Catalyst that converts carbon dioxide to carbon monoxide in water

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The conversion of carbon dioxide to carbon monoxide requires a catalyst to prohibit the formation of an energetically unfavorable radical anion (CO$_2$$^-$$^-$$^-$). Iron porphyrins are a desirable candidate for a catalyst because the iron can be reduced from Fe(I) to Fe(0) using electrochemistry. Fe(0) can then bind with the unwanted radical anion intermediate, allowing for the production of carbon monoxide. However, porphyrins are not water soluble. Furthermore, acid promotes the catalytic reaction, but the presence of acid also risks the formation of hydrogen gas. The formation of carbon monoxide and hydrogen gas are competitive and therefore, the more hydrogen gas that is produced, the lower the product yield of carbon monoxide.

Prior studies showed that phenols are a good candidate for providing an acidic proton while not promoting the formation of hydrogen gas. The authors decided to incorporate phenol groups into the porphyrin structure. However, the phenol-modified catalyst was still insoluble in water. To overcome this, Costentin, et al. incorporated a para-substituted trimethylamine into the phenol groups. This final product is a water soluble modified porphyrin.

Cyclic voltammetry studies of their catalyst in the absence of CO$_2$ showed three waves, characteristics of iron's three oxidation states. The wave of interest is the one that represents the oxidation of Fe(I) to Fe(0). Fe(0) is necessary for catalyzing the CO$_2$-to-CO reaction. Cyclic voltammetry studies of the catalyst in the presence of CO$_2$ shows a large increase in current, indicating catalytic activity.
Cyclic voltammetric and preparative-scale electrolysis studies clarified the reaction mechanism and demonstrated the reaction's pH dependence. The first electrolysis study was over a four hour period in which CO₂ was added to an aqueous solution of the catalyst at -0.97 V vs. NHE. The pH was increased using KOH. The resulting products showed CO as the predominant product (90%) with a small amount of H₂ (7%) present, as well as other bi-products. A second study over a longer period of time but at potential of -0.87 V vs. NHE lead to a near-quantitative production of CO. Additional pH studies showed that at lower pH, more H₂ forms.

While additional kinetic studies need to be done, the authors believe that at neutral pH CO formation is competitively favored over the formation of H₂CO₃ which leads to H₂ production. While porphyrins typically catalyze H₂ production, the production of H₂CO₃ is energetically unfavorable and kinetically slow with this particular catalyst.

Finally, Costentin, et al. estimated overpotential and turnover frequency of their catalyst using methods that they had previously reported in which overpotential and turnover frequency are related to each other via a catalytic Tafel plot. These plots allow comparison and analysis of catalysts based on intrinsic chemical properties while also minimizing the effects of side reactions. Using a catalytic Tafel plot, they were able to estimate a maximum turnover frequency for their catalyst at 10⁷ s⁻¹. Additionally, Tafel plots that compare their catalyst with other catalysts in aprotic solvents showed that their modified porphyrin is the best catalyst for this reaction.

While additional studies need to be done to understand the mechanism involved, Costentin, et al. report a novel catalyst that is able to convert CO₂ to CO in near quantitative yields in a neutral aqueous environment. This finding is key step in the process of taking a renewable source, CO₂, and converting it into a usable energy source.

**More information:** "Efficient and selective molecular catalyst for the CO₂-to-CO electrochemical conversion in water" *PNAS*, DOI: 10.1073/pnas.1507063112