

DARE2X



Decentralised Ammonia production from Renewable Energy utilising novel sorption-enhanced plasma-catalytic Power-to-X technology

D2.1 – Report on rational catalyst design and results

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Abstract: In this report, we depict a modelling-based rational catalyst design. Based on extensive DFT modelling of ammonia synthesis from nitrogen hydrogenation, a reaction mechanism is postulated. Furthermore, the kinetics and energetics of the individual steps are calculated for nine prospective transition metals are calculated. These calculations are then used to find correlations with easy-to-compute properties of the metals, which allow the screening to be expanded to the entire periodic table. Using these correlations, other metallic elements are also screened. Based on those, we identify prospective catalyst materials for ammonia production. These are used for a rational catalyst design.



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ABBREVIATIONS AND ACRONYMS

EC	European Commission	GA	Grant Agreement
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1. Introduction

Catalysis plays a central role in the production of ammonia, a cornerstone of the global chemical industry and a critical component in fertiliser production. Traditionally, the development of catalysts for ammonia synthesis was based on empirical trial-and-error methods, which led to significant advances but often failed to provide fundamental mechanistic insights. However, with the advent of density functional theory (DFT) calculations, a paradigm shift towards rational catalyst design has changed the landscape of catalyst development for ammonia synthesis.

Ammonia synthesis, first commercialised over a century ago by Fritz Haber and Carl Bosch, revolutionised agriculture by enabling the large-scale production of nitrogen-based fertilisers. The process involves the reaction of nitrogen and hydrogen over a catalyst, usually iron-based, at high temperatures and high pressure. In the past, the development of catalysts for ammonia synthesis was based on empirical experiments in which researchers investigated different metal compositions, supports and reaction conditions to improve catalytic performance. While this trial-and-error approach was successful in developing industrially viable catalysts, it often required laborious screening processes and lacked mechanistic understanding, limiting further optimisation.

In recent decades, the advent of computational techniques, in particular density functional theory (DFT), has revolutionised catalyst design by providing unprecedented insights into the underlying molecular mechanisms of catalytic reactions. In the context of ammonia synthesis, DFT calculations allow researchers to clarify the energetics of nitrogen and hydrogen activation, adsorption and reaction pathways on catalyst surfaces. By simulating these processes at the molecular level, DFT provides a rational framework for the design and optimisation of catalysts and enables the identification of active sites, tuning of electronic properties and prediction of catalytic activity with remarkable accuracy.

The transition from trial-and-error to DFT-based catalyst design in the field of ammonia production offers several distinct advantages. First, DFT calculations facilitate the rapid screening of a wide variety of catalyst compositions and configurations, which greatly accelerates the discovery of new catalytic materials. In addition, DFT provides mechanistic insight into reaction pathways and surface interactions, enabling the rational design of catalysts with improved activity, selectivity and stability. This predictive capability not only accelerates the development of catalysts, but also reduces the reliance on costly experimental iterations, ultimately simplifying the path to more efficient and sustainable ammonia synthesis processes.

The first aspect of catalyst design within this report delves into the atomistic realm, where a comprehensive exploration is undertaken, drawing upon recent Density Functional Theory (DFT) studies of plasma catalysis. The investigation not only evaluates the efficacy of existing methodologies but also integrates innovative strategies, such as those proposed by DARE2X. Notably, previous modeling endeavors have highlighted nickel (Ni) and cobalt (Co) as the most active metals in plasma catalysis, establishing them as benchmarks for validating the developed model. This endeavor entails close collaboration with T2.1, leveraging ongoing experimental

data to refine and validate the DFT model. Subsequently, the validated model will serve as a tool for screening potential catalyst formulations, paving the way for a rational design approach.

2. Methodology

Calculations of the entire reaction mechanism were first performed using DFT for nine metals. Subsequently, BEP correlations were drawn with simple descriptors (adsorption energies of H and N) to expand this to the entire periodic table.

2.1 DFT calculations

The computations were conducted utilizing plane-wave Density Functional Theory (DFT), employing VASP 5.4.1 software. Electron-ion interactions were simulated using the projector-augmented wave method, while electron exchange and correlation were modeled using the RPBE functional with an energy cut-off of 450 eV. To account for dispersion effects, the Grimme D3 dispersion correction along with the dipole correction were implemented. Transition states were initially located through a nudge elastic band calculation and subsequently refined using the dimer method, with a force threshold of 0.03 eV/Å. Vibrational analysis was conducted using the finite difference method with the Hessian matrix and a displacement of 0.01 Å. This analysis, employed for calculating reaction rates, utilized partition functions under the harmonic oscillator approximation. Spin-polarized calculations were carried out for molecular oxygen adsorption and dissociation on all catalysts, as well as for all reaction steps on Co and Ni. The nine catalysts subjected to full DFT calculations crystallized in either the fcc (Ag, Au, Cu, Ni, Pd, Pt, Rh) or hcp lattice (Co, Ru). Metals screened assumed various lattice structures, including fcc, bcc, hcp, tetragonal, and rhombohedral lattices. Lattice parameters were determined from bulk calculations using a 16×16×16 Monkhorst–Pack mesh of k points, with slight underestimation due to the dispersion correction employed. Metal surfaces were modeled in four layers, representing the most extended facets of each lattice type. Unique surface sites were probed for all surface species, encompassing different lattice types and surface orientations.

Table 1: The comparison involves the lattice constants determined from calculations (using RPBE+D3 with a 16×16×16 grid) and those obtained experimentally for metals where the entire mechanism was scrutinized with DFT. All measurements are presented in angstroms. Metals marked with asterisks exhibit magnetic moments.

Metal	Lattice type	Calculated a	Calculated c	Experimental a	Experimental c
Ag	fcc	4.1660	/	4.085	/
Au	fcc	4.1730	/	4.078	/
Co*	hcp	2.476	4.004	2.507	4.070
Cu	fcc	3.577	/	3.615	/

Fe*	bcc	2.8190	/	2.8670	/
Ni*	fcc	3.487	/	3.524	/
Pd	fcc	3.916	/	3.897	/
Pt	fcc	3.939	/	3.924	/
Re	hcp	2.681	4.444	2.761	4.456
Rh	fcc	3.796	/	3.803	/
Ru	hcp	2.695	4.254	2.706	4.281

2.2 BEP correlations

Computational-led catalyst design has been the holy grail of catalysis and is being made possible with recent advances in computing power and theoretical concepts, such as scaling relations and Brønsted–Evans–Polanyi (BEP) relations and single-atom alloys models (SAA), which have been used for computationally-led catalyst design. While scaling relations and BEP relations form a solid theoretical foundation for the reduction of variables in the description of catalytic properties of different materials, they are usually used for modeling individual rate-determining reactions on immutable catalyst surfaces.[26] Herein, we extend such endeavors to predicting the entire reaction pathway using density functional theory (DFT).

BEP correlations state that there is a correlation between the reaction enthalpy and activation barrier. Moreover, it is possible to find correlations between simple-to-calculate values, such as adsorption of H or N, with activation barrier for more complex steps involving these atoms. This means that in essence, it is possible to compute just the two values – called descriptors – and recover the entire reaction mechanism kinetics and thermodynamics to a very good degree of reproducibility.

In order to discover these correlations, the full mechanism is computed for ten metals along with their descriptors. Then, linear correlations are found. Lastly, the descriptors are calculated for the entire periodic table and the kinetics is back-calculated based on the assumption that the reaction mechanism is the same and that BEPs hold true.

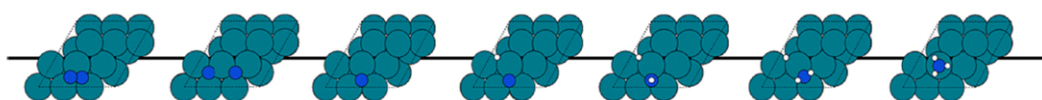


Figure 1: Dissociative reaction mechanism for N_2 hydrogenation to ammonia (shown on Ru, but universal).

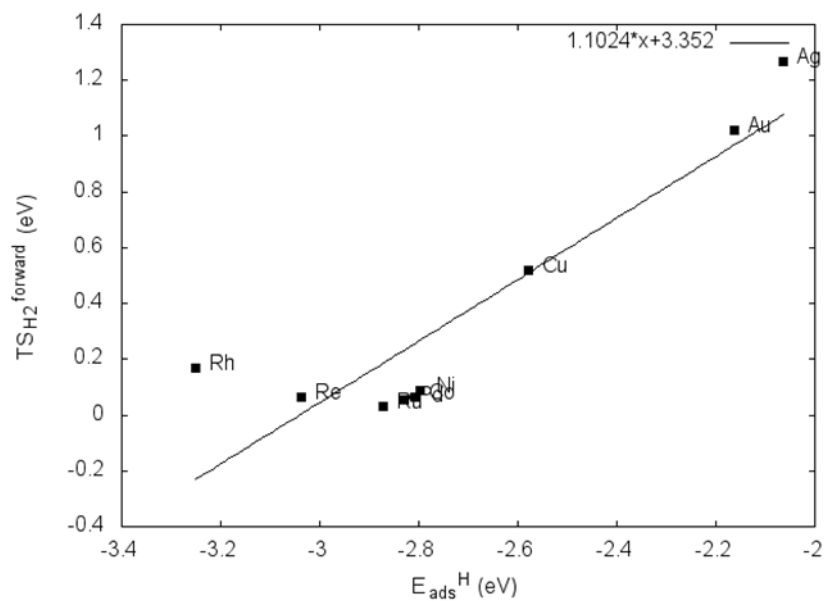


Figure 2: BEP correlation for H₂ dissociation.

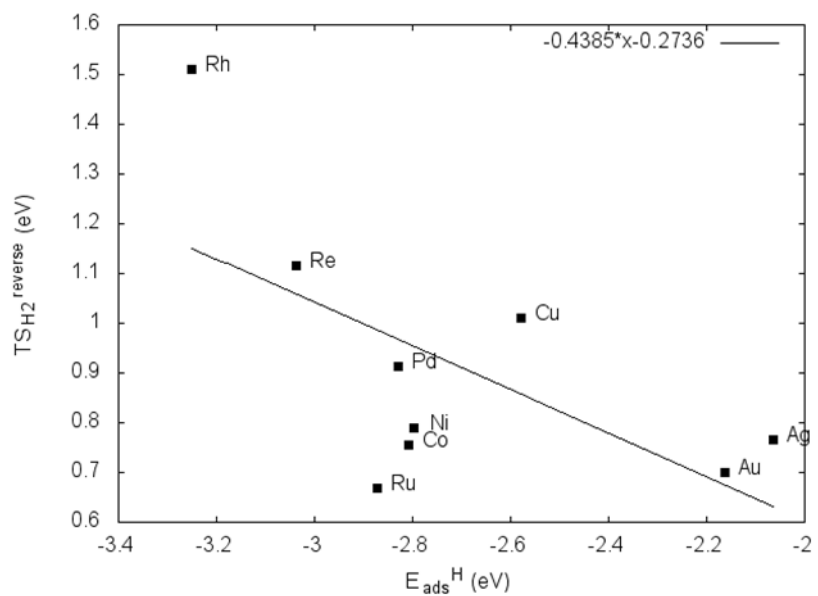


Figure 3: BEP correlation for reverse H₂ dissociation (H₂ formation).

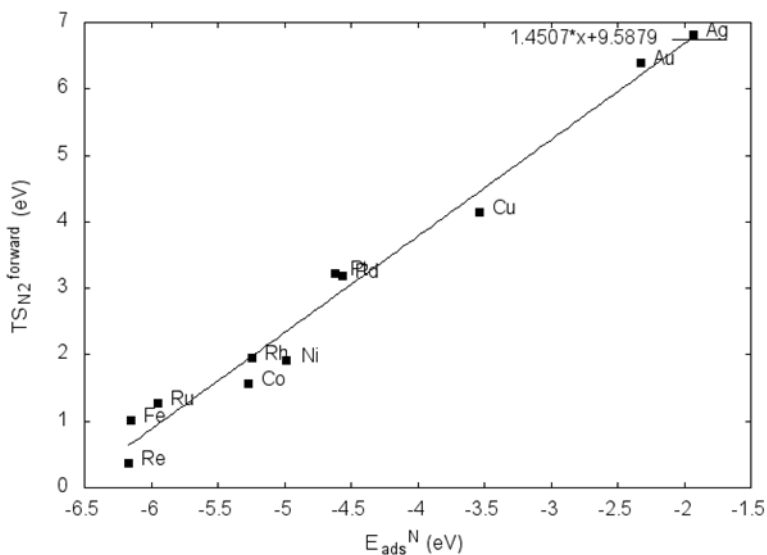


Figure 4: BEP correlation for N2 dissociation.

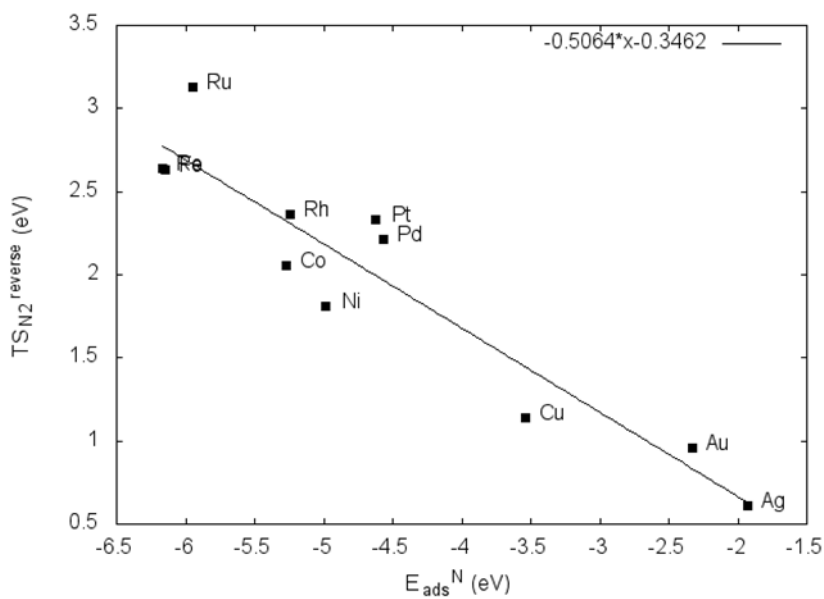


Figure 5: BEP correlation for reverse N2 dissociation (N2 formation).

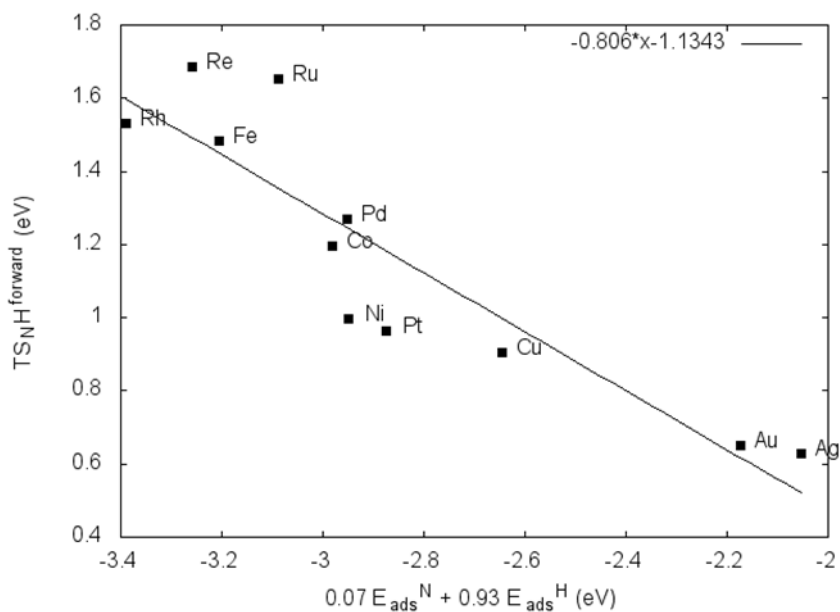


Figure 6: BEP correlation for N+H reaction.

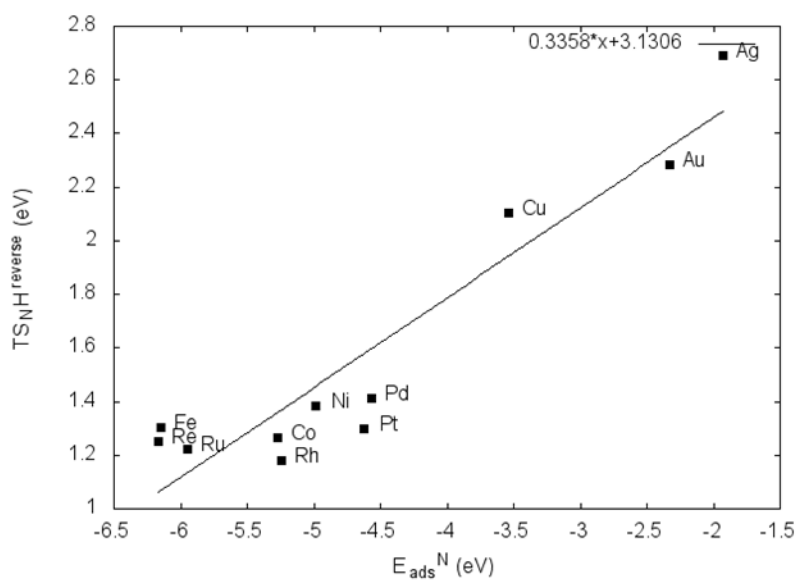


Figure 7: BEP correlation for NH dissociation.

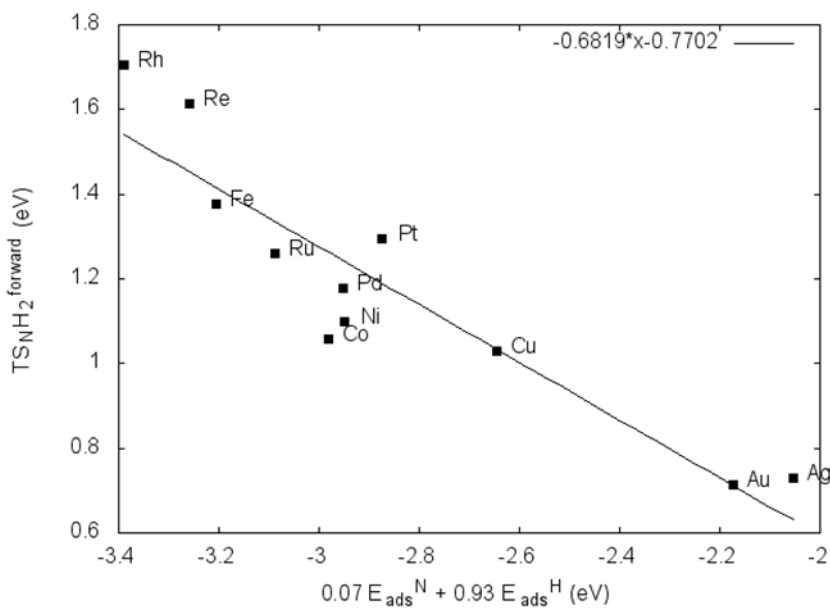


Figure 8: BEP correlation for NH+H reaction.

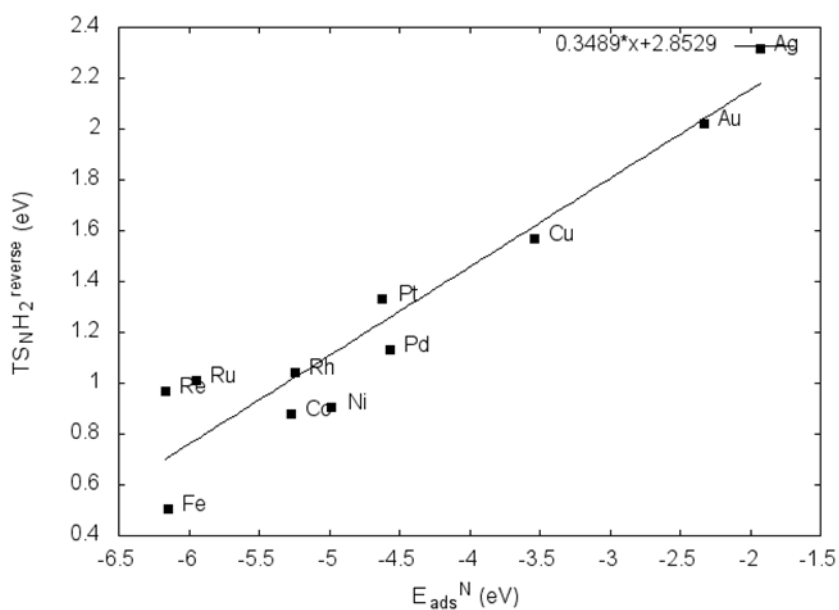


Figure 9: BEP correlation for NH₂ dissociation.

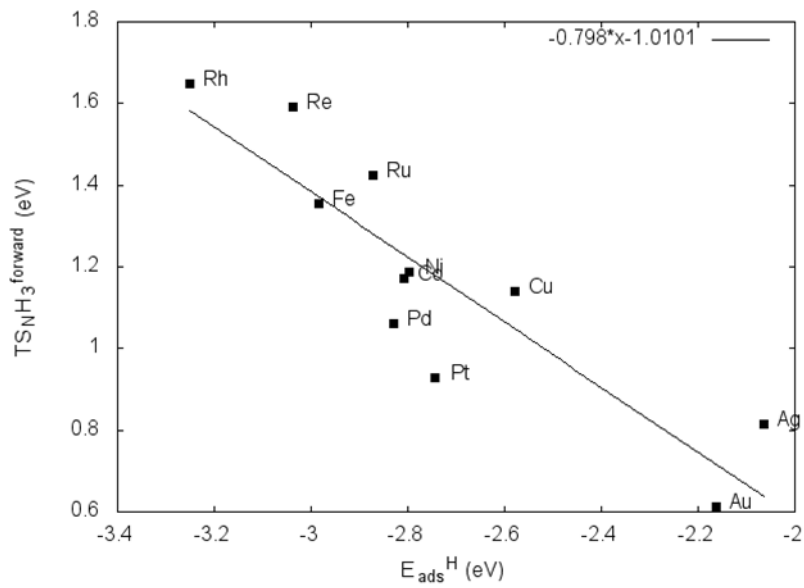


Figure 10: BEP correlation for NH_2+H reaction.

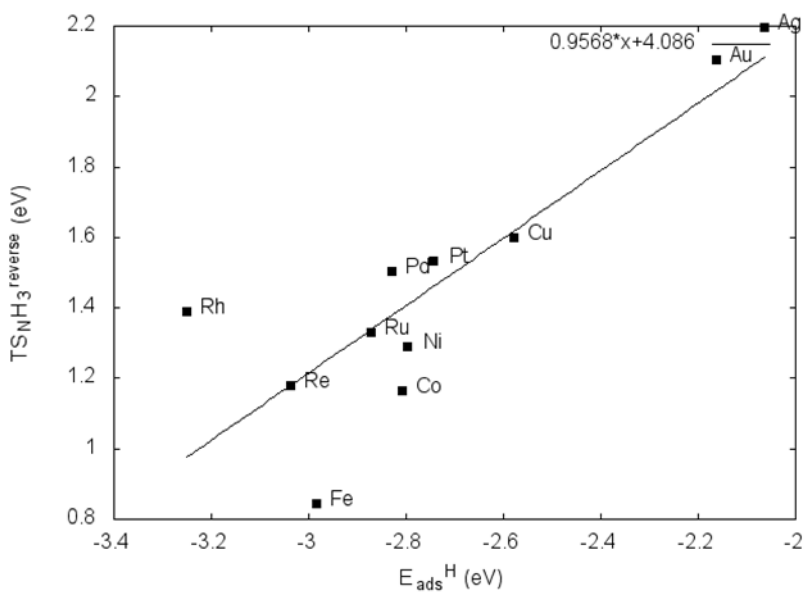


Figure 11: BEP correlation for NH_3 dissociation.

3. Screening the periodic table

Table 2: Calculated adsorption energies of H and N – descriptors – for all metals in the periodic table.

Metal	Adsorption energy H (in eV)	Adsorption energy N (in eV)
Zr	-3.34	-7.80
Zn	-1.65	-3.40
Y	-3.29	-7.90
Tl	-1.55	-3.02
Ti	-3.37	-7.70
Tc	-2.93	-6.11
Sc	-3.34	-8.04
Ru	-2.87	-5.95
Re	-3.04	-6.17
Os	-2.82	-5.85
Mg	-2.31	-5.68
Hf	-3.32	-7.85
Co	-2.28	-5.27
Cd	-1.71	-2.87
Rh	-3.25	-5.24
Pt	-2.74	-4.62
Pd	-2.83	-4.57
Pb	-1.47	-3.03

Ni	-2.80	-4.98
Ir	-2.72	-4.97
Cu	-2.58	-3.54
Ce	-2.92	-6.90
Ca	-3.00	-6.65
Au	-2.16	-2.33
Al	-2.02	-6.05
Ag	-2.06	-1.93
W	-3.03	-6.73
V	-3.29	-7.74
Ta	-3.25	-7.76
Rb	-2.18	-2.92
Nb	-3.14	-7.25
Na	-2.21	-3.56
Mo	-2.98	-6.49
Li	-2.86	-6.18
K	-2.24	-2.99
Fe	-2.98	-6.15
Cs	-2.26	-3.01
Cr	-3.07	-6.88
Ba	-2.79	-5.98

Based on the correlations discovered, the most promising candidates for N₂ reduction to NH₃ have a very negative value of E_{ads}(N) descriptors and a value of E_{ads}(H) that is not too low to poison the catalyst entirely with H*, limiting its performance.

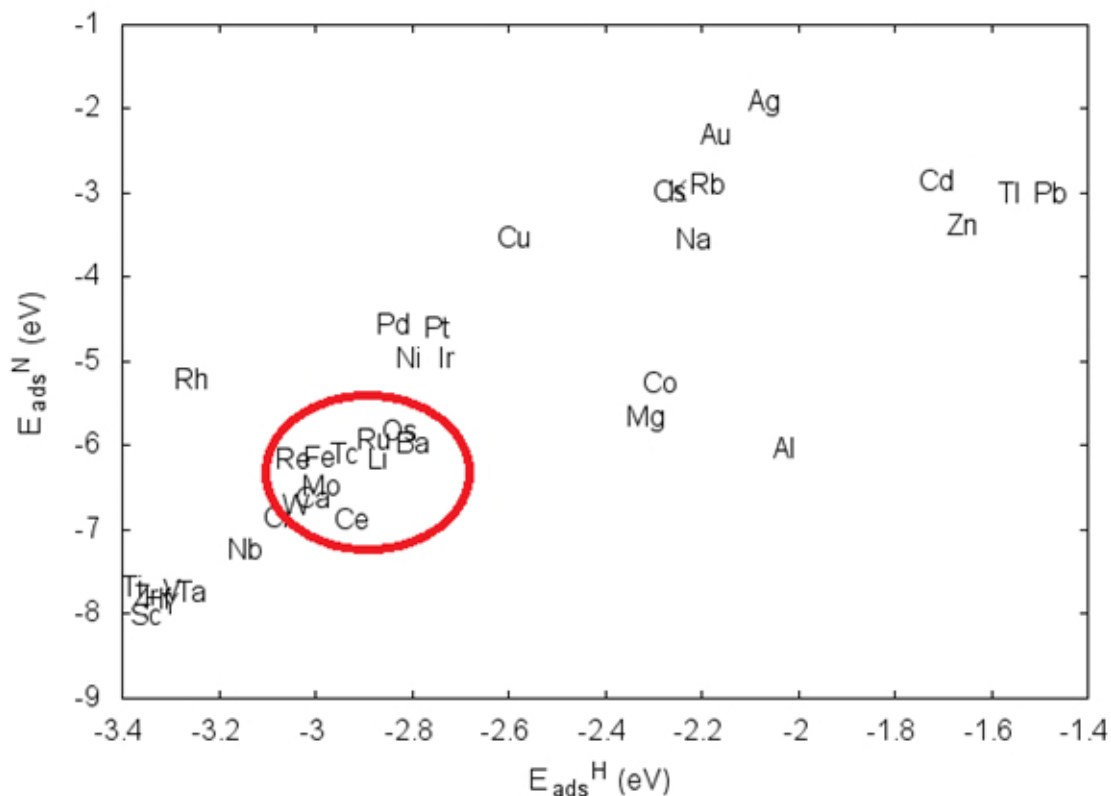


Figure 12: Values for descriptors.

Based on these data, the following materials are predicted to perform best: Re, Fe, Mo, W, Ru, Os.

4. Conclusions

In conclusion, recent strides in computational-led catalyst design, empowered by advances in computing power and theoretical frameworks like scaling relations, Brønsted–Evans–Polanyi (BEP) relations, and single-atom alloys models (SAA), signify a significant breakthrough in the field of catalysis. By harnessing BEP correlations and identifying links between simple-to-calculate descriptors and complex reaction steps, we've showcased a pathway towards efficient catalyst design. Our utilization of density functional theory (DFT) extends beyond traditional approaches, enabling the prediction of entire reaction pathways rather than just individual rate-determining reactions on fixed catalyst surfaces.

Through meticulous computational analyses across multiple metals and the extrapolation of descriptors to encompass the entire periodic table, we've established a systematic framework for catalyst design. This approach, rooted in fundamental principles and bolstered by computational prowess, not only advances our understanding of catalytic processes but also promises practical implications for developing tailored and highly efficient catalysts. Looking ahead, continued advancements in computational techniques and theoretical frameworks hold the key to unlocking even greater precision and efficacy in catalyst design, thereby fueling innovation across a spectrum of industries reliant on catalysis.

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