Electrocatalysis Under Confinement: CO_2-Reduction with Molecular Catalysts Immobilized on Ordered Mesoporous Carbons

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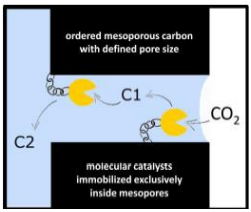
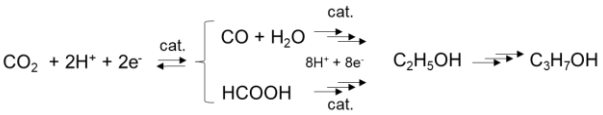
The goal of this work is to investigate confinement effects and maximize activity and selectivity for the formation of C_{2+} products using molecular catalysts tethered inside the pores of ordered mesoporous carbons (OMCs). Three primary confinement effects are studied: **1. Amplification of Intermediate Concentration:** Confined geometries enable further electron and proton transfers beyond the 2-electron reduction products CO and HCOOH (formic acid). **2. CO_2 "Over Solubility" in Confined Geometries:** Gas solubility increases in liquids confined within mesopores compared to bulk liquid.**3. Electrical Field Effects in Nanoconfined Electrolytes:** Changes in the electrical double layer and potential decay occur in the radial direction of the pores.

Metal porphyrinoid catalysts like iron porphyrin (Fe-por) and cobalt corrole (Co-cor) tethered inside OMC pores will be used to study and utilize confinement effects, focusing on intermediate amplification to control the product spectrum. Our study compares the performance of Fe-porphyrin as a molecular catalyst within OMC pores versus dissolved in electrolyte. Using an H-type cell setup, we investigated how this configuration impacts the electrochemical CO_2 reduction reaction (CO_2RR), emphasizing confinement engineering and tethered molecular catalysts in OMCs.





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