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QM-Mechanism-Based Hierarchical High-Throughput in silico Screening Catalyst Design for Ammonia Synthesis

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Abstract

We propose and test a hierarchical high-throughput screening (HHTS) approach to catalyst design for complex catalytic reaction systems that is based on quantum-mechanics (QM) derived full reaction networks with QM rate constants, but simplified to examine only the reaction steps likely to be rate-determining. We illustrate this approach by applying it to determine the optimum dopants (our of 35 candidates) to improve the turn-over-frequency (TOF) for the Fe-based Haber-Bosch ammonia-synthesis process. We start from the QM-based free-energy reaction network for this reaction over Fe(111) which contains the 26 most important surface configurations and 17 transition states at operating conditions of temperature and pressure, from which we select the key reaction steps that might become rate-determining for the alloy. These are arranged hierarchically by decreasing free-energy reaction barriers. We then extract from the full reaction network a reduced set of reaction rates required to quickly predict the effect of the catalyst changes on each barrier. This allows us to test new candidates with only 1% of the effort for a full calculation. Thus we were able to quickly screen 34 candidate dopants to select a small subset (Rh, Pt, Pd, Cu) that satisfy all criteria, including stability. Then from these four candidates expected to increase the TOF for NH₃ production, we selected the best candidate (Rh) for a more complete free-energy and kinetic analysis (10 times the effort for HHTS but still 10% of the effort for a complete analysis of the full reaction network). We predict that **Rh doping of Fe will increase the TOF for NH₃ synthesis by a factor of ~3.3 times compared to Fe(111)**, in excellent agreement with our HHTS predictions, validating this approach.

1. Introduction

In order to significantly accelerate the rate of discovery and optimization of novel catalyst systems required to meet the urgent problems in energy and environment faced by society^{1,2}, we need to employ quantum-mechanics (QM) based rational design (*in silico* optimization) so that experiment can focus on the most promising candidates. Previously, a great deal of progress on simpler catalytic processes has been made by using the Sabatier principle³ as translated into volcano curve modeling,^{4,5} which has provided useful guidelines and general trends to help identify promising candidates for improving simple catalysts. But this analysis is based on a simplified scenario of the catalysis process, essentially presenting one key rate-determining step.^{6,7} In contrast, the mechanisms involved in many realistic, industrially-relevant catalytic processes are often extremely complex with many competing pathways.

Fortunately QM computational methods are becoming sophisticated and powerful enough to successfully master this level of complexity. Thus we recently reported a complete analysis of the Haber-Bosch (HB) synthesis of NH₃ based on Fe catalysts at high pressure and temperature.⁸ Here we considered the most efficient Fe(111) surface for the HB reactions.⁸ This required full quantum-mechanics-based free-energy calculations of the 26 most important surface configurations at operating conditions of temperature and pressure and including the free energy based reaction rates between these species. This was followed by full kinetic Monte Carlo analysis for 45 minutes, allowing the ensemble of configurations to come to steady state at reaction conditions. The final Turn-over-Frequency (TOF) of 17.7/sec per site for the Fe(111) single crystal at 400 C and 20 atm compares well with the experimental TOF=9.7/sec per site. This excellent agreement is a testament to the accuracy of the PBE-D3 QM, to the completeness of the reaction network, and to the robustness of the kinetic Monte Carlo (kMC) predictions. However, such a complete set of QM calculations takes an enormous effort in personnel, computer resources, and time to completion, and is not practical to use on 10's to 1000's of possibilities.

To make rapid progress in dramatically accelerating our discovery of improved catalysts, we need to be able to quickly estimate the TOF of new candidates, say at 1% of the effort for a full

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3 analysis, and then to validate the most promising cases with a more compete but still fast and
4 reliable procedure, say at 10% of the effort for a full calculation. We present here this general
5 procedure which we illustrate by applications to discover binary alloys to improve the HB
6 process. We aim to achieve sufficiently quantitative accuracy that the experiments can examine
7 just the few candidates we identify as most promising and focus on optimizing process and
8 operating conditions of these selected cases.
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14 Here we propose the hierarchical protocol for rapid high-throughput screening (HHTS), which
15 we demonstrate by application to discovering improved catalysts for energy intensive HB
16 ammonia synthesis⁹⁻¹². Our experimentally validated full reaction network for the HB process⁸
17 at industrial conditions, identified 10 potentially rate determining steps in the full network,
18 which we partition here into 4 distinct and diverse processes that might most likely become
19 rate-determining as we dope the Fe catalyst:
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27 (i) activation of the N-N bond (itself composed of 4 different steps, from adsorption
28 from the gas phase to interconversion between different adsorption modes),
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30 (ii) hydrogenation of NH_x -adsorbed species (itself also distinguished into 3 different
31 steps with $x=0-2$),
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33 (iii) desorption of the NH_3 product (in 2 different points along the catalytic path),
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35 (iv) poisoning of catalytically active sites by reactant (H_2) or product (NH_3) species.
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38 All 10 of these distinct steps could be rate-determining. As the first step, we use our full kMC
39 kinetic analysis to simplify this reaction network to single out the minimum number of
40 processes (4) and corresponding reaction free energies required to estimate the overall catalytic
41 rate with minimum computational effort but simultaneously with sufficient accuracy to avoid
42 missing any potential candidates. This reduces the computational effort to 1% of the full QM
43 calculation, making it practical to examine a large set (34) of dopants that might accelerate the
44 rates by reducing the barriers for all of the 4 distinct reaction steps most likely to become rate-
45 determining. From these 34 alloying elements our protocol discovers 4 that are very promising
46 to significantly accelerate HB rates with respect to the pure Fe catalyst: Rh, Pt, Pd and Cu, all
47 of which are novel and not yet tested experimentally.
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3 Then as the next step for *in silico* design, we select the case (Rh) predicted to be most
4 promising and compute an extended (but still not the full set) of QM-based free-energy rates
5 that we use in kMC simulations to predict the NH₃ production rate. This extended calculation
6 requires ~10% of the full calculation. We predict that the Rh doped system will have a TOF 4.7
7 times faster than the pure Fe(111) system, in excellent agreement with HHTS expectations,
8 thus validating our approach. **This HHTS process provides a breakthrough advance, with**
9 **quantitative measure of how much improvement can be obtained, to trigger experiments**
10 **focused on optimizing reaction conditions, knowing that an improved performance is**
11 **guaranteed.**
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23 **2. The hierarchical high-throughput screening (HHTS) approach**

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25 As starting points of our HHTS approach, we assume to have available:

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27 (i) a complete free-energy network (for Fe(111) HB this includes 26 surface configurations)
28 for the target catalytic reaction, including reaction rates between them (17 for this case); and
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30 (ii) a strategy to change the catalyst composition over a chosen set of possibilities.
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34 To test our approach, (i), we use the free-energy reaction network for ammonia synthesis (HB)
35 process over Fe(111) derived in Ref.8, in which density-functional theory (DFT) predictions¹³⁻
36 ¹⁶ free energies and reaction rates used the (2x2) unit cell of Fe(111) (PBE-D3)^{13,14} exchange-
37 correlation functional, see Ref.8 and the Supplementary Information, SI, for computational
38 details). This is one of the most extensive first-principles-based investigation of a
39 heterogeneous catalytic reaction ever reported. This free-energy reaction network, evaluated at
40 673 K, P(H₂) = 15 atm, P(N₂) = 5 atm, P(NH₃) = 1 atm, is shown as a linear diagram in Figure
41 1. The predicted Turn-Over-Frequency (TOF) of 17.7 NH₃/sec for our 2x2 computational cell
42 is in excellent agreement with the TOF = 9.7 NH₃/sec from single crystal experiments⁸
43 (changing the barrier for the rate determining step by 0.04 eV, would reduce the predicted rate
44 to 9.7 showing the sensitivity of TOF to the reaction barriers).
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3 The energy diagram shown Fig.1 suggests that the barrier for N₂ absorption/desorption is the
4 highest. But the kinetic Monte Carlo analysis show that the dissociative chemisorption of H₂
5 and the desorption of NH₃ play an essential role in providing the empty sites required for the N₂
6 to bind and as the NN bonds are reduced from 3 to 0. As a result, the desorption of NH₃ is also
7 rate limiting for Fe(111). Additional potential RDSs involve the successive addition of H* to
8 NH_x* via Langmuir-Hinshelwood (LH) additions, leading to 4 possible RDSs, that also depend
9 on H₂ chemisorption and NH₃ desorption of H. Thus, there are at least 10 potential RDS, each
10 of which may require specific types of sites.
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18 The strategy (ii), we adopt to modify the Fe(111) catalyst is to replace one of the 4 topmost Fe
19 atoms in the (2x2) unit cell with one from a set of 34 metal elements covering a large portion of
20 the periodic table (substitutional surface doping, see Figure 2-A,B, with the set of dopants
21 shown in Figure 2-C). We consider as dopants the 29 transition metal elements, plus selected
22 lanthanides for a total of 34 elements (alkalis such as K are not considered since they adopt
23 non-substitutional configurations, other main group metal and non-metal elements will be
24 considered in future work).
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32 Our HHTS protocol then consists of the following steps:

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34 (a) analyze the free-energy diagram to single out the largest barriers and arrange them in
35 decreasing order;
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38 (b) define a simple criterion to estimate the effect of the proposed change in the catalyst on
39 each barrier;
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42 (c) evaluate each criterion in sequence in the order of decreasing barrier over the set of
43 candidates, at each step restricting only to candidates which have passed previous (higher-
44 level) screening by leading to a decrease in the overall barrier, thus sequentially sifting out
45 potential candidates;
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48 (d) test the stability of the proposed catalyst change with respect to possible degradation
49 mechanisms;
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3 (e) for candidates which have survived all previous criteria, reconstruct a significant
4 portion of the free-energy diagram and perform explicit kinetic Monte Carlo (kMC)
5 simulations to predict actual increase in catalytic efficiency.
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9 We now discuss these steps in more detail.
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11 Step (a) is illustrated in Figure 1, in which the largest barriers are assigned different colors to
12 make the analysis clearer. We use the Dijkstra's algorithm¹⁷ to single out the shortest
13 (minimum-barrier) path between initial and final states within the given reaction network,
14 which gives the largest contribution to the rate constant under steady-state conditions.¹⁸ We
15 then section this path into a sequence of lowest-free-energy resting states and highest-free-
16 energy transition states, in which the resting states are local minima of the free-energy profile
17 while transition states are the highest-free-energy points between two resting states. The free-
18 energy difference between each couple of transition and resting states defines our set of free-
19 energy barriers, which we then arrange in decreasing order. It can be noted in this connection
20 that, for the largest barrier, its resting state exhibits the most negative degree of rate control
21 (DRC) index and its transition state exhibits the most positive DRC index as defined by
22 Campbell *et al.*,¹⁹ but the second-largest and lower barriers typically exhibit negligible DRC
23 indexes. We note that the free-energy diagram and thus the associated hierarchy of reaction
24 barriers depend also on the experimental conditions, i.e., temperature and pressure of reactants
25 and products. Here we select for definitiveness $T = 673$ K, $P(\text{H}_2) = 15$ atm, $P(\text{N}_2) = 5$ atm, and
26 $P(\text{NH}_3) = 1$ atm. The ideal goal of current research on HB is to drastically reduce the extreme
27 conditions of industrial ammonia synthesis (HB) process, typically held at 773-823 K and total
28 pressure of 150-250 atm, by reducing temperature by 100-150 K and pressures by a factor of
29 10. This first step has analogies with and has been inspired by previous work, in particular the
30 concept of DRC in catalysis¹⁹, i.e., the analysis of the overall catalytic process to single out
31 which are the rate-determining mechanistic steps on which effort should be concentrated to
32 achieve acceleration.
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53 The previous volcano approaches^{5,6} typically assume linear scaling in the reaction rates to focus
54 on a specific rate-determining step (RDS) and identify catalysts that improve (accelerate) this
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3 step or to reconstruct the energy diagram on given catalysts so as to identify the optimum
4 catalyst, while the DRC approach could use a combination of RDSs depending on the DRC
5 indexes but only focuses on steps that are relevant for a specific catalyst.¹⁹ Therefore, these
6 approaches provide a fast catalyst screening for reactions that have relatively simple
7 mechanisms. In contrast, HHTS considers that there may be a number of potential RDSs, so
8 that improving one of them may lead to a very different RDS. Thus, we arrange all the
9 potentially rate-determining steps of any complex reaction mechanism in hierarchical order,
10 and then we sequentially filter candidate catalysts that accelerate the overall reaction rate also
11 when the largest barrier corresponding to the previous RDS is no longer rate determining. For
12 example in NH₃ synthesis over Fe(111) we found 4 distinct steps in the N₂ reduction, three
13 distinct steps in adding H* to NH_x* and two distinct NH₃ desorption steps. Based on the relative
14 barriers we reduced this to two potential RDS for N₂ desorption, one for H* plus NH_x, and one
15 NH₃ desorption. This is especially important when optimization approaches the ideal catalyst
16 presenting a uniform energy landscape, in which all the potentially rate-determining steps
17 exhibit similar barriers and similar rates. Thus, HHTS must consider a diversity of energetic
18 and barrier calculations. This makes HHTS much more likely to succeed for a much wider and
19 rigorous applicability. The only assumption in HHTS is that the dopants can change the relative
20 energies of the configurations and therefore the kinetics, but do not significantly change the
21 overall reaction mechanism.
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39 In step (b), for each barrier we define a simple criterion to estimate how the given barrier will
40 be affected by a change in the catalyst. We do so by associating a reaction to each barrier and
41 using the corresponding electronic reaction energy (same DFT approach and VASP software²⁰
42 as in Ref.8) to estimate the change in free-energy barrier. In other words, we explicitly
43 calculate only the free-energy of reference states. In general, the free-energy of transition states
44 can be explicitly calculated or estimated via Brønsted–Evans–Polanyi (BEP) relations.^{4,5,19} But
45 we found that the key barriers for N₂ adsorption and hydrogen migration are essentially
46 constant (independent of the dopant), which corresponds to assuming unitary slope BEP linear
47 relationship between free-energy barrier and reaction free energies.²¹⁻²³ Of course, for the
48 predicted best dopant, Rh, we actually calculate the barriers. The good correspondence of this
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3 full predicted with the in-silico estimates justifies the approximation. Simple DFT geometry
4 relaxations are needed to evaluate such criteria for each element. Figure 3 illustrates the
5 configurations used in the screening procedure, as discussed in detail in the next Section.
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9 Step (c) defines our hierarchical or sequential systematic screening procedure, in which we use
10 the estimated barriers from step (b) to sift out candidates expectedly leading to a decrease in the
11 overall barrier. This step is illustrated as an Eratosthenes' sieve or Wenn diagram in Figure 2
12 and Figure S1 of the SI. We apply the first criterion, corresponding to the largest barrier, to the
13 complete set of 34 dopant elements. We apply the second criterion only to the elements that
14 have passed the first criterion showing the potential to decrease the overall barrier. We apply
15 the third criterion only to the elements that have passed the first and second criteria, and so on.
16 Restricting lower-level criteria only to candidates that have passed higher-level ones
17 significantly reduces the total computational effort.
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21 As for step (d), we test one common catalyst degradation mechanism for alloy systems, i.e.,
22 inverse segregation of the dopant from the surface into the bulk of the catalyst. Clearly, other
23 catalyst degradation mechanisms are possible. E.g., some dopants are expected to vaporize as
24 hydrides under the given conditions so we have not included these in the set of dopants (e.g.,
25 As transforming into AsH₃), while others may aggregate into clusters, etc. Other degradation
26 mechanisms could be considered after defining a chemical potential for competing species or
27 mechanisms, but we do not consider them in this proof-of-principle study.
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31 In the final step (e), for the most promising candidate which has survived all screening criteria
32 (i.e., Rhodium, Rh) we evaluate entropic terms and explicit energy barriers for steps that have
33 proved to be important to kinetics⁸. In this way we check that our rapid-screening estimates
34 hold, and we quantitatively predict the expected increase in catalytic efficiency.
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40 41 **3. *In silico* strategy for doped Fe(111) catalysts for HB synthesis**

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43 The previous QM studies for HB on Fe(111) found 4 important reaction barriers that could
44 potentially become rate determining. Two are involved in adsorbing/dissociating N₂, one is
45 involved in H_{ad} reacting with NH_x to form NH_{x+1}, one is associated with H₂ poisoning, and one
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involves NH₃ adsorption/desorption. But in analyzing the rates using kMC these rates can be related back to fundamental differences in free energies of various intermediates which allows us to minimize the states that must be analyzed.

Criterion 1. Triple bonded N₂ adsorption over 2N state

The largest free-energy barrier in the diagram of Figure 1 – yellow line, barrier (1) – is associated with N₂ adsorption over the 2N state. The system first transforms from its low-energy resting state with a high coverage of NH_y-adsorbed species into the 2N[zig-zag] configuration (Figure 3A), which has two nearest-neighbor vacant bridge sites so that it can dissociate N₂, which is followed by N₂ adsorption and dissociation. We recall⁸ that the 2N[zig-zag] configuration is named “zig-zag” because an alternative “linear” configuration with the same stoichiometry exists, as illustrated in Figure S2(a,b) of the SI (the same alternative applies to configurations with different stoichiometry such as 2N_NH₂_H, 2N_N₂[γ], etc.). A high energy price is associated with generating the 2N[zig-zag] configuration on Fe(111). An improved catalyst should decrease this energy price and thus the stability of N adatoms on the surface, while still exhibiting a sufficiently large affinity to nitrogen to be able to dissociate N₂ effectively. We identify our first criterion, connected with the N₂ adsorption/dissociation barrier, with the electronic reaction energy from the 2N_NH₂_H[zig-zag] (Figure 3 B-D) resting state to 2N[zig-zag]: “2N_NH₂_H[zig-zag] → 2N[zig-zag] + NH₃” (see Figure 3 for pictorial illustrations). Note that the highest saddle point for subsequent N₂ dissociation is 0.3 eV below the saddle point corresponding to barrier(1). This might become rate determining when the N₂ adsorption energy onto the catalyst surface is too small. We thus complement our first criterion by evaluating the N₂ adsorption energy on 2N[zig-zag], i.e., the energy difference between the “2N[zig-zag]+ N₂ gas-phase” and 2N_N₂[γ,zig-zag] configurations, and ensuring that this adsorption energy is > 0.5 eV as an additional constraint. We finally estimate barrier(1) via the formulae:

$$\text{barrier}(1) = \Delta E \{ 2N_NH_2_H[\text{zig-zag}] \rightarrow 2N[\text{zig-zag}] + NH_3 \} - 0.104 \text{ eV} \quad (1)$$

$$\text{constraint} : \Delta E \{ 2N_N_2[\gamma, \text{zig-zag}] \rightarrow 2N[\text{zig-zag}] + N_2 \} > 0.5 \text{ eV} \quad (2)$$

where $2N_NH_2_H$ [zig-zag], $2N$ [zig-zag], and $2N_N_2$ [\(\gamma\),zig-zag] (Figure 3 M-O) correspond to the surface configurations discussed above, N_2 and NH_3 refer to molecules in the gas phases, and “ ΔE ” refers to the electronic energy difference between the states after arrow and states before arrow. The energy value “0.104 eV” was computed based on the free energy corrections of the pure Fe(111) surface. The barrier (1) corresponds to the energy barrier (1) values in Figure 1 for the pure Fe(111) surface. All the electronic energies of the doped configurations are listed in the xsl file in the SI.

Criterion 2. H_2 poisoning N_2 dissociation via the $2N_2H$ resting state

The second highest barrier in Figure 1 – blue line, barrier(2) – is associated with the same saddle point, but is connected with the observation that the $2N_2H$ [linear] (Figure 3 E-F) configuration can represent a resting state under some conditions (e.g. at low NH_3 pressure) which can slow down catalysis (H_2 poisoning). Therefore, the second criterion is expressed by the formula:

$$\text{barrier}(2) = \Delta E \{2N_2H[\text{linear}2] \rightarrow 2N[\text{zig-zag}] + H_2\} + 0.113 \text{ eV} \quad (3)$$

where $2N_2H$ [linear2] corresponds to the surface configuration (Figure S2) discussed above, and H_2 refers to hydrogen in the gas phase. The energy value “0.113 eV” was computed based on the free energy corrections of the pure Fe(111) surface.

Criterion 3. H_{ad} migration to NH_{2ad} to form NH_{3ad}

The conversion of adsorbed N into NH_y species is also associated with high energy barriers, the third largest in the free-energy diagram of Figure 1 – green line, barrier(3) –, and our third criterion estimates these barriers. We focus on the highest-barrier hydrogenation (or hydrogen migration) mechanistic step, which is the hydrogenation of $2N_NH_2_H$: “ $2N_NH_2_H \rightarrow 2N_NH_3$ ”. We use the Brønsted–Evans–Polanyi principle and assume that the energy barrier of this step will be a linear function of the energy difference between $2N_NH_2_H$ and $2N_NH_3_H$ configurations (Figure 3 G-H), thus estimating the third barrier with the formula:

$$\text{barrier}(3) = \Delta E \{2N_NH_2_H[\text{zig-zag}] + \frac{1}{2} H_2 \rightarrow 2N_NH_3_H[\text{zig-zag}]\} + 1.549 \text{ eV} \quad (4)$$

where the 2N_NH₃_H[zig-zag] corresponds to the surface configuration discussed above. The energy value “1.549 eV” was computed based on the free energy corrections of the pure Fe(111) surface.

Criterion 4. NH₃ desorption. Finally, NH₃ desorption can be rate-limiting – red line, barrier(4) –, so the fourth criterion ensures that a high NH₃ desorption energy does not decrease in the overall rate. The largest NH₃ desorption barrier is expected close to the 2N[zig-zag] state, for the 2N_NH₃_H[zig-zag] configuration, and is estimated with respect to the 2N_NH₂_H[zig-zag] resting state as follows:

$$\text{barrier}(4) = \Delta E \{2N_NH_2_H[\text{zig-zag}] + \frac{1}{2} H_2 \rightarrow 2N_NH_3_H[\text{zig-zag}]\} + \Delta H \{2N_NH_3_H[\text{zig-zag}] \rightarrow 2N_H[\text{zig-zag}] + NH_3\} + 0.425 \text{ eV} \quad (5)$$

where 2N_H[zig-zag] (Figure 3 K-L) corresponds to the surface configuration discussed above. The energy value “0.425 eV” was computed based on the free energy corrections of the pure Fe(111) surface.

Criterion 5. Preference of dopant in top layer versus second layer

The above criteria assume that the overall free-energy diagram is only altered quantitatively, not qualitatively, by the proposed change in the catalyst. The fifth and last criterion tests that the catalyst change does not introduce qualitative alterations of the diagram, i.e., the insurgence of degradation mechanisms. Inverse segregation of the dopant element into the bulk is a common mechanism for dopants that reduces the interaction of the catalyst surface with NH_y-adsorbed species.²⁴ We evaluate this degradation mechanism only for the 4N configuration (Figure 3I) and for the dopant going from the top surface layer into the subsurface layer (Figure 3J). We estimate the increase in the previous barriers as follows:

$$\text{barrier}(1-4) = \text{barrier}(1-4) + \max \{ \Delta E \{4N[\text{subsurface-dopant}] \rightarrow 4N[\text{surface-dopant}]\}, 0 \} \quad (6)$$

where 4N[subsurface-dopant] and 4N[surface-dopant] correspond to the configurations discussed above, “max” refers to the maximum between the two numbers in the bracket, and “barrier(1-4)” refers to the the maxium barrier for steps 1 to 4.

4. Application of hierarchical in silico screening to 34 dopants.

The application of the rapid in silico screening to HB over singly-top-surface-substitutionally-doped Fe(111) is illustrated in Figures 2 and S1 using the original free energy diagram.⁸ The electronic energy results of the five criteria are listed in Table 1 (with a complete report in the xsl file in the SI).

Criterion 1. N₂ desorption/dissociation

Of the 34 dopants, only 12 led to a barrier lower than the 1.68 eV for Fe, but we kept an additional 3 that were only a little above 1.68, as shown in Table 1. The other 19 cases were not examined further. Of these 19, 14 are more electropositive than Fe (electronegativity (χ)=1.8), while Mo is the same and Tc, Re, and Hg (all χ =1.9) are only slightly more electronegative. This indicates that alloying a more electronegative element helps with N₂ dissociation. Thus the elimination of Os (χ =2.2) is the only outlier. It is interesting that Haber found that pure Os does do NH₃ synthesis. Of these 12 selected dopants, none violate the constraint equation (2).

We note here that the best two, Rh and Pd, with a barrier lower by 0.17 eV might lead to a rate increase by a factor of 18.75 for our target conditions.

Criterion 2. H₂ poisoning to the N₂ adsorption

Here we eliminate 6 more. This includes the 4 closed shell elements (Cd, Au, Ag, and Zn). This suggests that we want open-shell d-electrons for good N₂ dissociation barriers. It is not obvious why Ir and Ru have a high barrier. It is interesting that pure Ru (hcp crystal structure) does do NH₃ synthesis.

Criterion 3. NH_x hydrogenation

All 6 remaining candidates are better than Fe.

Criterion 4. NH₃ desorption

All 6 remaining candidates are better than Fe. It is important to note that criterion NH₃ desorption becomes an important step for some (e.g. Pt-) doped systems. Note that these steps

would not be considered within a DRC approach because of their low DRC indexes on the undoped catalyst.

Criterion 5. Surface stability

Here two cases: Co and Ni, prefer subsurface. This may be because they are slightly smaller than Fe.

The Winners

We are left with four winners: Rh and Pt predicted to be 4 times better than pure Fe and Pd and Cu predicted to be 2 times better than pure Fe.

Rh and Pt lead to a reduction in the overall barrier of 0.06 eV: hydrogen poisoning limits the potential reduction of 0.17 or 0.13 eV according to criterion (1). Reducing the overall barrier by 0.06 eV would not allow dramatically less extreme industrial conditions, but – if realized – should guarantee a reduction by a factor of ~ 4 in the energy consumption even maintaining the same conditions (≈ 200 atm total pressure and 773-823 K temperature) and industrial plants as used presently. Further improvements can likely be achieved by implementing multiple doping strategies. The HHTS-estimated NH_3 production rates for optimal dopants are also listed in Table 1.

As discussed in Ref.8, the barriers associated with these phenomena are also intimately related to the charge and magnetic state of surface atoms, as we confirm by reporting an analysis of the changes in charges and spins of surface atoms upon doping, illustrated in Figure S3.

5. Full QM analysis and Kinetic Study of Rh-Doping

The above *in silico* analysis focused on 11 key states that determine the major barriers. This allowed us to reduce the candidates from 34 to 4. Now we will consider the full analysis for one of the winners, Rh, which we estimated would be 4 times better than Fe. To this end we extend the study from the 11 configurations considered above and consider the 21 configurations and 13 barriers most important for the kinetics (Figure S4 and S5 of SI).

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3 We performed QM simulations on a (2x2) unit cell of the Fe(111) surface substitutionally
4 doped in the top layer with one Rh atom and reconstructed a substantial portion of the reaction
5 energy diagram, as shown in Figure 4. A simplified reaction pathway is illustrated pictorially in
6 Figure S4 showing the surface structure step by step, to clarify the nature of each adsorption
7 site and the interactions between these adsorbed species. The favorable mechanistic paths are
8 the same as on the pure Fe surface.⁸ Figure 4 plots a standard state free energy diagram which
9 does not include the configurational entropy of adsorbates.²⁵ However, configurational effects
10 are taken into account in our kMC simulations model by including the configuration counting
11 into the rate constants.
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20 To validate our assumptions, we compare the 4 key reaction steps used in our HHTS approach
21 between pure Fe and Rh-doped catalysts. For the pure Fe catalyst, the free energy barriers for
22 N₂ adsorption (step1), H₂-poisoning (step2), H migration (step3), and NH₃ desorption (step4)
23 are 1.68, 1.57, 1.52, and 1.43 eV, respectively. Based on our assumptions, the estimated
24 barriers from HHTS for Rh-based catalyst are 1.51, 1.60, 1.31 and 1.44 eV for these 4 steps,
25 respectively, whereas explicit calculations on the Rh-doped catalyst give values of: 1.44, 1.62,
26 1.31 and 1.35 eV, respectively. The difference between estimated and explicit calculations is
27 within a maximum error of 0.09 eV, thus validating our free-energy barrier estimates.
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36 We used the energetics from the free-energy diagrams of Figures 1 and 4 as input to kinetic
37 Monte Carlo (kMC) simulations, using the same set of 21 configurations and 13 barriers for
38 both pure and Rh-doped Fe(111).
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42 On pure Fe(111), this leads to production of 2441 NH₃ molecules produced by our (2 × 2) unit
43 cell, corresponding to a predicted TOF = 4.6 NH₃/sec per (2 × 2) site, which can be compared
44 to TOF=3.68 for our simplified model
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48 On Rh-doped Fe(111), this leads to production of 35980 NH₃ molecules produced by our (2 ×
49 2) unit cell, corresponding to a predicted TOF = 9.7 NH₃/sec per (2 × 2) site, which can be
50 compared to 14.6 in our simplified model.
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54 However, the Rh-doped system can be further improved by exploiting its sensitivity to H₂
55 poisoning and working in a lean-H₂ régime. Thus reducing the H₂ pressure from 15 to 6.5 atm:
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3 under conditions of $T = 673$ K, $P(\text{H}_2) = 6.5$ atm, $P(\text{N}_2) = 5$ atm, and $P(\text{NH}_3) = 1$ atm, we predict
4 TOF = $15.3 \text{ NH}_3/\text{sec}$ per (2×2) site, which is a factor of 3.3 larger than on Fe(111), in good
5 agreement with expectations from the HHTS estimates. **Thus we estimate that Rh doped Fe**
6 **might lead to an overall TOF that is ~3.3 times the current Fe based catalysts.** We note
7 here that reducing H_2 pressure slows down the reaction rate for Fe, but increases it for Rh.
8 Given the high cost of H_2 , working under lean- H_2 conditions may be beneficial in terms of
9 production costs.
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11 Finally, to provide information on mechanistic details, the steady-state apparent ΔG (i.e., the
12 logarithm of the relative populations or residence times) for the most important states are
13 reported in Table S1 for both pure and doped Fe(111).
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17 **6. Modifications of the PBE-D3(BJ) free-energy diagram**

18 Any HTS approach depends on the accuracy of the assumed free-energy diagram. The one
19 employed here was derived using the DFT/PBE-D3 method,⁸ and leads to excellent agreement
20 with experimental ammonia production rates at low NH_3 pressure²⁶ (theory: $17.7/\text{sec}$ for a 2×2
21 surface cell; experiment 9.7). We now test how robust our analysis is with respect to a change
22 in the system energetics. In particular, one issue of Figure 1 is that the overall free-energy
23 change (δG) for the ammonia synthesis reaction $[\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3]$ is predicted by PBE-
24 D3(BJ) to be -0.54 eV at 673°K , and 5:15:1 atm of N_2 , H_2 and NH_3 , respectively. In contrast
25 the experimental value is $\delta G = -0.06$ eV under the same conditions.²⁷ To test how sensitive the
26 HHTS predictions are to this issue, we use an empirical correction²⁸ and modify the free-energy
27 diagram of Figure 1 by adding a quantity of $[0.08 \cdot y]$ eV to the free energy of NH_y surface
28 species. This corresponds to assuming that PBE-D3(BJ) overestimates the N-H vs. N-Fe bond
29 strength by this quantity (for transition states corresponding to hydrogenation mechanisms we
30 use half of the 0.08 eV correction). The overall gas-phase energetics of the HB reaction is so
31 recovered by distributing the PBE-D3(BJ) error in δG uniformly over the energetics of surface
32 species. The free-energy diagram resulting after applying these corrections is reported in Figure
33 S6 of the SI, under the same conditions of Figure 1: $T = 673$ K, $P(\text{H}_2) = 15$ atm, $P(\text{N}_2) = 5$ atm,
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3 $P(\text{NH}_3) = 1 \text{ atm}$ (thermodynamic equilibrium conversion using experimental energetics
4 corresponds to 1.7 atm NH_3 pressure, thus $P(\text{NH}_3) = 1 \text{ atm}$ is consistent with roughly 50%
5 conversion typically used in the industrial HB process). The five basic criteria singled out in
6 Section 3.a need to be only slightly modified after applying these corrections (the main
7 difference being that the resting state of the system is now the 4N configuration), and are
8 detailed in the SI.
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15 We applied the high-throughput screening protocol using these new criteria. Interestingly, the 5
16 elements (Rh, Pt, Cu, Pd, with the addition of Ni which is roughly identical to Fe) which are
17 suggested as promising using the free-energy diagram of Figure 1 are still present in the final
18 HHTS set derived using the diagram of Figure S6, as illustrated in Figure S7. The major
19 difference is that:
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25 (1) the NH_3 production rate at $P(\text{NH}_3) = 1 \text{ atm}$ by the Fe(111) surface is decreased (the
26 production rate at low NH_3 pressure using Figure S6 does not change much and is also
27 consistent with the experiment²³),
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31 (2) therefore, the expected acceleration due to doping is increased, and
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33 (3) more elements are included in the set of potentially promising dopants, such as Zn, Ag, Au,
34 Cd. In particular Zn seems particularly appealing due to its small size mismatch with Fe.
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38 Apart from calling for a proper experimental validation of the accuracy of DFT for this system,
39 these finding suggests that, overall, the set of optimal dopants determined in Figure 2 is
40 reasonably robust to a change in the theoretical method. Much larger enhancements in
41 production rates are predicted when using the free energy diagram of Figure S6. The expected
42 maximum in catalytic activity is realized for Cu, Ni, and Pd, with a reduction in overall barrier
43 amounting to 0.35-0.37 eV, thus translating into a potential speed-up by more than factor of
44 100 in HB process rate.
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51 To conclude, we note that, clearly, several variants of HHTS can be conceived. For example,
52 the kinetic model can be analyzed and solved via other methods not considered in this work,
53 such as micro-kinetic modeling as in the DRC approach.^{19,29} In this connection, note that, to
54 implement our hierarchical approach, DRC indexes could be defined for each section of the
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3 free-energy diagram potentially leading to rate-determining steps. The screening criteria can be
4 improved by explicit transition state calculations. The free-energy diagram can be made more
5 accurate, e.g., by improving over the harmonic approximation to evaluate entropic
6 contributions, using more accurate exchange-correlation functionals or higher-level
7 computational methods, or adjusting empirical corrections to the energetics of different
8 metals.³⁰ Other strategies for changing the catalyst³¹ such as multiple (ternary, etc.) doping can
9 be investigated. Finally, catalytic selectivity rather than simple activity can be targeted for
10 optimization.¹⁹
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21 **7. Conclusions**

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23 A goal of current research in theoretical materials science is to devise new computational
24 approaches that can be appropriate to complex (and thus realistic) materials design, going
25 beyond simple outlining of general trends towards the completion of a fully predictive
26 theoretical modeling. In the catalysis field, this thrust faces significant challenges. First, the
27 property to be optimized (catalytic activity) is connected with saddle points in the potential
28 energy surface (PES) and corresponding energy barriers, that intrinsically require a higher
29 computational effort with respect to description of local minima and equilibrium states.
30 Second, the free energy diagram of a realistic catalytic mechanism is often so complex and
31 with so many competing paths that the behavior of activity or selectivity in terms of any given
32 descriptor cannot be represented with a single volcano curve, i.e., the property/variable
33 function becomes so rugged that its optimum value is to be found in a pocket or niche of this
34 fragmented free-energy landscape, at the intersection of several Brønsted–Evans–Polanyi
35 (BEP) energy relationships. In these realistic cases, high-throughput screening seems the only
36 viable path to predictive rational catalyst design.
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50 Here we answer these challenges by developing a hierarchical high-throughput screening
51 (HHTS) protocol for rapid *in silico* design of novel catalysts, and demonstrate its usefulness by
52 applying it to the ammonia synthesis (Haber-Bosch) process over doped Fe(111) surface. The
53 approach starts from a complete free-energy diagram of the given catalytic reaction, which is
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3 then analyzed to single out and arrange the barriers of key mechanistic steps in hierarchical
4 order, defining for each of these steps a simple energy criterion for deciding whether a
5 proposed change in the catalyst composition will lead to an increase or a decrease of the
6 corresponding barrier, and sequentially screening a set of doping elements according to these
7 criteria, to finally arrive at a subset of promising candidates satisfying all criteria. Promising
8 candidates can then be tested by reconstructing larger portions of the free-energy diagram
9 followed by kMC simulations of steady-state production rates (100 time the effort).
10 **Application of this protocol to ammonia synthesis over doped Fe(111) surface identifies a**
11 **set of promising dopants: Rh, Pt, Cu, Pd, that might dramatically improve the TOF**
12 **compared to the current Fe catalysts.** Most of these candidates are quite novel, providing a
13 set for experimental confirmation. We followed this prediction from HHTS that Rh doping of
14 Fe might significantly enhance NH₃ TOF, with complete calculations including all 44 surface
15 configurations, free energy reaction barriers and full kMC to predict that **Rh doping of Fe**
16 **might increase the TOF by ~3.3 times compared to pure Fe.** This provides a focused target
17 for experimental confirmation, that may potentially **reduce in HB energy consumption by**
18 **several fold**, even with the same conditions and industrial plants as used presently.
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33 Future developments include variants of the screening criteria, refinement of the free-energy
34 diagram analysis via micro-kinetic model techniques,^{19,29} adjustments of empirical corrections
35 to the energetics of different metals,³⁰ or other strategies for changing the catalyst,³¹ such as
36 multiple (ternary, etc.) doping.
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44 ASSOCIATED CONTENT

45 46 47 48 Supporting Information

49 The Supporting Information is available free of charge on the ACS Publications website at
50 DOI:xxx.
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3 Computational details, in silico strategy for doped Fe(111) catalysts for HB synthesis, KMC
4 simulations details, and energy diagram of Rh-doped Fe catalyst.
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7 Figures include Alternative illustration of the screening protocol; “Linear” vs. “zig-zag” 2N
8 configurations for the 2N system; Atomic charges and spins for selected configuration; Surface
9 structure for reaction steps in Figure 4; N₂ dissociation steps on Rh-doped Fe(111) surface;
10 DFT/PBE-D3 free energy diagram including semi-empirical correction; and Barriers for
11 promising dopants estimated (A) without or (B) including empirical corrections.
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17 Xlsx files with all raw energy data.
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23
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46 **Competing interests**

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48 The authors declare no competing interests.
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Figure Captions

Figure 1. The standard state free energy diagram at the DFT/PBE-D3 level for ammonia synthesis over a (2x2) unit cell of the Fe(111) surface, evaluated at 673 K, $P(\text{H}_2) = 15$ atm, $P(\text{N}_2) = 5$ atm, $P(\text{NH}_3) = 1$ atm. The barriers selected for high-throughput screening are highlighted in color and numbered. Black is the linear pathway and orange is the alternative pathway from the optimum reaction barriers. The notations for the adsorbed species represent the key configurations (Figure S4 of SI) along the reaction path. Free energies in eV.

Figure 2. (A,B) Schematic depictions of the (2x2) unit cell of Fe(111) both pure (A) and with one substitutional dopant (B). Bronze spheres represent the top layer, dark grey spheres represent the second layer, while white spheres are third layer Fe atoms. In (B) one dopant atom colored in purple replaces one topmost (bronze) Fe atom. **(C)** Portion of the periodic table selected for catalyst screening (34 elements). In the top row the screening criteria are indicated in colors, and the elements are also highlighted using the color of the criterion which has sifted them out.

Figure 3. Schematic depiction of the configurations used for reaction energies (the numbers are electronic energies (eV) from DFT simulations) for estimating barriers (energies for Rh-doping case). The Rh, N and H atoms are represented by purple, blue and red balls, respectively. Bronze, dark and white spheres represent the top, the second, and the third layer Fe atoms, respectively. To represent the complexity of various doping sites, we use different symbols here for adsorbed species than Figure 1 and 4. The symbol (l) represents the linear $2\text{N}_2\text{H}$ structure and the c (or f) represents the doping close (or far) to the N, H, NH_2 and NH_3 species.

Figure 4. The standard state energy landscape for NH_3 synthesis reactions on Rh-doped Fe(111) surface under 673 K and 20 atm conditions. The lowest energy state $3\text{N}_2\text{NH}_2$ is taken as reference, with a free energy of zero. Black is the linear pathway and orange is the alternative pathway from the optimum reaction barriers. The notations for the adsorbed species represent the key configurations (Figure S4 of SI) along the reaction path. To be consistent with Figure 1, we used the same symbols for adsorbed species.

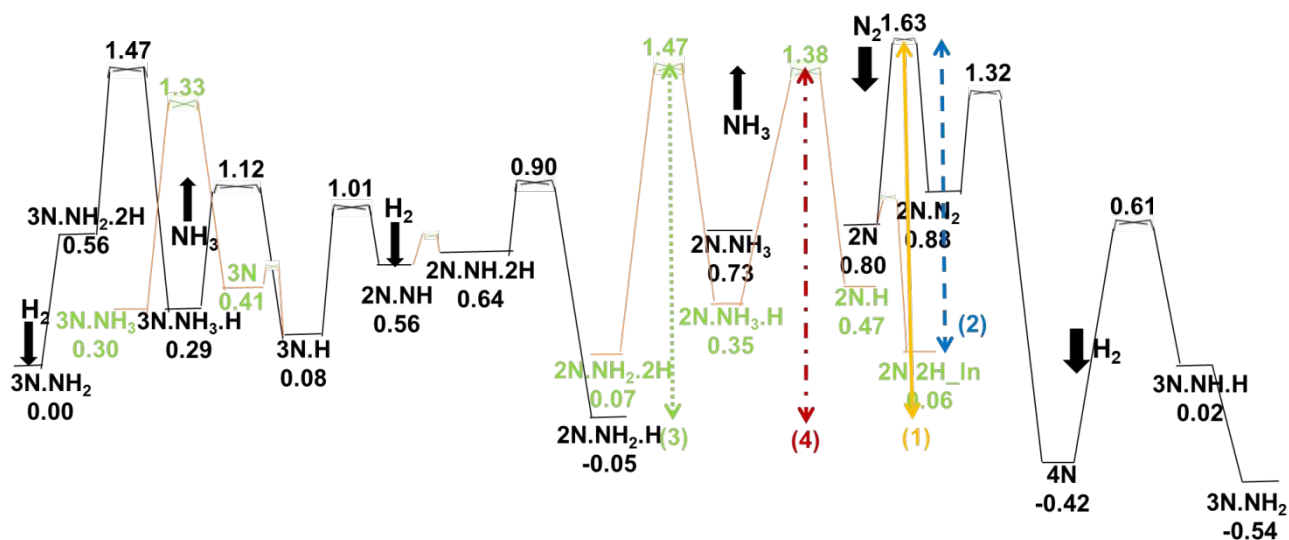


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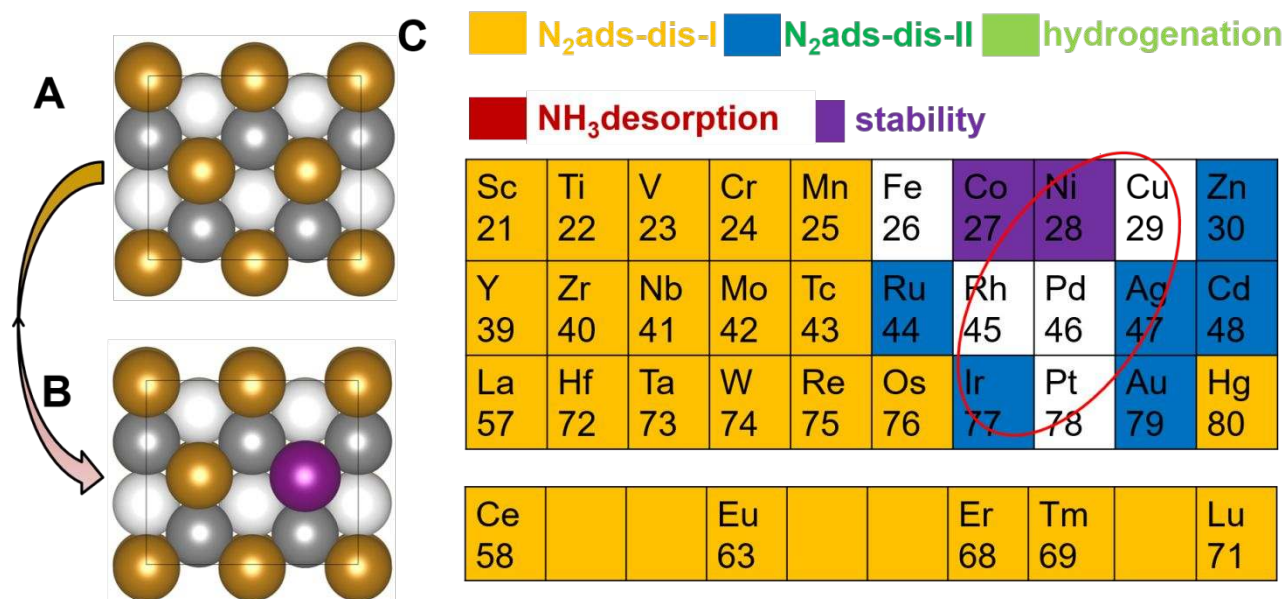


Figure 2. (A,B) Schematic depictions of the (2x2) unit cell of Fe(111) both pure (A) and with one substitutional dopant (B). Bronze spheres represent the top layer, dark grey spheres represent the second layer, while white spheres are third layer Fe atoms. In (B) one dopant atom colored in purple replaces one topmost (bronze) Fe atom. **(C)** Portion of the periodic table selected for catalyst screening (34 elements). In the top row the screening criteria are indicated in colors, and the elements are also highlighted using the color of the criterion which has sifted them out.

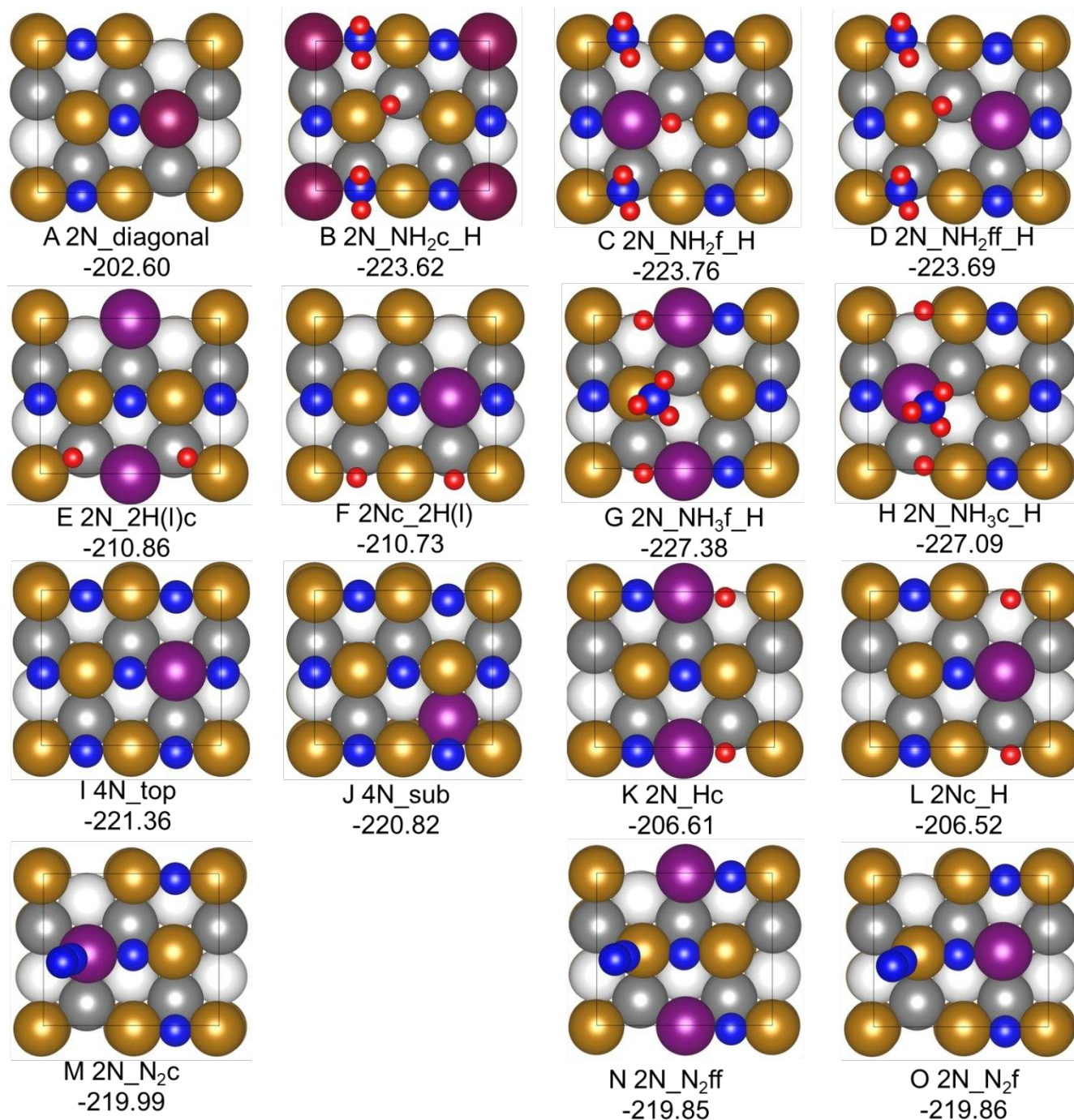


Figure 3. Schematic depiction of the configurations used for reaction energies (the numbers are electronic energies (eV) from DFT simulations) for estimating barriers (energies for Rh-doping case). The Rh, N and H atoms are represented by purple, blue and red balls, respectively. Bronze, dark and white spheres represent the top, the second, and the third layer Fe atoms, respectively. To represent the complexity of various doping sites, we use different symbols here for adsorbed species than Figure 1 and 4. The symbol (l) represents the linear 2N_2H[linear2] structure while the symbol c (or f) represents a doping element put close to (or far from) the N, H, NH₂ and NH₃ species.

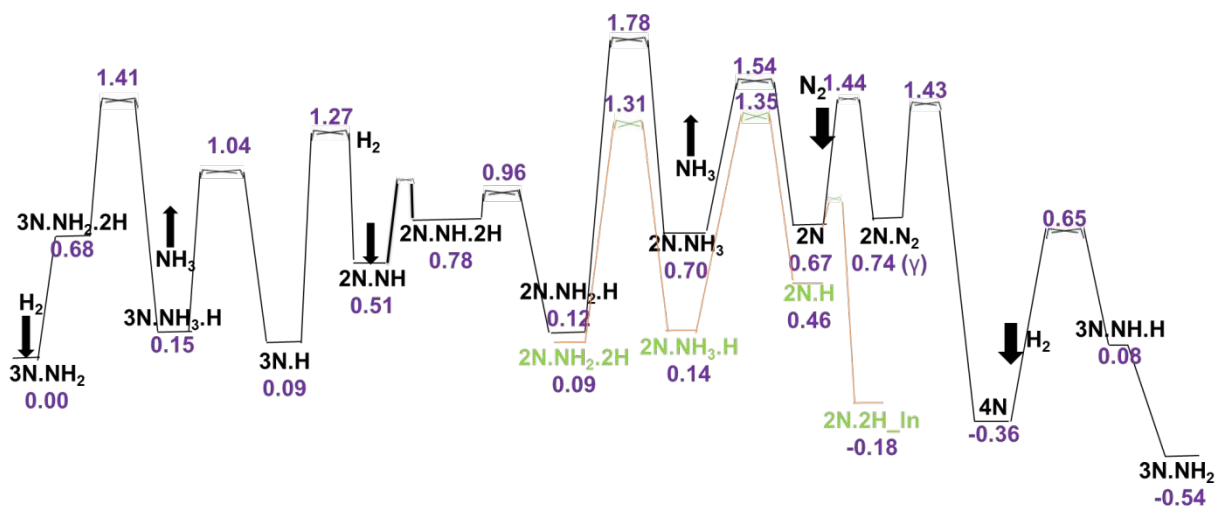


Figure 4. The standard state energy landscape for NH₃ synthesis reactions on Rh-doped Fe(111) surface under 673 K and 20 atm conditions. The lowest energy state 3N_NH₂ is taken as reference, with a free energy of zero. Black is the linear pathway and orange is the alternative pathway from the optimum reaction barriers. The notations for the adsorbed species represent the key configurations (Figure S4 of SI) along the reaction path. To be consistent with Figure 1, we used the same symbols for adsorbed species.

Table 1. Barriers of rate-determining steps in ammonia synthesis over pure and doped Fe(111) surface estimated via the Brønsted–Evans–Polanyi (BEP) principle as discussed in the text. Barrier-5 corresponds to the maximum of barrier(1-4) plus the stability penalty term. Rightmost column is the expected NH₃ production rate per (2x2) unit cell per second. Free energies in eV.

Element	barrier-1	barrier-2	barrier-3	barrier-4	barrier-5	Rate(S ⁻¹ , 673 K)
Rh	1.51	1.60	1.31	1.44	1.60	14.61
Pd	1.51	1.63	1.42	1.51	1.63	8.71
Pt	1.55	1.59	1.36	1.60	1.60	14.61
Cd	1.55	1.84				
Au	1.57	1.82				
Co	1.58	1.51	1.42	1.45	1.76	
Ag	1.59	1.81				
Ni	1.60	1.39	1.48	1.53	1.68	
Cu	1.64	1.61	1.56	1.52	1.64	7.33
Zn	1.64	1.79				
Ir	1.65	1.88				
Ru	1.67	1.76				
Fe	1.68	1.57	1.53	1.43	1.68	3.68
Os	1.73					
Mn	1.73					
Ce	1.74					

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