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Hydrogen adsorption trends on Al-doped Ni₂P surfaces for optimal catalyst design

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Nanoparticles of nickel phosphide are promising materials to replace the currently used rare Pt-group metals at cathode-side electrodes in devices for electrochemical hydrogen production. Chemical modification by doping can be used to fine-tune the electrocatalytic activity, but this path requires theoretical, atomic-level support which has not been widely available for Ni-P. We present a density functional theory analysis of Al-doped Ni₂P surfaces to identify structural motifs that could contribute to the improved behavior of the catalyst. Based on formation energies of substitutionally Al-doped Ni sublattices, we find doping to take place preferably at the topmost layers. The Ni-Ni bridge and the P-top sites are the optimal ones in terms of hydrogen bonding energies. The Ni-Ni bridge site is not present on pristine surfaces but a consequence of Al doping and provides a candidate to explain the experimentally observed high activities in doped Ni-P nanoparticles. Similar structural motifs can be recommended to be engineered for other Ni-P structures for improved electrocatalytic activity.

1 Introduction

Fully clean production of hydrogen as energy carrier from water can be realized by using electrocatalytic devices that are powered by renewable energy sources such as photovoltaics.^{1,2} In the electrocatalytic process of water splitting the cathode side of the device produces molecular hydrogen via the two-step hydrogen evolution reaction (HER).³ In HER, aqueous protons interact with the catalyst and the reaction is driven by cathodic overpotential. The electrodes in current water-splitting devices rely still heavily on Pt-group metals, which exhibit high efficiencies but pose major challenges due to their scarcity in Earth's crust.⁴ The search for Pt-group free electrodes is thus active and spans a wide variety of non-precious materials (see, for example^{2,5}). Nickel phosphides in various forms such as nanorods, -particles and -films are recent promising nanomaterials for catalysing HER in acidic conditions.^{6–10}

Chemical doping of Ni-P, which results in mixed anion or cation sublattices, is a new interesting way to modify the material further to optimize its performance.^{5,10} We studied recently MoS₂ surfaces modified by transition metal doping by density functional theory simulations (DFT) and showed that the H adsorption strength is strongly dependent on the nature of the dopant and the microscopic details of the surface.¹¹ This framework is used in the present research to elucidate doping-based modifica-

tions in nickel phosphides. Experimentally, successful doping of Ni-P systems by Al has been demonstrated by Lado *et al.*¹² The resulting foam electrodes were found to significantly outperform those of pure Ni-P nanoparticles, but the atomic-level origin of this improvement is not clear. In this work we elucidate the Al doping effects in detail in terms of formation and hydrogen adsorption energies. We aim to answer what kind of structural motifs on nickel phosphide surfaces, induced by doping, are the ones that are responsible for the experimentally observed improved HER performance compared to the pristine surfaces.

From a computational perspective, we use the Gibbs free energy of H adsorption (ΔG_H , hereafter ΔG) on the electrode surface with respect to molecular H₂ as reference as a descriptor for predicting relative HER activities.¹³ Finding catalysts with ΔG close to zero is widely used (as an example, see Ref.¹⁴) and encompasses the idea in Sabatier's principle of 'a not too weakly or a not too strongly adsorbed intermediate species', which is beneficial for HER. For more accurate and computationally involved approaches, one can include various electronic descriptors (see, for example¹⁵) or quantum dynamical simulations. A direct *ab initio* molecular dynamics calculation of reaction barriers and rate constants is appealing to model the two-step HER, but such an approach is computationally demanding. In modeling HER in Ni-P systems, a ΔG -based approach has been the most often used.^{16–19} Hansen *et al.*¹⁸ calculated also barriers for the surface recombination (Tafel) step. Wexler *et al.* investigated the formation and hydrogen adsorption energies of Ni₂P and Ni₅P₄ in detail by taking into account the thermodynamic equilibrium with the electro-

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chemical environment.^{19,20}

In this work we study the effects of Al doping on the actual surface structures and H adsorption characteristics in the Ni_2P phase, which is the predominant phase in the Al-Ni-P foam electrodes of Lado *et al.*¹² We focus on the theoretically predicted²⁰ stable surface structures Ni_3P_2 and phosphorized $\text{Ni}_3\text{P}_2 + \text{P}$ (Fig. 1). We study Al doping at substitutional Ni sites following the procedures of our recent studies on MoS_2 and doped MoS_2 .^{11,21} We calculate formation energies of the substitutional dopants and analyze how the surfaces change in terms of H adsorption characteristics. Particularly we find evidence that Al doping changes the H adsorption landscape beneficially, which correlates with the experimentally observed improved activity.

Fig. 1 $\text{Ni}_3\text{P}_2 + \text{P}$ surface (view from the top). The unit cell in the x-y plane is drawn in the lower left corner. The P adatom (Pad) and the atoms in the topmost layer are indicated. The Ni_3 triangular motif at the topmost layer is also separately emphasized. The Ni_3P_2 surface corresponds to the same structure without the P adatom.

The paper is organized as follows. The computational details are provided in Sec. 2. Sec. 3 reports the H adsorption results for the pristine surfaces, the formation energies of substitutional Al-dopants and the H adsorption results for Al-doped surfaces. Since the relative energy differences are often very small, in Sec. 3 we also discuss the sensitivity of ΔG values to the change of the exchange-correlation functional and to the inclusion of van der Waals forces. In Sec. 4 we discuss the implications of our results to understanding the effect of Al doping on HER on Ni_2P surfaces. Sec. 5 concludes the work.

2 Computational details

Density functional theory calculations were performed using the PBE functional.²² All calculations were carried out with the CP2K/Quickstep software.^{23,24} The kinetic energy cutoff was 700 Ry and the cutoff of the reference grid 60 eV. Double-zeta plus polarization level molecularly optimized basis sets (MOLOPT-SR-DZVP)²⁵ and norm-conserving Goedecker-Teter-Hutter (GTH) pseudopotentials^{26–28} were used. The Poisson equation for the electrostatic potential was solved with periodic boundary conditions. In structural minimizations the atomic positions were optimized using the Broyden-Fletcher-Goldfarb-Shanno algorithm until the force on any atom was less than 0.023 eV/Å.

For Ni_2P bulk lattice parameters, a supercell of 4x4x4 unit cells was allowed to freely relax with pressure tolerance of 0.1 kbar. Orbital transformation (OT) method and spin-polarization calculations were used. The cell parameters were obtained as $a=b=5.860$ Å and $c=3.332$ Å (experimental values²⁹ 5.86 Å and 3.39 Å) and the system relaxed to a nonferromagnetic state. For reference total energies for Ni and Al in the crystalline phase, supercells of 10x10x10 units were used with PBE lattice parameters from literature.³⁰

For surface calculations we used the diagonalization method with an electronic smearing of 75 K and the DFT-D3(BJ) method to take into account the van der Waals interactions.^{31,32} At least a 10 Å wide vacuum layer was used on both sides of the slab. We focused on the (0001) surface and its Ni_3P_2 termination, which is the preferred termination in the bulk Ni_2P stability region according to Wexler *et al.*²⁰ In addition to Ni_3P_2 , we study the $\text{Ni}_3\text{P}_2 + \text{P}$ termination, which is the most prevalent phase at cathodic overpotentials $U < -0.21$ V and consistent with experimental observations for phosphorus enrichment of Ni_2P surfaces. We modeled the surfaces with 1x1 surface unit cells with some tests with 2x2 surfaces to assess H...H repulsion effects on adsorption energies. For the Ni_3P_2 surface we employed a symmetric slab with seven layers and fixed the atoms at the bottom layer to their bulk positions. We used 5x5x1 Monkhorst-Pack *k*-points. For $\text{Ni}_3\text{P}_2 + \text{P}$, we used the Ni_3P_2 slab and added the extra P on one side at the Ni_3 hollow sites. With these choices the H adsorption energies were estimated to be converged within 0.1 eV. Fig. 2 illustrates the slab used in the calculations for pristine and doped surfaces.

Fig. 2 Supercell used for the seven-layer slab calculations for (a) pristine and (b) singly Al-doped $\text{Ni}_3\text{P}_2 + \text{P}$ surface (view from the side, optimized atomic positions are shown). The three first atomic layers are indicated.

To sample H adsorption sites on a given surface we used a set of roughly 14 different starting initial H positions above the slab. We analyzed the H coverage and differential Gibbs free energies of H adsorption following the self-consistent scheme as presented in the literature.^{18,33} In this scheme for a given chemical potential μ of protons and electrons, the relevant H coverage is determined by the minimum of the total adsorption energy ΔG_{tot}

$$\Delta G_{\text{tot}}(n) = G(n) - G(0) - n\mu \quad (1)$$

as a function of n adsorbed hydrogens. Above, $G(n)$ is the free energy of the surface with n hydrogens and $G(0)$ the same for the

uncovered surface. The chemical potential is given by

$$\mu = 1/2G(\text{H}_2) - q_e U, \quad (2)$$

where $G(\text{H}_2)$ is the free energy of molecular hydrogen in the gas phase, U the potential of the cathode and q_e the elementary charge. The differential Gibbs free energy of H adsorption that is relevant for analysing the hydrogen evolution reaction at a given n is given by¹⁸

$$\Delta G_{\text{diff}}(n) = G(n) - G(n-1) - \mu \quad (3)$$

This can be approximated as

$$\Delta G_{\text{diff}}(n) \approx E(n) - E(n-1) - 1/2E(\text{H}_2) + 0.24 \text{ eV} + q_e U, \quad (4)$$

where E is the DFT-calculated total energy at 0 K and the term 0.24 eV takes into account the zero point energy and entropy differences following Ref.¹⁸ We note that Wexler *et al.*¹⁹ calculated the zero-point corrections explicitly and found that the total correction factor was of the same order, 0.19 eV for H adsorption at the Ni_3 -hollow site and 0.24 eV at the P adatom site.

The minimum overpotential to adsorb hydrogen at a given H coverage n is given as

$$\eta(n) = \Delta G_{\text{diff}}(n)/e. \quad (5)$$

In the following we drop the subscript and use simply ΔG to denote ΔG_{diff} . In the subsequent tables we report values at $U = 0$ V.

Our test calculations for charged pristine and Al-doped surfaces did not suggest any charge trapping. In other words, the supercell in the neutral charge state is energetically the lowest against the +1 or -1 charged ones, and we thus consider only neutral charge states in the current work.

3 Results

3.1 H adsorption on pristine surfaces

On the Ni_3P_2 (1x1) surface, stable at the lowest overpotentials,²⁰ the DFT calculations reveal a strongly binding Ni_3 -hollow site and a few weaker binding sites similarly as in the previous studies^{16,19} (see Table 1). After the hollow site is occupied by one H, the lowest adsorption energies for the next sites are slightly above 0 eV. Fig. 3 (a) shows this situation for the energetically lowest one. On the $\text{Ni}_3\text{P}_2 + \text{P}$ (1x1) surface, which was predicted to be the most stable at overpotentials $-0.21 \text{ V} > U > -0.36 \text{ V}$,²⁰ a P adatom occupies the Ni_3 -hollow site. We find, similarly to Wexler *et al.*, that this adatom is the active site and can bind up to three hydrogens (Fig. 3 (b)). The corresponding ΔG values are close to 0 eV (Table 2). There are other adsorption sites in addition to those reported but they are higher in energy.

It is instructive to consider if the ΔG values would change in the case of a larger surface area of the supercell for which the H...H image interactions are weaker. The calculated values for two cases for a (2x2) surface area are reported in Tables 1 and 2: the finding is that the adsorption energy is negligibly lower, 0.02 eV and 0.06 eV, respectively. The finding indicates only weak H...H interactions and we will consider our results for the (1x1)

Fig. 3 Relevant H adsorption configurations for (a) Ni_3P_2 at $n_{\text{H}} = 2$ and (b) $\text{Ni}_3\text{P}_2 + \text{P}$ at $n_{\text{H}} = 3$. n_{H} denotes the number of hydrogens adsorbed on the surface.

Table 1 ΔG for the Ni_3P_2 (1x1) surface according to Eq. 4. n_{H} denotes the number of hydrogens adsorbed on the surface. The value in parentheses [ ] corresponds to (2x2) surfaces. Asterisk * denotes an energetically close alternative site. The values by Wexler *et al.*¹⁹ correspond to a $\sqrt{3} \times \sqrt{3}$ surface unit cells

n_{H}	ΔG (eV)	
	This work	Wexler <i>et al.</i>
1	-0.49 (Ni_3 hollow)	-0.47
2	0.16 [0.14] (Ni-Ni bridge x 2)	-
2*	0.22 (Ni_3 hollow + Ni-P bridge)	0.26
3	0.19 (H_2 formation)	-

surface as sufficiently representative. These results for the pristine systems form a reference against which we compare our Al-doping results.

A few differences in our findings compared to the Wexler *et al.*'s results can be identified. For the Ni_3P_2 surface our relevant ΔG value is 0.16 eV for the second adsorbed H, whereas they find this energy to be 0.26 V. In contrast, for the $\text{Ni}_3\text{P}_2 + \text{P}$ surface our ΔG of 0.23 eV (for $n_{\text{H}} = 2$) is higher than their value. Our results thus suggest that Ni_2P could be HER-active already at low overpotentials (-0.16 V), before the $\text{Ni}_3\text{P}_2 + \text{P}$ phase becomes prevalent (at -0.21 V according to Wexler *et al.*). However, energy differences below 0.1 eV level are subject to computational uncertainties which needs to be taken carefully into account when making interpretations. These aspects are discussed in Section 3.4 below.

3.2 Al doping

The question to be answered by simulations is on which layers Al is preferentially located in the case that it substitutes Ni. For bulk we study single substitutional Al atoms in Ni_2P 4x4x4 supercells, whereas for surfaces we study the 1x1x7 slabs with substitutional atoms in different layers.

In the case of bulk crystals, a single Al dopant is found to energetically prefer the Ni_3P layer instead of the Ni_3P_2 one (total energy difference ~ 0.7 eV favors the Ni_3P layer, see Table 3 bottom). At surfaces, a single Al dopant in the topmost layer of Ni_3P_2 has a slightly negative formation energy, suggesting a relatively easy doping, whereas doping in the layers below has a clearly higher cost. In contrast, at $\text{Ni}_3\text{P}_2 + \text{P}$ surfaces, single Al doping of the topmost two layers have rather similar formation energies. For both the surfaces, in deeper layers the formation energy becomes progressively higher. Preference for the Ni_3P layer is similar as observed for the bulk crystal.

Based on the formation energies, Al doping is thus the most

Table 2 ΔG for the $\text{Ni}_3\text{P}_2+\text{P}$ (1x1) surface according to Eq. 4. See caption of Table 1

n_{H}	ΔG (eV)	
	This work	Wexler <i>et al.</i>
1	0.06 [0.00] (P-top)	0.01-0.06
1*	0.12 (Ni-top)	-
2	-0.03 (P-top)	0.01-0.06
3	0.23 (P-top)	0.01-0.06
4	0.08 (H_2 formation)	0.14

Table 3 Formation energy of single Al dopants on the surface and deeper layers of Ni_3P_2 (left two columns) and $\text{Ni}_3\text{P}_2+\text{P}$ (right two columns). The values corresponding to a bulk crystal are given. The formation energy of three Al's in the topmost layer (all Ni sites substituted by Al) is also reported (second line in the table)

Ni_3P_2		$\text{Ni}_3\text{P}_2+\text{P}$	
Layer	E_{F} (eV)	Layer	E_{F} (eV)
Ni_3P_2 , top	-0.31	$\text{Ni}_3\text{P}_2+\text{P}$, top	0.44
Ni_3P_2 , top, 3 x Al	0.97	$\text{Ni}_3\text{P}_2+\text{P}$, top, 3 x Al	1.31
Ni_3P_2 , 2nd	0.29	Ni_3P_2 , 2nd	0.67
Ni_3P_2 , 3rd	1.69	Ni_3P_2 , 3rd	1.87
Ni_3P_2 , 4th	0.89	Ni_3P_2 , 4th	0.98
bulk, Ni_3P layer	1.01	-	-
bulk, Ni_3P_2 layer	1.67	-	-

favorable in the two topmost surface layers. Moreover, the Ni_3P_2 surface is more likely to be Al doped (by 0.7 eV) than the $\text{Ni}_3\text{P}_2+\text{P}$ one. Since for both the Ni_3P_2 and $\text{Ni}_3\text{P}_2+\text{P}$ cases doping with three Al in the topmost layer has considerably larger formation energy (Table 3) than doping with one Al, our result suggests that the general doping level remains low.

3.3 H adsorption on Al-doped surfaces

Based on the findings for the formation energies in Section 3.2, we focus on surfaces in which only the topmost layer is doped. We consider either one or three dopants and carry out the same analysis for ΔG as for the undoped surfaces. Tables 4 and 5 report the results.

Table 4 ΔG for Al-doped Ni_3P_2 surface in the case of one and three Al dopants in the topmost layer. n_{H} denotes the number of hydrogens adsorbed on the surface. The values for the pristine surface are given for reference

n_{H}	ΔG (eV), Ni_3P_2 surface	
	one Al	three Al
1	-0.02 (Ni-Ni bridge)	-0.37 (Al-Al bridge)
2	0.32 (Ni-Ni + P-top)	0.16 (Ni-Ni x 2)

The fact that ΔG ($n_{\text{H}} = 1$) is close to 0 eV on the weakly Al-doped Ni_3P_2 surface is very interesting as compared with the pristine surface with the strongly adsorbing hollow site. Al doping effectively weakens the hollow site's binding energy and H becomes coordinated just to two nickels instead of three (Fig. 4 (a)). However, when all the Ni atoms in the topmost surface are replaced by Al dopants, the adsorption energy becomes again stronger (-0.37 eV). Secondly, as in the case of pristine $\text{Ni}_3\text{P}_2+\text{P}$, the adatom P creates an efficient first adsorption site with $\Delta G \sim 0.05$ eV independent of the surface being doped by one or three Al atoms. In the weak doping case H binds to the midway between the P

Table 5 ΔG for Al-doped $\text{Ni}_3\text{P}_2+\text{P}$ surface in the case of one and three Al dopants in the topmost layer. See caption of Table 4. The value with asterisk * corresponds to an energetically close alternative site

n_{H}	ΔG (eV), $\text{Ni}_3\text{P}_2+\text{P}$ surface	
	one Al	three Al
1	0.07 (P-top - Al bridge)	0.05 (Al-Al bridge)
1*	-	0.11 (Al-top)
2	0.20 (P-top x 2)	0.25 (H_2 formation)

Fig. 4 Relevant H adsorption configurations for singly Al-doped (a) Ni_3P_2 at $n_{\text{H}} = 1$ and (b) $\text{Ni}_3\text{P}_2+\text{P}$ at $n_{\text{H}} = 1$.

adatom and the Al dopant (Fig. 4 (b)). We thus identify both the Ni-Ni bridge and P-top sites as the most promising structural motifs in terms of H adsorption in Al-doped Ni_2P .

3.4 Sensitivity to computational parameters

To have an idea of the sensitivity of the adsorption energies to the used level of theory (PBE+vdW correction), in Table 6 we report a set of cases for which (i) the van der Waals correction is switched off and (ii) the RPBE functional³⁴ is used instead without van der Waals correction. The RPBE values for Ni_3P_2 reported by Liu *et al.*¹⁶ are given for comparison (0.24 eV correction is added to bring their values to the scale of Gibbs free energy of adsorption).

Table 6 Effect of exchange-correlation functional and van der Waals correction on ΔG for selected cases. The values by Liu *et al.*¹⁶ are given for comparison for Ni_3P_2 . Asterisk * denotes an energetically close alternative site

n_{H}	site	Ni_3P_2			
		PBE+vdW	PBE	RPBE	Liu <i>et al.</i>
1	Ni_3 hollow	-0.49	-0.41	-0.15	-0.30
2	Ni-Ni bridge x 2	0.16	0.23	0.35	0.33†
		Ni_3P_2 , Al-doped			
n_{H}	site	PBE+vdW	PBE	RPBE	
1	Ni-Ni bridge	-0.02	0.03	0.00	
1*	Ni-Al bridge	0.10	0.17	0.14	
		$\text{Ni}_3\text{P}_2+\text{P}$			
n_{H}	site	PBE+vdW	PBE	RPBE	
1	P-top	0.06	n/a	0.22	
1*	Ni-top	0.12	n/a	0.21	

† Ni_3 hollow + Ni-P bridge site

For these test cases the RPBE functional leads to similar or slightly weakened H binding. For Ni_3P_2 the ΔG values by RPBE are similar to the values by Liu *et al.*¹⁶ Van der Waals correction, on the other hand, is not found to influence significantly the adsorption energies. The slight reduction of binding by using the RPBE functional is typical for chemisorbed atoms and molecules.³⁴ In the third case (pristine $\text{Ni}_3\text{P}_2+\text{P}$) the RPBE-predicted configuration of the energetically lowest adsorption site does not make a difference between the P-top and Ni-top sites, unlike in PBE.

These issues are most probably case specific. We note that even when a set of starting H positions converges to the same nominal final adsorption site, one may still observe some variation in the ΔG values. As an example, on the $\text{Ni}_3\text{P}_2 + \text{P}$ surface for the Ni-top site (Table 6, lowest panel) we found, in addition to 0.12 eV, also a local minimum with 0.17 eV adsorption energy with PBE+vdW correction. This observation thus suggests that a careful analysis should be carried out when small relative energy differences are critical for structural and reaction interpretations.

4 Discussion

We discuss first the nature of the adsorption sites in pristine and Al-doped Ni_2P and then the general implications for HER as analyzed through ΔG values. We postpone until the end the discussion of the uncertainties of this approach. First, regarding strongly binding adsorption sites (i.e., those that can be considered to lead to H 'poisoning' the surface), from our analyses it appears that there are only two surfaces that exhibit this feature: the pristine Ni_3P_2 and the fully Al-doped Ni_3P_2 (in the latter all Ni atoms in the topmost layer are replaced by Al atoms). On pristine Ni_3P_2 the strong-binding site is the Ni_3 -hollow site ($\Delta G = -0.49$ eV and on fully Al-doped one the Al-Al bridge site ($\Delta G = -0.37$ eV). Binding the next H's on these surfaces will require overpotentials -0.16 V and -0.20 V, respectively. Neither of these surfaces is thus optimally close to 0 eV in terms of ΔG . For the rest of the surfaces and adsorption sites the binding energies are generally small, either close to 0 eV or somewhat above it.

We identified Ni-Ni bridges (Fig. 4 (a) and P adatoms (Fig. 3 (b) and 4 (b)) as the most promising structural motifs since the corresponding binding energies for H adsorption are very close to 0 eV. Of major interest regarding chemical modification is the Ni-Ni bridge site at the weakly Al-doped Ni_3P_2 surface. Al substitution breaks the symmetry of the Ni_3 triangle motif and allows hydrogen to be bound by two nickel atoms instead of three (in other words, Al doping weakens the original Ni_3 hollow site's adsorption strength). Second, the P adatom was already recognized by Wexler *et al.* as playing an active role in HER on the pristine $\text{Ni}_3\text{P}_2 + \text{P}$ surface.¹⁹ We have now showed that this adatom plays an equally active role in the Al-doped $\text{Ni}_3\text{P}_2 + \text{P}$ surface. It creates energetically optimally adsorbing P-adatom-Al-bridge and Al-Al bridge sites with ΔG around 0.05-0.10 eV.

To strengthen the relevance of the above findings to real experimental situations, we refer to the formation energies of Al in Ni_2P , Sec. 3.2. Table 3 shed light on which surfaces Al prefers to be located. To recapitulate those results, Al doping is best favored at low concentration levels at the topmost Ni_3P_2 surface, and the doping probability decreases deeper from the surface. Doping at the third and fourth layers was energetically roughly of similar cost as doping inside the bulk crystal. We thus believe that the experimentally synthesized samples will be predominantly surface enriched by Al. Qualitatively, a similar doping level at the topmost layer was observed in cobalt doped synthesized MoS_2 nanolayers: the doping concentration (substitutional doping of Mo atoms) was about 25% at the MoS_2 edge surface.³⁵

Our formation energies thus support the view that the topmost surface layer of Ni_3P_2 is weakly doped by Al, and we have seen

that this creates Ni-Ni bridge sites for H adsorption at optimal energies. If the ΔG criterion were the only explaining factor for good electrocatalytic behavior, our result would align well with the experimental finding by Lado *et al.*¹² for Al-Ni-P nanoparticles. Technically, Lado *et al.* observed the minimum required overpotential $\eta \sim -0.02$ V for driving 1 mA/cm² current density for their Al-doped sample (Ni_2P as the major crystal phase), which is in good agreement with our finding of $\Delta G \sim 0$ eV. On the other hand for undoped Ni-P samples, which consist predominantly of Ni_5P_4 crystal phases, they observed $\eta \sim -0.08$ V. This latter result is in qualitative agreement with the predicted value of -0.16 V for the lowest overpotential for the (000 $\bar{1}$) surface by Wexler *et al.*¹⁹ Interestingly, in our results the ΔG for the phosphorized Ni_2P surface ($\text{Ni}_3\text{P}_2 + \text{P}$) does not seem to be strongly affected by Al doping.

Recommendations for experimental synthesis of nickel phosphides in general (not limited to Ni_2P) can be made based on our current results. We recommend that by chemical and/or structural modification one attempts to create Ni-Ni bridge motifs and low-coordinated P adatoms. Firstly, for creating the Ni-Ni motifs, substitutional doping on Ni sites clearly serves the purpose. In this work we have verified that Al doping in the topmost surface layer leads to Ni-Ni bridge sites, an effect which can be related to Al's lack of 3d electrons. For future studies and to build up systematic understanding of doping effects, other substitutional dopants should be attempted. Doping by magnesium (one *p* electron less than Al) or antimony (a closed d shell and two additional *p* electrons compared with Al) are some candidates. Secondly, engineering more P adatoms on the surface is the route that can be experimentally exploited, either by tuning the phosphorization conditions or possibly by intentional creation of defects.

Finally we discuss some of the factors that need to be taken into account when making further analysis and conclusions regarding HER electrochemistry in nickel phosphides. While the ΔG criterion is often used and is able to explain trends, predicting electrocatalytic behavior solely based on a single descriptor is challenging.^{15,36–38} In the present work, one clear uncertainty remains regarding what is the rate-limiting step in HER of nickel phosphides and what are the related activation energies. Realistic reaction and activation energy analysis would require for example *ab initio* molecular dynamics. Regarding the precision of our ΔG values, we estimated that the chosen calculation parameters (cut-off parameters, size of vacuum, thickness of the slab etc.) lead to convergence within 0.01 eV in our adsorption energies ΔG for the present level of theory. Our ΔG values for the relevant sites are similar to the results by Wexler *et al.*¹⁹ who also used the PBE + vdW approach. We studied in Sec. 3.4 separately the effect of XC functional and van der Waals correction on some of our adsorption configurations. The choice of the XC functional in our case may lead to a rough uncertainty of the order of 0.1-0.15 eV in the ΔG values. We thus see it risky to make strong conclusions based on relative differences in the ΔG values below the 0.1 eV level.

5 Conclusions

We performed a theoretical analysis to understand and explain Al-doping effects on Ni_2P surfaces in terms of improved electro-

chemical behavior as observed in HER experiments. We analyzed by DFT calculations the formation and hydrogen adsorption energies on Al-doped Ni_3P_2 and $\text{Ni}_3\text{P}_2 + \text{P}$ surfaces. At low doping levels Al is most likely to be located only at the topmost layer and at deeper layers the formation energies quickly increase to the level of corresponding bulk values. We observed two distinct structural motifs that promote optimal ($\Delta G \sim 0$ eV) adsorption energies in view of the hydrogen evolution reaction: Ni-Ni bridge sites and P adatom sites. The Ni-Ni bridge site is a consequence of substitutional doping and provides a candidate for explaining the low HER overpotentials in synthesized Al-Ni-P foams.¹² We recommend that these and analogous motifs should be explored further and engineered into synthesized phosphide nanostructures to maximize the chances to improve the electrocatalytic activity.

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