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Mechanism of CO₂ Electroreduction to Multicarbon Products over Iron Phthalocyanine Single-Atom Catalysts

Reza Khakpour, Kaveh Farshadfar, Si-Thanh Dong, Benedikt Lassalle-Kaiser, Kari Laasonen, and Michael Busch*



ABSTRACT: Carbon dioxide reduction reaction (CO_2RR) is a promising method for converting CO_2 into value-added products. CO_2RR over single-atom catalysts (SACs) is widely known to result in chemical compounds such as carbon monoxide and formic acid that contain only one carbon atom (C1). Indeed, at least two active sites are commonly believed to be required for C-C coupling to synthesize compounds, such as ethanol and propylene (C_{2+}), from CO_2 . However, experimental evidence suggests that iron phthalocyanine (PcFe), which possesses only a single metal center, can produce a trace amount of C_{2+} products. To the best of our knowledge, the mechanism by which C_{2+}



products are formed over a SAC such as PcFe is still unknown. Using density functional theory (DFT), we analyzed the mechanism of the CO₂RR to C1 and C₂₊ products over PcFe. Due to the high concentration of bicarbonate at pH 7, CO₂RR competes with HCO_3^- reduction. Our computations indicate that bicarbonate reduction is significantly more favorable. However, the rate of this reaction is influenced by the H₃O⁺ concentration. For the formation of C₂₊ products, our computations reveal that C–C coupling proceeds through the reaction between in situ-formed CO and PcFe("0")–CH₂ or PcFe("-I")–CH₂ intermediates. This reaction step is highly exergonic and requires only low activation energies of 0.44 and 0.24 eV for PcFe("0")–CH₂ and PcFe("-I")–CH₂. The DFT results, in line with experimental evidence, suggest that C₂₊ compounds are produced over PcFe at low potentials whereas CH₄ is still the main post-CO product.

INTRODUCTION

Electrocatalytic CO₂ reduction relies on multiple proton and electron transfers to form a variety of reduction products. Considering the number of carbon atoms, the products in CO₂ electroreduction can be classified into C1 (carbon monoxide, formic acid, methanol, etc.) and C₂₊ (ethylene, ethanol, propylene, propanol, etc.) paths.¹ Compared to C1, the C₂₊ products exhibit a higher energy density. Furthermore, some multicarbon products are highly demanded chemical feed-stocks. For instance, ethylene is used in the production of polyethylene as well as ethylene oxide and diesel fuel.²

Among the various transition metals, copper appears to be particularly effective in the formation of C_{2+} compounds.³⁻⁵ For instance, Cu-nanoplate catalysts reported by Ajmal et al. display selectivity toward C_2H_4 and C_2H_6 formation.⁶ In comparison with the Cu-planar, the Cu-nanoplate catalyst exhibited a 24 times increase in faradaic efficiency. Koper et al. investigated the reaction mechanism of electrochemical CO_2 reduction to C1 and C_{2+} on copper electrodes.⁷ According to their suggestion, the key intermediate for the C_{2+} pathway is the formation of a CO dimer through electrochemical C-Ccoupling. This CO dimer is then reduced to form the C_{2+} products. In addition to uniform Cu catalysts, copper alloy materials, which have tunable adsorption strengths for key intermediates, can facilitate CO_2 reduction to C_{2+} products. Using density functional theory (DFT), Zhi et al. analyzed the challenging kinetics of C–C coupling for electrochemical CO₂ reduction on copper alloys with Pt, Pd, or Au.⁸ They concluded that OC–COH coupling is kinetically more favorable than OC–CHO coupling on the copper alloy surfaces due to the increase in the reactivity of the adsorbed CO species. However, effective CO₂ reduction to C₂₊ species remains a challenge^{9–12} due to the following factors: (1) it competes with the undesired hydrogen evolution reaction (HER),^{13,14} (2) a high activation barrier needs to be overcome for C–C couplings to form long hydrocarbon chains (C₂₊ products),¹⁵ and (3) there is a high number of possible reaction pathways for C₂₊ formation.¹⁵

At this point, it appears from most of the literature that at least two active sites on the catalyst are required to produce C_{2+} . This is due to the fact that C_{2+} formation requires two nearby active sites for carbonous intermediates, which then can couple. However, our previous study¹⁶ surprisingly demonstrated that C_{2+} products can also be formed over single-atom molecular catalysts like iron phthalocyanine (PcFe) albeit with

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a very low faradaic efficiency, while these systems are wellknown to only produce C1 products.^{17,18} Based on the abovementioned study,¹⁶ PcFe is capable of producing light hydrocarbons such as C_2H_4 and C_3H_6 through the electrocatalytic CO₂ reduction in aqueous solutions under neutral pH conditions. Based on their experimental evaluations, we suggested that CO is an essential reactant in the pathways of CO₂ reduction to C_{2+} . There is, however, no clear understanding of how C–C coupling occurs over PcFe, which contains only one active site (Fe). Developing a deeper understanding of the C–C coupling mechanism over PcFe could lead to the design of more effective single-atom catalysts (SACs) with a higher faradic efficiency for C₂₊.

Independent of the target products, CO_2 is commonly believed to be the starting point of the carbon dioxide reduction reaction (CO_2RR) .^{19,20} However, under neutral pH, CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} are in equilibrium.^{21–23} As a result of carbonate equilibrium in the aqueous solution, CO_2 reduction competes with carbonate reduction.²¹ Indeed, HCO_3^- and CO_3^{2-} dominate the equilibrium at neutral to alkaline pH, while CO_2 and H_2CO_3 dominate at acidic pH. According to our previous studies,^{21,24} bicarbonate is one of the key reactants in CO_2 reduction reactions over Fe porphyrins. Accordingly, it is necessary to consider bicarbonate or carbonic acid reduction when studying the CO_2 reduction reaction in an aqueous solution.

In this study, we will present the mechanisms of the CO_2RR toward C_{2+} products over PcFe (Figure 1a). The under-



Figure 1. (a) Structure of PcFe. (b) Redox potential for the transition from PcFe("I") to PcFe("0") and PcFe("-I") and H_2O adsorption in water at pH = 7.

standing of the detailed mechanisms for the formation of C_{2+} products on PcFe facilitates the development of more effective catalysts. The mechanisms presented in this study are derived from DFT calculations.

COMPUTATIONAL DETAILS

All DFT calculations were performed using Gaussian 16^{25} at the M06-L level of theory.²⁶ The accuracy of M06-L in calculating the energy of organometallic reactions has been shown in numerous studies.^{27–33} For all the calculations,

solvent effects were considered using the SMD solvation model³⁴ with water as the solvent. The SDD basis set^{35,36} with effective core potential was chosen to describe iron. The 6-31G(d) basis set³⁷ was used for all other atoms. Frequency calculations were carried out at the same level of theory as those for structural optimization. Transition states were located by using the Berny algorithm. Intrinsic reaction coordinate calculations were used to confirm the connectivity between transition structures and minima.^{38,39} To further refine the energies obtained from the SMD/M06-L/SDD,6-31G(d) calculations, we carried out single-point energy calculations using the M06-L functional method with the SMD solvation model in water along with the def2-TZVP basis set³² on all atoms for the optimized structures. The tight convergence criterion and ultrafine integral grid were utilized to enhance the accuracy of the single-point calculations. In the case of bicarbonate reduction, where we were unable to find the TS, potential energy scans were utilized (see Supporting Information). The most likely spin states were also tested, and the reaction profiles have been developed based on the most energetically favorable spin state. Accordingly, we assume that the spin changes only by $\pm 1/2$ in electrochemical steps. In chemical steps, the spin sate remains the same.

A computational normal hydrogen electrode was used to model proton-coupled electron transfer (PCET), which assumes that H_2 in the gas phase is a reference.⁴⁰ In order to compare to the experimental results, all potentials were then converted to RHE. With formic acid as a reference compound, pK_a values were determined by the isodesmic method.⁴¹ To correct the deficiencies of the implicit solvation model, eq 1 was used to scale the obtained pK_a values.⁴²

$$pK_a(scaled) = 0.49pK_a(DFT) + 3.2$$
 (1)

The effective absolute potential method was used to compute pure electron transfer steps which were not followed by an acid-base reaction.⁴³ Transition states for proton transfer reactions were modeled using an explicit water cluster containing two H₂O and one H₃O^{+44,45} in conjunction with the SMD. The TS values were then calculated based on the Gibbs free energy difference between the TS and the optimized structures of the reactant solvated by the same water cluster. A water solution with a pH of 7 was assumed as the electrolyte.

RESULTS AND DISCUSSION

Speciation. To determine the active form of PcFe under the reaction conditions (pH = 7), pure electron transfer without protonation was calculated.^{21,24} According to our computations, the reduction of formal PcFe("II") to PcFe("I") by electron transfer requires a potential of -0.48 V (Figure 1b). Upon receiving the second electron, PcFe("I") forms PcFe("0") at a potential of -0.73 V. In a subsequent step, PcFe("0") is reduced to PcFe("-I") at -0.91 V (Figure 1b). The oxidation states mentioned in this study are formal, and the additional electrons in each step can be delocalized to the ligand. As determined by DFT calculations, H₂O weakly binds to the catalyst in all oxidation states and the PcFe–O distance is almost 3 Å in all cases. Therefore, binding of water to PcFe can be neglected.

Using these calculations, it is possible to identify the most likely oxidation state of the active species under the reaction conditions. Considering a potential window of -0.6 to -1.0 V, PcFe("1"), PcFe("0"), and PcFe("-I") would appear to be the most likely active species. In order to simplify the explanation,

we will refer to each intermediate by its oxidation state at the beginning of the mechanism, e.g., the PcFe("-I")-COOH intermediate originated from a bare PcFe("-I") catalyst. The same logic is applied to the naming of other intermediates. All voltages in this study are expressed vs RHE.

Hydrogen Evolution Reaction. The HER is always in competition with the CO_2RR .^{46,47} It is therefore crucial to evaluate the HER before discussing the CO_2RR mechanism. As the first step, the Volmer reaction (reaction 2) initiates the HER by forming PcFe–H.

 $PcFe + H^{+} + e^{-} \rightarrow PcFe - H$ ⁽²⁾

This PCET over PcFe("I"), PcFe("0"), and PcFe("-I") entails potentials of -0.68, -0.62, and -0.45 V, respectively (Figure 2). Therefore, the HER is thermodynamically feasible

-0.91 V _{RHE}
V _{RHE}
H_2 Fe 1 TS_{1H-1} $0.16 eV$ barrierless

Figure 2. HER over PcFe("I"), PcFe("0"), and PcFe("-I") at pH = 7. Potentials are reported vs RHE. In all steps, the TS values are only calculated for chemical reactions.

within the assumed potential range (-0.6 to -1 V). The Volmer reaction, however, exhibits a relatively high activation energy of 0.88 eV for PcFe("I") using H₃O⁺ as a proton source (Figure 2). This activation energy combined with the low concentration of H₃O⁺ at pH 7 renders the first PCET an unlikely path over PcFe("I"). The calculated pK_a value of -3 is a further indication that Fe("I") remains unprotonated at pH = 7, which effectively blocks the HER. For PcFe("0"), the PcFe–H formation activation energy decreases to 0.50 eV and becomes barrierless for PcFe("-I") (Figure 2). Furthermore, PcFe("0")–H and PcFe("-I")–H remain protonated at pH 7 owing to the high calculated pK_a values of 8 and 12. The second PCET is then performed on PcFe–H to form H₂ through a Heyrovsky reaction, as illustrated in reaction 3.

 $PcFe - H + H^{+} + e^{-} \rightarrow PcFe + H_{2}$ (3)

Owing to the likely thermodynamic and almost barrierless reaction, the second PCET is both thermodynamically and kinetically favorable over all PcFe oxidation states.

Overall, the HER is blocked over PcFe("I") at pH = 7 as a result of the very acidic pK_a of PcFe("I")-H. The low activation energies for more reduced complexes, on the other hand, indicate that H_2 is produced over PcFe("0") and PcFe("-I"). Therefore, H_2 is, in line with experimental evidence, likely to be formed at applied potentials lower than -0.7 V.

Indeed, the lower the applied potential, the greater the amount of H_2 formed in experiments.

CO2 Reduction Reaction. PcFe-CO Formation. Considering different configurations of CO2 over PcFe (see Supporting Information for details), carbon dioxide most likely binds via the carbon atom to form a PcFe-C bond.^{48,49} This reaction is highly endergonic by 0.61 eV over PcFe("I"). Fe("I")'s poor nucleophilicity limits its ability to donate electron density for a PcFe-C bond formation, which is confirmed with the 0 net Mulliken charge transfer from PcFe to CO_2 . The O-C-O angle and the 3.2 Å PcFe-C distance are further indications that CO₂ is not activated on PcFe("I"). An electron transfer to PcFe("I") forms PcFe("0") and decreases the PcFe-C bond formation energy to 0.49 eV (Figure 3; left arrow). However, $PcFe("0") - CO_2$ formation is still fairly endergonic. Indeed, the considerable loss of entropy associated with CO₂ adsorption contributes to the endergonic reaction energy. CO_2 is activated on PcFe("0") by altering the linear O-C-O bond angle (180°) to 138° , but still a high activation energy of 0.96 eV must be overcome (Figure 3; left arrow). This is accompanied by a charge transfer of -0.64electrons to CO₂. Over PcFe("-I"), PcFe-C bond formation is, finally, exergonic by -0.09 eV and possesses a rather low activation energy of 0.41 eV (Figure 3; left arrow). The significant Mulliken charge transfer of -0.97 e from PcFe("-I") to CO₂ indicates the formation of a PcFe-COO carboxylate and a strong PcFe-C bond. Overall, the CO₂RR is inherently slow in all oxidation states when assuming CO₂ as the only reactant. The only exception is PcFe("-I"). This is in line with our previous works on Fe porphyrins.^{21,24} An alternative to direct CO_2 reduction is the reduction of bicarbonate or carbonic acid through an $S_N 2$ mechanism^{21,24} (Figure 3; right arrow). Bicarbonate is present in high concentrations in the electrolyte at pH = 7. As shown in Figure 3 (right arrow), the $S_N 2$ reaction for bicarbonate to form PcFe("0")-COO and PcFe("-I")-COO is exergonic by -0.82 and -1.41 eV, respectively. Similar to CO₂ activation, bicarbonate is not activated over PcFe("I") for the PcFe("I")-COO intermediate formation.

The activation energies for bicarbonate reduction are however 0.56 and 0.36 eV over PcFe("0") and PcFe("-I") assuming H_3O^+ as the proton donor. The energy barrier is much lower than that required for CO₂ activation over PcFe("0"). This, combined with the higher HCO_3^- concentration, renders the bicarbonate reduction path more likely for PcFe("0") (Figure S3). However, the bicarbonate reduction rate is sensitive to the proton concentration (Figures S3 and S4). This results in the reduction of CO_2 over PcFe("-I") being more likely than bicarbonate reduction (Figure S4). As reported in the recent study by our group,⁵⁰ in a control experiment with Ar-saturated 0.1 M KHCO₃ at pH \approx 8.5 (without purging any CO₂ gas), we only observed an extremely faint signal of CO, C_{2+} over PcFe. Since there is almost no CO_2 in this experimental condition, the trace amount of carbon products is likely the result of bicarbonate reduction. Compared to pH = 7 where the calculations are performed, raising the pH reduces the proton concentration, which is critical in the suggested mechanism for bicarbonate reduction.²¹ Therefore, the rate of bicarbonate reduction also declines at higher pH values (Figures S3 and S4).

Overall, only PcFe("0") and PcFe("-I") are able to activate CO_2 with the formation of PcFe-COO. Considering the speciation, it is most likely that PcFe-COO is formed only at

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Figure 3. CO_2 reduction vs bicarbonate reduction to the PcFe-CO intermediate over PcFe("I"), PcFe("0"), and PcFe("-I") at pH = 7. Potentials are reported vs RHE. Pure chemical steps are specified by red arrows. In all steps, the TS values are only calculated for chemical reactions.



Figure 4. CO release (left arrow) vs further reduction of PcFe-CO (right arrow) over PcFe("1"), PcFe("0"), and PcFe("-1") at pH = 7. Potentials are reported vs RHE. Pure chemical steps are specified by red arrows. In all steps, the TS values are only calculated for chemical reactions.

potentials almost below -0.73 V. When comparing PcFe-COO formation with HER, both are favorable. Indeed, more

negative applied potentials result in higher selectivity toward HER, as can be seen by comparing Figures 2 and 3.

form PcFe–COOH. This reaction proceeds on PcFe("I") and PcFe("0") already at relatively high potentials of -0.45 and -0.47 V (Figure 3; right arrow). However, due to a very low pK_a of 0, PcFe("I")–COO quickly loses its proton at pH = 7. In the case of PcFe("-I"), a potential of -0.91 V is required for the formation of PcFe("-I")–COOH, which is still achievable within the range of assumed applied potentials (-0.6 to -1 V).

PcFe("0")-COOH and PcFe("-1")-COOH species remain protonated due to the high pK_a value of 9. Regardless of PcFe's oxidation states, PcFe-COOH formation is barrierless using H₃O⁺ as the proton source (Figure 3; right arrow). This is not surprising since the lone pair electron of oxygen in PcFe-COO is easily shared with H₃O⁺. The second proton-coupled electron attacks OH in PcFe-COOH to form PcFe-CO through water elimination. This reaction requires even more positive potentials of 0.14 and 0.13 V for PcFe("0") and PcFe("-I"). Additionally, the formation of PcFe-CO is almost barrierless for both oxidation states (Figure 3; right arrow).

Overall, PcFe("I") is unable to activate CO_2 . The highly endergonic PcFe-COO formation over PcFe("0") renders the binding of CO₂ unlikely. In addition, CO₂ binding to PcFe("0") requires the overcoming of a high activation barrier of 0.96 eV. This is in contradiction to the experiment 16 in which CO is produced already at a moderately negative potential of -0.7 V. Bicarbonate reduction, on the other hand, requires a lower reaction energy of -0.82 eV and an activation energy of 0.56 eV over PcFe("0"). Accordingly, the experimental results for the CO formation at -0.7 V can only be explained by considering bicarbonate as the reactant. It is noteworthy that bicarbonate reduction is, even for PcFe("-I"), still the kinetically favorable route. In addition, the concentration of bicarbonate is considerably higher than that of CO_2 at pH = 7. Therefore, bicarbonate is, regardless of the oxidation states, the most likely reactant for the CO₂RR.

CO Release vs Post-CO. Once PcFe–CO has been formed, it can either release CO or be converted into post-CO intermediates. The route to the post-CO products is initialized by hydrogenation. PcFe–CO can form either PcFe–COH (reaction 4) or PcFe–CHO (reaction 5). Alternatively, it may also be released as CO (reaction 6).

$$PcFe - CO + H^{+} + e^{-} \rightarrow PcFe - COH$$
(4)

 $PcFe - CO + H^{+} + e^{-} \rightarrow PcFe - CHO$ (5)

$$PcFe - CO \rightarrow PcFe + CO$$
 (6)

CO is almost thermoneutral over PcFe("0") and PcFe("-I"). Thus, CO formation is overall favorable (Figure 4; left arrow). However, the activation barrier required for CO release increases from 0.29 eV (PcFe("0")) to 0.44 eV for PcFe("-I") (Figure 4; left arrow). Accordingly, at lower potentials, the release of CO is less likely. This can be explained with the higher electron density on Fe, which enhances the π backdonation to the π^* orbital of CO. This increases the PcFe–CO bond strength which, in turn, is responsible for the larger activation barrier. This effect is also visible in the PcFe–C bond length, which decreases from 1.88 to 1.82 Å, while the C–O bond length increases from 1.18 to 1.20 Å for PcFe("0") to PcFe("-I"), respectively (Figure 5). Therefore, more negative potentials shift the selectivity from CO toward post-CO products, which is observed experimentally.¹⁶





Figure 5. Summary of important bond lengths for the Fe-CO intermediate.

PcFe-COH formation is unlikely due to the very low potential of almost -2.10 V independent of the formal oxidation state (see Supporting Information). The hydrogenation of PcFe-CO to form PcFe-CHO has a potential of approximately 0 V for all oxidation states (Figure 4; right arrow). Owing to the pK_a values of 12 and 16, PcFe("0")-CHO and PcFe("-I")-CHO stay protonated at pH = 7. PcFe-CHO formation is a barrierless reaction for both formal oxidation states using H_3O^+ as the proton source (Figure 4; right arrow). The high reactivity of PcFe-CO toward H₃O⁺ is attributed to the bent Fe–C–O angle of 149° (Figure 5), which indicates the existence of a nonbonding electron in the valence shell of the carbon. These results clearly indicate that the hydrogenation of PcFe-CO to form PcFe-CHO is more likely than CO release. Accordingly, a greater amount of post-CO products than the trace amounts observed experimen- $\mathsf{tally}^{1\delta}$ could be expected. This is, however, contrary to the experiment, which indicates that, irrespective of the applied potential, always the amount of CO is significantly higher than that of post-CO products.¹⁶ Thus, the activation energy cannot solely explain the observed selectivity. Indeed, the proton supply is highly limited by the very low concentration of H₃O⁺ at pH = 7 ($[H^+]$ = 10⁻⁷). The CO release reaction, on the other hand, is independent of H_3O^+ and consequently is more likely than PcFe-CHO formation. Although the CO release is a more favorable path, PcFe-CHO formation is still feasible over PcFe("0") and PcFe("-I").

Once the barrier associated with the initial hydrogenation step is overcome, subsequent PCET can result in the formation of either PcFe–CHOH (reaction 7) or PcFe– CH_2O (reaction 8).

 $PcFe - CHO + H^{+} + e^{-} \rightarrow PcFe - CHOH$ (7)

 $PcFe - CHO + H^{+} + e^{-} \rightarrow PcFe - CH_2O$ (8)

The formation of PcFe–CHOH is unlikely due to the very low potential of -1.39 and -1.57 V required for PcFe("0")– CHOH and PcFe("-I")–CHOH, respectively. A much higher potential of -0.29 V and a moderate activation barrier of 0.63 eV are, on the other hand, required for PcFe–CH₂O formation from PcFe–CHO on PcFe("0") (Figure 4; right arrow). The potential increases to 0.11 V and the activation energy decreases to 0.52 eV, which result in even more likely PcFe–CH₂O formation on PcFe("-I"). This is followed by a PCET to the O atom in PcFe–CH₂O, leading to PcFe– CH₂OH (reaction 9). This reaction requires a potential of -0.05 and -0.50 V over PcFe("0") and PcFe("-I"),

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Figure 6. Methanol release (left arrow) vs further reduction of the $PcFe-CH_2OH$ intermediate to CH_4 release (right arrow) over PcFe("0") and PcFe("-I") at pH = 7. Potentials are reported vs RHE. In all steps, the TS values are only calculated for chemical reactions.

respectively, which is in the range of the experimentally applied potentials (Figure 4; right arrow). The hydrogenation of $PcFe-CH_2O$ to form $PcFe-CH_2OH$ is barrierless for all relevant oxidation states (Figure 4; right arrow).

$$PcFe - CH_2O + H^+ + e^- \rightarrow PcFe - CH_2OH$$
(9)

Overall, a lower applied potential results in a stronger PcFe– CO bond, which then requires a higher activation energy to release CO. Thus, the post-CO pathway opens at lower potentials as CO is more strongly bound to Fe in PcFe–Pc. Accordingly, the stronger the PcFe–CO binding, the greater the probability of entering the post-CO pathway. Indeed, the reaction is not limited by an overly high activation barrier or a too negative onset potential but is merely a result of the limited proton supply.

Methanol vs Methane Formation. Once $PcFe-CH_2$ is formed, the mechanism can bifurcate toward either CH_3OH or CH_4 formation. Both paths are shown in Figure 6. Methanol is formed through hydrogenation of the carbon in PcFe- CH_2OH , which then leads to CH_3OH release from the catalyst (reaction 10).

$$PcFe - CH_2OH + H^+ + e^- \rightarrow PcFe + CH_3OH$$
(10)

This reaction is energetically favorable, as indicated by the very positive potential of 1.09 and 1.16 V for PcFe("0") and PcFe("-I"), respectively (Figure 6; left arrow). The very high TS value of 1.03 eV associated with this protodemetalation

reaction, however, inhibits the formation of methanol over PcFe("0") (Figure 6; left arrow). For $PcFe("-I")-CH_2OH$, H⁺ is immediately drawn to the OH group and water elimination occurs; thus, it follows the CH₄ pathway (reaction 11).

$$PcFe - CH_2OH + H^+ + e^- \rightarrow PcFe = CH_2 + H_2O$$
(11)

The proton attack on the OH in $PcFe-CH_2OH$ causes water elimination and yields the $PcFe-CH_2$ metal Schrock carbene.⁵⁶ This reaction requires a potential of -0.69 and -0.50 V for PcFe("0") and PcFe("-I"), respectively (Figure 6; right arrow). This reaction is barrierless for both oxidation states (Figure 6; right arrow). The subsequent PCET step from $PcFe-CH_2$ to $PcFe-CH_3$ then requires only very high potentials of 1.71 V (PcFe("0")) and 1.57 V (PcFe("-I")) (reaction 12 and right arrow in Figure 6).

$$PcFe - CH_2 + H^+ + e^- \rightarrow PcFe - CH_3$$
(12)

According to our kinetic analysis, $PcFe-CH_3$ is rapidly formed through a barrierless proton transfer process for both oxidation states using H_3O^+ as the proton source. Methane is then released in a final PCET step, which again requires only potentials of 1.44 and 1.45 V for PcFe("0") and PcFe("-I"), respectively (reaction 13 and right arrow in Figure 6).

$$PcFe - CH_3 + H^+ + e^- \rightarrow PcFe + CH_4$$
(13)

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Figure 7. CH_4 release (left arrow) vs C-C coupling on PcFe-CH₂ (right arrow) over PcFe("0") and PcFe("-I") at pH = 7. Potentials are reported vs RHE. Pure chemical steps are specified by red arrows. In all steps, the TS values are only calculated for chemical reactions.

This protodemetalation reaction exhibits modest activation energies of 0.67 and 0.59 eV over PcFe("0") and PcFe("-I") (Figure 6; right arrow).

Overall, the methanol pathway requires activation energies much higher than those of the $PcFe-CH_2$ pathway. Thus, the CH_4 pathway is more favorable than methanol formation. Based on our DFT calculations and in line with experimental evidence,¹⁶ it appears that no methanol is produced over PcFe, while CH_4 is the major post-CO product.

C–C Coupling. Thus far, we have evaluated only the possible mechanisms for H_2 , CO, and CH_4 formation over PcFe in different formal oxidation states. Nevertheless, experiments clearly show that also minor amounts of C_{2+} products are formed.¹⁶ It remains unclear how and where C_{2+} is formed in the CO₂RR mechanism over FePc. To address this key question, we first evaluated the CO insertion reaction, a common reaction in organometallic chemistry.⁵⁷ However, in the present case, this very common mechanism was found to be unfavorable (see Supporting Information). This is not surprising since Fe does not possess a free adsorption site for CO.

Another route proceeds through the direct attack of CO on the carbon atom in $PcFe-CH_2$ (for other considered routes, see Supporting Information). This CO attack is in competition with the hydrogenation of $PcFe-CH_2$ (CH₄ formation path). Identical to the formation of CH₄, the mechanism is divided into a CO attack (reaction 14 and the right arrow in Figure 7) and hydrogenation steps (reaction 12 and the left arrow in Figure 7).

$$PcFe - CH_2 + CO \rightarrow PcFe - C_2H_2O$$
(14)

CO on the carbon in PcFe-CH₂ is strongly exergonic by -1.09 eV for PcFe("0") and -1.12 eV for PcFe("-I") (Figure 7; right arrow). This reaction led to the formation of a PcFe-C2H2O intermediate. Only small activation energies of 0.44 and 0.24 eV need to be overcome for PcFe("0") and PcFe("-I") (Figure 7; right arrow). Solely based on activation energies, $PcFe-CH_3$ (left arrow) and, thus, CH_4 are the most likely products. Accordingly, C2+ products should not be formed (Figure 7). However, the TS energy is again not the only parameter that affects the rate of the reactions. In fact, low concentrations of the reactants may significantly reduce the rate of the reaction. According to our DFT results and in line with experiment,¹⁶ CO is extensively produced and released into the double layer; thus, a high concentration of CO is expected close to the catalyst surface. The recent study by us demonstrated, using finite element calculations, that the concentration of CO close to the electrode (almost within 5 mm from the working electrode) is in the range of 1.5-4.5 mM.¹⁶ Meanwhile, the CH_4 path entails the use of H_3O^+ as a proton source. In pH = 7, the concentration of H_3O^+ is 10^{-7} M, which is 30,000 times less than that of CO. Furthermore, the catalyst continuously consumes H_3O^+ in the double layer,

thereby resulting in a concentration of H₃O⁺ even lower than 10^{-7} M. The C–C coupling (Figure 7; right arrow) is therefore feasible, but the formation of CH_4 (Figure 7); left arrow) is still a more likely path due to the exponential effect of the activation energy in the Arrhenius rate equation. Consequently, CH₄ is the main post-CO product, while a trace amount of C_{2+} products are also expected only at very negative applied potentials where the activation energy decreases to 0.24 eV for the CO attack on PcFe("-I"). The C₂₊ formation path is very unlikely over PcFe("0") owing to the high energy barrier of 0.44 eV for PcFe("0")-C₂H₂O formation compared to the barrierless reaction for the formation of PcFe("0")-CH₃. These are in good agreement with the experimental evidence of CO₂RR over PcFe where the formation of CH₄ is observed starting from -0.8 V, while that of C₂₊ products only starts from -0.9 V.¹⁶

In PcFe("-I")-C₂H₂O, the PcFe-C bond readily switches from one carbon to another through a rearrangement reaction (reaction 15 and Figure 7). This reaction is barrierless and exergonic by -0.96 eV (Figure 7; right arrow). In the subsequent PCET, the O side in PcFe("-I")-C₂H₂O is hydrogenated to form PcFe("-I")-C₂H₂OH at the potential of -0.57 V. Using H₃O⁺ as the proton source, this reaction is again barrierless.

$$PcFe - C_2H_2O + H^+ + e^- \rightarrow PcFe - C_2H_2OH$$
(15)

 $PcFe("-1")-C_2H_2OH$ then forms $PcFe("-1")-C_2H_2$ metal carbene through a water elimination reaction at the potential of -0.63 V (reaction 16 and Figure 7).

$$PcFe - C_2H_2OH + H^+ + e^- \rightarrow PcFe - C_2H_2 + H_2O$$
(16)

The protonation of $PcFe("-I")-C_2H_2OH$ to form $PcFe("-I")-C_2H_2$ requires a very low activation energy of 0.36 eV. Chemically, the $PcFe("-I")-C_2H_2$ intermediate is quite similar to the $PcFe("-I")-CH_2$ intermediate with respect to the metal carbene type complexes. Hence, the same reaction mechanism observed may also be active for the formation of longer carbon chains.

$$PcFe - C_2H_2 + CO \rightarrow PcFe - C_3H_2O$$
(17)

A PCET to $PcFe("-I")-C_2H_2$ forms $PcFe("-I")-C_2H_3$. This reaction is barrierless and takes place at a very high potential of 1.18 V (reaction 18 and Figure 8; right arrow). However, this PCET step rate is limited by the concentration of the proton at pH = 7. Both the CO attack for C3 formation and a PCET to $PcFe("-I")-C_2H_2$ are feasible. The latter reaction is, however, slightly more favorable unless there is a limitation on proton supply.

$$PcFe - C_2H_2 + H^+ + e^- \rightarrow PcFe - C_2H_3$$
(18)

From the PcFe("-I")– C_2H_3 intermediate, the mechanism is again divided into C_2H_4 release (reaction 19 and Figure 9; left arrow) and C_2H_6 formation (reaction 20 and Figure 9; right arrow) paths. A PCET on the carbon bonded to Fe in PcFe("-I")– C_2H_3 releases C_2H_4 at a very positive potential of 0.77 V and a low activation energy of 0.26 eV associated with the protodemetalation reaction (Figure 9; left arrow). The PCET to the second carbon (the carbon that is not bonded to Fe) in PcFe("-I")– C_2H_3 is even more kinetically favorable with an energy barrier of 0.07 eV (Figure 9; right arrow). In the end, this pathway leads to the formation of C_2H_6 . Thus, PcFe("-I") is expected to produce a greater amount of C_2H_6 than C_2H_4 .



Figure 8. C3 formation path (left arrow) vs C_2H_4 and C_2H_6 formation (right arrow) over PcFe("-1") at pH = 7. Potentials are reported vs RHE. Pure chemical steps are specified by red arrows. In all steps, the TS values are only calculated for chemical reactions.

This is in line with experimental evidence demonstrating that the amount of C_2H_6 produced is almost two times that of C_2H_4 .¹⁶

$$PcFe - C_2H_3 + H^+ + e^- \rightarrow PcFe + C_2H_4$$
(19)

$$PcFe - C_2H_3 + H^+ + e^- \rightarrow PcFe - C_2H_4$$
(20)

In the next step of C_2H_6 formation, $PcFe("-I")-C_2H_4$ forms $PcFe("-I")-C_2H_5$ through PCET with a high potential of 1.21 V. As this reaction is barrierless, it is also kinetically quite likely (Figure 9; right arrow). In the following reaction, C_2H_6 is released by another PCET. This reaction requires an activation energy of 0.37 eV and a positive potential of 1.41 V (Figure 9; right arrow).

Overall, the CH₄ pathway wins the competition over the formation of C_{2+} products. However, given the very low concentration of H₃O⁺ at pH = 7 and the high concentration of CO produced by CO₂ close to the electrode, C_{2+} pathways are also feasible at low potentials since they mostly depend on the C–C coupling step. This is also consistent with the experimental observations where only trace amounts of C₂₊ products are observed at low potentials.¹⁶ The overall proposed mechanism is illustrated in Figure 10.

CONCLUSIONS

In conclusion, our study has shed light on the unexpected formation of C_{2+} compounds during CO_2 reduction over a SAC, namely, PcFe. While the CO_2RR over SACs is typically associated with the generation of single-carbon (C1) products, PcFe has shown the ability to yield small amounts of larger C_{2+} products, thereby challenging the conventional understanding that C–C coupling necessitates multiple active sites. Our

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Figure 9. C_2H_6 release (left arrow) vs C_2H_6 formation path (right arrow) over PcFe("-I") at pH = 7. Potentials are reported vs RHE. In all steps, the TS values are only calculated for chemical reactions.



Figure 10. Overall suggested mechanism for CO_2 reduction over Fe Phthalocyanine. Only paths to products which are thermodynamically and kinetically accessible are displayed.

investigations, employing DFT, have elucidated key aspects of C_{2+} products formation mechanism over SACs, particularly the C–C coupling step. According to our results, we suggest a pathway involving a reaction between in situ-generated CO and a PcFe–CH₂ carbene intermediate with nucleophilic

character. These reactions were found to be highly exergonic, requiring low activation energies of 0.44 and 0.24 eV for $PcFe("0")-CH_2$ or $PcFe("-I")-CH_2$. This study contributes to the understanding of how C-C coupling is achievable over SACs and molecular catalysts and provides opportunities for

further research in the conversion of CO_2 into high-value products within sequential reaction schemes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c08347.

All considered mechanisms and structures and their total Gibbs free energies (PDF)

Optimized structures (ZIP)

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Notes

The authors declare no competing financial interest.

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