Supplementary Information of Reaction modelling of hydrogen evolution on nickel phosphide catalysts: Density functional investigation

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1 Phosphorus chemical potential limits

The chemical potential of phosphorus (μ_P) depends on the operating temperature and partial pressure of phosphorus, as described by the equation:

$$\mu_P = \frac{1}{4}\left[E^{tot}_{\mathrm{P_4}} + \tilde{\mu}_{\mathrm{P_4}}(T, p^0) + k_B T \ln\left(\frac{p_{\mathrm{P_4}}}{p^0}\right)\right] \tag{1}$$

Here, $\tilde{\mu}_{\mathrm{P_4}}$, the temperature-dependent chemical potential change at standard pressure, can be obtained from the JANAF Thermochemical Tables [1]. A detailed analysis of the chemical potential of phosphorus as a function of temperature and pressure is provided in [2]. In experiments aiming to prepare Ni_2P, the chemical potential of phosphorus is controlled by varying temperature and the concentration of phosphorus [3, 4].

In the present study, the lower (P-poor) and upper (P-rich) μ_P limits are set at 0 K such that the chemical potential of phosphorus will lead to the formation of Ni_2P. Below the P-poor limit, the chemical potential of phosphorus would lead to the formation of solid Ni, while above the P-rich limit, it would lead to the formation of P_4.

The following thermodynamic relationship is used to describe the formation of Ni_2P:

$$\frac{E^{bulk}_{\mathrm{Ni_2P}}}{3} = 2 \times \frac{E^{bulk}_{Ni}}{4} + \frac{E^{bulk}_{P}}{4} - \Delta H_f \tag{2}$$

$$\frac{E^{bulk}_{\mathrm{Ni_2P}}}{3} = 2 \times \mu_{Ni} + \mu_P \tag{3}$$

$$\mu_P^{lowerlimit} = \frac{E^{bulk}_{\mathrm{Ni_2P}}}{3} - 2 \times \frac{E^{bulk}_{Ni}}{4} = -7.89\ eV \tag{4}$$

$$\mu_P^{upperlimit} = \mu_{\mathrm{P}}(0K) = -4.22\ eV \tag{5}$$

In the above, ΔH_f is the heat of formation [5], $\mu_P^{lowerlimit}$ and $\mu_P^{upperlimit}$ are defined as the P-poor and P-rich limits of the chemical potential of phosphorus. The total energies used in these calculations are $E^{bulk}_{\mathrm{Ni_2P}} = -53.38$ eV, $E^{bulk}_{Ni} = -19.81$ eV [6], and $E^{molecule}_{\mathrm{P_4}} = -17.74$ eV [7]. It should be noted that if the energy of the crystalline P_4 ($E^{bulk}_{\mathrm{P_4}} = -21.50$ eV[8]) is used instead of molecular energy, the $\mu_P^{upperlimit} = -5.37$ eV.

Other expressions and values used to obtain the μ_P limits include the zero-point energy $E^{ZPE}_{\mathrm{P_4}} = 0.169$ eV [9], $\tilde{\mu}_{\mathrm{P_4}}(0K) = 0.69$ eV [1], and $E^{tot}_{\mathrm{P_4}} = E^{molecule}_{\mathrm{P_4}} + E^{ZPE}_{\mathrm{P_4}}$.

2 Calculation of Gibbs Free energy

The differential Gibbs free energy ($\Delta G_{diff}(n)$, eq. (13)) as a function of hydrogen coverage (n) is obtained using the free energy of vibrations in the systems (F_{vib}, eq. (8)). $E_{vib}(T, \omega)$ and $S_{vib}(T, \omega)$ are energy and entropy of vibrations in the system as a function of temperature and frequency. S_X represents the entropy of vibrations of species X, where nH stands for the number of adsorbed hydrogens at coverage n. The configurational entropy S_{nH} is neglected in the calculations. The below formalism is adapted from [10–12].

$$E_{vib}(T,\omega) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right) \tag{6}$$

$$S_{vib}(T,\omega) = k\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln(1-e^{-\beta\hbar\omega})\right] \tag{7}$$

$$F_{vib}(T) = \sum_{\omega} E_{vib}(T,\omega) - TS_{vib}(T,\omega) \tag{8}$$

$$\begin{aligned}\Delta G_{nH} = &\left[E_{slab+nH} + F_{vib(slab+nH)} - TS_{nH}\right] \\ &- \left[E_{slab} + \frac{nH}{2}\left(E_{H_2} + F_{vib(H_2)} - TS_{H_2}\right)\right]\end{aligned} \tag{9}$$

$$\begin{aligned}\Delta G_{nH} = &\left[E_{slab+nH} - E_{slab} - \frac{nH}{2}E_{H_2}\right] \\ &+ \left[F_{vib(slab+nH)} - \frac{nH}{2}F_{vib(H_2)}\right] \\ &- \left[TS_{nH} - \frac{nH}{2}TS_{H_2}\right]\end{aligned} \tag{10}$$

$$\Delta G_{nH} = \Delta E_{ads} + \Delta F_{vib} - T\Delta S_H \tag{11}$$

$$\Delta G(n) = \frac{\Delta G_{nH}}{nH} \tag{12}$$

$$\Delta G_{diff}(n) = \Delta G_{nH} - \Delta G_{(n-1)H} \tag{13}$$

2.1 Vibration energy values

Table 1: Vibrational free energy (eq. (8)) at 298 K, with dispersion corrections in parentheses. Ni-Ni bridge and Ni-top sites are unstable for 1H adsorption. Ni-Ni bridge values average 2H and 3H coverages; Ni-top values are from 2H coverage (one H at the hollow site, one at Ni-top). "adatom P - nH" indicates n hydrogens on adatom P.

Adsorption site	Vibration Free energy $F_{vib}(298K)$(eV)	
	Ni_3P_2	Ni_3P_2 + 4P*
Ni-Ni bridge	0.18 (0.18)	-
Ni hollow	0.15 (0.15)	-
Ni top	0.13	0.26
P top	0.19	0.29
Ni-P bridge	0.17 (0.17)	0.28
adatom P - 0H	-	0.12 (0.06)
adatom P - 1H	-	0.31 (0.29)
adatom P - 2H	-	0.50 (0.50)
adatom P - 3H	-	0.71 (0.73)

* Vibrations of phosphorus adatoms are included.

3 Adsorption results

3.1 Adsorption coverage visualisation

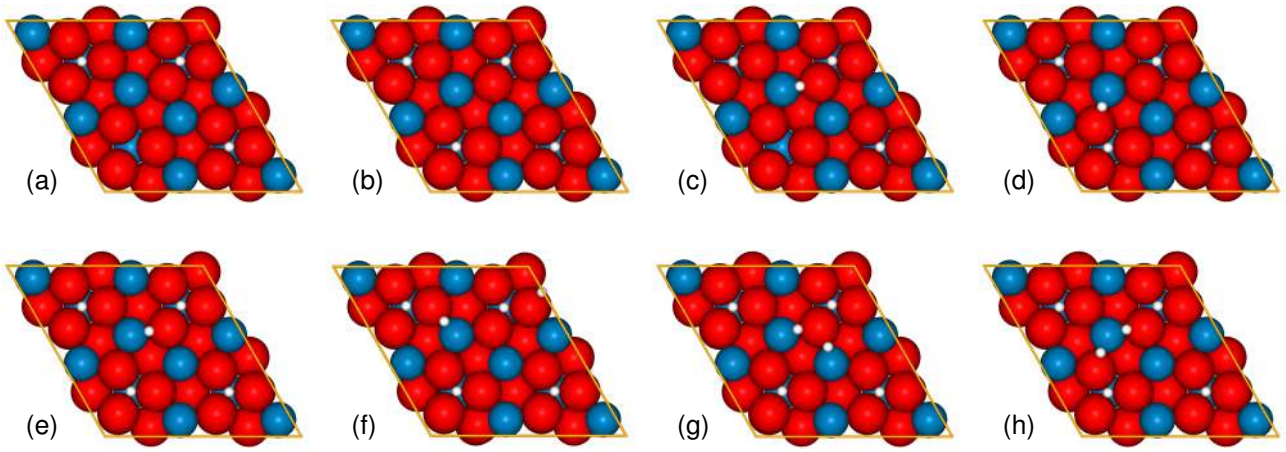

Figure 1: Hydrogen adsorption coverage configurations a) 3H(0), b) 4H(0), c) 4H(I), d) 5H(0), e) 5H(I), f) 6H(0), g) 6H(I), h) 6H(II) on Ni_3P_2 (pristine) surface termination. The colours red, blue and white represent Ni, P and H atoms, respectively.

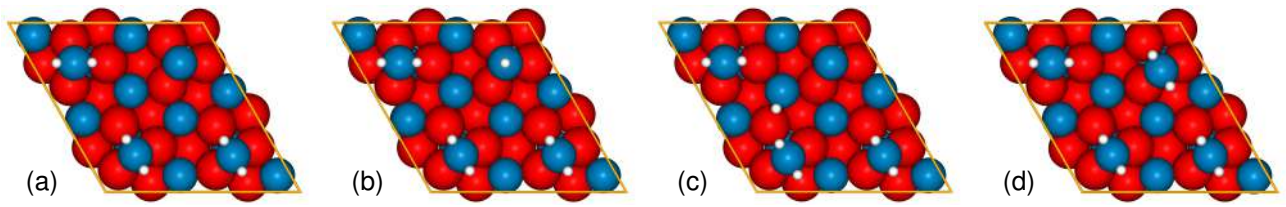

Figure 2: Hydrogen adsorption coverage configurations a) 6H(0), b) 7H(0), c) 7H(I), d)8H(0) on Ni_3P_2+4P (reconstructed) surface termination. The colours red, blue and white represent Ni, P and H atoms, respectively.

3.2 Adsorption energies in the literature

Table 2: Adsorption energy (ΔE_{ads}) and Gibbs Free energy ($\Delta G(1)$) of single H atom adsorption without (with) dispersion correction from various references.

Ads. site	Ni_3P_2	
	ΔE_{ads}(eV)	ΔG(eV)
Ni hollow	-0.65 [13], -0.64 [14]	-0.47 [15], -0.49 [16]
P top	0.09 [13], 1.09 [14]	-
Ni-P bridge	-0.05 [13]	-
Ads. site	Ni_3P_2+4P	
	ΔE_{ads}(eV)	ΔG(eV)
P top	0.15 [13]	-
Ni top	-0.04 [13]	0.12 [16]
Ni-P bridge	0.23 [13]	-
adatom P	-0.22 [13]	0.01-0.14 [15], 0.06 [16]

4 Reaction Calculations

The results of hydrogen evolution (HER) reaction calculations are provided below which are discussed in the main text. The data for all the reaction calculations presented in the main and supplementary text is available [17].

4.1 Reaction pathway visualisations

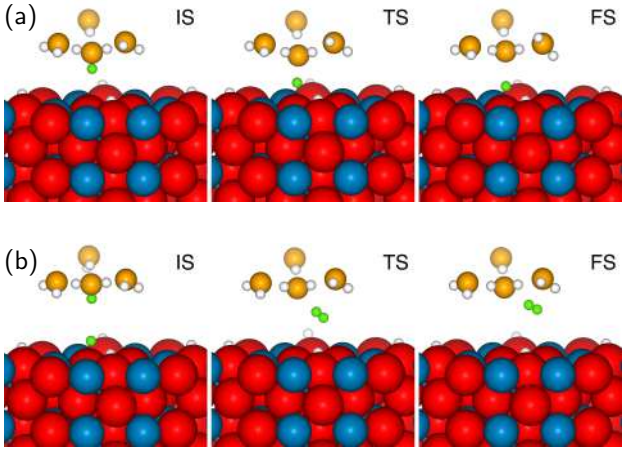

Figure 3: Volmer-Heyrovsky reaction pathway $P4_{VH}$ on Ni_3P_2 via surface H coverages (a) 4 to 5 and (b) 5 to 4.

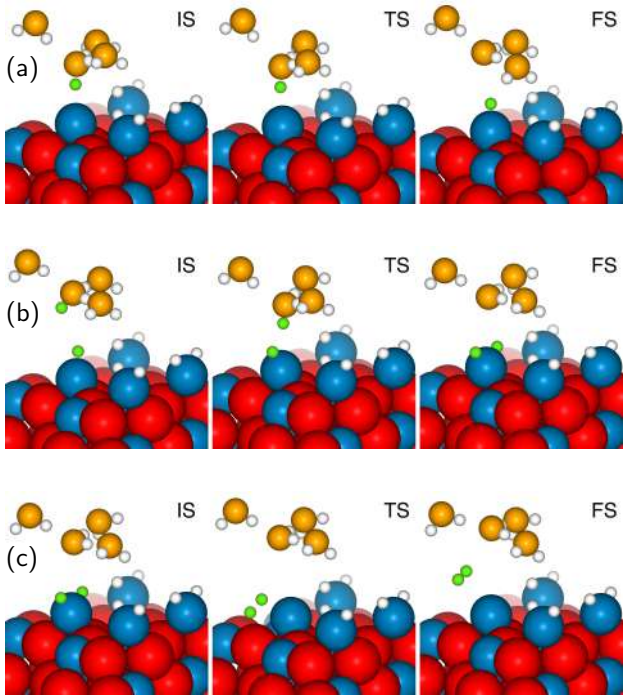

Figure 4: Volmer-Volmer-Tafel reaction pathway $R6_{VVT}$ on Ni_3P_2+4P via surface H coverages (a) 6 to 7, (b) 7 to 8 and (c) 8 to 6.

4.2 Reaction and activation energy of Volmer, Tafel and Heyrovsky steps

Table 3: Reaction (E_r) and activation (E_a) energies of Volmer, Tafel and Heyrovsky mechanisms, without proton-corrections, at various coverages on pristine (Ni_3P_2) and reconstructed (Ni_3P_2+4P) surface terminations. The most (least) favourable step is indicated by green (red) for each reaction.

		Configurations		Energy (eV)	
		Initial	Final	E_r	E_a
Pristine	Volmer	3H(0)	4H(0)	0.14	0.51
		4H(0)	5H(I)	0.68	0.72
		4H(0)	5H(0)	0.67	0.71
		5H(I)	6H(I)	0.72	0.80
		5H(I)	6H(II)	0.56	0.67
	Tafel	5H(0)	3H(0)	0.47	0.47
		6H(I)	4H(0)	-0.19	0.05
		6H(II)	4H(I)	0.43	0.45
	Hey	5H(I)	4H(0)	0.46	0.62
		5H(0)	4H(0)	0.56	0.64
Reconstructed	V	6H(0)	7H(I)	0.11	0.28
		6H(0)	7H(0)	-0.25	0.03
		7H(0)	8H(0)	-0.59	0.16
	T	8H(0)	6H(0)	0.28	1.38
	H	7H(I)	6H(0)	-0.22	0.40
		7H(0)	6H(0)	-0.22	0.66

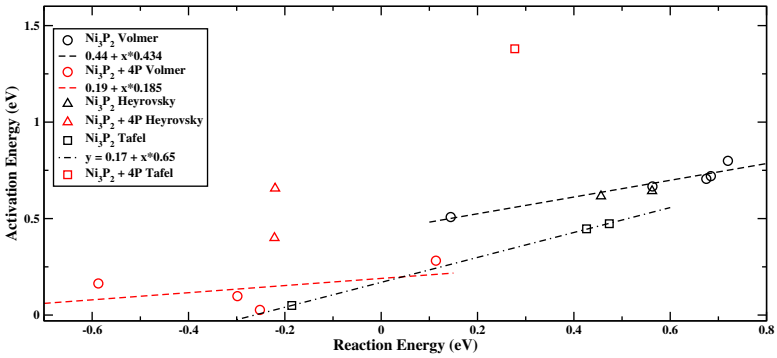

Figure 5: The bare reaction and activation energies of Volmer, Tafel and Heyrovsky steps of HER are plotted to investigate the Bell–Evans–Polanyi (BEP) principle. The BEP linear relation is observed for the Tafel steps of Ni_3P_2 and Volmer steps of both Ni_2P_3 and Ni_3P_2+4P terminations. Due to insufficient data, the remaining reaction steps could not be assessed.

4.3 HER energy profiles

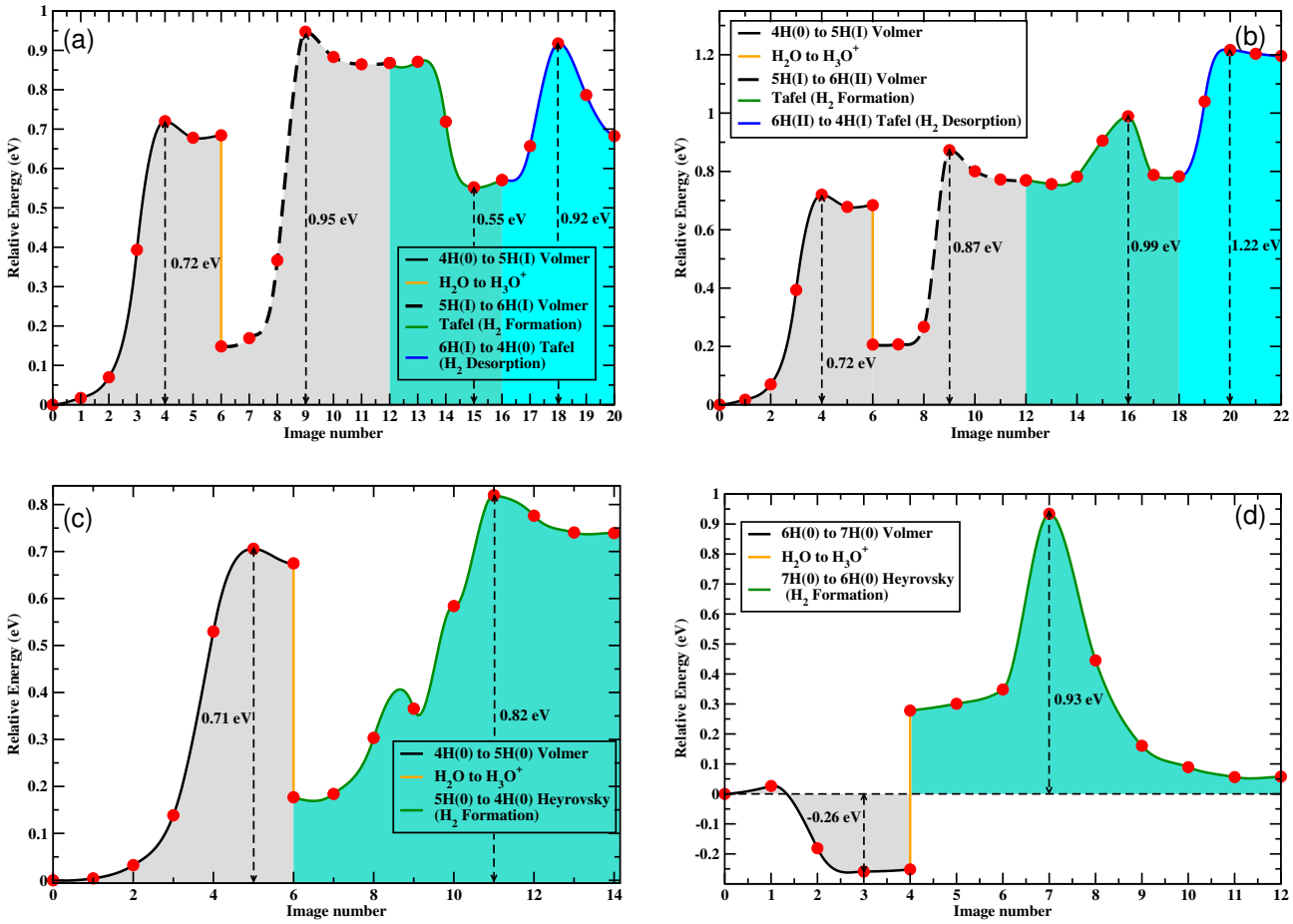

Figure 6: Hydrogen evolution reaction energy profile on the a), b), c) pristine (Ni_3P_2) and d) reconstructed (Ni_3P_2+4P) surface terminations of $Ni_2P(0001)$. a), b) depicts the Volmer-Volmer-Tafel (VVT) cycle and c), d) depicts the Volmer-Heyrovsky (VH) cycle. a) Adsorption coverage transitions from 4H(0) to 6H(I) through 5H(I), ending at 4H(0) coverage with reaction (E_r)/activation (E_a) energy 0.68/0.95 eV. b) Adsorption coverage transitions from 4H(0) to 6H(II) through 5H(I), ending at 4H(I) coverage with E_r/E_a equals 1.20/1.22 eV. c) Adsorption coverage transitions from 4H(0) to 5H(0) during the Volmer steps. Beginning with 5H(0) coverage, the system concludes at 4H(0) coverage with E_r/E_a equals 0.74/0.82 eV. d) Adsorption coverage transitions from 6H(0) to 7H(0) during the Volmer steps. Beginning with 7H(0) coverage, the system concludes at 6H(0) coverage with E_r/E_a equals 0.06/0.93 eV.

4.4 Reaction and activation energies in the literature

Table 4: Activation (E_a) and reaction (E_r) energy of Volmer (Vol), Tafel (Taf) steps (React) of hydrogen evolution reaction (HER). Ni hollow (Ni hol) and Ni-P bridge (Ni-P B) adsorption sites are specified.

React	Surf coverage transition	E_a (eV)	E_r (eV)
Vol	0H→1H (Ni hol)	0.01 [14]	-0.16 [14]
Vol	1H (Ni hol)→2H (Ni hol)	0.32 [14]	-0.48 [14]
Vol	1H (Ni hol)→2H (Ni-P B)	0.15 [14]	-0.47 [14]
Vol	0H→1H (Ni hol)	-	-0.54 [18]
Vol	1H (Ni hol)→2H (Ni-P B)	-	0.09 [18]
Taf	2H (Ni hol, Ni-P B)→0H	-	0.45 [18]
Vol	0H→1H (Ni hol)	-	-0.12 [12]
Vol	1H (Ni hol)→2H (Ni-P B)	-	0.41 [12]
Taf	2H (Ni hol, Ni-P B)→0H	0.32 [12]	-0.29 [12]

5 Average Gibbs free energy of adsorption data

The average Gibbs free energy data discussed in the word is provided below. The complete dataset for the hydrogen adsorption calculations and corresponding analysis code is available [19].

Table 5: Average Gibbs free energy $\Delta G(n)$ (eq. (12)) as a function of adsorption coverage n on pristine (Ni_3P_2) surface termination of $Ni_2P(0001)$.

n	$\Delta G(n)$	Adsorption sites
1	-0.4	1@hol
1	0.22	1@NiPbrdg
1	0.36	1@Ptop
2	-0.39	2@hol
2	-0.39	2@hol
2	-0.05	1@NiPbrdg-1@hol
2	-0.05	1@NiPbrdg-1@hol
2	-0.03	2@NiNibrdg
2	-0.01	1@Ptop-1@hol
2	-0.01	1@Ptop-1@hol
2	-0.01	1@hol-1@Ptop
2	0.03	1@Nitop-1@hol
2	0.03	1@hol-1@Nitop
2	0.31	1@NiPbrdg-1@Ptop
2	0.4	2@Ptop
3	-0.38	3@hol
3	-0.18	2@hol-1@NiPbrdg
3	-0.14	1@hol-2@NiNibrdg
3	0.05	2@NiNibrdg-1@NiPbrdg
3	0.12	3@NiNibrdg
4	-0.37	4@hol
4	-0.21	3@hol-1@NiPbrdg-1
4	-0.21	3@hol-1@NiPbrdg-2
5	-0.24	4@hol-1@NiPbrdg-5
5	-0.23	4@hol-1@NiPbrdg-1
5	-0.23	4@hol-1@NiPbrdg-2
5	-0.23	4@hol-1@NiPbrdg-3
5	-0.23	4@hol-1@NiPbrdg-4
5	-0.23	3@hol-2@NiNibrdg-1
5	-0.23	3@hol-2@NiNibrdg-2
5	-0.23	3@hol-2@NiNibrdg-3
5	-0.2	4@hol-1@Ptop
6	-0.14	3@hol-2@NiNibrdg-1@NiPbrdg-1

Table 5 – continued

n	$\Delta G(n)$	Adsorption sites
6	-0.14	3@hol-2@NiNibrdg-1@NiPbrdg-2
6	-0.14	3@hol-2@NiNibrdg-1@NiPbrdg-3
6	-0.14	3@hol-2@NiNibrdg-1@NiPbrdg-4
6	-0.14	4@hol-2@NiPbrdg-2
6	-0.14	4@hol-2@NiPbrdg-3
6	-0.14	4@hol-2@NiPbrdg-4
6	-0.14	4@hol-2@NiPbrdg-5
6	-0.13	3@hol-2@NiNibrdg-1@NiPbrdg-5
6	-0.13	4@hol-2@NiPbrdg-1
6	-0.13	4@hol-2@NiPbrdg-7
6	-0.13	4@hol-2@NiPbrdg-8
6	-0.13	2@hol-4@NiNibrdg
6	-0.12	3@hol-2@NiNibrdg-1@Ptop-1
6	-0.12	3@hol-2@NiNibrdg-1@Ptop-2
6	-0.12	3@hol-3@NiNibrdg
6	-0.12	4@hol-2@NiPbrdg-6
6	-0.12	4@hol-1@Ptop-1@NiPbrdg-1
6	-0.11	4@hol-1@Ptop-1@NiPbrdg
6	-0.09	4@hol-1@Ptop-1@NiPbrdg-2
6	-0.09	4@hol-1@Ptop-1@NiPbrdg-3
6	-0.09	4@hol-1@Ptop-1@Ptop
7	-0.07	2@hol-4@NiNibrdg-1@NiPbrdg
7	-0.07	1@hol-6@NiNibrdg
7	-0.07	2@hol-4@NiNibrdg-1@NiPbrdg-1
7	-0.07	3@hol-2@NiNibrdg-2@NiPbrdg-1
7	-0.07	4@hol-3@NiPbrdg-2
7	-0.07	4@hol-3@NiPbrdg-3
7	-0.06	2@hol-4@NiNibrdg-1@NiPbrdg-2
7	-0.05	2@hol-5@NiNibrdg
7	-0.05	2@hol-4@NiNibrdg-1@NiPbrdg-3
7	-0.05	3@hol-2@NiNibrdg-2@NiPbrdg-2
7	-0.05	4@hol-3@NiPbrdg-1
8	-0.02	4@hol-4@NiPbrdg-3
8	-0.01	8@NiNibrdg
8	-0.0	7@NiNibrdg-1@hol
8	0.01	4@hol-4@NiPbrdg-1
8	0.02	4@hol-4@NiPbrdg-2
9	0.02	4@hol-5@NiPbrdg-3
9	0.03	4@hol-5@NiPbrdg-1
9	0.03	4@hol-5@NiPbrdg-2
9	0.03	4@hol-5@NiPbrdg-5
9	0.03	4@hol-5@NiPbrdg-6
9	0.03	4@hol-5@NiPbrdg-8
9	0.03	8@NiNibrdg-1@NiPbrdg-2
9	0.04	9@NiNibrdg
9	0.04	8@NiNibrdg-1@NiPbrdg-1
9	0.04	8@NiNibrdg-1@Ptop
9	0.04	4@hol-5@NiPbrdg-4
9	0.04	4@hol-5@NiPbrdg-7
9	0.04	4@hol-5@NiPbrdg-9
10	0.06	8@NiNibrdg-2@NiPbrdg-1
10	0.06	8@NiNibrdg-2@NiPbrdg-2
10	0.06	4@hol-6@NiPbrdg-2
10	0.06	4@hol-6@NiPbrdg-5
10	0.06	4@hol-6@NiPbrdg-6
10	0.06	4@hol-6@NiPbrdg-7

Table 5 – continued

n	$\Delta G(n)$	Adsorption sites
10	0.06	4@hol-6@NiPbrdg-8
10	0.07	4@hol-6@NiPbrdg-1
10	0.07	8@NiNibrdg-2@NiPbrdg-3
10	0.07	4@hol-6@NiPbrdg-3
10	0.07	4@hol-6@NiPbrdg-4
10	0.07	4@hol-6@NiPbrdg-9
10	0.08	9@NiNibrdg-1@NiPbrdg
10	0.08	9@NiNibrdg-1@Ptop
11	0.09	8@NiNibrdg-3@NiPbrdg-1
11	0.1	4@hol-7@NiPbrdg-1
12	0.11	8@NiNibrdg-4@NiPbrdg-1
12	0.13	4@hol-8@NiPbrdg-1
13	0.13	8@NiNibrdg-5@NiPbrdg-1
13	0.15	4@hol-9@NiPbrdg-1
13	0.15	4@hol-9@NiPbrdg-2
13	0.15	4@hol-9@NiPbrdg-3
13	0.15	4@hol-9@NiPbrdg-4
13	0.16	12@NiNibrdg-1@NiPbrdg-1
14	0.16	8@NiNibrdg-6@NiPbrdg-1
14	0.18	12@NiNibrdg-2@NiPbrdg-1
15	0.19	8@NiNibrdg-7@NiPbrdg-1
15	0.21	12@NiNibrdg-3@NiPbrdg-1
16	0.2	8@NiNibrdg-8@NiPbrdg-1
17	0.22	8@NiNibrdg-9@NiPbrdg-1
18	0.24	8@NiNibrdg-10@NiPbrdg-1
19	0.26	8@NiNibrdg-11@NiPbrdg-1
20	0.27	8@NiNibrdg-12@NiPbrdg-1

Table 6: Average Gibbs free energy $\Delta G(n)$ (eq. (12)) as a function of adsorption coverage n on the reconstructed (Ni_3P_2+4P) surface termination of Ni_2P(0001).

n	$\Delta G(n)$	Adsorption sites
1	0.08	1@0P
1	0.21	1@Nitop
1	0.44	1@Ptop
1	0.52	1@NiPbrdg
2	0.11	2@PH2
2	0.15	2@0P
2	0.26	2@Nitop-1
2	0.26	2@Nitop-2
3	0.13	2@PH2-1@0P
3	0.17	3@PH3
3	0.18	3@0P
4	0.14	4@PH2
4	0.16	2@PH2-2@0P
4	0.21	4@0P
4	0.36	2@PH2-2@Ptop
4	0.37	2@PH2-2@NiPbrdg-1
4	0.4	2@PH2-2@NiPbrdg-2
5	0.18	3@0P-2@PH2
5	0.18	3@PH3-2@PH2
5	0.19	4@PH2-1@0P
5	0.28	4@0P-1@Ptop
5	0.32	4@0P-1@NiPbrdg

Table 6 – Continued from previous page

n	$\Delta G(n)$	Adsorption sites
6	0.15	6@PH2
6	0.16	4@PH2-2@0P
6	0.2	6@PH3
7	0.16	6@PH2-1@0P
7	0.18	3@PH3-4@PH2
7	0.20	6@PH2-1@NiPbrdg
8	0.16	8@PH2
8	0.18	3@PH3-4@PH2-1@0P
8	0.19	6@PH3-2@PH2
8	0.2	6@PH3-2@0P
9	0.17	3@PH3-6@PH2
9	0.19	6@PH3-2@PH2-1@0P
9	0.22	9@PH3
10	0.2	6@PH3-4@PH2
10	0.21	9@PH3-1@0P
10	0.25	8@PH2-1@Ptop-1@NiPbrdg-1
10	0.25	8@PH2-1@Ptop-1@NiPbrdg-2
10	0.26	8@PH2-2@NiPbrdg
11	0.22	9@PH3-2@PH2
11	0.3	8@PH2-3@Ptop
11	0.3	8@PH2-3@NiPbrdg-1
11	0.3	8@PH2-3@NiPbrdg-2
12	0.24	12@PH3
12	0.29	6@PH2-3@PH3-2@Ptop-1@NiPbrdg
12	0.34	8@PH2-4@Ptop
12	0.34	8@PH2-4@NiPbrdg-1
12	0.34	8@PH2-4@NiPbrdg-2

References

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