

Electrochemical Synthesis of Urea: Co-reduction of Nitric Oxide and Carbon Monoxide

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Abstract

Electrocatalytic conversion is a promising technology for storing renewable electricity in the chemical form. Substantial efforts have been made on the multi-carbon feedstock production, while producing nitrogen-containing chemicals like urea via C-N coupling little is known. Here, we elucidate the possible urea production on metals through co-reduction of nitric oxide (NO) and carbon oxide (CO). Based on adsorption energies calculated by DFT, we find that Cu is able to bind both *NO and *CO while not binding *H. During NO + CO co-reduction, We identify two kinetically and thermodynamically possible C-N couplings via *CO + *N and *CONH + *N, and further

hydrogenation leads to urea formation. A 2-D activity heatmap has been constructed for describing nitrogen conversion to urea. This work provides a clear example of using computational simulations to predict selective and active materials for sustainable urea production.

The electroreduction of CO_2 is a promising technology for carbon utilization. In the electrolysis of CO_2 or CO_2 -derived CO , most efforts have been devoted to promoting C-C bond formation to generate important industrial multi-carbon feedstock such as ethylene, ethanol, n-propanol and acetate. However, bonding the C atom of CO_2 with other valuable heteroatoms (e.g., N) is an alternative strategy to produce value-added products which is highly beneficial for expanding the application of CO_2RR .¹⁻³

N-containing chemicals, such as urea, amides, amines, and nitriles, are of widespread importance for the bulk chemicals, synthetic intermediates, fertilizers, agrochemicals, and pharmaceuticals.⁴⁻⁶ Currently, the synthesis of these molecules is all dominated by thermocatalytic transformation of NH_3 precursors under harsh conditions.³ Especially, the production of urea (NH_2CONH_2) consumes approximately 80% of the global NH_3 .⁷⁻⁹ In principle, the formation of C-N bonds for urea should be possible mixing CO_2 or CO with nitrogen species (NO_x), like NO_3^- , NO_2^- and NO , when suitable catalysts are utilized. Nevertheless, the formidable challenge is that the direct electroreduction of CO_2 or NO_x to single carbon or nitrogen species competes with the urea formation. This results in a complex products distribution with low Faradaic efficiency (FE) of urea and also with a need for product separation.¹⁰

The concept of electrocatalytic co-reduction of CO_2 and NO_x was to the best of our knowledge tested in 1995 by Shibata *et al.* to produce urea¹¹ and more recently has gained interest in the community.¹² The product distribution as a function of potential, as measured by Shibata *et al.* with a Cu loaded gas-diffusion electrode (GDE), is shown in Fig. 1.^{11,13,14} With simultaneous reduction of $\text{CO}_2 + \text{NO}_3^-$ (Fig. 1(a)) or $\text{CO}_2 + \text{NO}_2^-$ (Fig.

1(b)), the observed dominant product in both experiments from CO_2 reduction in this GDE setup is CO, which increases with increasing the overpotential. Note that today, research groups report high hydrocarbon production and FE from Cu electrode in GDE.^{15,16} For NH_3 and urea formation, similar current efficiency trend is observed and it decreases with increasing the overpotential. At potential of -0.25 V vs. RHE (reversible hydrogen electrode), the current efficiency of urea with approximately 37% was obtained for $\text{CO}_2 + \text{NO}_2^-$ co-reduction.¹¹ However, the absolute current for each product was not reported. Besides, experimentally, the detection of urea in presence of NO_x species usually involves a two-step process, in which urea is firstly decomposed by ureases into ammonia, and then the amount of ammonia measured by spectrophotometer.^{13,14} The pre-quantification of ammonia is thus crucial, since ammonia is also the product of direct reduction of NO_x . In another word, a rigorous protocol for experimental urea detection is highly demanded.

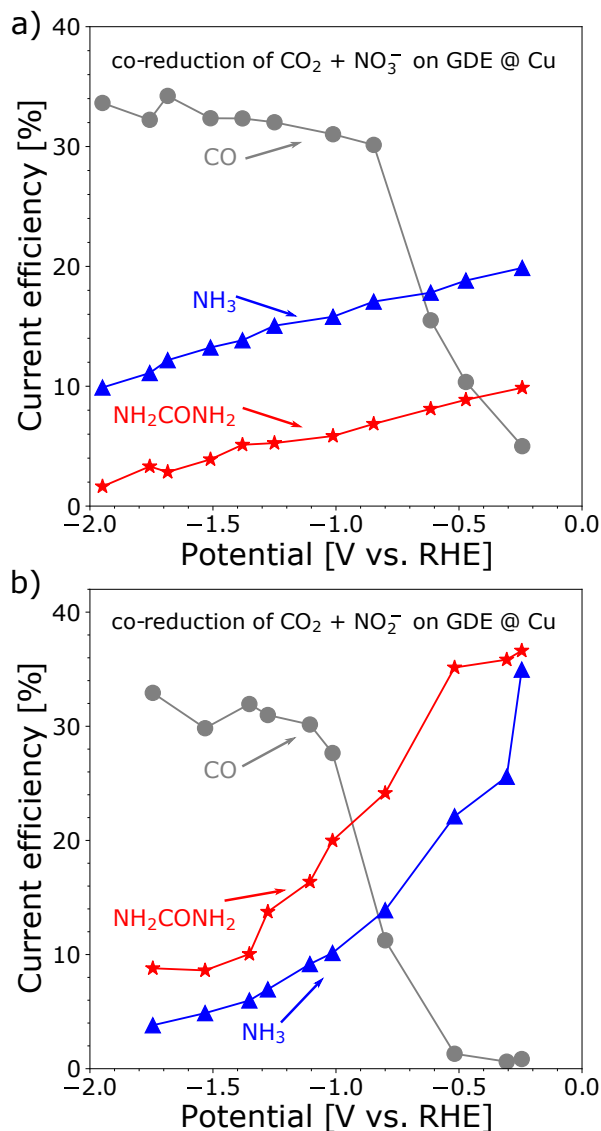


Figure 1: Experimentally determined major product distribution (current efficiency) from electrocatalytic (a) co-reduction of CO₂ + NO₃⁻ and (b) co-reduction of CO₂ + NO₂⁻ at a Cu loaded gas-diffusion electrode (GDE) as a function of electrode potential (versus reversible hydrogen electrode, RHE), as measured by Shibata *et al.*^{11,13,14}

Cu-based materials represent as an important category of electrochemical CO₂ reduction catalysts, allowing the production of hydrocarbons with adsorbed CO as a key intermediate.^{17,18} Furthermore, Cu-based electrocatalysts have been investigated for electrochemical reduction of nitrogen species (NO_x) with high FE (greater than 90%) for NH₃ formation.^{19–22} For electrocatalytic NO₃⁻/NO₂⁻ reduction, adsorbed nitric oxide (*NO, * denotes the active site.) has been suggested as a divergent center, which may control the electrocatalytic

selectivity towards NH_3 production.²²⁻²⁷ As a result, electrochemical NO reduction might provide a more sufficient way for NH_3 formation.²³⁻²⁶

In this work, we investigate the C-N couplings for urea formation during the electrocatalytic co-reduction of $\text{NO} + \text{CO}$ among a group of metals via density functional theory (DFT) simulations. The co-reduction of $\text{NO} + \text{CO}$ provides a study model for understanding the fundamentals of electrocatalytic C-N coupling reactions, developing amides or more specifically, sufficient urea production technologies. The classification mapping has been previously utilized to understand the selectivity on metals for CO ^{28,29} and NO reduction²² with two descriptors. Cu is the only metal that binds both $\ast\text{NO}$ and $\ast\text{CO}$ molecules, but does not have a strong affinity to $\ast\text{H}_{\text{UPD}}$ (under potential deposited $\ast\text{H}$). Essentially meaning that Cu has a lower coverage of $\ast\text{H}$ at reduction conditions allowing CO and NO reduction to take place relative efficiently. Utilizing this knowledge, we investigate the selectivity during co-reduction of $\text{NO} + \text{CO}$, by possible C-N couplings for urea production. We simulate activation barriers for C-N couplings, and construct a 2-D activity heatmap for describing nitrogen conversion towards urea.

In the electrochemical co-reduction of $\text{NO} + \text{CO}$, multiple reactions are possible. Here, we list four important ones:



For each reaction, the standard reduction potential *versus* RHE is shown on the right. Thermodynamically, urea formation has the highest equilibrium potential, which should result in a large driving force for urea. However, due to the existence of overpotential and the large amount of proton electron transfers, the other reactions are still competitive. With

aim to conduct electrocatalytic NO + CO reduction on catalysts, both NO and CO species are expected to be adsorbed on the surfaces. In addition, the competition from hydrogen evolution reaction (HER) also has to be avoided at negative potentials.

Fig. 2(a) shows the classification scheme²⁸ of adsorption energies of *CO plotted against *H adsorption energy. The horizontal line in Fig. 2(a) shows the equilibrium between CO gas and adsorbed *CO while the vertical line depicts the equilibrium between (1/2)H₂ and adsorbed *H under standard conditions. The blue dotted line describes the linear fitting between *CO and *H adsorption energies of transition metals, except metals from group 12 and above which do not bind *CO and hence these values are much too low as compared to how their binding in reality is. Note that the crossing point (indicated by (1)) between the linear fit and the vertical line is important.

Fig. 2(b) illustrates the classification scheme²² of adsorption energies of *NO plotted against *H adsorption energy. The horizontal line illustrates the equilibrium between NO (gas) and adsorbed *NO and the vertical line shows the equilibrium between (1/2)H₂ and adsorbed *H. The blue dotted line is obtained from the linear fitting between *NO and *H adsorption energies without including metals from group 12 and above. The crossing point between the linear fit and the vertical line is indicated by (2). In combination, it is found that Cu is the only metal binding both *NO and *CO but not *H below the equilibrium line of 1/2H₂ ↔ *H. This could lead to a selective NO + CO reduction. Metals on the left of vertical line (both in Fig. 2(a) and (b)) like Pt, Pd, bind *CO, *NO and *H very strongly, resulting in HER, especially at potential below 0 V vs RHE. For the metals above the horizontal line in 2(b), such as Au or Ag, it is unfavourable to bind *CO or *NO, which does not allow CO or NO reduction.

Fig. 2(c) presents a direct adsorption energy comparison between *NO and *CO. The diagonal line in Fig. 2(c) exhibits the equal adsorption strength for *NO and *CO adsorption. Metals are at or below the diagonal line, indicating that the adsorption of *NO is always stronger than *CO adsorption. Using the linear fittings of *CO vs. *H and *NO vs. *H

in Fig. 2(a) and (b), allows to co-plot two lightblue lines. These two blue lines show the equilibrium between $(1/2)\text{H}_2$ and adsorbed $*\text{H}$. Metals on the right of vertical blue line (1) and also above the horizontal blue line (2), are required in order to avoid high $*\text{H}$ adsorption, and hereby H_2 evolution. Utilizing the information of $*\text{NO}$ and $*\text{CO}$ binding with the linear fittings, allows the construction of an area where we can classify urea formation for catalysts. As observed, for all metals they lie below the diagonal line showing a preferred stronger binding of NO than CO. This indicates that NO reduction is easier than CO, even without considering the thermodynamic potentials. Here, the urea production area is marked with blue color and for metal catalysts only Cu metal leads to possible urea conversion. Here, it has to be mentioned that the classification analysis is a necessary properties to fulfill, but may not be sufficient, to describe urea formation on metal catalysts.

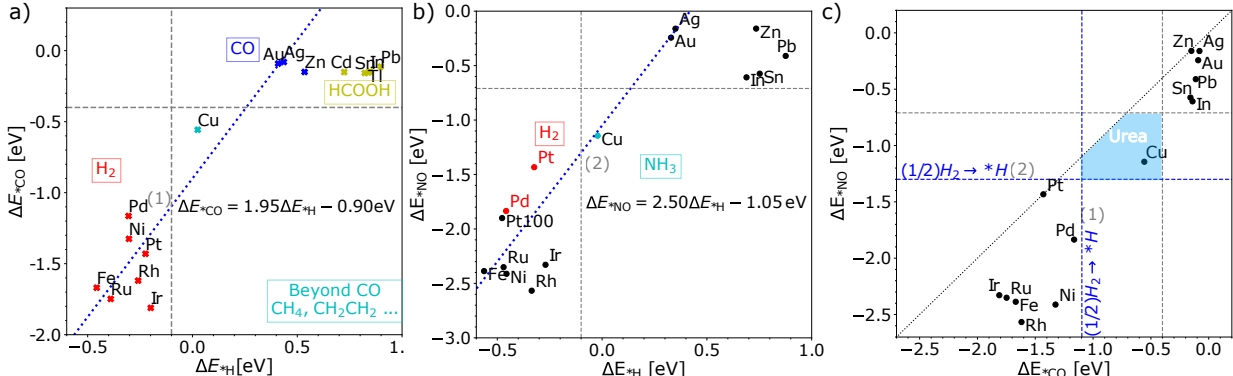


Figure 2: The adsorption energies of the intermediates on metals: (a) $*\text{CO}$ and $*\text{H}$; (b) $*\text{NO}$ and $*\text{H}$; (c) $*\text{CO}$ and $*\text{NO}$. The vertical lines in (a) and (b) show the equilibrium between $(1/2)\text{H}_2$ and adsorbed $*\text{H}$ under standard conditions. The horizontal line in (a) exhibits the equilibrium for $\text{CO} \rightarrow *\text{CO}$ with $\Delta G_{*CO} = 0$ which is also indicated in the vertical gray line in (c). The horizontal lines in (b) and (c) illustrate the equilibrium for $\text{NO} \rightarrow *\text{NO}$ with $\Delta G_{*NO} = 0$ and the diagonal line in (c) shows the equal adsorption strength of $*\text{CO}$ and $*\text{NO}$. Line (1) in (a) describes the linear fitting between $*\text{CO}$ and $*\text{H}$ adsorption energies with ΔE_{*H} below 0.5 eV. Line (2) in (b) is obtained from the linear fitting between $*\text{NO}$ and $*\text{H}$ adsorption energies with ΔE_{*H} below 0.5 eV. The lightblue lines in (c) are obtained from scaling relations on $*\text{CO}$ vs. $*\text{H}$ (line (1)) and $*\text{NO}$ vs. $*\text{H}$ (line (2)). Data is obtained from ref. 22,28,29.

For electrochemical co-reduction of $\text{NO} + \text{CO}$, C-N coupling can happen via CO and NO reduction intermediates. Using the observation that $*\text{NO}$ binds stronger and NO protonation

proceeds at lower overpotential than CO protonation,^{22,28} we investigate the first C-N bond formation via the coupling between *CO and *NHO, *NOH, *NHOH, *N, *NH, *NHH intermediates.

Fig. 3 illustrates the activation barriers (E_a) for C-N bond formation. In Fig. 3(a), the *CO + *N coupling barrier is plotted against the reaction energies (ΔE). A Brønsted-Evans-Polanyi (BEP) scaling relation between the reaction and transition-state energies for this C-N bond formation is obtained, shown in a dotted line. Au has the lowest barrier whereas Pd or Pt have the highest barrier. The barrier for Cu is between the two extremes. The activation barrier between *CO + *N on Cu is around 0.50 eV which is acceptable since the rate of 1 s^{-1} can be obtained at the activation barrier of 0.75 eV (gray dashed horizontal line) at room temperature.³⁰ Furthermore, other C-N couplings between *CO and *NH_x (x = 1,2) on Cu are all energetically downhill (Fig. S1) and with an increase in x, the ΔE also increases.

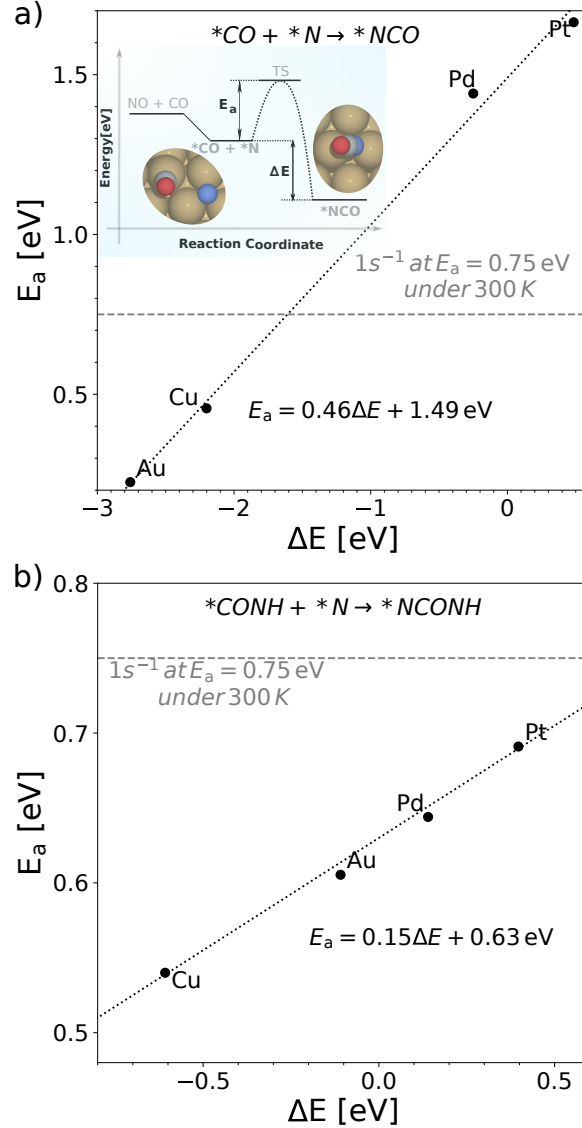


Figure 3: Activation barriers for C-N coupling on (111) facets (a) between $*CO$ and $*N$; (b) $*CONH$ and $*N$ intermediates. Inset in (a) illustrates the energy diagram for $*CO$ and $*N$ coupling activation on a catalyst. The atomically adsorbed ($*CO + *N$) and $*NCO$ states, as well as the transition state (TS) are indicated. Two Brønsted-Evans-Polanyi (BEP) scaling relations between the reaction and transition-state energies for C-N bond formation are exhibited in dashed lines. The horizontal lines show the activation barrier of 0.75 eV at 300K which provides a rate of $1 s^{-1}$.

Fig. 3(b) shows the relation between $*CONH + *N$ coupling barrier and reaction energy. Compared to $*CO + *N$ coupling, the favorable BEP scaling for $*CONH + *N$ coupling, indicates its fast kinetics. For Cu, C-N coupling via $*CONH + *N$ intermediates is energetically downhill while it is unfavourable to form C-N bond for other metals like Au, Pt

and Pd. Further urea production is achieved on Cu through continuous hydrogenation of a *NCONH intermediate.

The analysis above, suggests possible reaction path for urea formation on Cu during co-reduction of NO + CO. Fig. 4 demonstrates the energy diagram for (a) NO to NH₃, (b) CO to CH₄ and (c) NO + CO towards urea formation. The potential for NO reduction, CO reduction and NO + CO co-reduction is 0.23 eV, 0.52 eV and 0.23 eV respectively. This suggests that NO reduction is more favorable than CO during NO + CO co-reduction process. This data is supported by experimental observations of NO reduction towards NH₃ on Cu starting at 0.3 V vs. RHE²¹ and CO reduction to hydrocarbons formation on Cu starting at potential below -0.4 V vs. RHE.^{31,32} Furthermore NO and NO+CO reductions share a common limiting potential, making NO reduction and the co-reduction in direct competition - which is also observed in Figure 1 by these two products having the same behaviour with potential.

Fig. 4(c) presents the reaction path for urea formation from co-reduction of NO + CO via two C-N couplings: (1) *CO and *N coupling; (2) *CONH and *N coupling. Three energy uphill steps are identified: (1): hydrogenation of *NO is potential dependent with 0.23 eV; (2) and (3): C-N couplings are potential independent and have a barrier with 0.50 eV and 0.52 eV respectively. The hydrogenation of *NO is a shared step for NH₃ and urea production, indicating a competition between those two products. Therefore, activation barriers for C-N and N-H bond formation have been also compared here. A higher activation energy (0.72 eV, see Fig. 4(a)) for N-H bond formation than *CO and *N coupling (0.50 eV) is observed, suggesting a fast kinetics for C-N bond formation. In addition, a more negative reaction energy for *CO and *N coupling (-2.23 eV) than *N and *H coupling (-1.53 eV) provides a higher driving force for C-N bond formation. Second C-N bond formation happens with 0.52 eV energy barrier via coupling between *CONH and *N intermediates where *CONH is formed through the hydrogenation of *NCO. Further protonation towards *NCONH and *NHCONH leads to urea formation. Overall, for C-N bond formation, the first C-N

bond formation can be treated as the rate determining step. This computational analysis above suggests possible explanation for the experimental reports where electrocatalytic C-N coupling is widely observed on Cu-based catalysts with acceptable Faradaic efficiency for amides formation, such as urea.^{2,3,11,13,14,33}

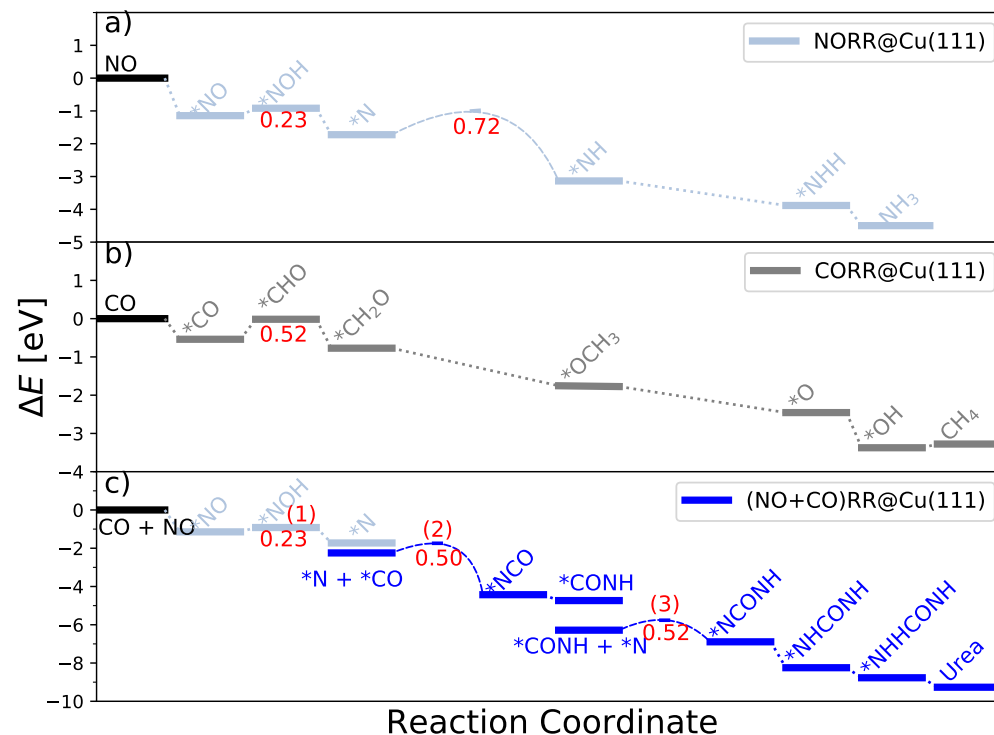
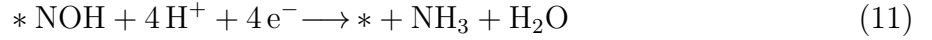
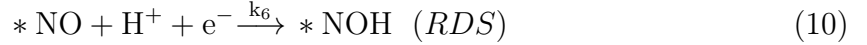
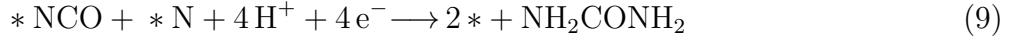
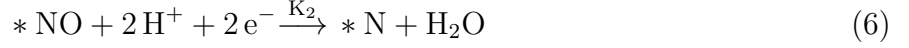


Figure 4: The energy diagram on Cu(111) for (a) NO reduction to NH₃; (b) CO reduction towards CH₄; (c) Co-reduction of NO + CO for urea production with barriers for *CO and *N coupling and *CONH and *N coupling considered. This is made without free energy and solvation corrections

Here, with aim to investigate how to control the reaction towards urea as compared with NH₃ formation, since they are really linked in this process, the efficiency for nitrogen conversion to urea but not the FE for all products in the NO + CO co-reduction has been considered. A 2-D reaction activity heatmap has been constructed for urea formation, where BEP relation from Fig. 3(a) and intermediates scaling relations (Fig. S3) are utilized to reduce the complexity. Further, to keep the microkinetic model simple but still capturing the important chemistry, we consider the following reactions: urea formation with the first

C-N bond formation (*CO and *N coupling) as the rate-determining step (RDS) and for NH₃ formation using the *NOH formation as RDS which is potential dependent²² while the former is not. Here, CO reduction is not included.



From where we can find that, the analytical expression for the rate (R) in the area where *NO and *CO adsorbed but not binding *H can written as:

$$R_{\text{urea}} = k_4^+ K_1 K_2 (U) K_3 P_{\text{NO}} P_{\text{CO}} P_{\text{H}_2\text{O}}^{-1} \theta_*^2 \quad (12)$$

$$R_{\text{NH}_3} = K_1 k_6 (U) P_{\text{NO}} \theta_* \quad (13)$$

$$\text{Nitrogen conversion to Urea} = R_{\text{urea}} / (R_{\text{urea}} + R_{\text{NH}_3}) \times 100\% \quad (14)$$

where $\theta_* = (1 + K_1 P_{\text{NO}} + K_3 P_{\text{CO}} + K_1 K_2 P_{\text{NO}} P_{\text{H}_2\text{O}}^{-1})^{-1}$ and U (vs. RHE) is applied potential.

with

$$\begin{aligned} K_1 &= \exp\left(-\frac{\Delta G_{* \text{NO}}}{k_B T}\right) & K_2(U) &= \exp\left(-\frac{\Delta G_{* \text{N}} - \Delta G_{* \text{NO}} - 2eU}{k_B T}\right) \\ K_3 &= \exp\left(-\frac{\Delta G_{* \text{CO}}}{k_B T}\right) & k_4^+ &= \frac{k_B T}{h} \exp\left(-\frac{\Delta E_a}{k_B T}\right) \\ k_6(U) &= \frac{k_B T}{h} \exp\left(-\frac{\Delta G_{* \text{NOH}} - \Delta G_{* \text{NO}} - eU}{k_B T}\right) \end{aligned}$$

E_a stands for the activation barrier for *CO and *N coupling (see Fig. 3(a)). Under a certain temperature, pressure of the reactants (P_{NO} , P_{CO}), and applied potential (U), the rate depends exactly on two electronic energy parameters: ΔE_{*CO} and ΔE_{*NO} . Fig. 5 shows the nitrogen conversion to urea ($R_{urea}/(R_{urea} + R_{NH_3}) \times 100 \%$) as a function of *NO and *CO adsorption energies with Eq. 12 and Eq. 13 applied in the area where *NO and *CO adsorbed but not binding *H. The kinetic model is calculated at a temperature of 300K, and Fig. 5(a) and (b) are under $P_{NO} = 1$, $P_{CO} = 1$. It is important to note that the coverage of *N is kept fixed by applying a potential of $-(\Delta G_{*N} - \Delta G_{*NO})/2e$ with Cu, Cu(110), and Cu(100) at 0.34, 0.29, and 0.27 V vs. RHE respectively. These potentials indicate that it is fair to not consider hydrocarbons formation from CO reduction where a much more negative potential is demanded (below -0.4 V vs. RHE).¹⁷ Note that in supporting information heatmaps (Figure S4) are presented at lower potentials, showing a clear decay in NO conversion towards urea with respect to potential. This is also observed in the experiment (Figure 1).

In Fig. 5(a), three regions can be classified in this model framework. Region (1) shows H_2 as a major product and region (2) represents urea production and NH_3 formation. Region (3) illustrates little activity for co-reduction of $NO + CO$ due to unfavourable adsorption of NO and CO even though there are low activation barriers for *CO and *N coupling. In region (2), a higher rate (red area) can be obtained from a weakening *NO or *CO adsorption, although without having desorption. As for the formation of NH_3 , our previous study has shown that a stronger *NO relative to Cu is demanded in order to obtain a higher rate or FE.²² As a result, a slightly weaker *NO adsorption relative to Cu, like Cu(100) in Fig. 5(b), not only improves selective urea production, but also promotes a high rate. Additionally, lowering the partial pressure of NO relative to CO (see Fig. 5(b), (c) and (d)) increases the selectivity of $NO + CO$ co-reduction towards urea production. As our model current reply on the observations in Shibata's experiments, it is highly relevant to reproduce those data in the near future to make the data and model valid. Notably, even quantifying urea versus ammonia can be a challenge to confirm sufficiently.

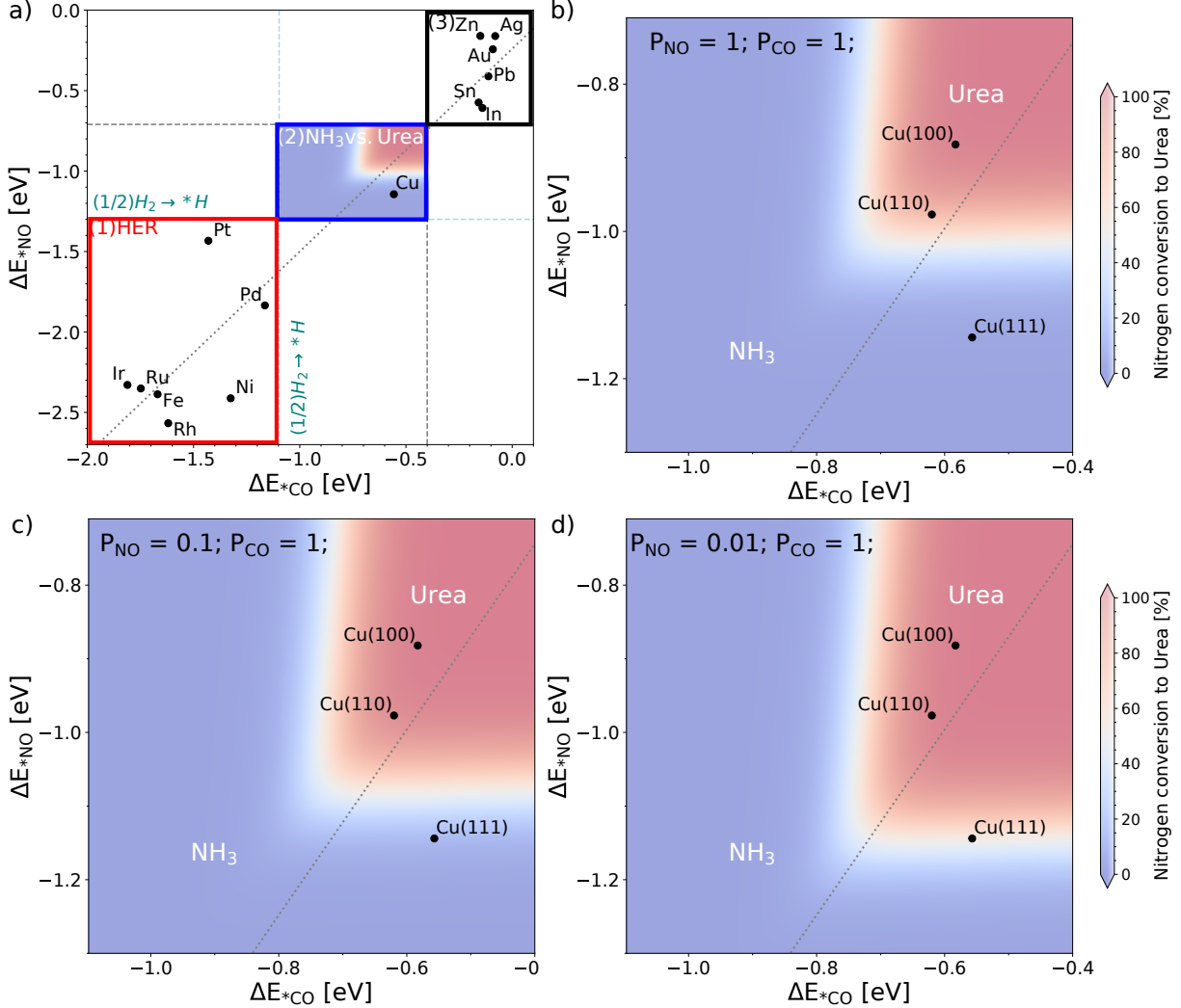


Figure 5: 2-D activity heatmap describing the nitrogen conversion for urea production as a function of ΔE_{*CO} and ΔE_{*NO} , computed at a temperature of 300K with (a) and (b) under $P_{NO} = 1, P_{CO} = 1$; (c) $P_{NO} = 0.1, P_{CO} = 1$; (d) $P_{NO} = 0.01, P_{CO} = 1$. The coverage of $*N$ is kept fixed by applying a potential of $-(\Delta G_{*N} - \Delta G_{*NO})/2$ with Cu, Cu(110), and Cu(100) at 0.34, 0.29, and 0.27 V vs. RHE respectively. Here, $R_{urea}/(R_{urea} + R_{NH_3}) \times 100\%$ equation has only been utilized in the area where $*NO$ and $*CO$ adsorbed but not binding $*H$. Region (1): Hydrogen evolution; Region (2): Urea and NH_3 production; Region (3): little activity. The gray dotted line is the linear fitting for $*NO$ and $*CO$ adsorption energies. It can be noted here Cu(100) not only benefits that the C-C coupling in CO reduction³⁴ but also favours C-N coupling during NO + CO co-reductions.

In this study, we use DFT simulations to investigate electrocatalytic NO + CO co-reduction over metal catalysts. Analogous to classifying CO_2 reduction by $*CO$ vs. $*H$ and NO reduction by $*NO$ vs. $*H$, we utilize the classification scheme by plotting $*NO$ vs. $*CO$.

Direct comparison of *NO vs. *CO shows that *NO binds stronger. Cu stands out with the unique property that it can bind both *NO and *CO but not having H_{upd} , leading to NO or CO reduction taking place prior to HER.

We show that C-N coupling is possible in the narrow window of *NO and *CO adsorbed but not binding *H. Among all the metals investigated here, Cu is predicted to be the most selective catalyst to produce urea. The results suggest that the key enabling steps on Cu in the formation of urea from co-reduction of NO + CO are first the hydrogenation of *NO and following the *CO + *N coupling. Firstly, if adsorbed *NOH can be stabilized relative to adsorbed *NO on Cu, the necessary overpotential can be reduced, which indicates a more efficient process. Besides, a relatively weaker *CO adsorption is needed in order to have a lower activation barrier for the coupling between *CO and *N. However, the hydrogenation of *NO is a shared limiting step both for urea and ammonia production, making a fundamental challenge in the formation of urea versus the conversion towards NH_3 . This is also observed experimentally. These descriptor-based analysis in this work provides a description of NO + CO co-reduction or even $\text{CO}_2 + \text{NO}_3^-/\text{NO}_2^-$ reduction network on metals at atomic scale. The results presented in the current study will form the basis of a search for improved understanding of the co-reduction of NO + CO on metals, suggesting a promising technology for amides especially urea formation.

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Graphical TOC Entry

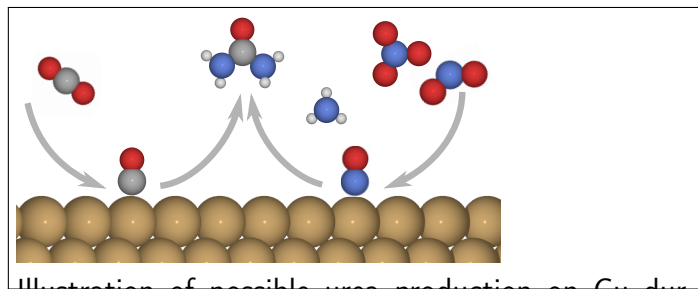


Illustration of possible urea production on Cu during electrocatalytic co-reduction of nitric oxide and carbon monoxide