Supporting Information

Deep Learning Assisted Investigation of Electric Field-Dipole Effects on Catalytic Ammonia Synthesis

Mingyu Wan†, Han Yue†, Jaime Notarangelo1, Hongfu Liu2, Fanglin Che1*

1Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, 01854, USA

2Michtom School of Computer Science, Brandeis University, Waltham, MA, 02453, USA

*Email: fanglin_che@uml.edu
1. Computational Setup

DFT calculations were conducted using the Vienna Ab-initio Simulation Package (VASP). These calculations were used to determine the ground state energy and the most favorable configuration of each species in the process of ammonia synthesis over Ru. There were two Ru surfaces tested, including the most thermodynamic favorable flat surface – Ru(0001), and the most active stepped surface for ammonia synthesis – Ru(1013). In particular, the Ru(1013) surface is equivalent to a periodic “ladder” with B5 type adsorption sites (Figure S1). The Ru(0001) surface has four adsorption sites for which species can adsorb, including top, bridge, hcp, and fcc. The Ru(1013) surface has seven adsorption sites for the reaction-related species to adsorb, including hollow site between one upper top atom and two lower top atoms (h1), hollow site between two upper top atoms and one lower top atom (h2), four-fold hold site (S4), upper top (Ut), lower top (Lt), upper bridge (Ub), lower bridge (Lb) and upper-lower bridge (ULb).

For all calculations we used the Generalized Gradient Approximation with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The projector-augmented wave method was applied to solve the Kohn-Sham equations. A first-order Methfessel-Paxton smearing method with width of 0.1 eV was used to account for partial occupancies around the Fermi level and to speed up the convergence. We chose the k-point Monkhorst-Pack mesh (3 × 3 × 1) for p(4 × 4) Ru(0001) surface and Ru(1013) surface and the plane-wave energy cutoff (500 eV) for DFT calculations. For four-layer Ru(0001) and Ru(1013) slabs, we fixed the bottom two layers to their bulk position and relaxed the top two layers to electronically interact with the surface adsorbates. The lattice constant of Ru was calculated as 2.726 Å, which is consistent as experimental work and other theoretical works. Geometries were considered optimized when the energy had converged to 10⁻⁵ eV and the forces were smaller than 0.03 eV/Å.

We have examined the energetics of the possible reaction paths for ammonia synthesis (Figure S2) from dinitrogen reduction over Ru(0001) and Ru(1013) surfaces. Based on the thermodynamic energetics, the 1st and 2nd most favorable reaction paths are presented in Figure S3. Thus, in our work, we only examine the electric field effects on the 1st and 2nd most favorable reaction paths.

To simulate the field-induced energetics through DFT calculations, we use the approach as proposed by Neugebauer and Scheffler, wherein the uniform electric fields are generated without
adding or removing any charge from the supercell.\textsuperscript{11} Regarding the ‘field emissions’ effects,\textsuperscript{12} our vacuum width is \( \sim 11 \) Å. This leads to a charge density in the vacuum, which is less than the magnitude of the Gibbs’ oscillations (0.001 e/Å\(^3\)) associated with plane-wave cutoffs.

We first examined the possible adsorption configurations for the reaction intermediates during ammonia synthesis over Ru surfaces (\textit{Figures S4 – S19}). To examine the electric field effects on the energetics (i.e., adsorption, reaction) of ammonia synthesis, we applied the negative electric fields from 0 to \(-1\) V/Å with the interval of 0.2 V/Å and applied the positive electric fields from 0 to 1 V/Å with the interval of 0.2 V/Å to the most favorable adsorption geometries and optimized them. The adsorption energy \( (E_{\text{ad}}(F)) \), in the presence and absence of electric fields, could also be calculated according to Eqn. (S1):

\[
E_{\text{ad}}(F) = E_{\text{total}}(F) - E_{\text{surface}}(F) - E_{\text{adsorbate}},
\]

where \( E_{\text{total}}(F) \) represents the total energy of the species over the surface with fields, \( E_{\text{surface}}(F) \) represents the energy of the surface (either Ru(0001) or Ru(1013)) with fields, and \( E_{\text{adsorbate}} \) represents the energy of the adsorbate in the absence of electric fields. Here, our assumption is that when an external electric field is present, only the energetics of adsorbates after adsorption and catalyst surfaces will be influenced by the fields. While the energetics of the gas phase molecules won’t be influenced by the electric field effects due to the full degree of freedoms (rotation, translation, vibration) of the molecules in the gas phase. More negative value of the \( E_{\text{ad}}(F) \) represents strong bonding between the adsorbates and the surface. The field-dependent adsorption energies of the ammonia synthesis-related reaction intermediates are presented in \textit{Figures S20 – S21}.

We then examined the co-adsorption configurations of the intermediates for the 1\textsuperscript{st} and 2\textsuperscript{nd} most favorable reaction mechanism during ammonia synthesis over Ru(0001) and Ru(1013) surfaces (\textit{Figures S22 – S30}). The co-adsorption configuration setup of two species was based on the most favorable stable sites of each involved species, found previously in \textit{Figures S4 – S19}. The field-dependent reaction energy \( (\Delta H_{\text{rxn}}(F)) \) was calculated using Eqn. (S2):

\[
\Delta H_{\text{rxn}}(F) = E_{FS}(F) - E_{IS}(F),
\]
where $E_{FS}(F)$ and $E_{IS}(F)$ are the total energies of the final state (FS) and the initial state (IS) of one elementary step during the ammonia synthesis process with and without electric fields. Endothermic reactions are accompanied by positive values of $\Delta H_{rxn}(F)$ and vice versa.

In the presence of a uniform electric field $(F)$, we can expand $E_{ad}(F)$ and $\Delta H_{rxn}(F)$ in Taylor series in terms of electric fields using Eqn. (S3) and (S4):\textsuperscript{13-17}

$$E_{ad}(F) = E_{ad} - \vec{\mu} \cdot \vec{F} - \frac{1}{2} \alpha |\vec{F}|^2,$$

(S3)

$$\Delta H_{rxn}(F) = \Delta H_{rxn} - \Delta \vec{\mu}_{rxn} \cdot \vec{F} - \frac{1}{2} \Delta \alpha_{rxn} |\vec{F}|^2,$$

(S4)

where $\vec{\mu}$ and $\alpha$ are the effective dipole moment and polarizability for surface adsorbates.\textsuperscript{18-25} $E_{ad}$ and $\Delta H_{rxn}$ are the adsorption and reaction energies without fields. $\Delta \vec{\mu}_{rxn}$ and $\Delta \alpha_{rxn}$ are the effective dipole moment change and polarizability change between final and initial states of an elementary reaction.\textsuperscript{18-25} In theory, the adsorption (or reaction) with larger $\vec{\mu}$ ($\Delta \vec{\mu}_{rxn}$) and larger $\alpha$ ($\Delta \alpha_{rxn}$) will have larger electric field effects.

\textbf{Figure S1.} Top and side views of Ru(0001) and Ru (1013) catalytic surfaces. All possible adsorption sites over Ru(0001) and Ru(1013) surfaces are marked in red. Blue area refers to B5 site.
**Figure S2.** Possible reaction mechanisms of ammonia synthesis over Ru catalytic surfaces.

![Reaction Mechanism Diagram](image)

**Figure S3.** The energetics of possible reaction paths during ammonia synthesis over Ru(0001) and Ru(1013). This shows that a for Ru(0001) surface, the most energetics favorable path for dinitrogen reduction is dissociative pathway ($N_2^* \leftrightarrow 2N^*$); and b for Ru(1013) surface, the most energetics favorable path for dinitrogen reduction is dissociative pathway ($N_2^* \leftrightarrow 2N^*$), while the 2nd most energetics favorable path is associative pathway ($N_2^* + H^* \leftrightarrow N_2H^*$). Asterisk (*) represents the empty surface site.

![Energy Diagram](image)
The most favorable adsorption geometry is when N* sits at the hcp site on the Ru(0001) surface. When N* adsorbs over the bridge site, it is not stable and it shifts to the most favorable hcp site.

The most favorable adsorption geometry is when N* sits at the Ub1 site on the Ru(1013) surface. When N* adsorbs over Ut or Lt site, it is not stable and it shifts to the nearby favorable site.

The most favorable adsorption geometry is when H* sits at the fcc site on the Ru(0001) surface. When H* adsorbs over the bridge site, it is not stable and it shifts to the nearby fcc site.
**Figure S7.** The possible adsorption configurations of H\(^+\) over the Ru(1013) surface and its corresponding energetics. The most favorable adsorption geometry is when H\(^+\) sits at the Ub site on the Ru(1013) surface. When H\(^+\) adsorbs over the S4 site, it is not stable and it shifts to the nearby Ub site.

**Figure S8.** The possible adsorption configurations of N\(_2^+\) over the Ru(0001) surface and its corresponding energetics. The most favorable adsorption geometry is when N\(_2^+\) sits at the hcp site on the Ru(0001) surface.

**Figure S9.** The possible adsorption configurations of N\(_2^+\) over the Ru(1013) surface and its corresponding energetics. The most favorable adsorption geometry is when N\(_2^+\) sits at the S4 site on the Ru(1013) surface.
**Figure S10.** The possible adsorption configurations of H$_2^*$ over the Ru(0001) surface. The only stable adsorption geometry is when H$_2^*$ sits at the top site on the Ru(0001) surface. For example, when H$_2^*$ sits at the fcc site, it is not stable and it breaks into 2H$^*$. 

**Figure S11.** The possible adsorption configurations of H$_2^*$ over the Ru(1013) surface. The only stable adsorption geometry is when H$_2^*$ sits at the Ut site on the Ru(1013) surface. For example, when H$_2^*$ sits at the Lt site, it is not stable and it breaks into 2H$^*$. 
**Figure S12.** The possible adsorption configurations of NH\(^{+}\) over the Ru(0001) surface and its corresponding energetics. The most favorable adsorption geometry is when NH\(^{+}\) sits at the hcp site on the Ru(0001) surface. When NH\(^{+}\) adsorbs over the bridge site, it is not stable and it shifts to the nearby hcp site.

**Figure S13.** The possible adsorption configurations of NH\(^{+}\) over the Ru(1013) surface and its corresponding energetics. The most favorable adsorption geometry is when NH\(^{+}\) sits at the h2 site on the Ru(1013) surface.

**Figure S14.** The possible adsorption configurations of NH\(_2^{+}\) over the Ru(0001) surface and its corresponding energetics. The most favorable adsorption geometry is when NH\(_2^{+}\) sits at the bridge site on the Ru(0001) surface. When NH\(_2^{+}\) sits at the fcc or hcp site, it is not stable and it shifts to the nearby bridge site.
Figure S15. The possible adsorption configurations of NH$_2^*$ over the Ru(1013) surface and its corresponding energetics. The most favorable adsorption geometry is when NH$_2^*$ sits at the Ub site on the Ru(1013) surface. When NH$_2^*$ sits at the S4 site, it is not stable and it shifts to the nearby ULb site.

Figure S16. The possible adsorption configurations of NH$_3^*$ over the Ru(0001) surface and its corresponding energetics. The most favorable adsorption geometry is when NH$_3^*$ sits at the top site on the Ru(0001) surface. When NH$_3^*$ sits at the hcp site, it is not stable and it shifts to the nearby top site.

Figure S17. The possible adsorption configurations of NH$_3^*$ over the Ru(1013) surface. The only stable adsorption geometry is when NH$_3^*$ sits at the Ut site on the Ru(1013) surface. For example, when NH$_3^*$ sits at the Lt site, it is not stable and it shifts to the nearby Ut site.
Figure S18. The possible adsorption configurations of N\textsubscript{2}H\textsuperscript{+} over the Ru(0001) surface and its corresponding energetics. The most stable adsorption geometry is when N\textsubscript{2}H\textsuperscript{+} sits at the hcp site on the Ru(0001) surface. When N\textsubscript{2}H\textsuperscript{+} sits at the top site, it is not stable and it shifts to the fcc site.

Figure S19. The possible adsorption configurations of N\textsubscript{2}H\textsuperscript{+} over the Ru(1013) surface and its corresponding energetics. The most stable adsorption geometry is when N\textsubscript{2}H\textsuperscript{+} sits at the hcp site on the Ru(1013) surface.
Figure S20. The electric fields effects on altering the adsorption energies of the most favorable adsorption configurations of a H*, b H₂*, c N*, d N₂*, e NH*, f N₂H*, and g NH₂* over Ru(0001).
Figure S21. The electric fields effects on altering the adsorption energies of the most favorable adsorption configurations of a H$^\ast$, b H$_2^\ast$, c N$^\ast$, d N$_2^\ast$, e NH$^\ast$, f N$_2$H$^\ast$, and g NH$_2^\ast$ over Ru(1013).
Figure S22. The possible co-adsorption configurations of $2N^*$ over the Ru(0001) surface and its corresponding energetics. The most stable co-adsorption geometry is when $2N^*$ sits at the hcp site on the Ru(0001) surface.

Figure S23. The possible co-adsorption configurations of $2N^*$ over the Ru(1013) surface and its corresponding energetics. The most stable co-adsorption geometry is when $2N^*$ sits at the Ub_h2 site on the Ru(1013) surface.

Figure S24. The possible co-adsorption configurations of $N^*$ and $H^*$ over the Ru(0001) surface and its corresponding energetics. The most stable co-adsorption geometry is when $N^*$ and $H^*$ sit at the hcp_fcc site on the Ru(0001) surface.
**Figure S25.** The possible co-adsorption configurations of N* and H* over the Ru(1013) surface and its corresponding energetics. The most stable co-adsorption geometry is when N* and H* sit far away and adsorb at the Ub_Ub site on the Ru(1013) surface.

**Figure S26.** The possible co-adsorption configurations of NH* and H* over the Ru(0001) surface and its corresponding energetics. The most stable co-adsorption geometry is when NH* and H* sit at the hcp_fcc site on the Ru(0001) surface.
Figure S27. The possible co-adsorption configurations of NH\textsuperscript{+} and H\textsuperscript{+} over the Ru(1013) surface and its corresponding energetics. The most stable co-adsorption geometry is when NH\textsuperscript{+} and H\textsuperscript{+} sit at the h2\_Ub site on the Ru(0001) surface.

Figure S28. The most favorable co-adsorption configurations of NH\textsubscript{2}\textsuperscript{+} and H\textsuperscript{+} over the Ru surfaces.

Figure S29. The most favorable co-adsorption configurations of N\textsubscript{2}\textsuperscript{+} and H\textsuperscript{+} over the Ru surfaces.
Figure S30. The most favorable co-adsorption configurations of NH* and N* over the Ru surfaces.
2. Large Electric Field in Experimental Setups

In the research field of electric field-enhanced catalysis, to the best of our knowledge, there are three ways to generate a large electric field in the experimental works.

- **Highly localized electric field within the catalyst structure.** Large oriented electric fields can be created over molecular length scales in (metallo-)enzyme and zeolite catalytic active sites, on the order of >0.1 V/Å. These fields may decrease activation barriers in enzymatic and zeolite catalysis and in turn, govern the selectivity of the desired reaction path. Especially, the Boxer group has identified the highly localized electric field, > 1.5 V/Å, in the enzyme’s active site via calibrating the shifts in molecular vibrational frequencies, known as Stark shifts, of CO molecules.

- **External electric fields generated in gas/solid heterogeneous catalytic system.** Scanning tunneling microscope tips (STM) or field ion/emission microscopes (FIM or FEM) can generate such fields in ultra-high vacuum conditions, and these tools have been used to study field-dependent catalysis. For example, an electric field on the order of 1 V/Å can be generated with an applied electrical bias of 10 V if a metal tip with a 1 nm diameter is used. Because of this property and their relative ease of use and measurement, STM probes are well-suited as “nanoreactor” systems for testing the effects of electric fields on catalytic reactions. Such an experiment involving a Diels-Alder reaction was recently reported by Aragones et al.

Electric field effects have also been probed in flow reactor systems via probe-bed-probe reactor, coaxial capacitor reactor, dielectric barrier discharge reactor, and microwave reactor. However, in practice, applying a large electric field, > 0.1 V/Å to a reaction is challenging because large voltages applied over macroscopic distances result in dielectric breakdown (e.g., air brakes down at the electric field of ~ 3 × 10⁻³ V/Å, but electric field of > 0.1 V/Å is needed to alter the catalytic thermodynamic and kinetic properties). Similar to ultrahigh vacuum conditions in STM/FIM/FEM (i.e., few gas molecules to breakdown under the high electric field at low pressure), it is possible to avoid the breakdown and apply such large electric fields at the microscopic scale by controlling the surface charge difference of the polarized electrode within a very short electrode-electrode distance (few molecules in a small path length). Moreover, the strength of electric
fields increases as increasing the curvature of the catalyst. Thus, small metal nanoparticles can help achieve desired strengths of the local electric fields for field-induced catalysis.\textsuperscript{45, 65-70}

- **Interfacial electric fields generated at gas/liquid/solid triple phase boundary.** In an electrochemical cell, a large potential drop (i.e., 1.2 V) is generated due to the opposite charges at each side of the interface layer between the electrode and the electrolyte (the so-called "Helmholtz layer"). As a result, a very high electric field on the order of 0.1 to 0.4 V/Å is produced within this thin interfacial layer (i.e., 3 to 8 Å\textsuperscript{71}). Such an interfacial electric field can be further strengthened by the local pH\textsuperscript{72} and the ion/cation\textsuperscript{73-74} of the solution. The Kanan group induced an interfacial static electric field by applying a constant voltage between two Si electrodes, which significantly changed the selectivity of a Rh porphyrins-TiO\textsubscript{2} catalyst for the carbine reaction to favor the cyclopropanation product rather than the insertion product from maximum ratio of 100/1 to minimum ratio of 1/2.\textsuperscript{75-76} Furthermore, Román-Leshkov and Surendranath groups\textsuperscript{72} showed that ethylene hydrogenation rates can be modified when local electric field at Pt/C particles suspended in an electrochemical cell was varied (by modifying the pH of the solution) and monitored via vibrational Stark effect\textsuperscript{26-27, 45, 77-78} for CO and by open-circuit potential of the cell.
3. Field-Dependent Reaction Barriers

The elementary reactions over Ru(1013) to calculate the field-dependent activation barriers are shown below:

\[
\begin{align*}
\text{H}_2^* + * &\leftrightarrow 2\text{H}^*, \\
\text{N}_2^* + * &\leftrightarrow 2\text{N}^*, \\
\text{N}_2^* + \text{H}^* &\leftrightarrow \text{N}_2\text{H}^* + *, \\
\text{N}_2\text{H}^* + * &\leftrightarrow \text{N}^* + \text{NH}^*, \\
\text{N}^* + \text{H}^* &\leftrightarrow \text{NH}^* + *, \\
\text{NH}^* + \text{H}^* &\leftrightarrow \text{NH}_2^* + *, \\
\text{NH}_2^* + \text{H}^* &\leftrightarrow \text{NH}_3^* + *.
\end{align*}
\]

where the asterisk (*) represents the surface empty site. All field-dependent activation barrier results from DFT are shown in Figure S31. It is noticed that H$_2^*$ over Ru(1013) doesn’t exist. This is because when H$_2$ adsorbs over the surface, it automatically breaks into 2H$^*$ with the electric field of -1 V/Å, while H$_2$ dissociation with the electric field of 0 and 1 V/Å is also a barrier-free process (Figure S31a). The convergence criteria of TS are the same as that of the adsorption geometry optimization, i.e., the energy converged to $10^{-5}$ eV and the forces smaller than 0.03 eV/Å. For the elementary reaction of NH$_2^* + \text{H}^* \leftrightarrow \text{NH}_3^* + *$, we used CI-NEB method to get a better initial guess for the minimum energy pathway and used Dimer$^{79}$ method to find the true TS. The true TS was further verified by calculating their vibrational frequencies confirming that a single unique normal mode eigenvector was obtained which corresponds to the negative curvature at the saddle point.
Figure S31. Transition state calculations with and without the electric fields for the ammonia synthesis-related elementary reactions over Ru(1013). a $\text{H}_2^* + * \leftrightarrow 2\text{H}^*$ (Note: $\text{H}_2^*$ over Ru(1013) with the electric field of -1 V/Å doesn’t exist. This is because when H$_2$ adsorbs over the surface, it automatically breaks into 2H* under the negative field of -1 V/Å); b $\text{N}_2^* + * \leftrightarrow 2\text{N}^*$; c $\text{N}_2^* + \text{H}^* \leftrightarrow \text{N}_2\text{H}^* + *$; d $\text{N}_2\text{H}^* + * \leftrightarrow \text{N}^* + \text{NH}^*$; e $\text{N}^* + \text{H}^* \leftrightarrow \text{NH}^* + *$; f $\text{NH}^* + \text{H}^* \leftrightarrow \text{NH}_2^* + *$; g $\text{NH}_2^* + \text{H}^* \leftrightarrow \text{NH}_3^* + *$ (Note: The hollow squares represent the converged TS after applying Dimer method).

We then corrected the field-dependent activation barrier ($\Delta G^\dagger(F)$) and field-dependent reaction energy ($\Delta G_{\text{rxn}}(F)$) with zero-point energy (ZPE), entropy (S) and temperature (T) corrections as follows:

$$\Delta G^\dagger(F) = G_{TS}(F) - G_{IS}(F),$$  \hspace{1cm} (S12)

$$\Delta G_{\text{rxn}}(F) = G_{FS}(F) - G_{IS}(F),$$  \hspace{1cm} (S13)
where \( G_{IS}(F), G_{TS}(F) \) and \( G_{FS}(F) \) are field-dependent free energies of IS, TS and FS, respectively. The field-dependent free energy \( G(F) \) can be written as Eqn. (S14):

\[
G(F) = E_{DFT}(F) + E_{ZPE}(F) - TS(F), \tag{S14}
\]

where \( E_{DFT}(F) \) is the ground state energy from DFT. \( E_{ZPE}(F) \) is the field-dependent zero-point energy (ZPE). The formula of \( E_{ZPE}(F) \) for each examined species refers to Eqn. (S15). For the surface reactions, since all the involved species adsorb over the catalytic surface, the transitional and rotational degree of freedom become restricted translation- and rotational-vibrational modes. Thus, only field-dependent vibrational entropy contribution \( (S_{\text{vib}}(F)) \) is considered for the temperature-entropy correction for surface reactions (Eqn. (S16)). The entropy for gas phase molecule (i.e., NH\(_3\)) at a certain temperature (T) and standard pressure (0.1 MPa) can be referred to the JANAF thermochemical table.\(^{80}\) We also fixed all Ru atoms and relaxed only the surface adsorbates to avoid vibrational frequency noise form the surface for vibrational frequency calculations. It is worth mentioning that the vibrational frequencies \((\nu_i(F))\) for the surface species were calculated with and without electric fields.

\[
E_{ZPE}(F) = \frac{1}{2} \sum_i h\nu_i(F), \tag{S15}
\]

\[
S_{\text{vib}}(F) = R \sum_i [\frac{h\nu_i(F)}{k_BT} e^{\frac{h\nu_i}{k_BT}} - ln(1 - e^{\frac{h\nu_i(F)}{k_BT}})], \tag{S16}
\]

where \( k_B \) is Boltzmann constant and \( R \) is gas constant. We presented the ZPE and TS corrected field-dependent activation barriers in Table S1 and field-dependent reaction energies in Table S2. Here, temperature conditions of 473 K\(^{81}\) and 773 K\(^{52}\) are to estimate low temperature and high temperature field-accelerated energetics of ammonia synthesis.

The field-dependent forward reaction rate constants \((k_f(F))\) and backward reaction rate constants \((k_b(F))\) for an elementary reaction are estimated using Eqn. (S17 – S18):

\[
k_f(F) = \frac{k_B T}{h} e^{-\frac{\Delta G_i(F)}{k_B T}}, \tag{S17}
\]

\[
k_b(F) = \frac{k_B T}{h} e^{-\frac{\Delta G(F) - \Delta G_{\text{rxn}}(F)}{k_B T}}. \tag{S18}
\]

Finally, the field dependent equilibrium constant \((K(F))\) can be obtained by:
\[ K(F) = \frac{k_f(F)}{k_b(F)}. \] (S19)

**Table S1.** The field-dependent reaction barriers (\(\Delta G^\ddagger(F)\)) for ammonia synthesis-related elementary reactions over Ru(1013) (all energies in eV).

| Reactions | F = -1 V/Å | F = 0 V/Å | F = 1 V/Å |
|-----------|------------|------------|------------|
|           | 473 K | 773 K | 473 K | 773 K | 473 K | 773 K |
| \(N_2^* + * \leftrightarrow 2N^*\) | 0.56 | 0.59 | 0.62 | 0.65 | 0.68 | 0.72 |
| \(N_2^* + H^* \rightarrow N_2H^* + *\) | 1.19 | 1.23 | 1.15 | 1.18 | 1.08 | 1.12 |
| \(N_2H^* + * \leftrightarrow N^* + NH^*\) | 0.25 | 0.27 | 0.3 | 0.32 | 0.35 | 0.37 |
| \(N^* + H^* \leftrightarrow NH^* + *\) | 1.04 | 1.05 | 1.01 | 1.02 | 0.95 | 0.96 |
| \(NH^* + H^* \leftrightarrow NH_2^* + *\) | 1.07 | 1.09 | 1.05 | 1.04 | 0.98 | 0.99 |
| \(NH_2^* + H^* \leftrightarrow NH_3^* + *\) | 1.37 | 1.38 | 1.26 | 1.28 | 1.13 | 1.15 |

**Table S2.** The field-dependent reaction energies (\(\Delta G_{rxn}(F)\)) for ammonia synthesis-related elementary reactions over Ru(1013) (all energies in eV).

| Reaction | F = -1 V/Å | F = 0 V/Å | F = 1 V/Å |
|---------|------------|------------|------------|
|         | 473 K | 773 K | 473 K | 773 K | 473 K | 773 K |
| \(N_2^* + * \leftrightarrow 2N^*\) | -0.24 | -0.26 | -0.15 | -0.16 | -0.05 | -0.06 |
| \(N_2^* + H^* \leftrightarrow N_2H^* + *\) | 0.56 | 0.59 | 0.32 | 0.35 | 0.01 | 0.05 |
| \(N_2H^* + * \leftrightarrow N^* + NH^*\) | -0.62 | -0.67 | -0.51 | -0.57 | -0.39 | -0.44 |
| \(N^* + H^* \leftrightarrow NH^* + *\) | 0.16 | 0.17 | -0.02 | -0.03 | -0.29 | -0.29 |
| \(NH^* + H^* \leftrightarrow NH_2^* + *\) | 0.01 | 0.02 | -0.11 | -0.08 | -0.26 | -0.23 |
| \(NH_2^* + H^* \leftrightarrow NH_3^* + *\) | 0.7 | 0.62 | 0.49 | 0.39 | 0.22 | 0.23 |
4. Charge Analysis

Differential charge density analysis and Bader charge analysis for various coverages of NH$_3$ over Ru(0001) surfaces are shown in Figure S32.

Figure S32. Differential Charge density analysis and Bader charge analysis for various coverages of NH$_3$ over Ru(0001) surfaces. The isosurface of the differential charge density is 0.01 e/Bohr$^3$. 
5. Deep Learning Method

Let \( X_M \) denote the features and \( A_M \) stand for the similarities, where \( M = (g, s, o) \) is the set of adsorbates in the gas phase, catalytic surfaces, and adsorbate adsorption over the catalytic surfaces, respectively. Let \( F_M \) be the electric fields, and \( E_M \) be the field-dependent total energy, then our goal is to find a function \( f : (X_g, X_s, X_o, A_g, A_s, A_o, F_g, F_s, F_o, E_g, E_s) \) to predict the \( E_o \) under various electric field values.

We designed a novel deep learning framework for predicting the field-dependent adsorption energies. Specially, we employed the Graph Neural Network (GNN) to capture the relationship among the geometries of adsorbate in the gas phase, pure catalytic surface, and adsorbate adsorption over the catalytic surface. The reason of applying GNN is a special deep learning architecture widely used to capture the information-exchange among the relational data. Then we adopted Multi-Layer Perceptron (MLP) for regression analysis. Let \( \theta = \{\theta_G, \theta_H, \theta_P\} \) be the learnable parameters in the model, where \( \theta_G, \theta_H, \theta_P \) are learnable parameters for GNN, hidden layers and prediction layers, respectively. Detailed objective function is as follows.

**Graph Neural Network.** We built a graph for each structure, where each node denotes an atom, and each edge is represented by the similarity between two atoms. The adjacency matrix of the graph is defined by:

\[
A_M(i, j) = 1/Dist^2(i, j),
\]

where \( Dist^2(i, j) \) is the squared distance between atom \( i \) and atom \( j \). With this adjacency matrix, we then applied Graph Convolutional Network (GCN), a concrete algorithm of GNN, to incorporate similarities of all atoms with their corresponding features, as follows:

\[
G_M^{(l+1)} = ReLU(\tilde{D}^{-1/2}\tilde{A}\tilde{D}^{-1/2}G_M^{(l)}\theta_G^{(l)}),
\]

where \( \tilde{A} = A + I \) is the adjacency matrix \( A \) with added self-connections, \( I \) is the identity matrix, \( \tilde{D} \) is the degree matrix of \( \tilde{A} \), and \( \theta_G^{(l)} \) is a layer-specific trainable weight matrix. \( G_M^{(l)} \) denotes the matrix in the \( l^{th} \) layer for \( M, G_M^{(0)} = X_M \). In experiments, we adopted a 2-layer GCN for simplicity.
**Multilayer Perceptron.** Multilayer Perceptron (MLP)\(^{83}\) is a universal non-linear function approximator for regression analysis. We first built an MLP on top of the GCN and incorporated the electric field values as the hidden layer to get hidden representations:

\[
H_M = ReLU(Concat(G_M, F_M)\theta_H).
\]  
(S22)

Then for each of the three parts, i.e., adsorbate in the gas phase, pure catalytic surface, and adsorbate adsorption over the catalytic surface, we got a hidden representation. Combining them with the energy of adsorbate and surface, we adopted another MLP as the prediction layer:

\[
P_o = ReLU(Concat(H_g, H_s, H_o, E_g, E_s)\theta_P),
\]  
(S23)

where \(P_o\) is the predicted energy for adsorbate adsorption over the catalytic surface. Finally, we adopted Equation (S1) to calculate the adsorption energy of reactive intermediates under various electric fields.

**Objective Function.** We adopted absolute error as our objective function, which can be written as:

\[
min_{\theta}|P_o - E_o|.
\]  
(S24)

We adopted Adam optimizer\(^{84}\) to minimize the objective function.

**Detailed Architecture.** The detailed architecture of our deep model in Scheme 1c is presented in Figure S33. Here, “#sample” of Input/Output Dimension in all layers (i.e., 2-layer Shared GNN, Max pooling, Shared MLP, and 2-layer MLP) denotes the number of molecules. For example, the molecules in our deep learning model for ammonia synthesis over Ru(1013) and Ru(0001) surfaces include (1) the radicals/molecules in the gas phase (19 species) under no electric fields; (2) the pure catalytic surfaces under no electric fields and electric field of ± 0.6 V/Å (2 surfaces × 3 electric fields = 6 scenarios); and (3) the adsorbate over the surface under no electric fields and electric field of ± 0.6 V/Å (51 species × 3 electric fields = 153 scenarios). “#node” of Input/Output Dimension in 2-layer Shared GNN denotes the maximum number of atoms within a structure. The maximum number of atoms within a structure in our system is 8 NH\(_3\) over Ru(1013), which is 48. And “#feature” of Input Dimension 2-layer Shared GNN is the number of chemical element types.
In our case, ammonia synthesis over Ru, the number of chemical element types is 3 since we only have Ru, N, and H. The purpose of 2-layer Shared GNN is to capture the relationship among the configurations in adsorbate in the gas phase, pure catalytic surface, and adsorbate adsorption over the catalytic surface (Total). The purpose of Max Pooling is to get structure-level features from atom-level features. After employing GNN, a shared multiple-layer perception aims to predict field-induced adsorption energetics, dipole moments, and polarizabilities of reactive intermediates over surfaces for catalytic ammonia synthesis. The final output dimension of the 2-layer MLP is the field-dependent adsorption energy of certain sample. The dimensions of hidden layers are 64 and 32, which are popular used in computer science area. It is also worth mentioning that the shared GNN and MLP mean they have the same weights for adsorbate, surface, and adsorbed systems.

*Figure S33.* The detailed architecture of our deep model in *Scheme 1c.*
6. Implementation Details

We adopted Adam optimizer\textsuperscript{84} with a learning rate of 0.003, and run 8000 epochs to train the model. The experiments were run on a physical machine with Ubuntu 18.04, total memory of 64GB, AMD Ryzen Threadripper 2920X 12-Core Processor, and an NVIDIA GP102 GPU.
7. Training Structures

Our deep learning model for ammonia synthesis over Ru(1013) and Ru(0001) surfaces has three components, including the optimized geometries and the corresponding energies of (1) the radicals/molecules in the gas phase (19 species) under no electric fields; (2) the pure catalytic surfaces under no electric fields and electric field of ± 0.6 V/Å (2 surfaces × 3 electric fields = 6 scenarios); and (3) the adsorbate over the surface under no electric fields and electric field of ± 0.6 V/Å (51 species × 3 electric fields = 153 scenarios). Using the above data, our deep learning model is able to predict the field-dependent adsorption energies, dipole moments and polarizabilities of the ammonia synthesis-related intermediate adsorption system over Ru under the electric field ranges of -1 to 1 V/Å. All the species are involved in the elementary steps (Eqn. (S5 – S11)) of ammonia synthesis. More specifically, the adsorption system includes H adsorption, H₂ adsorption, H-H co-adsorption, N adsorption, N₂ adsorption, N-N co-adsorption, N₂-H co-adsorption, N₂H adsorption, N-NH co-adsorption, N-H co-adsorption, NH adsorption, NH-H adsorption, NH₂ adsorption, NH₂-H co-adsorption and NH₃ adsorption with various coverage (1/16 monolayer (ML), 2/16 ML, 4/16 ML, and 8/16 ML) at their most favorable adsorption sites. We also include some species (e.g., NH, N-NH co-adsorption, etc.) at their less favorable adsorption sites. Considering that there is no public train/test split for this dataset, we adopted 10-fold cross validation, which splits all structures into 10 folds and perform the fitting procedure a total of ten times. Each fit is performed on a training set consisting of 9 folds of structures and the remaining fold as the test set. The training structures are shown in Tables S3 and S4.

Table S3. The training structures over Ru(0001) with no electric field and ± 0.6 V/Å.

| Species | Ru (0001) | No Electric Field | Electric Field ± 0.6 V/Å |
|---------|-----------|-------------------|--------------------------|
| H-H (2fcc) | H-H (fcc hcp) | N-N (fcc hcp) | N-N (2hcp) | NH₃ (top) | 2NH₃(top) |
| N (hcp) | N-H (hcp hcp) | N-H (fcc hcp) | N-NH (2hcp) | N-NH (fcc hcp) | H₂ (top) |
| N₂ (hcp) | N₂ (top) | N₂H (fcc) | N₂H (hcp) | NH (fcc) | NH (hcp) |
| NH₂ (bridge) | NH₂-H (fcc hcp) | NH-H (hcp fcc) | NH-H (fcc hcp) | NH₂ (hcp) |

Table S4. The training structures over Ru(1013) with no electric field and ± 0.6 V/Å.

| Species | Ru (1013) | No Electric Field | Electric Field ± 0.6 V/Å |
|---------|-----------|-------------------|--------------------------|
| H-H (ub-ub) | N-N (ub-h2) | 2NH₃ (ut) | 4NH₃ (ut) | NH₃ (ut) | H (ub) |
| H₂ (h1) | H₂ (st) | N (ub) | N-H (ub-ub) | N-NH (ub ub) | N-NH (ub h1) |
| N₂ (B5) | N₂-H (B5-ub) | N₂-H (B5) | NH (b) | NH-H (ub ub) | NH-H (h1 ub) |
| NH (h1) | NH₂-H (ub-ub) | NH₂ (ub) | 8NH₃ (ut) |
To broaden the impacts of our developed deep learning model, we show here that our deep learning model has the transferability to predict field-dependent adsorption energies, dipole moments, and polarizabilities of ammonia synthesis-related intermediates over other catalytic surfaces (e.g., Fe). The possible adsorption sites over Fe(110) and Fe(111) are shown in Figure S34. We applied the Ru-trained deep learning model to predict the energetics of ammonia synthesis over Fe(110) and Fe(111) surfaces under electric fields. The results show that with 10%, 20%, and 30% training data of ammonia synthesis related intermediate adsorption energy over Fe(110) and Fe(111), we can predict the rest adsorption data of field-dependent ammonia synthesis over Fe with the mean absolute error of 0.17 eV, 0.14 eV, and 0.09 eV, respectively (Figure S35). The training structures of the Fe system are shown in Tables S5 – S7.

Figure S34. Top and side views of Fe(110) and Fe(111) catalytic surfaces. All possible adsorption sites over Fe(110) and Fe(111) surfaces are marked in red.
Figure S35. The performance of the Ru-trained deep learning model on predicting field-dependent energetics over Fe(111) and Fe(110) surface with 30% training data. a The comparison between the DFT-calculated adsorption energies and the deep-learning predicted ones over Fe(111) and Fe(110) surfaces; b The mean absolute errors (5% outliers removed) for adsorption energy (no fields), dipole moment and polarizability for ammonia synthesis related intermediates over Fe(110) and Fe(111) are 0.08 eV, 0.08 eÅ, and 0.07 eÅ²/V, respectively. Our deep learning model was first trained with the DFT data using the system of Ru and further tuned with 30% training data – the configurations and the corresponding adsorption energies of ammonia synthesis-related intermediates over Fe(110) and Fe(111) at 0.0 V/Å and ±0.6 V/Å.; and c Pearson correlation coefficients for the field-dependent energy diagrams of DFT and deep learning results over Fe surfaces. Yellow area refers to a strong positive relationship with r greater than 0.85.

Table S5. The 10% training structures over Fe(111) and Fe (110) with no electric field and ± 0.6 V/Å.

|                | Fe(111) | Fe(110) |
|----------------|---------|---------|
|                | H-H (hcp-hcp) | NH-H (bri-hcp) | NH₂ (bri) |
|                | H-H (hol-hol) | NH-H (lb-hol) | NH₂ (lb) |

Note: hol represents hollow site and bri represents the bridge site.

Table S6. The 20% training structures over Fe(110) and Fe (111) with no electric field and ± 0.6 V/Å.

|                | Fe(111) | Fe(110) |
|----------------|---------|---------|
|                | H-H (hcp-hcp) | NH-H (bri-hcp) | NH₂ (bri) |
|                | H-H (hol-hol) | NH-H (lb-hol) | NH₂ (lb) |

Note: hol represents hollow site and bri represents the bridge site.

Table S7. The 30% training structures over Fe(110) and Fe (111) with no electric field and ± 0.6 V/Å.

|                | Fe(111) | Fe(110) |
|----------------|---------|---------|
|                | H-H (hcp-hcp) | NH-H (bri-hcp) | NH₂ (bri) |
|                | NH₂ (hcp-hcp) | N-N (bri-hcp) | N-H (bri) |
|                | NH₃ (bri) | NH₂-H (bri-hcp) |
| Fe(110) | H-H (hol-hol) | NH-H (lb-hol) | NH₂ (lb) |
|                | N-N (lb-hol) | N-H (lb) |
|                | NH₂ (lb) | NH₂-H (lb-hol) |
|                | NH₃ (top) | |

Note: hol represents hollow site and bri represents the bridge site.
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