

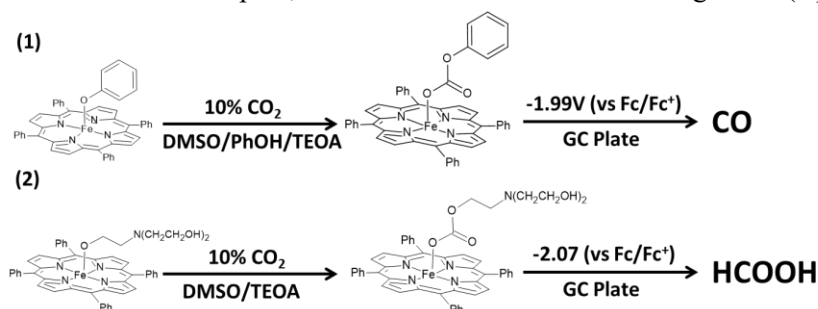
Electrocatalytic Reduction of Low Concentration CO₂ by Iron Porphyrins

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Transition Metal Complexes are one of the effectively utilized systems for the selective conversion of CO₂ with high efficiency, and most of these catalyst systems can function effectively under electrochemical and photochemical conditions. For the practical realization of these systems for the direct conversion of CO₂ in the flue gas, the catalyst should work under low concentrations of CO₂.¹ The Re(I) complexes with a deprotonated triethanolamine are efficient catalysts for direct reduction of low-concentration CO₂; the versatility of this system is attributed to the fast CO₂ insertion reaction to the Re-O bond.² However, considering the elemental strategy, we should identify other efficient catalysts based on earth-abundant elements that can work under low CO₂ concentrations.

Porphyrin complexes of iron are efficient catalysts for CO₂ reduction under electrochemical and photochemical conditions. Selective electrochemical reduction of CO₂ to CO is observed in most iron porphyrin-based catalyst systems under pure CO₂ atmosphere when a Brønsted acid is employed as an additive or prepositioned near the catalyst by ligand modification.³ In this report, we could successfully observe CO formation using the commercially available iron porphyrin catalyst Fe(III) tetraphenyl porphyrin (FeTPP), under 10% CO₂ concentration with a 91% faradic yield and 23 TON in the presence of phenol and TEOA (trace,) indicating the possibility phenyl carbonate formation with FeTPP-Phenol system (eq. 1). The formation of Fe-CO₂-OPh was confirmed using FTIR by observing the C=O stretching upon CO₂ bubbling to the FeTPP-OPh complex. Another aspect is the possibility of low-concentration CO₂ reduction in the presence of triethanolamine (TEOA); the reaction produced HCOOH as the major product with a 52% faradic yield and 12 TON, in this case also, the CO₂ inserted complex, Fe-CO₂TEOA was observed using FTIR (eq. 2).



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