

# Methane Activation and Coupling Pathways on Ni<sub>2</sub>P Catalyst

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## S1. Details of density functional calculations of thermochemical properties

Frequency calculations were performed on gas phase molecules and all optimized adsorbed species to determine zero-point vibrational energies (ZPVE), and vibrational, translational and rotational enthalpy and free energy. These terms were then used, together with electronic energies ( $E_0$ , provided by VASP), to estimate enthalpies ( $H$ )

$$H = E_0 + \text{ZPVE} + H_{\text{vib}} + H_{\text{trans}} + H_{\text{rot}} \quad (\text{S1})$$

and free energies ( $G$ )

$$G = E_0 + \text{ZPVE} + G_{\text{vib}} + G_{\text{trans}} + G_{\text{rot}} \quad (\text{S2})$$

for reactants, products, and transition states at 1123 K. For calculations which include a periodic surface, there are no translational or rotational degrees of freedom and DFT-derived vibrational frequencies can be used to determine the ZPVE,  $H_{\text{vib}}$ , and  $G_{\text{vib}}$

$$\text{ZPVE} = \sum_i (\frac{1}{2} \nu_i h) \quad (\text{S3})$$

$$H_{\text{vib}} = \sum_i \left( \frac{\nu_i h e^{-\frac{\nu_i h}{kT}}}{1 - e^{-\frac{\nu_i h}{kT}}} \right) \quad (\text{S4})$$

$$G_{\text{vib}} = \sum_i \left( -kT \ln \frac{1}{1 - e^{-\frac{\nu_i h}{kT}}} \right) \quad (\text{S5})$$

For gaseous molecules, translational and rotational enthalpies and free energies were also computed from statistical mechanics:

$$H_{\text{trans}} = \frac{5}{2} kT \quad (\text{S6})$$

$$H_{\text{rot,linear}} = kT \quad (\text{S7})$$

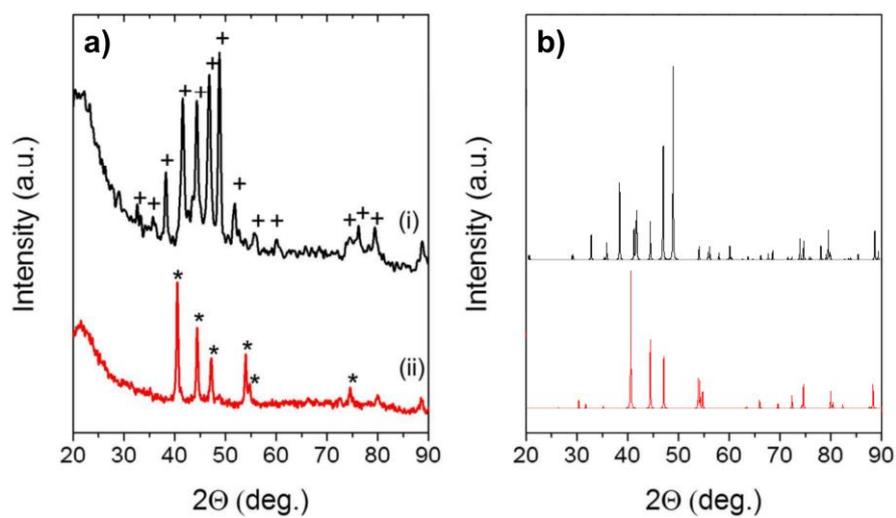
$$H_{\text{rot,nonlinear}} = \frac{3}{2} kT \quad (\text{S8})$$

$$G_{\text{trans}} = -kT \ln \left[ \left( \frac{2\pi M kT}{h^2} \right)^{3/2} V \right] \quad (\text{S9})$$

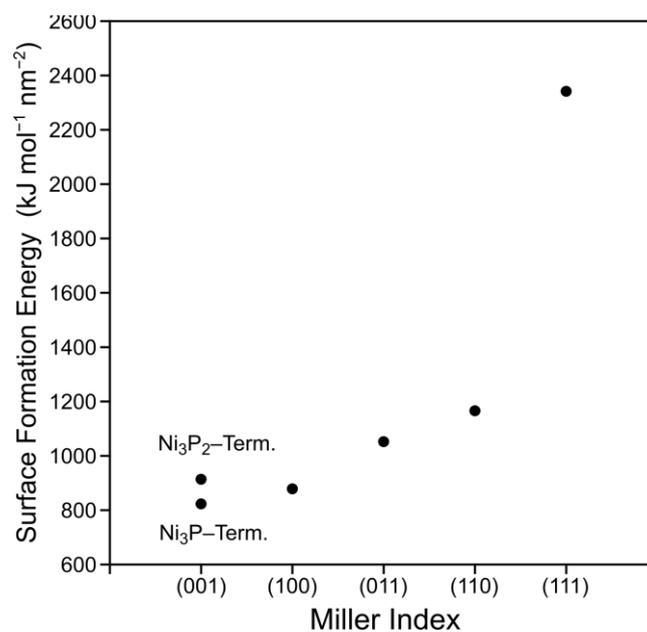
$$G_{\text{rot}} = -kT \ln \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\theta_x \theta_y \theta_z} \right)^{1/2} \right] \quad (\text{S10})$$

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \quad (\text{S11})$$

where  $I_i$  is the moment of inertia about axes  $x$ ,  $y$  or  $z$  and  $\sigma$  is the symmetry number of the molecule (2 for H<sub>2</sub> and 6 for C<sub>2</sub>H<sub>6</sub>). Equations S10–S12 obtained from: McQuarrie, D. A.; Statistical Mechanics; Sausalito, CA.



**Figure S1.** (a) Experimental and (b) DFT-simulated XRD patterns of bulk  $\text{Ni}_2\text{P}$  (red) and  $\text{Ni}_{12}\text{P}_5$  (black).



**Figure S2.** DFT-derived surface formation energy for Ni<sub>2</sub>P. Lower surface formation energy indicates more stable surface.

The bulk Ni<sub>2</sub>P structure was cleaved along different Miller indices and the surface formation energy was calculated by

$$E = \left( E_{surf} - \frac{N_{surf}}{N_{bulk}} E_{bulk} \right) \frac{1}{2A} \quad (1)$$

where N is the number of atoms and A is the area of the surface. For the Ni<sub>2</sub>P(001), surface there is an alternation of planes in the z direction that have different Ni and P composition: 1) Ni<sub>3</sub>P and 2) Ni<sub>3</sub>P<sub>2</sub>.