

CO₂ ReductionInternational Edition: DOI: 10.1002/anie.201808593
German Edition: DOI: 10.1002/ange.201808593Reaction Mechanisms of Well-Defined Metal–N₄ Sites in Electrocatalytic CO₂ ReductionZheng Zhang⁺, Jianping Xiao⁺, Xue-Jiao Chen, Song Yu, Liang Yu, Rui Si, Yong Wang, Suheng Wang, Xianguang Meng, Ye Wang, Zhong-Qun Tian, and Dehui Deng*

Abstract: Electrocatalytic CO₂ reduction to CO emerges as a potential route of utilizing emitted CO₂. Metal–N–C hybrid structures have shown unique activities, however, the active centers and reaction mechanisms remain unclear because of the ambiguity in true atomic structures for the prepared catalysts. Herein, combining density-functional theory calculations and experimental studies, the reaction mechanisms for well-defined metal–N₄ sites were explored using metal phthalocyanines as model catalysts. The theoretical calculations reveal that cobalt phthalocyanine exhibits the optimum activity for CO₂ reduction to CO because of the moderate *CO binding energy at the Co site, which accommodates the *COOH formation and the *CO desorption. It is further confirmed by experimental studies, where cobalt phthalocyanine delivers the best performance, with a maximal CO Faradaic efficiency reaching 99 %, and maintains stable performance for over 60 hours.

In recent centuries, the combustion of fossil fuels has released excessive amounts of carbon dioxide (CO₂) into the atmosphere, leading to severe environmental problems such as global warming and ocean acidification. Recycling CO₂ to produce valuable chemicals is considered a promising and sustainable route to alleviate these problems and maintain carbon neutrality.^[1] The electrocatalytic CO₂ reduction reaction (CO₂RR) is a promising strategy for CO₂ conversion

owing to its high efficiency and mild reaction conditions.^[2] Among various catalysts reported previously,^[3] metal-containing nitrogen-doped carbon (metal–N–C) has exhibited promising catalytic activity for the electrocatalytic CO₂RR to deliver carbon monoxide (CO).^[4] The reactivity and selectivity of different metal–N–C catalysts have been systematically studied for CO production.^[5] The metal–N₄ center in metal–N–C structures was considered to be the possible active site.^[6] However, because of the challenge in controllable synthesis, the metal–N–C catalysts usually contain complex structures, such as metal–N_x (x = 1–4), metal–C, and defects in the carbon matrix, resulting in difficulty in identifying the real active sites and reaction mechanisms. Metal phthalocyanines (MePcs) have a clear metal–N₄ coordination structure, and provide an excellent model catalyst for studying the active center and reaction mechanism for the electrocatalytic CO₂RR. Moreover, MePcs are a potential class of electrocatalysts for CO₂RR because of their low cost, accessibility, and high thermal and chemical stabilities.^[7] However, a clear understanding of the catalytic nature and activity trends of metal–N₄ structures is lacking, as well as a confirmation of the optimum MePc catalyst for CO₂RR.

In this work, by using well-defined MePcs with transition-metal centers (Mn, Fe, Co, Ni, and Cu) as model catalysts, we performed systematic density functional theory (DFT) calculations and studies on the reaction system to investigate the catalytic nature and activity trends of the electrocatalytic CO₂RR. Theoretical calculations show that CoPc has a moderate *CO binding energy at the Co site, which accommodates the reaction steps of *COOH formation and *CO desorption, rendering it the optimum catalyst for selective electrocatalytic CO₂RR to deliver CO. Experimental tests of the corresponding MePc monomer as the electrocatalyst for the CO₂RR match well with our theoretical predictions.

DFT calculated free-energy pathways of CO₂ reduction to CO at the metal sites of MePcs, and the intermediate structures are shown in Figures 1a,d–g. Among the four elementary reaction steps, the CO₂ adsorption step is always exergonic regardless of the MePc, whereas the *COOH formation and *CO desorption reaction energies depend significantly on the MePc types, alternately playing the role of the rate-limiting step as the intrinsic activity variation. To display the trend more clearly, we established the linear relations of reaction energies of *COOH formation and *CO desorption as functions of the *CO adsorption energy, as shown in Figure 1b. For Fe, Mn, and Co Pcs, the *CO desorption is the most endergonic step and determines the overall reaction rate. However, for Ni and Cu Pcs with relatively weak CO adsorption, the *COOH formation

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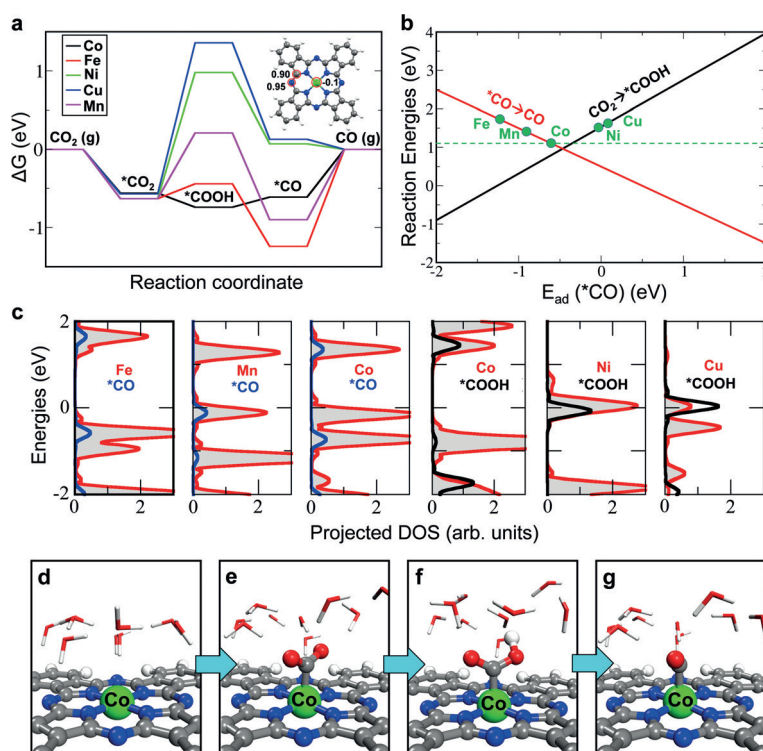


Figure 1. Theoretical analysis of the electrocatalytic CO₂RR to CO by DFT calculations. a) Calculated free-energy diagram for all the MePc electrodes. The inset shows the adsorption energy of *COOH (in eV) on different sites of CoPc. b) Fitted *CO desorption (*CO → CO) and *COOH formation (CO₂ → *COOH) trends over all five MePc electrodes. c) Projected density of states for crucial structures from *CO and *COOH adsorption. The initial condition of CoPc (d), adsorbed CO₂ (e), formed *COOH (f), and adsorbed *CO (g) on CoPc in presence of a hydronium in the water layer. The solvation and electric effect have been considered in all energies. The balls in green, blue, grey, red and white represent Co, N, C, O and H atoms, respectively.

becomes the most endergonic and thus the rate-limiting step. The two linear relations reveal an inverted volcano curve in the activity trend of MePcs for CO₂ reduction to CO, with the optimum *CO binding energy close to −0.5 eV. CoPc locates at the position closest to the volcano peak, and thus shows the best intrinsic activity for CO₂ reduction to CO in the series of MePcs. The activity of other sites in the CoPc besides the Co center were also investigated using the *COOH adsorption energy as a probe, as shown in Figure 1a inset. The *COOH adsorbed on the N site adjacent to the central Co site is not stable and migrates to the Co site readily. On other N and C sites surrounding the Co–N₄, the adsorption energies of *COOH is 0.95 eV and 0.90 eV, respectively, compared to that of −0.1 eV on the Co site, demonstrating that the metal center is the most preferable adsorption site.

The electronic structures of *COOH and *CO adsorbed onto MePcs were also calculated to understand the activity trend, as shown in Figure 1c. Taking the *CO on FePc, MnPc, and CoPc as examples, the d orbitals were split in the planar fourfold coordination into two obvious energetic states below the Fermi level. For the CoPc case, the electronic states of adsorbed *CO have a resonance at a lower energy level, resulting in weaker binding strength with respect to the FePc and MnPc cases. Hence, our theoretical studies show the

CoPc is the best candidate for CO₂ electroreduction to CO. In contrast, we have examined the kinetic barrier of CO₂ protonation to *COOH over CoPc, compared to that of hydrogen adsorption (Volmer process) on the surface of electrode. The protonation barrier of CO₂ to *COOH is surmountable with 0.30 eV, while it is much higher with 0.93 eV in the Volmer process, indicating high CO selectivity for CoPc over the hydrogen evolution reaction (HER) in CO₂ electroreduction. In addition, we have calculated barriers for both Volmer and CO₂ to *COOH over other catalysts, as shown in Figure S1 (see the Supporting Information). For Cu and Ni, as the barriers of CO₂ to *COOH are pretty high, thus the intrinsic activity of the CO₂RR is low. However, the barriers for the Volmer process are quite low and comparable to CO₂RR process for both Fe and Mn. Therefore, the CO selectivity is not competitive to HER as diffusion limiting in these CO₂RR process. Overall, the CoPc has the best activity and selectivity for CO₂RR.

To assess our theoretical predictions on the CO₂RR activity of MePcs, we conducted experimental tests of the corresponding MePc cathode catalysts. Figure 2a and Figure S6 show the linear sweep voltammetry (LSV) and controlled potential electrolysis tests of different MePcs in a CO₂-saturated 0.5 M KHCO₃ electrolyte, in which the CoPc catalyst exhibits the lowest onset potential and largest current density. Both the CO₂RR and HER contribute to the current density (see Figure S7). Obviously, CoPc shows the largest activity, namely, CO current density, in a wide potential range compared with other MePcs (Figure 2b).

According to the computational hydrogen electrode, the activity for CO production should be proportional to the charge transfer amount and applied potential, explaining well our observations.^[8] Additionally, on CoPc, the CO₂RR to CO dominates over the HER, with Faradaic efficiency reaching the maximum value of 99% at −0.8 V versus RHE (Figure 2c). However, on other MePcs, the Faradaic efficiency of CO production is much lower than that of CoPc at the same potential and goes even lower as the potential increases, owing to the more competitive HER on these catalysts (see Figure S8). For direct comparison, the Faradaic efficiency of CO production on different MePc samples at the potential of −0.8 V versus RHE is depicted in Figure 2d, showing that CoPc is best catalyst for the CO₂RR to deliver CO. In addition, the calculated turnover frequency (TOF) of CoPc at all the applied potentials is at least one order of magnitude larger than those of other MePcs (see Figure S11), consistent qualitatively with the DFT results in Figure 1. Additionally, the TOF based on electrochemical active surface area also demonstrates the conclusion (see Figure S13). The electrochemical impedance spectroscopy results in Figure S15 further confirmed that the CoPc possesses the optimum catalytic activity for the CO₂RR compared with other MePcs.

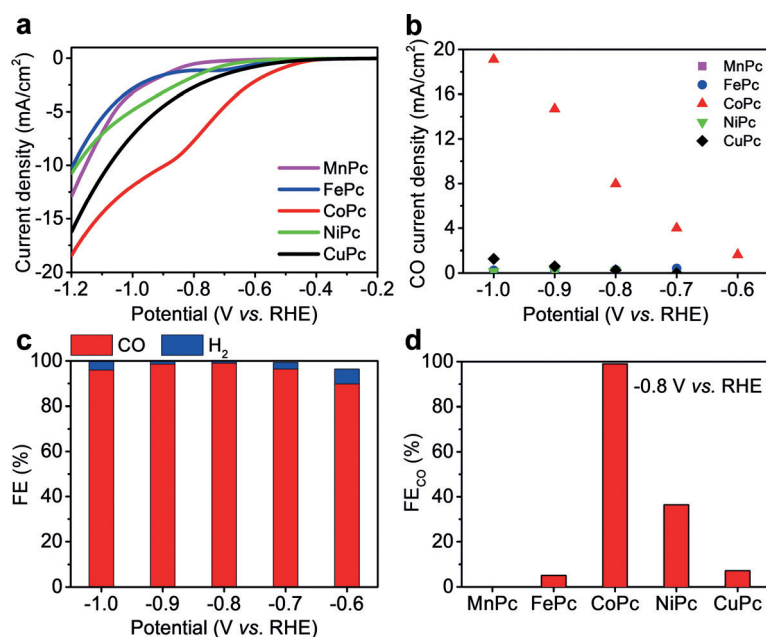


Figure 2. Activity of the MePc samples in the electrocatalytic CO₂RR to deliver CO in 0.5 M KHCO₃ solution at 25 °C. a) LSV tests in CO₂-saturated electrolyte. b) CO current density of MePcs at various potentials. c) Faradaic efficiency of CO and H₂ formation at different potentials for the CoPc sample. d) Faradaic efficiency of CO formation at -0.8 V versus RHE for the different MePc samples.

In addition, CoPc can achieve a low onset overpotential of 170 mV (see Figure S16). And it has a much higher Faradaic efficiency of CO production (99%) compared with other metal-N₄ molecular catalysts reported previously in the literature (Table S1). A pure Pc molecule shows a poor selectivity for CO₂ reduction with a Faradaic efficiency of CO production below 5% at the potential range from -0.7 to -1.0 V versus RHE (see Figure S17), and suggests that the Co center is the active site for CO₂ reduction, further demonstrating the DFT results.

Moreover, we carried out the in situ X-ray absorption spectroscopy (XAS) to probe the valence state and coordination structure of CoPc catalysts under real electrocatalytic CO₂RR conditions.^[9] No significant changes were detected in either X-ray absorption near-edge structure (XANES) profiles (Figure 3a) or extended X-ray absorption fine structure (EXAFS) spectra (Figure 3b; see Table S2) at the Co K-edge of the CoPc catalyst when exerting -0.6 V versus RHE to reduce CO₂. The results indicate that the valence state and the coordination structure of Co²⁺ remained at the reduced potential. Recently, Daasbjerg et al. found that the Co²⁺ remains during electrocatalytic CO₂RR in heterogeneous systems,^[10] consistent with our observations.

The long-term stability test of the CoPc showed that the Faradaic efficiency of the CO₂RR to deliver CO is maintained above 90% for 60 hours at a working potential of -0.8 V versus RHE (Figure 4a). In the UV/Vis test of CoPc before and after the long-term stability test, there is no variation in the featured sharp Q-band at 600–700 nm, indicating that the

monomeric molecular CoPc^[11] was maintained (Figure 4b). Furthermore, the vibration modes in the Raman spectra of the CoPc before and after the stability test are almost identical (Figure 4c). These results demonstrate that the CoPc is a robust catalyst for electrocatalytic CO₂RR to CO.

In summary, combining DFT calculations and experiments, we have systematically studied the electrocatalytic CO₂RR mechanisms for the model catalysts MePcs with well-defined metal-N₄ structures. Theoretically, the CoPc exhibits the optimum activity for CO formation, owing to the moderate *CO binding energy at the Co site, and benefits the overall reaction thermodynamics by compromising on the key reaction steps of *COOH formation and *CO desorption. Electrochemical experiments further confirm the unique activity of the CoPc catalyst, which achieves a much higher Faradaic efficiency of 99% for CO₂RR to CO with a mild potential of -0.8 V versus RHE among the MePcs and other analogous electrocatalysts possessing metal-N₄ structure in the literature. Our study provides an understanding of the intrinsic activity of catalysts, with well-defined structures, in the electrocata-

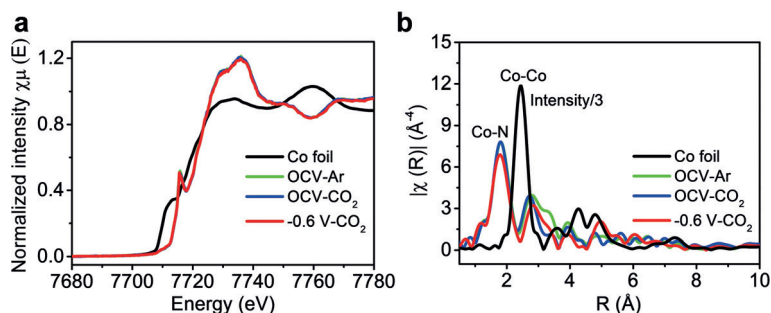


Figure 3. In situ XAS characterizations of MePcs. a) In situ Co K-edge XANES profiles for the electrocatalytic CO₂RR on CoPc sample. b) Fourier transformed EXAFS spectra in the R space of the CoPc catalyst during the CO₂RR. OCV: open circuit voltage.

lytic CO₂RR, and paves a way towards optimization of the highly efficient electrocatalyst.

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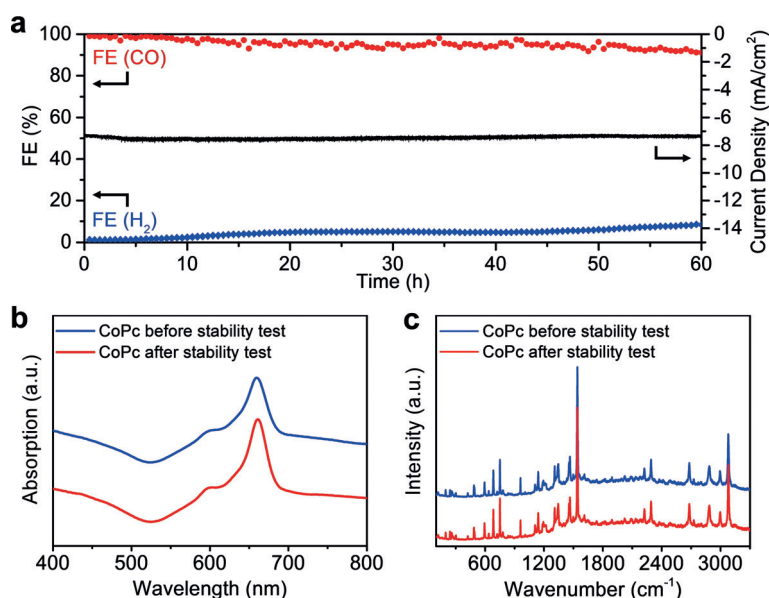


Figure 4. Stability tests for CoPc catalyst in the electrocatalytic CO₂RR at the potentials of -0.8 V versus RHE for 60 hours. a) Faradaic efficiency and current density. UV/Vis absorptions (b) and Raman spectra (c) for CoPc catalyst before and after the stability test.

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Conflict of interest

The authors declare no conflict of interest.

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