First-principles Study of the Products of CO2 Dissociation on Nickel-based Alloys: Trends in Energetics with Alloying Element

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Oxidation and corrosion of nickel and Ni-based alloys are a problem for many industrial applications, such as power plants that use supercritical CO\(_2\) as the working fluid. In supercritical CO\(_2\) environments, CO\(_2\) dissociates on the surface forming adsorbed CO and O, which can oxidize the surface. The adsorbed CO can further breakdown via direct CO dissociation or via the Boudouard reaction to form adsorbed C, which can in turn carburize the surface. Understanding how the adsorbed species interact with different Ni-based alloys can help guide the design of future alloys. The interactions of adsorbed O, C, and CO on the (100) and (111) facets of pure Ni and Ni individually alloyed with Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ti, V, and W are examined using density functional theory. We find that the binding of CO is energetically similar across all alloy surfaces and both facets, while O binding varies across the different alloy surfaces and C binding varies between the different facets. The binding of O is weaker on pure Ni and Ni alloyed with Cu, Co, Fe, Al, or Mn and stronger on Ni alloyed with Nb, Cr, Mo, Ti, V, or W, while the binding of C is weaker on the (111) facet than the (100) facet. The difference in the binding energies of the adsorbates across the different alloy surfaces is due mainly to the ensemble effect, rather than the ligand effect. The breakdown of CO via direct CO dissociation is endothermic on the (111) facet and exothermic on the (100) facet, with the alloy surfaces that bind O strongly having the most exothermic reaction energies. The breakdown of CO via the Boudouard reaction has similar reaction energies across the different alloy surfaces of a single facet and is endothermic on both facets, with the (111) facet being most endothermic. This comprehensive study presents a summary of the current literature as well as a well-rounded view of the products of CO\(_2\) breakdown on Ni surfaces alloyed with the most common alloying elements used in industrial applications.

1. Introduction
Nickel-based alloys are commonly used in industrial applications as structural materials and as heterogeneous catalysts. In catalysis, Ni-based alloys are common in applications such as the oxidation of hydrocarbon fuels in solid-oxide fuel cells (SOFC) [1-3] and in the catalytic dry reforming of CH4 with CO2 to make syngas [4, 5]. Ni-based alloys are also widely used as structural materials in industrial applications such as heat exchangers, pipework, combustion cans, and engine blades due to their corrosion-resistance, high-strength, and high-temperature properties [6, 7]. An emerging application for Ni-based alloys is in supercritical carbon dioxide (sCO2) power production cycles. Compared to conventional steam power production cycles, sCO2 cycles offer an improved plant efficiency due to less compressive work because of higher CO2 densities. Other advantages of sCO2 cycles include lower cost, reduced emissions, fewer and smaller energy conversion components, and a simpler cycle layout [8, 9]. A major limitation to implementing this step-changing technology is the identification and development of high-strength, corrosion-resistant materials for high temperature (650-800°C) power plant components. Herein, we use density functional theory to study the surface chemistry of a dozen Ni-based alloys that are promising materials for such power plants, and discover trends in the thermodynamic stabilities of the surface species, which give insights into how to improve the long-term stability of these materials.

There are many commercially available Ni-based alloys and superalloys that are currently being considered for sCO2 applications such as 740H, 282, 230, 625, 214, 224, and C276 [9-14]. In these Ni-based alloys, the highest concentration alloying elements are Cr, Fe, Co, Mo, W, Al, Nb, Ti, Mn, Si, Cu, C, and V, which are taken as the starting point for the Ni-based alloy surfaces studied herein. All metallic elements, which excludes Si and C, are included in this study giving twelve different alloy surfaces.

The initial step in the degradation of Ni-based alloys in sCO2 conditions is expected to be through the dissociation of CO2 to make adsorbed CO plus O (COads + Oads). We find this reaction to be quite exothermic with a reaction energy of -1.38 eV on the (100) facet and -1.07 eV on the (111) facet, and therefore CO2 dissociation is expected to be fast. This is followed by carbon deposition from COads dissociation into Cads + Oads or from the Boudouard reaction where two COads react to form Cads + CO2,gas. Deposition of O on the surface leads to oxidation of the surface and the formation of metal oxides while deposition of C on the surface leads to carburization of the surfaces and the formation of metal carbides, which change the chemistry of the surface and eventually the properties of the bulk metal. Herein we study the adsorbed products of CO2 dissociation (Oads, Cads, and COads) and uncover how their stabilities depend on the nature of the alloying element used to make the Ni-based alloy. The effects of alloying elements on the interactions of CO, O, and C with Ni surfaces are also of great interest in catalysis where the strength of surface interactions has been related to catalytic activity [15, 16].

The adsorption of O [17-20] and CO [20-25] has been studied extensively on the low-index facets of pure Ni surfaces. More recently studies have included Ni-based alloys looking at the adsorption of O, C, and CO on the (111) facet [1-7, 26, 27], however the (100) facet [28, 29] is less studied. In order to develop new Ni-based alloys, it is essential to understand the fundamental interactions of the corrosive species with the surface. Herein we focus on the Ni(100) and Ni(111) facets with Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ti, V, or W alloying elements and examine their interactions with adsorbed O, C, and CO. To better understand the direct interaction between the adsorbate and the alloying element, a low concentration alloy is modeled by replacing a single Ni surface atom with the alloying element, leading to a mole fraction of 1/9 in the surface layer but
only 1/63 and 1/54 in the (100) and (111) simulation slabs, respectively. Binding energies and binding sites for all adsorbates, ligand and ensemble effects of the alloying atom, and CO dissociation and Boudouard reaction energies are determined on all facets and surfaces.

2. Methods

2.1 Computational Details

All results are calculated using density functional theory (DFT) via the Vienna Ab-initio Simulation Package (VASP) [30-33], with some of the calculations run on the Extreme Science and Engineering Discovery Environment (XSEDE) [34]. Electronic structures are calculated for the adsorption of one C, O, or CO adsorbate on the (100) and (111) facets of Ni-based alloys. A p(3x3) unit cell is used to represent the 12 Å thick surface slabs, containing 7 layers for the (100) facet and 6 layers for the (111) facet, with 20 Å of vacuum between slabs. The top 4 metal layers and the adsorbate are allowed to relax while the bottom 3 layers for the (100) facet and 2 layers for the (111) facet are held fixed. Atomic Simulation Environment (ASE) was used to create the initial simulation cells [35].

The exchange correlation potential and energy is described by the generalized gradient approximation (GGA) as defined by the Perdew-Burke-Ernzerhof (PBE) functional [36, 37], and the projector augmented wave (PAW) method is used to represent the core electrons [38, 39]. Spin polarization and magnetization effects are included. Plane-wave calculations are employed with a kinetic energy cutoff of 400 eV for the Kohn-Sham orbitals and the surface Brillouin zone is sampled using a Monkhorst-Pack grid with 5x5x1 k points. Increasing the energy cutoff to 500 eV changes the binding energies of O, C, and CO on Ni(100) by 3 meV, 10 meV, and 3 meV and on Ni(111) by 8 meV, 8 meV, and 1 meV, respectively. Increasing the number of k points to 7x7x1 changes the O, C, and CO binding energies on Ni(100) by 0.04 eV, 0.02 eV, and 0.002 eV and on Ni(111) by 0.03 eV, 0.02 eV, and 0.01 eV, respectively. All calculations for binding energies are relaxed until the forces are converged below 0.01 eV/Å. The calculated lattice constant for Ni is 3.52 Å, in agreement with the experimental value of 3.52 Å [40].

Density of states calculations are performed using 15x15x1 k points to sample the Brillouin zone. Increasing to 19x19x1 k points changes the d-band center of the pure Ni surface by 0.04 eV for the (100) facet and 0.03 eV for the (111) facet. The electron density is converged until the energy is below 10^{-6} eV for the clean surfaces. Only the top one surface layer is considered when calculating the d-band center of each Ni-based alloy surface.

2.2 Surface Models

The 3x3 surfaces bind one adsorbed species, corresponding to a 1/9 monolayer adsorbate coverage. For the alloy surfaces, one of the Ni atoms in the top layer is exchanged for the alloying metal atom (Ti, V, Nb, Cr, Mo, W, Mn, Fe, Co, Cu, or Al), setting the alloy surface concentration at 1/9. Figure 1 shows the different adsorption sites on the alloyed (100) and (111) facets. There are three unique hollow sites, three unique top sites, and four unique bridge sites on the (100) facet and three unique hcp hollow sites, three unique fcc hollow sites, three unique top sites, and four unique bridge sites on the (111) facet. The numbers in Figure 1 represent the unique binding locations for each site and increase moving away from the alloying atom. Alloy-rich sites have the adsorbate adjacent to the alloying atom and include the top-1, hollow-1, hcp-1, fcc-1, and bridge-
1 sites. Ni-rich sites correspond to sites in which the adsorbate is bound to only Ni atoms and include all remaining sites.

**Figure 1.** Unique binding sites on the (100) and (111) facets. Light blue circles represent top sites, medium blue rectangles represent bridge sites, dark blue squares represent (100) hollow sites, dark blue up-pointing triangles represent (111) hcp hollow sites, and dark blue down-pointing triangles represent (111) fcc hollow sites. The numbers increase moving away from the alloying atom and label the unique binding locations for each site.

Binding energies of O, C, and CO at each unique site are calculated to determine the most stable binding location for each adsorbate on every alloy surface. The binding energy is defined as

\[
E_{\text{bind}} = E_{\text{surf}+\text{ads}} - E_{\text{surf}} - E_{\text{ref}}
\]

where \(E_{\text{surf}+\text{ads}}\) is the total energy of the surface and adsorbate system, \(E_{\text{surf}}\) is the energy of the clean surface, and \(E_{\text{ref}}\) is the adsorbate reference energy. The reference energy is the energy of 1/2 O\(_2\) in vacuum, one graphite atom, or CO in vacuum for the O, C, or CO adsorbate, respectively. With this notation, a negative \(E_{\text{bind}}\) value indicates a release of energy upon adsorption and a positive \(E_{\text{bind}}\) value represents an increase in energy upon adsorption.

Binding energy differences are also reported for adsorbates on the different Ni-based alloy surfaces relative to the pure Ni surface when the adsorbate is in its most stable adsorption site on each surface. The difference in binding energy is calculated as

\[
\Delta E_{\text{bind}} = E_{\text{bind}}^{\text{alloy}} - E_{\text{bind}}^{\text{Ni}} = E_{\text{surf}+\text{ads}}^{\text{alloy}} - E_{\text{surf}}^{\text{alloy}} - E_{\text{surf}+\text{ads}}^{\text{Ni}} + E_{\text{surf}}^{\text{Ni}}
\]

where the superscripts indicate the alloy surface or the pure Ni surface. In this notation, a negative \(\Delta E_{\text{bind}}\) value indicates that the adsorbate binds stronger to the alloy surface than the pure Ni surface and a positive \(\Delta E_{\text{bind}}\) value signifies that the adsorbate binds weaker to the alloy surface than the pure Ni surface. The advantage of calculating the binding energy difference is that it is independent of the choice of reference species, which is useful when comparing to other literature values.
The binding energies of the reactants and the products in the CO dissociation reaction \((\text{CO} \rightarrow \text{C} + \text{O})\) and the Boudouard reaction \((2\text{CO} \rightarrow \text{C} + \text{CO}_2)\) are calculated relative to CO in the gas phase. The binding energy of a single CO reactant follows Equation 1 and is calculated as

\[
E_{\text{bind,CO}} = E_{\text{surf}+\text{CO}} - E_{\text{surf}} - E_{\text{CO}}
\]  

where \(E_{\text{CO}}\) is the energy of CO in vacuum. The binding energy of the products of CO dissociation, C+O, is calculated as

\[
E_{\text{bind,C+O}} = E_{\text{surf}+\text{C}} + E_{\text{surf}+\text{O}} - 2E_{\text{surf}} - E_{\text{CO}}
\]  

making the overall CO dissociation reaction energy

\[
E_{\text{rxn,COdiss}} = E_{\text{bind,C+O}} - E_{\text{bind,CO}} = E_{\text{surf}+\text{C}} + E_{\text{surf}+\text{O}} - E_{\text{surf}+\text{CO}} - E_{\text{surf}}.
\]  

The binding energy of the Boudouard reaction products, C+CO\(_2\), is calculated as

\[
E_{\text{bind,C+CO}_2} = E_{\text{surf}+\text{C}} + E_{\text{CO}_2} - E_{\text{surf}} - 2E_{\text{CO}}
\]  

where \(E_{\text{CO}_2}\) is the energy of CO\(_2\) in vacuum, making the overall Boudouard reaction energy

\[
E_{\text{rxn,Boudouard}} = E_{\text{bind,C+CO}_2} - 2E_{\text{bind,CO}} = E_{\text{surf}+\text{C}} + E_{\text{CO}_2} + E_{\text{surf}} - 2E_{\text{surf}+\text{CO}}.
\]  

A positive reaction energy, \(E_{\text{rxn}}\), represents an endothermic reaction, with CO being the most energetically stable species, and a negative reaction energy represents an exothermic reaction, where C+O for CO dissociation or C+CO\(_2\) for the Boudouard reaction is energetically more favorable. Herein the adsorbates are assumed to be far apart and non-interacting.

3. Results and Discussion

The aim of this study is to understand the relative stabilities of CO\(_2\) dissociation products on Ni-based alloy surfaces. The binding energies reported below reveal that the dissociation of CO\(_2\) gas on these alloy surfaces to produce CO\(_{\text{ads}}\) + O\(_{\text{ads}}\) is quite exothermic, with a reaction energy of -1.38 eV on Ni(100) and -1.07 eV on Ni(111). This is in good agreement with a previous study that found the reaction to be exothermic by -1.00 eV on Ni(100) and -1.33 eV on Ni(111) [41]. Herein we focus on the relative energies of the CO\(_2\) dissociation products (CO\(_{\text{ads}}\) and O\(_{\text{ads}}\)) and further CO reaction products (C\(_{\text{ads}}\)) which can be produced by either CO dissociation, CO \(\rightarrow \text{C} + \text{O}\), or the Boudouard reaction, 2CO \(\rightarrow \text{C} + \text{CO}_2\), and analyze how these energies depend on the nature of the alloying element.

The binding energies of O, C, and CO are presented in Sections 3.1-3.3, respectively, and include binding of the adsorbates to the (100) and (111) facets of pure Ni and eleven Ni-based alloy surfaces. Section 3.4 focuses on understanding the effect of the alloying element on the adsorbate binding energies by exploring the ligand effect and the ensemble effect. In Section 3.5 the reaction energies for CO dissociation and the Boudouard reaction are determined and key findings are highlighted and discussed.
3.1 Oxygen Binding

The binding of O is most stable at a hollow site (-3.20 eV) and less stable at a bridge site (-2.50 eV) or a top site (-1.30 eV) on the Ni(100) facet. On the Ni(111) facet, O binds slightly stronger at an fcc hollow site (-2.91 eV) than an hcp hollow site (-2.80 eV) and weaker at a top site (-1.06 eV). The O binding energy at a bridge site on the (111) facet could not be determined. This is in good agreement with previous DFT studies that also found the hollow site on Ni(100) and the fcc site on Ni(111) to be the most stable binding sites for O [20, 41-43]. Experimentally, O is also found to be most stable at a four-fold hollow site on Ni(100) with a binding energy of -2.85 eV and at three-fold hollow sites on Ni(111) with a binding energy of -2.28 eV [18]. This is in good agreement with the results presented here, however non-hybrid DFT functionals, such as PBE, are well known to overbind chemisorbed systems [44, 45], so slightly stronger calculated binding energies are not surprising. Comparing the two facets, O adsorbs 0.29 eV stronger on the (100) facet than on the (111) facet, in agreement with previous DFT studies that found O adsorption is stronger on Ni(100) than Ni(111) by 0.28 eV [42], 0.31 eV [41, 43], 0.32 eV [20], or 0.44 eV [46].

Replacing a Ni surface atom with an alloying atom changes the properties of the surface and influences the way O interacts with the surface, as shown in Table 1 by different binding energies and binding sites for adsorbed O. A complete list of O binding energies for all surfaces at different sites can be found in the Supporting Information. The most stable binding site for O adsorption is adjacent to the alloying atom at the hollow-1 site and fcc-1 site on the (100) and (111) facets, respectively, for all Ni-based alloy surfaces except when the alloying element is Cu, Mo, or W. On the Cu alloy surface, O binds stronger at a Ni-rich hollow site than the hollow site adjacent to the Cu atom by 0.13 eV on the (100) facet and by 0.34 eV on the (111) facet. On both facets of the Mo and W alloy surfaces, O binds strongest at the top-1 site right above the alloying atom. On the Mo alloy surface, O is more stable at the top-1 site by 0.26 eV and 0.15 eV than the hollow-1 site on the (100) facet and the fcc-1 site on the (111) facet, respectively, which are the second most stable sites. O is not stable at the hollow-1 site on the (100) facet of the W alloy surface so a comparison cannot be made, however on the (111) facet O binds 0.21 eV stronger to the top-1 site compared to the fcc-1 site. The energetic favorability of O at top-1 sites can be explained by the stronger oxophilic nature of both Mo and W compared to Ni. Oxophilicity is hard to measure, but has been correlated with electronegativity [47]. Mo, which is 13% more electronegative than Ni, and W, which is 24% more electronegative than Ni, are the only two elements considered herein that are more electronegative than Ni on the Pauling electronegativity scale [48-50], causing O to bind most strongly on top of the Mo and W atoms.

Table 1. Effects of substituting an alloying atom for a single Ni surface atom on oxygen adsorption. Binding energy (eV) referenced to 1/2 O_2 in vacuum, binding energy difference relative to pure Ni (eV), and binding site for O adsorption on the (100) and (111) facets of Ni-based alloys at 1/9 ML coverage. For site locations, refer to Figure 1.
All the alloying elements strengthen the O-surface interactions on both the (100) and (111) facets, shown by the negative $\Delta E_{\text{bind}}$ values in Table 1, except Ni(100) alloyed with Cu in which the O binding energy is not affected. The range over which an alloying element affects the binding energy of O on the surface is broad, with the largest increase being 1.07 eV and 1.10 eV for Ni alloying with W on the (100) and (111) facets, respectively. The order in which the alloying element increases the binding strength of O on the Ni-based alloy surfaces is similar on both facets, increasing with the alloying atom as (Ni, Cu) < Co < (Fe, Al) < Mn << (Nb, Cr) < (Ti, V) < Mo < W on the (100) facet and as (Ni, Cu) < Co < Fe < Al < Mn << Nb < Cr < Ti < (Mo, V) < W on the (111) facet. The Ni-based alloy surfaces can be divided into two groups on each facets: those that bind O weaker (binding strength $\leq$ 3.39 eV including the pure Ni surface and Ni alloyed with Cu, Co, Fe, Al, or Mn) and those that bind O stronger (binding strength $\geq$ 3.67 eV including Ni alloyed with Nb, Cr, Ti, V, Mo, or W). This divide among transition metal alloying elements occurs between groups 6 and 7 in the periodic table in which alloying elements in groups $\leq$ 6 bind O strongly and alloying elements in groups $\geq$ 7 bind O weakly.

Table 2 summarizes previous studies of O adsorption on the (111) facet of Ni-based alloy surfaces, with two of the most comprehensive studies of O adsorption on different surface alloys performed by Alexandrov et al. [6] and An et al. [1]. On the (111) facet, Alexandrov et al. [6] found that O binding strength increases with the alloying atom as Cu < Ni < Fe < Al < Mn < Cr at a 1/16 surface alloy concentration, while An et al. [1] found the O binding strength to increase with the alloying atom as Mo < Co < Fe < Ni < Cu at a 1/4 surface alloy concentration and as Cu < Ni < Co < Fe < Mo at a 2/4 surface alloy concentration. The discrepancies among these studies and our study lie in the use of different O binding sites. Alexandrov et al. [6] used the equivalent of an fcc-1 site for all surfaces, An et al. [1] used the equivalent of an fcc-2 or hcp-2 site (they did not distinguish between the two) for their study at 1/4 alloy concentration and an fcc-1 or hcp-1 site for their study at 2/4 alloy concentration, while herein we use the most favorable O binding site for each surface. Comparing our results at the fcc-1 site or the fcc-2 site, with data in the Supporting Information, gives the exact same results as that of Alexandrov et al. [6] and An et al. [1]. While studies of the same adsorption site for different alloy surfaces give insight into the ligand effects, the most stable binding site needs to be used to determine differences in reaction energies on the different surfaces.

Table 2. Summary and comparison to previous studies of the change in binding energy, $\Delta E_{\text{bind}}$, of atomic O on (111) Ni-based alloy surfaces compared to a pure Ni(111) bulk/surface. An[1] and Das[7] did not differentiate between fcc and hcp hollow sites in their studies and refer to the adsorption sites as three-fold hollow (3fh) sites. The number in parentheses after the binding site indicates the number of alloying atoms at the adsorption site.
As seen in Table 2, our findings are in good agreement with previous DFT studies at identical adsorption sites with the exception of Alexandrov et al. [6] when the alloying element is Mn or Cr. It is unclear why their results are significantly different than all other results, including the results presented here and the results by Das et al. [7] for Ni alloyed with Cr. As the
concentration of the alloying element increases, the number of alloying atoms bound to O also increases, influencing the binding energy of O on the surface. An increase in the number of Cu atoms bound to O weakens the binding energy of O, while increasing the concentration of all remaining alloying elements strengthens the O binding energy.

The (100) facet of Ni-based alloys is less investigated, although a few studies have made a comparison to the (111) facet. Das et al. [7, 29] studied Ni alloyed with Cr and determined that O adsorbs stronger on the (100) facet than the (111) facet by 0.02 eV at a 1/4 surface alloy concentration and 0.04 eV at a 2/4 surface alloy concentration. These results indicate that O binds almost equally strong on the (100) and (111) facets of Ni alloyed with Cr, in good agreement with our findings. Wu et al. [28] studied Ni alloyed with Al at a 1/4 bulk alloy concentration, but different (100) and (111) surface alloy concentrations, and found that O adsorbs 0.125 eV stronger on the (100) facet than the (111) facet, in good agreement with our calculations where O adsorbs 0.21 eV stronger on the (100) facet than the (111) facet. The largest difference between binding energies on the two facets is 0.29 eV, on the pure Ni surface, while the smallest difference is 0.06 eV, when the alloying element is Cr.

3.2 Carbon Binding

The binding of C is only stable at a hollow site (-0.36 eV) on the (100) facet and has positive binding energies at a bridge site (1.84 eV) and a top site (3.37 eV) relative to a single graphite atom. All binding energies are positive on the (111) facet with a slightly more favorable interaction at an hcp hollow site (1.04 eV) than an fcc hollow site (1.09 eV) and a very unfavorable interaction at a top site (3.45 eV). The interaction energy of C at a bridge site on the (111) facet could not be calculated. Different reference species shift the binding energy of C; for example, using atomic C in gas phase as a reference species instead of graphite lowers the binding energy by 9.11 eV, which would make all the C binding energies herein negative. Many previous DFT studies of C binding on Ni alloy surfaces use atomic C in the gas phase as a reference species and get very negative binding energies for C on the (111) facet [1, 4, 5, 41-43, 46, 51], while a study using graphite as a reference species gets positive C binding energies on the (111) facet [27], similar to what is calculated here. Herein we use graphite as the reference species because it is a more realistic material than a gas phase C species. However, we mostly discuss the difference in binding energies rather than absolute binding energies in order to normalize the choice of reference species.

The most stable sites for C binding on Ni is at hollow sites, similar to O binding but with C at hcp hollow sites and O at fcc hollow sites on the (111) facet, although the energy difference between the two (111) hollow sites is small for both adsorbates. Previous DFT studies have also found that C is most stable at hollow sites on the (100) facet and hcp sites on the (111) facet of a pure Ni surface [41-43, 51]. C binds 1.40 eV stronger to the (100) facet than the (111) facet, which is in good agreement with previous DFT studies that have found C adsorption to be 1.05 eV [51], 1.44 eV [41, 43], 1.51 eV [42], and 1.57 eV [46] stronger on Ni(100) than Ni(111). Both O and C are more stable on the (100) facet than the (111) facet, but the increase in stability on the (100) facet is 5 times larger for C than O.

When the pure Ni surface is alloyed, the binding energy and the most stable binding sites of C on the surface can change, as shown in Table 3. A complete list of binding energies for all surfaces at different sites can be found in the Supporting Information. For all Ni-based alloy surfaces, C is most stable at hollow sites and hcp sites on the (100) and (111) facets, respectively, and in general the Ni-rich sites are more stable, in contrast to O adsorption. The binding of C on
the (100) facet is most stable at the hollow-3 site for the majority of the surfaces, with the exceptions being the Cu alloy surface, where the hollow-2 site is 0.02 eV more stable than the hollow-3 site, and the Al alloy surface, where the hollow-2 and hollow-3 sites are equally stable. The hcp-2 site is the most stable site on all (111) surfaces, except when the alloying element is Co or Cr in which the hcp-1 site is more stable by 0.03 eV and 0.02 eV, respectively.

Table 3. Effects of substituting an alloying atom for a single Ni surface atom on carbon adsorption. Binding energy (eV) referenced to a single graphite atom, binding energy difference relative to pure Ni (eV), and binding site for C adsorption on the (100) and (111) facets of Ni-based alloys at 1/9 ML coverage. For site locations, refer to Figure 1. The binding energy of C on Ni(100) alloyed with Al is equally stable at hollow-2 and hollow-3 sites.

<table>
<thead>
<tr>
<th>Alloying Atom</th>
<th>(100) facet</th>
<th>(111) facet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E&lt;sub&gt;bind&lt;/sub&gt;</td>
<td>ΔE&lt;sub&gt;bind&lt;/sub&gt;</td>
</tr>
<tr>
<td>Ni (no alloy)</td>
<td>-0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>Co</td>
<td>-0.38</td>
<td>-0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.39</td>
<td>-0.03</td>
</tr>
<tr>
<td>Cu</td>
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</tr>
<tr>
<td>Mn</td>
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<td>-0.21</td>
</tr>
<tr>
<td>Ti</td>
<td>-0.52</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

All alloy surfaces calculated increase the binding strength of C on both the (100) and (111) facets, shown by the negative ΔE<sub>bind</sub> values in Table 3. The largest increase in C binding strength is 0.24 eV on the (100) facet, by alloying with W, and 0.15 eV on the (111) facet, by alloying with Ti. The changes in binding energy on the alloy surfaces are much smaller for the C adsorbate than the O adsorbate, with the average C binding energy difference over both facets 19% that for O. The binding energy of C increases with the alloying atom on the (100) facet as (Ni, Cu, Co, Fe) < Mn < Al < Cr < (V, Ti) < (Nb, Mo) < W and on the (111) facet as (Ni, Fe, W, Co) < (Mo, Cu, Al, Mn) < (Nb, V) < Cr < Ti. Unlike O adsorption, the trends for C adsorption are quite different for the different facets, however the range of C binding energies is less than 0.25 eV, so small fluctuations in the binding energy have a larger effect on the trend. The average binding energy of C on the (100) facet is five times stronger than on the (111) facet, with the largest difference being 1.63 eV, when the alloying element is W, and the smallest difference being 1.36 eV, when the alloying element is Cu.

Table 4 compares our findings for C adsorption on Ni-based alloys with previous DFT studies in the literature. An et al. [1] found that the C binding strength on the (111) facet increases with the alloying atom as Mo < Co < Fe < Ni < Cu for a 1/4 surface alloy concentration with C at sites equivalent to our hcp-2 or fcc-2 sites and as Mo < Cu < Fe < Co < Ni for a 2/4 surface alloy concentrations with C at sites equivalent to our hcp-1 or fcc-1 sites. Here we calculate the binding strength of C to increase with the alloying atom as Co < (Ni, Fe) < (Mo, Cu) at the hcp-2 site and as Cu < Fe < (Mo, Ni, Co) at the hcp-1 site, in good agreement with the results presented by An et
al. [1]. The only exception is the Mo alloy surface which is on the opposite side of the trends for
the two studies, and it is unclear why this discrepancy occurs. None of the other previous DFT
studies, shown in Table 4, are directly comparable to this work due to different bulk and surface
alloy concentrations, yet are included here for completeness.

Table 4. Summary and comparison to previous studies of the change in binding energy, $\Delta E_{\text{bind}}$, of
atomic C on (111) Ni-based alloy surfaces compared to a pure Ni(111) bulk/surface. An[1] did not
differentiate between fcc and hcp hollow sites in their study and refer to the adsorption sites as
three-fold hollow (3fh) sites. The number in parentheses after the binding site indicates the number
of alloying atoms at the adsorption site.

<table>
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<th>Surface Alloy Conc.</th>
<th>Second Layer Conc.</th>
<th>Bulk Alloy Conc.</th>
<th>Adsorbate Conc. (ML)</th>
<th>Binding Site</th>
<th>$\Delta E_{\text{bind}}$ (eV)</th>
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<td>0/9</td>
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</table>
3.3 Carbon Monoxide Binding

The adsorption of CO on the (100) facet of pure Ni is most stable at a hollow site (-1.97 eV) compared to a bridge site (-1.88 eV) or a top site (-1.69 eV), in agreement with previous DFT studies on Ni(100) [41, 42, 52]. CO on the (111) facet binds slightly stronger at an hcp hollow site (-1.94 eV) than an fcc hollow site (-1.93 eV), and weaker at a top site (-1.57 eV). The binding energy of CO at a bridge site on the (111) facet could not be calculated. Previous DFT studies on Ni(111) also found the hcp site [41, 42, 52] or the fcc site [53] to be most stable, in agreement with experimental studies [54, 55]. The adsorption of CO is 0.03 eV more stable on the (100) facet than the (111) facet, in good agreement with previous DFT studies that find CO adsorption to be 0.03 eV [41, 43], 0.07 eV [20, 52], 0.08 eV [42], and 0.14 eV [46] stronger on Ni(100) than Ni(111). Hammer et al. [56] calculated CO binding energies of -2.00 eV on Ni(100) and -1.88 eV on Ni(111) when using the same PBE functional, in excellent agreement with the results obtained here. Experimental results find slightly weaker CO binding energies of -1.27 eV [57] or -1.30 eV [58] on Ni(100) and -1.30 eV [59] or -1.35 eV [57] on Ni(111), however it is well known that DFT overbinds chemisorbed systems, especially with the PBE functional [44, 45].

The binding energies at the most stable binding sites for CO on the different Ni-based alloy surfaces are shown in Table 5. A complete list of binding energies for different sites on all surfaces can be found in the Supporting Information. The lowest energy CO binding sites are Ni-rich hollow sites for all surfaces and both facets, similar to C binding, with the exception of the Ni(100) facet alloyed with V, Cr, or Ti in which the hollow-1 site is more stable by 0.02 eV, 0.15 eV, and 0.18 eV, respectively. The binding of CO on all (111) surfaces is strongest at the hcp-2 site compared to the other Ni-rich hollow sites, however the binding strength is within 0.06 eV at the fcc-2, fcc-3, hcp-2, and hcp-3 sites for each surface.

Table 5. Effects of substituting an alloying atom for a single Ni surface atom on carbon monoxide adsorption. Binding energy (eV) referenced to CO in vacuum, binding energy difference relative to pure Ni (eV), and binding site for 1/9 ML CO adsorption on the (100) and (111) facets of Ni-based alloys. For site locations, refer to Figure 1. On many surfaces, the CO binding energy is equal at multiple sites indicated by multiple site assignments.

<table>
<thead>
<tr>
<th>Alloying Atom</th>
<th>(100) facet</th>
<th>(111) facet</th>
</tr>
</thead>
<tbody>
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<td>Ni (no alloy)</td>
<td>E\textsubscript{bind} = -1.97, ΔE\textsubscript{bind} = 0.00, site = hol</td>
<td>E\textsubscript{bind} = -1.94, ΔE\textsubscript{bind} = 0.00, site = hcp</td>
</tr>
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<td>E\textsubscript{bind} = -1.93, ΔE\textsubscript{bind} = 0.01, site = hcp-2</td>
</tr>
<tr>
<td>Fe</td>
<td>E\textsubscript{bind} = -1.97, ΔE\textsubscript{bind} = 0.00, site = hol-3</td>
<td>E\textsubscript{bind} = -1.94, ΔE\textsubscript{bind} = 0.00, site = hcp-2, fcc-2</td>
</tr>
<tr>
<td>Cu</td>
<td>E\textsubscript{bind} = -1.98, ΔE\textsubscript{bind} = -0.01, site = hol-2</td>
<td>E\textsubscript{bind} = -1.96, ΔE\textsubscript{bind} = -0.02, site = hcp-2</td>
</tr>
<tr>
<td>Mn</td>
<td>E\textsubscript{bind} = -1.98, ΔE\textsubscript{bind} = -0.01, site = hol-2</td>
<td>E\textsubscript{bind} = -1.97, ΔE\textsubscript{bind} = -0.03, site = hcp-2</td>
</tr>
<tr>
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<td>Mo</td>
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<td>E\textsubscript{bind} = -1.99, ΔE\textsubscript{bind} = -0.05, site = hcp-2, fcc-3</td>
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</tbody>
</table>

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The addition of many of the alloying elements on the (100) and (111) facets strengthens the CO bond to the surface, shown by the negative ΔE_{bind} values in Table 5. Ni alloyed with Fe has no effect on the binding strength of CO on either facet, while Ni alloyed with Co slightly weakens the CO bond by 0.01 eV on the (111) facet. The alloying elements affect CO binding similarly on both facets, with the binding strength of CO increasing with the alloying atom as (Ni, Fe, Co, Cu, Mn) < Al < (Nb, V, Mo, W) < Cr < Ti on the (100) facet and as (Co, Ni, Fe) < (Cu, Mn) < (Mo, W, Nb, Al, Cr, V) < Ti on the (111) facet. The maximum CO binding energy difference, due to alloying with Ti on both facet, is 0.23 eV on the (100) facet and 0.10 eV on the (111) facet. This is five times smaller than the maximum change in O binding energy caused by alloying the Ni surface and about equal to the change in C binding energy. CO binds stronger to the (100) facet than the (111) facet for all Ni-based alloy surfaces, with the largest difference being 0.16 eV, when Ni is alloyed with Ti, and the smallest difference being 0.01 eV, when Ni is alloyed with Al or Mn. Overall, CO binds similarly on both facets and across all Ni-based alloy surfaces.

A comparison of the results presented here of CO binding energy on the (111) facet with previous DFT studies is shown in Table 6. The results by Wang et al. [3] show excellent agreement with the results here for CO adsorption on Ni alloyed with Cu, and are the only results with a comparable binding site and bulk composition. Although the other results in Table 6 cannot be compared as easily, it is still evident that alloying Ni with Co or Fe decreases the binding strength of CO, alloying with Cu has a neutral effect, and alloying with Al increases the strength of CO binding.

Table 6. Summary and comparison to previous studies of the change in binding energy, ΔE_{bind}, of CO on (111) Ni-based alloy surfaces compared to a pure Ni(111) bulk/surface. A three-fold hollow (3fh) site designation in this work indicates that the hcp and fcc hollow sites are energetically equal. The number in parentheses after the binding site indicates the number of alloying atoms at the adsorption site.
3.4 Alloying Atom Effect

The ligand effect and ensemble effect are analyzed in order to understand the trends in binding energy of the adsorbates to the different alloy surfaces. The ligand effect attributes changes in the chemical properties of the alloy surfaces to different electronic structures of the surfaces while the ensemble effect attributes changes in the surface properties to changes in the ensemble of atoms that make up the binding site [60]. Herein we assess the ligand effect by calculating changes in the d-band center of the alloy surfaces relative to the pure Ni surface. According to Hammer and Nørskov’s d-band model [61-63] the adsorption energy of an adsorbate scales with the d-band center of the surface. In general, a higher d-band center, closer to the Fermi level, indicates a stronger bond between the adsorbate and the surface.

The d-band center of the top layer of the pure Ni surface is calculated to be -1.17 eV and -1.21 eV for the (100) and (111) facets, respectively. Including the top two layers changes the d-band center to -1.33 eV and -1.34 eV for Ni(100) and Ni(111), respectively. This is in good agreement with previous calculations for the Ni(111) d-band center of -1.16 eV [3, 64], -1.32 eV [65], and -1.87 eV [66]. The d-band center for the (111) facet is lower than for the (100) facet, which has been shown to be the trend for many metals including Ni [51], Pd [67], Pt [68], Cu [69-71], and Ag [72], and correlates well with weaker binding of O, C, and CO on the (111) facet relative to the (100) facet.

The d-band center for the top layer of the (100) and (111) facets for each Ni-based alloy surface is shown in Table 7. The shift in d-band center is similar on both facets and increases with the alloying atom as Cu < Ni < Co < (Al, Fe) < (W, Mo, Mn) < V < (Nb, Cr, Ti) on the (100) facet and as Cu < (Co, Ni) < Fe < (Mo, W, Al) < Mn < (Nb, V, Ti) < Cr on the (111) facet. The surfaces can be divided into two groups on each facet: those with lower d-band centers (d-band center shift ≤ 0.16 eV including Ni alloyed with Cu, Co, Fe, Al, W, Mo, and Mn) and those with higher d-band centers (d-band center shift ≥ 0.17 eV including Ni alloyed with V, Nb, Ti, and Cr). In general, the d-band center is lower for Ni alloyed with elements that are farther to the right in the periodic table and higher when the alloying elements are farther left.
Table 7. Effects of substituting an alloying atom for a single Ni surface atom on the d-band of the top surface layer for the (100) and (111) facets. The d-band center relative to the Fermi level, \( \varepsilon_d \) (eV), the change in the d-band center relative to the pure Ni surface, \( \Delta \varepsilon_d \) (eV), the width of the d-band, \( w_d \) (eV), and the number of d-electrons per surface transition metal atom, \( n_d \), are shown.

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<th>( \Delta \varepsilon_d ) (100)</th>
<th>( w_d ) (100)</th>
<th>( n_d )</th>
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<th>( \Delta \varepsilon_d ) (111)</th>
<th>( w_d ) (111)</th>
<th>( n_d )</th>
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<td>Ti</td>
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<td>-1.00</td>
<td>0.26</td>
<td>0.21</td>
<td>1.93</td>
<td>1.92</td>
<td>7.90</td>
<td>8.05</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.91</td>
<td>-0.82</td>
<td>0.26</td>
<td>0.39</td>
<td>1.91</td>
<td>2.13</td>
<td>8.24</td>
<td>7.92</td>
</tr>
</tbody>
</table>

Kitchin et al. [73] have shown, through alloying Pt with 3d transition metals, that alloying with elements to the left in the periodic table decreases the d-band center, which is opposite to the trend observed here. The difference between the two d-band center trends is related to the differences in the alloying systems and in the electron filling of the d-band. The alloying system studied by Kitchin et al. [73] contained a sandwich structure with the alloying atoms in the second layer so that the number of d-electrons per atom in the top layer remained constant. When alloying with elements to the left in the periodic table, the larger d-orbital overlap causes an increase in the d-band width, as seen by Kitchin et al. [73] and here in Table 7 (roughly going down the column). In the work by Kitchin et al. [73], the d-band center must be shifted down with increasing d-band width in order to keep the d-band filling constant, so alloying with elements to the left in the periodic table shifts the d-band center down. Here the alloying atom is in the top layer and the number of d-electrons per surface transition metal atom is not constant, as shown in Table 7, and the d-band center shifts up for alloying elements farther left in the periodic table, as is observed for pure transition metal surfaces.

Cu has a completely filled d-orbital, unlike the remaining alloying elements considered herein, resulting in Ni alloyed with Cu having the most negative d-band center on both facets. The d-band center of Ni alloyed with Co is similar to the pure Ni surface, but is shifted slightly positive on the (100) facet and slightly negative on the (111) facet. This is in good agreement with previous DFT studies that found Ni(111) alloyed with Cu lowers the d-band center by 0.12 eV at a 1/4 alloy concentration [3, 64] while Ni alloyed with Co lowers the d-band center by 0.06 eV [65] or 0.11 eV [66] at a 1/2 alloy concentration. Here, the d-band center is lowered by 0.05 eV for the (111) Cu alloy and by 0.02 eV for the (111) Co alloy, which is expected for a lower 1/9 alloy concentration than the references cited above. Alloying Ni with all remaining elements shifts the d-band center in the positive direction.

The ensemble effect in an alloy surface accounts for changes in the catalytic properties of the surface due to changes in the chemical composition of the adsorption site. To understand the ensemble effect, the range of binding energies on the different alloy surfaces is calculated for each
adsorbate as the difference between the most strongly bound adsorbate and the most weakly bound adsorbate at each unique site. For example, at the fcc-1 site O binds most strongly (-3.89 eV) to Ni alloyed with V and most weakly (-2.60 eV) to Ni alloyed with Cu and has a range of 1.29 eV. The ranges for only the unique hollow sites are shown in Table 8, but the same trends are observed for all binding sites, as can be calculated from the Supporting Information.

Table 8. Binding energy range, eV, of O, C, and CO over the twelve alloy surfaces at each unique hollow site. For site locations, refer to Figure 1. CO binding at the hcp-1 and fcc-1 sites was not stable. The O binding range at the hollow-1 site does not include Ni alloyed with W and the C binding range at the hcp-1 and fcc-1 sites do not include Ni alloyed with Al, W, Nb, or Ti.

<table>
<thead>
<tr>
<th></th>
<th>O range</th>
<th>C range</th>
<th>CO range</th>
</tr>
</thead>
<tbody>
<tr>
<td>hollow-1</td>
<td>0.90</td>
<td>0.60</td>
<td>0.43</td>
</tr>
<tr>
<td>hcp-1</td>
<td>1.33</td>
<td>0.62</td>
<td>---------</td>
</tr>
<tr>
<td>fcc-1</td>
<td>1.29</td>
<td>0.53</td>
<td>---------</td>
</tr>
<tr>
<td>hollow-2</td>
<td>0.06</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>hcp-2</td>
<td>0.13</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>fcc-2</td>
<td>0.14</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>hollow-3</td>
<td>0.10</td>
<td>0.25</td>
<td>0.12</td>
</tr>
<tr>
<td>hcp-3</td>
<td>0.09</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>fcc-3</td>
<td>0.12</td>
<td>0.10</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The binding energy range for all adsorbates at sites neighboring an alloying atom are much larger than for Ni-only sites, suggesting that the chemical makeup of the adsorption site has a large influence on the binding energy of the adsorbate. The ranges of binding energies adjacent to the alloying atom are almost two times larger for O than for C or CO. At Ni-only sites, C has the largest range, although it is less than half the range of C at sites neighboring the alloying atom.

Figure 2 shows the binding energy of the C, CO, and O adsorbates on the (100) and (111) facets versus the shift in d-band center for each Ni-based alloy surface. The binding energies plotted in black, blue, and red are at the most common strongest binding sites across the alloy surfaces and correspond to the hollow-3 and hcp-2 sites for both C and CO on the (100) and (111) facets, respectively, and the hollow-1 and fcc-1 sites for O on the (100) and (111) facets, respectively. Plotted in gray are binding energies of each adsorbate at the most stable binding site if the binding site is different than the most common binding site. The trendlines are for each adsorbate at the most common binding site.
Figure 2. Binding energy of C, CO, and O adsorbates versus the shift in d-band center of the alloyed (100) and (111) surfaces. Colored points (dark in black and white) represent binding energies at the most common strongest site, as indicated in the figure. The binding of O on Ni(100) alloyed with W is not stable at the hollow-1 site. Gray points (light in black and white) represent binding energies at the most stable site if the site is different from the most common site.

All trendlines for the binding energies as a function of the d-band center shift in Figure 2 have a negative slope, indicating that surfaces with higher d-band centers bind adsorbates more strongly, in good agreement with the d-band model for different transition metals proposed by Hammer and Nørskov [61-63]. According to Hammer and Nørskov’s d-band model, surfaces with a high d-band center (Ni alloyed with V, Nb, Ti, and Cr) should bind the adsorbates strongest and surfaces with a low d-band center (pure Ni and Ni alloyed with Cu, Co, Fe, Al, W, Mo, and Mn) should bind adsorbates weakest, as is seen here. The only exception is Ni alloyed with W and Mo, which have a lower d-band center than would be expected for how strongly they bind the adsorbates. The most negative trendline slopes in Figure 2 are for O binding, which is bound adjacent to the alloying atom, while the C and CO binding slopes, with C and CO bound at Ni-only sites, have only a slightly negative slope. The difference between sites adjacent to the alloying atom and Ni-only sites suggests that the ensemble effect plays a role in the change in adsorbate binding. While the ligand effect plays a small role in changing the adsorbate binding energies, the difference in binding energies on the different alloy surfaces is dominated by the ensemble effect.

3.5 Carbon Monoxide Reactions

Multiple reaction mechanisms for C-Ni formation from CO have been proposed in the literature, such as the CO dissociation reaction $\text{CO} \rightarrow \text{C} + \text{O}$ and the Boudouard reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ [74, 75]. Both reactions are examined here from a thermodynamic perspective using gas phase CO as the reference species when comparing reactant and product energies.

For CO dissociation using the gas phase CO reference state, the CO reactant energy is the same as the CO binding energy reported in Section 3.3, but the C+O product energy is calculated differently than the individual O and C adsorbates reported in Sections 3.1 and 3.2. The reactant energy, product energy, and reaction energy for CO dissociation on the (100) and (111) facets of
all Ni-based alloy surfaces are shown in Table 9. In all instances, the binding energies correspond to the adsorbate being in its minimum energy adsorption site, and the C+O product energy corresponds to the two adsorbates being infinitely far apart.

Table 9. Effects of substituting an alloying atom for a single Ni surface atom on CO dissociation reaction energies on the (100) and (111) facets of Ni-based alloys. Reactant energy, product energy, and net reaction energy (eV) are shown relative to one CO molecule in the gas phase.

<table>
<thead>
<tr>
<th>Alloying Atom</th>
<th>E(CO&lt;sub&gt;ads&lt;/sub&gt;)</th>
<th>E(C&lt;sub&gt;ads&lt;/sub&gt;+O&lt;sub&gt;ads&lt;/sub&gt;)</th>
<th>E&lt;sub&gt;rxn&lt;/sub&gt;</th>
<th>E(CO&lt;sub&gt;ads&lt;/sub&gt;)</th>
<th>E(C&lt;sub&gt;ads&lt;/sub&gt;+O&lt;sub&gt;ads&lt;/sub&gt;)</th>
<th>E&lt;sub&gt;rxn&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (no alloy)</td>
<td>-1.97</td>
<td>-2.38</td>
<td>-0.42</td>
<td>-1.94</td>
<td>-0.71</td>
<td>1.23</td>
</tr>
<tr>
<td>Cu</td>
<td>-1.98</td>
<td>-2.40</td>
<td>-0.42</td>
<td>-1.96</td>
<td>-0.78</td>
<td>1.18</td>
</tr>
<tr>
<td>Co</td>
<td>-1.98</td>
<td>-2.46</td>
<td>-0.48</td>
<td>-1.93</td>
<td>-0.78</td>
<td>1.14</td>
</tr>
<tr>
<td>Fe</td>
<td>-1.97</td>
<td>-2.53</td>
<td>-0.56</td>
<td>-1.94</td>
<td>-0.85</td>
<td>1.10</td>
</tr>
<tr>
<td>Al</td>
<td>-2.02</td>
<td>-2.59</td>
<td>-0.58</td>
<td>-2.01</td>
<td>-0.97</td>
<td>1.04</td>
</tr>
<tr>
<td>Mn</td>
<td>-1.98</td>
<td>-2.63</td>
<td>-0.65</td>
<td>-1.97</td>
<td>-1.05</td>
<td>0.91</td>
</tr>
<tr>
<td>Cr</td>
<td>-2.14</td>
<td>-3.07</td>
<td>-0.92</td>
<td>-2.01</td>
<td>-1.66</td>
<td>0.35</td>
</tr>
<tr>
<td>Nb</td>
<td>-2.05</td>
<td>-3.18</td>
<td>-1.13</td>
<td>-2.00</td>
<td>-1.54</td>
<td>0.46</td>
</tr>
<tr>
<td>Ti</td>
<td>-2.20</td>
<td>-3.29</td>
<td>-1.09</td>
<td>-2.04</td>
<td>-1.74</td>
<td>0.30</td>
</tr>
<tr>
<td>V</td>
<td>-2.06</td>
<td>-3.32</td>
<td>-1.26</td>
<td>-2.02</td>
<td>-1.77</td>
<td>0.25</td>
</tr>
<tr>
<td>Mo</td>
<td>-2.06</td>
<td>-3.48</td>
<td>-1.41</td>
<td>-1.99</td>
<td>-1.72</td>
<td>0.28</td>
</tr>
<tr>
<td>W</td>
<td>-2.07</td>
<td>-3.70</td>
<td>-1.63</td>
<td>-1.99</td>
<td>-1.81</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The CO dissociation reaction is exothermic on the (100) facet and endothermic on the (111) facet for all Ni-based alloy surfaces. The reaction energy on the pure Ni surface is -0.42 eV on the (100) facet and 1.23 eV on the (111) facet, similar to previous calculations which find CO dissociation reaction energies of -0.36 eV [41], 0.12 eV [42], and 0.82 eV [52] on the (100) facet and 1.35 eV [43], 1.90 eV [42], and 2.60 eV [52] on the (111) facet. CO dissociation becomes more favorable in the presence of an alloying atom, with each alloying atom affecting CO dissociation similarly on both facets. The CO dissociation reaction becomes increasingly exothermic on the (100) facet with the alloying atom as (Ni, Cu) > Co > (Fe, Al) > Mn >> Cr > Ti > Nb > V > Mo > W and increasingly less endothermic on the (111) facet with the alloying atom as Ni > Cu > Co > Fe > Al > Mn >> Nb > Cr > (Ti, Mo) > V > W.

The CO reactant energy is similar for all surfaces and both facets, but a wide range of C+O product energies exists on the different alloy surfaces and facets, shown visually in Figure 3. The C+O products become more thermodynamically favorable with the alloying atom as Ni > (Cu, Co) > Fe > Al > Mn >> Nb > Cr > (Mo, Ti) > V > W on the (111) facet and as (Ni, Cu) > Co > Fe > Al > Mn >> Cr > Nb > Ti > V > Mo > W on the (100) facet. There is a divide on each facet between the surfaces that bind C+O weakly and have a more endothermic CO dissociation reaction energy (pure Ni surface and Ni alloyed with Cu, Co, Fe, Al, and Mn) and those that bind C+O strongly and have a more exothermic CO dissociation reaction energy (Ni alloyed with W, Mo, V, Ti, Nb, and Cr).
The trends in C+O product binding energies show similarities to the trends of both individual C binding and individual O binding behavior. The binding behavior of C+O is similar to C binding in that the adsorbate binding is much stronger on the (100) facet than the (111) facet. The difference in binding energies of both O and CO on the (100) and (111) facets is small compared to the difference of C binding on the two facets, so the binding of C dominates the reaction energy trends when comparing the two facets. The C+O products exhibit similar behavior to O binding in that they both have a wide range of binding energies over the different alloy surfaces. The difference in binding strength of either C or CO on the different Ni-based alloy surfaces is much smaller than the O binding energy differences for different alloy surfaces, so the binding of O dominates the reaction energy trends when comparing the surfaces of a given facet.

In the Boudouard reaction, the 2CO reactant energy comes from adsorbed CO while the C+CO₂ product energy comes from adsorbed C and gas phase CO₂, as previous DFT studies have found CO₂ to bind weakly to the Ni surface [76, 77]. The reactant energy, product energy, and reaction energy for the Boudouard reaction on the (100) and (111) facets for all Ni-based alloy surfaces are listed in Table 10. All reactant and product energies are relative to two gas phase CO molecules and correspond to the adsorbates being infinitely far apart at their lowest energy site.
Table 10. Effects of substituting an alloying atom for a single Ni surface atom on Boudouard reaction energies on the (100) and (111) facets of Ni-based alloys. Reactant energy, product energy, and net reaction energy (eV) are shown relative to two CO molecules in the gas phase.

<table>
<thead>
<tr>
<th>Alloying Atom</th>
<th>(100) facet</th>
<th>(111) facet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(2CO\text{ads})</td>
<td>E(C\text{ads}+CO\text{2})</td>
</tr>
<tr>
<td>Ti</td>
<td>-4.39</td>
<td>-3.13</td>
</tr>
<tr>
<td>Cr</td>
<td>-4.28</td>
<td>-3.04</td>
</tr>
<tr>
<td>Al</td>
<td>-4.03</td>
<td>-3.05</td>
</tr>
<tr>
<td>V</td>
<td>-4.11</td>
<td>-3.13</td>
</tr>
<tr>
<td>W</td>
<td>-4.15</td>
<td>-3.21</td>
</tr>
<tr>
<td>Mo</td>
<td>-4.13</td>
<td>-3.19</td>
</tr>
<tr>
<td>Cu</td>
<td>-3.96</td>
<td>-2.98</td>
</tr>
<tr>
<td>Nb</td>
<td>-4.10</td>
<td>-3.18</td>
</tr>
<tr>
<td>Ni (no alloy)</td>
<td>-3.93</td>
<td>-2.97</td>
</tr>
<tr>
<td>Fe</td>
<td>-3.94</td>
<td>-3.00</td>
</tr>
<tr>
<td>Co</td>
<td>-3.96</td>
<td>-2.99</td>
</tr>
<tr>
<td>Mn</td>
<td>-3.96</td>
<td>-3.02</td>
</tr>
</tbody>
</table>

The Boudouard reaction is endothermic on all surfaces and both facets, with the (111) facet having the most endothermic reactions. The reaction becomes less endothermic and more favorable with the alloying atom as (Ti, Cr) > (Al, Cu, V, Co, Ni, Mn, Mo, Fe, W, Nb) on the (100) facet and as (W, Al, V, Mo, Ti) > (Nb, Cr, Fe, Cu, Ni, Mn, Co) on the (111) facet. The reaction energies within each facet are very similar, with a total range of 0.34 eV on the (100) facet and 0.13 eV on the (111) facet, however between the two facets the reaction energies are very different, with an average reaction energy difference of 1.33 eV between the two facets. The small reaction energy ranges are due to small reactant energy ranges, 0.46 eV and 0.24 eV on the (100) and (111) facets, respectively, and small product energy ranges, 0.24 eV and 0.15 eV on the (100) and (111) facets, respectively. The small reactant energy ranges and small reactant energy differences between the two facets occur because CO binds similarly to all surfaces and both facets, as discussed in Section 3.3, with a total reactant energy range of 0.54 eV over both facets. The small product energy range on each facet and large product energy difference and reaction energy difference between the two facets are due entirely to differences in C binding, as discussed in Section 3.2, as the energy of the gas phase CO\text{2} product is the same for all surfaces. The reactant and product energies are shown visually in Figure 4.
In a microkinetic model study on steam methane reforming, Blaylock et al. [78] calculated energies of the Boudouard reaction and the CO dissociation reaction on the Ni(111) surface at 800°C, 1 bar, and 1 ML coverage, and determined the CO dissociation reaction enthalpy to be 1.49 eV, in reasonable agreement with our calculation of 1.23 eV. Blaylock et al. [78] calculated Boudouard reaction energies in a number of different ways and found a reaction enthalpy of 1.77 eV assuming the CO₂ product remains adsorbed, 2.06 eV with a desorbed CO₂ product, and 1.49 eV with dissociation of the CO₂ product into CO+O. Their calculation of 2.06 eV for the Boudouard reaction producing desorbed CO₂ is in reasonable agreement with our calculation of 2.30 eV.

The CO dissociation reaction is thermodynamically more favorable than the Boudouard reaction on the pure Ni surface by 1.38 eV on the (100) facet and 1.07 eV on the (111) facet. The addition of an alloying element on either facet causes the CO dissociation reaction to become more exothermic but has little effect on the Boudouard reaction energies, causing the CO dissociation reaction to become even more favorable than the Boudouard reaction. The largest difference between the two reaction mechanisms is when the alloying element is W, in which the CO dissociation reaction is more favorable than the Boudouard reaction by 2.56 eV on the (100) facet and 2.21 eV on the (111) facet.
The overall CO₂ breakdown starts with CO₂ dissociation into CO and O, followed by CO breakdown via either direct CO dissociation or the Boudouard reaction. Figures showing the energies for the complete CO₂ breakdown mechanisms via CO dissociation and the Boudouard reaction are included in the Supporting Information. These figures are similar to Figures 3 and 4, but are shifted down by the binding energy of O to account for the co-adsorption of CO and O and are referenced to gas phase CO₂ instead of gas phase CO.

4. Conclusions

The results presented herein give a well-rounded look at the products of CO₂ breakdown on Ni surfaces alloyed with the most common alloying elements in industrial applications. The binding of O occurs at alloy-rich sites for all surfaces except Ni alloyed with Cu, in which Ni-rich sites are more stable, while the binding of C and CO occur at Ni-rich sites for the majority of the surfaces. The O adsorption energy changes significantly with the alloying elements, dividing the surfaces into a group that binds O strongly (pure Ni and Ni alloyed with Cu, Co, Fe, Al, or Mn) and a group that binds O more weakly (Ni alloyed with W, Mo, V, Cr, Nb, or Ti). This divide also exists for the C and CO adsorbates, although it is much less pronounced. All three adsorbates bind stronger on the (100) facet than the (111) facet for the majority of the Ni-based alloy surfaces, with C binding significantly stronger to the (100) facet and O and CO binding only slightly stronger to the (100) facet. The CO binding energy is comparable for all Ni-based alloy surfaces studied and both facets. The effect that the alloying atom has on the binding energies of O, C, and CO is due mainly to the ensemble effect rather than the ligand effect.

The breakdown of CO can proceed via CO dissociation or the Boudouard reaction. The CO dissociation reaction is thermodynamically more favorable than the Boudouard reaction on the (100) and (111) facets of all Ni-based alloy surfaces considered herein. Both CO breakdown mechanisms are much more favorable on the (100) facet than the (111) facet, due to the adsorbed C product being much more stable on the (100) facet. CO dissociation is exothermic on the (100) facet and endothermic on the (111) facet, while the Boudouard reaction is endothermic on both facets. The Boudouard reaction energies are similar for all alloy surfaces within a given facet, while CO dissociation has a wide reaction energy range within each facet. The wide CO dissociation reaction energy ranges stem from the adsorbed O product having wide binding energy ranges, causing CO to dissociate more favorable on Ni alloyed with W, Mo, V, Cr, Nb, or Ti than on the pure Ni surface or Ni alloyed with Cu, Co, Fe, Al, or Mn.

The effect of substituting an alloying element into a Ni surface has been explored for the alloying elements Al, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ti, V, and W on the (100) and (111) facets. This is the first comprehensive study examining a wide range of Ni-based alloys on two common facets in a consistent manner. The knowledge gained from the binding energies of O, C, and CO on the different surfaces and the CO breakdown mechanisms via CO dissociation and the Boudouard reaction will be helpful for understanding corrosion by O and C on Ni-based alloy surfaces for applications such as those involving supercritical CO₂.

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