

Physics-Guided Design of Ammonia Decomposition Catalysts with Interpretable Machine Learning

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Abstract

Rational catalyst design for ammonia decomposition requires navigating coupled structural and electronic effects that govern reaction energetics across a large configurational space. Here, we integrate density functional theory (DFT), microkinetic modeling (MKM), and interpretable machine learning to establish a physics-guided screening framework. For the most active stepped Ru(10–13) surface, MKM identifies NH^* dissociation as the rate-limiting step and defines an NH^* binding-energy window of -4.47 to -3.84 eV that sustains near-maximal turnover frequency across 673–750 K and applied fields of 0 and -0.4 V/Å. A DFT database comprising 1,132 Ru and 270 Co configurations spanning surface structure, adatom coverage, and electronic state was used to train a gradient-boosted model, achieving a Ru test mean absolute error (MAE) of 0.082 eV. Although direct Ru-to-Co transfer yields a 0.397 eV error, incorporating only 45 Co configurations reduces the Co test MAE to 0.120 eV. SHAP analysis identifies charge, local site coordination, and surface energy as the dominant factors governing NH^* binding. Guided by these relationships, screening ~33,000 physically constructed candidates enriches the population within the kinetic target, while constrained-DFT validation supports the model's ability to identify promising configurations.

1. Introduction

While hydrogen has emerged as a promising zero-carbon fuel to replace fossil fuels in heavy transport and industry, its widespread adoption remains hindered by storage and transportation limitations.^{1–6} Ammonia (NH_3) circumvents these issues as a high-density, carbon-free hydrogen carrier, provided the hydrogen can be efficiently extracted via catalytic decomposition.^{7–9} Ruthenium (Ru)¹⁰ serves as the benchmark catalyst for this extraction, exhibiting maximum activity on pristine transition metal surfaces with a higher density of B5 sites.^{10–12} However, the identity of the kinetically relevant surface intermediate depends on surface structure, with N^* or NH^* accumulation reported under different catalytic environments.^{13, 14}

Catalytic activity is therefore strongly governed by the interaction between these nitrogen-containing intermediates and the catalyst surface. This interaction is not determined by catalyst composition alone, but emerges from the combined effects of surface facet, local coordination environment, adsorbate and adatom configuration, and surface electronic state.^{15–18} Structural modification through alloying,^{19–21} promoters,^{22, 23} and supports,^{13, 24} as well as electronic perturbations induced by external fields,^{25–29} can therefore alter the same underlying adsorption energetics.^{25, 30} Establishing quantitative relationships between these structural and electronic characteristics and catalytic performance is essential for rational catalyst design. The challenge is that these variables generate a vast configurational space, making systematic exploration by experiment alone impractical and exhaustive first-principles evaluation computationally prohibitive.³¹

First-principles calculations provide an atomic-level basis for connecting catalyst structure to reaction energetics. Density functional theory (DFT) quantifies adsorption energies and reaction barriers,^{32, 33} while microkinetic modeling (MKM) connects these elementary energetics to catalytic observables such as turnover frequency (TOF).^{34, 35} This mechanistic connection is important because the binding-energy descriptor governing activity can depend on the surface structure and the resulting dominant reaction intermediate.^{16, 36, 37} For ammonia decomposition, N* binding energy has been established as an activity descriptor on relatively flat metallic surfaces and subsequently used for catalyst screening and inverse design.^{19, 38, 39} On stepped surfaces containing B5-type sites, however, the reaction kinetics can shift toward NH* accumulation and kinetically limiting NH* dissociation,²⁵ motivating NH* binding energy (BE_{NH}) as the relevant descriptor for the surfaces considered here. Establishing this kinetically informed descriptor reduces the catalyst-design problem from evaluating a complete reaction network for every configuration to identifying structural and electronic environments that produce favorable BE_{NH} . Yet calculating BE_{NH} still requires DFT relaxation for each configuration, making exhaustive exploration of the large configurational space computationally prohibitive.

Machine learning provides a route to bridge this gap by learning the relationship between catalyst characteristics and adsorption energetics from a tractable set of first-principles calculations.^{40, 41} Beyond accelerating binding-energy prediction, interpretable machine-learning models can establish quantitative relationships between local coordination, surface structure, adsorbate environment, and electronic state, revealing how these factors collectively govern the kinetically relevant descriptor.^{42–44} Such relationships are particularly valuable for catalyst design because they identify which structural and electronic characteristics should be tuned to move candidates toward the desired binding-energy regime. Recent inverse-design approaches have extended machine learning toward the direct generation of candidate structures conditioned on target properties.^{45, 46} However, generative models can be challenging for the relatively small datasets typical of first-principles catalysis, and their application is further complicated when the relevant structural descriptors are geometrically coupled and cannot be independently specified.^{43, 46, 47} An alternative is to construct physically realizable structures directly and use an interpretable forward model to evaluate them. This strategy preserves the geometric relationships among descriptors while leveraging learned structure–property relationships to guide efficient screening toward the desired catalytic regime.^{48, 49}

In this work, we develop a physics-guided, interpretable machine-learning framework⁵⁰ for the design of ammonia-decomposition catalysts across coupled structural and electronic configurational spaces. Microkinetic modeling first establishes a kinetically relevant NH* binding-energy window as the catalyst-design objective. We then construct a first-principles database spanning diverse surface structures,⁵¹ local environments,^{52, 53} and electronic states and train a descriptor-based machine-learning model to predict NH* binding energetics. The framework is further extended from Ru to Co to examine its adaptability across catalyst chemistries. Model interpretation is used to uncover quantitative relationships between structural and electronic characteristics and NH* binding, providing physically

meaningful directions for catalyst design. These learned relationships are subsequently integrated with physically grounded structure generation and high-throughput screening to identify candidates within the kinetically favorable regime, followed by first-principles validation. Overall, this framework connects reaction kinetics, catalyst structure, electronic state, and adsorption energetics within an interpretable design workflow for navigating complex catalyst configurational spaces.

2. Methods

2.1 Computational Details

Density Functional Theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP).^{54, 55} For the exchange-correlation functional, we employed the Generalized Gradient Approximation (GGA)⁵⁶ with the Perdew-Burke-Ernzerhof (PBE)^{57, 58} parameterization. Valence states were expanded in plane waves with a cutoff energy of 500 eV, while core electrons were treated using the projector-augmented wave (PAW) method to solve the Kohn-Sham equation.^{59, 60} The bulk hexagonal close-packed Ru and Co were first optimized to determine their equilibrium lattice constants. The optimized lattice parameters were determined to be $a = 2.726 \text{ \AA}$ ($c/a = 1.58$) for Ru^{61, 62} and $a = 2.494 \text{ \AA}$ ($c/a = 1.62$) for Co,⁶³ which are in good agreement with experimental and previous theoretical reports.⁶⁴ Spin polarization was included in all calculations.

Six different surfaces, including flat and stepped (0001, 10–13, 10–10, 10–11, 11–21, and 2-1-12) of Ru and Co were modeled using a $p(4 \times 4)$ supercell. Surface energies calculated for the Ru facets were benchmarked against previously reported values, yielding a mean absolute deviation of 0.004 eV (**Table S1**).⁶⁴ Each slab model consists of four atomic layers with a vacuum of $\sim 11 \text{ \AA}$ in the z -direction to prevent interactions between periodic images. During geometry optimizations, the atoms in the bottom two layers were fixed to their bulk positions, while all other atoms in the slab and adsorbates were allowed to relax with the energy and force criteria of 10^{-5} eV and $0.03 \text{ eV/\AA}$, respectively. A Monkhorst-Pack k -point mesh of $(4 \times 4 \times 1)$ was used for sampling the Brillouin zone.⁶⁵

The binding energy of NH^* (BE_{NH}) on each surface was computed as:

$$BE_{ad} = E_{total} - E_{surface} - E_{adsorbate} \quad (1)$$

where E_{total} is the total energy of the NH -adsorbed slab (including any co-adsorbed adatoms), $E_{surface}$ is the energy of the corresponding bare slab in the identical charge and adatom configuration, and $E_{adsorbate}$ is the energy of an isolated NH radical computed with spin polarization. (**Figures S1-S6, Tables S2-S8**) Under this convention, a more negative BE_{NH} indicates stronger binding. More details on DFT modelling can be found in the SI section S1.

2.2 Microkinetic Modeling (MKM)

To identify the NH^* binding-energy window that maximizes catalytic activity, quantified as turnover frequency (TOF), we developed the MKM. Eight elementary steps were considered to define the ammonia cracking reaction network, for which the reaction rate and equilibrium constants were obtained from DFT-derived data using the Python Multiscale Thermochemistry Toolbox (pMuTT) under the harmonic oscillator approximation.⁶⁶ The obtained kinetic and thermodynamic parameters were then used to build the system of ordinary differential equations (ODEs) and solve for coverages of every molecule involved in the reaction with Cantera.⁶⁷ An isothermal, steady-state plug-flow reactor (PFR) model was employed for the catalyst bed, neglecting axial dispersion and pressure drops. The eight elementary steps in the reaction network included NH_x dehydrogenation, $\text{N} \equiv \text{N}$ and H-H bond formation, NH_3 adsorption, and the desorption of N_2 and H_2 , as detailed in **Tables S9-10**. To construct the activity volcano, BE_{NH} was scanned across approximately -5.11 to -3.64 eV range. TOF was evaluated at 673–750 K under applied electric fields of 0.0 and -0.4 V/Å (**Figure S7**). More details regarding MKM modeling are provided in SI Section S2.

2.3 Charged Surfaces and the Electric-Field Correspondence

The use of explicit charge as a descriptor is motivated by its ability to capture changes in surface electron density associated with an applied electric field. A negative field can enrich the metal surface with electrons, whereas a positive field can deplete surface electron density. Accordingly, explicit charge^{68, 69} and applied electric field provide complementary representations of electronic perturbation, although no one-to-one quantitative correspondence between a given charge state and field strength is assumed here. Because explicit charge can be systematically varied across the large DFT dataset at substantially lower computational cost, we use it as the electronic-state descriptor for subsequent machine-learning analysis.^{25, 28, 70}

2.4 Construction of Configurational Space

To construct a dataset spanning the structural and electronic degrees of freedom considered in this work, we systematically varied surface facet, adatom coverage, adsorption environment, and charge state. For each slab, we first identified the distinct NH^* adsorption sites (**Figures S1-S6**). Thereafter, to create the database with 1/16 ML adatom coverage, we identified the stable active site for adatoms over every Ru slab, with the selection criterion that the adatom must have $\text{CN} \geq 4$. Similarly, for 2/16 ML adatom coverage, with the already existing adatom on the surface, other nearby stable active sites were tested for the second adatom. To have an effective bi-adatom interaction, a valid second adatom had to be bonded with the first adatom; otherwise, two distant adatoms on the surface would only provide two separate mono-adatom interactions with the surface. Once these surfaces were ready, we placed NH^* as the binding species over the distinct active sites and construct the whole sample space.

In total, we calculated 1132 data points over Ru surfaces. Following similar steps with Co, we calculated 270 datapoints ($\sim 24\%$ of the Ru database). Together with the ten charge states per configuration, this

database spans six facets, adatom coverages of 0, 1/16, and 2/16 ML, and adsorption-site environments ranging from top and bridge to three-fold and four-fold hollows.

2.5 Machine-Learning Model Details

After the setup of the sample space, we featurized the dataset with 12 descriptors: charge, surface energy, coverage, GCN_{site}, θ_{NH} , Prox₁, Prox₂, Prox_{ad1-ad2}, GCN_{ad1}, GCN_{ad2}, CN_{slab}, and CN_{ad}. The full definition of each of these features is given in Section S4 of the SI. We then evaluated five machine-learning algorithms: Linear Regression (LR), Ridge Regression,⁷¹ Support Vector Machine (SVM),⁷² Random Forest (RF),⁷³ and XGBoost,⁵⁰ over the dataset. Mean Absolute Error (MAE) is used as the analytical metric to compare the models. Model interpretation was performed using SHAP⁴⁸ and LIME⁷⁴ analyses. More details of the construction of the machine learning models and hyperparameters (**Tables S11-S12**) tuning can be found in section S3 of SI. Whereas the complete details about the local, adatom, and global feature extraction from geometries or input (**Tables S13-S15**) are located in section S4 of SI. Model development was first performed using the Ru dataset, with an 80/20 training-test split. To evaluate cross-metal adaptation, increasing fractions of the Co dataset were subsequently added to the Ru training pool while the remaining Co configurations were retained as an independent test set. The Ru test partition was kept separate to assess whether incorporation of Co-specific data altered prediction accuracy for the original metal.

2.6 Generation of the screening dataset

To identify configurations within the target binding-energy window, we generated a large library of candidate structures directly as periodic slabs. This is a deliberate choice: several descriptors (GCN_{site}, the proximity terms, θ_{NH}) are emergent geometric quantities that cannot be assigned independently, so building the structures first ensures that every screened feature vector corresponds to a physically realizable configuration and is featurized by the same pipeline used for training.

Candidates were generated on the same six facets as the training set for both metals. For each facet, surface atoms were identified by coordination number and height, and adsorption sites (top, bridge, and three-fold hollow) were enumerated by Delaunay triangulation^{75, 76} of the surface-atom positions projected into the surface plane, following the approach used in automated adsorption-site frameworks.^{77, 78} NH* was placed at these sites over a range of tilt orientations to sample θ_{NH} . Adatoms over the surfaces were then built at coverages of 1/16 and 2/16 ML by placing one or two metal adatoms in three-fold hollow sites, with the NH* and adatom positions constrained to reproduce the bonded adatom clusters and NH-adatom coupling present in the training data. The explicit charge states were subsequently applied. Full details of the site-finding algorithm, the geometric constraints, and the placement parameters are given in SI Section 5.

Each generated structure was featurized with the training pipeline, and its BE_{NH} predicted using the trained XGBoost model. In total, ~ 33,000 structures were screened. Because these descriptors are computed from as-built geometries, we verified prediction reliability through the DFT validation in Section

3.6, where the NH^* and adatom positions are held fixed during relaxation so that the feature-defining geometry, and hence the predicted binding energy, is preserved. Additional details of the screening-dataset generation are provided in SI Section S5 (**Tables S16-17**).

3. Results and Discussion

3.1 Identifying the Target NH^* Binding-Energy Range

Ruthenium (Ru) is among the most active catalysts for ammonia decomposition, with its catalytic activity strongly dependent on surface structure. In particular, stepped Ru surfaces containing B5-type ensembles exhibit substantially higher activity than more closely packed surfaces because these sites facilitate N_2 formation. Among the Ru facets considered here, Ru(10–13) represents the most active surface and contains the characteristic B5 sites associated with high ammonia-decomposition activity. We therefore use Ru(10–13) as the representative surface to establish the kinetically relevant binding-energy target for catalyst design.

Microkinetic analysis of ammonia decomposition on Ru(10–13) shows that NH^* dehydrogenation remains the rate-limiting step across the investigated temperatures and applied electric fields, with NH^* accumulating as the dominant surface intermediate.²⁵ The catalytic activity is therefore strongly coupled to the NH^* binding energy (BE_{NH}). Excessively strong NH^* binding leads to surface accumulation and inhibits further turnover, whereas excessively weak binding destabilizes the adsorbed intermediate and suppresses the reaction pathway. These competing effects suggest that BE_{NH} can serve as a kinetic descriptor and motivate identifying a favorable binding-energy range.

To determine this range, we evaluated the steady-state TOF as a function of BE_{NH} using the microkinetic model described in Methods. At 673 K and zero applied field, the TOF increases sharply as NH^* binding weakens, followed by a broad high-activity plateau before decreasing at the weak-binding limit (Fig. 1a). On the strong-binding side, the TOF increases by more than an order of magnitude between -5.1 and -4.6 eV as NH^* accumulation is progressively alleviated. The activity then becomes nearly insensitive to BE_{NH} over a broad region from approximately -4.54 to -3.85 eV, across which the TOF varies by less than 1%. Only beyond this plateau does activity fall away again. Similar behavior is shown under an applied field of -0.4 V/Å (Fig. 1b), where the absolute TOF is roughly two orders of magnitude higher. Because the plateau is flat to within a fraction of a percent, the peak TOF is not a meaningful target, it shifts from -3.96 eV at zero field to -4.06 eV at -0.4 V/Å. We therefore define the objective target range by the extent of the saturated region. For each condition (673, 698, 723, 750 K temperature at each of zero and -0.4 V/Å) we take the contiguous BE_{NH} range over which TOF reaches at least 99% of its maximum (**Figure S7**, horizontal bars), averaging across all eight conditions gives an approximate target window of -4.47 to -3.84 eV generalized over different operating conditions. Across 673–750 K, with and without field, peak TOF varies by four orders of magnitude, yet the top 1% ranges overlap closely.

Having defined this kinetically informed binding-energy target that remains robust across the examined operating conditions, the challenge shifts to efficiently identifying structural and electronic configurations that yield a BE_{NH} within this window. To bypass the computational bottleneck of exhaustive DFT calculations, we constructed a comprehensive dataset and a feature engineering pipeline to enable rapid, machine-learning-driven screening.

3.2 Engineered Descriptors for the Configurational Space

Having established the target BE_{NH} window, we next require a physically meaningful representation of the configurational space that connects catalyst structure and electronic state to NH^* binding.^{79, 80} We featured the dataset using twelve descriptors designed to represent three physical regimes: the local binding environment, adatom lateral interactions, and the global surface state. Together, these descriptor families encode the principal dimensions varied in the DFT database: adsorption-site geometry, adatom-induced local modification, facet identity, and surface electronic state without explicitly specifying the metal identity.

Table 1
Configurational space of the DFT dataset.

Variables	Values
Surface facet	0001, 10–10, 10–11, 10–13, 11–21, 2-1-12
Base metal	Ru (1132), Co (270)
Applied charge ($ e $)	+ 3, + 2, +1, 0, -1, -2, -3, -4, -5, -6
Adatom coverage (ML)	0, 1/16, 2/16
Adsorption site	top, bridge, three-fold, four-fold (and adatom-involved variants)

The local binding environment was quantified by the number of first nearest-neighbor slab atoms (CN_{slab}) and adatoms (CN_{ad}), together with the generalized coordination number of the binding site (GCN_{site}) and of the first and second adatoms (GCN_{ad1} , GCN_{ad2}).^{52, 53, 81} To account for the geometric orientation of the adsorbate, the tilt angle of the N-H bond vector relative to the surface normal (θ_{NH}) was included.

A significant challenge in featuring adatom interactions across varying coverages is the handling of the no-adatom case. The simplest approach is to assign an arbitrarily large dummy distance to the missing adatom position, but this introduces a non-physical relation between feature and target that can degrade model performance. To resolve this, we employed inverse distance metrics ($Prox_1$, $Prox_2$, and $Prox_{ad1-ad2}$). Under this representation, the no-adatom case is equivalent to an infinitely large separation between the NH^* molecule and the adatom, for which the proximity metric converges smoothly to zero, maintaining a continuous and physically meaningful feature space.

Finally, the global state of the slab was described by the adatom coverage, the calculated surface energy of the facet,⁸² and the explicit system charge. Explicit charge captures variations in surface electron density analogous to those induced by an applied electric field and therefore provides a computationally tractable descriptor of the surface electronic state. Importantly, charge is used here to represent electronic-state variation instead of as a quantitative surrogate for a specific applied field strength.

3.3 Model Selection

Having established the descriptor set, we benchmarked five regression algorithms to identify the most suitable model for BE_{NH} prediction. Linear Regression, Ridge Regression, Support Vector Machine (SVM), Random Forest (RF), and XGBoost were each trained on the Ru dataset, and mean absolute error (MAE) was used as the comparison metric (Fig. 2a).

The two linear models perform poorly, with MAEs of 0.272 eV (Linear) and 0.282 eV (Ridge). The SVM improves this at 0.151 eV, while the two tree ensembles are significantly better with 0.041 eV for RF and 0.029 eV for XGBoost. The substantially lower errors of the tree-ensemble models indicate that a nonlinear mapping provides a more effective representation of the relationship between these descriptors and BE_{NH} than the linear models considered here.

XGBoost was therefore selected for all subsequent predictions. Trained on an 80/20 split of the Ru dataset, it reproduces the DFT binding energies with a training MAE of 0.029 eV and a test MAE of 0.082 eV (Fig. 2b), with predictions distributed evenly about the parity line across the full - 6.5 to -3.5 eV range and no systematic bias across the DFT test set at either binding extreme.

3.4 Cross-Metal Adaptation of the Descriptor-Based Model

Having established a predictive model for Ru, we investigated whether the same physically motivated descriptor representation can be adapted to another transition metal, Co. Generalizing binding-energy models across elements is challenging, as adsorption strength is sensitive to shifts in the lattice constant, atomic radii, electronic property and magnetic character.^{83, 84} To test whether our engineered descriptors capture fundamental physical interactions, we designed a cross-metal transfer learning experiment.

To bridge the configurational space, we integrated a small fraction (17%) of the total Co dataset into the primary Ru training pool, and the model was retrained on it. The predictive performance on the unseen Co data demonstrates the transferability of the chosen feature space. As shown in the parity plot (Fig. 3), the predictions for the held-out Co configurations align closely with the DFT-calculated BE_{NH} values, yielding a test MAE of 0.120 eV, while the Ru test error remains similar to that of the Ru-only model. These results show that the same descriptor representation and model architecture can accommodate Co adsorption energetics after exposure to a comparatively small amount of Co-specific data, hence the framework is able to adapt its established non-linear relationships to screen a second catalytic surface chemistry.

To track how the model learns cobalt chemistry, the Co training fraction was varied from zero to 17% on the partition used for the model in Fig. 3a, while the held-out 83% of the Co dataset was kept as the test set throughout (Fig. 3b). The model trained purely on Ru data points gives a Co test MAE of 0.397 eV demonstrating that the learned Ru mapping is not directly transferable to Co without metal-specific information. However, the Co error decreases systematically as a small number of Co configurations are introduced reaching 0.196 eV at 22 configurations (8% of the Co database) and 0.184 eV at 27 (10%) and eventually reaching 0.120 eV at 17%. The Ru test error stays within 0.084–0.097 eV across the entire sweep. Thus, the descriptor representation is not metal-independent, but it is efficiently adaptable: a relatively small amount of Co-specific data is sufficient to substantially reduce the cross-metal prediction error without materially degrading Ru performance. Notably the curve has not saturated at 17%, indicating that the transfer remains data-limited.

3.5 Feature Importance and Physical Interpretability

Having established predictive performance on Ru and adaptation to Co, we next examined which descriptors most strongly influence the model predictions. The objective here is not only to interpret the trained model, but to determine whether its dominant associations can provide physically meaningful directions for subsequent candidate screening. We unpacked its predictions using SHapley Additive exPlanations (SHAP) computed with the exact tree-ensemble algorithm.⁸⁵ Fig. 4 ranks the descriptors by global importance and shows their directional impact on BE_{NH} .

The model relies most heavily on Charge, GCN_{site} , and Surface energy, with the adatom GCN and proximity terms entering the top five. The prominence of the engineered descriptors: GCN_{site} , Surface energy, GCN_{ad1} , and the proximity metrics confirm the value of the feature-engineering pipeline.

Beyond ranking, the SHAP distribution reveals the direction in which each descriptor drives binding, which is what makes it actionable for design. Charge is the strongest electronic factor: positive charge shifts BE_{NH} toward stronger binding, whereas negative charge weakens NH^* binding. This trend is qualitatively consistent with the electronic effect associated with the negative applied field considered in the microkinetic analysis, as both perturbations enrich the surface electron density. We emphasize, however, that the explicit charge used in the DFT/ML framework represents electronic-state variation and is not assigned a quantitative one-to-one correspondence with the applied field strength in Fig. 1.

The geometric descriptors provide complementary information at different structural scales. GCN_{site} characterizes the local coordination environment of the adsorption site, whereas surface energy describes the facet-level environment. Their SHAP distributions indicate that both quantities contribute to the model prediction, although their effects should not be interpreted as causally independent because the descriptors can be structurally correlated. Within the model, facet identity therefore establishes a broader structural context while local coordination further differentiates NH^* binding among sites within that environment.

3.6 High-Throughput Screening and Validation

Having identified the dominant model descriptors and the direction of their associations with BE_{NH} , we next tested whether this information could be used to enrich the screening library in candidates within the target window. We deployed the trained model to screen $\sim 33,000$ generated structures for configurations within the target window (hereafter referred to as qualifying candidates, with predicted BE_{NH} between -4.47 and -3.84 eV). Among the three leading descriptors, charge is directly prescribed during candidate construction, whereas GCN_{NH} and surface energy emerge from the selected structure and facet. SHAP therefore provides the hypothesis that increasing electron enrichment should systematically weaken NH^* binding. We tested this prediction directly across the generated screening population. The resulting distribution of predicted BE_{NH} retains a peak near -4.5 eV, reflecting the intrinsic tendency of these surfaces to over-bind NH , but a substantial fraction is shifted into the target window, with 50.7% of the generated structures qualifying (Fig. 5), roughly double the 24.4% obtained over an unbiased charge range ($+3$ to -3 |e|; **Figure S8**), confirming that the negative-charge bias, not the structural sampling, drives the enrichment.

Before isolating individual descriptor effects over dataset as lever, we confirmed that the model reasons consistently within the qualifying region. Local (LIME) attributions computed separately for the qualifying and non-qualifying candidates both reproduce the top 3 global SHAP ordering, with charge, GCN_{site} , and surface energy as the leading descriptors (**Figure S9**). The model therefore applies a consistent attribution logic across the full configurational space.

Having confirmed the same features govern the qualifying region, we examined the dominant lever charge, which can be examined directly. As the applied charge becomes more negative, the mean predicted BE_{NH} shifts monotonically from -4.55 eV at -1 |e| into the target window, reaching -4.20 eV at -5 |e| (Fig. 6a), and the fraction of qualifying candidates rises, correspondingly from 31% to 77% (Fig. 6b). This is population-scale confirmation, on structures independent of the training set, of the negative-charge lever identified by SHAP, where making the surface more electron-rich systematically weakens NH^* binding toward the target.

The two geometric levers (GCN_{site} , surface energy) are emergent structural descriptors and are coupled to one another; their compensating behavior within the qualifying population, together with the effect of adatom coverage, is analyzed in detail in SI Section S6.3-6.4.

Finally, we verified the screening predictions against DFT. Nineteen qualifying Ru candidates were selected, and their binding energies recomputed, holding the NH^* and adatom positions fixed so that the validated geometry matches the one featurized during screening (Methods).⁸⁶ The predictions hold, with a deviation that is directional. The mean offset is $+0.104$ eV, so the constrained-DFT binding energies are on average weaker than predicted, while the mean absolute error of 0.172 eV reflects the statistical scatter of individual candidates around this shift. The positive bias is consistent with the constrained-relaxation protocol, in which fixing the NH^* and adatom positions prevents the adsorbate from fully

relaxing into its lowest-energy geometry and can therefore yield weaker computed binding. Twelve of the nineteen candidates fall within the target window under DFT, and the remainder lie just beyond its weak-binding edge, displaced onto the high-activity side of the volcano (Fig. 1). The constrained-DFT validation therefore supports the model's ability to enrich the generated library in candidates near the target window, while also revealing a systematic tendency toward weaker binding that should be considered when interpreting individual predictions.

4. Conclusions

This work establishes a physics-guided strategy for navigating catalyst configurational spaces by connecting reaction kinetics with interpretable structure-property relationships. Microkinetic modeling first defines the adsorption-energy regime required for high activity, after which an interpretable machine-learning model identifies the structural and electronic characteristics that favor this regime. Applied to ammonia decomposition, this framework reveals that NH^* binding is governed by coupled contributions from surface electronic state, local coordination, and facet-level structure. The ability to adapt the Ru-trained framework to Co with a relatively small amount of additional metal-specific data further suggests that physically motivated descriptors can provide a reusable foundation across related catalyst chemistries, even when direct cross-metal prediction is insufficient.

More broadly, the results demonstrate an alternative route to catalyst discovery for the small-data regime typical of first-principles modeling. Physically realizable candidates can be constructed directly and evaluated with an interpretable forward machine learning model, avoiding the need to learn a separate generative inverse mapping while preserving geometric constraints among descriptors. The resulting interpretation also provides design hypotheses: electronic-state modification offers a strong lever for tuning NH^* binding, while local coordination and facet selection provide complementary structural control.

Future work should extend this framework to broader and more complex reaction networks, particularly those in which both activity and selectivity must be optimized. Incorporating uncertainty-guided and active-learning strategies could further reduce computational cost by prioritizing the most informative new calculations, while improved connections between electronic-state descriptors and experimentally accessible perturbations would strengthen the link between computational design and operating conditions. Combined with experimental validation, these advances could enable iterative refinement among prediction, synthesis, and catalytic testing, ultimately establishing interpretable machine learning as a general framework for translating reaction kinetics into experimentally actionable catalyst-design principles.

Declarations

Competing Interests

The authors declare no competing interests.

Author Contribution

F.C. conceived the project, supervised the research, contributed to theoretical development and data analysis, and managed the project. P.S. performed the DFT calculations, developed the microkinetic model, and machine learning model development. J.Y. assisted the machine learning model development. All authors contributed to writing, reviewing, and editing the manuscript and supplemental information.

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Data Availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Code Availability

The code used in data generation and training the model can be requested from the corresponding author on request.

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Figures

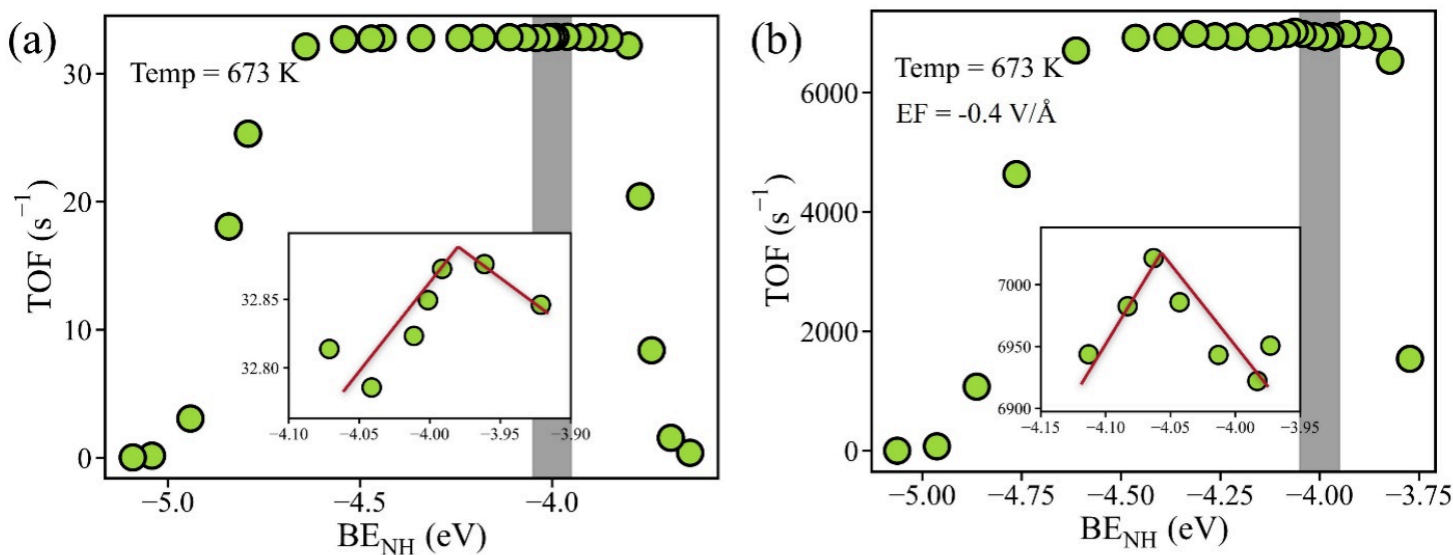


Figure 1

Steady-state TOF at 673 K under (a) zero applied field and (b) an applied field of $-0.4 \text{ V/\AA}$, with the shaded band marking the target window of -4.47 to -3.84 eV . Insets zoom on the high-activity plateau, across which the TOF varies by less than 1%.

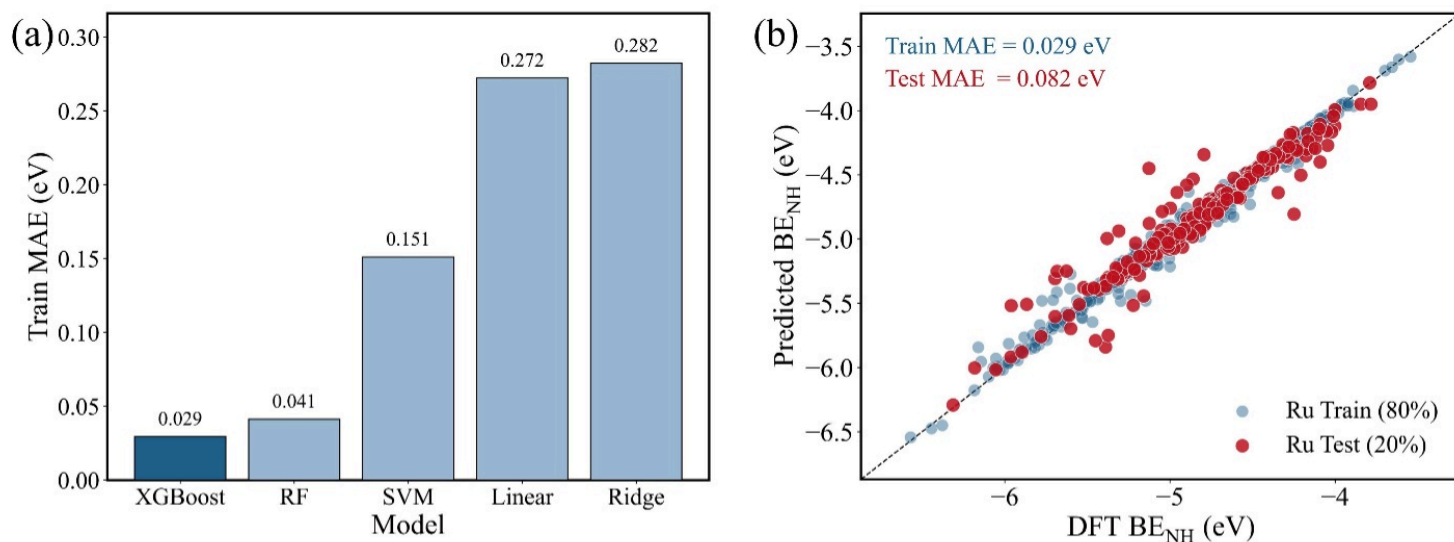


Figure 2

(a) Among the models evaluated, XGBoost provided the lowest test error and was therefore carried forward for subsequent evaluation. Its generalization performance was then assessed using the independent 20% Ru test set, yielding a test MAE of 0.082 eV. (b) Parity plot of XGBoost-predicted against DFT-calculated BE_{NH} for the 80/20 Ru split, with training and test partitions distinguished; the dashed line denotes exact agreement.

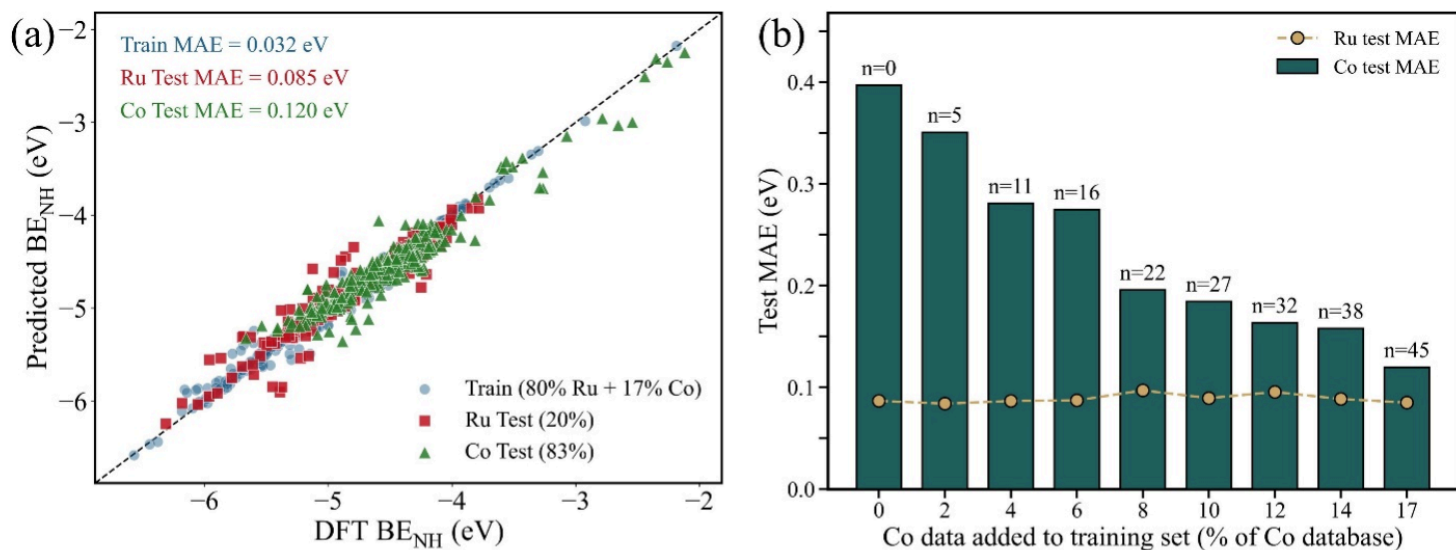


Figure 3

(a) Parity plot of predicted against DFT-calculated BE_{NH} for the held-out Co configurations, obtained from the model trained on the 80% Ru partition with additional 17% of the Co dataset. (b) Co test MAE as a function of the amount of Co data added to the Ru training pool, from zero-transfer to 17%.

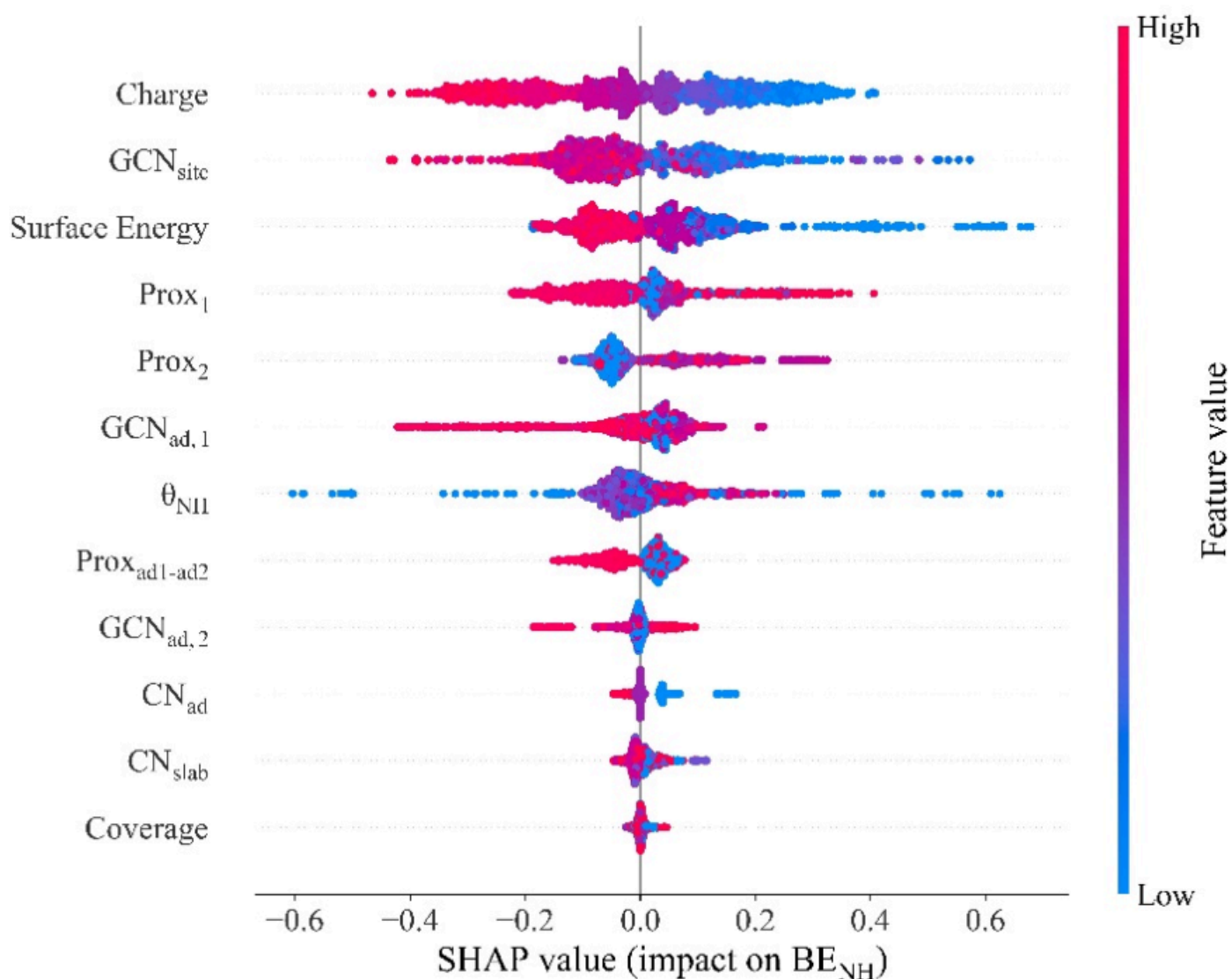


Figure 4

SHAP summary of the trained cross-metal model. Descriptors are ordered top to bottom by mean absolute SHAP value; each point is one configuration, positioned by its SHAP contribution to BE_{NH} and colored by the value of that descriptor, so that the horizontal spread gives the magnitude and the color gradient the direction of each descriptor's effect.

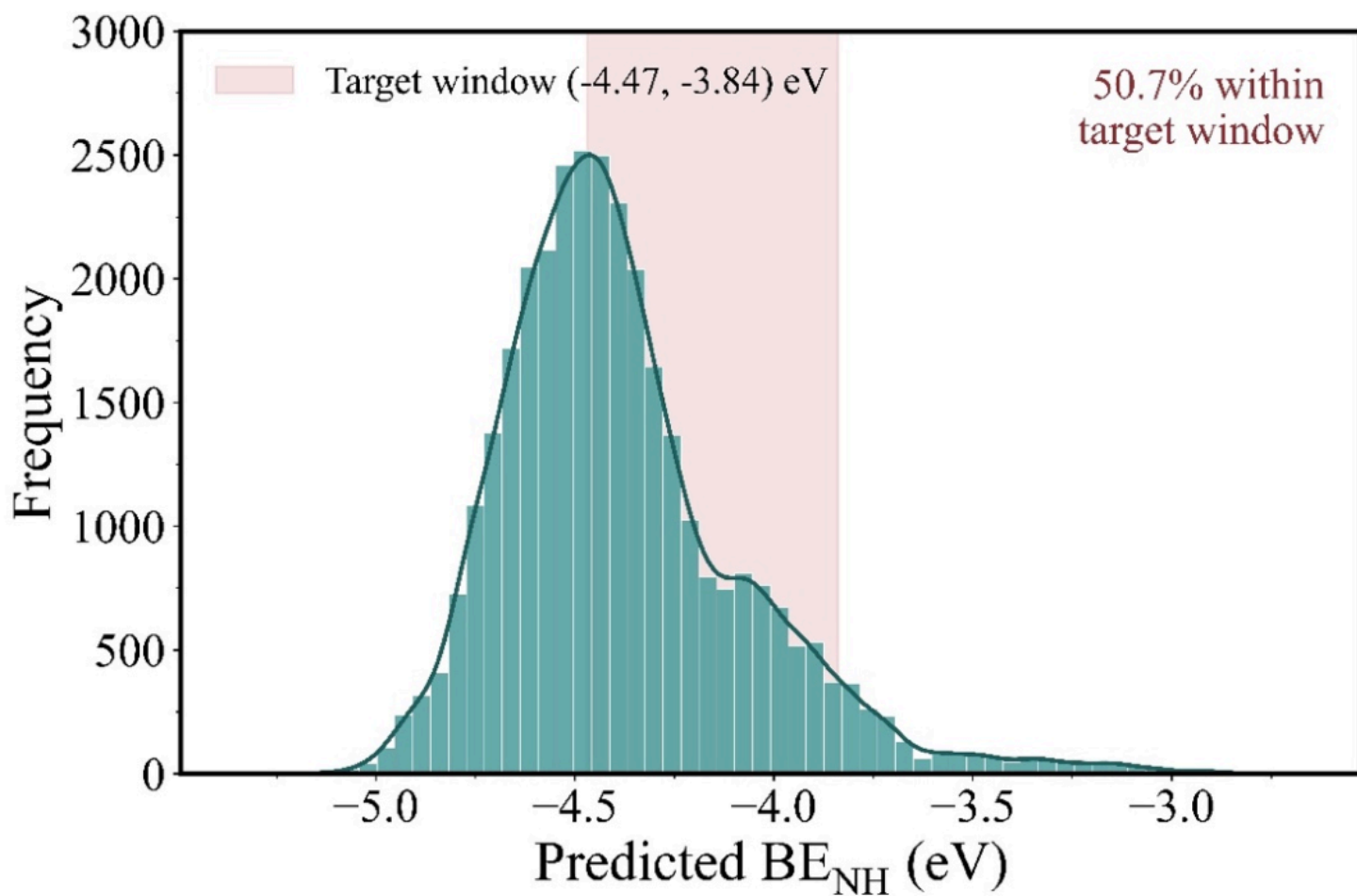


Figure 5

Distribution of predicted NH^* binding energies over the charge-biased screening library (-1 to -5 |e|, ~33,000 candidates). The shaded band marks the target window of -4.47 to -3.84 eV, within which 50.7% of candidates fall.

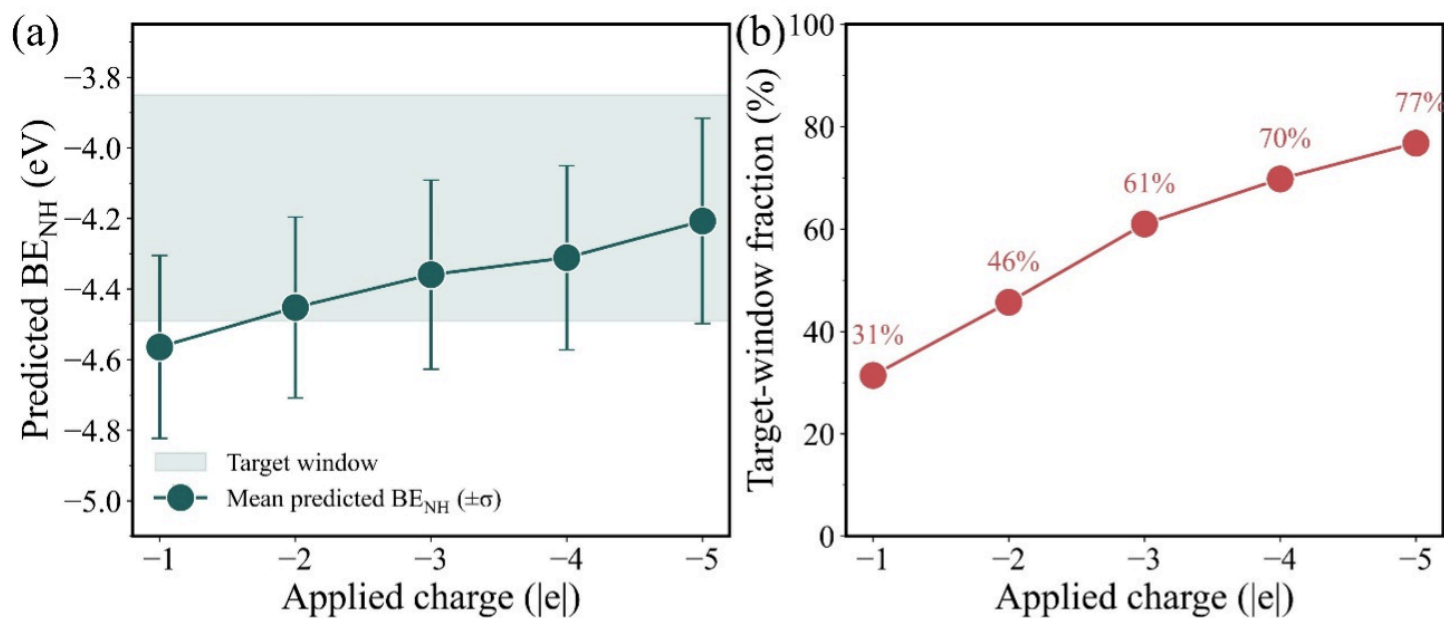


Figure 6

Charge as a design lever across the screening library. (a) Mean predicted BE_{NH} at each applied charge state, shifting monotonically from -4.55 eV at -1 |e| to -4.20 eV at -5 |e|, with the target window shaded. (b) Corresponding fraction of candidates falling inside the target window, rising from 31% to 77% over the same range.

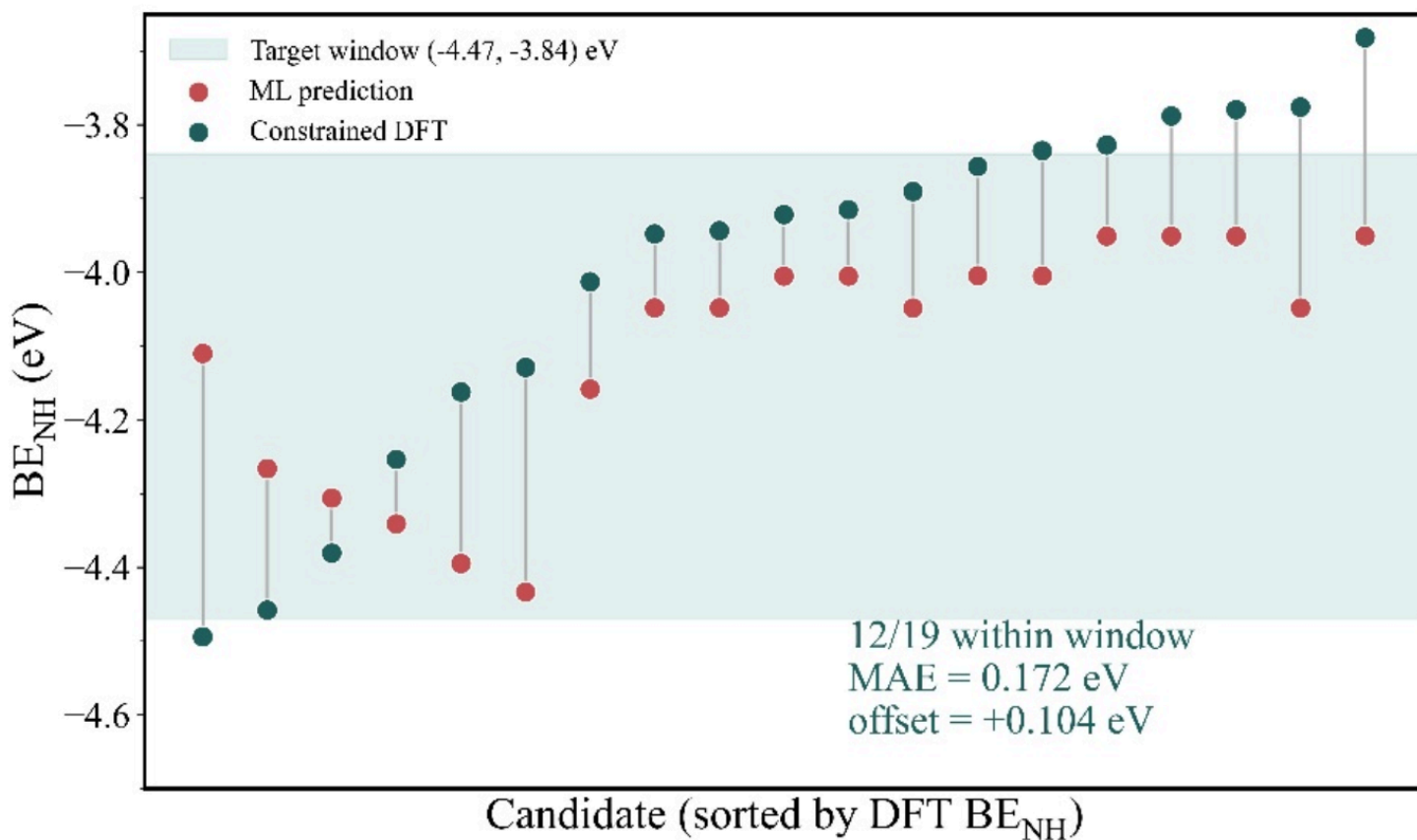


Figure 7

Constrained-relaxation DFT binding energies plotted against the model predictions for the nineteen randomly selected candidates, with the shaded band marking the target window.

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