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Catalysis of C-N Coupling on High-Entropy Alloys

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ABSTRACT

Catalyzing carbon–nitrogen (C-N) coupling using small abundant nitrogenous molecules is of growing interest to lessen the environmental impact of the industrial process. High-entropy alloys hold the potential to have surface sites optimized for each of the coupling intermediates and by varying the alloy composition of the catalyst it provides tunability to the adsorption energy distribution. We model the C-N coupling using adsorption energies of CO and NO and assume that *CO couples with an *NO-reduced intermediate. As more mechanistic insight is needed, we limit the model to the coverage of pairs of *CO and *NO, providing a necessary but not sufficient condition for catalytic activity. Two limiting cases for simulating the adsorption process are presented: one considering thermodynamic equilibrium and one considering out-of-equilibrium conditions. A Monte Carlo method connecting the two limits is suggested which reproduce trends observed in experiments. By varying the partial pressure of NO, the shape of the pair coverage function in the composition space, as well as its optima, are altered. Our method finds a ternary AuCuPd optimum at equal CO/NO partial pressures and copper to be the optimum at low NO partial pressures.

1. Introduction

Molecules containing C-N bonds are vital in pharmaceutical compounds and within agriculture as fertilizers, but the current synthesis methods require harsh conditions with both high temperatures and pressures, which leaves a great negative environmental impact from the chemical manufacturing industry in terms of greenhouse gasses [1-6]. The production of urea, an important fertilizer, is an example of a C-N coupling reaction at an industrial scale that consumes large amounts of energy. Urea is typically produced using the Bosch-Meiser process coupling CO₂ and NH₃, where production of NH₃ by the Haber-Bosch process in itself is an energy intensive process [7,1,8,6]. Furthermore, the hydrogenating agent H2 used in the Haber-Bosch process with N2 for procuring the consumed NH3 is typically produced through steam reforming of CH₄. Both processes are highly emissive [1,8,9]. Therefore, alternative synthesis routes under mild conditions are highly desired. In this regard, electrocatalysis has gained much interest recently as it has been shown that urea can be formed from co-reduction of CO2 and small nitrogenous molecules NO, NO₂, and NO₃ at mild conditions [1,10,2,6]. NO₂ and NO₃ also provides an extra benefit for the environment by the possibility of utilizing NO_2^- and NO_3^- from wastewater [7,10], although we note that NO_3^- itself is valuable as fertilizer.

The field of coupling C-N using electrocatalysis is still in its infancy, and while the seminal work from Shibata et. al. testing CO_2 co-reduction with NO_2^- , and NO_3^- in a GDE setup provides insights into the reaction [11,12,13,14], the coupling mechanism is a debated subject that needs to be determined to aid the design of new catalysts [1,7,2]. Most proposed mechanisms couple CO_2 reduced, and NO_x reduced intermediates. Often *CO with *NO, *N, *NH or *NH₂[7,15,10,16,17,18,19]. *COOH has also been proposed as the reduced carbon coupling intermediate [10,20]. The proposed mechanisms follow a Langmuir-Hinshelwood (LH) mechanism, which is also backed by experimental data as NH₃ and CO_2 /CO has been shown to not yield urea [10], which negates the Eley-Rideal (ER) mechanism. However, *CO reduced to *CCO has been reported to react with NH₃ in an ER mechanism to form acetamide [21]. The proposed mechanisms are summarized in Fig. 1a.

Most proposed mechanisms involving NO_x compounds has *CO and *NO as an intermediate step in the C-N coupling pathway (green paths in Fig. 1a). In CO_2 reduction reaction *CO is a key intermediate [22] and in both NO_2 and NO_3 reduction reactions *NO is a common intermediate [23,24]. Thus, choosing CO and NO as template molecules for C- and N-species, provides a simple model that keeps the key intermediate steps of both reduction pathways. We therefore employ CO and NO as starting reactants as also used in other works modelling

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Research article







Fig. 1. a) Compact scheme of proposed mechanism to form a C-N coupling with green indicating the pathways covered in this work. The proposed mechanisms are obtained from ref. [7,15,10,16,20,21,50,18,51] b) *CO–*NO pair as a necessary condition for C-N coupling from CO/CO₂ and various NO_x molecules to form an array of possible C-N containing compounds. c) Flowchart of the methodology. The black lines symbolize the backbone of the methodology, red indicates the input parameters, and blue the assumptions, which can be altered or removed, and work as rules for the simulation to obtain the number of C-N pairs on the surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the catalytic C-N coupling [16,15].

High-entropy alloys (HEAs) for catalysis is a new field gaining increasing attention and has shown great catalytic performances e.g., in electrocatalysis and can be used as a platform to discover new catalysts for different reactions through machine learning optimization schemes [25,26,27]. HEAs are multi-metallic alloys where the elements are randomly distributed, providing a wide range of unique sites. Thus, HEAs provide a near continuous distribution of adsorption energies depending on the molar composition offering tuneability and sites with potentially optimal catalytic properties [28,29,25,30,31]. The coreduction could be a reaction for which HEAs are well suited due to the difference in adsorption energies of each site, which theoretically could better accommodate the simultaneous adsorption of different species. Thus, the objective is sites accommodating CO₂/CO reduction to *CO next to sites optimal for reduced *NO-intermediates. A strategy also suggested in literature [10,6] and employed by Figueiredo et al. [32] and Sargent et al. [20] on binary CuO_xZnO_y and CuZn. The former found an activity and selectivity dependence on the Cu/Zn ratio with the equimolar being the most selective and active for urea production [32]. Likewise, by the latter, Cu/Zn hybrid catalyst was found to provide greater urea production than their monometallic counterparts [20]. HEAs thus hold the potential to aid in the discovery of suited multi

metallic catalysts for C-N coupling.

The random and heterogeneric nature of the HEA surface makes the modelling a great challenge, even for simpler reactions such as oxygen or carbon dioxide reduction reactions as previously modelled [30,25]. However, having non-scaling adsorption species react on the HEA surface is, to the best of our knowledge, a highly unexplored territory. As each adsorption site and its surrounding environment on a HEA is different, the Langmuir isotherm and microkinetic models cannot be used, as they are based on mean field approximations. The Langmuir adsorption model assumes a homogeneous surface with equal adsorption energies [33,34] and the mean field microkinetic models assume a uniform coverage and site distribution [35,36]. Moreover, Brønsted-Evans-Polanyi (BEP) relations are not reliable on HEAs [37]. In result, the reaction on HEAs becomes complicated with intermediates whose barriers will change by the surrounding composition, calling for much data and a new machine learning based model to predict activation energies in order to determine catalytic activity.

In this work we use *CO and *NO binding energies as template species to model $*CO_x$ and $*N_yO_z$ co-reduction to form C-N bonds. To keep the analysis simple, we study this co-reduction on HEAs as a gas phase reaction with high H₂ pressure and with varying ratios of NO to CO partial pressures while assuming an LH mechanism for the C-N



Fig. 2. Relation of adsorption energies for the same sites and slabs calculated with DFT for a) CO vs. H, b) NO vs. H and c) NO vs. CO. NO and H adsorption energies are obtained using equation S2, and CO adsorption energies by equation S6. The three surrounding hollow sites (*NO or *H) are shown against each *CO energy. The grey dashed lines indicate the $\Delta G_{*ads} = 0$ of the adsorbates. In b) a scaling relation is obtained from a linear fit shown in blue. In c) The horizontal blue line is the intersecting *NO energy between the blue line and the vertical grey line in b). For a) and c) the color coding indicates the metal of the on-top site, which CO is adsorbed to. In b the colors are displayed as the average RGB value of the ensemble constituting the site. Top sites blocked by *H in c) are shown as hollow. The big markers represent the single metals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

coupling. This gas phase reaction model allows for the generalization to other nitrogen and carbon containing reactants as well as to electrochemical setups. Modelling with other reactants can be achieved by altering the chemical potential through the partial pressures of the three gas phase species. For instance, if CO₂ is used as the carbon source instead of CO, the chemical potential of CO is adjusted so that the reaction $CO_2(g) + H_2(g) \Rightarrow CO(g) + H_2O(l)$ is at equilibrium. At CO_2 and H₂ partial pressures of 1 bar, a CO partial pressure $\operatorname{ofp}^{\ominus} e^{-\left(\Delta_{f} G_{CO}^{\ominus} + \Delta_{f} G_{H_{2}O}^{\ominus} - \Delta_{f} G_{CO_{2}}^{\ominus} - \Delta_{f} G_{H_{2}}^{\ominus}\right) / k_{B}T} = 3.2 \times 10^{-4}$ bar is needed. Similarly, in an electrochemical setup at an electrochemical potential of, say, -1.0 V vs. the reversible hydrogen electrode (RHE), the partial pressure of H₂ is adjusted to ensure that the reaction $2(H^+ + e^-) \Rightarrow H_2(g)$ is at equilibrium, which at this potential happens when the H₂ partial pressure assumes a value of tremendous $p^{\ominus}e^{-2eU_{RHE}/k_BT} = 3.4 \times 10^{33}$ bar, a number that reflects the relative ease with which the hydrogen adsorption can be strengthened in an electrochemical setup compared to the gas phase. We note that when limiting the objective to the necessary condition of *CO-*NO neighbor pairs, the reduction pathways towards *CO and *NO from other starting reactants are not accounted for in this work e.g., the oxophilicity of the surface, which is relevant for adsorption of NO₂ and NO₃ as they bind bidentate to the surface through oxygen [38]. Likewise for CO₂, which can have bidentate intermediates which influence product selectivity [39].

At the current stage the system is modelled as a gas-phase reaction, but with the perspective of adding electric potentials to make it electrocatalytic once the mechanism is better understood and thus an optimal operating potential can be determined. The purpose of the proposed model is to provide necessary but not sufficient conditions for catalytic activity of HEAs for a generalized C-N coupling. The subject of C-N coupling is currently of high interest, but still lacks much experimental data and theoretical knowledge.

We propose a minimalistic model to go beyond the Langmuir isotherm and microkinetic mean-field models by simulating the adsorption and counting sites that could facilitate C-N coupling. The model could be expanded to count potential sites for double coupling (N-C-N coupling), as showed in a recent theoretical study on triple-atom catalysts [40]. Instead of mathematical models, we set up a list of rules that the Langmuir adsorption model also follows but allows for circumventing the assumptions of the Langmuir model that does not hold for HEAs. Counting sites provides a necessary, but not sufficient condition for catalytic activity. Consequently, an estimation of the potential for the catalyst being active is obtained, in contrast to an explicit catalytic activity. It is important to note that only catalytic properties of random HEA structures are considered. Synthesizability and stability, although crucial, is outside the scope of this work.

2. Methods

To obtain an approximation to the distribution of adsorption energies of a given molar composition, we employ the workflow [41] summarized in Fig. 1c, where we simulate a 100x100 slab with the according composition. The adsorption energy for each site is predicted for H, NO and CO using a machine learning model trained on adsorption energies calculated with density functional theory (DFT) on (111) terminated HEA slabs of a face-centered cubic (fcc) crystal structure on periodically repeated unit cells sized 3x3x5 atoms. The adsorption energies obtained from DFT are corrected to free energies, as described in detail in section S1 in the Supporting information (SI), by adding zeropoint energies, heat capacities and entropies from ref. [42,43,44] In addition, the NO gas phase electronic energy is applied a functional error correction to its formation energy [45]. As CO adsorption energy on copper is close to $\Delta G_{*CO} = 0$, its accuracy is of great importance. Therefore, the CO adsorption free energies are adjusted in reference to experimental prediction for *CO on Cu obtained from ref. [46] *NO and *H are assumed to only occupy fcc threefold hollow sites and *CO to only occupy on-top sites. The assumptions for *CO and *H are obtained from previous work [30] and *NO in fcc hollow site from literature [47,48]. We note that CO favors adsorption in the fcc hollow site on Pd (1 1 1)[49], but unless the composition is primarily Pd, the amount of threefold Pd sites on a HEA will be negligible. A comparison of adsorption energies is given in section S1. The predictive model for adsorption energies is described in detail in section S2.

An estimation for the net energy distribution for each adsorbate is obtained by filling the surface with the adsorbates while considering a discrete adsorbate-adsorbate interaction where an adsorbate in an fcc hollow site is assumed to block its surrounding on-top sites and vice versa. All other sites are assumed to be non-interacting, implying that coverage dependency of adsorption energies and site preferences are not considered. First, the surface is filled with *H where the free energy is negative. In an electrochemical setup this corresponds to underpotential deposited hydrogen(*H_{UPD}), meaning that *H is adsorbed at positive potential as compared to $\frac{1}{2}H_2 \Rightarrow H^+ + e^-$. For filling the surface with *CO and *NO, two edge cases are studied: The first edge case we will refer to as the equilibrium limit. In this limit it is assumed that the adsorption is in an equilibrium state with the minimum net adsorption energy, corresponding to the reaction rate of the C-N coupling being slower than the adsorption rate. This case is obtained by filling the sites from lowest to highest adsorption energy. In the second edge case, referred to as the dynamic limit, the reaction rate of the coupling is faster than the



Fig. 3. Adsorption energy distribution of CO and NO for a) equimolar quinary composition, b) copper heavy quinary composition and c) equimolar binary composition of Au and Cu. The probability density denotes the probability of finding a specific combination of CO and NO adsorption energies within a specific area of adsorption energies. The dashed lines are the same as in Fig. 2. Sites occupied or blocked by *H has been removed from the distribution, leaving only available sites. The hatched area illustrates the viable energies for co-adsorption with the total probability within the area shown. The points show the DFT adsorption energies of the single metals. On the *CO energy axis the distribution is divided into bands with its position given by the ensemble i.e., the top atom, noted above and width from the ligand effects.

adsorption rate, making the distribution of net adsorption energies controlled by the adsorption dynamics. Adsorbates are picked one at a time with a probability according to their partial pressure, which will adsorb at a randomly picked site if it is free.

The two limits are connected by a Monte-Carlo simulation allowing the adsorbates to occupy blocked sites by desorbing blocking adsorbates with a Boltzmann factor probability given by the change in energy, in the dynamic filling scheme. The two limits are thereby connected by the number of iterations which serves as a unit of time: an infinite number of Monte Carlo steps corresponding to equilibrium, and no steps corresponding to the dynamic limit. The total energy and adsorption rate over time for $Ag_{20}Au_{20}Cu_{20}Pd_{20}Pt_{20}$ and pristine Cu is shown Figure S5. The direct adsorption onto free sites drops towards zero before the system converge to the equilibrium state. Here the adsorption process transitions from being dominated by adsorption directly onto free sites, to adsorption by exchanging blocking adsorbates with the new adsorbate. This is a third case studied, defined as the point in time with no new direct adsorptions for 1000 iterations (for a 100x100 atom surface), i.e. 1000 adsorption attempts.

Modelling the reaction on a HEA is complicated as the transition state energy at each reaction site would be different as with the case of adsorption energies. Moreover, the heterogeneity results in a lack of scaling relations between different adsorption sites (e.g. see Fig. 2), further resulting in no BEP relation [37]. Thus, as we deal with different adsorption sites, we cannot rely on scaling relations. In this work, the reaction process is simplified by assuming an infinitely low reaction barrier for the C-N coupling in a Langmuir-Hinshelwood (LH) mechanism, with the LH mechanism assumed due to being the predominantly proposed mechanism for *CO coupling with *NO_x reduced intermediates [7,15,10,16]. This allows for a simple screening of the HEAs, by only counting the number of *CO-*NO neighbor pairs, with a neighbor pair being defined as a top site *CO with *NO on the next nearest fcc hollow site as illustrated in the final box of Fig. 1c. The number of pairs will be normalized to a coverage with the maximum coverage being 0.75 (Figure S6). The three methods of filling the surface give consistently precise results, i.e. similar variance, for a 100×100 surface (Figure S7). For simplicity, no interaction between the *CO and *NO is included in the current model. A study found the change in adsorption energy of *CO from dipolar effects with neighboring *NO in fcc to be 0.19 eV on Pt(1 1 1) at 1/2 ML coverage versus an empty fcc site [52]. Not including these effect results in an overestimate of pair coverage.

We introduce relative pressures between CO and NO in order to change the chemical potential as *NO binds stronger than *CO on pure elements [15]. Varying the chemical potential simultaneously provides a means to simulate other NO_x species. By ignoring the reaction barriers and only counting adsorption pairs, an estimate of which HEA has the potential to be catalytically active is obtained, rather than estimating the actual catalytic activity, as the requirement that the adsorbates meet on the surface is only a necessary condition and not necessarily a sufficient one. For the model presented in this work to be general it rests on this assumption that CO/CO2 and various NOx molecules which can be modelled through varying the chemical potential, must go through the *CO-*NO pair in the process of forming C-N coupling for a variety of C-N containing products as illustrated by Fig. 1b. Moreover, without barriers the assumptions imply that when *NO is paired with *CO it will undergo C-N coupling, while all unpaired *NO will form NH₃ instead in an NO reduction reaction (NORR). Likewise, when considering an electrochemical setup where H⁺ in solution is the hydrogen source, all adsorbed H is assumed to form H₂ by the hydrogen evolution reaction (HER). Rather than constructing a mathematical law, predictions are made by simulating the adsorption according to the set of rules and assumptions, which can then be changed upon falsification and new information.

3. Results and discussion

The DFT calculated adsorption energies of each adsorption species within each site are plotted against each other in Fig. 2. *CO is adsorbed on-top, while *NO and *H are in the threefold fcc hollow sites. As the adsorption sites are not the same for CO and both H and NO, the adsorption energies of H and NO in the three surrounding fcc hollow sites containing the on-top site atom in its ensemble are shown against the CO adsorption energy in Fig. 2a and 2c, respectively. During the energy relaxation, mainly for NO and H, several cases of adsorbate changing site away from an fcc hollow site was identified. Only data with the adsorbate in fcc hollow sites are kept and in Fig. 2b, only sites occupied by both *NO and *H are used. The grey dashed lines show the zero Gibbs free energy of the respective adsorbate, meaning adsorption is only favorable at electronic adsorption energies below these lines. In Fig. 2a, showing CO vs. H adsorption energies, there is a correlation, but not a scaling relation.

On the HEAs, an estimate of the on-top site adsorption energy cannot be made from the hollow site, or vice versa. However, in Fig. 2b, where the adsorbates occupy the exact same site, there is a clear linear scaling,



Fig. 4. a, b) Distributions of adsorbed Gibbs free energies by filling the equimolar surface by a) the equilibrium method and b) the dynamic method. The gross energy distributions before filling the surface with *H and mutual blocking are shown as unfilled histograms and the resulting net energy distributions after filling as filled histograms. c, d) Adsorption energies of the obtained *CO-*NO pairs after filling the surface with c) the equilibrium method and d) the dynamic method displayed on the adsorption energy distributions from Fig. 3a.

obtained with linear regression, shown with the blue dashed line. The intersection of this line with the vertical grey line at $\Delta G_{*H} = 0$ represents the *NO energy at which H can adsorb and is shown with the blue line in Fig. 2c, where the energies of *NO is plotted against the *CO energies. This blue line represents the equilibrium adsorption energy between $\frac{1}{2}$ H₂ and *H at 1 bar partial H₂ partial pressure, or between H⁺ + e⁻ and *H at 0 V vs. RHE. Thus, in an electrochemical setup it is favorable to have *NO energies above this line to prevent the competitive HER.

In Wan et al. [15] this methodology was employed to define an area for which C-N coupling through *CO and *NO is favorable to form urea. However, since there is no scaling relation between *CO and *H, this method is not directly suited for HEAs. Instead, the *CO sites that have a neighbor fcc site in which H can adsorb, meaning it is to the left of the vertical line in Fig. 2a, are shown in Fig. 2c as unfilled markers. Thus, from Fig. 2c, to form C-N coupling, under the assumption that *CO and *NO are required on the surface, the desired sites have energies below the grey lines, above the blue line and are shown as filled markers, which are more likely for weaker CO adsorption. From this it is evident, that sites favoring C-N coupling, are most easily attained if the ensemble sites contain Cu.

From simulating a 100×100 surface with a given composition and predicting the adsorption energy of each site, adsorption energy distributions, shown in Fig. 3 are obtained. The adsorption energy of sites that are either occupied or blocked by *H are left out. The probability densities of three compositions are displayed with the equimolar quinary composition (Ag₂₀Au₂₀Cu₂₀Pd₂₀Pt₂₀) in Fig. 3a, a copper rich composition (Ag₁₀Au₁₀Cu₆₀Pd₁₀Pt₁₀) in Fig. 3b, and equimolar binary AuCu in Fig. 3c. The lines from Fig. 2c are plotted along with the distributions. From Fig. 3a, it is evident that from slightly below the blue line, all sites are blocked by *H. Likewise, the stronger the CO adsorption the less likely it is to find non-blocked sites. By integrating the probability density over the area below the $\Delta G_{*ads} = 0$ lines, the probability of adsorbing CO and NO simultaneously is obtained. Varying the composition causes the energy distributions to change which consequentially changes the probability. From Fig. 3a to 3b, the percentage of copper is increased, increasing the density in the copper *CO energy band, and heavily decreasing the density in the platinum band. As the Cu density is increased and the more likely to be blocked Pt and Pd densities are decreased along with the unfavorably adsorbing Ag and Au, the probability for simultaneous CO and NO adsorption is increased. For Au₅₀Cu₅₀ in Fig. 3c, the probability is increased even further as there are no sites blocked by hydrogen. The largest probability would be obtained for pure Cu, but it is important to note gold's ability to weaken the adsorption energy of NO relative to pristine Cu. This leaves many sites in the top-right corner of the hatched area, where the catalytic activity would presumably be greatest, as was also found by Wan et al. [15], who made a model for the activity on pure metals. (Ag/Au)Cu binary or possibly a AgAuCu ternary alloy could therefore be a potential candidate for a good catalyst for C-N coupling. An AuCu binary alloy was also suggested by Wan et al. [15] Adsorption energy distributions for AgCu, AgAuCu and AgAuCuPd alloys are displayed in Figure S8. AgCu, AuCu and AgAuCu, are similar in pattern but their distributions and probabilities vary. E.g., AgCu exhibits the highest probability, but is narrower and further from the ΔG_{*ads} lines than AuCu and AgAuCu.

Fig. 4 displays the result of the two edge case models, an equilibrium model and an out-of-equilibrium model, using the adsorption energies from 3a. Fig. 4a and 4b show the distribution of all simulated adsorption free energies on the 100×100 surface and at which energies *CO and *NO occupy. *H was assumed to be present in excess and therefore occupies or blocks adsorption on the most strongly adsorbing sites. A



Fig. 5. Contour maps of *CO–*NO pair coverage for 5 at% grids of the Ag-Au-Cu-Pd composition space shown as pseudo-ternary with Ag and Au combined. Each point with a multiplicity of AgAu combinations shows the highest pair coverage. a, b) displays the equilibrium limit, c, d) the dynamic limit and e, f) the MC model. Each at NO pressures of 1 and 0.1, respectively, and all with CO pressure of 1.

Table 1The best composition in the full quinary composition space found with Bayesianoptimization for each surface filling method at different NO pressures (P_{NO}) andCO pressure of 1.

	P_{NO}	Composition	pair coverage
Equilibrium	1	Ag ₆₁ Cu ₂₆ Pd ₁₄	0.1814
	0.5	Ag54Au6Cu26Pd14	0.1841
	0.1	Ag ₅₄ Au ₁ Cu ₂₉ Pd ₁₅	0.1871
	1	Cu	0.3306
Dynamic	0.5	Ag ₃₃ Cu ₆₇	0.2976
	0.1	Ag ₆₂ Cu ₃₈	0.1989
МС	1	Au59Cu22Pd19	0.1397
	0.5	Ag ₆ Au ₄₈ Cu ₃₁ Pd ₁₅	0.1624
	0.1	Cu	0.2830

notable difference in the distributions, is that CO is adsorbed at higher adsorption energies in the dynamic case, Fig. 4b and 4d, compared to the equilibrium case, Fig. 4a and 4c, resulting in more *CO–*NO pairs close to $\Delta G_{*CO} = 0$ in the dynamic method. The difference between the two methods: The equilibrium limit favors lower energies and will occupy those sites first, concentrating the pairs on the Pt and Pd bands, whereas the dynamic limit picks the adsorbing sites randomly and therefore favors pairs where the combined probability density between the two adsorption energy distributions is greater, which in this case is the Cu band. In the presented case, the number of pairs do not vary much, but rather their energy distributions, which would likely influence the catalytic activity if energetic barriers were included in the analysis.

The number of *CO–*NO pairs, presented as a coverage, for the dynamic and equilibrium limits for all ternary compositions in a 5 atomic percent (at%) grid for $P_{NO} = 1$, 0.5 and 0.1 is compared in Figure S9 and S10, where the pair coverage is plotted as a function of the composition space. In Fig. 5 the composition space for Ag-Au-Cu-Pd is shown for $P_{NO} = 1$ and 0.1 in a pseudo-ternary plot which combines Ag and Au into one component. In the equilibrium limit, Fig. 5a and 5b, the

best compositions are ternary and quaternary compositions, which are also found to be the global optimum in the composition space for the equilibrium limit using Bayesian optimization (Table 1). The methodology for Bayesian Optimization is described in an earlier paper [26]. The difference in pressure has little influence on the overall shape of the composition space as well as the optimum (when combining Ag and Au). It does however change the number of pairs towards the CuPd binary, with more pairs at lower pressure. Notably, pure Cu has zero pairs due to the surface being filled with *NO, the strongest binding adsorbate. In contrast, in the dynamic limit Cu has the highest number of pairs at high NO pressure, 5c. At lower NO pressure, 5d, the optimum is moved along the AgCu binary line (Table 1) and the shape towards resembling the equilibrium limit, with a high similarity to Fig. 5a.

These edge cases fail to follow trends found in literature, both theoretical and experimental. Firstly, Cu should show potential as a catalyst for the CO-NO co-reduction [15], but in the low energy limit, the equilibrium limit, all pure metals will have zero pairs as there will only be one energy for each adsorbate as there is assumed no interaction between sites. Thus, by this method under the current assumptions, the surface will be covered by the adsorption species with the lowest energy. Secondly, lowering the chemical potential of NO_x relative to CO/CO_2 e. g. by lowering pressure of NO or concentration of NO_2^- has shown to promote urea formation i.e. C-N coupling [15,53]. However, we also note that Shibata et al. found increasing concentration of NO_x species yielded a higher Faraday efficiency towards urea, although at a higher KHCO3 concentration [11,12,13,14]. Moreover, most experimental results reported uses lower concentration of the nitrogen source relative to the carbon source in the electrolyte [10]. Thus, Cu is expected to become a better catalyst at lower NO pressure, but the dynamic limit follows the reverse trend. Generally, for the dynamic method, equal pressure will be most favorable for creating as many *CO-*NO-pairs because each adsorbate is picked with equal likeliness, which is more likely a feature of the model than a natural description.

The pair coverage of all ternary composition spaces using the Monte

Table 2

Compositions with the highest selectivity found with Bayesian Optimization for $P_{NO} = 1$ and 0.1 in the full quinary composition space.

P _{NO}	Composition	C-N selectivity
1	Ag ₁₄ Au ₅₃ Cu ₁₉ Pd ₁₄	0.2165
0.1	Au ₂₄ Cu ₇₆	0.7938

Carlo (MC) method of filling the surface are displayed in Figure S11. In Fig. 5e and 5f, the pair coverage as function of the Ag-Au-Cu-Pd composition space obtained with the MC method. Here at equal partial pressures, Fig. 5e, the function is similar to the equilibrium limit in Fig. 5a. Meanwhile at low NO pressure, Fig. 5f, the function share similarity with the dynamic limit in Fig. 5c. In this model, the optima can be shifted by pressure like in the dynamic limit, but the optimum is not necessarily at equal CO and NO pressure. Furthermore, by lowering the pressure of NO, the optimum is now obtained to be Cu (Table 1). Thus, this model captures the aforementioned trends that the limit cases do not. By the chosen stopping criteria, of no direct adsorption, the system is captured in a state out of equilibrium, but not as far from equilibrium as the dynamic model, while also being influenced by change in relative pressure of the reactants.

In an interest to compare C-N coupling selectivity with competing reactions we use a counting scheme. Given that counting the CO-NO pairs provides the activity for the C-N coupling, further counting *H leads to H₂ (HER), and counting unpaired *NO the activity towards NH₃ (NORR). This allows us to setup a selectivity metric to optimize. The selectivity towards C-N coupling is then obtained by counting *NO that are a part of a pair versus the total number of sites producing a product (H₂, NH₃ and C-N coupling). Compositions with the highest selectivity found with Bayesian Optimization is listed in Table 2. The best selectivity found is the binary Au₂₄Cu₇₆ alloy.

In Fig. 6 the selectivity is shown for the Au-Cu-Pd composition space for $P_{NO} = 1$ (top) and 0.1 (bottom). The *H coverage is shown to the left in Fig. 6a and is independent of NO pressures and therefore the same for

both NO pressures. Increased *H coverage directly favors HER and should therefore be limited in an electrochemical setup. As only Pd adsorbs H, the coverage increases with the amount of Pd. The NO coverage panel shows the *NO reducing to NH₃ on the left (Fig. 6b and 6c) and *NO coupling with *CO on the right (Fig. 6d and 6e). The coverages of *NO forming C-N coupling are expectedly very similar to the pair coverages (Fig. 5e and 5f) as only the counting methods have changed such that here each *NO cannot be counted more than once. The resulting selectivities are displayed in the right panel in Fig. 6f and 6 g. At equal pressures (Fig. 6b) the NH₃ coverage increases towards Cu as NO does not bind to Au and H binds to Pd instead of NO while the coupled *NO coverage decreases, leaving a ternary composition as a relatively weak optimum in selectivity for this composition space, displayed in Fig. 6f, with comparable shape to the pair coverage in Fig. 5e. For lower pressure ($P_{NO} = 0.1$) un-coupled *NO coverage decreases while coupled *NO increases towards Cu, resulting in an increase in C-N coupling selectivity, shown in Fig. 6g. The shape of the C-N selectivity composition space is again similar to the pair coverages in Fig. 5e and 5f. In Figure S12 the number of pairs are plotted against the selectivity for each composition in 5 atm.% in the Au-Cu-Pd composition space. It shows a clear correlation with the selectivity setting an upper limit in a log-function shape for the number of pairs.

4. Conclusion

Using the machine learning model to predict sites for slabs of different compositions provides distributions of adsorption energies for different sites of *H, *CO and *NO. Changing the composition changes the distribution allowing for tunability towards a favorable distribution. From a qualitative analysis of the energy distributions, binary alloys of copper with silver or gold, (Ag/Au)Cu alloys, are suggested as possible candidates due to silver and gold's ability to weaken the adsorption energy of copper. By defining sets of rules, we can simulate the adsorption of CO and NO onto high-entropy alloy surfaces. First, two edge cases are defined: One controlled by minimum energy, the other by



Fig. 6. H and NO coverages and conversion ratio for C-N coupling within the Au-Cu-Pd subspace obtained using the MC model. Top shows $P_{NO} = 1$ and $P_{NO} = 0.1$ at the bottom (H is independent of NO pressure). a) displays the coverage of H as number of *H per surface atom, corresponding to a selectivity for HER. In the middle panel the NO coverage is divided into b, c) *NO not paired with a *CO showing selectivity towards NH₃ and d, e) paired *NO showing selectivity towards the C-N coupling. In the right panel f, g) the coverages are combined in a conversion ratio towards C-N coupling against the competing HER and NORR. For all color scales, yellow indicates the optimum in terms of the desired selectivity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the relative pressures. These two edge cases can be connected by a Monte Carlo simulation. Stopping the simulation before equilibrium provides results that align better with the trends in the current literature as well as avoiding obvious limitations in each of the two edge case methods. By counting sites, we go beyond the mean-field Langmuir adsorption model, which does not hold for a high-entropy alloy surface and obtains a necessary but not sufficient condition for the catalytic activity of C-N coupling through a Langmuir-Hinshelwood mechanism. In this quantitative analysis, the results point to pure copper with lower pressure of NO as the catalyst providing most coupling sites. However, extrapolating the site counting method to selectivity, an AuCu alloy, more precisely Au₂₄Cu₇₆, emerges as the most selective towards C-N coupling at low NO pressure relative to CO pressure.

To further develop the model, greater mechanistic insights are needed before further complicating this model with transition state activation energies, to obtain a catalytic activity. The model at its current state provides some general insights into C-N coupling on highentropy alloys by predicting possible suitable catalysts from the set of rules and assumptions presented in the methodology in Fig. 1c.

CRediT authorship contribution statement

Mads K. Plenge: . Jack K. Pedersen: . Alexander Bagger: . Jan Rossmeisl: Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2024.115322.

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