

Aggregation and the Significant Difference in Reactivity therein: Blocking the CO₂ to CH₃OH Reaction

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ABSTRACT: A CoPc/CNT system was recently reported to transform CO₂ to methanol via electrochemical reductions, despite the catalyst has been studied since the 1980s, such observations were not reported earlier. A clue to the high methanol selectivity is that CoPc exist as mainly as monomers in the new report while in earlier works CoPc aggregates dominate. Here we have studied the reactivity of monomeric and dimeric CoPc by DFT. The mechanism involves rate limiting CO₂ association, with the C-O cleavage step being having very similar activation free energy. Once the Co-CO⁻ intermediate is formed the reaction bifurcates with two possible paths, CO dissociation or further reduction and protonation to give the Co-CHO⁻ intermediate, which then leads to methanol by further reactions. For the monomeric species at low reduction potentials CO dissociation is favored, but the formation of Co-CHO⁻ becomes competitive at more negative applied potentials. For the dimer the CO dissociation is always favored, and the reduction needed to form the C-H bond is negative enough for it not to be observed. The more difficult reduction stems from repulsive interactions between the Co-Pc units and lower solvent stabilization of the charge in the aggregate.

Introduction

The conversion of CO₂ into value-added product such as CO¹ or methanol² is gaining more attention from the society as a result of the worsened environmental situation associated with high atmospheric CO₂ concentration³ as well as the increasing demand for energy globally⁴. Electrochemical CO₂ reduction is of particular interest as it allows mild operating conditions, which potentially enable on-demand industrial operation⁵ if stable and highly efficient catalysts are found. A wide selection of materials have been tested, ranging from transition metals such as copper⁶, silver⁷ or gold⁸; organometallic catalysts with macrocyclic ligands^{9,10} or ter/bipyridine ligands¹¹ etc. Some molecular catalysts^{9,12} exhibit dramatically improved reactivity under heterogenous conditions when they are immobilised on a non-reacting carbon-based electrode and using water as the reaction medium. For example, in terms of turnover frequency (TOF), a dramatic increase of 3 orders of magnitude¹³ was observed for cobalt phthalocyanine (CoPc). As a heterogenous catalyst, it exhibits superior reactivity, good stability as well as low overpotential when comparing to other hybrid catalysts. Moreover, it is the first transition metal complex reported that enables CO₂ to methanol reduction with good yields¹².

Hybrid molecular catalyst/carbon support materials rely on the π - π interactions between the catalyst and a carbon supporting material. However, such binding is by definition weak and low stability can limit larger scale production^{9,10}. Our previous work on a Co(TPP)/carbon nanotube (CNT) system¹⁴ illustrated that flat catalysts tend to aggregate on CNTs as a result of stronger π - π interactions among the catalysts as compared to between the catalysts and the CNTs. Therefore, the curvature of

the CNT plays an essential role in aggregation tendency: wider CNTs have better contact with the catalysts resulting in a reduced degree of aggregation. Apart from switching to flatter supporting materials, other proved methods that can minimise aggregation and hence improve TOF including (1) add bulky side groups to reduce the level of inter-catalyst π - π interactions; (2) grow a polymerised form of the catalyst¹⁵ on the CNT electrode, which can give as good TOF for CO₂ to CO conversion as the highly dispersed CoPc/CNT system; (3) incorporate the molecular catalyst in rigid structures such as metal organic frameworks (MOFs)¹⁶ or covalent organic frameworks (COFs)¹⁷. Furthermore, aggregation¹⁸ could in some cases block certain reaction pathways as demonstrated by Wang *et al* in a recent study¹². The sophisticated catalyst preparation method therein suggests that only when CoPc molecules are well dispersed, can methanol be obtained as the major product from CO₂ reduction at a relatively low reductive potential of -1.35V (vs. SHE). A few earlier reports^{19,20} together with some recent works^{21,22} of the same catalyst have only obtained trace amount of methanol (Faradaic Efficiency < 5%), if any. These observations highlight the importance of a highly dispersed system in CO₂ to methanol reduction.

Herein we present a computational study on the difference in reactivity between monomeric CoPc and dimeric CoPc, which is the simplest form of aggregates. In agreement with previous computational²³ and experimental studies^{23,24}, our results suggest that the catalyst-CO adduct is a key intermediate. We examined possible (further) reaction pathways of both monomer-CO and dimer-CO adducts, comparing reduction and

consecutive protonation, and the competing CO dissociation pathway which can limit further reduction to methanol.

Results and Discussions

Monomer Reactivity

We calculated the reductive potentials for the CoPc/CoPc⁻ (-0.30V vs. SHE) and CoPc/CoPc²⁻ (-0.96V vs. SHE) couple, which fit well with experimental measured reductive potentials obtained for a CoPc/graphite system (-0.34V, -0.71V) in water¹³. In agreement with previous DFT²⁵ and electron-spin resonance (ESR) spectroscopic studies²⁵⁻²⁷, we confirmed that the unpaired electron resides in the metal d_z^2 orbital for CoPc (Figure 1a) and that the first reduction fills the metal d_z^2 orbital forming (Co^IPc)⁻.

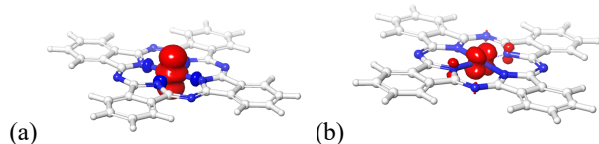


Figure 1. The spin density of (a) CoPc and (b) CoPc²⁻

Molecular orbital (MO) analysis of (Co^IPc)⁻ suggests that upon the full-filling of d_z^2 orbital, its energy is lowered and the degenerate d_{xz} , d_{yz} orbitals are now HOMOs. Since these three orbitals are very close in energy (Figure S1), shift in their alignment should be possible upon further reduction. The two degenerate LUMOs are ligand based but have some d_{xz}/d_{yz} character.

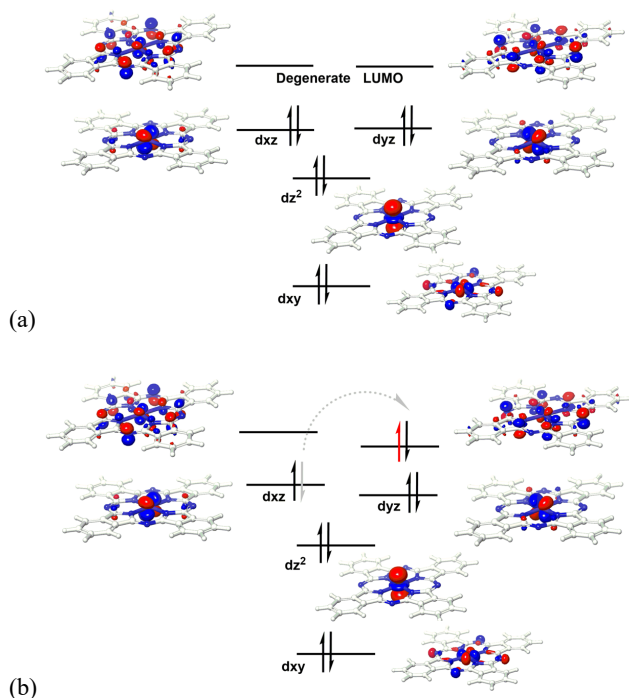


Figure 2. (a) Orbital-alignment in (Co^IPc)⁻ and (b) the proposed orbital occupation for (CoPc)²⁻

The nature of the second reduction is less clear^{27,28,29}, ESR spectrum yields a narrow resonance close to 2.0023 (i.e. g factor for the free electron), suggests the doublet nature of (CoPc)²⁻. However, no determine evidence exist in where exactly the

unpaired electron locates. The twice reduces CoPc exhibits new absorptions in the 900-1100 nm region³⁰ in the UV-vis spectrum, which was believed to be ligand based π - π^* transitions, suggesting the reduction being ligand-based. One should also note that the disproportionation energies for (CoPc)²⁻ is significantly lower than other MPcs where reductions are all ligand based, indicating the reversion back to Co^{II} after the second reduction²⁷. We used both electronic structures as the initial guess and got (CoPc)²⁻ with the unpaired electron in the previously fully occupied the d_{xz}/d_{yz} orbital as the optimised configuration irrespectively (Figure 2b). This indicates a certain level of metal-to-ligand electron transfer ($d_{xz}/d_{yz} \rightarrow \pi$) and the twice reduced species exists as (Co^{II}Pc)²⁻, which is further evidenced by partial charge analysis – Co becomes more positively charged upon the second reduction (Table 1).

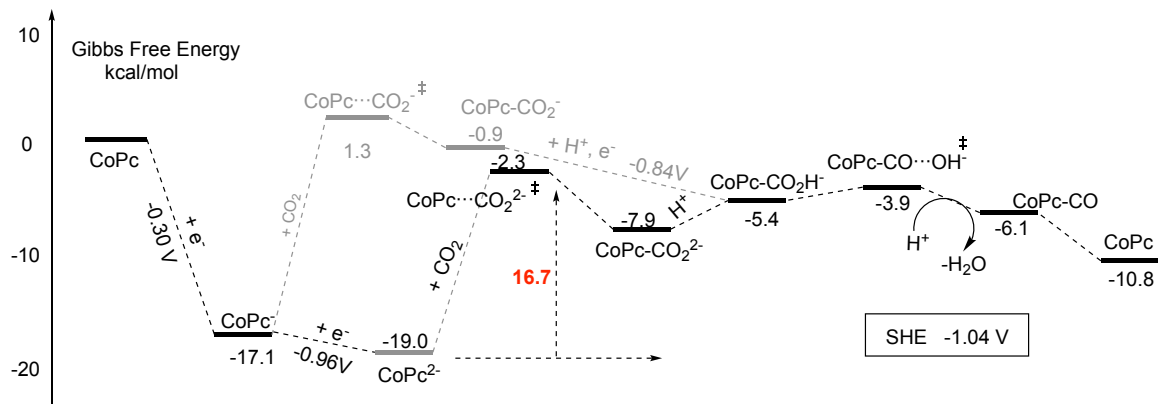
Species	Co ^{II} Pc	(Co ^I Pc) ⁻	(Co ^{II} Pc) ²⁻
Charge	0.41	0.25	0.36
Spin	1.03	N/A	0.78

Species	(CoPc-CO ₂) ²⁻	(CoPc-COOH) ⁻	CoPc-CO
Charge	0.25	0.40	0.45
Spin	0.092	0.025	1.02

Table 1. Mulliken partial charge and spin density analysis on the Co centre for relevant CoPc species

The calculated reaction profile at an applied potential of -1.04V (vs. SHE), which is the optimal reduction potential reported in experiment for CO production¹⁰, is shown in Scheme 1. In line with an experimental study¹⁸, our results indicate that CO₂ binding is the rate determining step. The calculated activation free energy of 16.7 kcal/mol is in very good agreement with experimental¹⁰ estimated value of 17.0 kcal/mol, which is converted from a TOF of 2.7s⁻¹ by transition state theory. CO₂ binding at the once reduced state as an alternative pathway is also possible as suggested by some studies^{18,25,31}, although it has to go through a slightly higher energy barrier (18.4 kcal/mol vs. 16.7 kcal/mol). Nonetheless, such difference is within the error range of DFT.

Upon CO₂ binding, d_z^2 electrons interact with an empty C sp^2 orbital, lowering the electron density on cobalt, which in turn leads to a charge transfer from the phthalocyanine ring back to the d_{xz} orbital. This re-generates Co^I (Table 1) and leaving the unpaired electron on the phthalocyanine ring (Figure 3a). Upon protonation, CO₂ is further polarised strengthening the Co-C bond, shifting more electron density away from cobalt centre (Table 1). The unpaired electron remains on the phthalocyanine ring (Figure 3b) until the second proton attack, which triggers C-O bond cleavage and releases water. In the CoPc-CO complex the unpaired electron resides in the d_z^2 orbital to avoid excessive repulsion with the CO lone pair (Figure 3c). Moreover, the doubly occupied d_{xz} and d_{yz} cab interact with CO via π back-bonding. Thereafter, as in-line with previous theoretical studies^{25,32}, spontaneous CO dissociation regenerates Co^{II}Pc and closes the catalytic cycle.



Scheme 1. Reaction Profile for CoPc monomer at -1.04V

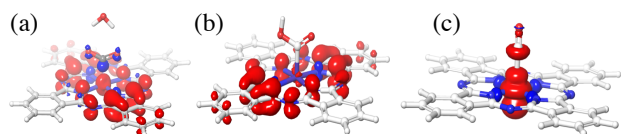


Figure 3. The spin densities of (a) CoPc-CO₂⁻, (b) CoPc-COOH and (c) CoPc-CO

Competing reactions for CO release are: (1) ligand-based reductions; and (2) protonation. The first reduction (-0.37V vs. SHE) is exergonic at both -1.04V (vs. SHE) and -1.34V (vs. SHE), while the preferred reaction afterwards is applied potential-dependent (Scheme 2). At -1.04V, spontaneous CO dissociation being the preferred pathway yielding (Co^IPc), which is -6.5 kcal/mol lower in free energy; while at -1.34V, we see a competition between CO dissociation (Scheme 2b, blue) and protonation (Scheme 2b, purple), explaining why a mixture of methanol and CO were obtained in the experiments¹².

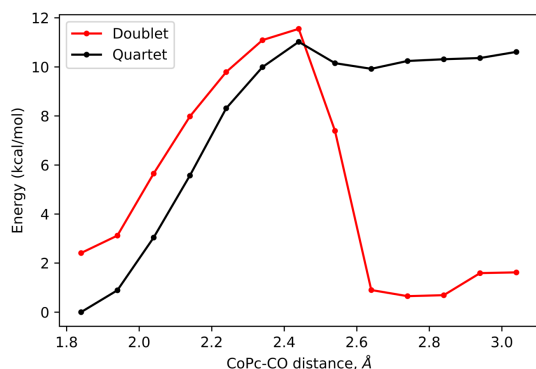
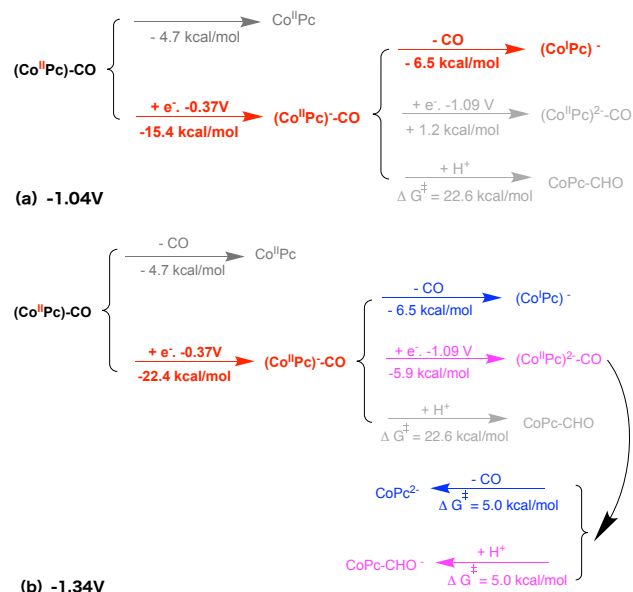


Figure 4. Relaxed coordinate scans showing a spin cross over during the CO dissociation process for CoPc²-CO at b3lyp-d3/lacvp** level of theory

A spin cross-over was observed for (CoPc)²-CO as CO dissociates (Figure 4), which resulted in a kinetic barrier of 5.0 kcal/mol. The same analysis was also performed for (CoPc)-CO, but no cross-over effect was observed (Figure S2).

Once the (CoPc)-CHO complex is obtained, an additional protonation leads to Co-C bond cleavage and releases HCHO, which spontaneously bond with Co centre on the O site with



Scheme 2. Possible Reaction Pathways beyond Co^{II} Pc-CO at (a) -1.04V and (b) -1.34V

a reaction free energy of -13.5 kcal/mol. HCHO as a key intermediate is also suggested by another experimental study²¹. Under a formaldehyde atmosphere as oppose to CO₂ atmosphere, the TOF to methanol was dramatically increased by more than 1000 times. This observation confirms that: 1) the rate determining step for CoPc catalysed CO₂ to methanol reduction (e.g. CO₂ binding, Figure 3) takes place before formaldehyde binding, which is in line with our calculations, with the caveat that no activation energies were calculated after (CoPc)-CHO formation; 2) formaldehyde binding as well as steps afterwards are very fast, meaning very low activation energies and/or negative reaction free energies are associated with these steps.

According to our calculations, the next proton assisted reduction has an equilibrium reductive potential of -1.47V which means that intermediate formed is merely 2.5 kcal/mol higher in energy at -1.34V. The final proton assisted reduction (-0.34V) is very facile. It affords methanol and closes the catalytic cycle (Figure 5). Overall, the proposed mechanism for CO₂ to CO then to methanol reduction agrees well with the experimental data available as discussed in the current section.

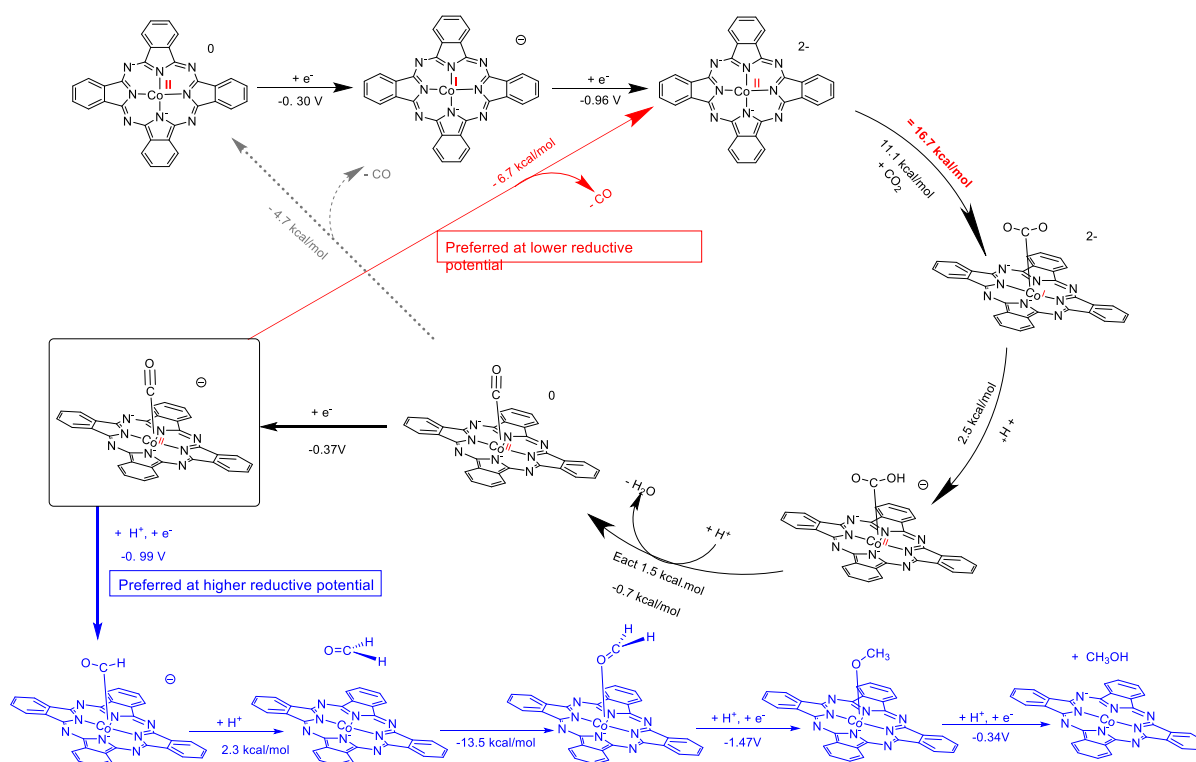


Figure 5. Proposed reaction mechanism for CoPc monomer

Dimer Reactivity

A dimer is the simplest form of aggregates. By exploring its reactivity, we can gain some insights in how aggregates differ from monomers in reactivity apart from the fact that not all active sites are accessible for CO₂ binding. In the case of CoPc, experimental results suggest that the monomer can further reduce CO to methanol while it is much less facile, if not impossible, for aggregates¹². It was previously proposed that the CoPc dimer exists in an eclipsed geometry as opposed to a metal-over-metal staggered fashion (Table S3)^{33,34}, to optimise the favourable electrostatic interactions while reducing the Pauli repulsion³³. Our DFT calculations suggest that the open shell singlet (Figure 6a) and the triplet state (Figure 6b) are very close in energy, as expected since the metals are well separated. Non-the-less, all spin alternatives were optimised, and the lowest energy spin-arrangement was selected for further investigation.

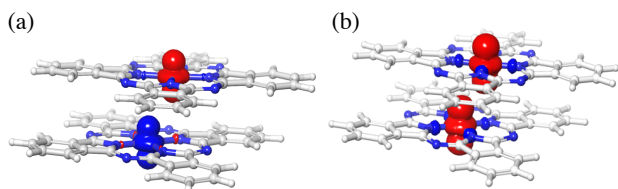
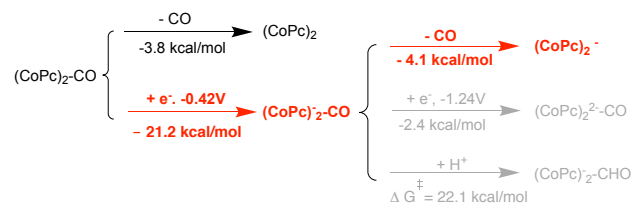


Figure 6. The geometry and spin density for (a) open shell singlet (CoPc)₂ and (b) triplet (CoPc)₂

We applied the same analogy to dimers, and found out that after the first reduction, CO dissociation remains the preferred reaction pathway even at -1.34 V. Compared to monomers, the reductions are harder here due to a lower degree of

solvation stabilisation (Table S10). Since the added charge is distributed on a larger system, it results in a lower charge density and hence weaker electrostatic interactions with water.



Scheme 3. The Reaction Profile for Dimer-CO complex at -1.34V

The negligible amount of methanol observed in previous studies at similar reductive potentials is likely produced by trace amount of monomeric CoPc presented in the system. In theory, a more negative applied potential can increase the driving force for proton assisted reduction and hence favours the formation of (CoPc)₂-CHO, which is a key intermediate for methanol production. Nonetheless, one should also bear in mind that proton reduction always acts as a competing reaction. Therefore, simply lowering the applied potential will not necessarily lead to a higher FE for methanol. In one study, where CO to methanol conversion (i.e. where CO dissociation route is suppressed) was studied²¹, when applied potential was further lowered to -1.76 V (vs. SHE), hydrogen production dominates, and no methanol was detected.

The high electric field close to the electrode surface attracts protons as well as other cations in the solution resulting in higher local concentrations³⁵ in a non-linear fashion. One can

imagine sites on larger aggregates are located slightly further away from the electrode surface where possibly experiences a lower proton activity than at the surface. This could be yet another reason making proton assisted reductions more difficult for aggregates, leaving spontaneous CO dissociation being the preferred reaction pathway. Furthermore, It is known that the presence of cation in an electric field stabilises the partial charges on the CO₂ oxygen atoms once it is activated, lowering the energy barrier for CO₂ binding³⁶. Hence CO₂ binding may also be slightly harder for larger aggregates, highlighting the superior activity of monomeric CoPc.

The present study explored the reaction mechanism for monomeric and dimeric CoPc, and demonstrated that dimers are harder to reduce due to a less-degree of solvation stabilisation, leaving CO dissociation being the preferred reaction pathway. Our findings should in theory apply to larger aggregates as well. Built on our previous work Co(TPP) aggregates in a Co(TPP)/CNT system, the current work deepens our understanding on aggregate reactivity in heterogeneous catalysts and explained that the formation of aggregates can, in certain cases, block reaction pathways that may be desirable. We believe this finding is helpful for further catalyst design.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Methodology, energies of optimized structures at different spin states, relevant analysis, relaxed coordinate scans for CO dissociation and solvation energy analysis (file type, PDF)

The optimized xyz coordinates of related species (file type, PDF)

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REFERENCES

- (1) Laitar, D. S.; Muller, P.; Sadighi, J. P., Efficient Homogeneous Catalysis in the Reduction of CO₂ to CO. *J. Am. Chem. Soc.* **2005**, *127* (49)
- (2) Ma, J.; Sun, N.; Zhang, X.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y., A Short Review of Catalysis for CO₂ Conversion. *Catal. Today* **2009**, *148* (3-4), 221-231.
- (3) Anagnostou, E.; John, H. E.; Edgar, K. M.; Foster, G. L.; Ridgwell, A.; Inglis, G. N.; Pancost, R. D.; Lunt, D. J.; Pearson, P. N., Changing Atmospheric CO₂ Concentration was the Primary Driver of Early Cenozoic Climate. *Nature* **2016**, *533*, 380-384.
- (4) Li, M., Peak Oil, the Rise of China and India, and the Global Energy Crisis. *J. Contemp. Asia* **2007**, *37*, 449-471.
- (5) Schiffer, Z. J.; Manthiram, K., Electrification and Decarbonization of the Chemical Industry. *Joule* **2017**, *1*, 10-14.
- (6) Lee, J.; Tak, Y., Electrocatalytic Activity of Cu Electrode in Electroreduction of CO₂. *Electrochim. Acta* **2001**, *385* (2), 209-225.
- (7) Rosen, J.; Hutchings, G. S.; Lu, Q.; Rivera, S.; Zhou, Y.; Vlachos, D. G.; Jiao, F., Mechanistic Insights into the Electrochemical Reduction of CO₂ to CO on Nanostructured Ag Surfaces. *ACS Catal.* **2015**, *5* (7), 4293-4299.
- (8) Zhao, S.; Jin, R.; Jin, R., Opportunities and Challenges in CO₂ Reduction by Gold- and Silver-Based Electrocatalysts: From Bulk Metals to Nanoparticles and Atomically Precise Nanoclusters. *ACS Energy Lett.* **2018**, *3* (2), 452-462.
- (9) Hu, X.-M.; Ronne, M. H.; Pedersen, S. U.; Skrydstrup, T. S.; Daasbjerg, K., Enhanced Catalytic Activity of Cobalt Porphyrin in CO₂ Electroreduction upon Immobilization on Carbon Materials. *Angew. Chem. Int. Ed.* **2017**, *56* (23), 6468-6472.
- (10) Zhang, X.; Wu, Z.; Zhang, X.; Li, L.; Li, Y.; Xu, H.; Li, X.; Yu, X.; Zhang, Z.; Liang, Y.; Wang, H., Highly Selective and Active CO₂ Reduction Electrocatalysts based on Cobalt Phthalocyanine/Carbon Nanotube Hybrid Structures. *Nat. Commun.* **2017**, *8*.
- (11) Johnson, B. A.; Agarwala, H.; White, T. A.; E., M.; Maji, S.; Ott, S., Judicious Ligand Design in Ruthenium Polypyridyl CO₂ Reduction Catalysts to Enhance Reactivity by Steric and Electronic Effects. *Chem. Eur. J.* **2016**, *22* (42), 14870-14880.
- (12) Wu, Y.; Jiang, Z.; Lu, X.; Liang, Y.; Wang, H., Domino Electroreduction of CO₂ to Methanol on a Molecular Catalyst. *Nature* **2019**, *575*, 639-642.
- (13) Lieber, C. M.; Lewis, S. L., Catalytic Reduction of CO₂ at Carbon Electrodes Modified with Cobalt Phthalocyanine. *J. Am. Chem. Soc.* **1984**, *106*, 5034-5035.
- (14) Chen, X.; Hu, X.-M.; Daasbjerg, K.; Ahlquist, M. S. G., Understanding the Enhanced Catalytic CO₂ Reduction upon Adhering Cobalt Porphyrin to Carbon Nanotubes and the Inverse Loading Effect *Organometallics* **2020**.

- (15) de Brito, J. F. A.; A. R.; Rajeshwar, K.; Zandoni, M.V.B., Photoelectrochemical reduction of CO₂ on Cu/Cu₂O films: Product distribution and pH effects. *Chem. Eng. J.* **2015**, *264*, 302-309.
- (16) Kornienko, N.; Zhao, Y.; Kley, C. S.; Zhu, C.; Kim, D.; Lin, S.; Chang, C. J.; Yaghi, O. M.; Yang, P., Metal-Organic Frameworks for Electrocatalytic Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **2015**, *137*, 14129-14135.
- (17) Lin, S.; Diercks, C. S.; Zhang, Y. B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M., Covalent Organic Frameworks comprising Cobalt Porphyrins for Catalytic CO₂ Reduction in Water. *Science* **2015**, *349*, 1208-1213.
- (18) Zhu, M.; Ye, R.; Jin, K.; Lazowski, N.; Manthiram, K., Elucidating the Reactivity and Mechanism of CO₂ Electroreduction at Highly Dispersed Cobalt Phthalocyanine. *ACS Energy Lett.* **2018**, *3*, 1381-1386.
- (19) Kapusta, S.; Hackerman, N., Carbon dioxide reduction at a metal phthalocyanine catalyzed carbon electrode. *Journal of The Electrochemical Society* **1984**, *131* (7), 1511-1514.
- (20) Kusuda, K.; Ishihara, R.; Yamaguchi, H., Electrochemical Investigation of Thin Films of Cobalt Phthalocyanine and Cobalt-4,4',4'',4'''-Tetracarboxyphthalocyanine and the Reduction of Carbon Monoxide, Formic Acid and Formaldehyde Mediated by the Co(I) Complexes *Electrochim. Acta* **1984**, *31*, 657-663.
- (21) Boutin, E.; Wang, M.; Lin, J. C.; Mesnage, M.; Mendoza, D.; Lassalle-Kaiser, B.; Hahn, C.; Jaramillo, T. F.; Robert, M., Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine. *Angew. Chem. Int. Ed.* **2019**, *58*, 16172-16176.
- (22) Xia, Y.; Kashtanov, S.; Yu, P.; Chang, L.-Y.; Feng, K.; Zhong, J.; Guo, J.; Sun, X., Identification of dual-active sites in cobalt phthalocyanine for electrochemical carbon dioxide reduction. *Nano. Energy* **2020**, *67*.
- (23) Shen, J.; Kolb, M.; Gottle, A. J.; Koper, M. T. M., DFT study on the mechanism of the electrochemical reduction of CO₂ catalyzed by cobalt porphyrins. *J. Phys. Chem. C* **2016**, *120* (29), 15714-15721.
- (24) Albo, J.; Alvarez-Guerra, M. A.; Castano, P.; Irabien, A., Towards the Electrochemical Conversion of Carbon Dioxide into Methanol. *Green Chem.* **2015**, *17*, 2304-2324.
- (25) Han, N.; Wany, Y.; Ma, L.; Wen, J.; Li, J.; Zeng, Z.; Nie, K.; Wang, X.; Zhao, F.; Li, Y.; Fan, J.; Zhong, J.; Wu, T.; Miller, D. J.; Lu, J.; Lee, S.-T.; Li, Y., Supported Cobalt Polyphtalocyanine for High-Performance Electrocatalytic CO₂ Reduction. *Chem* **2017**, *3*, 652-664.
- (26) Kroll, T.; Aristov, V. Y.; Molodtsova, O. V.; Ossipyan, Y. A.; Vyalikh, D. V.; Buchner, B.; Knupfer, M., Spin and Orbital Ground State of Co in Cobalt Phthalocyanine. *J. Am. Chem. A.* **2009**, *113*, 8917-8922.
- (27) Clack, D. W.; Hush, N. S.; Woolsey, I. S., Reduction Potentials of Some Metal Phthalocyanines. *Inorganica Chimica Acta* **1976**, *19*, 129-132.
- (28) Rollman, L. D.; Iwamoto, R. T., Electrochemistry, Electro Paramagnetic Resonance, and Visible Spectra of Cobalt, Nickel, Copper, and Metal-free Phthalocyanines in dimethyl sulfoxide. *J. Am. Chem. Soc.* **1968**, *90* (6), 1455-1463.
- (29) Clack, D. W.; Yandle, J. R., Electronic Spectra of the Negative Ions of Some Metal Phthalocyanines. *Inorg. Chem.* **1972**, *11*, 1738-1742.
- (30) Grodkowski, J.; Dhanasekaran, T.; Neta, P., Reduction of Cobalt and Iron Phthalocyanines and the Role of the Reduced Species in Catalyzed Photoreduction of CO₂. *J. Phys. Chem. A.* **2000**, *104*, 11332-11339.
- (31) Zeng, J. S.; Corbin, N.; Williams, K.; Manthiram, K., Kinetic Analysis on the Role of Bicarbonate in Carbon Dioxide Electroreduction at Immobilized Cobalt Phthalocyanine *ACS Catal.* **2020**, *10*, 4326-4336.
- (32) Pan, Y.; Lin, R.; Chen, Y.; Liu, S.; Zhu, W.; Cao, X.; Chen, W.; Wu, K.; Cheong, W.-C.; Wang, Y.; Zheng, L.; Luo, J.; Lin, Y.; Liu, Y.; Liu, C.; Li, J.; Lu, Q.; Chen, X.; Wang, D.; Peng, Q.; Chen, C.; Li, Y., Design of Single-Atom Co-N₅ Catalytic Site: A Robust Electrocatalyst for CO₂ Reduction with Nearly 100% CO Selectivity and Remarkable Stability *J. Am. Chem. Soc.* **2018**, *140*, 4218-4221.
- (33) Rosa, A.; Baerends, E. J., Origin and Relevance of the Staggering in One-Dimensional "Molecular Metals". A Density Functional Study of Metallophthalocyanine Model Dimers. *Inorg. Chem.* **1992**, *31*, 4717-4726.
- (34) Ge, X.; Manzano, C.; Berndt, R.; Anger, L. T.; Köhler, F.; Herges, R., Controlled Formation of a n Axially Bonded Co-Phthalocyanine Dimer. *J. Am. Chem. Soc.* **2009**, *131*, 6096-6098.
- (35) Bohra, D.; Chaudhry, J. H.; Burdyny, T.; Pidko, E. A.; Smith, W. A., Modeling the Electric Double Layer to Understand the Reaction Environment in a CO₂ Electrocatalytic System. *Energy. Environ. Sci.* **2019**, *12*, 3380-3389.
- (36) Liu, M.; Pang, Y.; Zhang, B.; Luna, P. D.; Voznyy, O.; Xu, J.; Zheng, X.; Thangdin, C.; Fan, F.; Cao, C.; Pelayo Garcia de Arquer, F.; Safaei, T. S.; Mepham, A.; Klinkova, A.; Kumacheva, E.; Filleter, T.; Sinton, D.; Kelly, S. O.; Sargent, E. H., Enhanced Electrocatalytic CO₂ Reduction via Field-Induced Reagent Concentration. *Nature* **2016**, *537*, 382-386.