

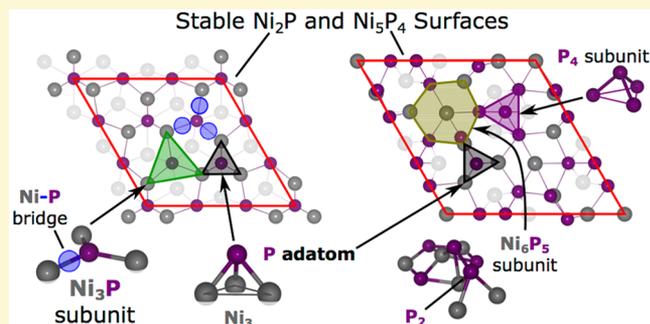
Stable Phosphorus-Enriched (0001) Surfaces of Nickel Phosphides

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S Supporting Information

ABSTRACT: In heterogeneous catalysis, catalyst synthesis precedes operation and, in most cases, is conducted in an altogether different chemical environment. Thus, determination of the structure and composition of the catalyst surface(s) due to fabrication is essential in accurately evaluating their eventual structure(s) during operation, which provides the origin of their catalytic activities and are therefore key to catalyst optimization. We explore the reconstructions of both Ni₂P(0001) and Ni₅P₄(0001)/(000 $\bar{1}$) surfaces with first-principles density functional theory (DFT). Most of the stable terminations under realistic synthesis conditions are determined to be P-rich on both materials. A P-covered reconstruction of the Ni₃P₂ termination of Ni₂P(0001) is found to be most stable, consistent with the current literature. By contrast, the most energetically favorable surfaces of Ni₅P₄ are found to be the Ni₃P₃ and Ni₄P₃ bulk-derived terminations with P-adatoms. The preferred excess P binding sites and their energies are identified on each surface. We find that the P₃ site, which is present on Ni₅P₄, and the Ni₃ site, which is present on both Ni₂P and Ni₅P₄, strongly bind excess P. Additionally, we predict the presence of stable P_{*n*} (*n* = 2, 4) agglomerates on Ni₅P₄ at the P₃-hollow and Ni–Ni bridge sites. This study highlights the importance of considering the aggregation behavior of nonmetal components in predicting the surface reconstruction of transition metal compounds.



INTRODUCTION

Elemental enrichment of the surfaces of transition metal oxides, sulfides, and phosphides is a desirable route to modify their physical and/or chemical properties. The ability to manipulate the amount of the transition metal component of a transition metal compound is believed to be the key to modifying the chemistry of its surface. Perhaps for oxides this is naively rooted in the fact that oxygen cannot stably form extended compounds or chains exceeding three atoms (e.g. ozone), and thus surfaces of oxides are most directly manipulated through their metallic components. Phosphorus and sulfur, however, can form extended chains or crystals on their own; thus P and S present possible sources of solid secondary phases when they form compounds with metals.^{1–3} This behavior may have deeper implications for the types of stable surfaces metal phosphides or sulfides form.

Surface composition and structure govern the key catalytic properties of nickel phosphides for a number of industrially important chemical reactions.^{4–8} The material properties of transition metal phosphides, including binary, ternary, and mixed-metal compounds, have been well characterized since the 1960s.^{9,10} They form binary phosphides M_xP_y (where *M* denotes a transition metal) with compositions usually ranging from M_3P to MP_3 including Ni₂P, Ni₅P₄, Ni₃P, Ni₅P₂, Ni₁₂P₅, NiP, and NiP₂.

The metal-rich phosphides (M_xP_y , where $x > y$) tend to exhibit better thermal stability, chemical inertness, electrical

conductivity,^{11–13} and hardness than P-rich phases; therefore we focus on Ni₂P and Ni₅P₄ in this study. Both solids have hexagonal crystal structures, as shown in Figure 1. Their low index (0001) facets are found to be the most stable terminations for both compounds. Ni₂P has two unique terminations on the (0001) plane, the Ni₃P and Ni₃P₂ layers, and they have distinct structure and stoichiometry. DFT calculations reveal that the latter is more stable under conditions where bulk Ni₂P is stable.¹⁴ Calculated scanning tunneling microscope (STM) images for this termination¹⁴ do not, however, match experimental data.^{13,15,16} This apparent inconsistency was resolved by dynamic low-energy electron diffraction (LEED) experiments, which revealed a surface reconstruction where nonstoichiometric additional P covers the Ni₃P₂ surface at the Ni₃-hollow sites (see Figure 5 in ref 27). They showed that this P-covered Ni₃P₂ termination (hereafter denoted as Ni₂P–Ni₃P₂+P) comprises ~80% of the surface, whereas the Ni₃P₂ (hereafter denoted as Ni₂P–Ni₃P₂) makes up the remaining 20%. Other reconstructions have been reported but only after annealing at higher temperatures, e.g., above 790 K.^{15,17} By contrast, Ni₅P₄ has a larger unit cell composed of Ni₃P₂, Ni₃P₃, and Ni₄P₃ layers (Figure 1b). Additionally, Ni₅P₄ lacks reflection symmetry with respect to

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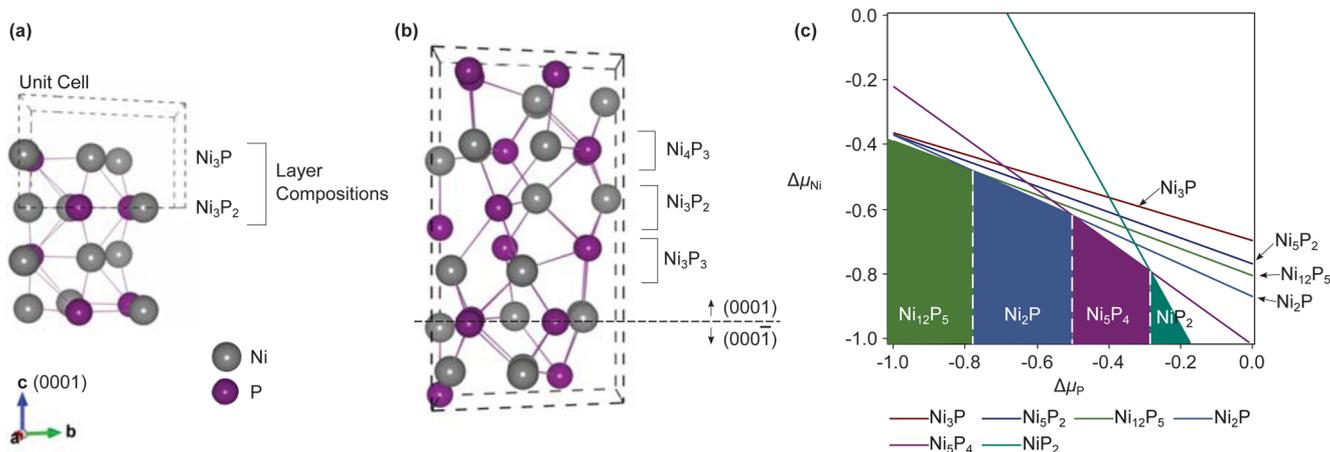


Figure 1. Crystal structures of (a) Ni_2P and (b) Ni_5P_4 , highlighting the layer stacking along the $[0001]$ direction. (c) Bulk phase diagram as a function of the relative chemical potentials (eV) of Ni and P for nickel phosphide phases that are stable under 850 K as has been found in the literature. Each solid line satisfies the equilibrium equation: $\Delta G_{\text{Ni}_x\text{P}_y} = x\Delta\mu_{\text{Ni}} + y\Delta\mu_{\text{P}}$ at 0 K. Each dotted vertical line denotes a phase coexistence point.

the $[0001]$ plane. The surface structures of Ni_5P_4 have not been studied previously. Although both are demonstrated to be efficient catalysts for H_2 evolution, Ni_5P_4 is much more active than Ni_2P , thereby igniting interest in the differences and similarities of these surfaces with the hope of elucidating their hydrogen evolution reaction (HER) catalytic activities.⁸

In this work, we conduct a comprehensive, systematic theoretical investigation of surface reconstruction on the (0001) and $(000\bar{1})$ facets of Ni_2P and Ni_5P_4 . First, we calculate the standard energy of formation for different bulk nickel phosphides (Ni_xP_y) with first-principles calculations so as to determine the region of P chemical potential ($\Delta\mu_{\text{P}}$) where bulk Ni_2P and Ni_5P_4 are stable. Then, we compute the free energy for a large number of distinct surface terminations. We show that both $\text{Ni}_2\text{P}(0001)$ and $\text{Ni}_5\text{P}_4(0001)$ prefer chemical and structural reconstructions of their bulk terminations, thereby providing a framework for the re-examination of the HER mechanism on these nickel phosphides.

COMPUTATIONAL METHODS

DFT^{18,19} calculations with periodic boundary conditions are performed using the Quantum ESPRESSO code.²⁰ The generalized gradient approximation (GGA) is employed to calculate the exchange-correlation energy using the method of Perdew, Burke, and Ernzerhof (PBE).²¹ Optimized,²² norm-conserving, designed nonlocal²³ pseudopotentials were generated using OPIUM²⁴ to represent the core electrons and soften the potential for the valence electron wavefunctions. Semicore 3p states are treated along with the 4s, 4p, and 3d for Ni, while 3s, 3p, and 3d valence states are included for P. The 3d orbitals of P are deemed necessary to model anionic electron configurations and complex coordination environments. The valence states are expanded in a plane-wave basis with a 50 Ry kinetic energy cutoff. For bulk calculations, $5 \times 5 \times 6$ and $5 \times 5 \times 4$ k -point grids, shifted along k_z , are used to sample the Brillouin zones of Ni_2P and Ni_5P_4 , respectively, and a small (0.005 Ry) Gaussian electronic smearing is applied to improve electronic convergence. All cells are allowed to fully relax, with a stress convergence threshold of 0.01 kbar. We perform spin-polarized calculations for bulk Ni_2P and Ni_5P_4 . The spin configuration is initially ferromagnetic, but both systems relax to a nonferromagnetic state.

Surfaces are modeled using slabs with 1×1 (for high surface defect concentrations) and $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ (for fractional defect concentrations) surface cells separated by ~ 15 Å of vacuum. For slabs, the k -point grid sampling is reduced to $5 \times 5 \times 1$ and $3 \times 3 \times 1$,

respectively. Orbital-projected density of states (DOS) calculations and Löwdin population analysis are performed on the stable surface reconstructions of Ni_2P and Ni_5P_4 using a finer k -point grid ($12 \times 12 \times 1$). A dipole correction²⁵ is applied to further remove the artificial electric field interactions between periodic images; its contribution to the total energy, however, is very small. We consider the (0001) surface of both Ni_2P and Ni_5P_4 . Seven-layer, up-down symmetric slabs are used to model $\text{Ni}_2\text{P}(0001)$ terminations. For Ni_5P_4 , asymmetric slabs of thickness ranging from 10 to 12 layers are constructed. In studying the reconstructions of the (0001) surface of Ni_5P_4 , the composition of the $(000\bar{1})$ is kept to be Ni_4P_3 . Likewise, in studying $(000\bar{1})$, the same type of termination is kept for (0001) . All atoms are allowed to fully relax with a force convergence threshold of 10^{-3} Ry/Bohr.

The surface free energy (Ω) is calculated under various environmental conditions using the following expression:

$$\Omega = \frac{1}{2A}(\phi + \Gamma_{\text{P}}\Delta\mu_{\text{P}}) \quad (1)$$

where A is the area of the surface unit cell, $\Delta\mu_{\text{P}}$ is the chemical potential of phosphorus relative to bulk phase white phosphorus, and ϕ and Γ_{P} are

$$\phi = E_{\text{slab}} - \frac{N_{\text{Ni}}E_{\text{Ni}_x\text{P}_y}^{\text{bulk}}}{x} + \Gamma_{\text{P}}E_{\text{P}}^{\text{bulk}} \quad (2)$$

$$\Gamma_{\text{P}} = N_{\text{Ni}}(y/x) - N_{\text{P}} \quad (3)$$

Here, E_{slab} is the DFT total energy of the slab, $N_{\text{Ni}/\text{P}}$ is the number of Ni/P atoms in the slab, x/y is the number of Ni/P atoms per formula unit of the bulk, and E^{bulk} is the formation energy of the bulk compound in the subscript. Equation 1 is governed by the equilibrium conditions defined by the dominant bulk phase and a secondary P chemical reservoir.

RESULTS AND DISCUSSION

Bulk Stability of Ni_2P and Ni_5P_4 . A prerequisite of the existence of a surface is the presence of a stable bulk phase that supports it. Thus, to be able to determine the chemical potential ranges where certain surfaces become relevant, we generate a bulk phase diagram from first-principles thermodynamic calculations (Figure 1c). Another P-rich phase, NiP, is expected to dominate in the same P chemical potential range as NiP_2 . However, NiP was demonstrated to only appear at high temperatures (>850 K)²⁶ and thus was not included in the

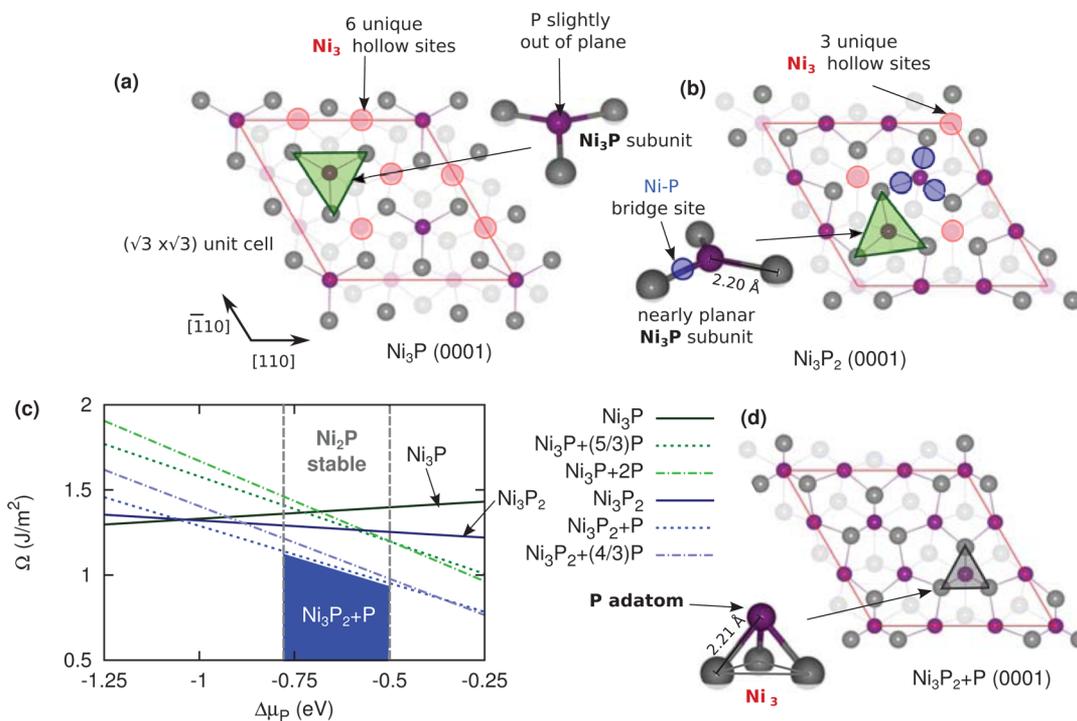


Figure 2. Surface crystal structures of $\text{Ni}_2\text{P}(0001)$ with either a (a) Ni_3P or (b) Ni_3P_2 termination. Only the atoms of the outermost layers are clearly shown. Structural insets highlight the basic subunits of each surface. Red lines outline the $\sqrt{3} \times \sqrt{3} R 30^\circ$ supercells. (c) Surface phase diagram for $\text{Ni}_2\text{P}(0001)$ as a function of $\Delta\mu_{\text{P}}$ (eV). Surface energies are reported in J/m^2 . Dashed gray vertical lines border the bulk stability region for Ni_2P .

phase diagram (Figure 1c), which represents only low temperature conditions since we neglect entropy contributions. It shows the values of $\Delta\mu_{\text{P}}$ and $\Delta\mu_{\text{Ni}}$ where bulk Ni_2P and Ni_3P_4 are stable compared to other nickel phosphide compositions. We find that Ni_2P is stable at $-0.78 \text{ eV} \leq \Delta\mu_{\text{P}} \leq -0.50 \text{ eV}$. At $\Delta\mu_{\text{P}} = -0.50 \text{ eV}$, bulk Ni_3P_4 becomes thermodynamically favored up to $\Delta\mu_{\text{P}} = -0.28 \text{ eV}$, at which point bulk NiP_2 becomes favored. The regions where these two phases are stable define the chemical potentials where their respective surfaces and their corresponding reconstructions are bound to exist. These surface reconstructions are discussed in the following sections.

Surface Structure and Stability of $\text{Ni}_2\text{P}(0001)$. First, we describe the bulk-derived terminations of $\text{Ni}_2\text{P}(0001)$. As shown in Figure 1a, bulk Ni_2P has two distinct layer compositions along the c -axis, Ni_3P and Ni_3P_2 , where two layers constitute a unit cell. The surface crystal structure of $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}$ is shown in Figure 2a for a $\sqrt{3} \times \sqrt{3} R 30^\circ$ surface unit cell. The outermost layer consists of repeating Ni_3P subunits (green shaded triangle) with the central P sticking slightly out of the surface plane (shown in the inset). This surface also possesses six unique Ni_3 hollow sites (red shaded circles), which are formed by the Ni corners of the Ni_3P subunits. Ni_3P subunits are also found on $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$ but adopt a geometry where the central P is nearly coplanar with the Ni corners (see Figure 2b). Owing to the increased surface P concentration on this termination, the number of unique Ni_3 hollow sites reduces to three. The center of the Ni_3P subunits in the $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}$ layer are above (and below) the Ni_3 hollows of the $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$ and *vice versa*. This stacking arrangement reveals a $\text{Ni}_3\text{P}-\text{Ni}_3$ pattern along the $[0001]$ direction. The surface energy of $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}$ and $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$ is plotted in Figure 2c as a function of $\Delta\mu_{\text{P}}$. In the bulk Ni_2P stability region,

$\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$ is the preferred bulk-like termination, which is consistent with previous DFT calculations in the literature.¹⁴

Given that there is experimental evidence for P-enrichment of Ni_2P surfaces,^{13,15,16,27,28} we investigate the possibility of stabilizing bulk terminations by systematically adding extra P to the surface and then identify the most stable reconstruction. We find that the adsorption of P at Ni_3 hollow sites in a trigonal pyramidal geometry decreases the surface free energy of both $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}$ and $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$ (see Figure 2c). This particular binding site and geometry is expected because it is analogous to creating a new, partial layer with P at bulk lattice positions. It is also different than the Ni_3P subunit, which has a nearly planar geometry. The Ni-rich (P-poor) $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}$ termination is maximally stabilized by the addition of P at five out of the six Ni_3 hollow sites to generate a surface composition of $\text{Ni}_3\text{P}+(5/3)\text{P}$ (defect concentration denoted per 1×1 surface unit cell). Higher coverages through further adsorption of P at the sixth Ni_3 hollow site ($\text{Ni}_2\text{P}-\text{Ni}_3\text{P}+2\text{P}$) causes the surface free energy to slightly increase, signaling P saturation. For $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2$, the surface energy is minimized by the addition of P at all three Ni_3 hollow sites ($\text{Ni}_3\text{P}_2+\text{P}$ in Figure 2d). If a fourth P is added to make $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2+(4/3)\text{P}$, it binds to a Ni-P bridge site, forms a surface adsorbed P_2 complex with P from the nearest Ni_3 hollow site (see Figure S1 in the Supporting Information), and increases the surface energy. Comparing the surface energies of both bulk-like terminations and their reconstructions, $\text{Ni}_2\text{P}-\text{Ni}_3\text{P}_2+\text{P}$ is the most stable surface phase whenever bulk Ni_2P is stable, *i.e.*, under relatively P-rich conditions. Thus, for a thermodynamically controlled synthesis of Ni_2P , this surface should be the most prevalent phase and, in fact, it is the same structure that ref 27 predicts, which they found to be the most consistent with the experimental STM among the surfaces they investigated.

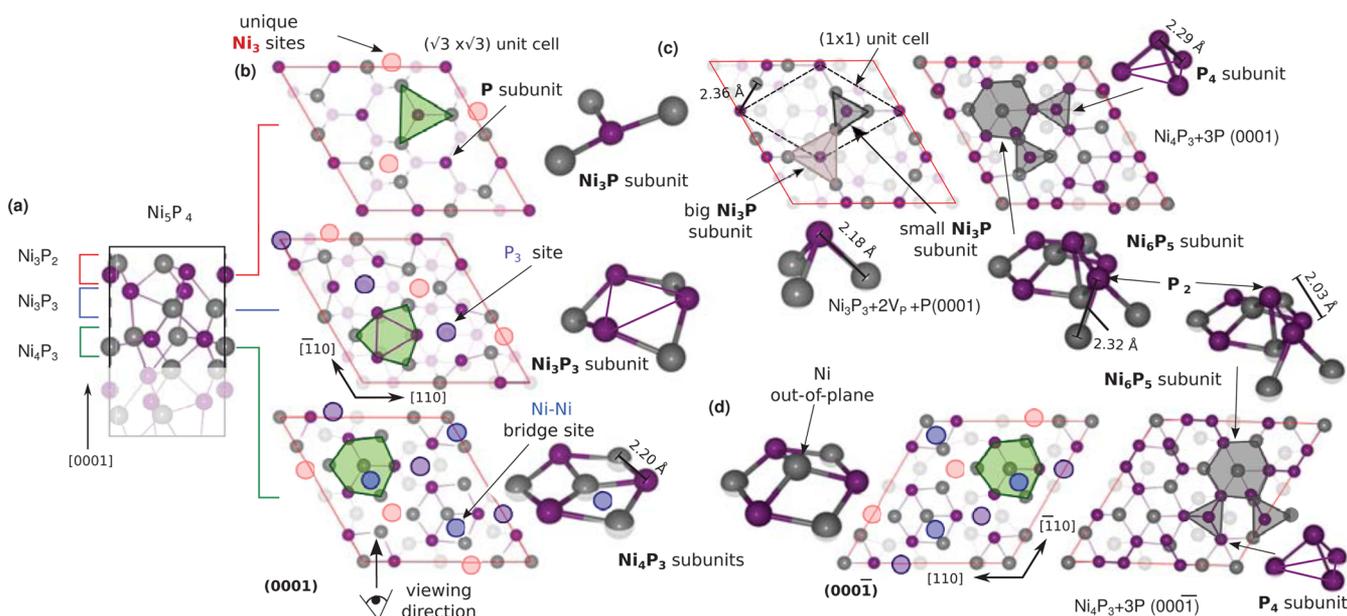


Figure 3. Surface crystal structure for bulk-derived terminations and reconstructions of $\text{Ni}_5\text{P}_4(0001)$ and $(000\bar{1})$. (a) Bulk layering in Ni_5P_4 . (b) Bulk-like (0001) terminations Ni_3P_2 (top), Ni_3P_3 (middle), and Ni_4P_3 (bottom) with shaded regions corresponding to the insets highlighting important structural features. (c) Stable (0001) reconstructions $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3+2\text{V}_p+\text{P}$ (left) and $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$ (right). (d) Bulk-like (left) and reconstructed (right) $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}(000\bar{1})$.

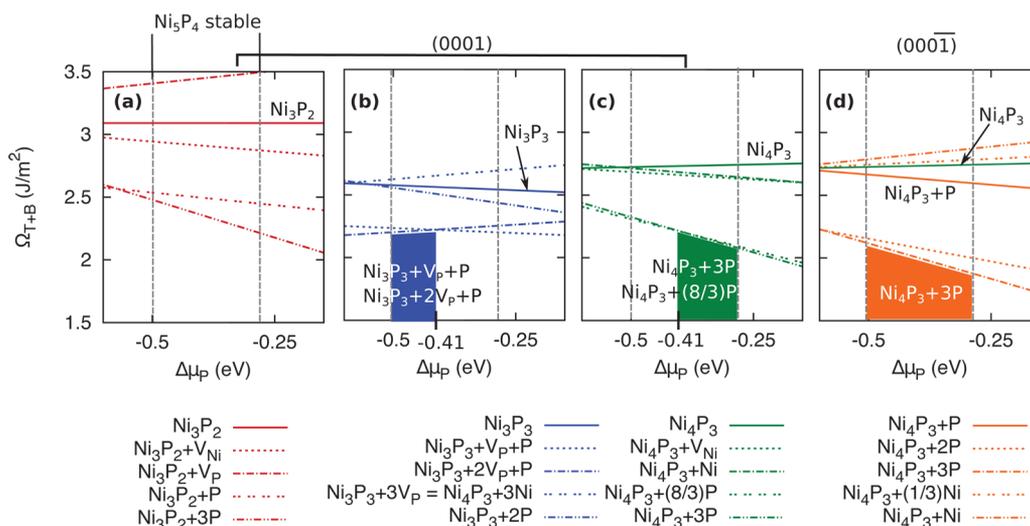


Figure 4. Surface phase diagram for $\text{Ni}_5\text{P}_4(0001)$ and $(000\bar{1})$ surfaces as a function of $\Delta\mu_p$ (eV). Ω_{T+B} corresponds to the combined surface energies (J/m^2) of the top (T) and bottom (B) surfaces of (a) $\text{Ni}_3\text{P}_2(0001)$, (b) $\text{Ni}_3\text{P}_3(0001)$, (c) $\text{Ni}_4\text{P}_3(0001)$, and (d) $\text{Ni}_4\text{P}_3(000\bar{1})$ and their respective reconstructions. Shaded areas denote regions of $\Delta\mu_p$ where certain reconstructions (as labeled) are favored.

The presence of P adatoms in Ni_3 -hollow sites on the reconstruction $\text{Ni}_2\text{P-Ni}_3\text{P}_2+\text{P}$ has important implications for the catalytic activity of $\text{Ni}_2\text{P}(0001)$ toward HER. It was proposed that H can adsorb at both Ni_3 -hollow and Ni-P bridge sites, where the latter offers more moderate binding.²⁹ H atoms at these two sites can diffuse to one another and subsequently desorb, forming $\text{H}_2(\text{g})$. Adlayer P offers a new site for H adsorption while also blocking the conventional bulk-like Ni_3 sites, thereby prompting a reconsideration of the HER mechanism on $\text{Ni}_2\text{P}(0001)$.³⁰ Ni_3 -hollow sites play a key role in the predicted mechanisms of other important chemical reactions such as hydrodesulfurization (HDS),^{31,32} water-gas shift (WGS),⁶ and hydrodeoxygenation (HDO).³³ Their catalytic mechanisms should be revisited on reconstructed

$\text{Ni}_2\text{P}(0001)$ surfaces since the above analysis shows that Ni_3 -hollow sites may not in fact be readily available.

Surface Structure and Stability of $\text{Ni}_5\text{P}_4(0001)$ and $(000\bar{1})$. As mentioned above, Ni_5P_4 lacks mirror symmetry along $[0001]$, giving rise to structurally distinct (0001) and $(000\bar{1})$ surfaces. Additionally, the structural layers of Ni_5P_4 are less clearly delineated. We choose to decompose the structure into three layers and refer to them according to their formula unit: Ni_3P_2 , Ni_3P_3 , and Ni_4P_3 (Figure 3a). A set of three layers forms half a unit cell, where the addition of a second set of three layers that are rotated 180° about the (0001) axis completes the full unit cell. Note that due to the absence of a reflection symmetry about the $[0001]$, the layer that comes before a given layer along the $[0001]$ becomes the layer that

comes after along the $[000\bar{1}]$. For example the layer below the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2(0001)$ surface is the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ layer, whereas the layer below the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2(000\bar{1})$ is the $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3$ layer. Therefore, the absence of reflection symmetry means different subsurface layers, which will affect the chemistry of the (0001) vs. $(000\bar{1})$ surface layer, despite having the same composition.

For brevity, we only discuss here in detail the structural and chemical features of the (0001) surfaces and their reconstructions, while the $(000\bar{1})$ layer that produces the most stable reconstruction is discussed. We discuss each bulk-derived layer and the different structural and compositional perturbations giving rise to their reconstructions. The compositional variations introduced include Ni vacancies (V_{Ni}), P vacancies (V_{P}), P adatoms ($+x\text{P}$, as in the Ni_2P surface reconstructions), and Ni adatoms ($+x\text{Ni}$). We also discuss the energetics involved in these reconstructions, revealing the most likely (thermodynamically stable) surfaces of $\text{Ni}_5\text{P}_4(0001)$.

Ni_3P_2 -Derived Surfaces of Ni_5P_4 . The upper panel of Figure 3b shows the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ (three unit cells) of the bulk-derived $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2$ layer. This layer is composed of repeated Ni_3P (green shaded triangle) and P subunits. Each isolated P subunit is coordinated to three P atoms found in the layer below. The removal of this lattice P, creating vacancies (V_{P}), is unfavorable and destabilizes the surface (Figure 4a, compare solid line, $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2$, and dash-dotted line, $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2+V_{\text{P}}$). The corners of three adjacent Ni_3P units surround a common point, which creates a Ni_3 hollow site (red shaded circle). Removal of one of these Ni atoms somewhat stabilizes the surface by about 0.25 J/m^2 ($\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2+V_{\text{Ni}}$, dotted line), while saturating all the Ni_3 hollow sites with one and up to three P per site, creating a P_3 staggered against the Ni_3 , ($\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2+(1,3)\text{P}$, double dotted and dash-double dotted lines, Figure 4) stabilizes the surface significantly more ($\approx 0.5\text{--}0.75 \text{ J/m}^2$).

Ni_3P_3 -Derived Surfaces of Ni_5P_4 . The middle panel of Figure 3b shows the $\sqrt{3} \times \sqrt{3} R 30^\circ$ $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ layer. Closed-chain Ni_3P_3 subunits compose this surface. The Ni_3P_3 subunit is characterized by a triangular P_3 overlaid on a Ni_3 that are rotated 60° relative to each other. The Ni corners of three Ni_3P_3 subunits also converge on a common point which also creates a trinuclear Ni hollow site (red shaded circles). The same is true for the three P corners which correspondingly create a trinuclear P hollow site (purple shaded circles). As in the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_2$ surface, saturation of these Ni_3 and P_3 sites with one P per site stabilizes this surface. Figure 4b shows the stabilizing effect of saturating both the Ni_3 and P_3 sites (solid, $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ vs dash-double dotted line, $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3+2\text{P}$). However, saturating the Ni_3 sites alone and removing one of the lattice P's ($\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3+V_{\text{P}}+\text{P}$) better stabilizes the surface, with one of the remaining P's displaced toward the center of the Ni_3P_2 subunit (see Figure S2 in the Supporting Information). The removal of another P from the Ni_3P_3 subunit further lowers the surface energy in the low $\Delta\mu_{\text{P}}$ regime (dotted line, $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3+2V_{\text{P}}+\text{P}$) and exhibits the same displacement of the remaining P to the center of the Ni_3 base, creating a big Ni_3P subunit (Figure 3c, left panel). The $nV_{\text{P}}+\text{P}$ where ($n = 1\text{--}2$) stabilizes the surface by $\sim 0.25 \text{ J/m}^2$, making these the most stable reconstructions of the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ layer. The dominance of these surfaces is made possible by a combination of low P chemical potential and the tendency of the system to maximize the number of Ni–P bonds.

Ni_4P_3 -Derived Surfaces of Ni_5P_4 . The bottom panel of Figure 3b shows the $\sqrt{3} \times \sqrt{3} R 30^\circ$ $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3$ layer. This layer is composed of Ni_4P_3 subunits with the same motif as the Ni_3P_3 subunits found in the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ layer, but with an additional Ni at the center. Also, similar to the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ layer, the subunits create Ni_3 (red shaded circles) and P_3 (purple shaded circles) hollow sites (one of each per 1×1 surface). However, the extra Ni, which makes this layer distinct from the $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$, gives rise to Ni–Ni bridge sites (blue shaded circle). Both Ni vacancies (V_{Ni}) and Ni adatoms ($+Ni$), marginally stabilize the surface. Saturation with P adatoms of all the Ni_3 and P_3 sites and one Ni–Ni bridge site per Ni_4P_3 subunit ($\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$) proved to be the most thermodynamically favorable. Partial occupation of the Ni–Ni bridge site may also be achieved, e.g., in the case of $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+(8/3)\text{P}$. The structure of P-saturated $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3$ ($\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$) is shown in the right panel of Figure 3c. A distinctive tetrahedral P_4 subunit forms from the adsorption of P at the P_3 site, while a P_2 moiety is stabilized from the bonding of the two P adatoms on a Ni–Ni bridge and a Ni_3 site.

Global Stability of the (0001) Reconstructions of Ni_5P_4 . Bulk Ni_5P_4 was calculated to be stable between $\Delta\mu_{\text{P}} -0.5$ and -0.28 eV , so we examine the surfaces with the lowest surface energy within this range. The $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3$ -derived surface with either the $2V_{\text{P}}+\text{P}$ or $V_{\text{P}}+\text{P}$ reconstruction is found to be the most stable (0001) termination from $\Delta\mu_{\text{P}} -0.5$ to -0.41 eV (blue shaded region in Figure 4b). At a higher $\Delta\mu_{\text{P}}$, -0.41 to -0.28 eV , the P-covered $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3$ -derived surfaces, $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$ and $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+(8/3)\text{P}$, dominate (green shaded region in Figure 4c).

$\text{Ni}_5\text{P}_4(000\bar{1})$ Reconstructions. Despite the change in the sublayer composition supporting each termination (due to the change of the layer sequence when going the opposite direction), the $(000\bar{1})$ surface is found to be also thermodynamically dominated by the P-covered $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3$ -derived surfaces. The $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3(000\bar{1})$ exhibits the same sites as the $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3(0001)$, i.e. Ni_3 and P_3 hollow and Ni–Ni bridge sites, and is similarly composed of the Ni_4P_3 subunit (Figure 3d, left panel). The difference between the (0001) and $(000\bar{1})$ surfaces is the direction of the corrugation of central Ni of the subunits. The central Ni points into the slab in the case of the (0001) , while it points outward to the vacuum in the case of the $(000\bar{1})$. Full saturation of the hollow sites and one Ni–Ni bridge site per Ni_4P_3 subunit ($\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$) also ultimately stabilizes this surface, in fact dominating the whole stability region of Ni_5P_4 (Figure 4d). The compositional and structural similarity of the most stable reconstructions of these (0001) and $(000\bar{1})$ surface isomers may render the two surfaces indistinguishable without the knowledge of the stacking direction within the bulk. However, at slightly lower P concentrations ($\Delta\mu_{\text{P}} < -0.41 \text{ eV}$), the (0001) undergoes a phase change into $\text{Ni}_5\text{P}_4\text{-Ni}_3\text{P}_3+2V_{\text{P}}+\text{P}$, while the $(000\bar{1})$ robustly remains as $\text{Ni}_5\text{P}_4\text{-Ni}_4\text{P}_3+3\text{P}$. See Supporting Information for a complete survey of the $(000\bar{1})$ layers and reconstructions.

Comparison of the Stable Ni_2P and Ni_5P_4 (0001) Reconstructions. We have shown that the enrichment of Ni_2P and Ni_5P_4 (0001) and $(000\bar{1})$ surfaces with P has a significant stabilizing effect. The most stable reconstruction for $\text{Ni}_2\text{P}(0001)$ is the $\text{Ni}_3\text{P}_2+\text{P}$ surface, which has an overall composition of Ni_3P_3 and a 1:1 ratio of Ni to P. The preferred reconstructions for Ni_5P_4 (0001) and $(000\bar{1})$, namely $\text{Ni}_3\text{P}_3+[1\text{--}2]V_{\text{P}}+\text{P}$ and $\text{Ni}_4\text{P}_3+[(8/3)\text{--}3]\text{P}$, are where Ni/P

varies from 0.66 to 1.5. The reconstructions of Ni₂P and Ni₅P₄ similarly exhibit P adsorption at Ni₃ hollows to generate a Ni₃P trigonal pyramid, the only difference being the number of Ni₃ hollow sites per unit area and the Ni–P bond distance (see Figures 2 and 3). Unlike Ni₂P reconstructions, however, Ni₅P₄–Ni₄P₃+3P (0001) and (000 $\bar{1}$) promote the formation of stable aggregates of P on their surfaces, such as P₄ subunits and P₂ moieties. The former closely resembles the tetrahedral P₄ structures in P (s, white), has a very similar P–P bond distance ($d_{\text{P(s)}} = 2.21 \text{ \AA}$ ³⁴ vs $d_{\text{surf}} = 2.29 \text{ \AA}$), and carries a nearly neutral charge (0.07e, Table 1), suggesting the possible nucleation of a

Table 1. Calculated Löwdin Charges for the Surface P Atoms for Some of the Stable Reconstructions of Ni₂P and Ni₅P₄

composition		location	no. electrons			net charge
bulk	surface		3s	3p	3d	[e]
Ni ₂ P	Ni ₃ P ₂ +P	Ni ₃ P subunit	1.60	3.19	0.88	−0.68
		Ni ₃ -hollow	1.75	3.09	0.48	−0.30
Ni ₅ P ₄ (0001)	Ni ₄ P ₃ +3P	Ni ₄ P ₃ subunit	1.46	3.06	1.09	−0.61
		Ni ₃ -hollow	1.55	3.05	0.72	−0.32
		P ₃ -hollow	1.55	2.77	0.61	0.07
		Ni–Ni bridge	1.63	2.93	0.49	−0.05

secondary pure P phase. The P₂ moiety ($d_{\text{surf}} = 2.03 \text{ \AA}$) has a similar bond length to gaseous P₂ ($d_{\text{P}_2(\text{g})} = 1.89 \text{ \AA}$)³⁵ and also possesses nearly neutral charge (−0.05e, Table 1).

From the dominant structures, we see that the major driving force for the P-rich reconstruction is to saturate Ni coordination where it achieves either a four-fold or five-fold coordination as in the bulk. The complexity of the Ni₅P₄ reconstructions, especially the Ni₄P₃+3P surface composition, presents other avenues for surface stabilization which include the expansion of surface P valency through bonding with additional P, e.g., at P₃ hollow sites. P–P bonds may act as possible nucleation centers for white P, P₂(g), and other P phases depending on the environmental conditions.

Unlike transition metal oxides which are more strongly ionic and whose surface reconstructions are governed by surface charge passivation,^{36–38} the metallic nickel phosphides are demonstrated to be primarily driven by saturation of the coordination chemistry of the surface atoms. Due to the much greater electronegativity of O compared to P, transition metal oxides also tend to have larger bond dipoles than Ni₂P and Ni₅P₄. Thus, at oxide surfaces, dangling bonds lead to the buildup of a large surface dipole, which can be screened by reconstruction with the constituent elements of the material or by cations or anions readily available in the environment.^{39–41} The geometry of oxide and phosphide reconstructions is also affected by their electron configurations. Since O has a lower valence than P, oxide reconstructions tend to involve O adatoms bridging between two metal atoms or forming coordinatively unsaturated sites,⁴² whereas P may easily form three bonds using its 3p orbitals while also expanding its valence shell using its energy-accessible 3d orbitals. On this basis, P can introduce modes of coordination beyond sp bonding. This is clearly demonstrated by the partial population of the P 3d orbitals (see Table 1 for the 3d charge population)

and their hybridization with the P 3p states (see Figure S5 in the Supporting Information for the projected density of states of some of the surfaces). Such flexibility in valence enables the formation of exotic surface structures including small covalent P clusters.

Because bulk-like terminations of Ni₂P and Ni₅P₄ tend to reconstruct, the previously proposed mechanism of HER^{29,30} on Ni₂P and Ni₅P₄, as well as other chemical reactions^{6,31–33} for which it is catalytically active, must be reevaluated. Depending on the chemical reaction catalyzed, the catalyst may be subsequently exposed to different solvents, ions, molecules, and even applied potentials during operation which would then facilitate further evolution of the surfaces. Here, we provide a set of chemically sound structures that lay the foundation for studying the effects of these additional variables on catalysis. A few of the most notable routes for additional reconstructions to consider are perhaps through hydration, protonation, and hydroxylation of surface Ni and P species once exposed to water. We show however that the non-stoichiometric P ad-species prevalent on these reconstructions already constitute strong Ni-bond-passivating components of the surface. This suggests that P redox and acid–base chemistries (instead of nickel's) are more relevant in determining the eventual transformation and activity of the surfaces during catalysis. Thus, for example, phosphine and phosphorous/phosphoric acid chemistries may very well hold the key in understanding Ni–P catalysis in an aqueous environment.

CONCLUSIONS

Both Ni₂P and Ni₅P₄ favor P-rich reconstructions on the (0001) facet, arising from the extended coordination of P and the tendency of Ni to remain saturated. For Ni₂P, the most stable surface termination is Ni₃P₂+P, where P adatoms rest on the Ni₃-hollow sites. On Ni₅P₄(0001), reconstructions of both the Ni₃P₃ and Ni₄P₃ surface layer compositions may form. For its (000 $\bar{1}$), Ni₅P₄–Ni₄P₃+3P is most stable. Ni₅P₄–Ni₄P₃+3P-(0001) and (000 $\bar{1}$) are furnished by stable P clusters, P₄ and P₂, which resemble phases of P, namely white P and P₂(g), respectively. The ability of P to agglomerate on Ni₅P₄(0001) sets this phase apart from Ni₂P(0001) and, more generally, from transition metal oxides, which are much more limited in their modes of reconstruction and more adherent to surface charge passivation requirements.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b01437.

Calculated bulk parameters, surface crystal structures of Ni₂P–Ni₃P₂+(4/3)P and Ni₅P₄–Ni₃P₃+V_P+P(0001), survey of the Ni₅P₄(000 $\bar{1}$) layers and reconstructions, and calculated Löwdin charges and orbital-projected density of states (PDOS) for the surface atoms for the stable surface reconstructions and some of the bulk-derived terminations of Ni₂P and Ni₅P₄(0001) and (000 $\bar{1}$) (PDF)

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Notes

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