Electrochemical formation of ammonia on transition metal surfaces

Egill Skúlason\textsuperscript{1,2}, Thomas Bligaard\textsuperscript{1,2}, Sigrídur Gudmundsdóttir \textsuperscript{1}, Anthony Goodrow \textsuperscript{2}, Jan Rossmeisl \textsuperscript{2}, Jens K. Nørskov\textsuperscript{2} and Hannes Jónsson\textsuperscript{3}

\textsuperscript{1}Science Institute, VR-III, University of Iceland, IS-107 Reykjavik, Iceland  
\textsuperscript{2}Center for Atomic-scale Materials Design, Department of Physics, Building 311, Technical University of Denmark, DK-2800 Lyngby, Denmark  
\textsuperscript{3}Faculty of Science, VR-III, University of Iceland, IS-107 Reykjavik, Iceland

Abstract

Theoretical studies of the possibility of forming ammonia electrochemically at ambient temperature and pressure are presented. Density functional theory calculations were used in combination with a model for describing the effect of an applied potential to calculate the free energy profile for the reduction of \( \text{N}_2 \) admolecules and \( \text{N} \) adatoms on several flat and stepped transition metal surfaces in contact with acidic electrolyte. Trends in the catalytic activity, so-called volcano curves, were calculated for a range of pure transition metal surfaces and applied potential under the assumption that activation energy barriers scale with free energy difference in each elementary step. Hydrogen gas formation is a competing reaction, but for the most favorable situation, a direct attachment of protons from the solution on a \( \text{N}_2 \) molecule adsorbed at a step on a Fe(110) surface, an applied potential of \(-0.6\) V should suffice to form more ammonia than hydrogen. Mechanism involving first the rupture of the \( \text{N}_2 \) bond as in the Haaber-Bosch process is less likely in the electrochemical reduction because of the high coverage of hydrogen on the surface.

1 Introduction

Ammonia is one of the most highly produced chemicals. It is primarily used in the subsequent production of fertilizer. Since early in the last century, ammonia has been produced by the Haber-Bosch process. This Nobel prize discovery has been directly linked to the explosive population growth of the 20th century [1]. Much work has gone into the industrial optimization of this process and today it is understood in great detail [2, 3, 4]. In the Haber-Bosch process, nitrogen and hydrogen gas molecules are heated to 430 °C, pressurized to 150 bar and passed over either an Fe or a Ru surface to catalyze the reaction [5, 6]

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]  

(1)

The relatively high temperature is necessary to provide an adequate reaction rate.
However, this shifts the equilibrium of the reaction towards the reactants. This results in an undesirable decrease in the conversion of the reactants to products. The high pressure is chosen to alleviate this problem, since it shifts the equilibrium in favor of the products.

Microorganisms exist in nature which use an enzyme called nitrogenase to produce ammonia from solvated protons, electrons and atmospheric nitrogen. In contrast to the transition metal catalyst used in the Haber-Bosch process, nitrogenase can synthesize ammonia at room temperature and atmospheric pressure. The active site in the enzyme is a $\text{MoFe}_7\text{S}_9\text{N}$ cluster (called FeMo-co), that catalyzes the electrochemical reaction

$$N_2 + 8H^+ + 8e^- \rightleftharpoons 2NH_3 + H_2.$$  

(2)

The source of energy for this reaction is at least 16 adenosine triphosphate (ATP) molecules (or approximately 5 eV) [7, 8]. This increases the chemical potential of the electrons and the protons compared to $H_2$ molecules. It has been hypothesized that nitrogenase acts as an ATP driven 'battery' for this reaction. It is conceivable that the natural process which occurs in bacteria could be emulated in a man-made system. A low-temperature and low-pressure process could make it possible to have a more decentralized ammonia production instead of the current situation where ammonia can only be produced in large factories. The protons could come from an acidic solution while the electrons would be driven to the electrode surface by the applied electrical potential. The reaction mechanism in enzymes is quite different from the industrial synthesis method. In the enzyme, $N_2$ molecules are hydrogenated (associative mechanism) [9]. However, in the Haber-Bosch method, the nitrogen and hydrogen atoms do not react until the strong $N_2$ triple bond and the $H_2$ bond have been broken (dissociative mechanism) [10].

There have been a number of theoretical studies on electrochemical ammonia synthesis, both on the active site of the enzyme [9, 11, 12] as well as low-temperature ammonia synthesis on transition metal surfaces using hydrogen gas [10, 13]. However, no practical low-temperature man-made process with reasonable yields of ammonia has yet been developed. For the electro-catalytic $N_2$ reduction, various types of electrolytes and electrode materials have been studied, but the electrode kinetics are too slow for practical applications [14, 15, 16, 17, 18, 19, 20, 21]. Little is known about the mechanism of this process and in most cases hydrogen gas is formed more readily than hydrogenation of $N_2$.

In the present study, reactions on the Ru(0001) surface were first studied, since this is the optimal pure metal catalyst under industrial conditions [22]. Density functional theory calculations of ammonia formation on both the flat and stepped surface were carried out. For each surface, the reduction of both the adsorbed $N_2$ molecule and adsorbed $N$ atoms were studied. The influence of an external potential was subsequently taken into account using a previously established model [23] and the negative electrode potential needed to reduce nitrogen into ammonia was estimated. The free energy of the various intermediates formed on the surfaces was calculated as a function of voltage.
Since the electrodes will be fully covered with hydrogen at a negative bias, it is not likely that \( \text{N}_2 \) molecules will dissociate on the surface, and hence the associative mechanism is the main focus of our study. The binding energy of the adsorbed species on a range of closed-packed and stepped transition metal surfaces was calculated and used to identify the most active transition metal catalyst and the ratio of ammonia to hydrogen formed.

## 2 Methodology

### 2.1 System and DFT calculations

A close-packed HCP(0001) surface was used to model the flat surfaces of Sc, Re, Os, Co, and Ru while a FCC(111) surface was used for Rh, Ni, Pt, Pd, Cu, Ag, and Au and a BCC(110) surface was used for W, Mo, Cr and Fe. The calculations were carried out using density functional theory (DFT) in the DACapo code with the RPBE functional [24, 25]. Plane wave basis sets were used to simulate a periodically repeated (2x2) three layer supercell. The stepped surfaces were modeled with \((6 \times 2)\) three layer cells, where three rows of the metal atoms in the top layer were removed to create a strip island three rows wide. Increasing the strip size to five rows was found to change the adsorption energy in a few test cases by less than 0.1 eV. The calculated lattice constants were: Sc 3.30 Å \((c/a\ ratio: 1.59)\), Re 2.76 Å \((c/a\ ratio: 1.62)\), Os 2.76 Å \((c/a\ ratio: 1.58)\), Co 2.48 Å \((c/a\ ratio: 1.62)\), Ru 2.75 Å \((c/a\ ratio: 1.58)\), Rh 3.85 Å, Ni 3.56 Å, Pt 4.02 Å, Pd 4.02 Å, Cu 3.71 Å, Ag 4.21 Å, Au 4.24 Å, W 3.20 Å, Mo 3.20 Å, Cr 2.87 Å, and Fe 2.91 Å. The slabs were separated by 10-12 Å of vacuum. For the flat surfaces the two bottom metal layers were fixed and the top layer was allowed to relax as was the adsorbed species. For the stepped surfaces the two top layers were allowed to relax whereas the bottom layer was fixed. \(6 \times 6 \times 1\) Monkhorst-Pack k-point sampling was used for the flat Ru surfaces and maximum symmetry was applied to reduce the number of k-points in the calculations. For all the other metals, \(4 \times 4 \times 1\) k-point sampling was used since the difference between this and the denser k-point sampling was less than 0.01 eV in test calculations. A \(2 \times 6 \times 1\) k-point sampling was used for all the stepped surfaces. The plane wave cutoff was 30 Ry for the wave function and 60 Ry for the density for the Ru calculations, whereas these values were 25 Ry and 36.7 Ry for all the other metals.

### 2.2 The electrochemical reactions

In the hypothetical electrochemical ammonia synthesis process, the anode reaction is

\[
H_2 \rightarrow 2H^+ + 2e^-.
\]  \hspace{1cm} (3)

Here, it is assumed that the concentration of hydrogen molecules is in thermodynamic equilibrium with the protons and the electrons. The protons are solvated in the electrolyte and the electrons are transported from the anode to the cathode through a wire. At the cathode the reaction is
\[ N_2 + 6H^+ + 6e^- \rightleftharpoons 2NH_3, \quad (4) \]

where nitrogen molecules, protons and electrons are in equilibrium with ammonia. The overall electrochemical reaction is, therefore, reaction (1).

First, we consider the possibility that the reaction follows a dissociative Heyrovsky mechanism, where the nitrogen molecules are first dissociated on the surface and subsequently hydrogenated by direct attachment of protons from the solution, (*) denotes an unoccupied site on the surface:

\[
2 \ast + N_2 \rightleftharpoons 2 \ast N \quad (5)
\]

\[
2 \ast N + 6(H^+ + e^-) \rightleftharpoons \ast N + \ast NH + 5(H^+ + e^-) \quad (6)
\]

\[
\ast N + \ast NH + 5(H^+ + e^-) \rightleftharpoons 2 \ast NH + 4(H^+ + e^-) \quad (7)
\]

\[
2 \ast NH + 4(H^+ + e^-) \rightleftharpoons \ast NH + \ast NH_2 + 3(H^+ + e^-) \quad (8)
\]

\[
\ast NH + \ast NH_2 + 3(H^+ + e^-) \rightleftharpoons 2 \ast NH_2 + 2(H^+ + e^-) \quad (9)
\]

\[
2 \ast NH_2 + 2(H^+ + e^-) \rightleftharpoons \ast NH_2 + \ast NH_3 + (H^+ + e^-) \quad (10)
\]

\[
\ast NH_2 + \ast NH_3 + (H^+ + e^-) \rightleftharpoons 2 \ast NH_3 \quad (11)
\]

\[
2 \ast NH_3 \rightleftharpoons \ast NH_3 + NH_3 + \ast \quad (12)
\]

\[
\ast NH_3 + NH_3 \rightleftharpoons 2NH_3 + 2 \ast \quad (13)
\]

Then, we consider an associative Heyrovsky mechanism, where the nitrogen molecules are hydrogenated by protons, analogous to the mechanism in the enzyme:

\[
\ast + N_2 + \ast \rightleftharpoons \ast N_2 \quad (14)
\]

\[
\ast N_2 + 6(H^+ + e^-) \rightleftharpoons \ast N_2H + 5(H^+ + e^-) \quad (15)
\]

\[
\ast N_2H + 5(H^+ + e^-) \rightleftharpoons \ast N_2H_2 + 4(H^+ + e^-) \quad (16)
\]

\[
\ast N_2H_2 + 4(H^+ + e^-) \rightleftharpoons \ast N_2H_3 + 3(H^+ + e^-) \quad (17)
\]

\[
\ast N_2H_3 + 3(H^+ + e^-) \rightleftharpoons \ast N_2H_4 + 2(H^+ + e^-) \quad (18)
\]

\[
\ast N_2H_4 + 2(H^+ + e^-) \rightleftharpoons \ast NH_2 + NH_3 + (H^+ + e^-) \quad (19)
\]

\[
\ast NH_2 + NH_3 + (H^+ + e^-) \rightleftharpoons \ast NH_3 + NH_3 \quad (20)
\]

\[
\ast NH_3 + \ast \rightleftharpoons NH_3 + \ast \quad (21)
\]

We then consider dissociative and associative Tafel mechanism where adsorbed hydrogen atoms react with N or N_2.

\textit{Dissociative Tafel mechanism:}

\[
2 \ast + N_2 \rightleftharpoons 2 \ast N \quad (22)
\]

\[
2 \ast N + \ast H \rightleftharpoons \ast N + \ast NH \quad (23)
\]

4


\[
*N + *NH + *H \rightleftharpoons 2 *NH
\]  
(24)

\[
2 *NH + *H \rightleftharpoons *NH + *NH_2
\]  
(25)

\[
*NH + *NH_2 + *H \rightleftharpoons 2 *NH_2
\]  
(26)

\[
2 *NH_2 + *H \rightleftharpoons *NH_2 + *NH_3
\]  
(27)

\[
*NH_2 + *NH_3 + *H \rightleftharpoons 2 *NH_3
\]  
(28)

\[
2 *NH_3 \rightleftharpoons *NH_3 + NH_3 + *
\]  
(29)

\[
*NH_3 + NH_3 \rightleftharpoons 2NH_3 + 2*
\]  
(30)

**Associative Tafel mechanism:**

\[
* + N_2 + \rightleftharpoons *N_2
\]  
(31)

\[
*N_2 + *H \rightleftharpoons *N_2H
\]  
(32)

\[
*N_2H + *H \rightleftharpoons *N_2H_2
\]  
(33)

\[
*N_2H_2 + *H \rightleftharas* *N_2H_3
\]  
(34)

\[
*N_2H_3 + *H \rightleftharpoons *N_2H_4
\]  
(35)

\[
*N_2H_4 + *H \rightleftharpoons *NH_2 + NH_3
\]  
(36)

\[
*NH_2 + NH_3 + *H \rightleftharpoons *NH_3 + NH_3
\]  
(37)

\[
*NH_3 + \rightleftharpoons NH_3 + *
\]  
(38)

Before each of the hydrogenation step of the Tafel reactions, Eq. 22-38, a hydrogen atom needs to adsorb on the surface via the Volmer reaction:

\[
H^+ + e^- \rightarrow H^*
\]  
(39)

DFT calculations were used to estimate the free energy of each elementary step. The calculations provide information about the stability of various possible surface intermediates, which is difficult to obtain by other means. The adsorption energy and vibrational frequencies for the most stable configuration of each intermediate were calculated and the free energy estimated as a function of applied potential. On this basis, we establish a reaction mechanism and estimate thermodynamic properties of the cathode reactions. A method was introduced in Ref. [23] for describing trends in electrochemical oxygen reduction. Here, we apply it to the reduction of N and N_2 in an electrochemical cell. The procedure involves 3 steps:

1. **The reference potential is** set to be that of the standard hydrogen electrode (SHE). The chemical potential (the free energy per H) of \((H^+ + e^-)\) is related to that of \(\frac{1}{2}H_2\) (Eq. 3 is in equilibrium). This means that at pH = 0, potential of \(U = 0\) relative to the SHE and 1 bar of \(H_2\) in the gas phase at 298 K, the reaction free energy of reaction (1) is equal to that of the net reaction of (5) - (13) or (14) - (21) at an electrode.

2. **The free energy of the intermediates is** calculated at zero potential and pH = 0
\[ \Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S, \]  

where \( \Delta E \) is the reaction energy and \( \Delta E_{ZPE} \) is a zero point energy correction.

3. The effect of an applied bias, \( U \), is included for all reactions involving an electron in the electrode by shifting the free energy by \(-nU\), where \( n \) is the number of electrons involved in the reaction

\[ \Delta G(U) = \Delta E + \Delta E_{ZPE} - T\Delta S - nU. \]  

The presence of water may help to stabilize some species more than others via hydrogen bonding. For example, \(^*\)NH is expected to be stabilized by hydrogen bonding, while the effect of the water layer on adsorbed nitrogen will be negligible. This effect has not been included here.

The effect of the electric field at the surface should also be taken into account. The simplest way to estimate its effect is to introduce an external sawtooth potential with a potential drop in the vacuum hence creating an electric field at the surface. This field interacts with the dipole moment of the adsorbed species. The effect on the free energy tends to be small. For example, the adsorption energy of O* and HO* has been estimated to change by less than 0.015 eV at 1 V bias [23]. This effect has not been included in the calculations presented here.

At a pH different from 0, we may correct the free energy of \( H^+ \)-ions by the concentration dependence of the entropy, \( G(pH) = -kT \ln[H^+] = kT \ln 10 \). All calculations presented here are for pH = 0.

2.3 Rate estimation

The adsorption energy of all intermediate states in (5) - (21) was calculated on a flat and a stepped Ru surface and in all intermediate states in (14) - (21) for flat and stepped Sc, Re, Pt, and Au surfaces. The adsorption energy of the N atom was calculated on both flat and stepped surfaces of Sc, Re, Rh, Co, Ni, Ru, Pt, Pd, Cu, Ag, and Au and only on stepped surfaces of Os, W, Mo, Cr, and Fe. These energy values for different species were then used to estimate the free energy change in the elementary reactions (14) - (21) and (31) - (38). The negative of the free energy difference of an elementary step, \(-\Delta G\), is used as a simple measure of the rate of these reactions by assuming that the prefactor \( \nu \) in the rate expression \( \nu e^{-\Delta G/k_BT} \) is the same for all the reactions and potential and material independent, and by assuming that the activation free energy barrier scales with the reaction free energy. Trends in catalytic activity of the transition metals can be summarized conveniently and interpolated using approximate linear relations for the adsorption energy [26]. It has been shown that the adsorption energy of simple hydrogen containing species \( A\text{H}_x \) (for example, \( \text{CH}_x \), \( x = 1, 2, 3 \), \( \text{NH}_x \), \( x = 1, 2 \), \( \text{OH}_x \), \( x = 1 \) and \( \text{SH}_x \), \( x = 1 \)) depend nearly linearly on the adsorption energy of the atom \( A \). In this paper we obtain linear relations for larger molecules, \( N_2\text{H}_x \) (\( x = 0, 1, 2, 3, 4 \)) using the chemisorption energy of the N.
adatom as a parameter. The slope is roughly consistent with the number of unpaired electrons in the gas-phase molecule. Within this approximate scheme, we construct so-called volcano plots where the rate-limiting steps and the most catalytically active metal surface can be identified. Furthermore, the variation of the volcano plots with applied voltage is obtained to identify the electrochemical conditions that are most likely to produce ammonia in appreciable yield.

3 Results

3.1 Ammonia formation at a flat and stepped Ru(0001) surface

We first present the results of DFT calculations of the free energy for reduction of nitrogen for the dissociative and associative mechanisms on the Ru(0001) surface, referenced to \( H_2 \) in the gas phase. All intermediates are included. Similar results have previously been published for the dissociative mechanism on flat and stepped Ru(0001) and the associative mechanism on flat Ru(0001) [10, 27, 28] but the results on the associative mechanism at a step are new. In the discussion section, we use these results to predict the electrochemical analogs of each step for these different mechanisms.

It is well established that in the industrial Haber-Bosch process, the dissociation of \( N_2 \) takes place at steps on the catalyst surface, because there is a very high energy barrier for dissociation on the flat terrace [27], on the order of 1.9 eV. Fig. 1 shows the free energy for the formation of ammonia at the stepped Ru(0001) surface via such a dissociative pathway at room temperature. Hydrogen atoms are added one by one to the adsorbed species and DFT calculations are used to find the minimum energy configuration, binding energy and vibrational frequencies. Several structures and adsorption sites were investigated in each case. In this case, the rate-limiting step would be the reduction of \( \ast NH_2 \) to \( \ast NH_3 \). Similar results were presented in [28], but are included here for completeness. In the discussion section below, we add the influence of an applied electrical potential. However, steps on a transition metal surface in contact with acidic solution at room temperature are expected to be fully covered with adsorbed hydrogen atoms [29, 30]. The probability of finding a large enough uncovered area on the surface to dissociate \( N_2 \) will, therefore, be low, so an associative mechanism where only one site is needed is more likely for ammonia production at ambient conditions. Below, we study the formation of ammonia by an associative mechanisms, first on a flat surface and then at a step.

The DFT calculations show that an intact \( N_2 \) molecule binds on the flat Ru(0001) surface with a binding energy of -0.4 eV. The free energy change increases to +0.08 eV because of the large loss in entropy in going from the gas phase to a surface bound molecule, see Fig. 2. The rate-limiting step in the reduction to form ammonia is the addition of the first hydrogen atom to form \( N_2 H \), assuming the prefactor is the same in all steps. This first hydrogenation step is 0.75 eV uphill in energy and 1.08 eV in free energy (after including ZPE and entropy). A large entropy loss is associated with the
binding of hydrogen from the gas phase.

The intact $N_2$ binds more strongly at a step on the Ru(0001) surface, with a binding energy of 0.71 eV. This drop in energy is sufficiently large for the free energy to decrease by 0.23 eV despite the loss in entropy. The addition of a hydrogen atom is again uphill in free energy and the addition of the second hydrogen atom even slightly more uphill.

The minimum energy configurations of the $N_2H_x$ admolecules at the step are shown in Fig. 4. A particularly stable and compact configuration of $N_2H$ molecule was found where the molecule bends down towards the surface so that both N atoms become bonded to metal atoms. This significantly reduces the free energy barrier for the reduction as compared to the flat surface and makes the addition of the second hydrogen atom rate-limiting for the reduction at a step.

### 3.2 Adsorption of N and $N_2H_x$ on other transition metals

To estimate the catalytic activity of other transition metals in the associative reduction of nitrogen, a DFT calculation of the binding of N and $N_2H_x$ ($x = 0, 1, 2, 3, 4$) molecules has been carried out for both the flat and stepped surfaces of Sc, Re, Ru, Pt and Au. This choice of metals gives a wide range in binding energy. The most stable binding
Figure 2: Free energy for the associative mechanism on a flat Ru(0001) surface, analogous to Fig. 1. The rate-limiting step is now the addition of the first proton to the adsorbed N$_2$ molecule. With an applied potential of $U = -1.08$ V, all the elementary steps involve either no change or a decrease in free energy.

Figure 3: Free energy for the associative mechanism at a step on the Ru(0001) surface, analogous to Figs. 1 and Figs. 2. The rate-limiting step is now the addition of the second proton to the N$_2$ molecule adsorbed at the step. With an applied potential of $U = -0.37$ V, all the elementary steps involve either no change or a decrease in free energy.

...site and configuration on the Ru surface (discussed above) was used as an initial guess for the other metals. The binding energy of N$_2$H$_x$ was found to scale quite well with
Figure 4: Minimum energy configurations of $N_2H$, $N_2H_2$, $N_2H_3$ and $N_2H_4$ adsorbed at a step on the Ru(0001) surface. Color code: Ru, grey; N, blue; H, yellow.

the binding energy of N, analogous to what has been found for AH$_x$ type molecules previously [26]. The results for flat surfaces are shown in Fig. 5a where the $N_2H_x$ energy is plotted against the adsorption energy of N in the FCC hollow site. Fig. 5b shows similar results for the steps.

The closed shell molecules $N_2$, $N_2H_2$ and $N_2H_4$ bind only weakly and with similar strength to all these transition metals, so their binding energy is largely independent of the binding energy of $N$. The adsorption energy of the $N_2H$ radical scales, however, directly with a slope of nearly one with that of $N$, consistent with the fact that both molecules would have three unpaired electrons in the gas phase. The linear relation of the adsorption energy of $N_2H_3$ has a smaller slope consistent with fewer unpaired electrons. The best-fit slopes are 0.98 and 0.55, respectively.

The linear relations of the $N_2H_x$ binding energy at a step are shown in Fig. 5b. The results are similar to the ones obtained for the flat surfaces. In most cases the slopes are similar whereas the intercepts are slightly more negative since the steps tend to bind stronger than the flat surfaces. One species behaves differently on the step than on the flat surface: the $N_2H_2$ admolecule. On the flat surface the H atoms are bonded one to each of the two nitrogen atoms, resulting in a closed-shell structure. At the step, the two hydrogen atoms are both attached to the outer nitrogen atom, resulting in a different electronic structure. Such a molecule would have two unpaired electrons in the gas phase. The slope on the linear relation plot is found to be 0.57, close to the 0.67 predicted by this simple argument.

In Fig. 5c the adsorption energy of H adatoms is plotted as a function of the chemisorption energy of N adatoms on selected metals in their closed packed surface structure. The relation is linear between these adsorption energies. In the Discussion section we use this linear relation to convert H adsorption energies into N adsorption energies.
4 Discussion

The DFT results presented in the previous section can now be used to estimate two possible variations in the system: (1) the effect of applying an electric potential, and (2) the effect of replacing Ru with some other pure transition metal to construct the so-called volcano plots. In the end, (1) and (2) are combined to calculate the variation in the volcano plots with applied potential.
4.1 Applied potential on Ru electrode

We now use the approach described in section 2.2 to estimate the effect of an applied electrical potential on the elementary steps in the reduction of nitrogen at a Ru electrode. Assuming an electrolyte solution with pH=0, room temperature and 1 bar pressure of H₂ gas, the results on the gas phase reduction steps can be directly related to the electrochemical reduction steps [23]. The only difference is the change in the free energy of the electrons in the electrode when the electrical potential is applied, as given in eqn. 41. By applying an electrical potential which raises the free energy of the electrons in the metal electrode and drives protons from the electrolyte towards the metal surface, the free energy rise in the rate-limiting steps can be eliminated. While there will also be activation energy barriers and variations in the prefactor, we will assume that they are small and that the onset of a significant reaction rate occurs at a potential where the free energy of the initial and final states of an elementary step is equal to ∆G = 0.

In the dissociative mechanism, see Fig. 1, it is enough to apply a potential of -0.16 V vs. SHE to eliminate the rise in the free energy at the rate limiting steps in the hydrogen gas reactions. After the dissociation of the N₂ molecule, all steps are then downhill in free energy to spontaneously form adsorbed ammonia molecules. The next steps would be to further protonate the adsorbed NH₃ to form NH₄⁺ which becomes solvated in the electrolyte. The last steps are not shown in the figure. This mechanism is, however, not likely to work because the surface will be covered with hydrogen and the probability of finding adjacent free sites where the N₂ molecule can dissociate will be low. We estimate from the Volmer reaction, Eq. 39, that the coverage of hydrogen on the surface will be θ = 0.96 at U = 0 V and 1.00 at U = -0.3 V [30].

We, therefore, focus on the associative mechanism. The free energy landscape in the presence of applied potential is shown in Fig. 2 for the flat Ru(0001) surface. When hydrogen is fed into the reaction in the form of H₂ molecules the reaction has significant free energy barriers, as has been noted previously [10]. This associative mechanism is analogous to the mechanism in the enzyme. There, however, hydrogen is not entering as H₂ but as protons and electrons, H⁺ and e⁻. The energy landscape changes significantly when the chemical potential of the protons and the electrons is increased by applying an electrical potential. With a potential of U = -1.08 V the free energy rise when the first proton is attached to N₂ is eliminated and all steps become downhill in free energy.

A much smaller potential is needed if the N₂ is bound to a step site. There, a potential of U = -0.37 V suffices to make the reduction path all downhill in free energy, as shown in Fig. 3. This associative mechanism at a step is the most likely mechanism for electrochemical ammonia formation emerging from our study.

4.2 Volcano plots for ammonia formation

The question now arises whether other transition metal surfaces can serve as better catalysts for the electrochemical reaction. By using the linear relations of N₂H₃ adsorption as a function of the binding energy of N adatoms, one can create volcano plots to see
which value of the binding energy of N adatoms would provide the highest activity for electrochemical ammonia synthesis. This method was first introduced in Ref. [31] where it was applied to the electrolysis of water on oxide surfaces.

Again, activation energy barriers are not taken into account, they are assumed to be low enough or scale with the reaction energy. The issue is to avoid intermediates with low free energy that would slow down the overall reaction. We also assume that all these single electron-proton transfer steps have the same prefactor. In this analysis the reaction free energy can be used directly as a simple measure of electro-catalytic activity. The reaction free energy for each elementary step can be expressed as functions of the applied potential \( U \) and the binding energy of the nitrogen adatom, denoted as \( N^* \), in the following way. First we consider a Heyrovsky-type reaction mechanism where solvated protons from the solution can directly react with an electron and \( N_2H_x \) or \( NH_x \) species on the surface:

\[
N_{2(g)} + 6(H^+ + e^-) \rightleftharpoons N_2H + 5(H^+ + e^-),
\]

\[
\Delta G_1 = \Delta G_{N_2H} - \Delta G_{N_{2(g)}}
\]
\[
= \Delta E_{N_2H} + 0.80 - 0 + eU
\]
\[
= 0.98\Delta E_{N} + 0.70 + eU
\]  

\[
* N_2H + 5(H^+ + e^-) \rightleftharpoons * N_2H_2 + 4(H^+ + e^-),
\]

\[
\Delta G_2 = \Delta G_{N_2H_2} - \Delta G_{*N_2H}
\]
\[
= \Delta E_{N_2H_2} + 1.11 - \Delta E_{*N_2H} - 0.8 + eU
\]
\[
= -0.80\Delta E_{N} + 1.06 + eU
\]  

\[
* N_2H_2 + 4(H^+ + e^-) \rightleftharpoons * N_2H_3 + 3(H^+ + e^-),
\]

\[
\Delta G_3 = \Delta G_{N_2H_3} - \Delta G_{N_2H_2}
\]
\[
= \Delta E_{N_2H_3} + 1.46 - \Delta E_{N_2H_2} - 1.11 + eU
\]
\[
= 0.37\Delta E_{N} - 0.46 + eU
\]  

\[
* N_2H_3 + 3(H^+ + e^-) \rightleftharpoons * N_2H_4 + 2(H^+ + e^-),
\]

\[
\Delta G_4 = \Delta G_{N_2H_4} - \Delta G_{N_2H_3}
\]
\[
= \Delta E_{N_2H_4} + 1.80 - \Delta E_{N_2H_3} - 1.46 + eU
\]
\[
= -0.45\Delta E_{N} + 0.12 + eU
\]  

\[
* N_2H_4 + 2(H^+ + e^-) \rightleftharpoons N_2H_2 + NH_3 + (H^+ + e^-),
\]

\[
\Delta G_5 = \Delta G_{N_2H_2} + \Delta G_{NH_3} - \Delta G_{N_2H_4}
\]
\[
= \Delta E_{N_2H_2} + 0.88 - 0.31 - \Delta E_{N_2H_4} - 1.80 + eU
\]
\[
= 0.31\Delta E_{N} - 1.21 + eU
\]
\[ *NH_2 + (H^+ + e^-) \rightleftharpoons NH_3(g), \]
\[ \Delta G_6 = \Delta G_{NH_3(g)} - \Delta G_{*NH_2} \]
\[ = -0.31 - \Delta E_{*NH_2} - 0.88 + eU \]
\[ = -0.41\Delta E_{*N} - 0.83 + eU \]

Then we consider a Volmer-Tafel-type reaction mechanism where a solvated proton from the solution first adsorbs on the surface and combines with an electron, the Volmer reaction, Eq. 39, and then a H adatom reacts with \(N_2H_x\) or \(NH_x\) species on the surface:

\[ N_{2(g)} + H \rightleftharpoons N_{2H}, \]
\[ \Delta G_1 = \Delta G_{*N_2H} - \Delta G_{N_{2(g)}} - \Delta G_{*H} \]
\[ = \Delta E_{*N_2H} + 0.80 - 0 - \Delta E_{*H} - 0.22 \]
\[ = 0.98\Delta E_{*N} - 0.10 + 0.80 - 0.24\Delta E_{*N} + 0.43 - 0.22 \]
\[ = 0.74\Delta E_{*N} + 0.91 \]

\[ *N_2H + H \rightleftharpoons *N_2H_2, \]
\[ \Delta G_2 = \Delta G_{*N_2H} - \Delta G_{*N_2H} - \Delta G_{*H} \]
\[ = -1.04\Delta E_{*N} + 1.27 \]

\[ *N_2H_2 + H \rightleftharpoons *N_2H_3, \]
\[ \Delta G_3 = \Delta G_{*N_2H_2} - \Delta G_{*N_2H_2} - \Delta G_{*H} \]
\[ = 0.13\Delta E_{*N} - 0.25 \]

\[ *N_2H_3 + H \rightleftharpoons *N_2H_4, \]
\[ \Delta G_4 = \Delta G_{*N_2H_3} - \Delta G_{*N_2H_3} - \Delta G_{*H} \]
\[ = -0.69\Delta E_{*N} + 0.33 \]

\[ *N_2H_4 + H \rightleftharpoons *NH_2 + NH_3, \]
\[ \Delta G_5 = \Delta G_{*N_2H_4} + \Delta G_{NH_3} - \Delta G_{*N_2H_4} - \Delta G_{*H} \]
\[ = 0.07\Delta E_{*N} - 1.00 \]

\[ *NH_2 + H \rightleftharpoons NH_3(g), \]
\[ \Delta G_6 = \Delta G_{NH_3(g)} - \Delta G_{*NH_2} - \Delta G_{*H} \]
\[ = -0.65\Delta E_{*N} - 0.62 \]

The free energy is expressed here as a sum of an energy contribution that scales as the adatom binding energy, a constant coming from zero point energy and entropy, and the energy shift due to the applied potential. The energy of all the different \(N_2H_x\) and \(NH_x\) species is now expressed in terms of the N adatom binding energy by using the linear scaling relations for flat surfaces in Fig. 5a and steps in Fig. 5b and for the H adatoms vs. N adatoms in Fig. 5c. The energy relations and the constants in Eqs. 42 - 53 are shown for flat surfaces, whereas similar equations may be written for stepped surfaces.
The negative of the change of the free energy, $-\Delta G$, which within our approximations gives the logarithm of the reaction rate, is shown in Fig. 6a and b for the six charge transfer reaction steps of the Heyrovsky-type reaction, Eq. 42 - 47 and in Fig. 6c and d for the Volmer-Tafel-type reactions, Eq. 48 - 53. A volcano plot is obtained in all cases, where the right side of the volcano is limited by the first proton transfer step (and adsorbing $N_2(g)$), Eqs. 42 and 48, (green lines) both for the flat and the stepped surface. The left side of the volcano is limited by the second proton transfer step, Eqs. 43 and 49, (red lines) for the flat surfaces whereas the fourth proton transfer step, Eqs. 45 and 51, (purple line) is the rate-limiting step for the stepped surfaces.

Figure 6: Negative of the change of the free energy, $-\Delta G$, which within our approximations is proportional to the logarithm of the reaction rate, for all the charge transfer steps of ammonia synthesis as a function of the nitrogen binding energy at $U = 0$ V vs. SHE. $\Delta G$ is calculated from linear relations as explained in the text. The resulting volcanos are indicated with the shaded areas. The best possible material would fall on the horizontal dashed line representing the equilibrium potential $+0.1$ V. a) is for flat surfaces and b) for stepped surfaces via the Heyrovsky-type mechanism and c) is for flat surfaces and d) for stepped surfaces via the Volmer-Tafel mechanism.

The predicted rate of formation of ammonia is much greater for the stepped surfaces than the flat surfaces, especially on the left side of the volcano. The right side is not affected as much by introducing steps. The Heyrovsky mechanism is predicted to be more active than the Volmer-Tafel mechanism from this analysis. But it remains to be

15
seen from detailed simulation of the elementary steps whether large activation energy barriers change this result. The top of the volcano is shifted slightly to the left, from around +0.20 eV for the flat surfaces to -0.55 eV for the stepped surfaces. Ru is closest to the top in all cases, and is, therefore, the best catalyst of those metals considered here. The free energy difference is reduced by 0.4 eV when going from the most active flat surface to the most active stepped surface via the Heyrovsky mechanism. The estimated electrical potential needed to form ammonia is about -1.05 V vs. SHE for the optimal flat surface but -0.65 V for the optimal stepped surface via the Heyrovsky mechanism. In Fig. 2 and Fig. 3 the values of -1.08 V vs. SHE and -0.37 V vs. SHE, were obtained for the Ru surfaces. The reason for the difference is that the volcanos are coming from the linear relations in Fig. 5 and this difference is within the scatter. It should be noted here that by turning Fig. 6 upside down the same analysis may be applied to the reverse reaction: ammonia decomposition (oxidation) into nitrogen gas, protons and electrons.

The main reason why the steps get more active than the flat surfaces is because of the stable species of $N_2H$ shown in Fig. 4 which is not possible to form on flat surfaces. This makes the first hydrogenation at a step much less endothermic than on the flat surface. At negative applied bias most surfaces will be fully covered with H adatoms [30] which will make this $N_2H$ configuration less likely to be formed. An H adatom needs to be discharged into a solvated proton and an electron (Volmer oxidation reaction: $*H \rightleftharpoons H^+ + e^-$) to create an empty site on the surface. This step is added to the rate-limiting step ($N_2(g) + H^+ + e^- \rightleftharpoons *N_2H$) on the right side of the volcano in Fig. 6b. Here we use the linear energy relations between adsorbed N and H adatoms in Fig. 5c to convert the H adsorption energies into N adsorption energies. This is explained in more details in the next section. Since here this rate-limiting step consist of two processes, where the electrons are transferred in opposite directions, this step is not affected by the applied bias.

The observation that the steps are more active than the flat surfaces indicates that more reactive and open structures may be needed to find the optimum electrochemical ammonia synthesis catalyst, e.g. nitrides, sullides, oxides, stepped surfaces or nanoparticles. A similar effect was also observed when comparing the volcano for electrochemical oxygen evolution on transition metal surfaces with the corresponding volcano for the metal oxides [31].

Recently we determined the mechanism of the hydrogen formation step when evolving $H_2$ from protons and electrons on various types of electrode materials, different metals and surface structures [30]. Two possible mechanism were studied; (1) where two H adatoms desorb into an $H_2$ molecule (Tafel reaction) and (2) where a solvated proton in water directly reacts with an H adatom and an electron from the surface and forms $H_2$ molecule (Heyrovsky reaction). We concluded that the Tafel mechanism will always have a considerable lower activation barrier than the Heyrovsky mechanism on any metal electrode and at a bias in the range from -1 V vs. NHE to +0.5 V vs. NHE. This observation has important consequences. It means that it might be possible to block the $H_2$ formation. Since the Tafel mechanism requires that the two H adatoms
sit close to each other on the surface, it may be possible to design a surface structure where e.g. only every other surface atom binds H. This would increase the activation barrier to form $H_2$.

### 4.3 Relative amount of hydrogen and ammonia

An important issue is the relative amount of ammonia to hydrogen produced. As in the enzyme, hydrogen formation is going to take place at the same time ammonia is formed. A volcano for hydrogen gas formation is shown in Fig. 7a, similar to that shown in Fig. 6 for ammonia formation. The binding of N atom on the surfaces is again used as the variable:

\[ H^+ + e^- \rightleftharpoons {}^*H \]

\[ \Delta G_1 = \Delta G_{*H} \]

\[ = \Delta E_{*H} + 0.22 + eU \]

\[ = 0.25 \Delta E_{*N} - 0.19 + eU \]

\[ {}^*H = \frac{1}{2} H_2(g) \]

\[ \Delta G_2 = \Delta G_{\frac{1}{2}H_2(g)} - \Delta G_{*H} \]

\[ = 0 - \Delta E_{*H} - 0.22 \]

\[ = -0.19 \Delta E_{*N} + 0.24 \]  

(54)  

(55)

Here we have fitted the data points to a straight line on each side of the volcano plot. Identical plot could be made from the linear relations in Fig. 5c. At $U = 0$ V vs. SHE, it is evident from Fig. 7a that hydrogen gas formation would dominate over ammonia formation for all pure metal catalysts. To obtain a more quantitative comparison, the free energy of ammonia formation in Fig. 6a (flat) and 6b (steps) for the Heyrovsky mechanism and in Fig. 6c (flat) and 6d (steps) for the Volmer-Tafel mechanism has been subtracted from the free energy of hydrogen evolution in Fig. 7a ($\Delta G_{H_2} - \Delta G_{NH_3}$) and plotted in Fig. 7b and c, respectively. For the flat surfaces, Rh, Ni, Co, and Ru are at the top of the volcano plot. The stepped surfaces are clearly much more active than the flat surfaces. The left leg of the volcano plot shows promising results where Fe is at the top.

The simple analysis presented here only takes into account the binding energy and vibrational entropy of each intermediate. The binding energy of the $N_2H_x$ and $NH_x$ species are modeled on clean surfaces (without any steric effects from surrounding H adatoms that are expected to adsorb on the surfaces at negative electrical potentials considered in this study). This analysis does not take into account effects of the local electric field at the surface and surface charges. Also, activation energy barriers are not included. All these effects are important for determining the absolute rate of the reaction and further studies are required to obtain a better estimate of the reaction rates.
Figure 7: a) Hydrogen evolution volcano for $U = 0$ V vs. SHE in the lower part and hydrogen oxidation volcano in the upper part, obtained with similar linear relations as in the ammonia volcano. A more accurate HER volcano obtained from calculated rates [30] is also included for comparison (dotted line). The difference in reaction free energy ($\Delta G_{H_2} - \Delta G_{NH_3}$) for hydrogen gas formation and for ammonia formation (Fig. 6a and 6b) for Heyrovsky mechanism b) and ammonia formation (Fig. 6c and 6d) for Tafel mechanism c) at $U = 0$ V vs. SHE. This gives the relative amount of hydrogen formed vs. ammonia, assuming the prefactors are the same.

For comparison we have added to Fig. 7a the volcano for hydrogen formation coming from a detailed study of reaction kinetics in Ref [30] where all parameters (reaction and activation energy for each step) have been estimated by DFT calculations and a more
detailed electrochemical model [32, 33, 30]. In this way, water, solvated protons, surface charges, electric fields and electrical potentials are all taken into account. Here, the rate of hydrogen formation is represented as $-E_a = k_B T (\ln r - \ln \nu)$ and is plotted vs. the binding energy of the N adatom on the same surface. The overall shape, in particular the location of the maximum, is the same as for the simple estimate obtained from the free energy analysis, supporting the validity of the approximate scheme. We expect the same will be true for the ammonia formation and that the present, approximate analysis can give a good indication of which metal catalyst and applied potential can be expected to lead to appreciable ammonia formation.

To estimate the effect of the applied potential on the relative amount of ammonia and hydrogen formation, the potential dependence of the volcano for $\Delta G_{H_2} - \Delta G_{NH_3}$ is shown in Fig. 8. Until now, the volcanos have been plotted for $U = 0$ V vs. SHE. In Eq. 42 - 47 and Eq. 54, the free energy is not only dependent on the N binding energy but also the applied electrical potential. Notice that the reaction free energy of desorbing $H_2$ from the surface, Eq. 55, is not dependent on the bias (for $\Delta E_{aN} < 1$ eV). The reaction free energy of the first protonation step to the $N_2$ molecule on a stepped surface via the Heyrovsky mechanism is also potential-independent as explained previously, see further the right side of the volcano in Fig. 6b. Also, both of the rate-limiting steps for the Tafel mechanism are not dependent on the bias (only the Volmer step is potential dependent in that process) and hence only the Heyrovsky mechanism for the ammonia formation is considered here. Fig. 8 shows the ratio of ammonia vs. hydrogen gas formation as a function of both the applied potential and the nitrogen binding energy. As larger negative bias is applied, the ratio of ammonia to hydrogen is predicted to increase. For the stepped surfaces, a smaller negative bias is needed to start forming more ammonia than hydrogen, $-0.6$ V vs. SHE for a stepped surface and $-1.2$ V vs. SHE for a flat surface. Notice that we show different range of values for the x-axis in Fig 8a and 8b. The reason why we do not show values above $-0.55$ eV in $\Delta E_{aN}$ for the stepped surfaces is that above that value the rate-limiting steps of both the hydrogen and ammonia formation are potential-independent as explained previously. Hence, we can not tune the bias to negative values in order to make the ammonia formation more favorable than hydrogen formation, and the Ru, Rh, Ni, Co, Pt, Pd surfaces are predicted to be inactive towards ammonia formation and the hydrogen evolution will be the dominant product. Only when going towards the more reactive metals the ammonia formation will be possible and Fe or Os are the most promising of the pure metal steps.

In the end, it is noted that the metals on the left side of the volcano are known to form oxides in contact with water. However, since here we are applying negative bias, the O and OH species become less stable compared to $H_2O$. This would need to be studied in more details, especially for stepped iron oxides.

These are promising results and a more detailed study including more accurate estimates of the rates of each elementary step is warranted and will be conducted in a continuation of this work.
5 Conclusions

We have used theoretical calculations to study the possible mechanisms for forming ammonia electrochemically on pure metal electrodes. The effect of an applied electrical potential and the trends over a range of transition metal electrodes have been identified. The results indicate that ammonia may be synthesized at a sufficiently negative applied potential, especially via an associative Heyrovsky mechanism at a step. At the same time, hydrogen gas will be formed, as is the case in nitrogen fixing enzymes. According to our analysis and within the approximations used (water molecules are not explicitly included, the effect of local electric fields, steric effects from H adatoms and activation barriers), more ammonia is formed than hydrogen when the applied potential is less than -0.6 V vs. SHE for a stepped surface of Fe(110) and less than -1.2 V vs. SHE for flat closed-packed surfaces of Ru, Rh, Co, and Ni.

References


