Active Role of Phosphorus in the Hydrogen Evolving Activity of Nickel Phosphide (0001) Surfaces

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Supporting Information

ABSTRACT: Optimizing catalysts for the hydrogen evolution reaction (HER) is a critical step toward the efficient production of H2(g) fuel from water. It has been demonstrated experimentally that transition-metal phosphides, specifically nickel phosphides Ni2P and Ni5P4, efficiently catalyze the HER at a small fraction of the cost of archetypal Pt-based electrocatalysts. However, the HER mechanism on nickel phosphides remains unclear. We explore, through density functional theory with thermodynamics, the aqueous reconstructions of Ni2P(0001) and Ni5P4(0001)/(0001̅), and we find that the surface P content on Ni2P(0001) depends on the applied potential, which has not been considered previously. At −0.21 V ≤ U ≤ −0.36 V versus the standard hydrogen electrode and pH = 0, a PHx-enriched Ni3P2 termination of Ni2P(0001) is found to be most stable, consistent with its P-rich ultrahigh-vacuum reconstructions. Above and below this potential range, the stoichiometric Ni3P2 surface is instead passivated by H at the Ni3-hollow sites. On the other hand, Ni5P4(0001̅) does not favor additional P. Instead, the Ni4P3 bulk termination of Ni5P4(0001̅) is passivated by H at both the Ni3 and P3-hollow sites. We also found that the most HER-active surfaces are Ni3P2+P+(7/3)H of Ni2P(0001) and Ni4P3+4H of Ni5P4(0001̅) due to weak H adsorption at P catalytic sites, in contrast with other computational investigations that propose Ni as or part of the active site. By looking at viable catalytic cycles for HER on the stable reconstructed surfaces and calculating the reaction free energies of the associated elementary steps, we calculate that the overpotential on the Ni4P3+4H surface of Ni5P4(0001̅) (−0.16 V) is lower than that of the Ni3P2+P+(7/3)H surface of Ni2P(0001) (−0.21 V). This is due to the abundance of P3-hollow sites on Ni5P4 and the limited surface stability of the P-enriched Ni2P(0001) surface phase. The trend in the calculated catalytic overpotentials, and the potential-dependent bulk and surface stabilities explain why the nickel phosphides studied here perform almost as well as Pt, and why Ni5P4 is more active than Ni2P toward HER, as is found in the experimental literature. This study emphasizes the importance of considering aqueous surface stability in predicting the HER-active sites, mechanism, and overpotential, and highlights the primary role of P in HER catalysis on transition-metal phosphides.

KEYWORDS: electrocatalysis, hydrogen evolution, metal phosphides, nickel phosphides, density functional theory, aqueous surface phase diagram

INTRODUCTION

Electrical energy produced from renewable sources (e.g., solar cells) can be used to split water to produce fuel (H2). The cathode half-reaction of water splitting is the hydrogen evolution reaction (HER), which can be performed in both acidic (shown below) and to some extent in basic aqueous media:

$$2H^+ + 2e^- = H_2(g)$$  

(1)

Pt is currently considered as the benchmark catalyst for the HER; however, it is both scarce and expensive. This has motivated many scientists in the past decade to search for earth-abundant, cheap alternatives to Pt as electrocatalysts for the HER.\(^4\)\(^-\)\(^10\)

There are two well-known mechanisms for the HER: Volmer–Tafel (VT) and Volmer–Heyrovsky (VH).\(^4\)\(^-\)\(^10\)

Their chemical representations are as follows:

$$H^+ + S + e^- \rightleftharpoons S-H$$  \hspace{1cm} (Volmer step)  

(2)

$$S-H + S' \rightleftharpoons S/S' + S' - H_2$$  \hspace{1cm} (Tafel step)  

(3)

$$S-H + H^+ + e^- \rightleftharpoons S-H_2$$  \hspace{1cm} (Heyrovsky step)  

(4)

$$S-H_2 \rightleftharpoons S + H_2(g)$$  

(5)

Both mechanisms start with the Volmer step, where one H binds to a site (S) on the electrocatalyst surface. From here, the reaction can proceed in two different ways. Either another H will bind at a separate site (Tafel step), where S and S’ may or may not be of the same type, or directly on top of an adsorbed H forming an H2 complex (Heyrovsky step). Both the Tafel
and Heyrovsky steps are followed by the desorption of H$_2$(g) or alternatively, lead to direct desorption of the molecule.

A few potential substitutes for Pt HER electrocatalysts are molybdenum sulﬁdes,$^{2,11,24}$ molybdenum and tungsten carbides,$^{35–37}$ nitrides,$^{36–42}$ and nickel and cobalt phosphides.$^{43–51}$ The hydrogen evolution activity of Ni$_5$P$_2$(0001) was originally predicted computationally$^{43}$ and then subsequently demonstrated experimentally.$^{44}$ It was proposed of metal-hollow sites (the so-called “ensemble effect”) while also providing weak binding for H at Ni−P bridge sites.$^{45}$ The electrostatic attraction between adsorbed H$^+$ (at Ni−P bridge sites) and H$^+$ (at trinuclear Ni$_3$-hollow sites) was proposed to facilitate HER on Ni$_5$P$_2$.$^{44}$

Surface phase stability is of utmost importance in predicting the performance of heterogeneous catalysts.$^{52–62}$ Different surface structures give rise to different sites for H adsorption, which may lead to different HER mechanisms and overpotentials. Therefore, it is essential to determine the structure and composition of the catalyst surface(s) under fabrication and operating conditions. Ni$_5$P$_2$ has two bulk layers, Ni$_4$P$_3$ and Ni$_5$P$_4$, along the crystal’s (0001) axis; accordingly, there are two bulk-like terminations: Ni$_3$P$_2$ and Ni$_5$P$_4$. DFT calculations predict that the latter is more stable under Ni$_5$P$_4$ bulk formation conditions.$^{63}$ Scanning tunneling microscopy (STM) and dynamic low-energy electron diffraction (LEED) experiments reveal that nonstoichiometric additional P covers ≈80% of this surface; hereafter, the surface found experimentally is denoted as Ni$_5$P$_2$(s)/Ni$_5$P$_4$(0001)+P (note that the naming scheme we adopt here is bulk/surface+adlayer where each term is the empirical formula).$^{64–68}$ Calculated adsorption energies for H at low coverage on different sites of Ni$_5$P$_2$(s)/Ni$_5$P$_4$(0001)+P show that H prefers to bind on these P adatoms.$^{66}$ We recently studied the reconstructions of both Ni$_5$P$_2$(0001) and Ni$_5$P$_4$(0001)/(0001) surfaces with DFT and discovered that the most stable terminations, subject to an inert environment, are P-enriched.$^{52}$ We predict$^{52}$ that Ni$_5$P$_2$(0001) prefers a P-covered reconstruction of the Ni$_5$P$_2$ termination that is consistent with STM and LEED experiments in the literature.$^{64–68}$ Ni$_5$P$_2$ has three bulk layers along the (0001) and (0001) axes: Ni$_3$P$_2$, Ni$_5$P$_4$, and Ni$_5$P$_4$. Ni$_5$P$_2$(0001)/(0001) favors P-enrichment of the Ni$_5$P$_4$ and Ni$_5$P$_4$ terminations. Ni$_3$- and P$_3$-hollow sites, the latter of which are only present on Ni$_5$P$_4$(s)/Ni$_5$P$_4$(0001)/(0001), bind additional P.

Recently, Ni$_5$P$_4$ was synthesized and was shown to exhibit exceptional, Pt-level performance for HER at pH ≈ 0 and applied potentials ranging from U ≈ 0 V to −0.1 V vs the standard hydrogen electrode (SHE).$^{38}$ The superior performance of Ni$_5$P$_4$ was attributed to a higher positive charge on Ni atoms and to the ensemble effect of P, where the number of Ni$_3$-hollow sites that bind H very strongly is decreased due to the abundance of P, which therefore leads to more thermoneutral adsorption.$^{43,45,49}$ Additionally, it was shown that monodisperse Ni$_5$P$_4$ nanocrystals have higher surface area and greater stability in acidic media than Ni$_5$P$_4$. In this work, we only consider Ni$_5$P$_2$ and Ni$_5$P$_4$ because they are experimentally demonstrated to be the most HER-active nickel phosphate polymorphs.$^{49,50,72}$ Additionally, these two compounds do not have strong differences between their crystal structures and structural motifs in the bulk, and both compounds also have comparable electronic conductivities.$^{64,71,72}$ Therefore, conclusions on their relative HER activities based on the compositional and structural properties of their surfaces, as well as the relative stabilities of their bulk and surfaces, can be made. A better understanding of the atomistic mechanism of the HER for various Ni phosphate systems will accelerate the design and fabrication of robust HER electrocatalysts.

To address this need, we apply DFT calculations and thermodynamics to predict the most stable surface phases under normal synthetic conditions and in an electrochemical environment, that is, aqueous solution at speciﬁed pH and applied potential U (hereafter U is implicitly relative to SHE). Each of the phosphides we model has been electrochemically investigated in aqueous solution$^{44,48}$ and is found to be stable. Thus, we model the catalytic properties of each bulk phase and evaluate which surfaces are responsible for their respective activities. We calculate the free energy of reaction of the elementary steps involved in the electrochemical HER via first-principles, and consequently, we reveal the lowest-energy pathways on Ni$_5$P$_2$(0001) and Ni$_5$P$_4$(0001)/(0001).

## METHODS

### First-Principles Calculations.

DFT$^{73,74}$ calculations were carried out using the Quantum ESPRESSO (version 5.1) software.$^{75}$ Geometric relaxation of the bulk and surface structures was performed until changes in the total energy and force were less than 1.4 × 10$^{-3}$ eV/cell and 2.6 × 10$^{-2}$ eV/Å respectively. Optimized,$^{76}$ norm-conserving, designed non-local pseudopotentials were constructed using the OPIUM (version 3.7) software$^{77}$ to replace the core electrons and nucleus with a smoother, effective potential. We used the generalized gradient approximation (GGA) as formulated by Perdew, Burke, and Ernzerhof (PBE) to calculate electron exchange and correlation energies.$^{78}$ The valence orbital wave functions were expanded in a plane-wave basis with a cutoff energy of 680 eV. Gaussian electronic smearing of 0.07 eV was applied to the band occupations near the Fermi energy to improve electronic $k$-point convergence. We used the semiempirical DFT-D2 method$^{80}$ to include van der Waals (vdW) interactions, which are vital for modeling catalytic transformations.$^{81,82}$

Bulk lattice constants were also relaxed with a pressure convergence threshold of 6.3 × 10$^{-6}$ eV/Å$^3$. The total energies of bulk Ni$_5$P$_2$ and Ni$_5$P$_4$ were found to be converged with 5 × 5 × 6 and 5 × 5 × 4 $k$-point grids respectively, offset along $k_z$. Calculated lattice constants and formation energies of Ni(s), P(s,white), Ni$_5$P$_2$(s), and Ni$_5$P$_4$(s) are found to be in good agreement with experimental values.$^{52}$ Slab models for Ni$_5$P$_2$(0001) and Ni$_5$P$_4$(0001)/(0001) were generated with $\sqrt{3} \times \sqrt{3} \times 30^\circ$ surface unit cells and $\approx 25$ Å of vacuum space separating layers. Accordingly, the $k$-point grid was reduced to $3 \times 3 \times 1$. A dipole correction was added to the center of the vacuum region to cancel any artificial electric fields between the slabs.$^{83}$ Vibrational frequencies of adsorbates and surface atoms directly coupled to them were calculated (from truncated Hessian matrices) using density functional perturbation theory (DFPT). The charge densities used for these calculations were obtained by lowering the total energy convergence threshold for SCF calculations from 1.4 × 10$^{-3}$ eV/cell for geometry relaxations to 1.4 × 10$^{-9}$ eV/cell.

### Theory.

In order to accurately model catalysis, it is necessary to construct a realistic model of the surface under experimental conditions, i.e. in aqueous solution with electrochemical driving forces, pH and U.$^{84}$ This can be achieved by considering the equilibrium between surface atoms and adsorbates, and their aqueous counterparts. When a surface is
in contact with an aqueous solution, the surface can lose atoms to or gain atoms from the solution. The chemical equation defining the equilibrium between a surface and aqueous solution where atom A is being exchanged is as follows

\[ S - A + n_h H_2O = S + [H_2AO]^{z+} + n_h H^+ + n_e e^- \]  

where S is the surface, \( n_e \) is the number of water molecules needed to oxidize (reduce) and/or solvate A in the solution, \([H_2AO]^{z+}\) is the most stable aqueous phase of A, \( z \) is the charge of the A-complex which can either be positive, negative, or zero, \( n_h \) is the number of protons formed, and \( n_e \) is the number of electrons released. Note that the latter two can be negative in which case proton(s) and electron(s) are gained to form \([H_2AO]^{z+}\). The free-energy change for this dissolution reaction of one A ion is

\[
\Delta G_{\text{A,diss}} = (G_S - G_{\text{SA}}) + (G_{[H_2AO]}^{z+} + n_h G_{H^+} + n_e G_{e^-}) - n_h G_{H_2O} 
\]  

where \( n_h \) is the free energy of formation of Ni\(_2\)P(0001) in equilibrium with 1 M Ni\(_2^+\) or Ni(\(\delta\)) and 1 M H\(_2\)PO\(_4\) at 298.15 K. (B)–(D) show the evolution of the surface through adsorption–desorption equilibrium of P. P dissolves off the surface as phosphates (B). As the potential is lowered it redeposits as phosphines (C), up to a point where PH\(_3\) becomes very soluble and re-exposes the Ni sites for H to bind (D). Average bond lengths are indicated.

\[
\Delta G_{\text{A,diss}} = \Delta G_{\text{diss}} + \Delta G_{\text{A,(std)/}[H_2AO]}^{z+} + \Delta \mu_{H_2AO}^{z+} + n_h \Delta \mu_H + n_e \Delta \mu_e 
\]  

where \( \Delta \mu_{H_2AO}^{z+} = k_B T \ln a_{H_2AO}^{z+}, \) \( \Delta \mu_H = -2.303 k_B T \ln H^+ \), and \( \Delta \mu_e = -q U \). These terms can be thought of as knobs that control the chemical potentials of \( H_2AO^{z+} \) for phosphates.

Note here we simply add \( G_{\text{A,(std)}} \) to the first term and subtract it from the second term. We define the second term as the differential desorption (diss) free energy \( \Delta G_{\text{diss}} \) for A to leave the surface and form A\(_{\text{(std)}} \). We re-express the second term with respect to the standard oxidation/reduction free energy \( \Delta G^{0\text{c}}_{\text{A,(std)/}[H_2AO]}^{z+} \) of A\(_{\text{(std)}} \) to form \([H_2AO]^{z+}\) (see additional theoretical details and Table S1 in the Supporting Information). Our final expression is

\[
\Delta G_{\text{A,diss}} = \Delta G_{\text{diss}} + \Delta G^{0\text{c}}_{\text{A,(std)/}[H_2AO]}^{z+} + k_B T \ln a_{H_2AO}^{z+} - 2.303 n_h k_B T \ln H^+ - n_e q U 
\]  

The last three terms represent the deviation of the chemical potentials due to concentrations of the aqueous species: H\(_2\)AO\(_{\text{std}}\) and H\(^+\) from the standard condition, and of the electronic energy relative to SHE.
\[ \Delta G_{\text{Ni}_2P}^f \leq a \Delta G_{\text{Ni}(s)/\text{H}_2\text{NiO}_x} + b \Delta G_{\text{P(white)/H}_2\text{PO}_4^-} \]  

(12)

The bulk phase diagrams of Ni₂P and Ni₅P₄ are shown in Figure S2 in the Supporting Information. Finally, we calculated the free energies of hydrogen adsorption (see reaction in eq 2)

\[ \Delta G_{\text{ads}} = G(n_H + 1) - G(n_H) - G(\text{H}^+ + e^-) \]  

(13)

at 298.15 K, pH = 0, and U = 0 V.

**RESULTS AND DISCUSSION**

**Structure and Aqueous Stability of Ni₃P₄(0001) Surfaces.** For this study, we consider an acidic aqueous environment (pH = -0.1 to 1.0) because of typical experimental conditions for HER in acid, i.e., [H₂SO₄ = 1-0.1 M]⁴⁴,⁴⁸ and calculate the free energy of Ni₃P₄(0001) surfaces in equilibrium with 1 M Ni²⁺ or Ni(s), and 1 M PH₃ or 1 M H₂PO₄ at 298.15 K (see Table S2 in the Supporting Information). For the purpose of our discussion, we choose the standard concentration of 1 M for the aqueous species as a suitable reference to define the bulk and surface phase stability boundaries. The results for 0.01 and 0.001 M concentrations are plotted in Figure S6 in the Supporting Information, where we show that qualitatively the observed trends in stability and reactivity are unaffected, while quantitatively, the upper bound for the applied potential where the phases are stable varies by 0.02 to 0.05 V. In the regions of U and pH where solubility is greater than 1 M, it is reasonable to conclude that the catalyst would no longer be practical, as it would experience significant material loss during catalysis and after prolonged use (see Figure S2 for the calculated solubility of the bulk as a function of U and pH). Also, we note that the overpotential calculated for an HER elementary step for a given surface is independent of these concentrations. Figure 1A shows the phase diagram for the (0001) surface of Ni₃P₄. At U > -0.21 V, Ni₃P₄(s)/Ni₃P₄(0001) with one H per surface unit cell, hereafter denoted as Ni₃P₄(s)/Ni₃P₄(0001)+H, is the dominant surface phase. The \( \sqrt{3} \times \sqrt{3} \) R30° surface has one H bonded to each Ni₃-hollow site (labeled 1-3 in Figure 1B). Ni₃-hollow sites strongly bind H, with an adsorption free energy (see eq 13) of -0.47 eV/H. We summarize \( \Delta G_{\text{ads}} \) for different sites on Ni₃P₄(0001) and Ni₅P₄(0001) in Table 1.

<table>
<thead>
<tr>
<th>Bulk</th>
<th>Surface</th>
<th>Orientation</th>
<th>Active Site</th>
<th>( \Delta G_{\text{ads}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃P</td>
<td>Ni₃P₄+H</td>
<td></td>
<td>Ni₃-hollow</td>
<td>-0.47</td>
</tr>
<tr>
<td>Ni₅P</td>
<td>Ni₃P₄+P+(7/3)H</td>
<td>(0001)</td>
<td>adamant P</td>
<td>0.01 to 0.14</td>
</tr>
<tr>
<td>Ni₅P</td>
<td>Ni₅P₄+H</td>
<td>(0001)</td>
<td>Ni₅-hollow</td>
<td>-0.57</td>
</tr>
<tr>
<td>Ni₅P</td>
<td>Ni₅P₄+4H</td>
<td>(0001)</td>
<td>P₃-hollow</td>
<td>-0.27 to -0.06</td>
</tr>
</tbody>
</table>

For \( -0.21 \leq U \leq -0.36 \) V, a P-enriched phase, Ni₅P₄(s)/Ni₅P₄(0001)+P+(7/3)H is most stable. Aqueous P reacts with the surface, replacing the H atom at each Ni₃-hollow site with P. This surface is similar to the UHV reconstruction Ni₅P₄(s)/Ni₅P₄(0001)+P, but here P-adatoms are also hydrogenated. More specifically, one adatom P forms a surface PH₃ moiety, whereas the other two form PH₂ for a total of seven H atoms (labeled 1-7 in 1C) per \( \sqrt{3} \times \sqrt{3} \) R30° surface unit cell. These units, with an average P-H bond length of 1.43 Å, form the precursor for phosphine molecule (\( d_{\text{PH}} = 1.42 \) Å⁵⁰), desorption, which occurs at \( U < -0.36 \) V. The side view in Figure 1B reveals that P is exposed and able to react with more H than the Ni₃P₄(0001) surface. The bond length between in-plane Ni and P is 2.19 Å, whereas the bond length between Ni and adatom P is elongated (2.35 Å), signaling a weaker bond. As such, adatom P is able to form a stronger bond with H (\( \Delta G_{\text{ads}} = 0.05 \) eV/H) than the lattice P (\( \Delta G_{\text{ads}} = 0.27 \) eV/H). H-binding is much weaker on adatom P sites than Ni₃-hollow sites, in agreement with the literature.⁴⁶

Below U = -0.36 V, PH₃ desorbs and re-exposes the Ni₃-hollow sites again for H to bind, one H per Ni₃. Two additional H adsorb on the surface (labeled 4 and 5 in Figure 1D) forming Ni₃P₄(s)/Ni₃P₄(0001)+4H, where Ni forms a complex with H₂, pushing the central H to a Ni-bridge site. The average Ni-H bond length involving atomic H decreases from 1.79 Å on Ni₃P₄(s)/Ni₃P₄(0001)+H to 1.67 Å on Ni₃P₄(s)/Ni₃P₄(0001)+4H because of the reduced coordination of number of H. The H-H bond length (0.82 Å) is only slightly larger than that of H₂(g) (0.74 Å⁵⁰), highlighting the weak adsorption of this species.

**Structure and Aqueous Stability of Ni₅P₄(0001) Surfaces.** For Ni₅P₄(0001), only two different surface phases are observed under acidic (pH = -0.1 to 1.0) conditions (see Figure 2A). For U ≥ -0.37 V, the predominant surface phase is Ni₅P₄(s)/Ni₅P₄(0001)+4H. The structure of this surface is shown in Figure 2B, and it consists of repeating Ni₅-hollows connected by central Ni atoms. The P₃-hollow sites are unique to Ni₅P₄ and specifically the Ni₅-hollow termination. There are two different types of Ni-P bonds, one with a bond length of 2.09 Å between P and the central Ni and another with a bond length of 2.26 Å between P and a Ni from a Ni₃-hollow. The average of these two Ni-P bond lengths is near the bond length between in-plane Ni and P on Ni₅P₄(s)/Ni₅P₄(0001) surfaces. Three H atoms adsorb, per \( \sqrt{3} \times \sqrt{3} \) supercell, one at each Ni₃-hollow with equal bonding contributions from all three Ni atoms and an average bond length of 1.74 Å. H binding is stronger at the Ni₅-hollow site on Ni₅P₄(s)/Ni₅P₄(0001)+4H, with an adsorption free energy of -0.57 eV/H. Nine additional H atoms per supercell adsorb, three per P₃-hollow site (circled and shaded in light purple in in Figure 2B). Each H makes a single P-H bond of length 1.42 Å, and the H atoms point toward the center of the P₃-hollow. We find a positive correlation between \( \Delta G_{\text{ads}} \) and H coverage \( n_H \) at the P₃-hollow sites (see Figure 3), and we attribute this to repulsive interactions between H adsorbates. As H coverage at P₃-hollows increases, surface H species are forced into close proximity, thereby increasing the P-P-H angle (see inset in Figure 3), destabilizing H adsorption, and shifting it toward thermoneutrality. This coverage-dependent chemisorption energy is the key feature that makes P₃-hollows superior to other P-based active sites. At more negative potentials, U < -0.37 V, two additional H atoms per supercell bind to one of the Ni₅-hollows, generating a Ni-H₃ complex (\( d_{\text{Ni-H}} = 0.86 \) Å) identical to that on Ni₅P₄(s)/Ni₅P₄(0001)+4H/3/3H, as shown in Figure 2C. Consequently, there are three domains of binding energy on Ni₅P₄ (colored red, blue, and green in Figure 3). The maximum coverage of Ni₅P₄(0001) is 1.5 times larger than that of Ni₅P₄(0001). We also consider P-enriched (0001) surfaces in our stability analysis (see Table S4 in the Supporting Information) but find that they are not stable in acidic aqueous media, unlike in Ni₅P₄(0001), where an adlayer of P forms. P₃-hollows, however, are more advantageous for the HER than adatom P because they exist at less negative overpotentials.
We defer our discussion of Ni$_5$P$_4$(0001) surfaces to the Supporting Information (see Figure S3) because the (0001) faces on Ni$_5$P$_4$(0001) and Ni$_2$P(0001) surfaces offer lower HER overpotentials, which will now be discussed.

**HER Mechanism of Ni$_5$P$_4$(0001) and Ni$_2$P(0001) Surfaces.** In general, the most efficient catalytic mechanisms occur between nearly isoenergetic surface phases, such that each step in the reaction is thermoneutral or low-energy. For electrochemical reactions that do not occur spontaneously, an applied potential can be used to drive the reaction. Here, we define the overpotential $\eta$ as the potential required to make all elementary steps in the HER spontaneous and ensure catalyst stability, since a prerequisite for catalysis is a regenerable surface that supports it. In the following discussion on the mechanism of the HER, the predictions we make satisfy these criteria.

The HER mechanism on Ni$_5$P is still debated in the literature. Computational studies have focused on stoichiometric Ni$_5$P surfaces, with none considering the influence of surface reconstruction driven by the aqueous phase in contact with the catalyst. There are two main proposals for the HER active site on Ni$_5$P: cooperative Ni$_3$-hollow and Ni$_2$P bridge sites on the (0001) facet,$^{43,44}$ and Ni–Ni bridge sites on the (1120) and (1120) surfaces.$^{47}$ Here, we present alternative mechanisms that exhibit the lowest overpotentials for HER on the (0001) surfaces of Ni$_5$P and Ni$_2$P. A less favorable mechanism on Ni$_5$P(0001) is reported in the Supporting Information.

For Ni$_2$P(0001), we find that the H-covered, P-enriched Ni$_2$P$_2$H$_4+$P+(7/3)H surface offers the lowest overpotential for HER via the Volmer–Heyrovsky mechanism. Figure 4A shows the free energies and structures of reaction intermediates. The first step of this reaction involves two concerted events: (a) reaction of a proton in solution and electron with H at a PH$_3$ moiety and (b) desorption of H$_2$(g) to form PH$_2$. In the second step, the PH$_2$ subunit is replenished by another proton and electron. At $U = 0$ V, this reaction has a 0.14 eV barrier (black line in Figure 4A), and consequently, the application of $-0.14$ V (red line) makes each step spontaneous. Ni$_2$P$_2$H$_4+$P+(7/3)H, however, is only stable for $-0.21$ V $\leq U \leq -0.36$ V. Therefore, we portray an overpotential of $-0.21$ V (green line) for Ni$_5$P(0001), since the reaction is limited by the stability of the active surface phase (the dominant surface at $U = -0.14$ V has a larger overpotential requirement, $U = -0.26$ V, see Figure S4 in the Supporting Information). This mechanism is different from those previously proposed in the literature for Ni$_5$P,$^{45,47}$ highlighting the importance of considering aqueous phase stability in the prediction of catalytic mechanisms. It was also predicted that Ni–P bridge sites on Ni$_5$P(0001) offer weaker binding for H. However, we find that these sites are not stable.

Ni$_5$P$_4$(0001) offers a surface phase that provides efficient HER catalysis, Ni$_5$P$_2$H$_4+$H. Like Ni$_2$P(0001), this surface favors a Volmer–Heyrovsky mechanism, as shown in Figure 4B. This mechanism involves the simultaneous addition of H and abstraction of H$_2$(g) from a P$_3$-hollow site followed by H...
adsorption to replenish the third H at the P₃-hollow site. At U = 0 V, this HER mechanism has a smaller barrier (0.07 eV at U = 0 V, black line in 4B) and consequently requires a smaller overpotential (−0.07 V, red line) to make each step spontaneous. Bulk Ni₅P₄(s), however, is only stable with respect to dissolution for −0.16 V ≤ U ≥ −0.48 V at pH = 0, whereas Ni₃P(s) is stable for −0.11 V ≤ U ≥ −0.66 V. This prediction agrees with an experiment where it has been shown that applying negative potential (≈ −0.2 V vs RHE) suppresses degradation of Ni₅P₄. If positive potentials, i.e. U ≈ 0.3 V vs RHE, the compound dissolves with a rate of 1 ng/s/cm². Therefore, the performance of Ni₅P₄ is expected to degrade over time for potentials higher than the stabilizing potential. Therefore, the lowest HER overpotential for Ni₅P₄(0001) is −0.16 V, as the reaction is limited by the stability of bulk Ni₅P₄(s). From this, we see that the (001) planes of Ni₅P₄ are more HER active than that of Ni₃P(0001), in agreement with experimental reports. If one were only to consider thermodynamic barriers associated with the catalytic cycle, Ni₅P₄(0001) would still have a lower overpotential (−0.07 V) than Ni₃P(0001) (−0.14 V). Since we find that the adsorption energy of H on Ni₅P₄ is nearly thermoneutral, i.e. −0.07 eV, the intrinsic activity of Ni₅P₄ should be comparable to that of Pt. However, while it is experimentally found that the overall activity of nanocrystalline Ni₅P₄ approaches that of Pt on an electrode-basis, the surface-area-normalized turnover frequency (TOF) of Pt, i.e. performance on the basis of intrinsic activity (irrespective of morphology), is 2 orders of magnitude higher than that of Ni₅P₄. This apparent inconsistency between the calculated catalytic overpotential and the experimentally measured TOF can be explained by the limited aqueous stability of bulk Ni₅P₄, requiring an applied potential U ≤ −0.16 V. Therefore, potentials are expected to degrade the phosphides’ performance. This reconciles the “apparent” intrinsic activity of Ni₅P₄ being below that of Pt, although we predict that purely on the basis of catalytic activity of the active surface, Ni₅P₄(0001) is comparable to that of Pt. Synthetic methods, e.g. chemical doping, that would allow for Ni₅P₄ to be stable near 0 V vs SHE are therefore expected to lead to higher performance for the phosphide.

Since our calculations indicate that the P₃-hollow is the most active site for HER catalysis, we propose high-throughput searching for materials that express this motif. P₃-hollows form on Ni₅P₄(0001)/Ni₃P₃(0001) because of the high P content in Ni₅P₄ relative to other bulk nickel phosphides and the ability of bulk P(s) to form stable clusters. Clustering behavior in nonmetals is not unique to P, as S(s) also exhibits many different allotropes with various clustering geometries. As such, we believe that multinonmetal sites in general may hold promise for HER catalysis and should be a focal point for researchers studying the HER. Another way to improve the efficiency of nickel phosphides for HER therefore would be to subtly modulate the metal–P bond strength so as to indirectly shift the free energy of H adsorption toward thermoneutrality. This opens a clear path for materials design of new materials to improve HER activity by tuning metal–P bond strength via lattice strain (e.g., epitaxial film growth) or low concentration doping/ion exchange with other elements. To date, however, there has only been one study of the relationship between Fe and Co-doping on the H adsorption free energy. Since we find P to be the active site for HER on Ni₃P and Ni₅P₄, we recommend anionic substitutions for P as a more straightforward path to tune the catalytic activity, in contrast with the transition metal substitution approach proposed recently. For example, the presence of the more electronegative S can directly (through the formation of S–H) or indirectly (through modulation of the Ni–P bond strength) affect the binding of H onto the surface. Given that Ni₅P is a hydrodesulfurization catalyst, surface substitution with S should be possible. Nickel phosphate HER catalysts are reported to have nearly quantitative Faradaic efficiencies. Therefore, the formation of reduction side products from the electrolyte leading to the formation of reduced sulfur species is assumed not to occur and not included in our models. Further studies are necessary to develop a robust theory of chemical bonding between metal, P, and H in transition-metal phosphides, which could ultimately provide systematic guidance for designing improved HER catalysts.

### CONCLUSIONS

The (001) surface of Ni₅P₄ provides lower HER overpotentials and therefore greater HER activity than Ni₃P(0001), which can be attributed to the thermodynamics and structure of surface P. For Ni₃P(0001), the most stable aqueous surface reconstructions are Ni₃P(s)/Ni₅P₃(0001)+nH (n = 1, 5/3) and Ni₅P₃(s)/Ni₅P₄(0001)+P+(7/3)H, with the latter having an HER overpotential of −0.21 V. For Ni₅P₄, the (0001) facet is more catalytically active than (001), and the most stable aqueous reconstruction is Ni₅P₄(0001)+nH (n = 4, 14/3). This surface has the lowest overpotential for HER at −0.16 V, and not Ni, is the most active site, with adatom P and P₃-hollows providing low overpotential HER via the Volmer–Heyrovsky mechanism on Ni₅P₄(0001) surfaces. The P₃-hollow site on Ni₅P₄(s)/Ni₅P₄(0001) is present at low overpotential and offers nearly optimal H adsorption, is the origin of the superior catalytic activity of Ni₅P₄. The structural flexibility of P, i.e. its ability to form surface adlayers (adatom P) and in-plane multi-P clusters (P₃-hollow), provides a new frontier for improving the catalytic activity of transition-metal phosphides by embarking on high-throughput computational searches for catalysts that express these motifs and modulating the interaction strength between the metal and phosphorus via strain and surface doping.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b02761. Additional computational details, additional theoretical details, tabulated experimental standard formation free energies of solid and aqueous Ni and P species, Pourbaix diagrams for Ni and P, bulk phase diagrams for Ni₅P and Ni₅P₄, free energies of Ni₅P(0001) and Ni₅P₄(0001) surfaces, structure and aqueous stability of the Ni₅P₄(0001) surfaces, additional hydrogen evolution reaction mechanisms, and surface phase diagrams of Ni₅P₄(0001) and Ni₅P₄(0001) in equilibrium with different molar concentrations of solvated species (PDF)

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Notes
The authors declare no competing financial interest.

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