

Acetylene Semi-Hydrogenation on Intermetallic Ni-In Catalysts: Ni Ensemble and Acetylene Coverage Effects from a Theoretical Analysis

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DFT-based reaction profiles and microkinetic simulations were used to describe the catalytic selective hydrogenation of acetylene on Ni, Ni₃In, NiIn, and Ni₂In₃ model intermetallic surfaces. Among the Ni_xIn_y intermetallic catalysts, NiIn showed the highest ethylene yield. Decreased formation of ethane was observed on NiIn and Ni₂In₃ accompanied by increased formation of oligomers compared to Ni and Ni₃In. This emphasizes the significance of accounting for the oligomerization reactions when evaluating the selectivity of the catalysts. Inconsistent acetylene coverage was obtained when performing microkinetic simulations using free energy values calculated at low acetylene coverage, while a fully consistent coverage was obtained using high coverage free energy values. Results from the high coverage microkinetic model showed that the presence of In on the catalytic surface decreased the rate of acetylene consumption with a trade-off relation between activity and selectivity. Simulations in the absence of ethylene in the feed confirmed that ethylene hydrogenation and acetylene C-C coupling were the primary sources for ethane and oligomers formation respectively. This study highlights the importance of considering oligomerization reactions, coverage effect, and feed composition when describing the activity and the selectivity of catalysts during the competitive hydrogenation of alkynes.

1. INTRODUCTION

Naphtha steam cracking is one of the primary sources of ethylene production.¹ Ethylene streams that come from steam crackers are the building blocks for polyethylene products and other key polymers. Acetylene is present in ethylene streams at levels of 1% and must be removed to an acceptable level of less than 5 ppm before the polymerization process.²⁻⁴ If not removed, acetylene impurities impact the life span of the polymerizing catalyst and the quality of the polymeric products. To purify streams from acetylene, highly active catalysts are needed to selectively hydrogenate acetylene to ethylene. As shown in **Figure 1**, a selective catalyst converts acetylene to ethylene without forming ethane through ethylene over-hydrogenation or converting acetylene to oligomers.

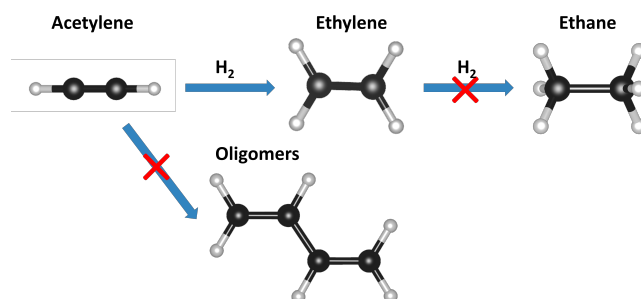


Figure 1. Possible products during acetylene hydrogenation reaction: ethylene (desired), ethane (undesired) or 1,3-butadiene, and other oligomers (undesired).

Intermetallic catalysts have been the subject of intensive research interest recently.⁵⁻⁷ An intermetallic is a phase of a binary system where atoms are in an ordered arrangement, and they offer several advantages over disordered alloys. For example, when evaluating the catalytic performance of the Pd-Cu catalyst in the ordered and disordered phases, a 40% increase in ethylene selectivity was obtained when Pd and Cu atoms were in an ordered arrangement due to the improved surface dispersion.⁸ Moreover, intermetallics are known to exhibit high thermodynamic stability and less risk of surface segregation.⁹⁻¹² Surface segregation presents a major drawback in the highly industrially utilized Pd-Ag alloys, where Pd islands create an ideal environment for acetylene oligomerization.¹³

Intermetallics are also distinct from Single Atom Alloys (SAAs), which are limited to mononuclear assemblies and require low surface densities for site isolation. In contrast,

intermetallics offer more control over the ensemble of active sites and consistent site isolation with a high density of active sites on the surface.^{9,14-16} Most importantly, the controlled composition of intermetallics allows for a direct comparison with theoretical predictions, making them suitable and practical model catalysts.¹⁴

Pd and Pt based catalysts have been used for decades for hydrocarbon hydrogenation.^{2,17} The promotion effect of In on Pd catalysts was studied experimentally and theoretically by Cao *et al.* and Luo *et al.*^{12,18} The Pd-In intermetallic catalyst showed a remarkable activity and selectivity improvement in the acetylene hydrogenation reaction in comparison to the monometallic Pd catalyst, as well as high stability under reaction conditions.¹² The intermetallic compound also suppressed the formation of palladium hydrides, which were precursors to producing ethane.^{12,19} However, the cost and the scarcity of these metals motivate the need to find economical and noble metal-free alternatives.

Ni was identified as a promising low-cost and abundant replacement. However, its utilization as a catalyst was limited due to its low selectivity and susceptibility to produce high levels of ethane and oligomers, mainly attributed to its strong adsorption of acetylene and ethylene relative to hydrogen.^{20,21} Therefore, it is important to reduce the adsorption strength of acetylene and ethylene to suppress oligomerization and enhance ethylene selectivity. To do this, a second metal can be added to modify the electronic properties and reduce the adsorption energy of molecules.^{18,22-24}

To accelerate the discovery of a selective Ni-based catalyst, many screening descriptors were proposed in the literature focusing on the formation of ethylene versus ethane as the sole factor in determining selectivity.^{14,17,25-28} A wide computational screening of bimetallic catalysts was reported by Studt *et al.*²⁶ where NiZn was identified as a selective catalyst based on the low levels of ethane production. Later on, a study done by Spanjers *et al.*²⁰ proved that ethane production was an inaccurate descriptor for ethylene selectivity when the facile formation of oligomers was neglected. Also, despite the fact that NiZn was more selective to ethylene than monometallic Ni during experimental testing, the DFT-based energy diagrams were indicating otherwise.²⁰ This could be ascribed to discounting the coverage effect in DFT calculations, meaning that adsorption energies and activation barriers were assumed to be coverage independent and were evaluated at low coverage. Thus, the impact of adsorbate-adsorbate interactions on the surface was not considered. This assumption may cause disagreement between experimental and theoretical studies and mispredict the selectivity of catalysts, which introduces the need to study the coverage

effect in microkinetic models to reconcile theoretical calculations with experimental observations and provide more accurate insights.

Inconsistencies in the literature may also arise from using a pure acetylene and hydrogen feed when screening catalysts,^{29,30} which is not representative of the ethylene-rich feed utilized in industrial settings. Isotopic labeling of acetylene and ethylene showed that ethane was mainly produced through the hydrogenation of the ethylene in the feed.²⁰ Thus, testing catalysts with pure acetylene may give the wrong impression about the selectivity of catalysts under real reaction conditions.

Even though acetylene hydrogenation reactions were studied extensively both experimentally and theoretically, there is still a lack of understanding of the reaction kinetics on the emerging intermetallic Ni-based catalysts. In this work, we present DFT-based modeling of Ni, together with Ni₃In, NiIn, and Ni₂In₃ intermetallics to describe the key hydrogenation and oligomerization reactions of acetylene. We show that the formation of the Ni-In intermetallic compounds may result in favorable geometric and electronic effects that can tune the hydrogenation activity and potentially enhance the selectivity for ethylene. The Ni-In phase diagram in **Figure S1** shows that Ni₃In, NiIn, and Ni₂In₃ all exist as an intermetallic phase.³¹ The selected formulations have a reasonable bulk unit cell size for computation (**Table S1-S3**) and available synthesis recipes in the literature.^{23,32} Additionally, these formulations exhibit a range of low, intermediate, and high In incorporation on Ni surfaces allowing us to understand trends. We studied the promotional effect of introducing In to metallic Ni against a monometallic Ni surface. We constructed reaction profiles at low and high coverage of acetylene based on the elementary steps of the hydrogenation and oligomerization reactions and addressed the competition between them when evaluating the selectivity of the catalysts. We also developed a microkinetic model to predict the activity and the selectivity of the catalysts under reaction conditions and investigated the impact of feed composition. Our study aims to unravel the promotional effect of In on Ni-based intermetallic catalysts while considering oligomerization reactions, coverage effect, and feed composition. We highlight the importance of accounting for these factors to develop a comprehensive understanding of the catalytic selectivity in acetylene hydrogenation reactions.

2. METHODS

2.1 Density Functional Theory (DFT) Methods

All DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP).^{33,34} The interaction between the ionic core and the valence electrons was described by the projector-augmented wave (PAW) method.^{35,36} The valence one electron functions were developed on a basis set of planes waves with an energy cutoff of 400 eV. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional in the framework of the generalized gradient approximation (GGA)³⁷ was employed to calculate the electronic structures. Dispersion interactions were included using the DFT-D3 method of Grimme.^{38,39} The force convergence threshold was set to 0.03 eV/Å and spin polarization was considered. Surfaces were modeled by 4×4 supercells^{27,28} and four-atomic-layer slabs. The two topmost layers and adsorbates were relaxed, and the rest of the layers were fixed to bulk composition except when calculating surface energies.

Sampling of the Brillouin zone was performed by 3×3×1 Gamma-centered **k**-point mesh for NiIn and Ni₂In₃. 4×4×1 and 5×5×1 Gamma-centered **k**-point mesh were used for Ni₃In and Ni surfaces, respectively. **K**-point mesh sizes were scaled based on bulk unit cell optimization. Each slab was separated from the next one in the z-direction by a vacuum of 15 Å to eliminate the interaction between them.

To determine the most exposed facet during the hydrogenation reaction, surface energies of the low-index facets for Ni₃In (Table S4) and Ni₂In₃ (Table S5) were calculated using equation 1.

$$\gamma = \frac{(E_{\text{slab}} - NE_{\text{bulk}})}{2A} \quad (1)$$

where E_{slab} is the total energy of the clean slab, N is the number of equivalent bulk unit cells for the slab and E_{bulk} is the energy of a single bulk unit cell. A is the area of the slab multiplied by a factor of two to account for the top and bottom surface area. This equation assumes that the top and bottom surfaces are equivalent and that the slab is stoichiometric.

Possible adsorption sites for reactants, intermediates, and products were explored on Ni₃In (Table S6), NiIn (Table S7), and Ni₂In₃ (Table S8). The adsorption energy of the gaseous molecules was calculated following equation 2.

$$\Delta E_{\text{adsorption}} = E_{\text{adsorbate/surface}} - E_{\text{surface}} - E_{\text{adsorbate}} \quad (2)$$

where $\Delta E_{\text{adsorption}}$ is the adsorption energy, $E_{\text{adsorbate/surface}}$ is the total energy of the gaseous molecule adsorbed on the surface of the slab, E_{surface} is the energy of the clean slab surface and $E_{\text{adsorbate}}$ is the energy of the gaseous molecule. Adsorption sites for Ni are studied in the literature.^{20,24,40,41}

The Gibbs free energy for acetylene hydrogenation and oligomerization reactions was calculated according to [equation 3](#) while treating all vibrational degrees of freedom harmonically.

$$G = E + E_{\text{vib}} + PV - T \times S \quad (3)$$

where G is Gibb's free energy, E and E_{vib} are the internal energy and vibrational energy of the system. The contribution of pressure and volume (PV) is assumed to be negligible.^{24,42} T is the reaction temperature (433 K) and S is the entropy.

The vibration analysis package in the Atomic Simulation Environment (ASE)⁴³ was used to calculate E_{vib} and vibrational entropy. All atoms were frozen except adsorbates. Transition states (TS) were calculated using the climbing image-nudged elastic band (CI-NEB) method with 8 images.⁴⁴ CI-NEB calculations were subsequently converged by the Quasi-Newton method or the dimer method by Henkelman *et al.*⁴⁵ Vibrational frequency calculations were also used to verify transition states, resulting in a single imaginary frequency along the reaction coordinate.

2.2 Microkinetic Model

The microkinetic model was constructed based on the nine elementary steps presented in [Table 1](#) with no assumption of a rate-determining step. The system of ordinary differential equations resulting from the elementary steps and the calculated reaction constants was solved in MATLAB (version R2022b) using an in-build solver "ode15s", which is fit for solving a set of stiff differential equations.⁴⁶

One monolayer coverage of C_2H_2 on Ni, NiIn, and Ni_3In was assumed to be 8 C_2H_2 molecules (one C_2H_2 molecule for two surface metal atoms) and 10 C_2H_2 molecules for Ni_2In_3 because the surface unit cell for Ni_2In_3 is larger. For H atom, one monolayer coverage was assumed to be 16 H atoms on Ni, NiIn, and Ni_3In and 20 H atoms on Ni_2In_3 . For the high coverage model, a single type of adsorbate, in this case, C_2H_2 , was used to simulate all the adsorbate-adsorbate interactions

in the systems. C₂H₂ was selected as the high coverage environmental species because the microkinetic model showed that it was the most abundant surface intermediate. It was also proven that using C₂H₂ to describe the multi-adsorbate systems for this reaction was appropriate because C₂H₂ and C₂H₄ showed similar self and cross-interactions.²⁷

The low coverage kinetic simulations used free energy profiles calculated on bare surfaces, with one acetylene and one H atom on the considered 4x4 unit cell, and the initial condition for the kinetics was a bare surface. In contrast, the high coverage simulations used free energy profiles calculated with 0.5 ML of acetylene for Ni, Ni₃In, and NiIn and 0.6 ML for Ni₂In₃, as justified later. Hence, the coverage of available empty sites was 0.5 ML (0.4 ML respectively). An additional acetylene molecule was adsorbed, together with two H atoms and the free energy pathways correspond to the reaction of that additional acetylene molecule. These pathways show differential adsorption and reaction free energies with reference to a surface pre-covered by 0.5 ML (or 0.6 ML) of acetylene, and these differential reaction energies were used for the kinetic simulations. Higher coverage of environmental acetylene was used for Ni₂In₃ because it was significantly more stable than the 0.5 ML case (Figure S2 (c)), allowing the reaction to take place between 0.6 ML and 0.7 ML, which were the most stable coverages. Kinetic simulations at high coverage were initiated with a total coverage of C₂H₂ (environmental + reacting) of 0.75 ML for Ni, NiIn, and Ni₃In and 0.8 ML for Ni₂In₃.

For the surface reaction steps, the rate constants were calculated according to the conventional transition state theory in equation 4.

$$k_i = \frac{k_B T}{h} e^{-\Delta G_i^\ddagger / k_B T} \quad (4)$$

where k_B is the Boltzmann constant, T is the reaction temperature, h is the Planck's constant and ΔG_i^\ddagger the change of standard molar Gibbs free energies between the TS and the initial state for step i , where $i = 1, \dots, 9$.

For the adsorption steps, the rate constants were assumed to be non-activated and were limited to the flux of molecules to the surface according to equation 5 and following the kinetic theory of gases.

$$k_{\text{adsorption}} = \frac{\sigma P^0 A}{\sqrt{2\pi m k_B T}} \quad (5)$$

Where σ is the initial sticking probability taken here as 1, P° is the standard pressure and m is the mass of the adsorbate. A is the surface area for one active site, a typical value of 10^{-19} m^2 was used here.^{47,48} For the desorption steps, rate constants were calculated from the adsorption equilibrium, $K_{\text{adsorption}}$ and the rate constant for adsorption ensuring thermodynamic consistency as shown in **equation 6**. All k values were expressed in s^{-1} .

$$k_{\text{desorption}} = \frac{k_{\text{adsorption}}}{K_{\text{adsorption}}} \quad (6)$$

The microkinetic model was embedded in a batch reactor model²⁰ to provide a more realistic and accurate representation of the reaction system and enable the prediction of key performance indicators such as conversion, selectivity, and yield. To mimic the industrial feed composition, a total pressure of ~ 10 bar and a partial pressure ratio of 1:1:100 $\text{C}_2\text{H}_2:\text{H}_2:\text{C}_2\text{H}_4$ was employed. All kinetic and thermodynamic calculations were done at a reaction temperature of 433 K to reflect the experimental conditions.²⁰

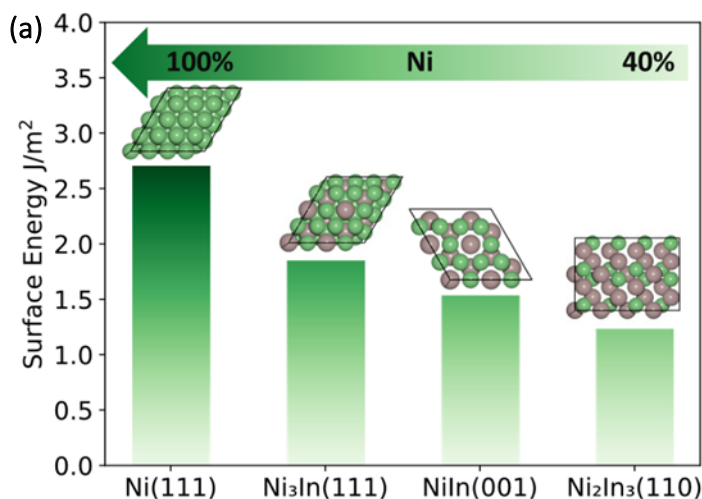
Table 1. Elementary steps and rate equations of acetylene hydrogenation and oligomerization reactions used in the microkinetic modeling (* represents the free site on the surface)

surface reaction	rate equation
1 $\text{C}_2\text{H}_2(\text{g}) + * \leftrightarrow \text{C}_2\text{H}_2^*$	$r_1 = k_1\theta_*P_{\text{C}_2\text{H}_2} / P^\circ - k_{-1}\theta_{\text{C}_2\text{H}_2}$
2 $\text{H}_2(\text{g}) + 2* \leftrightarrow 2\text{H}^*$	$r_2 = k_2\theta_*^2P_{\text{H}_2} / P^\circ - k_{-2}\theta_{\text{H}}^2$
3 $\text{C}_2\text{H}_2^* + \text{H}^* \leftrightarrow \text{C}_2\text{H}_3^* + *$	$r_3 = k_3\theta_{\text{C}_2\text{H}_2}\theta_{\text{H}} - k_{-3}\theta_{\text{C}_2\text{H}_3}\theta_*$
4 $\text{C}_2\text{H}_3^* + \text{H}^* \leftrightarrow \text{C}_2\text{H}_4^* + *$	$r_4 = k_4\theta_{\text{C}_2\text{H}_3}\theta_{\text{H}} - k_{-4}\theta_{\text{C}_2\text{H}_4}\theta_*$
5 $\text{C}_2\text{H}_4^* \leftrightarrow \text{C}_2\text{H}_4(\text{g}) + *$	$r_5 = k_5\theta_{\text{C}_2\text{H}_4} - k_{-5}\theta_*P_{\text{C}_2\text{H}_4} / P^\circ$
6 $\text{C}_2\text{H}_4^* + \text{H}^* \leftrightarrow \text{C}_2\text{H}_5^* + *$	$r_6 = k_6\theta_{\text{C}_2\text{H}_4}\theta_{\text{H}} - k_{-6}\theta_{\text{C}_2\text{H}_5}\theta_*$
7 $\text{C}_2\text{H}_5^* + \text{H}^* \leftrightarrow \text{C}_2\text{H}_6(\text{g}) + 2*$	$r_7 = k_7\theta_{\text{C}_2\text{H}_5}\theta_{\text{H}} - k_{-7}\theta_*^2P_{\text{C}_2\text{H}_6} / P^\circ$
8 $\text{C}_2\text{H}_2^* + \text{C}_2\text{H}_3^* \leftrightarrow \text{C}_4\text{H}_5^* + *$	$r_8 = k_8\theta_{\text{C}_2\text{H}_2}\theta_{\text{C}_2\text{H}_3} - k_{-8}\theta_{\text{C}_4\text{H}_5}$
9 $\text{C}_4\text{H}_5^* + \text{H}^* \leftrightarrow \text{C}_4\text{H}_6(\text{g}) + 2*$	$r_9 = k_9\theta_{\text{C}_4\text{H}_5}\theta_{\text{H}} - k_{-9}\theta_*^2P_{\text{C}_4\text{H}_6} / P^\circ$

3. RESULTS AND DISCUSSION

3.1 Surface Energy and Adsorption Sites

The surface energy of low-index facets of Ni, Ni₃In, NiIn, and Ni₂In₃ was calculated to determine the most stable and energetically favorable facet for each material. Symmetry on the Ni₃In surface reduced the number of studied surfaces to three facets only (Table S4), while Ni₂In₃ had a less symmetric nature with five distinguished facets (Table S5). For NiIn, the (001) facet was selected according to the study by Song *et al.*²⁴ Ni (111) was selected because it is the most energetically favorable facet⁴⁹ and was extensively studied in the literature, particularly in the contexts of acetylene hydrogenation reactions.^{5,20,24,40} The as-cut composition was preserved for all the facets. The most stable facets were Ni₃In (111), NiIn (001), and Ni₂In₃ (110) and these facets are assumed when referring to these surfaces for the rest of this work. As shown in Figure 2 (a), the lowest surface energy among all the explored surfaces was for Ni₂In₃ (110) with 1.23 J/m² and the largest surface energy was for Ni (111) with 2.71 J/m². Overall, surface energies were increasing with increasing the Ni content of the surface. These findings may have important implications for understanding the behavior of these surfaces during chemical reactions.



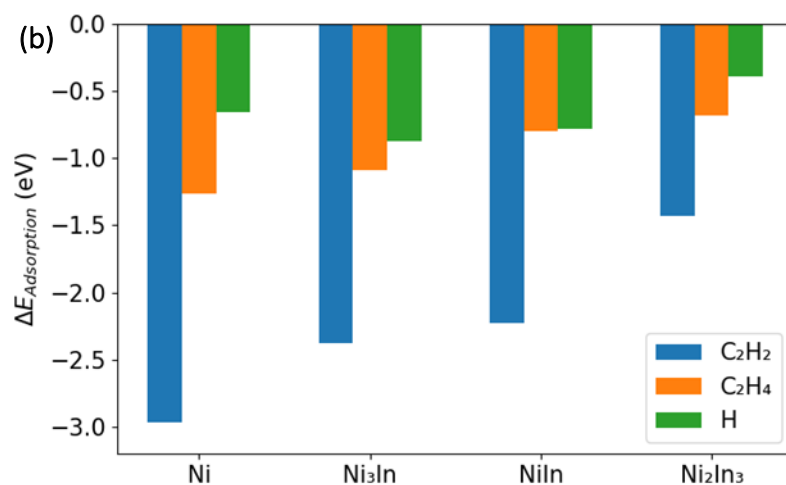


Figure 2. (a) Surface energies (J/m^2) of the most stable low-index facets of Ni, Ni₃In, NiIn, and Ni₂In₃. Color coding: Ni (green) and In (brown). Surface energies were increasing with increasing the Ni content of the surface. (b) Adsorption energies (eV) of C₂H₂, C₂H₄, and H at low coverage (only one species adsorbed on the unit cell). Adsorption energies of acetylene and ethylene were increasing with increasing the Ni content of the surface.

The shortest Ni-Ni distances, the corresponding Ni-Ni coordination numbers and d-band centers (ϵ_d) for Ni (111), Ni₃In (111), NiIn (001), and Ni₂In₃ (110) were calculated to understand the structural and electronic properties of these surfaces and are presented in Table 2. The Geometric effect caused by the isolation of Ni active sites is demonstrated by the shortest Ni-Ni distance on the surfaces as well as the Ni-Ni coordination numbers. The Ni-Ni coordination number was determined by counting the nearest neighbors of Ni atoms. Table 2 shows that Ni₂In₃ (110) exhibited complete isolation of the Ni active sites while Ni₃In (111) and NiIn (001) exhibited partial isolation. Modifications on the electronic structures of the 3d orbital of Ni are shown by the Density of States (DOS) calculations (Figure S4). The electronic properties of Ni are significantly modified upon the formation of intermetallic compounds, resulting in narrower d-bands and higher d-band centers when the In content on the surface increases.

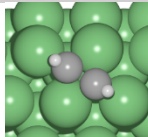
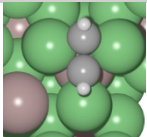
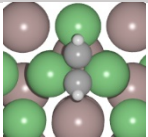
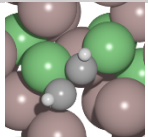
Table 2. Shortest Ni-Ni distances (Å), Ni-Ni coordination number, and d-band centers (ϵ_d) with respect to the Fermi level of Ni 3d orbitals on Ni (111), Ni₃In (111), NiIn (001), and Ni₂In₃ (110).

surface	shortest Ni-Ni distance (Å)	Ni-Ni coordination number	ϵ_d
Ni (111)	2.45	9	-1.66
Ni ₃ In (111)	2.50	6	-1.29
NiIn (001)	2.61	4	-1.36
Ni ₂ In ₃ (110)	2.87	2 ^a	-1.10

^a one Ni atom was at distance of 2.93 Å.

The evaluation of the possible adsorption sites on the most stable facets (Table S6-S8) revealed that In atoms were less active than Ni atoms. The most stable acetylene configurations on all the surfaces are shown in Table 3. Acetylene was always adsorbed on the Ni atoms or bridging with In atoms at high In content surfaces. The bond distances (also shown in Table 3) refer to the nearest Ni or In atom to a carbon atom in the acetylene molecule. The large distances between In and C atoms on Ni₃In, NiIn, and Ni₂In₃ indicate the lack of bonding between acetylene and In atoms thus, proves their lower catalytic activity compared to Ni. The overall weak adsorption energies and the low activity of In atoms came in agreement with the previous computational and experimental findings.^{24,30}

Table 3. Most stable configurations, low coverage adsorption energies (eV) and corresponding bond distances (Å) for acetylene. Color coding: Ni (green), In (brown), H (white), and C (gray). The large distances between In and C atoms indicate the low catalytic activity of In.

	Ni	Ni ₃ In	NiIn	Ni ₂ In ₃
acetylene configuration				
ΔE_{ads}	-2.97	-2.38	-2.23	-1.43
C-Ni bond (Å)	2.01	2.10	2.00	1.99
C-In bond (Å)	-	3.51	2.42	2.28

Low coverage adsorption energies of acetylene, ethylene, and hydrogen on the most stable facets are presented in **Figure 2 (b)**. Results show that the adsorption energy of acetylene decreases as the surface composition changes from Ni to Ni₂In₃, with the strongest adsorption energy value of -2.97 eV observed on Ni and the weakest adsorption energy value of -1.43 eV observed on Ni₂In₃. This could be caused by the Ni ensemble effect. Acetylene adsorbs on 4 Ni atoms on Ni, but it can only interact with Ni₃ ensembles on Ni₃In and NiIn, and with Ni₂ ensembles for Ni₂In₃. However, the difference in the adsorption energy of acetylene between Ni₃In and NiIn was small (0.15 eV) as they exhibit a similar Ni ensemble.

Notably, the hydrogen adsorption energy on Ni₃In and NiIn was slightly stronger than the hydrogen adsorption energy on Ni. Furthermore, the adsorption energy of hydrogen and ethylene was found to become similar on NiIn. The change in adsorption energies with surface composition was less pronounced in the case of ethylene in comparison to acetylene, but both followed the same trend and became stronger with increasing the Ni content of the surfaces, in line with the increase of the accessible Ni ensemble size for acetylene. Previous theoretical and experimental research has established the presence of strong electron interactions between Ni and In in Ni-In intermetallic compounds. Electron transfer from the electropositive In atoms to the Ni atoms was evidenced in electron density contour maps.^{22,23,50} Thus, the charge transfer from In to Ni and the active-site isolation of Ni in Ni-In intermetallics resulted in reduced adsorption strength of acetylene and ethylene in comparison to Ni.

3.2 Low Coverage Acetylene Reaction Profiles

Reaction profiles with low coverage of reactants, acetylene and hydrogen, were calculated to provide insights about the adsorption properties and activation barriers of individual molecules or atoms on the surface. The first step in the hydrogenation pathway is the C-H bond formation on the adsorbed acetylene molecule producing vinyl. Vinyl is then further hydrogenated to form ethylene. Ethylene will either desorb from the surface or over-hydrogenate and form ethane. Similarly, ethylene in the reaction feed can adsorb on the catalyst and be hydrogenated, which is undesirable. A selective catalyst should have a small ethylene desorption energy and a high ethylene hydrogenation barrier to avoid over-hydrogenation. The hydrogenation reaction profile is shown in **Figure 3**. The reaction profiles start with acetylene adsorption on the surface and follow the Horiuti–Polanyi mechanism.³⁵ In the Horiuti–Polanyi mechanism, the acetylene is being sequentially hydrogenated by the addition of atomic H.⁵ The adsorption energy of acetylene is weakened with the presence of In on the surface with Ni₂In₃ exhibiting the lowest binding energy. The first two activation energies in the reaction profile control the activity of the surface.²⁸ NiIn exhibits the highest acetylene hydrogenation barrier (1.00 eV), while the energy barriers for the other surfaces range from 0.82-0.84 eV (**Table S9**). Surfaces also show comparable second hydrogenation barriers except for Ni₂In₃ (**Table S9**); Ni₂In₃ has a high energy barrier for vinyl hydrogenation (1.12 eV), which poses a challenge for the hydrogenation reaction to proceed.

The calculated values of energy barriers of ethylene hydrogenation and ethylene desorption energy are presented in **Table 4**. Ethylene hydrogenation barriers and ethylene desorption energies are both decreased in the Ni-In surfaces in comparison to Ni. The enhanced ethylene desorption on Ni-In catalysts could be ascribed to the Ni site-isolation effect (**Table 2**), which is one of the advantageous characteristics of intermetallic compounds. This is because extended active sites are typically responsible for the strong adsorption of unsaturated hydrocarbons which subsequently catalyze undesired reactions.^{2,20,51} The Gibbs free energy difference (ΔG) between the ethylene hydrogenation barrier (ΔG_{TS}) and ethylene desorption energy (ΔG_{des}) has been used as a descriptor for ethylene selectivity in previous studies.^{17,52,53} A higher ΔG value is expected to indicate a greater preference for the formation of ethylene. However, further investigation showed that this descriptor was inaccurate as the microkinetic model revealed that Ni₃In had the highest ethylene yield despite having the lowest ΔG value, as discussed later.

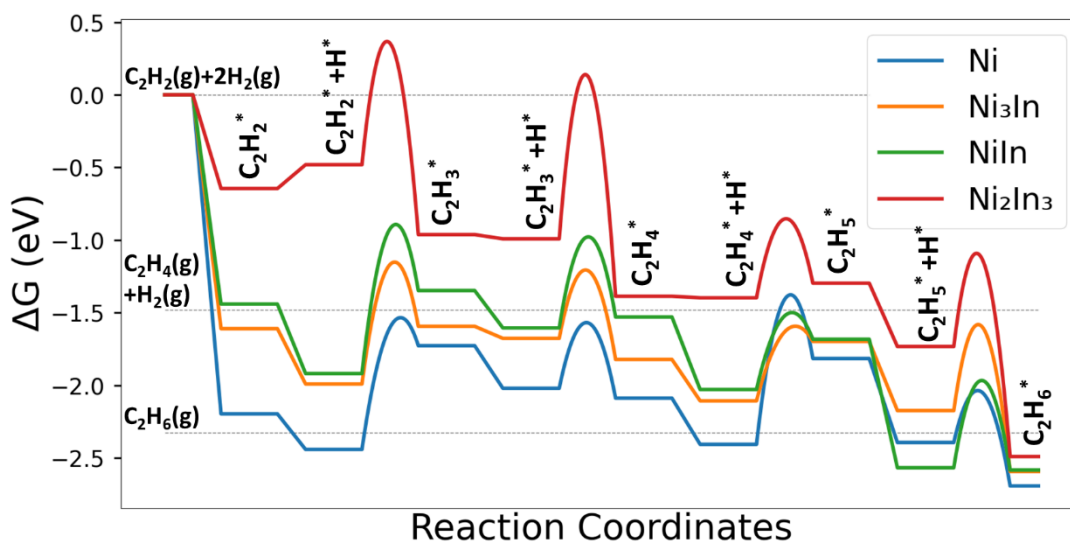


Figure 3. Gibbs free energy profiles of acetylene hydrogenation on Ni, Ni₃In, NiIn, and Ni₂In₃ at 433 K at low coverage. Energies are relative to bare surface, C₂H₂(g) and 2H₂(g) (dotted line). The gas phase reaction energy to form C₂H₄ and C₂H₆ is indicated with thin dotted lines. The reaction profiles follow the Horiuti-Polanyi mechanism where acetylene is sequentially hydrogenated by atomic H.

Table 4. Ethylene over hydrogenation barrier ΔG_{TS} (eV) (elementary step 6 in **Table 1**), desorption energy ΔG_{des} (eV) (elementary step 5 in **Table 1**), and the difference between the two values (ΔG). (ΔG) was proposed as a selectivity descriptor in previous studies,^{17,52,53} where a higher ΔG value is expected to indicate a greater selectivity to ethylene.

ΔG eV	Ni	Ni ₃ In	NiIn	Ni ₂ In ₃
over hydrogenation barrier ΔG_{TS}	1.00	0.48	0.51	0.54
desorption ΔG_{des}	0.62	0.34	0.05	-0.09
$\Delta G = \Delta G_{TS} - \Delta G_{des}$	0.38	0.14	0.46	0.54

The formation of C₄ hydrocarbon oligomers through C-C coupling is a key step in determining the overall selectivity of the catalysts, as it competes with the hydrogenation of acetylene and the formation of ethylene. **Figure 4** shows the reaction profiles of C-C bond formation between

adsorbed acetylene and vinyl. The proposed mechanism starts with the adsorption of an acetylene molecule, followed by the addition of a hydrogen atom to form vinyl. Next, a carbon-carbon bond is formed between vinyl and another adsorbed acetylene molecule, and the final step is the hydrogenation of C_4H_5 to produce butadiene. While there are other possible reactions for C-C coupling between molecules such as acetylene, vinylidene, and vinyl, the literature agrees that the most kinetically favorable precursors for oligomers were acetylene and vinyl.²⁰

In comparison to Pd surfaces, on which C4 hydrocarbon was stabilized by four Pd atoms,⁵⁴ Ni_2In_3 showed C4 hydrocarbon stability with only two isolated Ni atoms as shown in [Figure S5](#). The smallest C-C coupling barrier was observed on NiIn (0.75 eV), which also exhibited the largest acetylene hydrogenation barrier (1.00 eV) ([Table S9](#)). Thus, acetylene seems more likely to oligomerize than to hydrogenate over NiIn. The complexity of the reaction network and the different parameters that contributed to the selectivity of the catalysts introduce the need for microkinetic modeling to provide more insights, as discussed later.

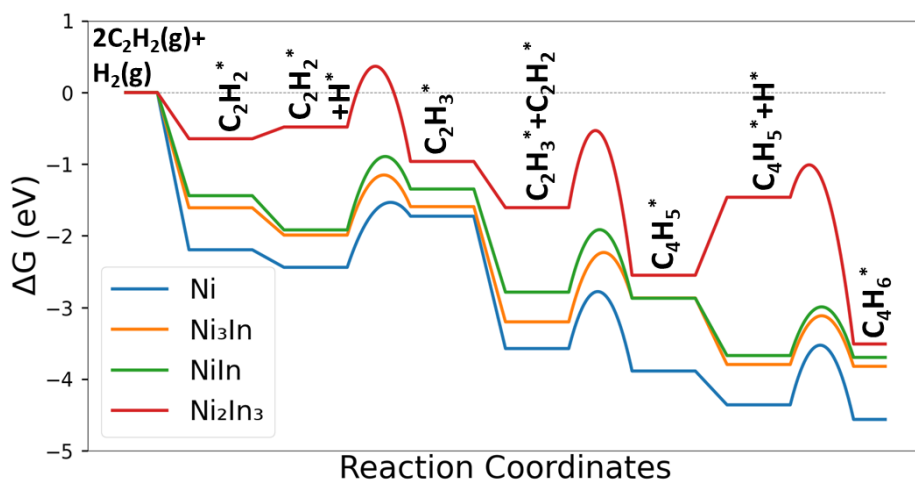


Figure 4. Gibbs free energy profiles of acetylene oligomerization on Ni, Ni_3In , NiIn, and Ni_2In_3 at 433 K at low coverage. Energies are relative to bare surface, $2C_2H_2(g)$ and $H_2(g)$ (dotted line). The reaction starts with the hydrogenation of adsorbed acetylene molecule to form C_2H_3 followed by a C-C bond formation between C_2H_3 and another adsorbed acetylene. The last step is C_4H_5 hydrogenation to form butadiene.

3.3 Coverage-Dependent Binding Energies

To accurately describe the surface species population under reaction conditions, it is important to understand how the adsorption energy changes with the coverage of adsorbates. It was found from previous studies^{27,28,55} that the coverage-dependent behavior of adsorption energies was only apparent when a specific coverage threshold was reached.

The exploration of high coverage situations was done by manually generating initial configurations. Surveying the adsorption sites at low coverage provided an idea about the stability of each site e.g. molecules do not adsorb at the top of In atom. Also, the symmetry of the surface may reduce the possible configurations as some adsorption sites can be equivalent. Resulting configuration geometries and energies for Ni, Ni₃In, NiIn and Ni₂In₃ for acetylene coverages of 0.5, 0.625/0.6 and 0.75/0.7 ML are shown in [Tables S10-S13](#).

The average adsorption free energies of acetylene as a function of coverage are shown in [Figure S3](#) to allow for a better comparison with experimental data. Here, NiIn was selected as a model system to investigate the change in binding energies with respect to coverage, while other systems can be found in [Figure S2](#). Initially, the total adsorption free energy of acetylene on a 4×4 slab of NiIn increases in absolute value linearly with increasing coverage ([Figure 5 \(a\)](#)). However, once the threshold coverage ($\Theta=0.5$ ML) was surpassed, the total adsorption free energy for C₂H₂ was weakened as indicated by the reduced slope of the linear fit. [Figure 5 \(a\)](#) does not include data for a C₂H₂ coverage of 1 ML, as the aggregation of the C₂H₂ molecules on the surface caused oligomerization after the placement of 8 C₂H₂ molecules in the unit cell ([Figure S6](#)). A similar two-slope behavior was found for H adsorption free energy versus coverage, with the same threshold coverage ($\Theta=0.5$ ML). However, the total adsorption free energy for H becomes positive (destabilizing) after this threshold ([Figure 5 \(b\)](#)).

The decrease in adsorption free energy after the threshold coverage varied in its extent between C₂H₂ and H due to the different properties of these molecules. This is because all the favorable adsorption sites for H were occupied at 0.5 ML coverage ([Figure S7](#)). As a result, the added hydrogen atoms resided on less stable sites when the coverage was above the threshold. H atoms in general exhibit negligible repulsive interactions with themselves and other adsorbates due to

their small size which deemed them unsuitable to describe the coverage effect on reaction at surfaces.^{5,55,56}

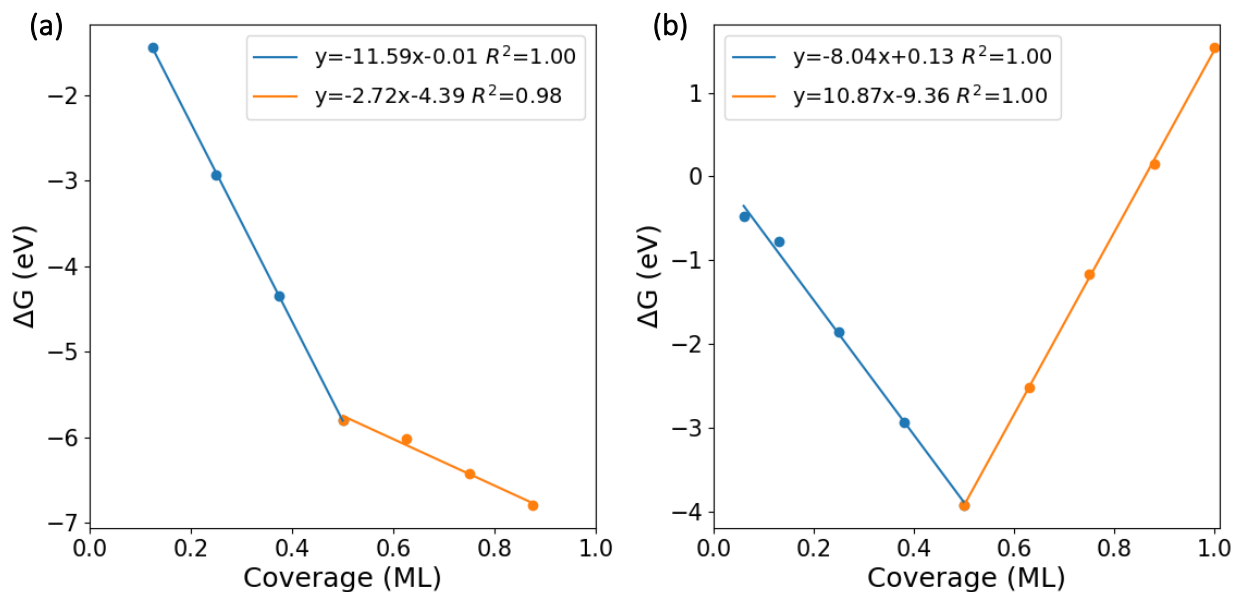
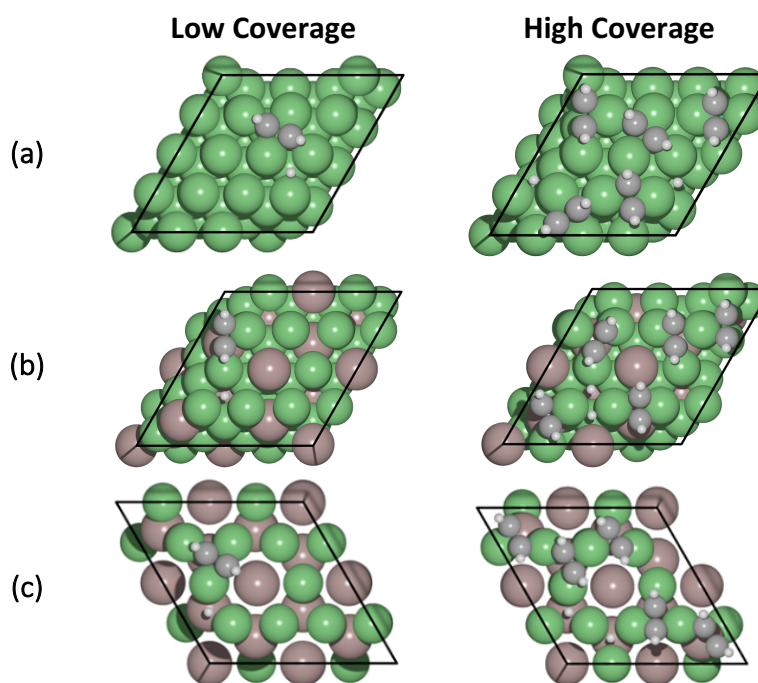


Figure 5. Total chemisorption free energies at 433 K versus coverage of (a) C_2H_2 and (b) H on a 4×4 supercell of NiIn. Data for a C_2H_2 coverage of 1 ML is not shown because the aggregation of the C_2H_2 molecules on the surface caused oligomerization. Low coverage data points and linear fit are shown by the blue line. High coverage data points and linear fit are shown by the orange line. In both cases, adsorption of C_2H_2 and H is weakened after a threshold coverage of 0.5 ML.

3.4 Acetylene Reaction Profiles at High Coverage

Going beyond the traditional modeling simplifications is essential in determining an accurate activity and selectivity descriptor and accelerating the discovery of hydrogenation catalysts. One commonly made simplification is the assumption that the reaction is not influenced by the degree of surface coverage. In this section, all adsorption energies and energy barriers were recalculated in the presence of 0.5 ML or (0.6 ML in the case of Ni_2In_3) initial coverage of acetylene species. The coverage of 0.5 ML is not thermodynamically the most stable for acetylene on the surfaces. It was selected because it represents the crossover between strongly bound and weakly bound molecules. Selecting 0.5 ML or (0.6 ML in the case of Ni_2In_3) as the initial coverage for the high coverage model was also validated retrospectively through the kinetic simulations as shown in the next section. From there an additional (weakly bound) acetylene molecule was added (bringing the coverage to 0.625 ML for Ni, Ni_3In , and NiIn , and to 0.7 ML for Ni_2In_3) and one H_2 molecule was dissociated in the favorable remaining sites to construct the structures used for the hydrogenation pathway (Table S14-S15). Figure 6 presents the surface species just before the first hydrogenation step at low and high coverage.



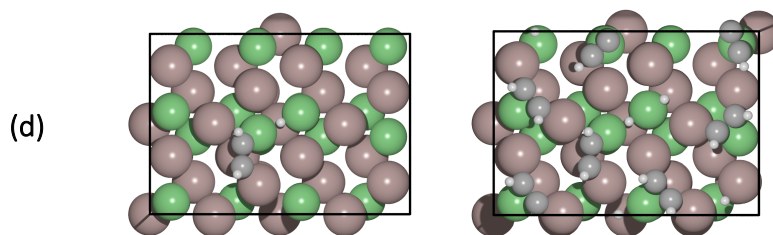


Figure 6. Coadsorbed acetylene and hydrogen, which is the starting configuration for the first hydrogenation step, at low (left) and high (right) acetylene coverage: (a) Ni (b) Ni₃In (c) NiIn (d) Ni₂In₃. Color coding: Ni (green), In (brown), H (white), C (gray).

Overall, the energy barriers were reduced at high coverage for both the hydrogenation (Figure 7, Table S9) and the oligomerization pathway (Figure 8, Table S9). Significant reductions in energy barriers were observed in the first hydrogenation step and the C-C coupling step. Although the second hydrogenation energy barrier was reduced from 1.12 eV to 0.93 eV on Ni₂In₃, it remains relatively high, presenting a challenge for the hydrogenation reaction to continue. The reduction of energy barriers at high coverage could be explained by the fact that these are bond-forming associative reactions that decrease the number of adsorbates on the surface and, hence, lower the lateral repulsions between them.

The step with the highest local barrier along the hydrogenation pathway changes at high coverage for Ni and Ni₃In. In the case of Ni, the highest local barrier shifts from the over-hydrogenation step at low coverage (Figure 3) to the first hydrogenation step at high coverage (Figure 7). In the case of Ni₃In, the highest local barrier shifts from the first hydrogenation step at low coverage (Figure 3) to the second hydrogenation step at high coverage (Figure 7). For NiIn and Ni₂In₃ the highest local barriers are the first hydrogenation step and the second hydrogenation step, respectively, regardless of the coverage.

Figure 8 shows that, at high coverage, Ni is highly prone to form oligomers, with a small C-C coupling energy barrier of 0.25 eV (Table S9). Conversely, Ni₂In₃ has the largest C-C coupling energy barrier, with a value of 0.57 eV. However, the substantial vinyl hydrogenation energy barrier (0.93 eV) in Ni₂In₃ is likely to steer the reaction towards oligomerization, rather than hydrogenation as was later confirmed by the microkinetic model.

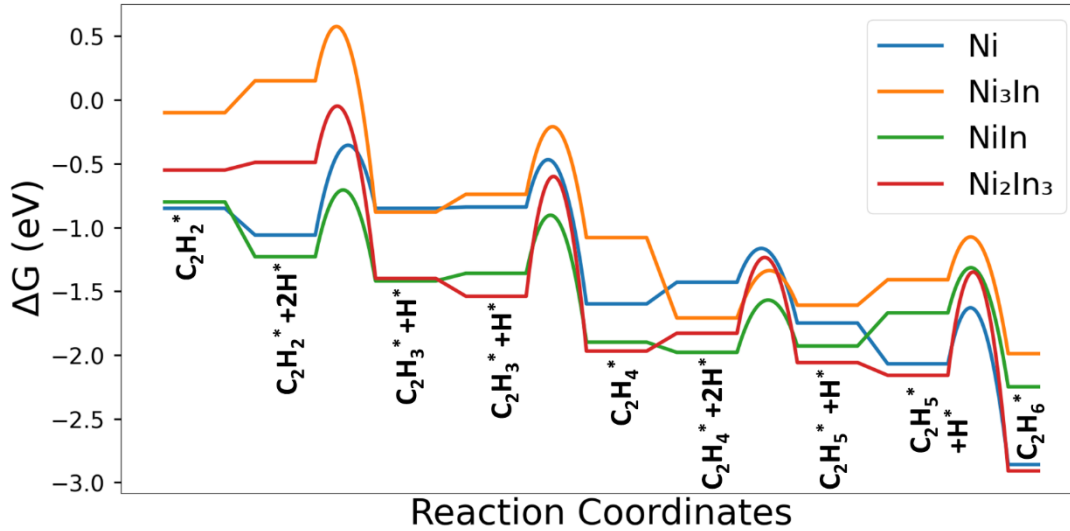


Figure 7. Gibbs free energy profiles of acetylene hydrogenation on Ni, Ni₃In, NiIn, and Ni₂In₃ at 433 K at high coverage. Energies are relative to surfaces with 0.5/0.6 ML of environmental C₂H₂. The labels assigned to each step denote the corresponding reacting species.

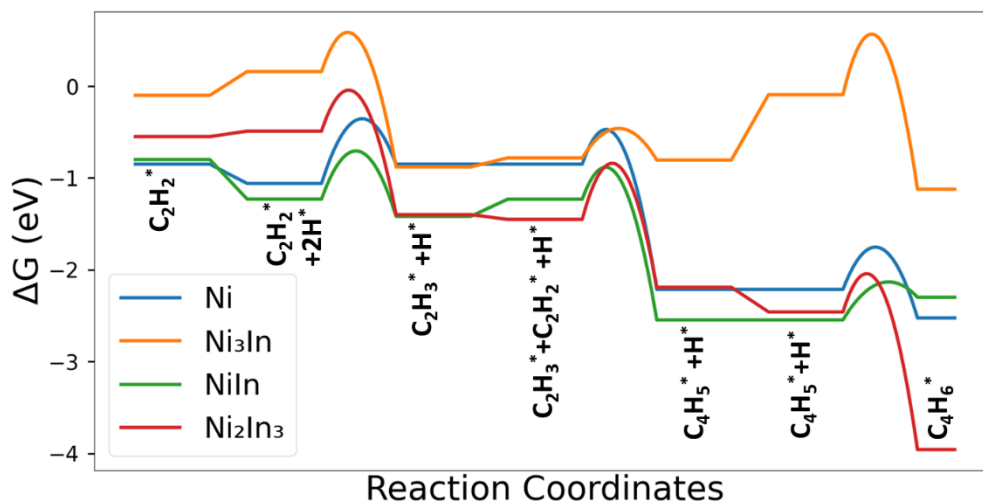


Figure 8. Gibbs free energy profiles of acetylene oligomerization on Ni, Ni₃In, NiIn, and Ni₂In₃ at 433 K at high coverage. Energies are relative to surfaces with 0.5/0.6 ML of environmental C₂H₂. The labels assigned to each step denote the corresponding reacting species.

3.5 Microkinetic Simulations

Kinetic modeling was then performed to study the effect of the surface reactant coverage on the activity and the selectivity of the catalysts. Species distribution for Ni₃In and Ni₂In₃ is shown in (Figure S8). Figure 9 (a) shows species distribution on Ni and NiIn as an example. At low coverage, acetylene is the dominant species on the reaction surface (Figure 9 (a)) and because of its high adsorption energy, it saturates the surface until 1 ML and, hence, poisons the catalysts.

With regards to catalytic conversion, Figure 9 (b) shows that the low coverage assumption for Ni and NiIn resulted in rapid full coverage of the catalytic surface by C₂H₂, indicating that the reaction was limited by acetylene poisoning caused by the high adsorption energy, evaluated at low coverage. Ni showed minimal conversion (6%) as the coverage of acetylene on the surface was increasing until it reached 1.0 ML (Figure 9 (b) (bottom)). This contrasts with the reported experimental results, which show acetylene conversion on Ni to range between 35% and 100%.^{20,21,30}

Figure 9 (b) (top) shows that surface poisoning happened at a slower rate in the case of NiIn allowing the reaction to proceed until 80% acetylene conversion in comparison to Ni (6%). This is simply related to the fact that acetylene is adsorbed more strongly on Ni than on NiIn. In the case of Ni₃In, the reaction proceeded to completion (100% conversion), however, the coverage of acetylene continually increased as the reaction progressed, reaching 1 ML (Figure S9). Ultimately, acetylene poisoning was observed in all the low coverage simulations except in Ni₂In₃ because of the very weak acetylene adsorption.

The high coverage kinetic simulation was performed using an initial coverage of 0.5 or 0.6 ML, which equates to 4 C₂H₂ molecules for a surface with 8 active sites for Ni, Ni₃In, NiIn, and 6 C₂H₂ with 10 active sites for Ni₂In₃. 0.5 ML coverage corresponds to the pivotal point at which the adsorption free energy per molecule shifts from high to low, as illustrated in Figure 5. It is worth noting, however, that 0.5 ML coverage does not necessarily correspond to the most stable thermodynamic state, as additional molecules can still weakly adsorb to the surface. In addition, the choice of 0.5 ML as the initial coverage for the high coverage model, was justified a posteriori by the kinetic simulations.

The high coverage model showed no increase in acetylene coverage for the surfaces and maintained the initial coverage of 0.5 ML throughout the simulations (Figure 9 (a) and Figure S8). Ni showed a conversion value of 45%, which is compatible with the experimental values.^{20,21,30} According to the high coverage model, hydrogen was covering a fraction of the surface on NiIn as shown in Figure 9 (a). Gibbs free energies of hydrogen and acetylene co-adsorbed on NiIn surface (Figure S10) show that acetylene adsorption was favored without accumulation of hydrogen on the surface which agrees with the microkinetic model.

The unchanged coverage at steady state, compared to the initial coverage of acetylene molecules stems from the weak differential adsorption energy (Table S16) and the enhanced desorption rates facilitated by the preadsorbed species on the surface. The different results obtained by the two models highlight the lack of consistency in the acetylene coverage when low coverage was assumed, in contrast to the self-consistent nature of the high coverage approach, which aligns with the initial conditions.

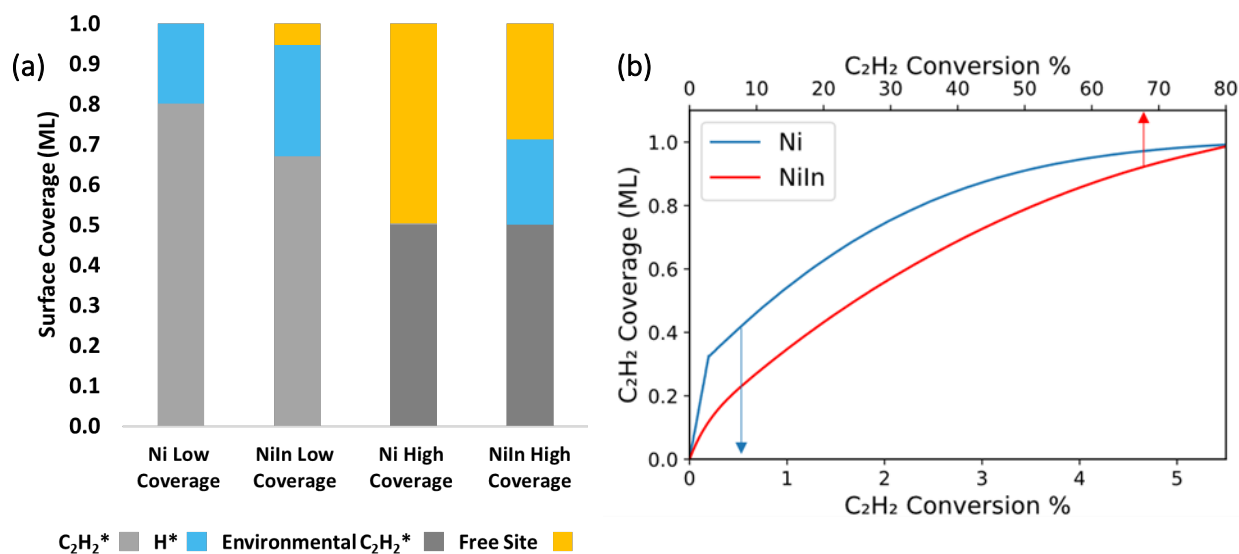


Figure 9. (a) Surface coverage distributions of main reaction species were taken at the same conversion value (40% C₂H₂ conversion except for Ni at low coverage for which it was taken at 2.5% conversion because the reaction stopped before reaching 40%). 40% was selected as the benchmark conversion, as it represents the lowest conversion observed in most of the catalysts, at both low and high coverage models. Environmental C₂H₂ corresponds to the initial 0.5 ML/0.6 ML coverage of acetylene considered for the simulations using the high coverage energy profiles, that can only access the remaining sites. **(b)** Coverage of acetylene

as a function of acetylene conversion on Ni (bottom) and NiIn (top) using data at low coverage.

Figure 10 shows the distribution of the products at the reactor outlet using the kinetic models established with energies obtained at low and high acetylene coverage. The ethylene levels presented in Figure 10 are the amount of ethylene generated during the reaction and do not account for the initial concentration of ethylene in the feed. NiIn exhibited the highest ethylene production in both models. NiIn and Ni₂In₃ showed a significant decrease in ethane levels in contrast to Ni and Ni₃In. However, this decrease in ethane production comes with a corresponding rise in the formation of oligomers (Figure 10(a-b)). This highlights the importance of considering the oligomerization reaction when assessing catalyst selectivity, rather than limiting selectivity to the amount of ethane produced.

The high selectivity to acetylene oligomerization on Ni₂In₃ presents it as a potentially promising catalyst for C-C coupling reactions. This could be resulting from the weak binding energies of acetylene on the surface. It was proven by Lausche *et al.* that transition metals with weak binding energies exhibited larger adsorbate–adsorbate interactions in comparison to transition metals with strong binding energies.⁵⁶ The strong binding between the molecule and the catalyst surface makes it more difficult for the molecule to react with other molecules. This is because the energy required to break the bond between the molecule and the catalyst surface is greater for a strong bond compared to a weak bond.⁵⁷ Thus, increased selectivity for oligomers was observed on NiIn and Ni₂In₃ (Figure 10).

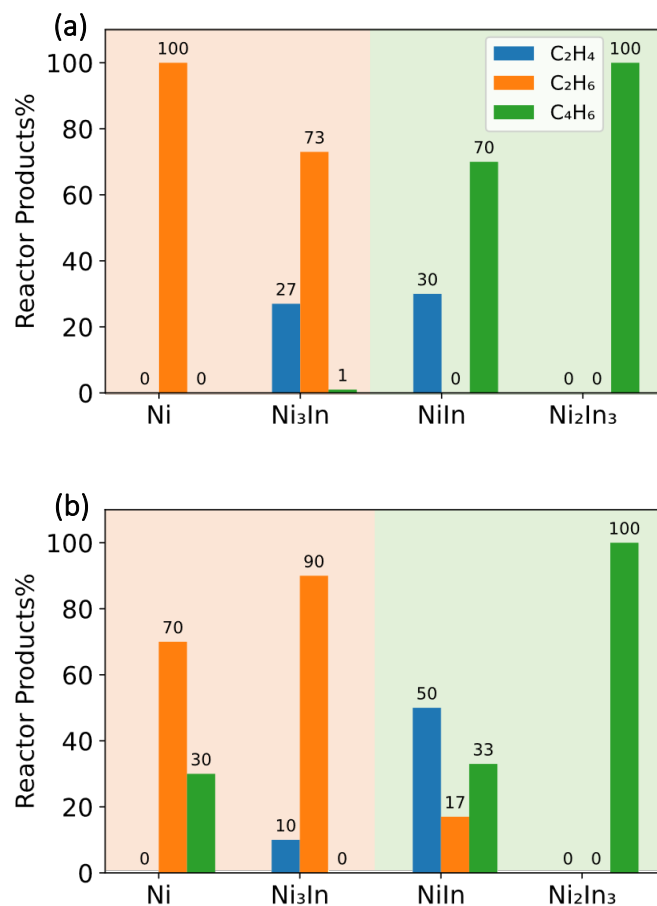


Figure 10. Calculated distribution of products at the reactor outlet at (a) low coverage and (b) high coverage. Feed composition (1:1:100 C₂H₂:H₂:C₂H₄) at 433 K and 10 bar. The ethylene levels denote the amount of ethylene generated during the reaction and do not include the initial concentration of ethylene in the feed. Orange regions (left) indicate surfaces with high selectivity to ethane and green regions (right) indicate surfaces with high selectivity to butadiene.

Figure 11 presents the acetylene consumption rates and yield of ethylene calculated using data at low and high acetylene coverage. All values were calculated at a 40% conversion except for the Ni at low coverage because the reaction only proceeded to a 6% conversion. 40% was selected as the benchmark, as it represents the lowest conversion observed among the catalysts, at both low and high coverage models.

The highly negative ethylene yield on Ni shown in **Figure 11 (a-b)** is due to the rapid hydrogenation of ethylene in the feed on Ni active sites. The low activity of Ni_2In_3 was attributed to the weak adsorption of acetylene and the substantial energy barriers for hydrogenation, even at high coverage as was discussed in the previous sections. In the low coverage model (**Figure 11 (a)**), Ni_3In was the most active catalyst with the highest ethylene yield. On the other hand, the most active catalyst and the highest ethylene yield in the high coverage model were Ni and NiIn , respectively (**Figure 11 (b)**). The microkinetic model using high coverage data showed that the presence of In on the catalytic surface decreased the rate of acetylene consumption, which is associated with the decrease in adsorption strength. A similar trend was found when alloying Pd with coinage metals.⁵⁸ Moreover, **Figure 11 (b)**, shows a tradeoff relationship between activity and selectivity. This relationship is not seen in **Figure 11 (a)** when the coverage effect was neglected.

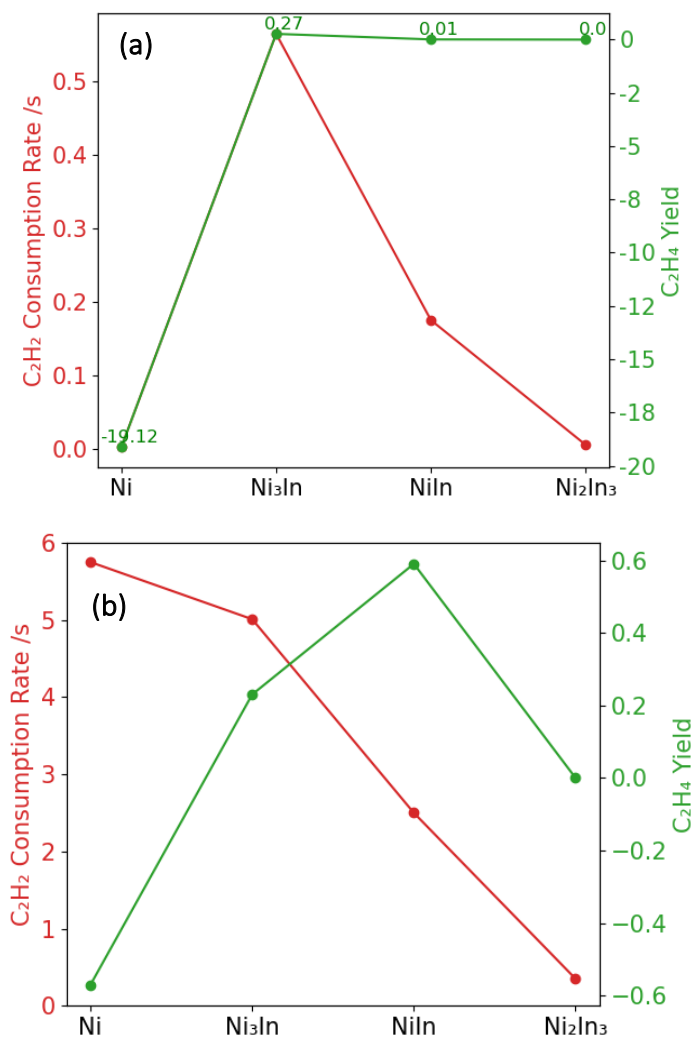


Figure 11. Acetylene consumption rates and yield of ethylene at 40% acetylene conversion using (a) low coverage energy data and (b) high coverage energy data. All values were calculated at a 40% conversion except for the Ni at low coverage because the reaction only proceeded to a 6% conversion. 40% was selected as the benchmark, as it represents the lowest conversion observed among the catalysts, at both low and high coverage models. A tradeoff relationship between activity and selectivity is observed when using the high coverage data. This relationship is not seen when the coverage effect was neglected.

Discrepancies in the literature regarding the origin of selectivity may be owed to the use of different feed compositions when evaluating catalysts. The results of the microkinetic simulations at high coverage, utilizing ethylene-rich feed (1:1:100 C₂H₂:H₂:C₂H₄) in comparison to C₂H₂ and H₂ feed only (1:1 C₂H₂:H₂) are presented in **Figure 12 (a-b)**. The formation of C₄H₆ was consistent when utilizing both feeds, which confirms that oligomers were primarily formed from acetylene C-C coupling reactions, in line with the isotopic labeling experimental results on Ni-Zn catalysts.²⁰ Experiments showed a ratio of 3:1 of the ethane produced from hydrogenating the ethylene in the feed to the ethane produced from the over-hydrogenation of acetylene.²⁰ This explains the C₂H₄ consumption on Ni when using the (1:1:100 C₂H₂:H₂:C₂H₄) feed (**Figure 12 (a)**). On the other hand, all surfaces showed minimal ethane formation and increased ethylene selectivity when utilizing the (1:1 C₂H₂:H₂) feed (**Figure 12 (b)**) confirming that the primary source of ethane was the hydrogenation of the ethylene in the feed. Therefore, testing catalysts with pure acetylene may provide an inaccurate representation of the selectivity of the catalysts under actual reaction conditions. Understanding the origin of side products, in this case, ethane and oligomers, provides insight into the reaction mechanism by identifying the key intermediates and pathways contributing to their formation and, thus, guides future optimizations to reduce or eliminate their production.

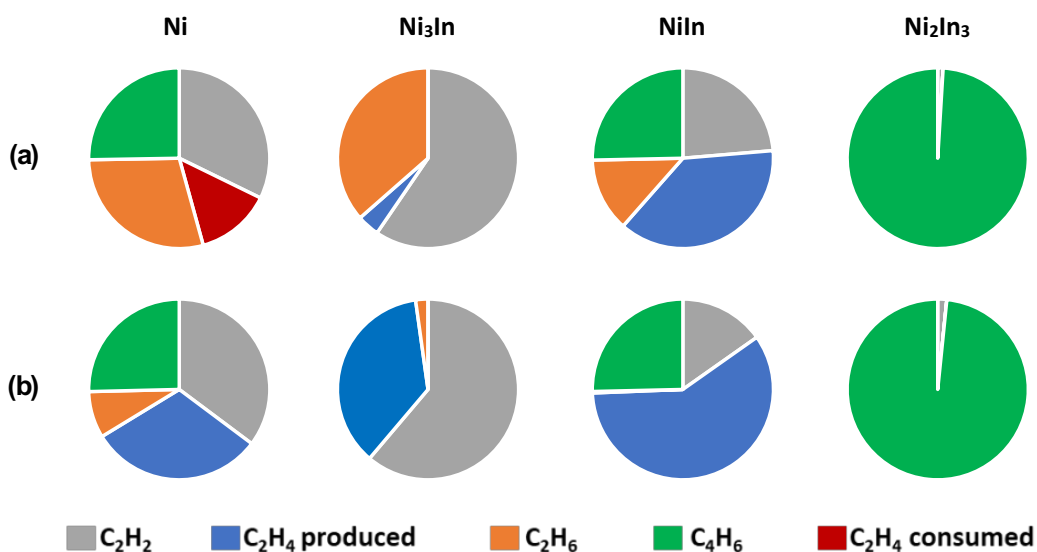


Figure 12. (a) Products distribution at the reactor outlet with a feed composition of (1:1:100 C₂H₂:H₂:C₂H₄) at 10 bar and 433 K. (b) Products distribution at the reactor outlet in the absence of ethylene with a feed composition of (1:1 C₂H₂:H₂) at 0.2 bar and 433 K. Significantly reduced levels of ethane formation were obtained in the absence of ethylene in the feed (b), in comparison to the results obtained with rich ethylene feed (a). These results were obtained using the high coverage model.

In summary, NiIn exhibited enhanced ethylene yield with reasonable activity regardless of the coverage model (Figure 10 and Figure 11) and feed composition (Figure 12) in comparison to Ni, Ni₃In and Ni₂In₃. A remarkable ethylene selectivity was achieved (95%) on NiIn in the absence of ethylene in the feed and at an increased pressure of 20 bar (Figure S11). It is important to recognize that product distribution results do not depict the optimum performance of the catalysts, but rather, they provide an understanding of their relative performance under standardized reaction conditions. The reaction conditions could be optimized for each catalyst individually; however, this falls outside the scope of this study.

4. CONCLUSION

DFT-based reaction profiles and microkinetic simulations were used to describe the reaction chemistry of acetylene hydrogenation on Ni-In intermetallic catalysts. NiIn showed the highest ethylene yield among the studied catalysts. In comparison to Ni, Ni₃In, and NiIn exhibited enhanced ethylene selectivity. While low ethane levels were formed on NiIn and Ni₂In₃ compared to Ni and Ni₃In, levels of C₄H₆ were also observed, which highlights the importance of accounting for oligomerization reactions when applying a selectivity descriptor to screen catalysts.

The high adsorption energies at low coverage resulted in the surface being saturated with acetylene and blocking the reaction. On the other hand, the high coverage model showed that surfaces were not poisoned by acetylene and maintained the initial coverage throughout the simulations. The contrasting outcomes of the two models demonstrate the inconsistent nature of acetylene coverage when assuming low coverage, while the high coverage model was self-consistent and accurately reflected the initial conditions. Results from the high coverage microkinetic model showed that the presence of In on the catalytic surface decreased the rate of acetylene consumption and a trade-off relation between activity and selectivity was observed.

The effect of feed composition on catalysts selectivity was also investigated. Reduced ethane production was observed in the absence of ethylene in the feed which confirmed that the origin of ethane formation was primarily from ethylene hydrogenation rather than acetylene over hydrogenation. The results also showed that the formation of oligomers was not impacted by the presence or absence of ethylene in the feed, thereby confirming that the source of oligomerization was acetylene. The study provides insights to better understand and evaluate the selectivity of catalysts and serves as a step towards developing a competitive alternative to the current Pd-Ag industrial catalyst for the semi-hydrogenation of alkynes.

5. SUPPORTING INFORMATION

Ni-In phase diagram, density of states calculations, details of bulk unit cells, surface facets calculations, adsorption sites, optimized structures, and additional microkinetic modeling results.

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