Toward a More Rational Design of the Direct Synthesis of Aniline: A Density Functional Theory Study

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Supporting Information

ABSTRACT: Plane-wave density functional theory (PW-DFT) calculations have been used to investigate the direct amination of benzene catalyzed by a Ni(111) surface to explore the reaction intermediates and to understand the role of nickel in this reaction. Adsorption structures, sites, energetics, and proposed reaction pathways relevant to the amination of benzene on the Ni(111) surface were investigated using the spin-polarized slab model with the Perdew−Burke−Ernzerhof functional. The dispersion-corrected DFT-D3 was used to examine the effect of van der Waals interactions on the adsorption energy. Detailed discussion of the adsorption behaviors of NH, NH$_2$, C$_6$H$_5$, C$_6$H$_5$NH$_2$, and C$_6$H$_5$NH on the Ni(111) surface is provided. Imide and benzene were predicted to be the most predominant adsorbed species on the Ni(111) surface, and a reaction process involving a surface-bound anilide as an intermediate was predicted to be more thermodynamically favorable than other reaction pathways. The electronic interactions and vibrational frequencies of isolated and adsorbed molecules were also investigated.

1. INTRODUCTION

Green chemical synthesis has been of significant interest for the development of safe and efficient reaction processes that reduce the generation of hazardous products and for economic benefits in the chemical industry. One process that has widely attracted the attention is the direct synthesis of aniline. Aniline (C$_6$H$_5$NH$_2$) is an important building block in the chemical industry as it can undergo numerous reactions involving either the amino group or the aromatic ring. These reactions can be extended for various industrial applications including the production of dyes, the production of polyurethane, use in the rubber industry, and in the manufacturing of pharmaceuticals, to name a few.$^{1,2}$ In 2013, the global annual production of aniline was $\sim$5 million tons and was anticipated to reach 6.2 million tons by 2015.$^{3}$ Eighty percentage of aniline goes to the production of methylene diphenylene isocyanate, which is used in the manufacturing of polyurethane.$^{1}$

The mass production of aniline demands an efficient, safe, and economical synthesis. Although the first reported production of aniline was in 1854 via the reduction of nitrobenzene, little improvements in this process have been reported, and hence, nitrobenzene remains the raw material used by almost all commercial producers of aniline.$^{1}$ Scheme 1 summarizes the industrial synthesis of aniline, which comprises multiple steps. It begins with the nitration of benzene using a mixture of nitric acid and sulfuric acid. The next step is the hydrogenation (reduction) of the nitro group in the presence of a catalyst (Pt/Pd on carbon or Raney Ni). Last, separation and distillation are performed to purify aniline.$^{1}$

The conventional route of the production of aniline, although it is practical and very exothermic, has drawbacks. It is not economical with respect to the capital cost and to atom economy. It also consumes a lot of energy, requires a large amount of corrosive acid catalysts and produces acid sludges, and can be accompanied by a great amount of by-products.$^{1,3}$ Thus, direct chemical synthesis of aniline is of significant importance as it reduces the generation of hazardous products and offers a more economical reaction process.

Scheme 1. Synthesis of Aniline$^a$

$^a$Adapted from ref 1.

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interest for the development of a more economic and environmentally friendly one-pot reaction process.

The direct route (Scheme 2) offers several advantages over the conventional process; however, it has several challenges.

Scheme 2. Proposed Direct Route of the Production of Aniline

The main challenge is the difficulty in activating the strong C−H bond of benzene [bond dissociation energy (BDE) = \( \sim 113 \) kcal mol\(^{-1}\)] and the strong N−H bond of ammonia (\( \sim 108 \) kcal mol\(^{-1}\)) simultaneously.\(^5\) Utilizing ammonia (NH\(_3\)) as an aminating agent is attractive because of its low cost and atom efficiency. Another issue associated with the direct process is that the production of hydrogen can drive the reaction toward the formation of benzene, which reduces the yield of aniline. Decomposition of ammonia into N\(_2\) and H\(_2\) at high temperature is also one of the challenges that must be inhibited to ensure a high yield of aniline.

Despite several experimental efforts,\(^4\)−22 a one-pot process has not been adopted yet for commercial applications, mostly because of low aniline yields. Most of the developments in this field are targeted toward the determination of an effective aminating agent, either ammonia or an ammonia derivative, in the presence of an effective catalyst. An oxidizing agent, such as oxygen gas, metal oxide, or hydrogen peroxide, is typically required. A significant advance includes the use of the Ni/NiO/ZrO\(_2\) cataloreactant,\(^19\)−22 to achieve direct amination of benzene to aniline. NiO is used as a reducible oxide that can oxidize the produced hydrogen while easily reducing to metallic Ni.\(^6\) The yield of aniline from this reaction is about 13.6% at 623 K and 300−400 atm. Hagemeier et al.\(^5\) conducted a large screening study and found that Rh/Ni−Mn/K−TiO\(_2\) cataloreactant produces the best benzene conversion and aniline selectivity. Both Hagemeier’s work\(^4\) and Hoffmann et al.\(^7,8\) emphasized the importance of metallic nickel as an active site for the formation of aniline. Hoffmann further proposed that elemental Ni is essential to activate the C−H bond of benzene and the N−H bond of ammonia simultaneously by conducting a temperature-programmed reaction (TPR) experiment of the direct amination of benzene on the Ni/ZrO\(_2\) catalyst at a temperature range of 523−873 K under standard pressure.\(^7\)

Although the cataloreactant of DuPont has been shown to produce aniline from the direct amination of benzene, no information about the thermodynamics and the electronic properties of some of the intermediates involved in this reaction is available.

To explore possible reaction intermediates and to better understand the role of nickel in direct aniline production, plane-wave density functional theory (PW-DFT) calculations were used to study the direct amination of benzene by a Ni(111) surface (Scheme 3). The DFT modeling of surface reactions has demonstrated the potential for providing molecular-level understanding of heterogeneous catalysts. Adsorption energies, structures, sites, and thermochemical analysis of the proposed reaction pathways relevant to the amination of benzene on the Ni(111) surface were investigated. Ni(111) is chosen because of its stability and its efficacy toward the adsorption of aniline.\(^26,27\) It is necessary to examine the adsorption behavior of aniline on the Ni(111) surface in detail, including its adsorption geometry and energy, which has not been, to our knowledge, reported before, to get information that can facilitate further catalyst design. This study also aims to compare and correlate a heterogeneous Ni(111)−imide model with the previous homogenous nickel−imide model for the C−H amination reaction.\(^28\)

2. RESULTS AND DISCUSSION

2.1. Method Calibration. To validate the utilized method for free molecules, the BDEs of the free molecules in the gas phase were calculated and compared with the available experimental data, as shown in Table 1. In addition to the calibration, these energies help to correlate the dissociation of these molecules in the gas phase and on the Ni(111) surface. For a molecule AB, the BDE is computed as follows: BDE = \( E_A + E_B − E_{AB} \) where \( E_A \) and \( E_B \) are the calculated total energies of molecule A and molecule B, respectively, and \( E_{AB} \) is the calculated total energy of molecule AB. Homolytic BDE calculations often represent a challenge for DFT owing to the difference in electron correlation between a molecule and its fragments. Calculating the reaction energies is usually more accurate because of the cancelation of error. Nevertheless, the calculated BDEs shown in Table 1 generally show a very good agreement with the experimental bond energies, especially when zero-point energy (ZPE) and thermal correction are added. The BDEs of Perdew–Burke–Ernzerhof (PBE) and PBE-D3 are very similar, with the largest difference between them being 1.1 kcal mol\(^{-1}\) for the C−N BDE of aniline, which is still within the experimental uncertainty. Therefore, as shown in Table 1, no notable improvement in the results is found when including the dispersion-corrected functional. From the BDE results, breaking one C−H bond of benzene in the gas phase is very endothermic, as expected, and requires a large amount of energy. We will show later how the use of a catalyst can help reduce this energetic demand. The same observation is true for the first N−H dissociation energy of ammonia and for NH\(_2\), NH, and aniline. The BDE of aniline shows that breaking the C−N bond of aniline requires higher energy than that required for N−H dissociation.

As the adsorption of ammonia and benzene on the Ni(111) surface has been studied before,\(^31,40\) their experimental adsorption energies were used to further validate the methods used in this study. Table 2 shows the calculated adsorption energies, structural, and thermodynamic properties for the adsorption of ammonia and benzene on a Ni(111) surface.
energies from this study using PBE-, PBE-D3-, ZPE-corrected adsorption energies, and the experimental adsorption energies for adsorbed ammonia and adsorbed benzene on the Ni(111) surface. Low-energy electron diffraction experiments\cite{31,32} and previous calculations\cite{33,34} confirmed that the nitrogen atom in ammonia is bound directly to the Ni(111) surface, whereas the hydrogen atoms point away from the surface, as shown in Figure 1a. The most stable adsorption site of NH$_3$ is atop, where the nitrogen atom is bound directly to a single Ni atom on the surface via the electron lone pair of the N atom of ammonia. In addition, previous experiments\cite{35,36} and calculations\cite{37} showed that the benzene ring adsorbs parallel to the surface, with all hydrogen atoms tilted away from the surface (Figure 1b). Our results agree well with these previous findings. The PBE adsorption energies (shown in Table 2) are in excellent agreement with experiments with $\leq$ 1.0 kcal mol$^{-1}$ difference. When adding the ZPE correction to the PBE adsorption energy of ammonia, the absorption energy is equal to that of the experiment, whereas the ZPE-corrected adsorption energy of benzene becomes 3.0 kcal mol$^{-1}$ lower than the experimental value. This is still in reasonable agreement with the experiment, as the experimental uncertainty associated with the use of temperature-programmed desorption spectroscopy to approximate the adsorption energy of large systems is estimated to be within 3 kcal mol$^{-1}$\cite{38,39}. This demonstrates the importance of including the ZPE correction in the calculations of the adsorption energies, and thus, the ZPE correction is included in all adsorption energies. To examine the effect of the van der Waals (vdW) interactions on the binding to the metal surface, the semiempirical PBE-D3 functional was used. The computed adsorption energies for ammonia and benzene using PBE-D3, shown in Table 2, show an overbinding of 9 kcal mol$^{-1}$ for ammonia and 38.4 kcal mol$^{-1}$ for benzene, which represents the dispersion energies that contribute to the molecule–metal bonding. A large dispersion energy of benzene on other (111) surfaces, such as Pt(111), Pd(111), Ag(111), and Au(111), was also previously obtained using different dispersion-corrected methods.\cite{40,41} Grimme et al.\cite{42} pointed out that DFT-D3 is a great tool to provide accurate adsorption energies for molecules and solids, in particular for weakly bounded systems (physisorption interactions), where dispersive interactions are dominant. For chemisorbed molecules, for example, all adsorbates in the present study, the interaction between a molecule and a metal surface may not be captured in the DFT-D3 parameterization, thereby leading to a large overbinding for the D3 corrections. DFT-D3 becomes more important when more than one molecule adsorb on the surface. Tonigold and Groß\cite{43} examined the performance of DFT-D3 on several water–metal systems as compared to that of PBE and found that pure PBE adequately described the adsorption behavior of pure water–metal system, but if additional adsorbates were added to the surface, then DFT-D3 would have been more reliable. Therefore, adding a dispersion correction to the molecule–Ni(111) adsorption systems in the current study would not be expected to improve the results relative to the experiment, which is demonstrated by the results in Table 2. Because the PBE adsorption energies are in excellent agreement with the experiment, they are used later to calculate the reaction thermodynamics.

2.2. Adsorption Geometries and Energies. The first step in surface reactions is usually the adsorption of the species involved in the reaction on the surface. Thus, it is of importance to study their adsorption behaviors. The adsorption behavior of the NH$_x$ ($x = 0–3$) species and the aromatic species involved in the direct amination of benzene on the Ni(111) surface is reported and discussed here. Geometry optimizations were performed for all adsorption systems to find the most stable structure of the molecule–surface interaction, that is, the most favorable surface site for each adsorption process, which has the lowest adsorption energy. The computed adsorption energy is defined as follows: $E_{\text{ad}} = E_{\text{adsorbate+Ni(111)}} - E_{\text{adsorbate}} - E_{\text{Ni(111)}}$, where $E_{\text{ad}}$ is the binding energy of a molecule bound to the surface, $E_{\text{adsorbate+Ni(111)}}$ is the calculated total energy of the optimized adsorption system, and $E_{\text{adsorbate}}$ and $E_{\text{Ni(111)}}$ are the calculated total energies of the isolated molecule and of the clean surface, respectively. As mentioned above, a ZPE correction was included in the calculations of the adsorption energies, and thus, the ZPE correction is included in all adsorption energies. To examine the effect of the van der Waals (vdW) interactions on the binding to the metal surface, the semiempirical PBE-D3 functional was used. The computed adsorption energies for ammonia and benzene using PBE-D3, shown in Table 2, show an overbinding of 9 kcal mol$^{-1}$ for ammonia and 38.4 kcal mol$^{-1}$ for benzene, which represents the dispersion energies that contribute to the molecule–metal bonding. A large dispersion energy of benzene on other (111) surfaces, such as Pt(111), Pd(111), Ag(111), and Au(111), was also previously obtained using different dispersion-corrected methods.\cite{40,41} Grimme et al.\cite{42} pointed out that DFT-D3 is a great tool to provide accurate adsorption energies for molecules and solids, in particular for weakly bounded systems (physisorption interactions), where dispersive interactions are dominant. For chemisorbed molecules, for example, all adsorbates in the present study, the interaction between a molecule and a metal surface may not be captured in the DFT-D3 parameterization, thereby leading to a large overbinding for the D3 corrections. DFT-D3 becomes more important when more than one molecule adsorb on the surface. Tonigold and Groß\cite{43} examined the performance of DFT-D3 on several water–metal systems as compared to that of PBE and found that pure PBE adequately described the adsorption behavior of pure water–metal system, but if additional adsorbates were added to the surface, then DFT-D3 would have been more reliable. Therefore, adding a dispersion correction to the molecule–Ni(111) adsorption systems in the current study would not be expected to improve the results relative to the experiment, which is demonstrated by the results in Table 2. Because the PBE adsorption energies are in excellent agreement with the experiment, they are used later to calculate the reaction thermodynamics.
correction is added to all total energies. Only the adsorption energies of the most stable structures on the Ni(111) surface are provided here.

2.2.1. NH₃⁺, NH₂⁺, NH⁺, N⁺, and H⁺. 2.2.1.1. Adsorption Sites and Energies. Both NH₃ and NH interact with the Ni(111) surface similar to ammonia (the same orientation), that is, via the nitrogen atom. However, each species interacts with different active sites (see Figures 1a and 2a,b). Duan et al. 33,47 studied the adsorption sites and energies of the NH species on the Ni(111) surface. They found that NH₂ and NH interact with the Ni(111) surface via bridge and face-centered cubic (fcc) sites, respectively, which is consistent with our findings. Duan reported the adsorption energies of the NH species in two publications. 33,47 The adsorption energies are different in those two papers. Their adsorption energies and the adsorption energies of the current study are listed in Table 3. The predicted gas-phase structural parameters of NH₃, NH₂, and NH from this work (using PW-PBE) are in excellent agreement with experiments (see Table 4). The predicted adsorbed structures of the NH species agree very well with the previous calculations by Duan et al. 33 The N–Ni bond distance in the NH₃/Ni(111) system is only 0.06 Å away from the experimentally measured distance. 35 The N–H bond length in NH₃ elongates by 0.004 Å when going from NH₃ to NH₂, as expected, given an increase in unsaturation of nitrogen in this order. This is evident, giving the different preferred interaction sites. This is evident, giving the different preferred interaction sites. This is evident, giving the different preferred interaction sites. This is evident, giving the different preferred interaction sites. This is evident, giving the different preferred interaction sites.
tetrahedral via adsorption. The distance between N and Ni decreases in the direction: NH$_3$ (2.03 Å), NH$_2$ (1.93 Å), and NH (1.84 Å), highlighting the strong binding of NH. In the N/Ni(111) system, the N−Ni bonds are the shortest among other N−Ni bonds (see Table 4); therefore, when nitrogen gets more unsaturated, it binds very tightly to the surface. Hydride, on the other hand, greatly overlaps with the Ni atoms, resulting in unsaturated, it binds very tightly to the surface. Hydride, on the other hand, greatly overlaps with the Ni atoms, resulting in each other.

Table 5. Vibrational Frequencies (in cm$^{-1}$) of Free and Adsorbed NH$_3$, NH$_2$, and NH

| adsorbate | adsorption sites | E$_{ad}^{\text{a}}$ (kcal mol$^{-1}$) | PBE | PBE-D3 | exp |
|-----------|-----------------|-------------------------------------|------|--------|-----|
| C$_3$H$_4$ (parallel) bridge | −21.4 | −59.8 | −18.0 |
| C$_3$H$_4$ (tilted) fcc | −51.1 | −88.1 |
| C$_3$H$_4$NH$_2$ (parallel) bridge and atop | −20.4 | −63.6 |
| C$_3$H$_4$NH (vertical) bridge | −38.7 | −56.9 |

Table 6. Adsorption Sites and Adsorption Energies (E$_{ad}$) (in kcal mol$^{-1}$) of the Aromatic Species Adsorbed on a Ni(111) Surface

interactions. The adsorption energy of phenyl on the Ni(111) surface is more stable than that of adsorbed benzene by ~30 kcal mol$^{-1}$ (see Table 6). The strong binding of phenyl compared to that of benzene is due to the strong σ interaction introduced in the phenyl/Ni(111) system, which is not present in the benzene/Ni(111) system (only π interactions), resulting in different adsorption structures between these two systems. The adsorption of phenyl appears tilted with respect to the surface on the fcc site (Figure 3a), which is a stronger binding site than the bridge site (most stable site of benzene). This adsorption orientation of phenyl was also found by Feng et al., but their adsorption energy of phenyl using the PBE method and the slab model is lower than ours by 92.8 kcal mol$^{-1}$ mainly because a larger surface unit (12.46 × 12.46 Å$^2$) was used in their study. The adsorption energy of phenyl when adsorbed nearly vertical to the Ni(111) surface on the hexagonal close-packed site is found to be less stable than that of the tilted phenyl by approximately 3 kcal mol$^{-1}$, as the former loses some of the π interactions (see Figure S5a). The adsorption energy of phenyl is predicted to be higher when adsorbed vertically on the bridge site, in which the π-electron interactions decrease the most (Figure S5b). The vertical orientation of phenyl may likely occur due to the few binding sites available on the Ni(111) surface.

Previous studies of the adsorption of aniline on nickel surfaces showed a slightly different adsorption behavior of aniline. On evaporated Ni films, aniline was found, using X-ray photoelectron spectroscopy, to adsorb molecularly by π electrons and dissociatively as an anion formed from losing a proton from the amino group. Studies by Huang and coworkers on the adsorption of aniline on the Ni(100) and the Ni(111) surfaces using fluorescence yield near-edge spectroscopy and TPR techniques revealed that the adsorption of aniline is a structure-sensitive reaction and that the Ni(111) surface is considered to be the most stable for the adsorption of aniline, where aniline does not easily undergo hydrogenolysis and hydrogenation until reaching the temperature of ~800 K and higher. Huang et al. concluded that aniline adsorbs on the Ni(111) surface at a small angle only via π interactions, whereas Myers and Benziger suggested that aniline forms an unreactive surface polymer (polyaniline) when adsorbed on the Ni(111) surface that is stable above 600 K. The same polyaniline was found on the Ni(100) surface. In the TPR

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2.2.2. C$_3$H$_4$, C$_3$H$_4$*, C$_3$H$_4$NH$_2$, and C$_3$H$_4$NH*. 2.2.2.1. Adsorption Sites and Energies. As mentioned above, benzene adsorbs parallel to the surface with all hydrogen atoms tilted away with respect to the surface (Figure 1b). The calculated adsorption energy of benzene including the ZPE correction is −21.4 kcal mol$^{-1}$ (see Table 6) obtained mostly from π interactions. The adsorption energy of phenyl on the Ni(111) surface is more stable than that of adsorbed benzene by ~30 kcal mol$^{-1}$ (see Table 6). The strong binding of phenyl compared to that of benzene is due to the strong σ interaction introduced in the phenyl/Ni(111) system, which is not present in the benzene/Ni(111) system (only π interactions), resulting in different adsorption structures between these two systems. The adsorption of phenyl appears tilted with respect to the surface on the fcc site (Figure 3a), which is a stronger binding site than the bridge site (most stable site of benzene). This adsorption orientation of phenyl was also found by Feng et al., but their adsorption energy of phenyl using the PBE method and the slab model is lower than ours by 92.8 kcal mol$^{-1}$ mainly because a larger surface unit (12.46 × 12.46 Å$^2$) was used in their study. The adsorption energy of phenyl when adsorbed nearly vertical to the Ni(111) surface on the hexagonal close-packed site is found to be less stable than that of the tilted phenyl by approximately 3 kcal mol$^{-1}$, as the former loses some of the π interactions (see Figure S5a). The adsorption energy of phenyl is predicted to be higher when adsorbed vertically on the bridge site, in which the π-electron interactions decrease the most (Figure S5b). The vertical orientation of phenyl may likely occur due to the few binding sites available on the Ni(111) surface.

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PBE adsorption energies. This overestimation may involve the length in adsorbed anilide.

The shortest C–Ni bond length in vertically adsorbed phenyl is 1.953 Å versus 1.974 Å for the N–Ni bond length in adsorbed aniline.

Similarly to benzene, the PBE-D3 predicts lower adsorption energies for phenyl, aniline, and anilide in comparison to the PBE adsorption energies. This overestimation may involve the contribution of the vdW interactions to the molecule–metal binding, which are known to be significant for aromatic systems (see Table 6). The dispersion energy of phenyl is very close to that of benzene, whereas aniline has about a 5 kcal mol$^{-1}$ larger dispersion energy than benzene as per the PBE-D3 results. As anticipated, anilide has the lowest dispersion energy among the adsorbed aromatic species because the ring is not very close to the surface. The difference in adsorption energy between parallel-adsorbed benzene and tilted-adsorbed phenyl is 30.0 kcal mol$^{-1}$ when using PBE and PBE-D3. Thus, PBE-D3 still provides correct qualitative trends of the adsorption energies.

2.2.2. Adsorption Geometry. Important structural parameters of the free and adsorbed aromatic species are shown in Tables 7 and 8. A full list can be found in Tables S1 and S2.

Table 7. Bond Lengths ($r$) in Å of Free and Adsorbed Benzene and Phenyl

| system                  | $r$(C–H) | $r$(C–C) | $r$(C–Ni) |
|-------------------------|----------|----------|-----------|
| C$_6$H$_6$              | 1.091    | 1.397    |           |
| C$_6$H$_6$ (expt)$^a$   | 1.084    | 1.397    |           |
| C$_6$H$_6$/Ni(111)      | 1.095    | 1.434    | 2.060, 2.085 |
| C$_6$H$_5$              | 1.091    | 1.405    | 1.376, 1.398 |
| C$_6$H$_5$ (tilted)/Ni(111) | 1.095    | 1.438    | 2.237, 2.002, 2.411, 2.076, 2.487, 2.305, 1.905 |

$^a$Reference 49.

The C–C bonds in phenyl elongate, similar to benzene, by 0.02–0.08 Å when adsorbed on the Ni(111) surface (see Table 7), resulting in a decrease in the bond order and a degree of molecular distortion that can also be seen from the changes in the CCH bond angles (Table S1). The C–H bond lengths of phenyl do not exhibit major changes via adsorption, except that they become tilted out of the plane of the aromatic ring, as shown in Figure 3a. The C–Ni bonds in adsorbed phenyl vary in length, ranging from 1.905 to ~2.5 Å. The gradual increase

![Figure 3. Adsorption sites of phenyl (a), aniline (b), and anilide (c) on the Ni(111) surface. * indicates an adsorbed molecule.](image)

![Figure 4. Top view of aniline adsorbed on the $p(3 \times 3)$ surface unit cell of Ni(111) on bridge site A (a) and on the $p(5 \times 5)$ surface unit cell on bridge site B (b) and a side view of aniline adsorbed on the large $5 \times 5 \times 4$ Ni(111) slab model (c).](image)
in the C−Ni bond lengths confirm that phenyl tilts from the surface, suggesting that it interacts with Ni(111) in both a σ fashion (through the short 1.905 Å bond) and π interactions with the remainder of the ring. This contrasts with the C−Ni distances in adsorbed benzene, which are all similar, \( \sim 2.1 \) Å.

Similarly, in aniline, the C−C bonds get longer upon the adsorption and the ring loses some degree of unsaturation. The C−Ni bond lengths in aniline range from 2.04 to 2.09 Å, almost similar to adsorbed benzene, except the two Cipso−Ni bond distances (Table 8). The carbon atom connected to the amino group (Cipso in adsorbed aniline interacts with two Ni atoms (bridge sites), making the two Cipso−Ni bond distances longer (2.585 and 2.133 Å). The perpendicular distance between the Cipso and the surface, though, is still \( \sim 2.1 \) Å, as shown in Figure 3b. Thus, the aromatic ring in aniline adsorbs parallel to the Ni(111) surface. The N−Ni distance in adsorbed aniline is also 2.1 Å, which is similar to the C−Ni bond lengths but longer by 0.07 Å than the N−Ni bond length in adsorbed ammonia. This is consistent with ammonia being a better σ donor than aniline. A steric effect may also play a role here in hindering the N atom from binding strongly to the Ni(111) surface. In addition, the HNH bond angle of the amino group in adsorbed aniline also opens as that in adsorbed ammonia to accommodate a more tetrahedral configuration about nitrogen.

In adsorbed anilide, four of the C−C bonds of the aromatic ring (two Cipso−C bonds and the other two C−C bonds that are parallel to them) become shorter instead of becoming longer via adsorption in contrast to that in aniline, benzene, and phenyl. The C−C bonds in adsorbed anilide are all longer than those in adsorbed aniline. The C−N bond in anilide elongates by 0.076 Å via adsorption, but it is still shorter than the C−N bond in adsorbed aniline. The nitrogen atom in adsorbed

Table 8. Bond Lengths \((r)\) in Å and Bond Angles \((\alpha)\) in Degree of Free and Adsorbed Aniline and Anilide

| system                  | \(r\)(C−H) | \(r\)(N−H) | \(r\)(C−C) | \(r\)(C−N) | \(r\)(C−Ni) | \(r\)(N−Ni) |
|-------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| \(\text{C}_6\text{H}_5\text{NH}_2 \) | 1.091     | 1.014     | 1.407, 1.393, 1.398 | 1.394     |           |           |
| \(\text{C}_6\text{H}_5\text{NH}_2 \text{ (expt)} \) | 1.084    | 1.397, 1.394 | 1.402     |           |           |           |
| \(\text{C}_6\text{H}_5\text{NH}/\text{Ni(111)} \) | 1.090, 1.096 | 1.021 | 1.433, 1.448, 1.456, 1.452 | 1.435     | 2.056, 2.094, 2.040, 2.585, 2.133 | 2.084     |
| \(\text{C}_6\text{H}_5\text{NH} \) | 1.091     | 1.032     | 1.407, 1.383, 1.437 | 1.340     |           |           |
| \(\text{C}_6\text{H}_5\text{NH}/\text{Ni(111)} \) | 1.103, 1.091 | 1.030 | 1.392, 1.398, 1.410 | 1.416     | 1.995, 1.974 |           |

\( ^a \)\( \text{(HNH)} = 112.7^\circ \). \( ^b \)Reference 61. \( ^c \)\( \text{(HNH)} = 113.1^\circ \). \( ^d \)\( \text{(HNH)} = 110.0^\circ \). \( ^e \)\( \text{(NiNCipso)} = 127.4^\circ \).

Table 9. C−H, C−C, C−N, and N−H Vibrational Frequencies (in \( \text{cm}^{-1} \)) of the Gas Phase and Adsorbed \( \text{C}_6\text{H}_6 \), \( \text{C}_6\text{H}_5 \), \( \text{C}_6\text{H}_5\text{NH}_2 \), and \( \text{C}_6\text{H}_5\text{NH} \)

|                  | gas phase\(^a\) | adsorbed on a Ni(111) surface\(^b\) | gas phase (expt)\(^c\) | adsorbed on a Ni(111) surface (expt)\(^d\) |
|------------------|----------------|---------------------------------|------------------------|---------------------------------|
| C−H stretch \((e_1^g)\) | 3122 | 3086 | 3062 | 3025 |
| C−C stretch \((e_1^g)\) | 3121 | 3084 | 3068 | 3072 |
| C−H stretch \((e_1^g)\) | 3106 | 3074 | 3063 | 3047 |
| C−C stretch \((e_1^g)\) | 3105 | 3065 | 3047 | 3051 |
| C−H stretch \((e_1^g)\) | 1586 | 1439 | 1596 | 1425 |
| C−C stretch \((e_1^g)\) | 1586 | 1422 | 1596 | 1497 |
| C−H stretch \((e_2^g)\) | 3580 | 3486 | 3500 | 3500 |
| C−C stretch \((e_2^g)\) | 3479 | 3394 | 3418 | 3418 |
| C−H stretch \((e_2^g)\) | 3125 | 3096 | 3053 | 3072 |
| C−H stretch \((e_2^g)\) | 3108 | 3087 | 3041 | 3041 |
| C−C stretch \((e_2^g)\) | 1612 | 1553 | 1639 | 1649 |
| C−C stretch \((e_2^g)\) | 1599 | 1446 | 1590 | 1590 |
| C−N stretch \((e_1^g)\) | 1280 | 1137 | 1279 | 1279 |
| C−H bending \((e_1^g)\) | 1168 | 1114 | 1173 | 1173 |
| C−H stretch \((e_2^g)\) | 3313 | 3291 |           |           |
| C−H stretch \((e_2^g)\) | 3129 | 3129 |           |           |
| C−H stretch \((e_2^g)\) | 3122 | 3113 |           |           |
| C−H stretch \((e_2^g)\) | 1551 | 1578 |           |           |
| C−H stretch \((e_2^g)\) | 1522 | 1566 |           |           |
| C−H stretch \((e_2^g)\) | 1303 | 1237 |           |           |
| C−H stretch \((e_2^g)\) | 1155 | 1196 |           |           |

\( ^a \)This work. \( ^b \)Reference 53 (for \( \text{C}_6\text{H}_6 \)), ref 62 (for \( \text{C}_6\text{H}_5 \)), and ref 63 (for \( \text{C}_6\text{H}_5\text{NH}_2 \)). \( ^c \)Reference 64.
aniline interacts with the Ni(111) surface via bridge sites similar to that in adsorbed amide (see Figures 1a and 3c). Because of the steric effect resulting from the aromatic ring in aniline, the N–Ni bonds in adsorbed aniline are longer by 0.065 and 0.044 Å than the N–Ni bonds of adsorbed amide. Also, the NiNC Ngo angle opens about 10° larger than the NiNH angle of adsorbed amide. This can explain why the adsorption energy of aniline is predicted to be higher than that of amide by 24 kcal mol⁻¹.

2.2.2.3. Vibrational Frequencies. The calculated vibrational frequencies of C–H, C–C, N–H, and C–N bonds of free and adsorbed benzene, phenyl, aniline, and anilide, as well as their experimental frequencies in the gas phase and the experimental frequencies of benzene adsorbed on the Ni(111) surface, are given in Table 9. A full list of the calculated frequencies can be found in Table S3. The calculated gas-phase frequencies are in good agreement with experiments, although they are not corrected for anharmonicity. From the lower C–C bond frequencies of adsorbed benzene, phenyl, and aniline compared to the C–C bond in the gas phase, it is reasonable to conclude that the adsorbed C–C bonds are not as strong as they are in the gas phase, mostly because of their contribution to the π interactions with the Ni(111) surface. The frequency of the C–C bond of aniline decreases only by 59 cm⁻¹ when adsorbed on the Ni(111) surface compared to a 147 cm⁻¹ decrease in the same frequency for benzene, which supports our proposal that aniline has higher adsorption energy than benzene because it involves weaker π interactions, which can also be seen from the slight differences in the C–Ni bond lengths in aniline compared to that in benzene, as mentioned in the former section. On the other hand, the C–C stretching frequencies of adsorbed aniline become higher by 27 cm⁻¹ versus the gas phase, indicating a stable aromatic ring. No large differences in the C–H stretching modes are seen between the gas phase and the adsorbed molecules, although they become slightly lower with adsorption. The C–H bond lengths do not change much via adsorption but they tilt away from the surface. Similar to the C–H stretching modes, the N–H stretching modes display no significant differences in the frequencies between the gas phase and the adsorbed molecules. The C–N stretching modes of aniline and anilide exhibit a high decrease in the frequencies between free and adsorbed molecules. Although the C–N bond becomes longer via adsorption, anilide was found to be stable against hydrogenolysis when adsorbed on the Ni(111) surface in the presence of hydrogen, but at very high temperature (more than 800 K).26

2.3. Decomposition Reactions. Reaction energies (ΔE), reaction enthalpies (ΔH) at 523 K, and reaction free energies (ΔG) at 523 K were all calculated for several decomposition reactions and are listed in Tables 10 and 11.

2.3.1. Decomposition of Ammonia. Decomposition of ammonia on close-packed surfaces of reactive transition metals requires high pressure and temperature to overcome the decomposition barrier.65 The use of NiO in DuPont’s cataloreactant may have favored the decomposition of ammonia into the NH₃ species, as Hoffmann et al. found that no NH₃ was detected above 523 K, meaning that the Ni surface was covered with NH₃ species. Adsorption of ammonia on the Ni(111) surface is an exergonic reaction but can be decomposed by increasing the heat. The reaction energy, enthalpies, and free energies are shown in Table 10. Breaking two N–H bonds of ammonia to produce imide (NH₂⁺ → NH⁺ + H⁺) shows the lowest reaction enthalpy (−20.1 kcal mol⁻¹), followed by breaking the N–H bond of amide (NH₂⁺ → NH⁺ + H₂), and NH₃ → NH₂⁺ + H⁺ (−6.4 kcal mol⁻¹). Finally, the decomposition of NH⁺ into H⁺ and N⁺ displays the highest reaction enthalpy. According to the present results, the decomposition of ammonia on the Ni(111) surface into imide is the most favorable; thus, imide is predicted to be the most prevalent species on the Ni(111) surface among the NH₃ species, although amide cannot be ruled out, while nitride seems less likely as does undissociated ammonia, which is consistent with the calculations of Duan of the activation energies.33 Duan found that the lowest energy barrier corresponds to the dehydrogenation of NH₂⁺ to give NH⁺ and H⁺, in which NH₂⁺ diffuses on the surface from the moderate binding bridge site to the strong binding fcc site. The adsorption energy of NH₃ on the fcc site is higher than that on the bridge site by 7 kcal mol⁻¹ (see Figures S4a,b), but the imide species bind more strongly and are more stable than amide on the fcc site (Table 3). A recent experimental study of the decomposition of ammonia on the closed-packed surface Co(0001), which is anticipated to carry reactivity similar to that of the Ni(111) surface, has found that imide is the most stable species among the NH₃ species and can be selectively produced using the electron-induced dissociation technique at low temperature.65 Gibbs free energies of the decomposition reactions of ammonia on the Ni(111) surface at 523 K predicted that these reactions are exergonic (except the dehydrogenation of imide) (see Table 10), with the imide–Ni(111) being the most favorable decomposition reaction of ammonia at this temperature. The differences between ΔH and ΔG are small as shown from the results in Table 10, indicating small contributions from the entropies.

2.3.2. Decomposition of Benzene. As shown in Table 11, the decomposition of benzene into phenyl and hydrogen on the Ni(111) surface is thermodynamically less favorable than the adsorption of benzene on the Ni(111) surface. This result is expected, given the difficulty in activating the C–H bond and the high stability of the benzene ring. However, compared to the energy required to break the C–H bond of benzene in the

### Table 10. Reaction Energies ΔE, Enthalpies ΔH, and Free Energies ΔG of the Adsorption and Decomposition Reactions of Ammonia on the Ni(111) Surface, All in kcal mol⁻¹

| reaction pathways | ΔE   | ΔH (523 K) | ΔG (523 K) |
|-------------------|------|-----------|-----------|
| NH₃ + * → NH₂⁺   | −17.02 | −22.0     | −19.0     |
| NH₂⁺ + * → NH⁺ + H⁺ | −4.1  | −6.4      | −3.5      |
| NH₂⁺ + 2* → NH⁺ + 2H* | −15.6 | −20.1     | −14.4     |
| NH⁺ + * → NH⁺ + H⁺ | −11.5 | −13.7     | −10.9     |
| NH⁺ + * → N⁺ + H⁺ | 5.1   | 3.3       | 5.4       |

* indicates an adsorbed molecule.

### Table 11. Reaction Energies ΔE, Enthalpies ΔH, and Free Energies ΔG of the Adsorption and Decomposition Reactions of Benzene on the Ni(111) Surface, All in kcal mol⁻¹

| reaction pathways | ΔE   | ΔH (523 K) | ΔG (523 K) |
|-------------------|------|-----------|-----------|
| C₆H₆ + * → C₆H₅⁺ | −21.4 | −25.1     | −22.1     |
| C₆H₅⁺ + * → C₆H₄⁺ + H⁺ | 5.3   | 1.8       | 6.8       |

* indicates an adsorbed molecule.
gas phase (113 kcal mol$^{-1}$) (Table 1), the use of the Ni(111) surface does reduce the endothermcity of breaking the C–H bond by ~99 kcal mol$^{-1}$. These results lead to the conclusion that benzene is more stable on the Ni(111) surface than phenyl and that the C–H bond can be possibly activated at high temperature.

2.4. Production of Aniline. Hoffmann et al. represented a kinetic study of the semibatch oxidative synthesis of aniline catalyzed by NiO/ZrO$_2$ and found that temperature is a critical parameter to move the reaction forward. Full coverage of the NH$_x$ species on the Ni surface is also required for the formation of aniline so that it can control the adsorption geometry of benzene on the nickel surface. Hoffmann suggested that an adsorbed phenyl-type intermediate would be possible for this process, yet no confirmation of this proposal has been provided. In this section, possible reaction pathways between imide and benzene, because they are likely the most prevalent (stable) species on the surface, are proposed and investigated based on their reaction enthalpies and reaction free energies at 523 K. Surface reactions generally go through a catalytic cycle comprising elementary steps, beginning with adsorption, then reaction, and finally desorption. Two mechanisms common in surface reactions are the Langmuir–Hinshelwood and Rideal–Eley mechanisms.

2.4.1. Langmuir–Hinshelwood Mechanism. In this mechanism, all reactants involved in the reaction are adsorbed on the surface before reacting. Under this scheme, two reaction processes for aniline production were proposed: insertion and stepwise (see Table 12 and Scheme 5). The first reaction produces aniline that would then be desorbed from the Ni(111) surface. The overall process is, of course, also endothermic by ~21.4 kcal mol$^{-1}$ at 523 K, but the calculations are interesting in that they suggest that the initial C–H activation step is disfavored ($\Delta H = 24.5$ kcal mol$^{-1}$) relative to the second C–N formation step ($\Delta H = -3.1$ kcal mol$^{-1}$). The uphill nature of the first step is consistent with the dehydrogenation of benzene on the Ni(111) surface being unfeasible, as shown earlier. In part, this disfavorability of the first step can be attributed to the loss of some of the $\pi$ interactions between the aromatic ring and the surface in phenyl as compared to that in the adsorbed benzene (Figures 1b and 3a). The $\Delta G$ of this reaction also favors the second step over the C–H bond activation of benzene, indicating that the formation of aniline is more entropically favored than the formation of phenyl.

### Table 12. Reaction Energies $\Delta E$, Enthalpies $\Delta H$, and Free Energies $\Delta G$ of the Proposed Reaction Processes of the Production of Aniline on the Ni(111) Surface, All in kcal mol$^{-1}$.a

| reaction processes of the production of aniline | $\Delta E$ | $\Delta H$ (523 K) | $\Delta G$ (523 K) |
|-----------------------------------------------|----------|------------------|------------------|
| **Langmuir–Hinshelwood Mechanism**            |          |                  |                  |
| I. Insertion                                   |          |                  |                  |
| NH$_x^+$ + C$_6$H$_5^+$ $\overset{\Delta}{\rightarrow}$ C$_6$H$_5$NH$_x^+$ + * | 17.0     | 21.5             | 14.8             |
| II. C–H Activation/C–N Formation              |          |                  |                  |
| NH$_x^+$ + C$_6$H$_5^+$ $\overset{\Delta}{\rightarrow}$ NH$_x^+$ + C$_6$H$_5^*$ | 24.9     | 24.5             | 25.2             |
| NH$_x^+$ + C$_6$H$_5$ $\overset{\Delta}{\rightarrow}$ C$_6$H$_5$NH$_x^*$ + * | -8.0     | -3.1             | -10.4            |
| **Rideal–Eley Mechanism**                      |          |                  |                  |
| NH$_x^+$ + C$_6$H$_5$ + * $\overset{\Delta}{\rightarrow}$ C$_6$H$_5$NH$_x^*$ + H$^*$ | 0.9      | -2.6             | -2.0             |
| C$_6$H$_5$NH$_x^*$ + H$^*$ $\overset{\Delta}{\rightarrow}$ C$_6$H$_5$NH$_x^*$ + * | -5.3     | -1.8             | -6.8             |

*a* indicates an adsorbed molecule.

Pathway entails direct insertion of the imide into the C–H bond of adsorbed benzene, generating new C–N and N–H bonds, and thus, aniline is coordinated. Then, aniline is desorbed. The overall reaction is endergonic and must be aided with heat and/or pressure, as it is also endothermic by 21.5 kcal mol$^{-1}$ at 523 K.

The second reaction pathway modeled is a stepwise formation of the C–N and N–H bonds. The first step proceeds by a C–H bond activation, in which a C–H bond of benzene breaks and a Ni–C bond forms, resulting in C$_6$H$_5$/Ni(111) and NH$_2$/Ni(111). These two species react in the second exothermic step akin to a C–N formation process to
pathway is highly likely to achieve the direct production of aniline, although high temperatures are needed for the desorption reaction.

2.5. Desorption of Aniline. Desorption of aniline is calculated to cost 25.1 kcal mol\(^{-1}\) thermal energy at 523 K, as shown in Table 13. Thus, heat is needed to overcome this barrier. Because the desorption reaction involves an increase in entropy owing to the conversion from being surface-bound to gas-phase aniline, the enthalpy barrier must be overcome for this reaction to proceed.

2.6. Density of States. To interpret the electronic structure of the NH/Ni(111) and NH₂/Ni(111) systems, the density of states (DOS) of these systems and of the clean Ni(111) surface were calculated. Furthermore, the local density of state (LDOS) was also calculated for the N atom in the isolated molecules and in the adsorption systems. The LDOS for the Ni atom interacting with the N atom in the adsorption system was also calculated. Because the findings of the DOS and LDOS for the NH₂/Ni(111) and NH/Ni(111) systems are similar, only the results of the later will be discussed. The results of the DOS and the LDOS of the NH₂/Ni(111) system are shown in Figure S6.

### Table 13. Reaction Energies \(\Delta E\), Enthalpies \(\Delta H\), and Free Energies \(\Delta G\) of the Desorption Reaction of Aniline on the Ni(111) Surface, All in kcal mol\(^{-1}\)

| reaction process | \(\Delta E\) | \(\Delta H\) (523 K) | \(\Delta G\) (523 K) |
|------------------|-------------|-------------------|-------------------|
| Desorption of Aniline | 20.3 | 25.1 | 22.1 |

*\(a^*\) indicates an adsorbed molecule.

Figure 5a,b shows the LDOS of the N atom in the isolated NH and NH/Ni(111) systems. Each LDOS shows the contributions from s, p, and d bands in the electronic structure. Figure 5c,d shows the DOS of the clean Ni(111) surface and the LDOS of one of the Ni atoms that interact with NH. The Fermi level is set to 0 eV; hence, all energies are relative to the Fermi energy, \(E_F\) which represents the energy of the highest occupied electronic state.

By comparing between Figure 5a and Figure 5b, it can be clearly seen that the two bands at \(-13\) and \(-10.5\) eV in the isolated molecule have shifted via adsorption. The band at \(-13\) eV corresponds to the \(2\sigma\) states (bonding) from the N atom in NH, whereas the band at \(-10.5\) eV corresponds to the \(3\sigma\) states (lone pair) from the N atom in NH. When NH adsorbs on the Ni(111) surface, the bonding band shifts away from the Fermi level (\(-16\) eV), whereas the lone-pair band shifts toward the Fermi level (\(-8\) eV). Therefore, the N bonding state does not contribute to the NH-surface bonding, whereas the N lone-pair state contributes to the bonding with the surface. In addition, the valence bands between \(-2\) eV and the Fermi level in the isolated NH lose their density and smear out via adsorption. These bands represent the \(1\pi\) states of the N atom (two unpaired electrons) and the \(3\sigma\) states of NH (in the triplet state). These states involve most of the NH-surface bonding character.

On the other hand, Figure 5d shows that the adsorption induces short and narrow bands at about \(-16\) and \(-8\) eV in the LDOS of the Ni atom in the adsorption system as compared to Figure 5c [the free Ni(111) surface]. These bands correspond to the N atom in the adsorbed NH [bonding states (\(-16\) eV) and lone-pair states (\(-8\) eV)]. The \(1\pi\) states of the N atom are also shown at \(-5\) eV, indicating that they are populated when interacting with the nickel surface. Figure 5d shows that the...
valence band is dominated by d states from Ni atoms. Therefore, the NH-surface bonding (the valence band) is a mixture of d states of the Ni atom, lone pair states of the N atom, and 1\(\pi\) states to which the d states contribute the most.

From the spin density plot, shown in Figure 6, the spin-up and spin-down densities of the N atom are very similar. This leads to the conclusion that NH interacts with the surface more as an imide (singlet NH\(^{-}\)) rather than as an imidyl (doublet NH\(\bullet\)) radical anion or as a nitrene (triplet NH\(\bullet\)\(\bullet\)) radical. NH\(_2\) also interacts with the surface as an amide (NH\(_2\)\(^{-}\)) rather than as an aminyl (NH\(_2\)\(\bullet\)) radical via analysis of its spin-up and spin-down densities (see Figure S7). Furthermore, from our calculations, anilide is found to adsorb in a way similar to that of amide based on its adsorption structure and vibration; thus, one may surmise that anilide interacts with the surface as an anion (C\(_6\)H\(_5\)(H)N\(^{-}\)) rather than as anilinyl (C\(_6\)H\(_5\)(H)N\(\bullet\)).

3. CONCLUSIONS

This study presents an initial step toward understanding and identifying relevant species involved in the direct amination of benzene using first principles density functional calculations. Calculations predict that aniline adsorbs parallel to the surface via the aromatic ring and the nitrogen atom. The adsorption energy of aniline is higher (less stable) than that of benzene, indicating a weaker \(\pi\) interaction with the surface. Among all species, imide (NH) and benzene are predicted to be the most stable on the Ni(111) surface. The DOS calculations predict that NH interacts with the surface as an imide (NH\(^{-}\)) and NH\(_2\) interacts with the surface as an amide (NH\(_2\)\(^{-}\)), and hence they are quite different from molecular analogues that have more radical character in the ligands. Three reaction pathways were proposed relevant to the direct amination of benzene on the Ni(111) surface, and on the basis of the thermodynamics, the reaction involves producing a surface-bound anilide, and then coupling between NH\(_2\)H\(_2\) and H on the Ni(111) surface seems most likely to produce aniline than the other reaction pathways. Anilide adsorbs vertically on the Ni(111) surface in a way similar to that of an amide; thus, one may surmise that anilide interacts with the surface as an anion (C\(_6\)H\(_5\)(H)N\(^{-}\)). More detailed conclusions about the catalytic potential of the Ni(111) surface for the direct amination of benzene cannot be drawn at this stage until the kinetic study of the transition states, coverage, and activation energies is completed.

4. COMPUTATIONAL DETAILS

4.1. Methods. All calculations were carried out using PW-DFT as implemented in the Vienna Ab initio simulation package.\(^{66-69}\) The electron exchange and correlation energies were addressed using the generalized gradient approximation as proposed by Perdew–Burke–Ernzerhof (GGA-PBE).\(^{70,71}\) The electron–ion interactions were described using the projector augmented-wave method,\(^{72,73}\) in which the inner core electrons are treated with pseudopotentials, whereas valence electrons are described by a plane-wave basis set. To examine the effect of vDW interactions on the adsorption energy, the dispersion-corrected DFT-D3\(^{34}\) approach was used in this study. To obtain accurate energies, convergence tests were run to ensure...
the optimal setting parameters of our calculations (see Figures S1−S3). Plane-wave basis sets were expanded within a 400 eV energy cutoff, the Brillouin zone was integrated using $S \times S \times 1$ $k$-point mesh for adsorption systems, and only the gamma point was used for gas-phase molecules. Because Ni has magnetic properties, spin polarization was considered for open-shell molecules and for all adsorption systems to ensure accurate adsorption energies, as recommended by Kresse and Hafner.48

The energy criterion for electronic minimization was $10^{-6}$ eV, and the ions were allowed to relax until all atomic forces were less than 0.02 eV/Å. The Methfessel−Paxton smearing method74 was used with $\sigma = 0.2$ eV. All calculations were performed at 0 K. Vibrational frequencies were calculated using a 600 eV energy cutoff at the gamma $k$-point, and the force convergence criterion was tightened to be less than $10^{-5}$ eV/Å. Vibrational modes were animated by animating the diatomic molecules and for all adsorption systems to ensure accurate thermal corrections. The ZPE correction that was added to all adsorption energies is calculated as follows

$$\text{ZPE} = \sum_{i=1}^{n} \frac{h\nu_i}{2}$$

where $\nu_i$ is the calculated real frequency of a system, $n$ is the number of vibrations, and $h$ is Planck’s constant. Vibrational assignments were made by animating the different vibrational modes and seeing which atoms moved. The assigned vibration was then compared with the available experimental assignments. For the electronic DOS calculations, the $k$-point grid was increased to $9 \times 9 \times 1$.

4.2. Surface Model. The DFT-optimized lattice constant of Ni used to build the slab is 3.52 Å (see Figure S1), which agrees well with the experimental lattice constant of Ni, 3.524 Å.75 The Ni(111) surface was modeled as a five-layer periodic slab in the (111) Miller plane, as shown in Scheme 4. A vacuum thickness of 10 Å along the $c$ axis was employed between repeated slabs. During the geometry optimization, the top three layers were relaxed and the bottom two layers were kept fixed. The total number of nickel atoms in a slab is 45 atoms per unit cell, and the surface unit cell is $p(3 \times 3)$. One molecule was adsorbed for each calculation.

4.3. Thermochemistry. As mentioned in Hoffmann’s study,7 the reaction temperature plays a critical role in the selectivity of aniline in the direct amination of benzene. DuPont’s direct synthesis reaction was conducted at 623 K and 300−400 atm.21 In an attempt to reduce the pressure needed, Hoffmann carried out a TPR experiment of the direct amination of benzene with a pre-reduced Ni/ZrO$_2$ as a catalyst at ambient pressure and temperature range 523−873 K. The onset formation of aniline was detected at temperatures lower than 600 K. Thus, to obtain realistic thermodynamics of the direct amination of benzene on the Ni(111) surface, statistical thermodynamics using the vibrational partition function were utilized to calculate the Gibbs free energies at 523 K as follows

$$G(T) = H(T) - TS$$

where $H(T)$ is the enthalpy of the system, calculated as

$$H(T) = E_{\text{total}} + \text{ZPE} + H_{\text{corr}}$$

where $E_{\text{total}}$ is the total energy of the system determined by DFT calculations, ZPE is the ZPE correction, calculated as shown in eq 1, and $H_{\text{corr}}$ is the thermal correction from 0 to 523 K and is calculated as

$$H_{\text{corr}} = \sum_{i=1}^{n} \frac{h\nu_i}{e^{h\nu_i/k_BT} - 1}$$

where $k_B$ is Boltzmann’s constant.

Because all molecules in this study are strongly bound to the Ni(111) surface, the translational and rotational modes are frustrated and replaced by vibrational modes, as suggested by Blaylock et al.76 The entropy correction to the energy of adsorbates $S$ (eq 2) includes the contribution only from the vibrational modes, and it takes the form

$$S = \sum_{i=1}^{n} \left[ \frac{h\nu_i/k_BT}{e^{h\nu_i/k_BT} - 1} - \ln(1 - e^{-h\nu_i/k_BT}) \right]$$

For gaseous molecules, the contributions from the translational and rotational modes are included within the thermal correction and entropy.

## Associated Content

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00356.

Convergence tests, adsorption structures, structural parameters, vibrational frequencies, and the DOS of the NH$_2$/Ni(111) system (PDF)

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**Notes**

The authors declare no competing financial interest.

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