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Thermodynamic Considerations for Optimizing Selective CO_2 Reduction by Molecular Catalysts

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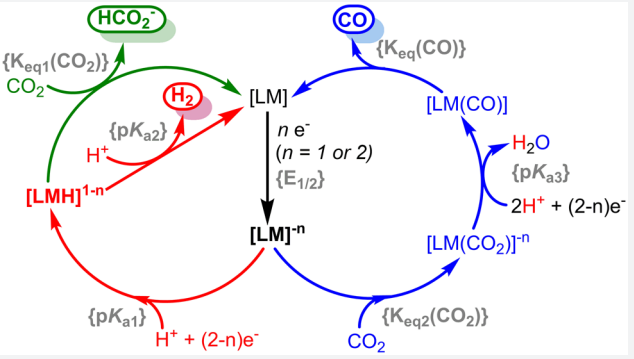
Supporting Information

ABSTRACT: Energetically efficient electrocatalysts with high product selectivity are desirable targets for sustainable chemical fuel generation using renewable electricity. Recycling CO_2 by reduction to more energy dense products would support a carbon-neutral cycle that mitigates the intermittency of renewable energy sources. Conversion of CO_2 to more saturated products typically requires proton equivalents. Complications with product selectivity stem from competitive reactions between H^+ or CO_2 at shared intermediates. We describe generalized catalytic cycles for H_2, CO, and HCO_2^- formation that are commonly proposed in inorganic molecular catalysts. Thermodynamic considerations and trends for the reactions of H^+ or CO_2 at key intermediates are outlined. A quantitative understanding of intermediate catalytic steps is key to designing systems that display high selectivity while promoting energetically efficient catalysis by minimizing the overall energy landscape. For CO_2 reduction to CO, we describe how an enzymatic active site motif facilitates efficient and selective catalysis and highlight relevant examples from synthetic systems.



The electrocatalytic reduction of CO_2 is a direct route to sustainable fuel production from renewable electricity.[1−3] Although protons are required to convert CO_2 to chemical fuels, direct proton reduction to H_2 siphons electrons away from CO_2 reduction, decreasing the Faradaic yield of carbon-containing products.[4,5]

Nonselective reduction is commonly the result of the competitive reactions with either H^+ or CO_2 at key intermediates that ultimately lead to divergent pathways and products (Scheme 1). Some of the earliest work investigating the mechanism of molecular electrocatalysts for CO_2 reduction suggested differential reactivity at common intermediates.[6] Additional studies quantified the relative reactivity of H^+ and CO_2 at these proposed electrocatalytic intermediates.[7−16] With the resurgence of interest in CO_2 reduction over the past decade, new mechanistic studies and catalysts have generated fresh insights into the varying factors that contribute to product selectivity.[3,17−29]

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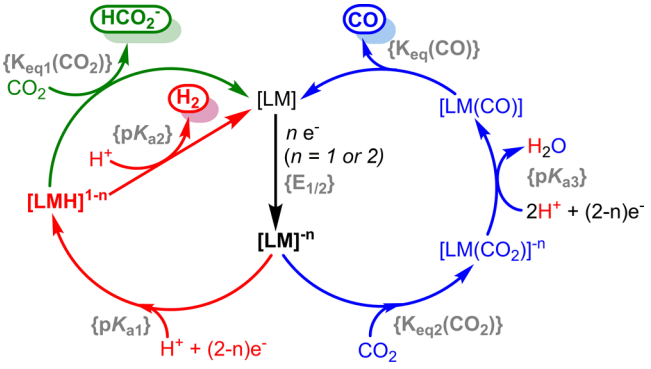
Scheme 1



Our analysis is focused on the thermodynamic considerations for key steps in the most commonly proposed catalytic cycles for the hydrogen evolution reaction (HER) and carbon dioxide reduction reaction (CO_2RR) to formate (HCO_2^-) and carbon monoxide (CO) by inorganic molecular electrocatalysts. Our evaluation includes general trends in catalyst properties and their broad impact on reactivity. We examine free energy considerations for the reaction of H^+ and CO_2 with proposed catalyst intermediates and the potential barriers for product release. These considerations provide guidelines for

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achieving selectivity at divergent reaction paths and are also essential for improving catalytic activity. Although our discussion is not focused on kinetic considerations, we note that intermediate steps in catalysis with high or low free energies intrinsically contribute to kinetic barriers in addition to the overall energetic efficiency (expressed in the overpotential). Thus, a quantitative understanding of the free energy contributions of each step is necessary to flatten the energy landscape and optimize activity.

We note that our analysis utilizes reported catalysts as examples but is not intended to be a complete description of the field. Instead, we refer the reader to more comprehensive reviews of molecular electrocatalysts for CO_2 reduction that have recently been published.[30−32]

Overall Reaction Scheme. A generalized scheme for the catalytic reduction of H^+ and CO_2 to H_2, HCO_2^-, and CO is shown in Scheme 1. Although other catalytic routes are possible, Scheme 1 represents the most frequently cited mechanisms. Upon electron transfer at a certain redox potential $\{E_{1/2}\}$, the reduced intermediate can either protonate to form a metal hydride or directly activate CO_2. In the *protonation-first pathway* (red), a metal hydride is formed which can react either with a second proton to form H_2, or with CO_2 to produce formate (green). Conversely, CO is typically the product in a *CO_2-activation-first pathway* (blue). Each of these possibilities will be described separately.

Metal Hydride Formation. The *protonation-first pathway* requires the ability to form a stable metal hydride upon protonation. The free energy of protonation is the difference in pK_a between the proton acceptor ($\{pK_{a1}\}$, or that of the targeted

$$\Delta G = -2.303RT(pK_{a(ext)} - pK_{a1}) \quad (1)$$

metal hydride intermediate) and proton donor ($\{pK_{a(ext)}\}$, or external acid source) as expressed in eq 1. We intuitively expect more electron-rich metal centers to have more negative reduction potentials and be more Brønsted basic (higher metal hydride pK_a values).

The measured pK_a values of metal hydrides with reported reduction potentials $\{E_{1/2}\}$ in acetonitrile are plotted in Figure 1.[33−53] The series represents a broad span of metal hydrides in different ligand environments (see Tables S1−S3 in the Supporting Information). Following the expected trend, more reducing metal centers are also stronger Brønsted bases. Since pK_a is a metric of heterolytic M−H bond free energy, Figure 1 also depicts the linear free energy relationship between redox potential and the bond dissociation free energy of the M−H bond.

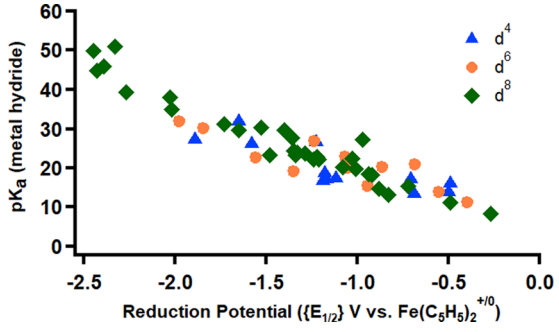

Figure 1. pK_a values of metal hydrides plotted versus the reduction potential required to access their conjugate bases. Blue triangles, orange circles, and green diamonds represent d^4, d^6, and d^8 metal hydrides, respectively. Compiled from refs 33−53.

R. H. Morris recently reported a valuable empirical model for calculating metal hydride pK_a values based on ligand acidity constants.[54,55] A review also compiled experimentally measured and calculated pK_a values for a broad range of metal hydrides (as well as dihydrogen complexes).[56] Additionally, he notes that since M−H bond dissociation free energies are typically ∼60 kcal/mol,[33−37,57,58] the pK_a values of metal hydrides are expected to correlate with the redox potential of the conjugate base as seen in Figure 1.[54]

H_2/HCO_2^- Formation. Upon metal hydride formation, it can react with either another proton or CO_2. M. R. Dubois and D. L. Dubois first described how the free energy for the reactions of a metal hydride with H^+ or CO_2 at a metal hydride is determined by the hydricity (ΔG_{H^-}, eq 2) of the metal hydride.[59,60] The hydricity is dependent on the two-electron reduction potential and pK_a of the transition metal hydride along with the reduction potential for H^+/H^- in the respective solvent.[48,61,62] As a result, hydricity values correlate with the average two-electron reduction potential of the metal (Figure S1).

The free energy for protonation of a metal hydride to evolve H_2 ($\Delta G(H_2)$) is shown in eq 3; it is dependent on its hydricity (ΔG_{H^-}), the pK_a of the external proton donor, and the heterolytic cleavage energy of H_2 (C_{H2}, a solvent-dependent constant). The free energy to reduce CO_2 to formate (eq 4) is dependent on the hydricity of the metal hydride "donor" (ΔG_{H^-}) and the hydricity of formate ($\Delta G_{H^-}(HCO_2^-)$), the "acceptor". The free energy of hydride transfer ($\Delta G(HCO_2^-)$) relates directly to $\{K_{eq1}(CO_2)\}$ in Scheme 1. Several recent perspectives have discussed these relationships in depth.[61−63]

The pK_{a2} in Scheme 1 delineates the proton activity in which $\Delta G(H_2)$ is close to zero, or ergoneutral. Using external acids with a lower pK_a than pK_{a2} will result in H_2 evolution

$$[MH]^n \rightarrow [M]^{n+1} + H^-$$
$$\Delta G_{H^-}\ (\text{hydricity}) \quad (2)$$

$$[MH]^n + H^+ \rightarrow [M]^{n+1} + H_2$$
$$\Delta G(H_2) = \Delta G_{H^-} - 2.303RT(\log[H^+]) - C_{H_2} \quad (3)$$

$$[MH]^n + CO_2 \rightarrow [M]^{n+1} + HCO_2^-$$
$$\Delta G(HCO_2^-) = \Delta G_{H^-} - \Delta G_{H^-}(HCO_2^-) \quad (4)$$

whereas the metal hydride will be stable to protonation with acids of a higher pK_a.[64−66] Since minimization of free energy leads to efficient catalysis, eq 3 was applied to optimize a class of catalysts for H_2 evolution.[67] A characteristic of a catalyst with a flattened energetic landscape is reversible reactivity (i.e., hydrogen evolution and oxidation), which was also illustrated in this class.[68−70]

An interesting aspect of eqs 3 and 4 is that the free energy of protonation of a metal hydride is dependent on the pK_a of the proton donor, while the reaction with CO_2 is not. As a result, there are conditions in which the reaction of a metal hydride with CO_2 is exergonic while protonation to form H_2 is endergonic. In these cases, if the pK_a of the proton donor is sufficiently low enough to form the metal hydride, selective CO_2 reduction can be accessed via thermodynamic consid-

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erations alone. These conditions exist because CO_2 reduction to formate is a $1H^+$, $2e^-$ process above the pK_a of formic acid, while H^+ reduction to H_2 is a $2H^+$, $2e^-$ process across all pK_a values. As a result, the thermodynamic potential for each reaction has a differential dependence on proton activity. We recently published a more detailed description on this topic.[64]

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We also note the thermodynamic values in eqs 2 and 4 are solvent-dependent, but do not quantitatively change to the same magnitude in different solvents.[41,61,71−76] For example, while the hydricity for metal hydrides and formate decreases from organic solvents to water (or become better donors), formate's hydricity decreases to a lesser extent. As a result, some metal hydrides that are insufficiently hydridic to reduce CO_2 in organic solvents will do so in water.[71,72,77]

In accordance to the Sabatier principle, the interactions between the catalyst and substrate/product are also important. A significant interaction between the catalyst resting state and formate would make a favorable (negative) contribution to the free energy in eq 4, permitting CO_2 reduction with weaker hydride donors. However, the interaction will also inhibit product release and catalyst turnover. Most putative hydride intermediates in successful CO_2 reduction catalysts are composed of electron-rich mid or late transition metals[18,26,64,78−81] which only weakly bind formate, so product release is not rate-limiting.

CO Production. The *CO_2-activation-first pathway* (blue in Scheme 1) requires CO_2 activation to outcompete protonation at the reduced metal center. While very little quantitative data exists on CO_2 binding constants $\{K_{eq2}(CO_2)\}$ at reduced metal centers, a small but instructive data set exists for Co(I) tetraaminemacrocycles.[82] In the absence of ligand steric effects, $\log\{K_{eq2}(CO_2)\}$ correlates with the Co(II/I) redox potential (Figure 2).[82−84] The relationship is also intuitive, where more electron-rich (reducing) metal centers activate CO_2 more strongly. In fact, no single transition metal site is known to react with CO_2 at potentials positive of −1.2 V vs $Fe(C_5H_5)_2^{+/0}$ in organic solvents.[30−32]

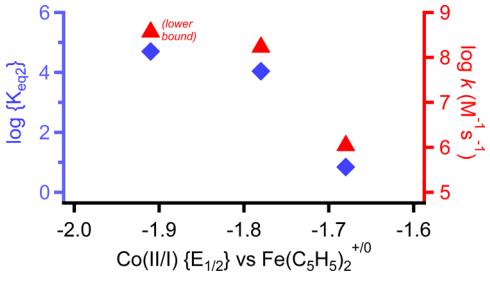


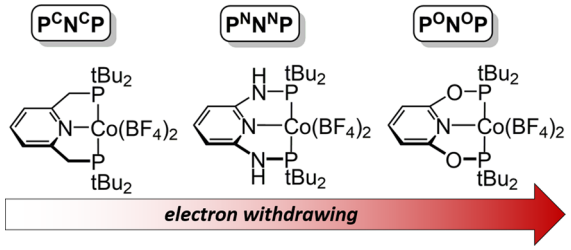
Figure 2. Relationship between $\{E_{1/2}\}$ of Co(I) macrocyclic complexes and thermodynamic ($\log\{K_{eq2}\}$) and kinetic ($\log k$) reactivity with CO_2. Data from ref 82.

The negative potentials required to activate CO_2 have several undesirable side effects for overall catalyst selectivity, efficiency, and rate. As illustrated in Figure 1, more reducing metal sites are also more Brønsted basic (with the caveat that protonation to form a metal hydride requires two-electron oxidation of the complex, which is not always accessible). Thus, more reducing metal centers favor both the *CO_2-activation-first* and the *protonation-first pathways*.

Another complicating factor is that in organic solvents the product, CO, is often a better ligand than CO_2. Thus, increasing the electron density of the metal for CO_2 activation often results in a more stable M−CO complex later in the catalytic cycle, inhibiting turnover. CO release has been shown to be rate-limiting in several known catalysts.[84−88] (We note that this is not always the case; an earlier study found CO_2 and CO equilibrium binding constants to cobalt macrocycles were competitive in water.)[14]

As a result, catalyst design for optimal CO_2 reduction to CO requires an intimate understanding of how CO_2, CO, and H^+ interact with reduced metal centers. The importance of these parameters was delineated by Schneider, Fujita, and coworkers in 2012 based on their experimental work with cobalt macrocycles.[82,84,87] Their analysis inspired our study on a series of isostructural cobalt pincer complexes, the results of which are summarized in Table 1.[89] Cobalt complexes with

Table 1. Interaction of CO_2, CO, and H^+ for an Isostructural Series of Cobalt Pincer Complexes (Data from Ref 89)



L	P^CN^CP	P^NN^NP	P^ON^OP
$E_{1/2}$, LCo(II/I)[a]	−1.03 V	−0.88 V	−0.61 V
$k[CO_2]$ (s^{-1}), [LCo][b]	10^{2-3}	10^{2-3}	no reaction
$[LCo(CO)]^+$, ν (cm^{-1})	1911	1923	1936
pK_a,[c] [LCo]	28		32

[a]vs $Fe(C_5H_5)_2^{+/0}$ in CH_3CN. [b]Reactivity with CO_2 occurs upon reduction of the Co(I) complex, which is electrochemically irreversible. $E_{1/2}$ for the reversible Co(II/I) couple is provided to illustrate the electronic trend. [c]Calculated for corresponding protonated complex.

more electron-donating ligands result in more negative reduction potentials and greater reactivity toward CO_2 (see Table 1). We were unable to obtain accurate rate constants, but the overall trend is similar to that observed in the cobalt macrocycles (Figure 2). The Co−(CO) bond strength, measured by the vibrational stretch (ν) of the CO bond by infrared spectroscopy, also increased with decreasing reduction potential.

The free energy relationships for metals and their association with CO_2, CO, and H^+ are comparable to scaling relationships more commonly used for analyzing heterogeneous catalysts. In this case, we find the general trends that relate redox potential with reactivity for the three key substrates follow opposing

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directions for catalyst optimization. Similar trends were also described for heterogeneous electrocatalysts.[90]

A generalized energy landscape for a single-site activation of CO_2 to CO is depicted in black in Figure 3. A strongly

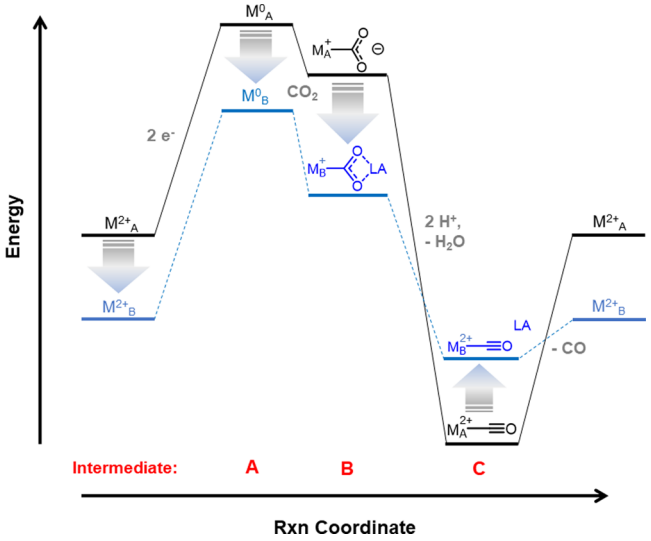

Figure 3. Free energy landscape for a single-site catalyst for CO_2 reduction to CO (black) and a catalyst that utilizes a cooperative interaction (blue) to stabilize the metal carboxylate intermediate B.

reducing (and thus higher energy) metal site (intermediate A) is utilized to activate the electrophilic carbon in CO_2. CO_2 can bind to metals in a few different orientations. The η^1 coordination is unstable in synthetic transition metal complexes[91,92] (although if there is another vacant coordination site, it can bind η^2).[93−96] The highly nucleophilic oxygen atoms on unstable metal carboxylates (intermediate B) can promote ligand decomposition[97] or disproportionation with another equivalent of CO_2 to give CO and CO_3^{2-}.[20,98−103] A characteristic of an unstable metal carboxylate is extreme Brønsted basicity (high $\{pK_{a3}\}$), which has been observed in some catalytic systems that scavenge protons from adventitious water or electrolyte.[104−107] If protonation and reduction of the metal carboxylate (intermediate B) is successful in cleaving a C−O bond, more electron-rich metals will result in a greater energetic barrier for CO release (intermediate C).

Given these factors, it is clear that activation of CO_2 at more positive potentials confers several benefits. In addition to catalysis at a milder potential, it inhibits the *protonation-first pathway* by lowering the Brønsted basicity of the metal while favoring product release.

Perhaps it is not surprising that a strategy for activating CO_2 at mild potentials can be found in nature, where efficient redox catalysis for energy transduction is a matter of survival. The electrocatalytic activity of Ni-CODH I, a carbon monoxide dehydrogenase of the anaerobic *Carboxydothermus hydrogenoformans* (*Ch*), displays reversible electrocatalysis of CO_2 to CO at high rates at the thermodynamic potential (no overpotential), or −520 mV vs SHE at pH 7.[108] The X-ray crystallographic structure of the enzyme under reducing conditions in the presence of CO_2 suggests cooperative binding by Ni and Fe, shown in Figure 4.[109] Electrophilic activation of CO_2 occurs at the redox active and Lewis basic reduced Ni^0, while the adjacent Fe^{2+} participates in nonredox substrate activation. Thus, the active site capitalizes on a

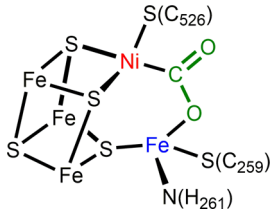

Figure 4. Active site of reduced *Ch* Ni-CODH II in the presence of CO_2 characterized by X-ray crystallography (adapted from ref 109).

secondary interaction to cooperatively bind CO_2 instead of a single metal site, contributing to its high rate and low overpotential.[32,109−111]

An energetic analysis of a cooperative CO_2 activation mechanism is shown in blue in Figure 3. Cooperative activation stabilizes the carboxylate intermediate, making a favorable free energy contribution to CO_2 activation. This results in reactivity at more positive potentials, which also destabilizes the subsequent metal carbonyl product, facilitating product release. Not represented in Figure 3 is the *protonation-first pathway*, but we would expect it to be less favorable as the Brønsted basicity of the reduced metal decreases, contributing to enhanced selectivity.

There is evidence that several synthetic catalysts cooperatively activate CO_2, which benefits their rate and/or selectivity. Bimetallic activation of CO_2 is proposed in a synthetic dipalladium system.[30] Single-site palladium complexes with a triphosphine ligand display a linear free energy relationship (LFER) between $K_{eq}(CO_2)$ and redox potential.[67] Addition of a hydrogen-bonding interaction or a second metal disrupted the LFER, leading to faster catalytic CO_2 reduction at a milder potential. Optimization of the cooperative interaction increased the rate of CO_2 to CO catalysis by 3 orders of magnitude compared to the monomer while lowering the overpotential almost 200 mV.[59,112−115] Additionally, the Faradaic efficiency improved from 10:90 CO:H_2 to 85:15 CO:H_2 upon introduction of the second metal center.[113,115]

However, the two symmetric homobimetallic sites have similar reduction potentials, which results in unproductive metal−metal bond formation, deactivating the catalyst. By using two different metals, the [NiFe] center of *Ch* Ni-CODH, promotes selective redox chemistry at the Ni site. Several other synthetic transition metal CO_2 reduction catalysts have shown substantial evidence for bimetallic CO_2 activation.[86,97,116−124] A dicobalt carboxylate complex was also structurally characterized from a cobalt macrocyclic catalyst.[125] We note several heterobimetallic systems utilize strong oxophilic Lewis acids to activate CO_2;[116,126] in some cases, the latter can bind the oxygen too tightly for catalyst turnover.

Other successful catalysts attribute improved activity to other types of cooperative CO_2 activation. Early mechanistic and computational studies for the catalysts $[Ni(cyclam)]^+$ and cobalt macrocycles indicate the importance of the protons on the macrocycle amines for facilitating CO_2 binding.[9,127] Savéant and co-workers have also shown that the incorporation of phenol moieties in the secondary coordination sphere of a previously investigated iron porphyrin complex results in a 50-fold rate increase at an overpotential 360 mV lower than the corresponding anisole substituted system.[128] Most recently, Dey and co-workers reported a low overpotential electrocatalyst which incorporates a proposed S−H functionality appropriately positioned to stabilize a metal carboxylate.[22] A

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key feature of these hydrogen-bonding interactions is that they are positioned appropriately to facilitate CO_2 binding (interaction with an O atom on the carboxylate) without enhancing direct proton delivery to the metal, which would favor the *protonation-first pathway*. Another system with proximal secondary amines was found to enhance protonation by generating a local hydrogen-bonding environment, even if they do not assist in CO_2 binding.[129] Although we are not discussing the second protonation event required to liberate water in detail, another possible route to H_2 is direct protonation of the metal carboxylic acid. Careful positioning of secondary sphere hydrogen-bonding functionalities is important for circumventing this possibility.

It has been suggested that cationic functionalities also lower the energetic requirement to access a metal carboxylate intermediate. Savéant and coworkers utilized cationic ammonium substituents to promote CO_2 reduction through electrostatic stabilization of a bound carboxylate species.[130] Iron porphyrin complexes featuring *o*-NMe_3^+ substituents function at 230 mV lower potential than the corresponding *p*-NMe_3^+ substituted complex, while operating at 100 times the rate. In contrast, catalyst activity was suppressed when the cationic amines were replaced with anionic sulfonate moieties, highlighting the effects of electrostatic interactions on CO_2 catalysis.[130] Electrostatic interactions have more recently been utilized for a similar beneficial effect in rhenium bipyridine systems.[131]

In addition to increasing the reaction rate and decreasing the required overpotential for catalysis, CO_2 activation involving cooperative interactions can also affect product selectivity. Large enhancements in CO selectivity have been observed in systems featuring hydrogen-bonding,[129,132,133] bimetallic,[113] and electrostatic interactions.[134]

Although synthetic catalysts have successfully utilized cooperative CO_2 activation to enhance their activity or selectivity, they have yet to achieve the lofty catalytic metrics exhibited by Ni-CODH I. We expect there are more secrets to be discovered for how the active sites of the carbon monoxide dehydrogenases (including the less studied MoCu class) balance key kinetic and thermodynamic factors for efficient, fast, and selective catalysis.

CONCLUSION

Efficiency, rate, and product selectivity are key figures of merit for electrocatalysts. Intermediate steps with large changes in free energy pay an energetic and intrinsic kinetic cost. A quantitative understanding of the free energy of each step in the catalytic cycle can be applied to minimize these energies. Thus, elucidating trends in metal−ligand properties is necessary for guiding catalyst development. The hallmark of efficient electrocatalysis—reversible reactivity—requires a flattened energy landscape.

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Selectivity for CO_2 reduction in the presence of protons is a complex challenge due to multiple possible reaction pathways. To simplify, we have discussed the most commonly cited mechanisms, detailing the thermodynamic parameters involved for each step and how they correlate with redox potential. We emphasize our generalized approach will not apply to all catalyst systems. Instead, we believe our analysis provides a useful framework for thoughtful and creative catalyst design and optimization. In the case of CO_2 reduction to CO, it is apparent that several key parameters are inversely related for single-site metals. However, these relationships can be broken using a secondary interaction, mirroring the approach used by a natural enzyme. Although it is not specifically discussed in our analysis, we also believe uncovering strategies for kinetic inhibition for undesirable reactions presents another fruitful area for targeted catalyst design.

> In the case of CO_2 reduction to CO, it is apparent that several key parameters are inversely related for single-site metals. However, these relationships can be broken using a secondary interaction, mirroring the approach used by a natural enzyme.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00095.

Detailed tables with compound identity and references for data used in Figure 1 as well as a figure depicting hydricity values and the average two-electron reduction potential (PDF)

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Notes

The authors declare no competing financial interest.

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