Elucidating the Role of Strain in Catalysis toward Modulating Surface-Adsorbate Interactions and Tuning Catalytic Activity

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Keywords: DFT, adsorption, ammonia synthesis, d-band, scaling relations, volcano plot
**Abstract**

Strain has been shown to modulate adsorption and reactions on metal surfaces. While its effect on surface-adsorbate interactions has been rationalized, an understanding of the electronic factors that drive these interactions and their consequences on catalytic activity is lacking. In this work, we use *ab initio* density functional theory (DFT) and microkinetic modeling (MKM) to develop electronic descriptors that govern the effect of biaxial strain in the modulation of interactions between adsorbate and transition states with catalyst surface and report its significance in enhancing the activity of fcc Pd(111) in the synthesis of ammonia (NH₃), an important renewable-energy and hydrogen (H₂) vector. We established the p-band center (p_{center}) of the adsorbates and transition states (TS) and the hybridized d-band center (d_{center}) of the surface metal as key electronic descriptors for adsorbate and TS energy variations with strain. Specifically, the p_{center} of the adsorbates is lowest for the sites with the strongest adsorption, and the upshift of the d_{center} of the surface metal atoms is greatest for the adsorption site with the highest strain susceptibility (*i.e.*, the change in adsorption energy per unit applied strain). Importantly, we showed significant deviations in scaling relations with strain compared to periodic scaling relationships, both for adsorption and reaction. Over a net 4% tensile strain (±2%), the d_{center} of Pd(111) moved upward by 0.21 eV, enhancing N₂ dissociation, the rate-determining step in NH₃ synthesis by ~37×, and the p_{center} in N bound to the catalyst surface moved downward in the adsorbed state and upward in the TS (*i.e.*, electron density shifted toward the bonding and anti-bonding states, respectively). Thus, tensile strain played a dual role in enhancing N₂ dissociation, strengthening the adsorption of atomic N and weakening the N-N bond in the TS. We then evaluated N₂ dissociation at 3/4 ML H-coverage under industrial conditions (150 atm H₂, 50 atm N₂, and 723 K), revealing the effect of tensile strain on the rate enhancement to be nearly two orders of magnitude greater (~3273× vs. ~37×) at
high surface coverages. Overall, this study highlights strain as a useful design tool to improve catalytic activity.
INTRODUCTION

In heterogeneous catalysis, the adsorption of adsorbates, reaction intermediates and the stability of transition states (TSs) directs the activity and selectivity of a catalyst.\textsuperscript{1, 2} For several reactions relevant to energy and chemical conversion, adsorption energies have been used as descriptors to predict catalytic performance.\textsuperscript{3-5} Catalytic activity is strongly linked to the adsorption of key reaction intermediates and limited by the peak of the Balandin-Sabatier “volcano”.\textsuperscript{6, 7} In simple terms, the adsorption of a key substrate must be strong enough to facilitate a reaction but not so strong that it hinders the reaction or acts as a poison. As such, the adsorption energy of a key intermediate could act as a descriptor of catalytic activity.\textsuperscript{8-11} For instance, in ammonia (NH\textsubscript{3}) synthesis, the adsorption energy of atomic N is used as a descriptor for catalytic activity on transition-metal surfaces.\textsuperscript{12, 13} The relation between adsorption energy and reaction rates can be represented using the Bronsted-Evans-Polanyi (BEP) relationship.\textsuperscript{14, 15} In NH\textsubscript{3} synthesis, BEP relationships for N\textsubscript{2} dissociation estimate the activation energy of N\textsubscript{2} dissociation from the enthalpy of N\textsubscript{2} dissociation (represented by the dissociative adsorption energy of N), thus enabling the use of N adsorption energy as a descriptor to estimate catalyst reactivity.\textsuperscript{16}

As adsorption is a key descriptor for the reactivity of a catalyst, the key to modulating catalytic activity hinges on understanding how adsorption is related to the fundamental electronic and structural properties of the adsorbate and the catalyst. The \textit{d-band} theory relates the electronic structure of the metal to its interactions with adsorbates.\textsuperscript{1, 17} Generally, as the \textit{d-band} of a metal narrows and gets closer to the Fermi level (moves upward), adsorption is strengthened. From left to right across the periodic table among the transition metals (TMs), as d-orbitals of the metals fill up, the d-band center (d\textsubscript{center}) moves downward, i.e., away from the Fermi level, decreasing the adsorption energy of a given adsorbate.\textsuperscript{1} Moving down from 3d to 5d TMs, the d-orbitals become
more localized, which raises the $d_{\text{center}}$ to maintain constant filling. Strategies such as alloying,\textsuperscript{18, 19} the use of single-atom-catalysts (SACs),\textsuperscript{20} and promoters\textsuperscript{21, 22} have been used to modulate the d-band of the catalyst and, consequently, tune the adsorption strength for key reaction intermediates. However, in such bi-metallic systems, the d-band structure is significantly altered from that of the bulk metals due to its interactions with “unlike” neighboring metal atoms.\textsuperscript{19, 23, 24}

For a bulk TM surface, strain can move the $d_{\text{center}}$ closer or farther away from the Fermi level.\textsuperscript{1, 25} As the atoms are pulled apart (i.e., undergo tensile strain), there is less spatial overlap between their d-orbitals, the d-band narrows (i.e., $d_{\text{width}}$ decreases), and moves upward (i.e., $d_{\text{center}}$ shifts up) to maintain constant filling.\textsuperscript{25} The effect of local strain of a metal surface on adsorption was reported by Gsell et al. for O/Ru(0001).\textsuperscript{26} Subsurface Ar bubbles were shown to create a region of tensile strain on a Ru(0001) surface, where O preferentially adsorbed, compared to the surrounding rim, which was locally compressed. Strain influencing adsorption was rationalized computationally by Mavrikakis et al.\textsuperscript{25}, where they investigated how the lattice expansion of Ru(0001) affected the strength of CO and O adsorption and CO dissociation. They reported that the adsorption of species like N, O, and CO and the dissociation of molecules including CO, CH$_4$, H$_2$, and NO was favored as the $d_{\text{center}}$ moved, establishing $d_{\text{center}}$ as an important descriptor in comparing catalytic surfaces and their relative adsorption energies.\textsuperscript{25}

A typical strategy to strain a catalytically active metal is growing it on a host metal with a different lattice constant.\textsuperscript{1} This can be achieved through a core-shell configuration wherein the core imposes its lattice constant onto the shell.\textsuperscript{27-30} Such implementations of strain using pseudomorphic (i.e., overlayer retaining the lattice constant of the substrate) catalysts have been employed to enhance electrocatalytic activity.\textsuperscript{28, 31} For instance, Strasser et al. investigated the effect of strain on the activity of a dealloyed Pt-Cu core-shell catalyst in the oxygen reduction
reaction (ORR). They created core-shell particles with a Pt shell and Pt-Cu core wherein the smaller lattice parameter of Cu was imposed on the Pt shell, causing compressive strains of up to ~4.5% in the exposed Pt layer, which lowered its d_{center}, and enhanced overall ORR activity.\textsuperscript{28}

Ultra-thin metal catalysts\textsuperscript{32,33} and alloying,\textsuperscript{34-36} to intrinsically strain the active metal centers are other strategies to implement strain to enhance catalytic activity. However, these approaches involve synthesis techniques requiring atomic-layer precision that can lead to secondary effects, such as structural inhomogeneity of the surface, contributing to changes in catalytic activity.\textsuperscript{32} In addition to strain, sub-surface metal atoms influence the electronic structure of the supported monolayer (i.e., shows the ligand effect), which stems from the hybridization of the d-states of the surface and sub-surface metal atoms.\textsuperscript{37-39} As such, decoupling the effect of strain from the ligand effect to evaluate its impact on catalytic activity is desired, and applying uniform external strain to the metal is a strategy toward that end.

Peterson and coworkers have extensively studied the effect of strain on adsorption and catalytic activity using experimental and computational tools.\textsuperscript{31,37,40-45} Experimentally, uniform strain was achieved by synthesizing TM thin-films on polymer substrates and applying strain onto the substrate. Computationally, they rationalized the effect of strain on adsorption to site coordination, adsorbate unsaturation, and mechanical models.\textsuperscript{44,46,47} Khorshidi et al. showed that adsorbates bonded to different adsorption sites could exhibit directionally opposite responses to strain and related the binding strengths to the strained surface using an “eigenstress” model. Briefly, an adsorbate either pushes the surface metal atoms outward or pulls them inward during adsorption. For instance, on Pt(100), NH\textsubscript{2} binds to the bridge site and N to the four-fold site. They exert directionally opposite forces on the unstrained surface atoms (NH\textsubscript{2} induces compression onto the surface atoms, and N induces tension). Thus, under externally applied tension, NH\textsubscript{2} is stabilized,
and N is destabilized. Scaling relationships predict similar directional responses for both adsorbates, while the eigenstress model indicates a directionally opposite response, thus suggesting strategies for breaking scaling relationships.\textsuperscript{42} Zeng et al. systematically investigated the adsorption of CH\textsubscript{x}, NH\textsubscript{x}, and OH\textsubscript{x} species on Cu, Pd, Ag, Pt, and Au fcc(111) surfaces under biaxial strain (-2\% to 2\%).\textsuperscript{44} They showed that metals with large d-orbitals have a larger d-d coupling matrix and, hence, larger adsorption strain susceptibilities (i.e., the slope of the adsorption energy vs. strain plot). The sites with higher coordination numbers (CN) on the fcc(111) surface were more susceptible to strain due to their larger d-d coupling matrices, as the number of metal atoms participating in adsorption increases with site CN.

While these studies explain how strain affects the binding of isolated substrates on various surfaces, they do not give insights into its consequences on catalytic activity and selectivity. A recent DFT study by Wittreich et al. applied dynamic strain on Ru and studied its impact on NH\textsubscript{3} synthesis activity.\textsuperscript{13} They showed that the dynamically strained catalyst could show similar activity at 320 °C and 20 atm compared to industrial reaction conditions (400 °C and 200 atm). A key to achieving this rate enhancement was that the rate-determining step (RDS) changed under tensile and compressive strains, which enabled both strain directions to contribute to the rate increase. However, if the RDS remains unchanged under both tensile and compressive strains, dynamic strain may not significantly enhance the overall rate. In this regard, understanding how strain affects adsorption and the stability of TSs and, therefore, the kinetics of a reaction with multiple elementary steps is desired. Furthermore, relating surface-adsorbate interactions using fundamental electronic properties of the adsorbate and metal surface could identify electronic descriptors to predict the effect of strain on adsorption on different metallic surfaces. Finally, a comparison of the rate enhancements achievable through strain and the established periodic
catalytic activity trends using BEP-like relationships is lacking and could elucidate the role of strain as a complementary catalyst design tool to improve catalytic activity.

In this work, we employ DFT calculations and microkinetic modeling (MKM) to detail the role of strain on the energies of adsorption and TSs and its net effect on modulating catalytic activity. The synthesis of NH₃, a promising renewable energy and hydrogen vector, was chosen as a model reaction.⁴⁸ The overall reaction on a catalyst is limited by NH₃ hydrogenation or N₂ dissociation, resulting in a volcano plot.¹², ⁴⁹ Pd is a widely used heterogeneous catalyst⁵⁰-⁵³ that shows relatively poor NH₃ synthesis activity due to its weak N binding and N₂ dissociation (the RDS) ability,¹⁶ thus being a suitable candidate to study the activity enhancement by strain. First, we highlight the electronic interactions between adsorbates and the catalytic surface and use electronic properties such as the p-band center (p_center) of the adsorbate and the hybridized d_center of the surface metal atoms to rationalize preferential adsorption and adsorbate strain susceptibilities. Using a mean-field MKM, we study the effect of strain on the NH₃ synthesis activity of Pd. To study the influence of lateral adsorbate interactions on the modulation of catalytic activity, we assess the effect of strain on reaction kinetics at surface coverage (3/4 monolayer H-coverage) under industrially relevant conditions (150 atm H₂, 50 atm N₂, and 723 K), uncovering the pronounced effect of strain in tuning surface reactivity at high coverages.
COMPUTATIONAL METHODS

Density-functional theory calculations: Density-functional theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP version 6.3.0). Exchange and correlation functions were described by the generalized gradient approximation (GGA) based on the Perdew-Burke-Ernzerhof (PBE) functional. Valence electron and ionic core interactions were described using the projector augmented wave (PAW) method. The plane-wave basis set was set to a kinetic energy cut-off of 800 eV for gas-phase calculations and 500 eV for cell optimizations and all the surface calculations. Dispersion corrections were added using the method of Grimme with zero damping (DFT-D3). 10^{-4} eV and 0.01 eV/Å were taken as the energy and force convergence criteria for electronic and ionic relaxations, respectively. Quasi-Newton algorithm was used to relax the ions, and Methfessel-Paxton smearing with a smearing parameter of 0.1 eV was applied with the energy extrapolated to zero smearing. A 4x4x1 Monkhorst pack k-point grid was used to sample the Brillouin zone for all surface calculations, while a 1x1x1 k-point grid was used for the gas-phase calculations.

The fcc Pd(111) surface was modeled with the aid of VESTA by first performing a bulk relaxation in VASP, followed by constructing a 2x2x1 supercell with the exposed (111) facet. The bulk Pd lattice constant was calculated to be 3.8859 Å, compared to an experimental value of ~3.8890 Å. The supercell consisted of 4 atomic layers, and surface calculations were performed by fixing the bottom two layers and relaxing the top two layers. The calculations performed were non-spin-polarized due to the non-magnetic nature of the system. We further compared the results from spin-polarized calculations with non-polarized calculations for the adsorption of H, N, N2, and NH on the Pd (111) surface, which showed insignificant energy differences (Table S1).
Biaxial strain was applied by varying the lattice parameters of the supercell in the x and y directions:

\[
 s = \frac{l - l_0}{l_0} \times 100\%
\]  

(1)

where \( l \) and \( l_0 \) are the imposed and equilibrium lattice parameters, respectively. Therefore, a biaxial strain of \( \varepsilon \% \) (-2% to 2%) was achieved by varying both lattice parameters by \( \varepsilon \% \) (-2% to 2%). A vacuum of 10 Å was introduced in the z-direction to remove the interactions from the neighboring periodic images in the z-direction. Adsorption energies were calculated as given in Equation 2 below:

\[
 E_{\text{ads}} = E_{s+a} - (E_s + E_a)
\]

(2)

where \( E_{s+a} \), \( E_s \), and \( E_a \) are the energies of the surface-adsorbate system, clean surface, and free adsorbate, respectively. The adsorbate energies were calculated with reference to the gas phase energies of \( \text{N}_2 \) and \( \text{H}_2 \). Zero-point energy (ZPE) and thermodynamic corrections were applied following a vibrational analysis using the VASPKIT package. Transition states (TSs) were identified using the climbing image nudged elastic band (CI-NEB) and improved dimer (IDM) methods and confirmed with vibrational analysis showing only one imaginary frequency.

**Microkinetic model:** The \( \text{NH}_3 \) synthesis reaction was modeled with the following elementary steps, consistent with literature and a mean-field approximation:

\[
 \text{H}_2(g) + 2* \rightarrow 2\text{H}^*
\]

(3)

\[
 \text{N}_2(g) + * \rightarrow \text{N}_2^*
\]

(4)

\[
 \text{N}_2^* + * \rightarrow 2\text{N}^*
\]

(5)

\[
 \text{N}^* + \text{H}^* \rightarrow \text{NH}^* + *
\]

(6)

\[
 \text{NH}^* + \text{H}^* \rightarrow \text{NH}_2^* + *
\]

(7)
\[ \text{NH}_2^* + H^* \rightarrow \text{NH}_3^* + * \] \hspace{1cm} (8)

\[ \text{NH}_3^* \rightarrow \text{NH}_3(g) + * \] \hspace{1cm} (9)

From the collision theory,\(^1\) rate constants for the adsorption steps (3 and 4) were calculated as:

\[ k_{\text{ads,H}} = (1 - \theta)^2 \frac{-\Delta G^\ddagger}{N_0 \sqrt{2 \pi m_H k_B T}} P_{\text{total}} \] \hspace{1cm} (10)

and,

\[ k_{\text{ads,N}_2} = (1 - \theta) \frac{-\Delta G^\ddagger}{N_0 \sqrt{2 \pi m_{N_2} k_B T}} P_{\text{total}} \] \hspace{1cm} (11)

where \((1 - \theta)^2\) and \((1 - \theta)\) is the fraction of vacant sites (represented by * in steps 3 and 4) for the dissociative and associative adsorption of H and N, respectively. \(\theta\) is the initial coverage (1/8 ML, i.e., one adsorbate on the surface), \(\Delta G^\ddagger\) is the free energy of activation for adsorption, \(P_{\text{total}}\) is the total reaction pressure (200 atm), \(N_0\) is the number of adsorption sites per surface area (supercell surface area), \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature (723 K), and \(m\) is the adsorbate mass. Exergonic adsorption for \(H_2\) (dissociative \(H_2\) adsorption) was assumed to proceed without activation (i.e., \(\Delta G^\ddagger = 0\)). For the surface reactions and \(\text{NH}_3\) desorption, the forward and backward rate constants were calculated from the Eyring equation:

\[ k = \frac{k_B T}{h} e^{-\frac{-\Delta G^\ddagger}{k_B T}} \] \hspace{1cm} (12)

where \(h\) is Planck’s constant and \(\Delta G^\ddagger\) is the free energy of activation. The equilibrium constant for all the elementary steps was calculated as follows:

\[ K_n = \frac{k_n}{k_{-n}} \] \hspace{1cm} (13)
where \( k_n \) and \( k_{-n} \) are the forward and backward rate constants, respectively. To identify the rate-determining step (RDS) and calculate the turnover frequency (TOF), all reactions were assumed to be irreversible, and the apparent rate constants were computed as follows:

\[
k'_1 = k_1 \tag{14}
\]
\[
k'_1 = k_1 \tag{15}
\]
\[
k'_3 = k_3 K_2 \tag{16}
\]
\[
k'_4 = k_4 (K_1 K_2 K_3)^{\frac{1}{2}} \tag{17}
\]
\[
k'_5 = k_5 K_4 K_1 (K_2 K_3)^{\frac{1}{2}} \tag{18}
\]
\[
k'_6 = k_6 K_5 K_4 K_1^2 (K_2 K_3)^{\frac{1}{2}} \tag{19}
\]
\[
k'_7 = k_7 K_6 K_5 K_4 K_1^2 (K_2 K_3)^{\frac{1}{2}} \tag{20}
\]

**Analysis of coverage effects:** To identify a representative coverage of adsorbates on the Pd (111) surface under reaction conditions, the free energy of the surface-adsorbate system was calculated when different adsorbates were singly and co-adsorbed at their preferred sites. The change in free energy of adsorption (\( \Delta G_{ads} \)) was then calculated with respect to the energy of the clean surface (no adsorbates) and the chemical potentials of the surrounding gas phase \( \text{N}_2 \) and \( \text{H}_2 \):

\[
\Delta G_{ads} = G_{s+a} - (E_s + \frac{n_H}{2} \mu_{\text{H}_2(g)} + \frac{n_N}{2} \mu_{\text{N}_2(g)}) \tag{21}
\]

where \( G_{s+a} \) is the free energy of the surface-adsorbate system, \( n_H \) and \( n_N \) are the number of H and N atoms adsorbed, respectively, and \( \mu \) the gas phase chemical potentials of \( \text{H}_2 \) and \( \text{N}_2 \), which are calculated as:

\[
\mu = G^0_{(g)} + k_B T + \ln \left( \frac{P}{P_0} \right) \tag{22}
\]
where $G^0_{\text{(g)}}$ is the gas phase free energy at standard pressure $P_0 = 1$ atm, and $P$ is the partial pressure under reaction conditions (150 atm H$_2$, 50 atm N$_2$, and 723 K).
RESULTS AND DISCUSSION

Adsorption and Strain. We first evaluated the electronic properties of the clean Pd(111) slab under strain by analyzing the density of states (DOS). As biaxial strain was applied to the Pd surface, its lattice parameters were disturbed from their equilibrium values (a=9.33 Å and b=5.38 Å of the Pd(111) supercell). Compressive and tensile strain both raised the total energy (i.e., the energy of the slab per Pd atom, shown in Figure S1). The projected DOS (PDOS) onto the d-orbitals of the Pd atoms are shown in Figure 1(a). In line with the d-band theory, the width of the d-band (dwidth, calculated here as energy range with ~97% occupancy about the d-band center (dcenter)) narrowed, and the dcenter moved up (i.e., closer to the Fermi level) as tensile strain was applied. Specifically, the dcenter moved up from -1.86 eV to -1.65 eV with respect to the Fermi level, and the dwidth reduced from 7.87 eV to 6.73 eV as the strain varied from -2% to 2%. Crucially, the shape of the d-band was well retained. The upward shift in dcenter and the narrowing of dwidth followed a linear trend with the applied biaxial tensile strain (Figure 1(b)). The values of dcenter and dwidth are summarized in Table S2. These features highlight the strong correlation between strain and the electronic properties of the metal surface and its use as a potential descriptor.
Figure 1. (a) Projected density of states (PDOS) on the d-orbitals of the surface Pd atoms of -2\%, 0\%, and 2\% strained Pd(111). The dashed lines are the d-band centers (d_{center}). (b) Variation of the d_{center} and the d-band width (d_{width}) with strain. The dashed lines are shown as linear fits.

The fcc Pd(111) surface has four types of adsorption sites based on site-coordination number (CN), namely top(t), bridge(b), fcc(f), and hcp(h). Figure 2(c) visualizes the adsorption of atomic N on the four sites. The site CNs are 1 for t, 2 for b, and 3 for f and h. Table 1 shows the adsorption energies (E_{ads}) of H, N, and NH_x (x=1,2,3) species on the four sites. Atomic H was adsorbed most favorably on the f site (E_{ads} = -0.59 eV). Atomic N had positive adsorption energies at all sites, with it being highest on the t site (E_{ads} = 3.03 eV). Akin to H, N too adsorbed most favorably on the f site (E_{ads} = 0.51 eV). NH adsorbed favorably on both three-fold sites (i.e., shows negative E_{ads}), with f being the most favorable (E_{ads} = -0.27 eV), while NH_2 and NH_3 were adsorbed on the
$b$ ($E_{ads} = -0.92$ eV) and $t$ ($E_{ads} = -2.03$ eV) sites, respectively. Overall, as the valence of N decreased from N to NH$_3$ (3 to 0), adsorption was preferred on sites with lower coordination. Specifically, N, NH, NH$_2$, and NH$_3$ adsorbed favorably on the $f$, $f$, $b$, and $t$ sites, respectively.

**Table 1.** Adsorption energies reaction intermediates relevant for ammonia (NH$_3$) synthesis with gas-phase N$_2$ and H$_2$ as a reference on the four sites (hcp($h$), fcc($f$), bridge($b$), and top($t$) sites) of Pd(111). Bolded values represent the most favorable adsorption site.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Top ($t$)</th>
<th>Bridge ($b$)</th>
<th>fcc ($f$)</th>
<th>hcp ($h$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.11</td>
<td>-0.44</td>
<td><strong>-0.59</strong></td>
<td>-0.55</td>
</tr>
<tr>
<td>N</td>
<td>3.03</td>
<td>1.28</td>
<td><strong>0.51</strong></td>
<td>0.59</td>
</tr>
<tr>
<td>NH</td>
<td>2.28</td>
<td>0.47</td>
<td>-0.27</td>
<td>-0.12</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>-0.22</td>
<td><strong>-0.92</strong></td>
<td>-$^a$</td>
<td>-$^a$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td><strong>-2.03</strong></td>
<td>-1.58</td>
<td>-1.56</td>
<td>-1.55</td>
</tr>
</tbody>
</table>

**Notes:**

$^a$Not applicable as the geometry optimization calculations for NH$_2$ adsorbed at the $f$ and $h$ sites converged to its nearby $b$ site.
Figure 2. Projected density of states (PDOS) on (a) d-orbitals of the surface Pd atoms that bind with N and (b) p-orbitals of the bonded N atom at the hcp(h), fcc(f), bridge(b), and top(t) sites on Pd(111). The bottom panels are PDOS on (a) d-orbitals of the clean surface Pd atoms and (b) p-orbitals of an isolated N atom in the gas phase. The dashed lines with values are the d- and p-band centers of Pd and N, respectively. (c) Top and isometric views of the optimized structures of N adsorbed on the four Pd(111) sites (grey=Pd and blue=N).

Here, we explain the difference in adsorption at different sites using the Newns-Anderson (NA) model. Three factors contribute to the adsorption strength: (1) the d-band filling of the surface metal, (2) the interaction matrix element between the adsorbate and the surface atoms, and (3) the energy difference between the original adsorbate energy level (represented by the p-band and its central moment, p_{center}, for N, and NH_{x} species) and the d_{center} of the surface metal atoms. As the composition of the Pd(111) surface is unchanged, the d-band filling remains constant. For a given surface-adsorbate pair, the energy difference between the original adsorbate level and the surface remains constant regardless of the adsorption site. However, the interaction matrix element between the adsorbate and Pd(111) depends on the adsorption site, as the number of surface atoms involved in the adsorption changes for the different adsorption sites.

When an adsorbate approaches the metal surface, its orbitals interact with the d-band of the metal, and its electron levels broaden and shift downward. The degree of downward movement from the original energy level indicates the strength of the adsorption. In the case of adsorbates binding to the surface through a p-element (e.g., C, N, O, etc.), the position of the p_{center} of the binding atom in the adsorbed state would thus indicate the adsorption strength. This would be the p_{center} of the N atom bonded to the surface Pd atoms in the adsorbed N and NH_{x} species. To evaluate the preferential adsorption of the adsorbates at the various sites, we performed DOS analyses of...
the adsorbed N-based species on the four sites. We have summarized the \( p_{\text{center}} \) of the binding N atom of these adsorbates in Table 2. For visualization, Figure 2(a and b) show the PDOS for the Pd-N bonds (adsorption of atomic N). Figure 2(a) shows the PDOS on the d-orbitals of the Pd atoms bonded to N, and Figure 2(b) shows the PDOS on the p-orbitals of the bonded N atom. The dashed lines indicate the central moments of the respective bands (\( d_{\text{center}} \) of Pd and \( p_{\text{center}} \) of N). Following the NA model, the PDOS in Figure 2(b) showed the splitting of the p-level of N into bonding and anti-bonding levels (above and below the Fermi level, respectively) when adsorbed. It was seen qualitatively that at the \( t \) site, a small electron density was in the bonding states, which increased on the \( b \) site and was greatest at the three-fold \( f \) and \( h \) sites. Here, a lower p-band moment, represented by \( p_{\text{center}} \), indicated greater electron density in the bonding states and, thus, stronger adsorption. The \( p_{\text{center}} \) for N and NH adsorption was lowest at the \( h \) site (also comparable to the \( p_{\text{center}} \) at the \( f \) site), which corresponded to the most negative adsorption energies (Table 1). We must note that while \( f \) was energetically the most favored adsorption site for N and NH, its \( p_{\text{center}} \) values suggest that they were most stable electronically on the \( h \) sites. In general, adsorption at the \( f \) and \( h \) sites were very close energetically and electronically as they both involve adsorption through three surface Pd atoms, and the additional electronic stability at \( h \) can be attributed to the influence of the Pd atom in the sub-surface layer directly below the \( h \) site.71 Importantly, the correlation held very well with respect to the CN, as both N and NH had significantly lower \( p_{\text{center}} \) on the \( f \) and \( h \) (CN=3) sites as compared to the \( t \) (CN=1) and \( b \) (CN=2) sites in line with the adsorption energies. For NH\(_2\) and NH\(_3\), the \( p_{\text{center}} \) was the lowest for the energetically preferred adsorption sites (\( b \) and \( t \), respectively). Taken together, the analysis revealed that the \( p_{\text{center}} \) of the binding adsorbate atom could be used as an electronic descriptor to explain preferential adsorption on specific fcc(111) sites.
Table 2. p-Band centers (p\textsubscript{center}) of the binding N atom of the adsorbed species on the four sites of Pd(111). The bolded values represent the most stable adsorbate electronic states.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Top (t)</th>
<th>Bridge (b)</th>
<th>fcc (f)</th>
<th>hcp (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-1.40</td>
<td>-2.04</td>
<td>-2.32</td>
<td>-2.43</td>
</tr>
<tr>
<td>NH</td>
<td>-2.44</td>
<td>-3.42</td>
<td>-3.81</td>
<td>-3.84</td>
</tr>
<tr>
<td>NH\textsubscript{2}</td>
<td>-3.65</td>
<td>-4.74</td>
<td>-a</td>
<td>-a</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>-6.28</td>
<td>-5.67</td>
<td>-5.59</td>
<td>-5.48</td>
</tr>
</tbody>
</table>

Notes: * p\textsubscript{center} was not calculated as these adsorption configurations were unfeasible (i.e., converged to the b site).

Next, we investigated the effect of strain on adsorption energies. Figure 3(a and b) show the change in adsorption energies with applied strain compared with the unstrained state for atomic H and N, respectively. The slope of these plots, *i.e.*, the change in adsorption energy per unit applied strain, is the strain susceptibility (eV/\%). A negative adsorption energy change indicates that adsorption is favored with tensile strain. Both H and N adsorption were favored with tensile strain. However, the magnitude of its effect depended upon the adsorption site, as seen from the strain susceptibilities. Specifically, the t site, which weakly adsorbed H and N, showed the least strain susceptibility (-0.8 eV/\% and -6.3 eV/\% for H and N, respectively), whereas the more stable sites (f and h) showed the highest strain susceptibilities (-3.2 eV/\% and -8.9 eV/\% for H and N of f, respectively). We again refer to the interaction matrix coupling element from the NA model to explain this, now looking at the influence the adsorbate has on the d-band of the surface atoms (*i.e.*, the hybridization of the d-band of the surface atoms upon adsorption)\(^1\) over strain. In Table 3, we summarize the change in the \(d_{\text{center}}\) of the Pd atoms involved in adsorption at the four sites for different adsorbates over a net 4\% tensile strain. Its change indicates how strain influences the hybridized d-band. A positive change indicates upward movement of the d-band, *i.e.*, the Pd atoms...
strongly participate in adsorption under tensile strain. The change in the hybridized d_{center}, i.e., the magnitude of its upward movement toward the Fermi level, increased with site CN. In general, the d_{center} of the bonded Pd atoms shifted upward the most at the f site, closely followed at the h site and then at the b and t sites. This trend was consistent with the strain susceptibilities shown in Figure 3(a and b), wherein f and h showed the highest slopes, followed by b and t. In general, for atomic and NH_x adsorption, strain susceptibility increased with the site CN. A similar trend was reported by Zeng et al. using the tight-binding model. Briefly, as the site CN increased from 1 to 3 (i.e., from t to f/h), the d-d orbital coupling matrix element of the surface metal atoms became larger due to the increasing number of metal atoms participating in adsorption. Thus, on the application of tensile strain, the larger d-d orbital coupling matrix at the higher CN sites showed a greater change than at the lower CN sites, resulting in increased strain susceptibility with site CN.44 Further, as seen from the strain susceptibilities, strain affected the adsorption of H and N to different magnitudes. Specifically, over net 4% tensile strain (2% compressive to 2% tensile), the adsorption energy of H and N on f site increased by 0.12 eV and 0.35 eV, respectively, i.e., N was affected ~3× as much as H over the same strain. The same held for the NH_x species, i.e., strain affected each species differently.

The change in adsorption energy (in eV) is plotted against strain values for NH_x on their preferred adsorption sites (Figure 3(c)), whose slope gives the strain susceptibility. The strain susceptibility was highest and comparable for atomic N and NH, followed by NH_2, and lowest for NH_3. In general, the slopes decreased with decreasing saturation of NH_x species. Figure 3(d) shows the strain-based scaling relationships relating the adsorption energies of NH_x (x=1-3) species with the adsorption energy of N. The trend, namely, the positive slopes, was similar to that observed in periodic scaling relationships.72 A key difference, however, was the value of the
scaling slopes. As compared to an NH scaling slope of 0.71 for the close-packed surface of various TMs reported by Abild-Pedersen et al., the strain-based scaling slope value was 1.1. For NH₂, the strain-based scaling slope was 0.5 compared to 0.41 for periodic scaling relationships. A detailed comparison of scaling relations and corresponding strain-based deviations was reported by Zeng et al. The greater scaling slopes obtained from strain versus the periodic scaling relationships demonstrate how increased and distinct variations in adsorption energy can be achieved with strain over altering the chemical composition of a catalyst surface, which is constrained by the periodic scaling relations.

![Figure 3](https://doi.org/10.26434/chemrxiv-2024-8ltp5)

**Figure 3.** Change in adsorption energy with respect to unstrained state for (a) H and (b) N at the four sites, and (c) NHₓ on their preferred sites with strain on Pd(111). The dashed lines are linear fits whose slopes represent strain susceptibilities. (d) Scaling relations for NHₓ species adsorption.
The dashed lines are linear fits whose slopes are the scaling slopes. The black squares in (d) are the variation of N adsorption energy with strain, and the dashed black line is its linear fit.

Table 3. Change in the hybridized d-band center (d_{center}) over net 4% tensile strain of the surface Pd atoms involved in adsorption at the four sites. The bolded values represent the highest strain susceptibility.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Top (t)</th>
<th>Bridge (b)</th>
<th>fcc (f)</th>
<th>hcp (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.215</td>
<td>0.228</td>
<td><strong>0.232</strong></td>
<td>0.229</td>
</tr>
<tr>
<td>N</td>
<td>0.084</td>
<td>0.165</td>
<td><strong>0.250</strong></td>
<td>0.224</td>
</tr>
<tr>
<td>NH</td>
<td>0.103</td>
<td>0.194</td>
<td><strong>0.259</strong></td>
<td>0.219</td>
</tr>
<tr>
<td>NH₂</td>
<td>0.163</td>
<td><strong>0.249</strong></td>
<td>-a</td>
<td>-a</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.158</td>
<td>0.176</td>
<td>0.179</td>
<td><strong>0.180</strong></td>
</tr>
</tbody>
</table>

**Notes:** a d_{center} was not calculated as these adsorptions were unfeasible (converged to the b site).

Strain-based scaling relations between the TS and adsorption energy of atomic N on the surface would enable the formulation of “BEP-like” relationships using strain as a descriptor to predict catalytic activity. To that end, we studied N₂ dissociation on the Pd (111) surface, which is reported to be the rate-determining step (RDS) in NH₃ synthesis. Molecular N₂ has two adsorption modes, namely, horizontal (i.e., with its molecular axis parallel to the Pd surface) and vertical (i.e., with its molecular axis perpendicular to the Pd surface). Our calculations showed that N₂ adsorbed more favorably in the vertical orientation on the t site (E_{ads} = -0.37 eV), compared to the horizontal orientation (E_{ads} = -0.20 eV on the f site) on Pd(111).

From the vertically adsorbed state, N₂ can dissociate directly by cleaving into two N atoms placed at adjacent f sites or indirectly by rotating to a horizontally adsorbed state, followed by cleavage. We found that both routes had highly positive dissociation energies (ΔE_{diss}) and showed
high activation energies ($E_a$). Furthermore, both routes showed nearly identical TS structures with the same energies. As such, we considered only direct N$_2$ dissociation. **Figure 4(a)** shows the N$_2$ dissociation reaction energy diagrams on the strained surfaces. The IS, TS, and FS were affected differently by strain. Adsorption of molecular N$_2$ was affected the least (i.e., N$_2$ has the least strain susceptibility). In contrast, the dissociated N atoms were affected the most, owing to the larger strain susceptibility of N at $f$. The energy differences under tensile strain lowered $\Delta E_{\text{diss}}$ from 2.92 eV (at -2%) to 2.24 eV (at 2%), making the reaction thermodynamically more feasible by ~0.68 eV. The TS also stabilized under tensile strain, with the $E_a$ reducing from 3.41 eV (at -2%) to 3.31 eV (at 2%). **Figure 4(b)** shows the strain-based linear scaling relationship (i.e., BEP-like) for N$_2$ dissociation obtained from the strained surfaces, with a slope of ~0.2. BEP relations for N$_2$ dissociation over various pure TMs and bulk alloys have been reported by Munter et al.\textsuperscript{16} On fcc (211) TMs, a BEP slope of 0.70 was reported over a 12 eV chemisorption energy range. A similar BEP-like plot is shown in **Figure S2**, having a slope of ~0.25, showing distinct scaling relations compared to BEP relationships. Further, as the adsorption energies are linearly related to the applied strain, strain can thus be used as a macroscopic descriptor to predict a change in the reaction rate on the Pd(111) surface using the activation energies and transition-state theory (TST) formalism of kinetic data.
Figure 4. (a) Reaction energy diagram of N$_2$ dissociation on the strained Pd(111) surfaces. The inset graphics are the initial, transition, and final state structures (grey=Pd and blue=N). (b) Brønsted-Evans-Polanyi-like (BEP-like) relationship for N$_2$ dissociation over strain. The dashed line is the linear fit whose equation represents the theoretical BEP-like relationship. The red triangles are the variation of N$_2$ dissociation energy with strain, and the dashed line is its linear fit.

To understand the underlying reason behind tensile strain reducing the activation energy for N$_2$ dissociation, we plotted the PDOS on the p-orbitals of the N$_2$ dissociation TS (N$_2$# TS) on the Pd surface (Figure 5). We compared it with the PDOS on the p-orbitals of the N bonded to Pd in the vertically adsorbed N$_2$ (green line in Figure 5). From the reference state of gas phase N$_2$ (purple line in Figure 5), the p-band of N split into a bonding state and a small anti-bonding state (below and above the Fermi level, respectively) as it was adsorbed on the Pd surface. As the adsorbed N$_2$
dissociated and approached the TS (blue line), its electron density split further into the bonding and anti-bonding states, indicating a weakening of the N-N triple bond. Interestingly, on the application of tensile strain, the p\text{center} of N\textsubscript{2}\# TS moved upward (Table 4), in contrast to it moving downward for both atomic N and molecular N\textsubscript{2}. This upward movement of the p\text{center} indicated electron density between the N atoms moving from the bonding states to the anti-bonding states, i.e., the N-N bond in the TS getting weaker on the application of tensile strain. This reduced the activation energy for dissociation as the weaker N-N bond was more readily cleaved. The variation of the p\text{center} of the bonded N atom in the different adsorbed states (atomic N, molecular N\textsubscript{2}, and N\textsubscript{2}\# TS) with strain are summarized in Table 4. The p\text{center} movement trends explain how the adsorption of intermediates was strengthened and dissociation enhanced with tensile strain. Specifically, with tensile strain, the downward movement of the p\text{center} in N and N\textsubscript{2} adsorption indicated stronger adsorption, while the upward movement of the p\text{center} in N\textsubscript{2}\# TS indicated facile dissociation.
Figure 5. Projected density of states (PDOS) on the Pd-N₂# transition state (TS) system. PDOS on - grey line: d-orbitals of the clean Pd surface atoms, red line: d-orbitals of the Pd atoms interacting with N₂# TS, blue line: p-orbitals of the N₂# TS on the Pd surface, and green line: p-orbitals of N atom of the vertically adsorbed N₂ on Pd.

Table 4. p-Band centers (p_{center}) of reference species (N and N₂ in vacuum) and binding N atoms of the adsorbed N species on Pd(111) and their variation with strain.

<table>
<thead>
<tr>
<th>Strain</th>
<th>Reference State</th>
<th>bonded to Pd (bonding site)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N</td>
</tr>
<tr>
<td>-2%</td>
<td>0.04</td>
<td>-3.13</td>
</tr>
<tr>
<td>-1%</td>
<td>0.04</td>
<td>-3.13</td>
</tr>
</tbody>
</table>
**Reaction Mechanism and Kinetics.** To observe the impact of the adsorbate strain susceptibilities and TS energies on the Pd(111) surface on the thermodynamics and kinetics (i.e., reaction rates), we built an MKM for NH₃ synthesis from the DFT-calculated activation energies and reaction energy changes. Specifically, we constructed the complete NH₃ synthesis free energy diagram (at reaction conditions of 150 atm H₂, 50 atm N₂, and 723 K) and observed the effect of strain on each surface reaction. **Figure 6** shows the free energy diagram on -2%, 0%, and 2% strained surfaces, along with the IS, TS, and FS structures for each surface reaction.
**Figure 6.** NH$_3$ synthesis reaction free energy diagram on Pd(111) on -2%, 0%, and 2% strained surfaces at 723 K and low surface coverage (~1/8 ML). The inset graphics are the initial, transition, and final state structures for each surface reaction (grey=Pd, blue=N, and pink=H).

Assuming all elementary steps to be irreversible, we calculated the apparent rate constants for each reaction (eqn. (14)-(20)) using zero-point energy (ZPE) and thermodynamics corrections corresponding to industrial synthesis conditions of 150 atm H$_2$, 50 atm N$_2$, and 723 K reaction temperature. The reaction free energy changes (ΔG$_{rxn}$), and free energies of activation (ΔG$^\ddagger$) versus strain of the surface reactions are presented in **Table 5**, respectively. The calculated rate and equilibrium constants are summarized in **Tables S3-S5**. Here, it is crucial to note that NH, NH$_2$, and NH$_3$ favorably adsorb to the $f$, $b$, and $t$ sites, respectively. As such, their formation involves more than one unique site (e.g., for NH hydrogenation, NH is on the $f$ site, NH$_2$ on the $b$ site, and the NH$_2$ formation TS in between the $f$ and $b$ sites). As such, the different strain susceptibilities at different sites compound the effect of strain on ΔG$_{rxn}$ and ΔG$^\ddagger$.

**Table 5.** Effect of strain on the thermodynamics (free energy of reaction, ΔG$_{rxn}$) and kinetics (free energy of activation, ΔG$^\ddagger$) of the surface reactions in NH$_3$ synthesis on Pd(111).

<table>
<thead>
<tr>
<th>Surface Reaction Free Energy Change and Free Energy of Activation (eV)</th>
<th>N$_2$ dissociation</th>
<th>N hydrogenation</th>
<th>NH hydrogenation</th>
<th>NH$_2$ hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain</td>
<td>ΔG$^\ddagger$</td>
<td>ΔG$_{rxn}$</td>
<td>ΔG$^\ddagger$</td>
<td>ΔG$_{rxn}$</td>
</tr>
<tr>
<td>-2%</td>
<td>3.68</td>
<td>3.26</td>
<td>0.56</td>
<td>-0.52</td>
</tr>
<tr>
<td>-1%</td>
<td>3.69</td>
<td>3.07</td>
<td>0.64</td>
<td>-0.47</td>
</tr>
<tr>
<td>0%</td>
<td>3.64</td>
<td>2.88</td>
<td>0.67</td>
<td>-0.43</td>
</tr>
<tr>
<td>1%</td>
<td>3.60</td>
<td>2.71</td>
<td>0.72</td>
<td>-0.39</td>
</tr>
<tr>
<td>2%</td>
<td>3.53</td>
<td>2.55</td>
<td>0.74</td>
<td>-0.36</td>
</tr>
</tbody>
</table>
Our calculations showed that N₂ dissociation is thermodynamically the most unfeasible and kinetically the slowest step. On the unstrained Pd surface, the apparent rate constant for N₂ dissociation was $1.42 \times 10^{-17}$ 1/s compared to the next slowest surface reaction, N hydrogenation, whose apparent rate constant was $4.82 \times 10^{-4}$ 1/s. The low apparent rate constant of N₂ dissociation stems from a slow intrinsic rate (due to a high activation energy of dissociation) coupled with the small N₂ adsorption equilibrium constant. As seen in Figure 6, all the hydrogenation steps were exergonic compared to the endergonic N₂ dissociation. Interestingly, N₂ dissociation was enhanced over tensile strain, while NH₃ hydrogenation was impaired (Table 5). As the apparent rate constant of each reaction consists of the equilibrium constants of the preceding reactions and their own intrinsic rate constants, the effect of strain is compounded. For example, despite tensile strain diminishing the intrinsic NHₓ hydrogenation reactions (i.e., $\Delta G^\dagger$ and $\Delta G_{\text{rxn}}$ increasing with tensile strain), their apparent rate constants increased. Specifically, N hydrogenation had the highest increase in apparent rate-constant ($\sim 229 \times$), followed by a $\sim 151 \times$ increase for NH hydrogenation, meaning that both these reactions were enhanced by more than two orders of magnitude over a net 4% tensile strain (-2% to 2%). The apparent rate constant of the RDS, N₂ dissociation, increased $\sim 37 \times$ (Table S5), implying that the overall NH₃ synthesis reaction was enhanced $\sim 37 \times$ by applying a net 4% biaxial tensile strain on the Pd (111) surface.
**Figure 7.** The logarithmic variation of apparent NH₃ formation rate and d-band center (d_{center}) of Pd with the atomic N adsorption energy. The dashed line is the linear fit.

The effect of tensile strain enhancing N₂ dissociation is shown using d_{center} as a descriptor in **Figure 7**, where we plot the logarithm of the apparent rate constant for N₂ dissociation as a function of atomic N adsorption energy (or d_{center}), a descriptor in constructing the NH₃ synthesis volcano plot.¹² The increasing rate constant with the application of tensile strain represents an upward path from the right side of the volcano.¹² The d_{center} descriptor can thus be used as a surrogate for the applied strain to predict the reaction rate. The strain-based BEP-like relationships for the N, NH, and NH₂ hydrogenation steps are plotted in **Figure S3** with slopes of 1.3, 0.4, and 0.7, respectively. These slopes are distinct from the slopes from BEP relationships for these steps over close-packed fcc(111) metals. The BEP slopes for N, NH, and NH₂ hydrogenation are 0.79, 0.68, and 0.46, respectively.⁷⁶ Overall, descriptors such as the d_{center} of strain-based catalysts and the formulation of linear scaling relationships enables the design of strain-based catalysts. Importantly, the strained metal catalysts show significant deviation from BEP relationships and provide another useful catalyst design tool.

**Surface Coverage Effects.** To understand how strain affects reaction kinetics at surface coverages relevant to industrial conditions (150 atm H₂, 50 atm N₂, and 723 K), we evaluated the change in free energy of adsorption (ΔG_{ads}) for the different reaction intermediates involved in NH₃ synthesis. Overall, among all the compositions considered, the one with complete coverage of H was most favorable under industrially relevant conditions. **Figure 8(a)** shows the ΔG_{ads} of the different species, calculated with respect to the clean surface and gas-phase chemical potentials of N₂ and H₂ at P_{H₂} = 150 atm, P_{N₂} = 50 atm, and T = 723 K (the values are summarized in **Table S6**). We found that only H (-0.27 eV) and NH₃ (-0.28 eV) had a negative ΔG_{ads}, meaning a
relatively more stable surface configuration than clean Pd(111). We then added H and NH₃ co-adsorbates to evaluate the extent of their coverage. A second adsorbed NH₃ molecule only slightly decreased ΔĜ_{ads} (-0.32 eV), while a third NH₃ molecule significantly destabilized the surface due to strong lateral interactions, leading to a positive ΔĜ_{ads} (0.87 eV). On the other hand, H adsorption was favorable (ΔĜ_{ads} decreased) up to 8H, corresponding to a complete ML coverage (Figure 8(b)). The ninth H would now adsorb onto an h site, as all f sites are occupied, which destabilized the surface and increased ΔĜ_{ads}.

Figure 8. Calculated change in free energy of adsorption for the adsorption of (a) species involved in NH₃ synthesis and (b) increasing the number of atomic H adsorbed on Pd(111).
To model N$_2$ dissociation, we considered a 6H surface (3/4 ML) rather than an 8H surface, leaving two free sites for the dissociated N atoms (Figure 9(a)). We calculated the $\Delta E_{\text{diss}}$ and $E_a$ for N$_2$ dissociation on the 3/4 ML H-covered surface and compared the kinetics with a mean-field model or a clean surface (Figure 9). Specifically, we performed TS calculations using molecular N$_2$ and two N atoms co-adsorbed with 6 H (3/4 ML) atoms on the Pd(111) surface as the IS and FS, respectively. As shown in Figure 9(a), N$_2$ adsorption was destabilized due to lateral interactions with the co-adsorbed H atoms. This was evident from the IS structures, wherein the 3/4 ML-covered surface adsorbed N$_2$ at an angle versus the axial N$_2$ adsorption on the clean surface (Figure 4(a)). Taking both IS as references, the dissociation energy change (3.69 eV vs. 2.56 eV) and activation energy (4.17 eV vs. 3.39 eV) were significantly higher on the 3/4 ML H-covered surface than on a clean surface. This resulted in a slower dissociation, with the apparent rate constant on the unstrained 3/4 ML H-covered surface being $3.16 \times 10^{-25}$ 1/s vs. $1.42 \times 10^{-17}$ 1/s on the clean surface. Interestingly, despite the lower reaction rates, the effect of tensile strain on facilitating N$_2$ dissociation was more pronounced. Figure 9(b) compares the apparent rate constants of the two surface states (clean and 3/4 ML H-covered) versus strain. The slopes of these curves revealed that the rate enhancement over a 4% net tensile strain on the 3/4 ML H-covered was $\sim 3273 \times$ compared to $\sim 37 \times$ on the clean surface. This demonstrated the elevated impact strain has on the NH$_3$ synthesis kinetics on a representative surface.

While we have studied the NH$_3$ reaction system, the varying strain susceptibilities, and TS stabilities over strain are a general phenomenon and could be applied to larger reaction networks. Leveraging the effect of strain (tensile or compressive) to enhance reaction rates opens interesting opportunities to use strain as a complementary catalyst design tool to fine-tune surface-adsorbate interactions and navigate reaction pathways.
Figure 9. (a) Reaction energy diagrams comparing N₂ dissociation on a clean and 3/4 ML H-covered Pd(111) surface. The inset graphics are the initial, transition, and final state structures for N₂ dissociation on the 3/4 ML H-covered surface (grey=Pd, blue=N, and pink=H). (b) Comparison of the effect of strain on the apparent N₂ dissociation kinetics on a clean and 3/4 ML H-covered Pd(111) surface. The dashed lines are linear fits.
CONCLUSION

In this study, we elucidated the electronic factors influencing surface-adsorbate interaction under the effect of biaxial strain on a pure metal and analyzed its impact on catalytic activity. For the Pd(111)-catalyzed NH\textsubscript{3} synthesis reaction, using DOS analysis, we found that the surface-adsorbate interaction matrix coupling element (that depends on the interaction between the orbitals of the adsorbate and the surface metal atoms during adsorption) plays a key role in describing the preferential bonding of the adsorbate at a particular site and its strain susceptibility. We found that the p\textsubscript{center} of the binding atom of the adsorbate and the hybridized d\textsubscript{center} of the surface metal atoms are strongly correlated to surface-adsorbate interactions. Specifically, the p\textsubscript{center} of the bonded adsorbate describes its preferential adsorption on particular fcc(111) sites, and the change in the hybridized d\textsubscript{center} of the adsorbing surface atoms corroborated the higher strain susceptibilities at sites with higher CNs. These trends can be extended across TM-adsorbate systems, enabling the use of the adsorbate p\textsubscript{center} and metal d\textsubscript{center} as descriptors to predict adsorption energies and strain susceptibilities.

Through microkinetic modeling (MKM), we then showed that the NH\textsubscript{3} synthesis activity of Pd increased ~37\times over a net 4% biaxial tensile strain (2% compressive to 2% tensile). N\textsubscript{2} dissociation, the RDS in NH\textsubscript{3} synthesis, was enhanced by making the dissociation more exergonic and lowering its activation energy, with the underlying reason being an upshift in the N\textsubscript{2} p\textsubscript{center} of the N\textsubscript{2} dissociation TS on the Pd(111) surface over tensile strain. The upshifted p\textsubscript{center} meant electron density moved into the anti-bonding states, which weakened the N\textsubscript{2} bond and favored dissociation. Surface coverage analysis revealed that a completely H-covered surface is the most representative under industrial reaction conditions of 150 atm H\textsubscript{2}, 50 atm N\textsubscript{2}, and 723 K. N\textsubscript{2} dissociation on such a surface (3/4 ML H-coverage) had a slower overall rate, but the effect of
strain was more pronounced than on the clean surface, with the apparent rate constant for N\textsubscript{2} dissociation increasing \(~3273\times\) versus \(~37\times\) on the clean surface over a net 4\% tensile strain, which can be attributed to the compounded effect of strain for each adsorbed species.

This study demonstrates using strain to fine-tune surface reactivity without altering the chemical composition of the catalyst and isolates its effect from the ligand effect. Importantly, our results highlight the ability of strain to potentially overcome periodic scaling limitations and present a useful catalyst design tool to climb up the volcano plot.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge at URL.

Total energy values for the clean Pd slab, BEP-like relationships for the NH\textsubscript{3} synthesis elementary steps over strained Pd(111), comparison of non-spin- and spin-polarized calculations, characteristics of the d-band of the strained Pd(111) slab, values of calculated rate constants for the NH\textsubscript{3} synthesis microkinetic model, and changes in free energy of adsorption on Pd(111). (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.
ACKNOWLEDGMENT

We are grateful to the Artie McFerrin Department of Chemical Engineering at Texas A&M University, the College of Engineering, Texas A&M Engineering Experiment Station (TEES) and the Provost for their financial support. We thank Texas A&M High Performance Research Computing (HPRC) for providing the computing resources for this work. MS acknowledges partial support from Texas A&M University System’s National Laboratory Office (NLO) for their Development Fellowship.

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