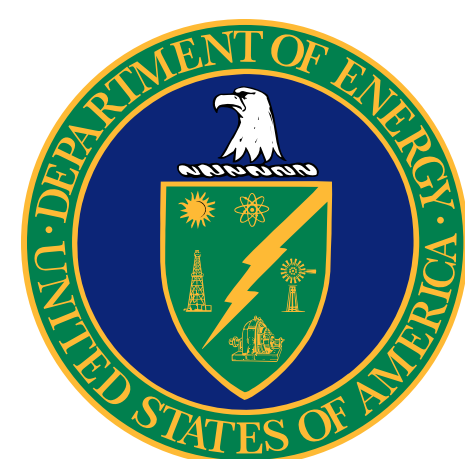


Managing Selective C-H Bond Formation with CO₂



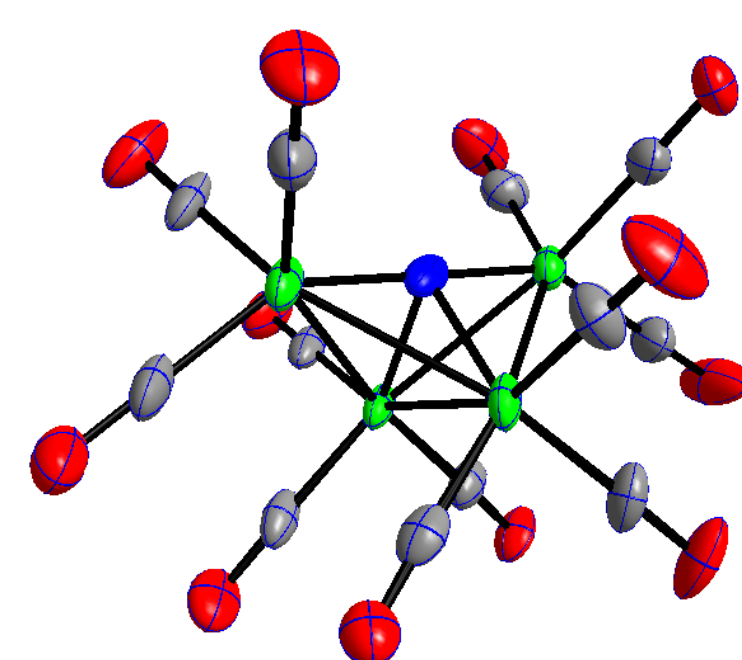
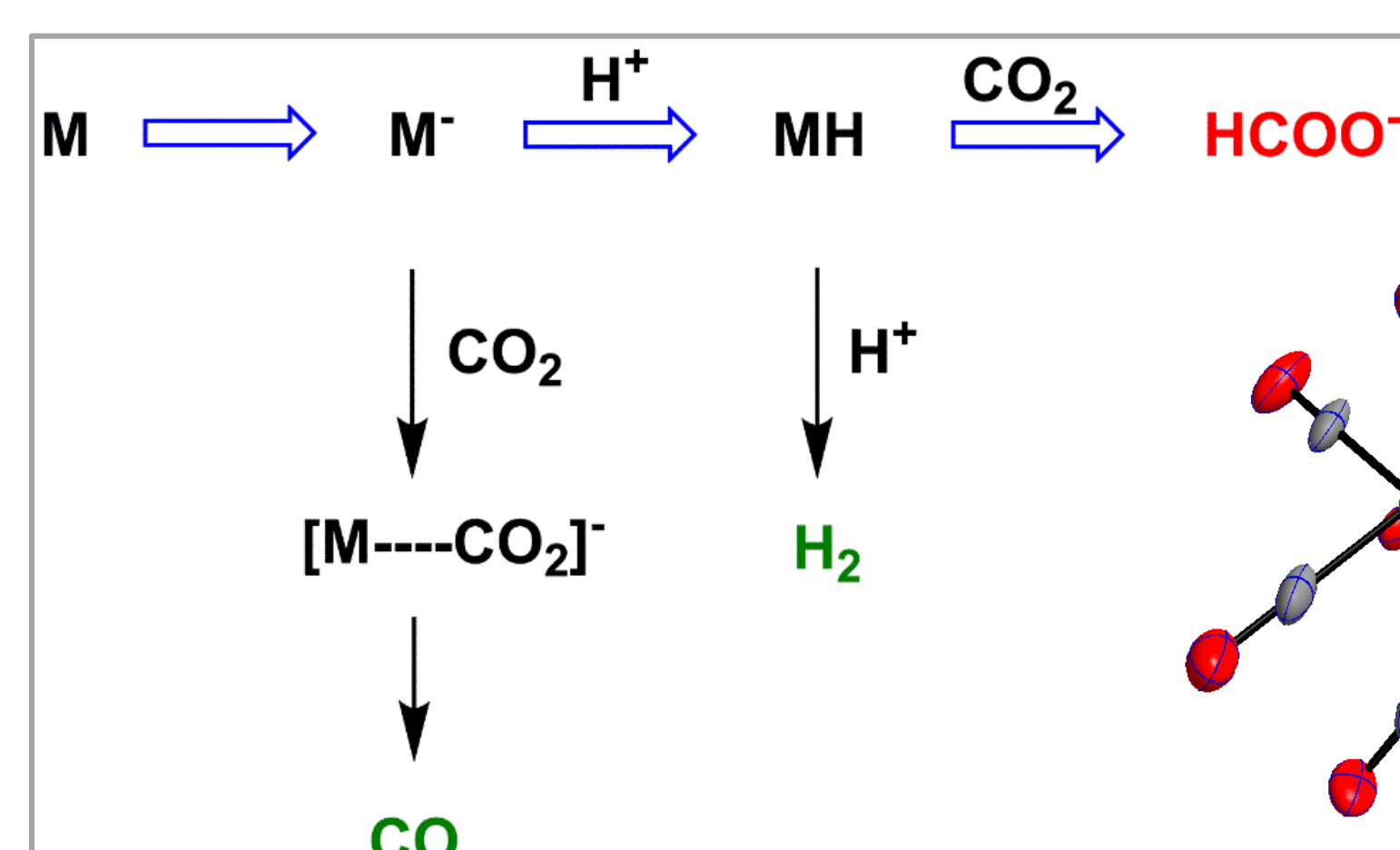
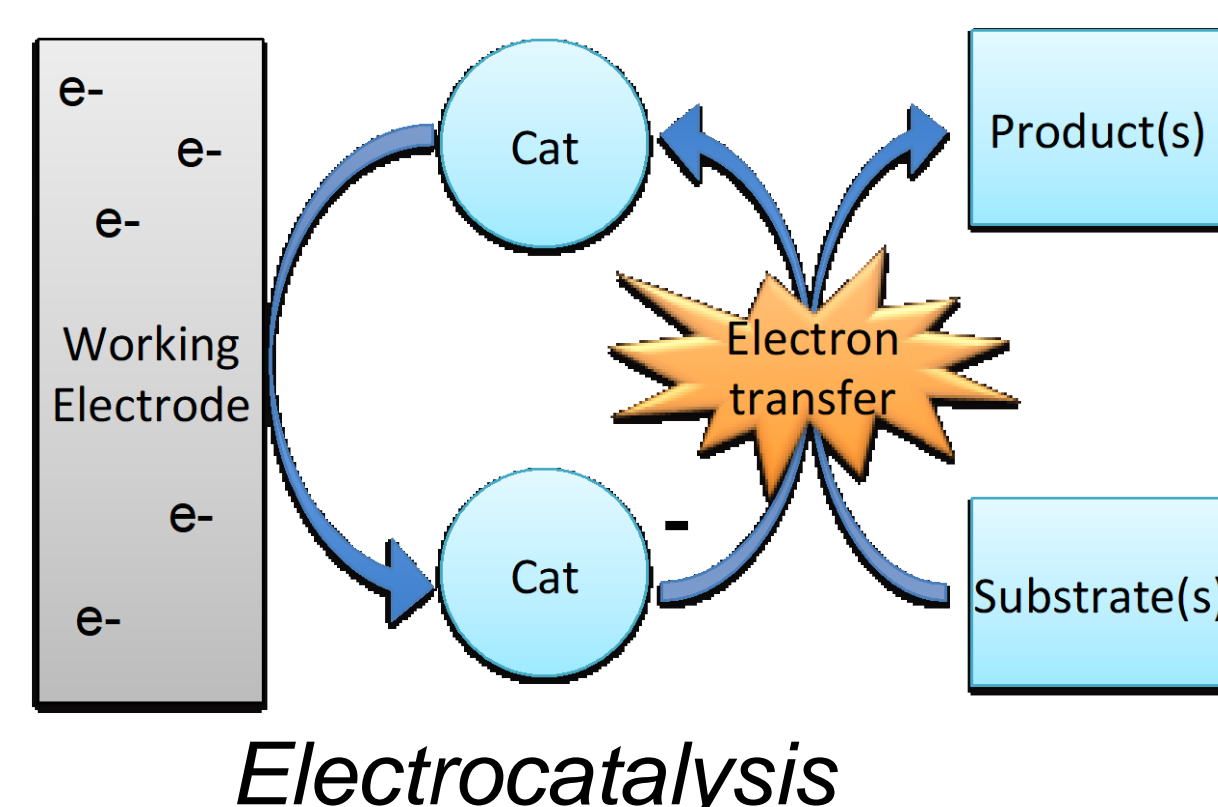
Louise A. Berben

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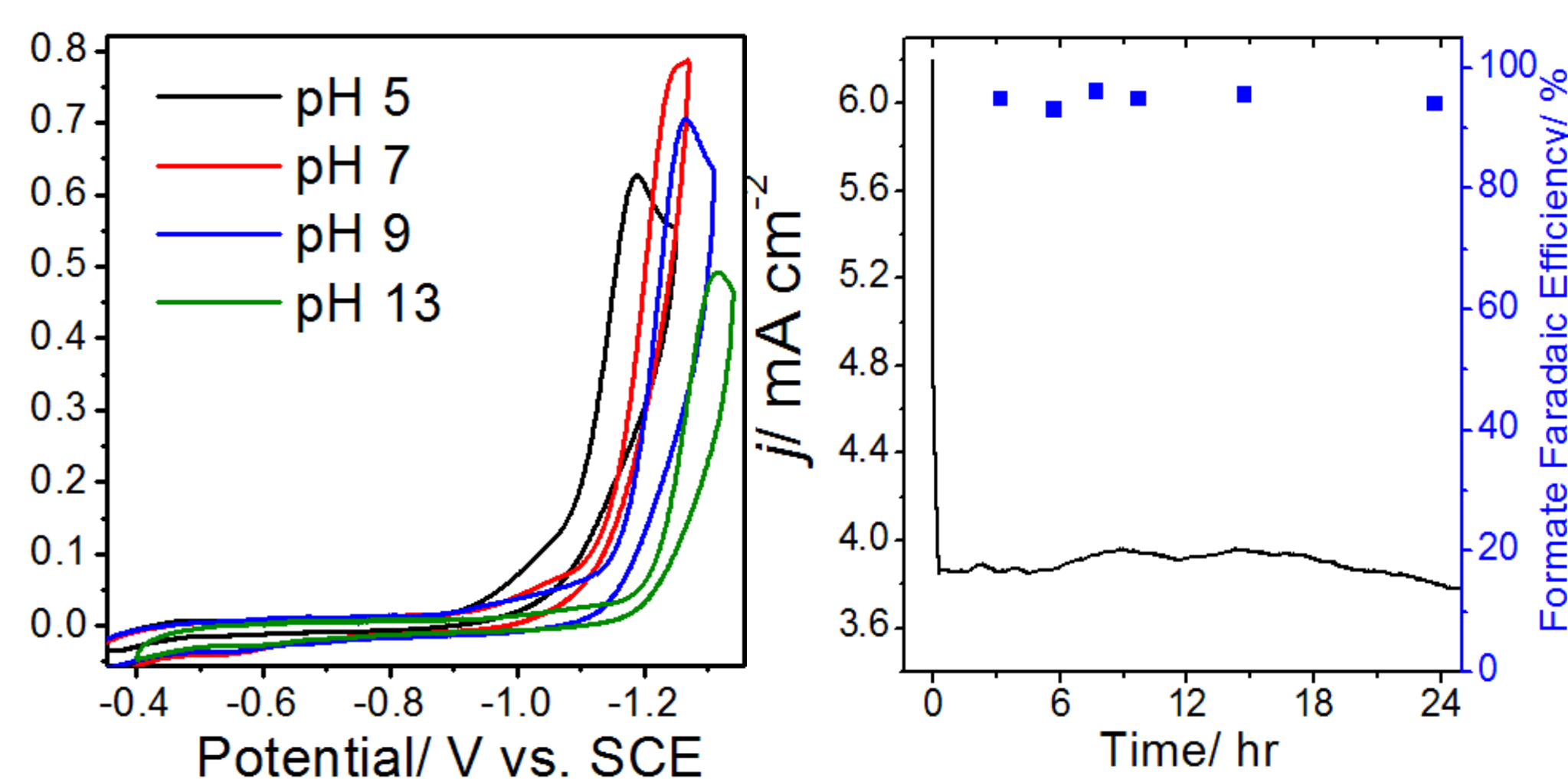
Introduction

- CO₂ reduction to formate, methanol, or methane promises **carbon neutral fuels**
- H₂, CO or HCOO⁻ formation are 2e-processes with similar energy input
- Both CO and H₂ formation are more likely when the catalyst is very reducing



- [Fe₄N(CO)₁₂]⁻ (**1**) catalyzes formate production with **96% efficiency** at pH 7 and -1.2 V vs. SCE ($\eta = 440$ mV)

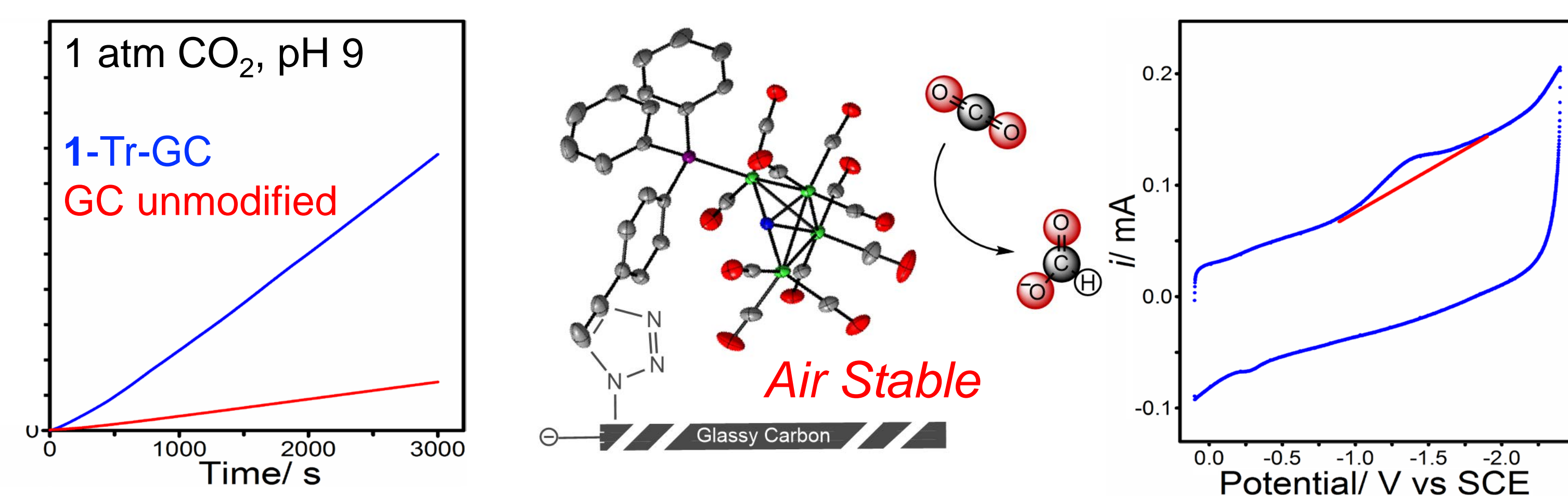
- Compared to highly selective heterogeneous catalysts, **1** has excellent FE, stability, and current density



(Left) Electrolysis plots showing superior catalyst performance at neutral pH (Right) Current density and formate produced over 24 hrs remained constant.

Homo/Heterogeneous Catalysis

- Heterogeneous catalysts allow easier product separation
- Surface coverage of 7.74×10^{-11} mol cm⁻² is ~50% of maximum theoretical value



- Under 1 atm CO₂, formate produced with 75% FE; 52,500 TON.
- Linear relationship between onset potential has $m \cong -59$ mV, suggesting proton-coupled electron transfer mechanism

References

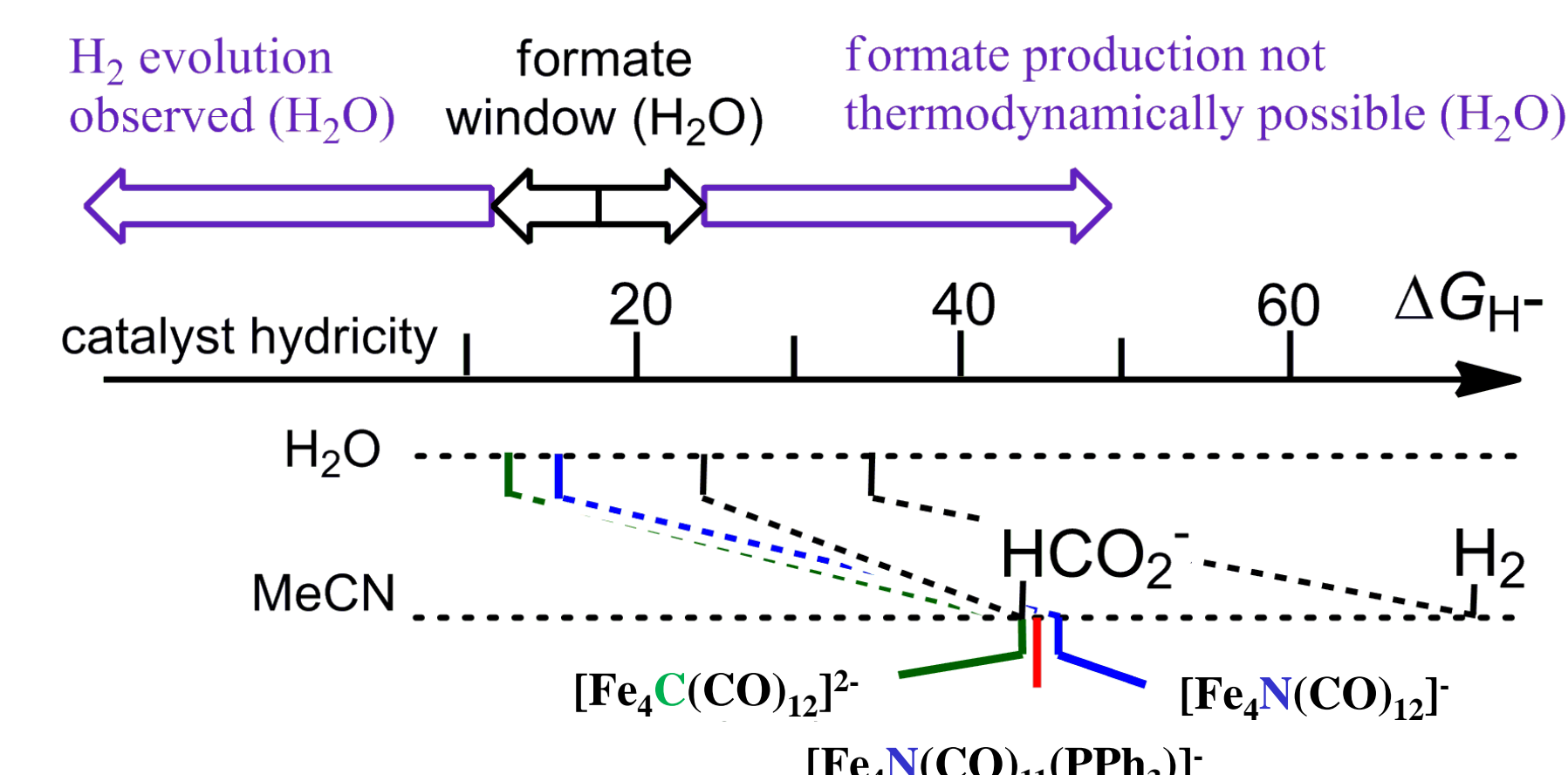
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Achieving Selective C-H Bond Formation

Thermodynamic Considerations:

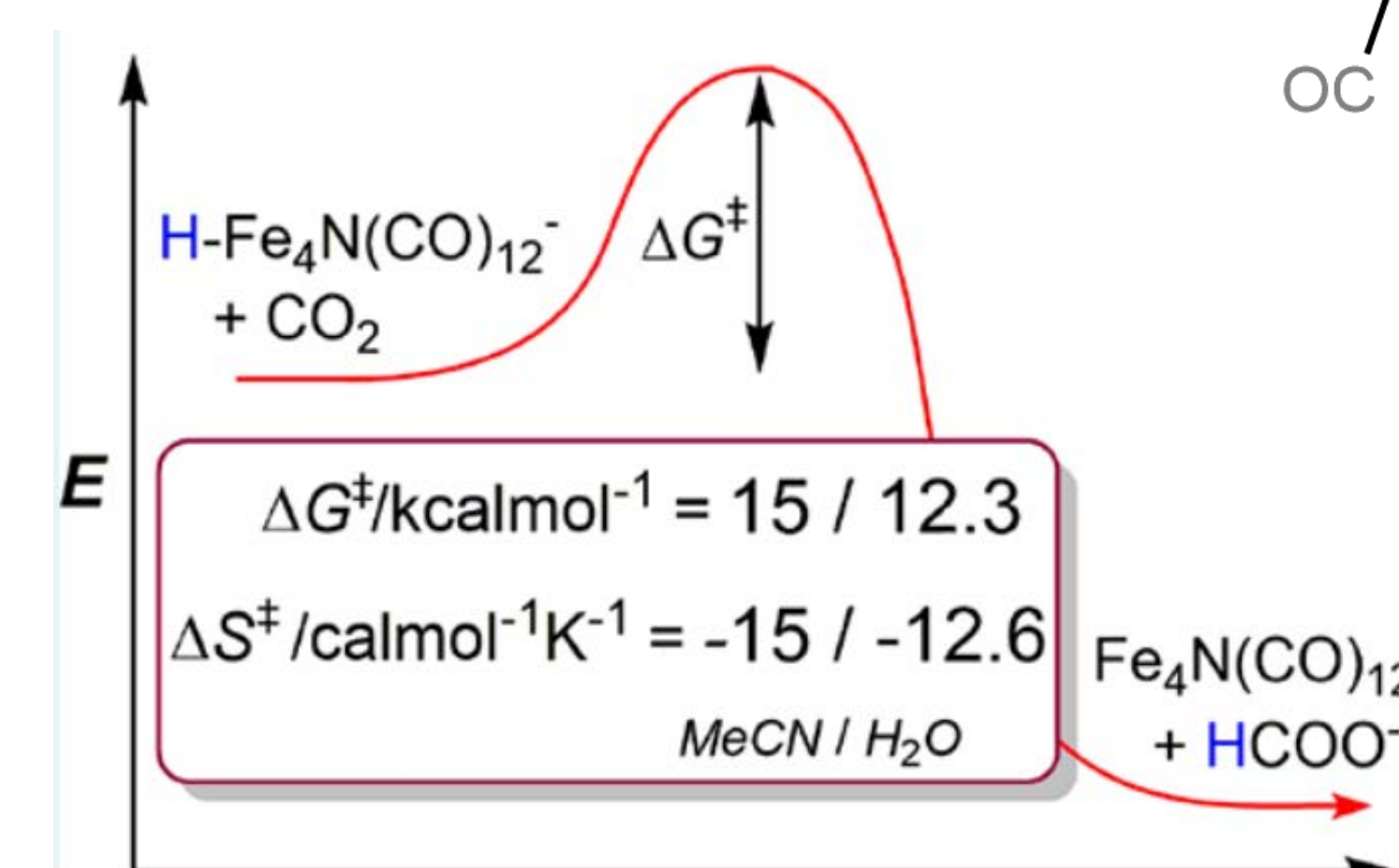
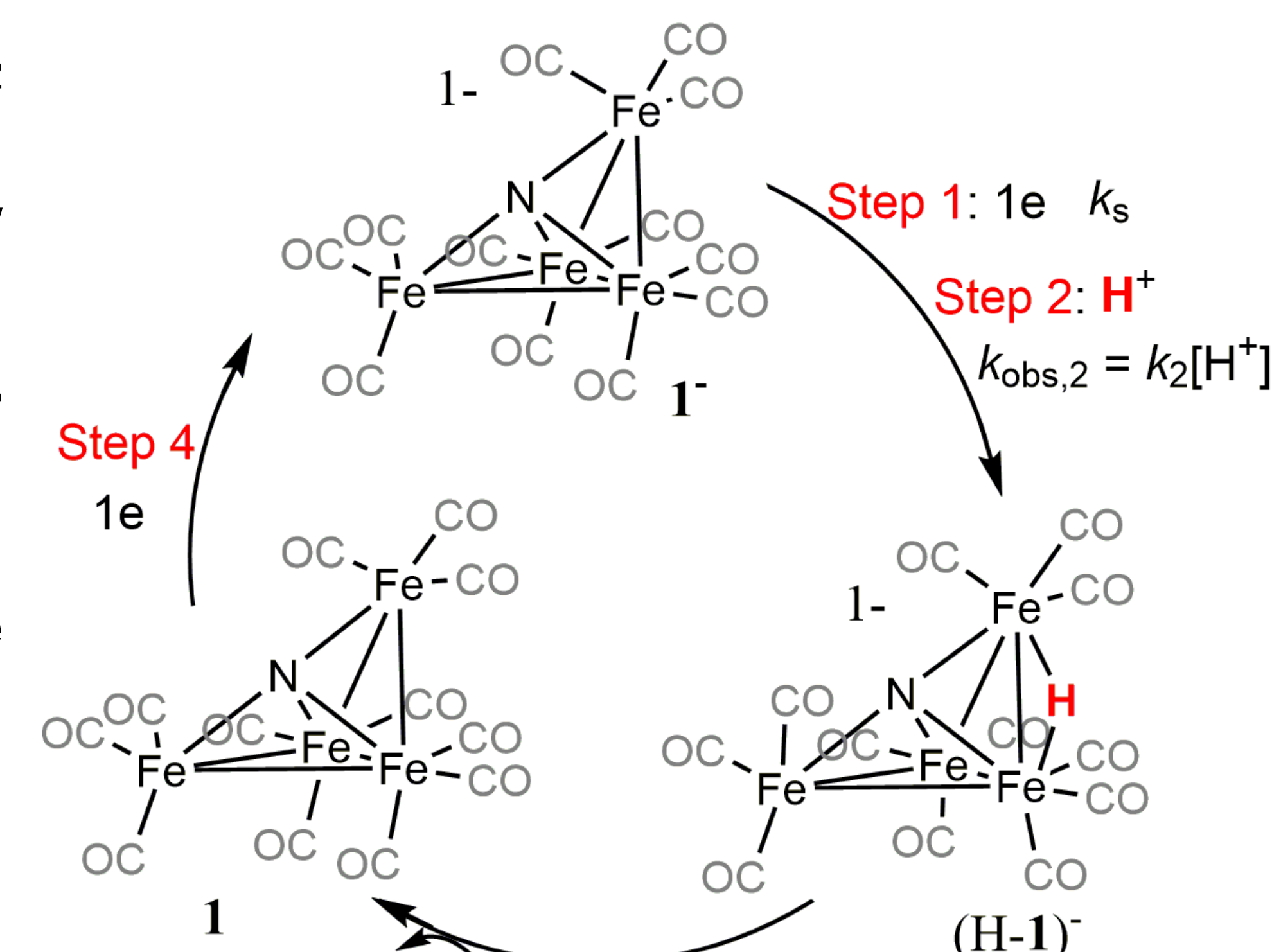


- Catalyst hydricity should be in the correct range to favor a product thermodynamically: H₂ vs HCOO⁻
- Catalysis may be low absent kinetic control



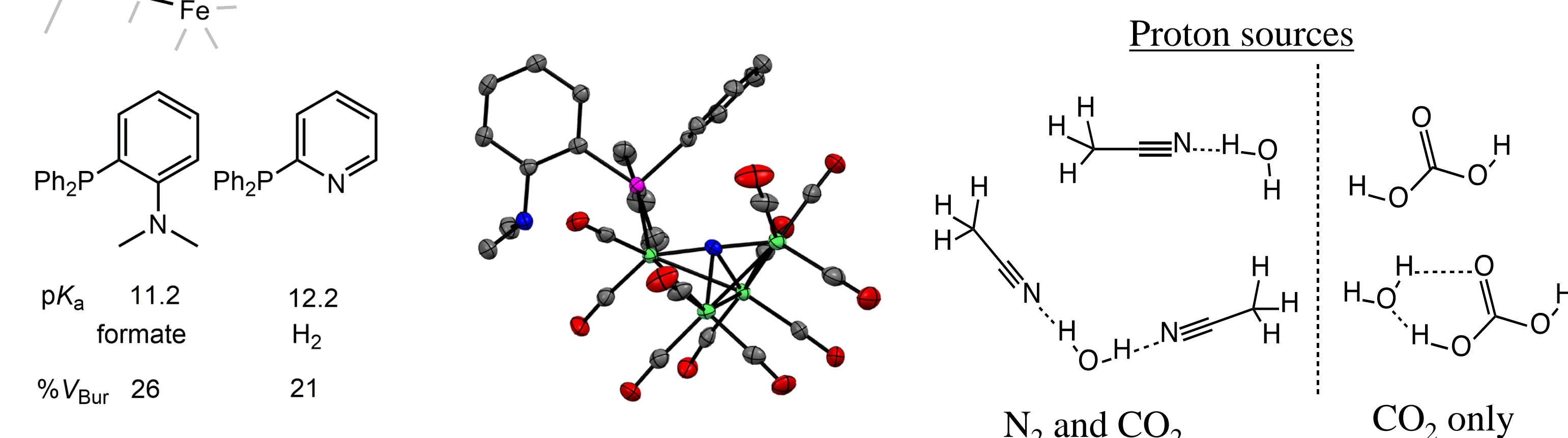
Kinetic Considerations:

- Hydride transfer to CO₂ (Step 3) is the RDS
- TOF limited by low solubility of CO₂ in H₂O
- Eyring analysis reveals an ordered transition state for hydride transfer
- Reaction more favorable in water



Tailoring the Proton Source:

- Steric effects around the catalyst active site can influence substrate transport.



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