

Methane Activation and Coupling Pathways on Ni₂P 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_{vib} , and G_{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 σ is the symmetry number of the molecule (2 for H₂ and 6 for C₂H₆). Equations S10–S12 obtained from: McQuarrie, D. A.; Statistical Mechanics; Sausolito, CA.

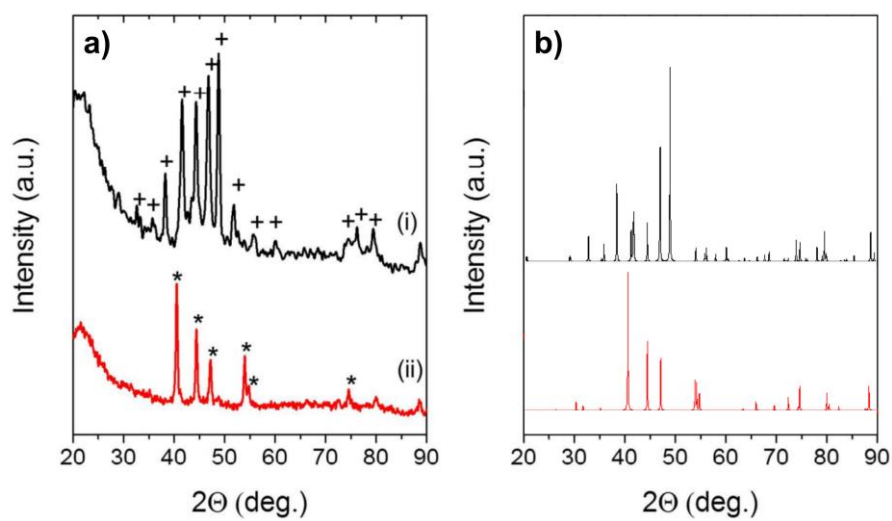


Figure S1. (a) Experimental and (b) DFT-simulated XRD patterns of bulk Ni_2P (red) and Ni_{12}P_5 (black).

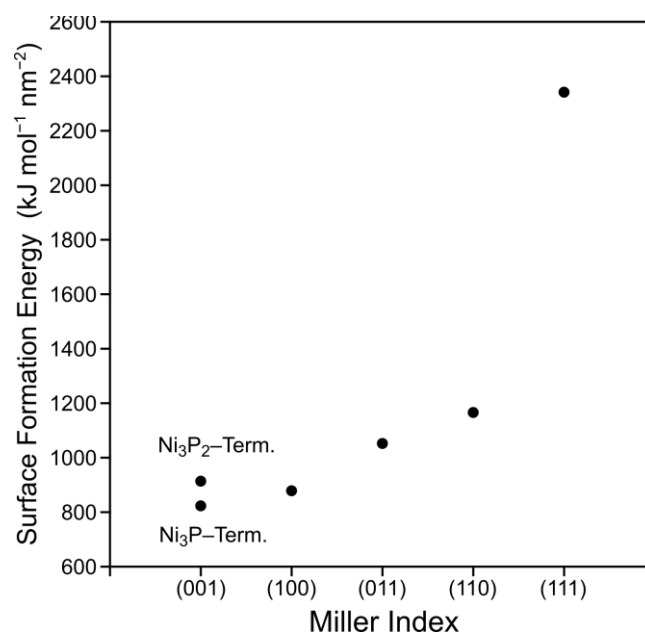


Figure S2. DFT-derived surface formation energy for Ni₂P. Lower surface formation energy indicates more stable surface.

The bulk Ni₂P 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 Ni₂P(001), surface there is an alternation of planes in the z direction that have different Ni and P composition: 1) Ni₃P and 2) Ni₃P₂.