

ELECTROCATALYSIS

The search for selectivity

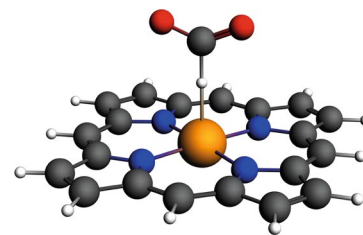
The $2\text{H}^+/2\text{e}^-$ electroreduction of CO_2 can give either CO and H_2O or HCO_2H — products that make fuels when combined with alkenes (the Fischer–Tropsch process) or sugars, respectively. The question of selectivity adds to the challenge of developing an electrocatalyst that is robust and active at low overpotentials. One notable class of molecular electrocatalyst for CO_2 reduction is the metalloporphyrins, which can feature a redox-active metal with apical sites available to substrates. But the metal is not the only redox-active component nor is it the only possible substrate binding site. Writing in *Journal of the American Chemical Society*, Adrien Göttle and Marc Koper use density functional theory to evaluate metal- and ligand-centred reactivity pathways. Their thermochemical calculations enable us to rationalize why different metalloporphyrins operate through different pathways and give rise to different selectivities.

Reducing a metalloporphyrin affords a complex of a low-valent and nucleophilic metal centre that can bind CO_2 at the electrophilic C atom to give a metallacarboxylate, with the $\eta^1\text{-CO}_2^{-/2-}$ ligand undergoing double protonation to liberate H_2O and CO . Yet, the low-valent metal is not only Lewis basic but also Brønsted basic, and can instead react with H^+ to give a hydrido. On reduction, this complex can donate H^- to CO_2 , a pathway that gives HCO_2^- and eventually HCO_2H , at sufficiently low pH. A third pathway, identified in metalloporphyrin-catalyzed H_2 evolution, can also be operative. Here, the reduced metalloporphyrin is protonated not at the metal but at a *meso*-C atom to afford a phlorinato, which transfers H^- to CO_2 to give

HCO_2^- in a similar way to the hydrido. Göttle and Koper knew of these pathways and wondered why porphyrinato complexes of middle first-row metals (such as Fe and Co) make CO , while those of late metals (such as Ni and Cu) are biased towards making HCO_2^- . “The project was based on experimental findings in my group that the selectivity of immobilized metalloporphyrins in the electroreduction of CO_2 is very sensitive to the nature of the metal,” says Koper.

The team predicted ΔG values associated with porphyrinatometal complexes accepting H^+ and e^- to give either a hydrido or the tautomeric phlorinato, as well as the situation in which CO_2 is added into the mix when one of two further products can form either a metallacarboxylate or an isomeric formate. Göttle and Koper used thermodynamic cycles and the computational hydrogen electrode method, thereby eschewing the need to use a value for $G(\text{H}^+)$. The duo reasoned that a thermodynamic preference for one pathway can hint at a kinetic preference because exergonic reactions typically have smaller activation barriers than endergonic reactions (the Brønsted–Evans–Polanyi relation).

The ΔG value for a porphyrinato converting into a phlorinato is independent of the metal present, an intuitive result for a ligand-centred pathway. Satisfyingly, the identity of the metal is influential when substrates land there. Metallacarboxylate and hydrido formation is more exergonic for Fe or Co than for Ni or Cu, with the former (more basic) metals giving lower ΔG values. The propensity



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for Fe and Co porphyrinatos to give metallacarboxylates is consistent with their high selectivity for CO evolution. Hydrido and phlorinato complexes give HCO_2^- (or H_2 at low pH), and formate intermediates are not involved at all. Alternatively, porphyrinatos can undergo net hydrogenation to give chlorinato intermediates that are unreactive to CO_2 but evolve H_2 . Each intermediate forms through stepwise transfers, which contrast earlier studies predicting concerted proton-coupled electron transfers for heterogeneous catalysts, which operate through metallacarboxylate and formate species en route to CO and HCO_2H , respectively. For metalloporphyrins, “Future work will focus on finding further experimental evidence for the importance of the hydrido intermediate,” says Koper. Indeed, experiments on these simple metalloporphyrins will help us tease out the mechanisms at play and perhaps inform the design of more active species with desirable selectivity.

David Schilter

“electroreduction of CO_2 is very sensitive to the nature of the metal



ORIGINAL ARTICLE Göttle, A. J. & Koper, M. T. M. Determinant role of the electrogenerated reactive nucleophilic species on the selectivity during the reduction of CO_2 catalyzed by metalloporphyrins. *J. Am. Chem. Soc.* <https://doi.org/10.1021/jacs.7b11267> (2018)

FURTHER READING Costentin C. & Savéant, J. M. Towards an intelligent design of molecular electrocatalysts. *Nat. Rev. Chem.* **1**, 0087 (2017)