spectra of γ -Al₂O₃ and P- γ -Al₂O₃ were acquired with a Thermo-Nicolet iS5 spectrometer (Thermo-Electron Corp., Madison, WI), using an iD7 ATR accessory with a diamond crystal plate, in the range of 400 to 4000 cm⁻¹. The spectra were recorded after 16 scans with a resolution of 4 cm⁻¹.

Computational details

Our simulations relied on Density Functional Theory (DFT), and specifically we employ the Quantum ESPRESSO software.⁵⁰ In the calculations, the PBE functional⁵¹ and Projector Augmented Wave (PAW) Pseudopotentials were employed with a kinetic energy cutoff of 50 Ry for the wavefunctions and a kinetic energy cutoff of 500 Ry for the charge density and potential. A Gaussian smearing to the occupations of the KS states was used, with a width (sigma) of 0.0001 Ry.⁵⁰ The self-consistent field calculations featured a Broyden mixing beta of 0.15. A *k*-point sampling on a 2 × 2 × 1 grid of points for geometry optimizations and a 4 × 4 × 1 grid

for all single-point computations were set.⁵² Additional non-self-consistent field (NSCF) was employed to generate smoother DOS plots.

The NMR calculations were carried out on the optimized bulk γ -Al₂O₃ structures by first performing a self-consistent field (SCF) calculation with pw.x. Computation of NMR spectra has been carried out using the DFT GIPAW (The Gauge-Including Projector Augmented Wave)³⁶ method using norm-conserving PPs (*e.g.* Al.pbe-tm-gipaw-dc.UPF) with the PBE functional.

IR spectra calculations were computed with PHONON⁴⁹ to generate vibrational frequencies and carried out with fixed occupations (no smearing). In these calculations we first performed a SCF calculation with pw.x, second, we calculated the vibrational frequencies (normal modes/phonons) with ph.x and finally using dynmat.x we collected the phonon information from ph.x output. The wavefunction kinetic energy cutoff for phonon calculation was 50 Ry on a 4 × 4 × 1 *k*-point grid with 1.0 × 10⁻¹⁴ threshold.

The chemical potentials (μ) were calculated as follows:

For P-doped and surface models (**O-sub**, **O-surf**, **OH-sub**, and **OH-surf**):

$$\mu_{\text{P-doped/surface}} = E_{\text{P-doped-}\gamma\text{-Al}_2\text{O}_3} - E_{\gamma\text{-Al}_2\text{O}_3} + (E_{\text{Al}} - E_{\text{P}}) \quad (1)$$

For monodentate (**O-md** and **OH-md**) and bidentate models (**O-bd** and **OH-bd**):

$$\mu_{\text{monodentate}} = E_{\text{P-doped-}\gamma\text{-Al}_2\text{O}_3} - E_{\gamma\text{-Al}_2\text{O}_3} - E_{\text{H}_3\text{PO}_4} + E_{\text{H}} + E_{\text{O}} \quad (2)$$

$$\mu_{\text{bidentate}} = E_{\text{P-doped-}\gamma\text{-Al}_2\text{O}_3} - E_{\gamma\text{-Al}_2\text{O}_3} - E_{\text{H}_3\text{PO}_4} + 2E_{\text{H}} + 2E_{\text{O}} \quad (3)$$

where the energy values were computed using the same cell for all species.

Conflicts of interest

There are no conflicts to declare.

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