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Tailoring Metal-Porphyrin-Like Active Sites on Graphene to Improve the Efficiency and Selectivity of Electrochemical CO₂ Reduction

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ABSTRACT: Density functional theory (DFT) calculations are performed to investigate the energetics of the CO₂ electrochemical reduction on metal (M) porphyrin-like motifs incorporated into graphene layers. The objective is to develop strategies that enhance CO₂ reduction while suppressing the competitive hydrogen evolution reaction (HER). We find that there exists a scaling relation between the binding energy of the catalyst to hydrogen and that to OCHO, a key intermediate in the reduction of CO₂ to CO; however, the M−H bond is stronger than the M−COOH bond, driving the reaction toward the HER rather than the reduction of CO₂ to CO. This scaling relation holds even with axial ligation to the metal cation coordinated to the porphyrin ring. When 4f lanthanide or 5f actinide elements are used as the reactive center, the scaling relation still holds but the M−COOH bond is stronger than the M−H bond, and the reaction favors the reduction of CO₂ to CO. By contrast, there is no scaling relation between the binding energy of the catalyst to H and that to OCHO, the key intermediate in CO₂ reduction to formic acid. Interestingly, we find that coordination of a ligand to an unoccupied axial site can make the M−OCHO bond stronger than the M−H bond, resulting in preferential formic acid formation. This means that the axial ligand effectively enhances CO₂ reduction to formic acid and suppresses the HER. Our DFT calculations have also identified several promising electrocatalysts for CO₂ reduction to HCOOH with almost zero overpotentials.

1. INTRODUCTION

One of the grand challenges in modern science and technology is the development of an artificial photosynthesis process that reduces CO₂ and stores the energy in the form of chemical bonds. This process requires electrocatalysts that are active, highly selective, inexpensive, and stable. Currently, copper and its alloys are the only catalysts capable of producing significant quantities of hydrocarbons from CO₂; however, these reactions require overpotentials in excess of 1 V. A further challenge is to identify catalyst that promotes the CO₂ reduction reaction (CO₂RR) rather than the hydrogen evolution reaction (HER). Therefore, there is a need to develop strategies for suppressing the HER relative to the CO₂RR.

In this study, we have used density functional theory (DFT) to develop strategies for enhancing the CO₂RR and suppressing the HER. For this effort, we considered a novel class of electrocatalysts consisting of metal atom coordinated to a porphyrin ring embedded in graphene. This type of catalyst is chosen for several reasons. N₄ macrocyclic complexes, such as porphyrins, corroles, and phthalocyanines, are known as electrocatalysts for the CO₂RR. For example, it has been shown by Savéant et al. that iron S,10,15,20-tetrakis(2′,6′-dimethoxyphenyl)-porphyrin is capable of electrochemical conversion of CO₂ to CO with high Faradaic yield (>90%) and high turnovers (~50 million) at low overpotentials (0.465 V). Cobalt and nickel phthalocyanines deposited on carbon electrodes have been found to catalyze the electroreduction of CO₂ to formic acid in acid solutions (pH 3–7), and they are also capable of reducing CO₂ to methanol at pH <4, although the current efficiency is <5%. Second, graphene and carbon nanotubes into which Fe-porphyrin-like motifs are embedded have been reported to be excellent electrocatalysts for the oxygen reduction reaction (ORR). For example, Lee et al. have synthesized carbon nanotubes incorporating porphyrin Fe−N₄ moieties and found that they exhibit excellent ORR catalytic activity as well as high structural stability over 10⁶ cycles. More recently it has been reported that nitrogen-doped carbon nanotubes are selective and robust electrocatalysts for CO₂ reduction to formic acid. The third key reason for selecting metal-porphyrin-functionalized graphene as...
catays motif is that the activity of the site can be tuned by changing the central metal (M) and through the choice of ligand (L) coordinated to the vacant axial site. It should be noted that, in addition to these \( N_4 \) macrocyclic complexes, there exist several metallic electrocatalysts (e.g., Au, Ag, and Pt/Pd alloys) that exhibit low overpotentials and high Faradaic efficiencies for CO\(_2\) reduction to CO\(^{20,21}\) or HCOOH\(^{22}\).

In this study, we only considered two-proton–two-electron (2H\(^+\)/2e\(^-\)) CO\(_2\) reduction reactions, namely, CO\(_2\) reduction to carbon monoxide (CO) and formic acid (HCOOH), and compared the energetics to those for the HER. These processes together with the equilibrium potential at pH 0 for each are shown in Scheme 1, and an illustration of the progress of these processes on metal-porphyrin-functionalized graphene (G-Por-M(L), M = Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\), Mn\(^{2+}\), and Cr and L = Py, IM, and NHC) is shown in Scheme 2.

We consider the metal-porphyrin-functionalized graphene (G-Por-M(L), M = Ni\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\), Mn\(^{2+}\), and Cr\(^{2+}\) and L = Py, IM and NHC) to consist of isolated active sites. As a result, the competition between the initial intermediates involved in the three target reactions (*H, *COOH, and *OCHO) for those active sites determines the fate of the electrocatalysis.

For example, if an active site is first occupied by *H as the applied voltage becomes more negative, then the HER would be the primary pathway and the CO\(_2\)RR would be minimized. Because the formation of those intermediates involves the transfer of one H\(^+/e^-\), the related stability of the *H, *COOH, and *OCHO intermediates is not affected by the change of the applied voltage or pH. As a consequence, the key to suppressing the HER and enhancing the CO\(_2\)RR is to develop strategies that strengthen the binding between the active sites and COOH (or OCHO) while weakening the interaction between those sites and H, leading to the requirement that \( \Delta G_{*COOH} < \Delta G_{*H} \) or \( \Delta G_{*COOH} < \Delta G_{*H} \). The goal of this paper is to show how this can be achieved.

The remainder of this paper is organized as follows. In Section 2, the density functional theory (DFT) methods used to perform our calculations are described. Our results are described in Section 3, beginning in Section 3.1 with a discussion of the role that active site composition (choice of M, L) has on the competition between the HER and the *COOH branch of the CO\(_2\)RR that yields CO (the gateway toward methanol, methane, etc.). It will be shown that the class of metal used (transition metal versus rare-earth metal) dictates the selectivity, while the choice of axial ligand is relatively inconsequential. In Section 3.2, we consider the additional issue of selectivity between HER and CO\(_2\)RR to yield CO and the other possible branch of the CO\(_2\)RR to yield formic acid, HCOOH, via the *OCHO intermediate. Selectivity toward formic acid production can be tuned by the choice of axial ligand. Finally, in Section 3.3, we consider the extent to which the overpotential for formic acid production can be minimized within the active-site paradigm studied here, and we show that very low overpotentials appear to be achievable.

### 2. COMPUTATIONAL DETAILS

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP)\(^{25-28}\) with the projector augmented wave pseudopotentials\(^{29,30}\) and the PBE functional.\(^{31}\) The plane wave energy cutoff was set to 400 eV, and electron smearing was employed using the Gaussian-smearing technique with a width of \( k_B T = 0.1 \) eV for the graphene systems and 0.01 eV for...
Table 1. Calculated Energetics for $^*\text{H}$ ($\Delta G_{^*\text{H}}$), $^\circ\text{COOH}$ ($\Delta G_{^\circ\text{COOH}}$), $^\circ\text{OCHO}$ ($\Delta G_{^\circ\text{OCHO}}$), and the Overpotentials Required for the Formation of $\text{H}_2$ ($\eta^{\text{HE}}$), CO ($\eta^{\text{CO}}$), and HCOOH ($\eta^{\text{HCOOH}}$)\textsuperscript{a}

<table>
<thead>
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<th>catalyst</th>
<th>$\Delta G_{^*\text{H}}$</th>
<th>$\eta^{\text{HE}}$</th>
<th>$\Delta G_{^\circ\text{COOH}}$</th>
<th>$\eta^{\text{CO}}$</th>
<th>$\Delta G_{^\circ\text{OCHO}}$</th>
<th>$\eta^{\text{HCOOH}}$</th>
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<tr>
<td>G-Por-Ni</td>
<td>1.75</td>
<td>1.75</td>
<td>1.85</td>
<td>1.73</td>
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<td>1.17</td>
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<td>0.18</td>
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<td>0.64</td>
<td>0.46</td>
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<td>0.19</td>
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<td>0.39</td>
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<tr>
<td>G-Por-Cr</td>
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<td>0.14</td>
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<td>0.09</td>
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<td>1.62</td>
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<td>1.57</td>
<td>1.84</td>
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<td>1.46</td>
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<td>G-Por-Co(NHC)</td>
<td>0.33</td>
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<td>0.95</td>
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<td>1.56</td>
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<tr>
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<td>0.36</td>
<td>0.43</td>
<td>0.31</td>
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<tr>
<td>Ac-Fe</td>
<td>0.53</td>
<td>0.53</td>
<td>0.56</td>
<td>0.44</td>
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<tr>
<td>Ac-Mn</td>
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<td>0.55</td>
<td>0.59</td>
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<td>Ac-Cr</td>
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<td>0.46</td>
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<td>$-0.62$</td>
<td>$-0.93$</td>
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<td>Ac-Pa</td>
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<td>0.61</td>
<td>$-0.89$</td>
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<td>0.24</td>
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<td>$-1.89$</td>
<td>2.07</td>
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<tr>
<td>Ac-Cm</td>
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<td>0.32</td>
<td>$-0.55$</td>
<td>0.67</td>
<td>$-1.84$</td>
<td>2.02</td>
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<tr>
<td>Ac-Ce</td>
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<td>0.27</td>
<td>$-0.22$</td>
<td>0.34</td>
<td>$-1.48$</td>
<td>1.66</td>
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<tr>
<td>Ac-Pr</td>
<td>0.38</td>
<td>0.38</td>
<td>$-0.10$</td>
<td>0.22</td>
<td>$-1.36$</td>
<td>1.54</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Units are electronvolts for energetics and volts for overpotentials.

molecules. All calculated values of energy were extrapolated to $k_B T = 0$. For the graphene systems, a Monkhorst–Pack $k$-point grid of $2 \times 2 \times 1$ was chosen to sample the reciprocal space, whereas for molecules only the gamma point was sampled. For graphene, at least $10 \text{Å}$ vacuum space between adjacent images was used to prevent the interaction between the replicas along the $z$ direction, while for all molecules, a $20 \text{Å} \times 20 \text{Å} \times 20 \text{Å}$ box was used for simulations. Spin-polarized wave functions were used for all calculations except H$_2$, CO, HCOOH, and CO$_2$. All possible spin states for each system were calculated by constraining the difference between the numbers of $\alpha$ and $\beta$ electrons ranging from 0 to 8, but only the most stable one was used for discussion.

Zero-point energy (ZPE), enthalpic, and entropic corrections and solvation energies are needed to convert electronic energies into Gibbs free energies. For graphene and organometallic systems, ZPE and thermodynamic corrections were taken as the numbers calculated for the G-Por-Mn system based on the finite difference method. Solvation corrections were calculated for each system using the Poisson–Boltzmann implicit solvation model\textsuperscript{32,33} with a dielectric constant $\varepsilon = 80$ for water. By contrast, the solvation energies for H$_2$O$_{(l)}$ and HCOOH$_{(aq)}$ were calculated by using their vapor pressure at 1 atm (3534 Pa for H$_2$O and 2 Pa for HCOOH).

Only concerted proton–electron transfer was considered because the materials studied here are metallic based on their DOS. The computational standard hydrogen electrode model proposed by Nørskov and coworkers was used to calculate potential- and pH-dependent free-energy surfaces.\textsuperscript{34} In the context of this model, the free energy of a proton and an electron is equal to half the free energy of H$_2(g)$ at an applied electric potential $U = 0 \text{V}$ versus SHE and pH 0. The overpotential ($\eta$) is estimated as the difference between the equilibrium potential and the least-negative applied potential at which each step on the pathway becomes exergonic. (See an example in the Supporting Information.) It should be noted that we only considered thermodynamics and ignored kinetics to obtain our estimates of $\eta$. We, therefore, assume that the barriers for electrochemical proton transfers are small and easily surmountable at room temperature. In fact, it has been shown computationally that the proton-transfer barriers for oxygen reduction reaction on Pt surfaces are small (0.15 to 0.25 eV) and diminished at higher applied voltages.\textsuperscript{35,36}

3. RESULTS AND DISCUSSION

3.1. Hydrogen Evolution versus CO$_2$ to CO Reduction (Competition between $^*\text{H}$ and $^\circ\text{COOH}$). Table 1 lists the calculated Gibbs free energies of the three intermediates ($\Delta G_{^*\text{H}}$, $\Delta G_{^\circ\text{COOH}}$, $\Delta G_{^\circ\text{OCHO}}$), referenced to the energies of proton and electron pairs (at pH 0 and $U = 0 \text{V}$) and CO$_2$$_{(g)}$ ($P = 1 \text{atm}$) and their corresponding overpotentials for H$_2$$_{(g)}$, CO$_{(g)}$, and HCOOH$_{(aq)}$ formation ($\eta^{^*\text{HE}}$, $\eta^{^\circ\text{CO}}$, $\eta^{^\circ\text{HCOOH}}$). The

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data in Table 1 includes a range of G-Por-M(L) active sites, corresponding to abundant first-row transition metals, with and without axial ligands, L, as well as some rare-earth elements. This large amount of computational data will be analyzed in the remainder of this subsection, as well as the following subsections.

We first compared \( \Delta G_{\text{H}_2} \) and \( \Delta G_{\text{COOH}} \) to identify the conditions under which \( \Delta G_{\text{COOH}} < \Delta G_{\text{H}_2} \) and therefore the reduction of CO\(_2\) to CO should be favored over the evolution of H\(_2\). Figure 1 summarizes these data for the transition metals and reveals that there is a good linear correlation between \( \Delta G_{\text{COOH}} \) and \( \Delta G_{\text{H}_2} \) for all of the G-Por-M sites; however, for all transition metals, \( \Delta G_{\text{COOH}} > \Delta G_{\text{H}_2} \) and correspondingly \( \eta^{\text{COOH}} < \eta^{\text{H}_2} \). This means that for all of the catalysts considered the HER would dominate over the CO\(_2\)RR. The same trend has been reported by Tripkovic et al. for the same system \(^{24}\) and reveals that there is a good linear correlation between \( \Delta G_{\text{COOH}} \) and \( \Delta G_{\text{H}_2} \) in the literature. \(^{40}\)-\(^{43}\) and some of these complexes have been demonstrated to exhibit activity for the reduction of CO\(_2\). \(^{44}\)-\(^{47}\)

Because of their much larger diameters, these rare-earth metal cations cannot fit in the N\(_4\) pocket of porphyrins. We therefore used a more flexible acetylacetonate ligand (Ac-M, M = Th\(^{4+}\), Pa\(^{4+}\), U\(^{4+}\), Cm\(^{4+}\), Ce\(^{3+}\), and Pr\(^{3+}\), Scheme 3b) to test the proposed idea. To assess the difference between the acetylacetonate and porphyrin macrocycles, we also repeated the calculations with the same five transition metals previously used. The results are plotted in Figure 2 and are also part of the comprehensive results given in Table 1. The transition-metal Ac-M results are very similar to those obtained previously with the G-Por-M site, with just a slight shift (~0.1 eV) toward stabilizing \( \Delta G_{\text{COOH}} \) versus \( \Delta G_{\text{H}_2} \).

We therefore applied the same approach here to determine whether axial ligands would bind with \( ^*\text{COOH} \) more tightly than \( \text{H}^* \), making \( ^*\text{COOH} \) a more favorable intermediate and driving the reaction toward the reduction of CO\(_2\) to CO. As illustrated in Scheme 3a, an N-heterocyclic carbene (NHC), imidazole (IM), and pyridine (Py) were chosen for investigation. These ligands were chosen because they have been shown both theoretically \(^{37}\) and experimentally \(^{38,39}\) to promote activity for the ORR. Table 1 and Figure 1 show, however, that active sites incorporating these ligands, G-Por-M(L) (L = Py, IM, NHC), still obey the same scaling relation, and \( \Delta G_{\text{H}_2} \) remains lower than \( \Delta G_{\text{COOH}} \). We conclude that these axial ligands do not change the outcome of electrocatalysis and that the HER remains the more favorable reaction pathway.

The next change in the active site design we considered was the introduction of rare-earth metal cations in place of transition-metal cations. In organometallic chemistry, it is well known that the small binding energy differences between M–H and M–C bonds in actinide alkyl complexes make them less prone to \( \beta \)-hydride elimination than transition-metal elements. \(^{40}\) This suggests that actinide-centered catalysts may result in \( \Delta G_{\text{COOH}} < \Delta G_{\text{H}_2} \) making CO\(_2\) reduction to CO more favorable than the HER. We evaluated this hypothesis by using 5f actinide cations Th\(^{4+}\), Pa\(^{4+}\), U\(^{4+}\), and Cm\(^{4+}\) and also 4f lanthanide cations Ce\(^{3+}\) and Pr\(^{3+}\) as catalytic centers. The synthesis of 5f actinide and 4f lanthanide metal complexes is well-documented in the literature. \(^{40-43}\) and some of these complexes have been demonstrated to exhibit activity for the reduction of CO\(_2\). \(^{44-47}\)

![Figure 1. Scaling relation between \( \Delta G_{\text{H}_2} \) and \( \Delta G_{\text{COOH}} \) for transition-metal ions, M, in a G-Por-M(L) (L = Py, IM, NHC) active site. In the gray shaded area, \( \Delta G_{\text{COOH}} < \Delta G_{\text{H}_2} \) and therefore, CO\(_2\) reduction to CO is more favorable than H\(_2\) evolution. In the orange shaded area, the overpotential, \( \eta^{\text{COOH}} \), is minimized. While a very good scaling relation is evident, no viable catalysts for selective CO\(_2\) reduction to CO emerge from this data (also shown in tabular form in Table 1).](Image 2)

![Scheme 3. (a) Axial Ligands Investigated in This Study and (b) Metal Acetylacetonates Complex](Image 3)
We consider next the problem of selective reduction of CO2(g) to HCOOH(aq) versus proton reduction to H2. The pathway for the reduction of CO2 to HCOOH has often not been considered in previous DFT studies, even though formic acid is a common product of CO2 reduction. In contrast with the nearly linear relation observed between ΔG_H and ΔG_OCHO (see Figure 1), we find that there is a much weaker scaling relation between ΔG_H and ΔG_OCHO as can be seen from Figure 3. This is not surprising because OCHO interacts with metals differently than do H and COOH. In addition to having an M−O σ interaction with metals, due to the lone pairs of electrons on O, OCHO also has a π interaction with metals, which is absent in M−H and M−COOH.

Axial ligation of Py, IM, and NHC with the metal has a significant effect on the reduction of CO2 to HCOOH, making ΔG_OCHO even smaller than ΔG_H. The average value of (ΔG_OCHO − ΔG_H) decreases from −0.06 eV for G-Por-M, to −0.20 eV for G-Por-M(Py), to −0.26 eV for G-Por-M(IM), respectively.

3.2. Hydrogen Evolution versus CO2 Reduction to Formic Acid. We consider next the problem of selective reduction of CO2(aq) to HCOOH(aq) versus proton reduction to H2(aq). The criterion for preferential reduction of CO2 to HCOOH versus the evolution of H2 is that ΔG_OCHO < ΔG_H. The averaged binding energy difference between M−H and M−CH3, (BE_M−H−BE_M−CH3) (BE is referenced to a vacant site and a hydrogen atom or methyl radical) bonds is 0.31 eV for M = Ni2+, Co2+, Fe2+, Mn2+, and Cr2+ and is only 0.16 eV for M = Th2+, Pa2+, U2+, Cm2+, Ce2+, and Pr2+. This means that moving from the first-row transition metals to the 4f and 5f elements indeed reduces BE_M−H−BE_M−CH3; however, the reduction is only 0.15 eV on average, which is too small to count for the big difference in ΔG_OCHO − ΔG_H (average value of 0.41 eV, comparing rare earths vs transition metals at the Ac−M sites).

Therefore, there must also be another factor contributing to the observed ΔG_OCHO < ΔG_H for the complexes involving 4f and 5f elements. Analysis of the structures of the *COOH intermediates shows that for the 4f and 5f complexes, the bond length between metal and oxo of COOH is smaller (R_M−O = 2.35−2.45 Å, red dashed line, Scheme 4a) than the Ni, Co, Fe, Mn, and Cr cases (2.90−2.74 Å). For example, for Ac−Th and Ac−Pa, the values of R_M−O are only 2.45 and 2.40 Å, respectively. This indicates that there is an additional orbital interaction between those metals and the O atom that stabilizes the *COOH intermediate and makes the reduction of CO2 to CO more favorable than the HER. This interaction can be seen from the electron density of one of the highest occupied molecular orbital of Ac−Th (Scheme 4b).

To evaluate the reliability of the PBE/PAW computational model, we changed the functional to the HSE and separately increased the plane-wave kinetic cutoff to 500 eV in the calculation done for Ac−Ce, Ac−U, and Ac−Th. We find that the results are similar to those based on the PBE/PAW with a 400 eV cutoff (Table S2 in the Supporting Information).
and to $-0.49 \text{ eV}$ for G-Por-M(NHC). In contrast with the G-Por-M series of complexes, $\Delta G_{\text{OCHO}}$ is lower than $\Delta G_{\text{H}}$ for the G-Por-M(L) (L = Py, IM, NHC) series, with the exception of only G-Por-Co(IM) and G-Por-Co(Py). This means that in the presence of axial ligands, particularly of only Por-M series of complexes, OCHO bind with metals tightly, pushing the empty 3d orbitals are either doubly occupied (for the *H) or singly occupied (for the *H, *COOH, and *OCHO intermediates), which results in a repulsive interaction with the incoming axial ligand, thereby significantly reducing the binding stabilization energy.

Because the CO$_2$RR occurs under strongly reducing conditions, the metallic center may be reduced from its original oxidation state of +2 to +1 or even zero. For this reason, we also calculated the energetics for G-Por-M$^+$ (by adding one more electron to G-Por-M). These calculations reveal that consistent with the results for G-Por-M there is still a strong scaling relation between $\Delta G_{\text{H}}$ and $\Delta G_{\text{COOH}}$ however, in contrast with the results for G-Por-M, *OCHO becomes relatively more stable than *H and *COOH (i.e., $\Delta G_{\text{OCHO}}$ is now lower than $\Delta G_{\text{H}}$ and $\Delta G_{\text{COOH}}$ Table 3). This means that reduction of the metallic center from +2 to +1 would make the reduction of CO$_2$ to HCOOH even more favorable.

### Table 2. Stabilization Energies for *H, *COOH, and *OCHO Intermediates by the Axial Ligands$^{a,b}$

<table>
<thead>
<tr>
<th>A/M</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-Por-M(Py) *</td>
<td>0.10</td>
<td>-0.26</td>
<td>-0.53</td>
<td>-0.35</td>
<td>-0.68</td>
</tr>
<tr>
<td>*H</td>
<td>-0.03</td>
<td>-0.23</td>
<td>-0.31</td>
<td>-0.32</td>
<td>-0.25</td>
</tr>
<tr>
<td>*COOH</td>
<td>0.11</td>
<td>-0.12</td>
<td>-0.26</td>
<td>-0.25</td>
<td>-0.18</td>
</tr>
<tr>
<td>*OCHO</td>
<td>0.03</td>
<td>-0.41</td>
<td>-0.56</td>
<td>-0.52</td>
<td>-0.40</td>
</tr>
<tr>
<td>G-Por-M(IM) *</td>
<td>0.13</td>
<td>-0.27</td>
<td>-0.51</td>
<td>0.23</td>
<td>-0.69</td>
</tr>
<tr>
<td>*H</td>
<td>-0.05</td>
<td>-0.23</td>
<td>-0.32</td>
<td>0.37</td>
<td>-0.30</td>
</tr>
<tr>
<td>*COOH</td>
<td>0.13</td>
<td>-0.15</td>
<td>-0.31</td>
<td>0.36</td>
<td>-0.24</td>
</tr>
<tr>
<td>*OCHO</td>
<td>0.05</td>
<td>-0.53</td>
<td>-0.65</td>
<td>-0.23</td>
<td>-0.52</td>
</tr>
<tr>
<td>G-Por-M(NHC) *</td>
<td>0.15</td>
<td>-0.77</td>
<td>-1.49</td>
<td>-1.41</td>
<td>-1.37</td>
</tr>
<tr>
<td>*H</td>
<td>-0.50</td>
<td>-0.62</td>
<td>-0.72</td>
<td>-1.38</td>
<td>-0.57</td>
</tr>
<tr>
<td>*COOH</td>
<td>-0.24</td>
<td>-0.59</td>
<td>-0.76</td>
<td>-1.35</td>
<td>-0.55</td>
</tr>
<tr>
<td>*OCHO</td>
<td>-0.18</td>
<td>-1.42</td>
<td>-1.41</td>
<td>-1.65</td>
<td>-0.97</td>
</tr>
</tbody>
</table>

### Table 3. Calculated Energetics for *H ($\Delta G_{\text{H}}$), *COOH ($\Delta G_{\text{COOH}}$), and *OCHO ($\Delta G_{\text{OCHO}}$) and the Overpotentials Required for the Formation of H$_2$ ($\eta^{H_2}$), CO ($\eta^{CO}$), and HCOOH ($\eta^{HCOOH}$) for G-Por-M$^+$ (M = Ni, Co, Fe, Mn, and Cr)$^a$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta G_{\text{H}}$ ($\text{eV}$)</th>
<th>$\eta^{H_2}$ ($\text{V}$)</th>
<th>$\Delta G_{\text{COOH}}$ ($\text{eV}$)</th>
<th>$\eta^{CO}$ ($\text{V}$)</th>
<th>$\Delta G_{\text{OCHO}}$ ($\text{eV}$)</th>
<th>$\eta^{HCOOH}$ ($\text{V}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-Por-Ni$^+$</td>
<td>1.46</td>
<td>1.46</td>
<td>1.50</td>
<td>1.38</td>
<td>0.56</td>
<td>0.38</td>
</tr>
<tr>
<td>G-Por-Co$^+$</td>
<td>0.79</td>
<td>0.79</td>
<td>0.95</td>
<td>0.83</td>
<td>0.34</td>
<td>0.16</td>
</tr>
<tr>
<td>G-Por-Fe$^+$</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.02</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>G-Por-Mn$^+$</td>
<td>0.23</td>
<td>0.23</td>
<td>0.27</td>
<td>0.15</td>
<td>0.56</td>
<td>0.74</td>
</tr>
<tr>
<td>G-Por-Cr$^+$</td>
<td>-0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.08</td>
<td>-0.57</td>
<td>0.76</td>
</tr>
</tbody>
</table>

*aUnit is electronvolts for energetics and volts for overpotentials.

3.3. Efficient Electrocatalysts for CO$_2$ Reduction to Formic Acid. Having demonstrated that selective reduction of CO$_2$ to formic acid is possible in the presence of protons, the final step in analyzing the data of Table 1 is to consider the associated overpotential. Our calculations predict $\eta^{HCOOH}$ to be very small for G-Por-Fe(IM) (0.02 V), G-Por-Mn(IM) (0.03 V), and G-Por-Mn(Py) (0.05 V) and small for G-Por-Fe(Py) (0.13 V), and G-Por-Cr(NHC) (0.15 V).

The discovery of an efficient electrocatalyst for converting CO$_2$ to formic acid is significant. Formic acid is a promising material for hydrogen storage due to its high volumetric capacity and its ease of handling and its relatively low toxicity, corrosiveness, and flammability. Hydrogen stored as formic acid can be released on demand with the help of homogeneous or heterogeneous catalysts to produced CO$_2$ and H$_2$, and the latter product can be used directly in a fuel cell. Moreover, formic acid can also be used as an ideal replacement of mineral acids such as HCl and H$_2$SO$_4$ for steel pickling and because it is biodegradable and therefore is environmentally friendly. Finally, formic acid fuel cells may be of future technological interest.

4. CONCLUSIONS

DFT calculations have been used to explore the nature of the active site required to achieve the electrochemical reduction of CO$_2$ in preference to proton reduction to generate H$_2$. As the active site, we have considered transition-metal cations held by homogeneous or heterogeneous catalysts, and both transition-metal cations and rare-earth metal cations complexes of acetylation (Ac-M). Our main conclusions are as follows.

(1) We find that a scaling relation exists between the Gibbs free energy of H and COOH binding to the metal cation center
in both G-Por-M and Ac-M; however, the binding of H atoms is stronger than that of COOH species, which drives the reaction toward H₂ generation rather than CO₂ reduction to CO. This scaling relation holds independent of the presence of an axial ligand and nearly independent of the choice of transition metal.

(2) When rare-earth metal cations (either 4f lanthanide or 5f actinides) are used as the reactive centers, the scaling relation still holds, but the catalysts bind more favorably with COOH than with H, resulting selective in CO₂ reduction to CO.

(3) By contrast, no scaling relation is found between the Gibbs free energy of H and OCHO binding to any of the metal complexes examined. Importantly, we find that when an axial ligand is coordinated to the metal site, the binding of OCHO becomes stronger than that of H, leading to formic acid formation. This means that the axial ligand effectively enhances CO₂ reduction to formic acid and suppresses the formation of H₂.

(4) We have also identified several promising electrocatalysts for selective CO₂ reduction to HCOOH with overpotentials approaching zero.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b05518.

Additional tables and details regarding computational methods. (PDF)

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Notes
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