Electrochemical Nitric Oxide Reduction on Metal Surfaces

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Abstract

Electrocatalytic denitrification is a promising technology for removing NO_x species (NO_3^- , NO_2^- and NO). For NO_x electroreduction (NO_xRR), there is a desire for understanding the catalytic parameters that control the product distribution. Here, we elucidate selectivity and activity of catalyst for NO_xRR . At low potential we classify metals by the binding of $\ast\text{NO}$ versus $\ast\text{H}$. Analogous to classifying CO_2 reduction by $\ast\text{CO}$ vs $\ast\text{H}$, Cu is able to bind $\ast\text{NO}$ while not binding $\ast\text{H}$ giving rise to a selective NH_3 formation. Besides being selective, Cu is active for the reaction found by an activity-volcano. For metals that does not bind NO the reaction stops at NO, similar to CO_2 -to-CO. At potential above 0.3 V vs RHE, we speculate a low barrier for N coupling with NO causing N_2O formation. The work provide a clear strategy for selectivity and aims to inspire future research on NO_xRR .

Keywords

NO_x Removal, Ammonia Synthesis, Metal Surfaces, DFT, Electrocatalysis

Introduction

Nitrogen can be transformed through biological and physical processes within the nitrogen cycle to form a broad spectrum of inorganic compounds, including ammonia (NH_3), hydrazine (N_2H_4), hydroxylamine (NH_2OH), nitrite (NO_2^-), nitrate (NO_3^-), nitric oxide (NO), and nitrous oxide (N_2O).^{1,2} While many of these processes are essential to life, large-scale commercial food production has led to over-fertilization and consequent accumulation of nitrate and nitrite ions in groundwater and in agricultural runoff streams. Both nitrate and nitrite ions are a source of pollution in groundwater, lakes, and coastal water, causing serious health problems, such as methemoglobinemia and cancer, when ingested in high concentrations.³⁻⁵ As a result, groundwater treatments to reduce the concentration of these ions have been developed and have become an important environmental consideration.^{6,7}

Meanwhile, the artificial N_2 fixation towards NH_3 is produced via the Haber-Bosch process. In the Haber-Bosch process, NH_3 is produced in a reaction between H_2 and N_2 at high pressure and temperature. As a consequence, the Haber-Bosch process depends on the use of gaseous H_2 which is commonly made from fossil fuel steam methane reforming (SMR). By contrast, the electrochemical conversion of NO_x ($x = 1, 2$, and 3) to NH_3 involves only H^+ and electrons from electricity that can be from sustainable sources, like wind and solar energy.

Electrochemical denitrification is a promising strategy for the removal of NO_x species from waste-water and constitutes a plausible alternative to traditional denitrification methods, such as biological and physical separations processes, due to its environmental compatibility, energy efficiency, safety, product selectivity, and potential for use in smaller-scale devices.⁶⁻¹⁴ Nitrate and nitrite electroreduction can produce a variety of products, such as N_2 , N_2O , NH_3 , and NH_2OH .^{7,9,15,16} The reduction of NO is an essential environmental reaction, since it determines the performance of waste-water treatment catalysts for NO_3^- , NO_2^- and NO removal.^{6,7}

Investigating electrochemical NO reduction is a first step toward understanding the fun-

damentals of electrocatalytic $\text{NO}_3^-/\text{NO}_2^-$ reduction and developing improved electrochemical denitrification or even sufficient NH_3 production technologies.^{6,7,9,17-19} In addition, the study of NO electrochemistry is of fundamental scientific interest because observations and developed methods can be straightforwardly applied to other environmentally friendly electrocatalytic reduction chemistries. Indeed, as we will show, the electrochemistry of NO has numerous analogies to CO_2/CO electroreduction, which has been reported before.^{20,21}

In this work, we study the potential dependence of the electrocatalytic reduction of NO among a group of metals via density functional theory (DFT) simulations. We classify metals for the electrochemical reduction of $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$, to understand what surface properties determine the main product during reduction, which has been found to be: H_2 , NH_3 , N_2 and N_2O . The analysis has been split into two potential regions according to experimental results as shown in Fig. 1: low and high potential. In each potential region, a descriptor-based method has been utilized to explain experimental observations of the various products formation. Especially under low potential, activity volcano has been constructed against the adsorption energy of $\ast\text{N}$, and Cu has been demonstrated as the most selective and active metal here for NO reduction since it adsorbs $\ast\text{NO}$ but not $\ast\text{H}$.

Figure 1: Schematic representation of experimental products from NO reduction on (a) Pt(111) and (b) Cu(111) and the relation to surface coverage. Two potential regions are shown with different product formation.

Electrochemical reduction of $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$

The electrochemical conversion of NO_3^- under reduction condition is complex, involving multiple reactions, products and stable intermediates (e.g., ammonia, nitrite, hydroxylamine, nitric oxide, nitrous oxide) spanning the many nitrogen oxidation states (from -III up to +V). With referring to the reversible hydrogen electrode potential (RHE), the reduction products

would be produced following the reactions below:

As for the NO_2^- reduction process:

Electrochemical NO reduction reaction (NORR) has been studied under a variety of reaction conditions, including reactions on different metal electrodes,^{22–25} and varying NO concentrations.^{22,26} Overall, there are four different products depending on potential observed during NORR process:

Except the reactions mentioned above, the competitive hydrogen evolution reaction (HER) becomes pronounced when potential goes below 0 V vs RHE:

Thus, below 0 V (vs RHE), the observed Faradaic efficiencies, or percent of electrons used in NORR, can be greatly impacted. All the reactions described above from $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$, illustrate that adsorbed nitric oxide (*NO) as divergent center, may control the electrocatalytic selectivity towards N_2O , N_2 , NH_2OH and NH_3 as illustrated in Fig. 2. As a result, the affinity to NO on metals will play an essential role in their reduction selectivity performance.

Figure 2: Schematic representation of $\text{NO}_3^-/\text{NO}_2^-/\text{NO}$ reduction pathways.

Results and Discussion

Fig. 1(a) shows for Pt that there are two major reaction regions for NO reduction:

- at low potential (< 0.3 V vs RHE) where both H_2 and NH_3 are observed, and at the potential below 0 V vs RHE, H_2 becomes the main product.
- at high potential (0.3 - 0.7 V vs RHE) which leads to N_2O formation.

Similar potential regions have been observed on other metals, such as Pd, Rh, Ru, Ir and Au. As a comparison, Fig. 1(b) shows Cu producing NH_3 as the main product at low potential (< 0 V vs RHE) and N_2O above 0 V vs RHE.

NORR under Low Potential

To conduct electrocatalytic NO_x reduction on catalysts, NO_x species are expected to be adsorbed on the surfaces. In addition, the competition from HER also has to be avoided, especially under low potential region.

Fig. 3(a) shows the adsorption energies of $\ast\text{NO}_3$ plotted against $\ast\text{H}$ adsorption energy. The horizontal line in Fig. 3(a) shows the equilibrium between NO_3^- and adsorbed $\ast\text{NO}_3$ while the vertical line depicts the equilibrium between $(1/2)\text{H}_2$ and adsorbed $\ast\text{H}$ under standard conditions. It is found that almost all metals investigated here can absorb $\ast\text{NO}_3$, except Au (Fig. 3(a)). As a result, all metals, except Au might obtain the electrocatalytic activity for NO_3^- reduction, while on Au, the electroreduction of NO_3^- is hardly detectable as reported experimentally.¹⁵ As for the adsorption of $\ast\text{H}$, there are three binding energy regimes: i) binding $\ast\text{H}$ weakly, limiting availability towards adsorbed $\ast\text{H}$ paves high barrier for their catalytic activity of NO_3^- reduction (Ag/Au); ii) binding $\ast\text{H}$ moderately but still above 0 eV (Cu) and iii) the remaining metals to the left of vertical line bind $\ast\text{H}$ strongly, mainly resulting in HER instead of NO_3^- reduction, especially at potential below 0 V vs RHE.

Figure 3: The adsorption energies of the intermediates (a): $\Delta E_{\ast\text{NO}_3}$; (b) $\Delta E_{\ast\text{NO}_2}$ and (c) $\Delta E_{\ast\text{NO}}$ are plotted against $\Delta E_{\ast\text{H}}$. The horizontal line shows the equilibrium between (a) NO_3^- and adsorbed $\ast\text{NO}_3$; (b) NO_2^- and adsorbed $\ast\text{NO}_2$; (c) $\text{NO}(\text{gas})$ and adsorbed $\ast\text{NO}$ while the vertical line depicts the equilibrium between $(1/2)\text{H}_2$ and adsorbed $\ast\text{H}$ under standard conditions. Red markers demonstrates H_2 produced as the main product while Cyan color markers shows NH_3 is the main product according to experimental results.^{9,10,25,27-29}

Fig. 3(b) illustrates the adsorption energies of $\ast\text{NO}_2$ is plotted against $\ast\text{H}$ adsorption energy. The horizontal line shows the equilibrium between NO_2^- and adsorbed $\ast\text{NO}_2$ and again the vertical line describes the equilibrium between $(1/2)\text{H}_2$ and adsorbed $\ast\text{H}$. The adsorption tendency towards $\ast\text{NO}_2$ are observed similar to $\ast\text{NO}_3$, except Au. Au binds $\ast\text{NO}_2$ stronger than $\ast\text{NO}_3$, and is close to the equilibrium between NO_2^- and $\ast\text{NO}_2$, leading to some catalytic activity of NO_2^- reduction¹⁷. Similar to NO_3^- reduction, for NO_2^- reduction, the metals to the left of vertical line binding $\ast\text{H}$ strongly, produces H_2 as the main product under low potential. For the metals to the right of the vertical line, binding $\ast\text{H}$ weakly, like Ag and Au, catalytic NO_2^- reduction is unfavorable due to limiting accessibility of adsorbed $\ast\text{H}$. As for Cu, it adsorbs $\ast\text{NO}_2$ and produces NH_3 with limited HER.

Fig. 3(c) shows the adsorption energies of $\ast\text{NO}$ plotted against $\ast\text{H}$ adsorption energy. The horizontal line illustrates the equilibrium between NO (gas) and adsorbed $\ast\text{NO}$ and the vertical line shows the equilibrium between $(1/2)\text{H}_2$ and adsorbed $\ast\text{H}$. Fig. 3(c) illustrates that metals can be classified into three groups in terms of the adsorption energies for $\ast\text{NO}$ and $\ast\text{H}$. Metals on the left of vertical line like Pt, Pd, bind both $\ast\text{NO}$ and $\ast\text{H}$ very strongly, resulting in HER at potential below 0 V vs RHE. For the metals above the horizontal line, it is unfavourable to bind $\ast\text{NO}$, which does not allow NO reduction. Only Cu metal binds $\ast\text{NO}$ while not having $\ast\text{H}$ upd, leading to NH_3 conversion.

The analysis above, shows that NO_x (NO_3^- , NO_2^- and NO) reduction on the metals to the left of the vertical line in Fig. 3 is greatly inhibited by HER, leading to low NO_x product faradic efficiency. For the metals above the horizontal line in Fig. 3(c), NO_x (NO_3^- , and NO_2^-) reduction can happen with sufficient potential applied, producing NO while further reduction of NO is hard. Cu stands out with the unique property that it can bind $\ast\text{NO}_3^-$, $\ast\text{NO}_2^-$ and $\ast\text{NO}$ but not $\ast\text{H}$, demonstrating its high selectivity for NO_x reduction over HER. This is similar to CO_2/CO electroreduction.²⁰

Fig. 4 demonstrates computational limiting potential for NO reduction towards NH_3 plotted against the adsorption energy of $\ast\text{N}$ ($\Delta G_{\ast\text{N}}$) with the utilization of the scaling re-

lations presented in Fig. S2. The red line represents the strong binding side of the volcano where the hydrogenation of $^*\text{NH}$ to $^*\text{NHH}$ is limiting step. The blue line shows metals with weak binding of $^*\text{N}$. For the metals on the weak binding side, $^*\text{NHO}$ is preferred in the protonation of $^*\text{NO}$, and NH_3 will be produced via $^*\text{NHHO}$ intermediate, leaving $^*\text{O}$ on the surface as shown in Fig. S4. On the weak binding side, Cu prefers $^*\text{NOH}$ while $^*\text{NHO}$ is formed on Ag or Au in the hydrogenation of $^*\text{NO}$. Further hydrogenation of $^*\text{NOH}$ on Cu produces $^*\text{N}$ and then continuous protonation of $^*\text{N}$ leads to the formation of NH_3 . Among all the metals investigated here, Cu is predicted to be the most active catalyst to produce NH_3 .

Figure 4: The limiting potential volcano for NO reduction to NH_3 . Limiting potential defined as the negative of the free energy change of each proton-coupled electron transfer step, which behaves as a function of the adsorption energy of $*N$ (ΔG_{*N}) at 0 V vs RHE. The left red line demonstrates the potential is limited by the strong binding of $*NH$ ($*NH$ towards $*NHH$) while the right blue line shows that the potential is limited by the weak binding of $*NHO$ (formation of $*NHO$ from $*NO$). The upper dashed horizontal line exhibits the equilibrium potential (0.71 V) which can be obtained from NO reduction to NH_3 . The vertical lines shows the $*H$ and $*NO$ adsorption respectively. Insert: Free energy diagram of NO reduction towards NH_3 on Cu(111), with blue line constructed under 0 V while red line constructed under equilibrium potential (0.71 V). Note Cu is the only metal on the weak binding side but prefers $*NOH$.

A closer catalytic reaction process on Cu(111) can be seen in the insert of Fig. 4. It proceeds via the protonation of the adsorbed $*NO$ to $*NOH$ intermediate, and further protonation of $*N$ and $*NH$ leads to NH_3 formation. The first hydrogenation of $*NO$ is the potential limiting step. As a result, Cu(111) provides the highest catalytic activity for NH_3 formation among all metals investigated here, and its catalytic activity can be still enhanced by strengthening its $*N$ adsorption, since it is still not on the top of the volcano.

Following the scaling relation between $*N$ and $*H$ and the scaling relation between $*N$

and *NO shown Fig. S5, the product selectivity (vertical dashed lines) can be also indicated in Fig. 4. When ΔG_{*N} is smaller than -1.5 eV, ΔG_{*H} becomes negative and H_2 will be the main product. For metals with ΔG_{*N} larger than -0.83 eV, the adsorption of *NO is unfavorable, leading to the formation of NO. Cu has ΔG_{*N} between -1.5 eV and -0.83 eV, leading to high selectivity for NH_3 production in the process of NORR, as also seen in Fig. Fig. 3.

This computational analysis explains that the experimental results with high faradaic efficiency ($> 90\%$) for NO_x (NO_3^- , NO_2^- and NO) reduction to NH_3 have been achieved on Cu-based catalysts.^{10,11,25,30-34} More interestingly, enhanced catalytic activity has also been observed when Cu is alloyed with strong *N adsorption metals, like Ni and Rh.^{11,31-33} This might be due to the stabilization of *NOH intermediate, getting close to the top of the volcano shown in Fig. 4(a) but still ΔG_{*N} in the region of -1.5 eV to -0.83 eV. At medium potentials (around 0 - 0.3 V vs RHE), the HER is thermodynamically impossible and NH_3 is reported as the major product²⁴. With limited access to adsorbed *H, much less current density is observed experimentally for the metals.^{15,17,24} Still, much higher current density at medium potential is reported on Cu for NO_x (NO_3^- , NO_2^- and NO) reduction under the same experimental conditions, compared to other transition metals.

NORR towards N_2O under High Potential

At high potential region, N_2O formation is observed. For this reaction to occur, N-N coupling is required. Fig. 5(a) shows that the *ONNO formation on metals from 2NO is unfavourable. Experimentally, it has been suggested that solution NO is involved in the reaction sequence to produce N_2O since N_2O is not produced during the reduction of adsorbed *NO.²⁴ It seems more reasonable to speculate N-N bond formation from *N and NO. As for the formation of *N, besides the continuous protonation of NO_x , the dissociation of NO_x can be another option. Fig. S3 (a-c) present the activation barriers for NO_x dissociation. Ni and Rh have the lowest barriers whereas Ag or Au have the highest barrier. Generally, the barriers for

Cu and the platinum group metals is between the two extremes. For the $*NO_x$ ($x = 1, 2$, and 3) dissociation reactions, E_a increases with decreasing x on a specific metal, implying that the final dissociation step has the highest activation energy. As a result, $*N$ might be produced via the dissociation of $*NO_3$ and $*NO_2$ and then the hydrogenation of $*NO$.

Figure 5: (a) Adsorption energy comparison between twice of $*NO$ and N-N coupling intermediate $*ONNO$. The horizontal line shows the equilibrium between $2NO(g)$ and $2*NO$, while the diagonal line illustrates the equal adsorption energy between $2*NO$ and $*ONNO$. (b) The activation barriers for N-N coupling between $*N$ and NO (gas) vs $*N$ and $*N$. where the unfilled markers show around 0.44 Monolayer of NO coverage is considered. (c) Adsorption energy comparison between $*NO$ and $*N_2O$. The horizontal line shows the equilibrium between $NO(g)$ and $*NO$ while the vertical line depicts the equilibrium between N_2O and $*N_2O$ under standard conditions.

Fig. 5(b) shows the activation barrier for N-N bond formation between adsorbed $*N$ and NO plotted against the activation barrier of N_2 formation from two adsorbed $*N$. There is almost no activation observed for N-N coupling between $*N$ and NO except Ru, no matter how strong $*N$ is adsorbed. Following the experiments, where 0.5 monolayer $*NO$ coverage has been suggested on strong adsorption metals like Ru,²⁴ $*N$ and NO coupling becomes feasible with this coverage consideration. In addition, the activation barrier of N_2 formation from adsorbed $*N$ is larger than N_2O formation.

Fig. 5(c) shows the adsorption energy comparison between $*NO$ and $*N_2O$. The horizontal line shows the equilibrium between NO (gas) and $*NO$ while the vertical line depicts the equilibrium between N_2O (gas) and $*N_2O$ under standard conditions. It shows that the adsorption of N_2O is not stable for all metals. As a consequence, N_2O will be the main

product during NO_x reduction at high potential.

Conclusions

In this study, we use DFT simulations to investigate electrocatalytic NO_x reduction selectivity and activity over metal catalysts. Analogous to classifying CO_2 reduction by $\ast\text{CO}$ vs $\ast\text{H}$, we classify metals by the adsorption energy of $\ast\text{NO}$ vs $\ast\text{H}$. Since the selectivity of the NO_x reduction is potential dependent, the products formation has been analysed in two different potential regions. At low potential, NO_x reduction competes with HER, leading to H_2 as the major product on strong $\ast\text{H}$ binding metals. For metals binding $\ast\text{H}$ weakly like Ag or Au, NO_3^- and NO_2^- reduction will stop at NO similar to CO_2 -to-CO. Cu stands out with the unique property that it can bind $\ast\text{NO}_3$, $\ast\text{NO}_2$ and $\ast\text{NO}$ but not having H_{upd} , leading to high selectivity for NH_3 formation.

With the utilization of scaling relations for intermediates adsorption energies, DFT simulated limiting potential is plotted against the adsorption energy of $\ast\text{N}$. Cu is predicted to be the most active metal to conduct NO reduction towards NH_3 and the potential limiting step is the hydrogenation of adsorbed $\ast\text{NO}$. The volcano shows that enhanced activity can be achieved by slightly strengthening the adsorption energy of $\ast\text{N}$ on Cu, like alloying Cu with metals binding $\ast\text{N}$ stronger but $\Delta G_{\ast\text{N}}$ still should be larger than -1.5 eV. At potential between 0 to 0.3 V vs RHE, the limiting adsorbed $\ast\text{H}$ results in much less current density compared to that under low potential for NO_x reduction. Still NH_3 is reported as the main product and Cu demonstrates higher current density under the same conditions as compared to other transition metals.

At high potential condition (> 0.3 V vs RHE), high coverage of adsorbed $\ast\text{NO}$ is observed for NO reduction. With free NO in the solution, the N-N bond formation from adsorbed $\ast\text{N}$ and NO, forming N_2O , is feasible while it is impossible to produce N_2 via the association of two adsorbed $\ast\text{N}$.

These descriptor-based analyses in this work provide a description of the NO reduction or even NO_3^- and NO_2^- reduction network on metals at atomic scale. These findings offer a guidance or inspiration for the design and discovery of both selective and active NO_x (NO_3^- , NO_2^- and NO) reduction electrocatalysts.

Computational Details

The computational analysis was carried out using the grid-based projector-augmented wave (GPAW) method, a DFT code based on a projected augmented wave (all-electron frozen core approximation) method integrated with the atomic simulation environment (ASE).^{35–37} The revised Perdew-Burke-Ernzerhof (RPBE) functional was used as an exchange-correlation functional.³⁸ The wavefunctions were represented on a uniform real-spaced grid with 0.18 Å grid-spacing. The electronic spins are treated separately, and a vacuum of minimum 7 Å was employed. Besides the calculation for climbing image nudged elastic band (NEB) was performed with GPAW code.³⁹ The quasi-Newton minimization scheme was employed for the geometry optimizations, and the systems were relaxed until the forces were less than 0.05 eV/Å. Structures, total energies, scripts to run calculations, and plotting methods are collected in the KatlaDB database available at this link: <http://nano.ku.dk/english/research/theoretical-electrocatalysis/katladb/>.

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Graphical TOC Entry

Illustration of selectivity and activity on metals for nitric reduction reaction