Progress Towards the Synthesis of Iron Catalysts for CO_2 Reduction to Methanol

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Background

- Atmospheric CO_2 raising global temperatures, causing climate change[1]
- One way to reduce CO_2 levels while simultaneously creating a new renewable energy source is by reducing it to MeOH

Purpose

Sequester atmospheric carbon dioxide; use as a renewable energy source

$$CO_2 + H_2 \rightleftharpoons CH_3OH + H_2O \quad \textbf{(Eqn 1)}$$

Desired Catalyst Properties

- Produces MeOH selectively
- High TON at low temperature and pressure
- Sustainable preparation methods
- Utilizes inexpensive, abundant metals (as opposed to noble metal catalysts)

Current Methods

Noble Metal Catalysis

Pros: High efficiency
Cons: Expensive and unsustainable

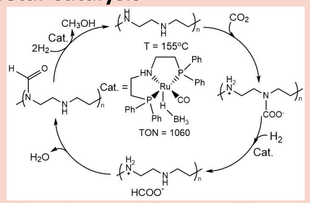


Figure 1. Established catalytic cycle for CO_2 reduction using noble metal.[2]

Non Noble Metal Catalysis

Pros: Low toxicity and high abundance
Cons: Low specificity and efficiency

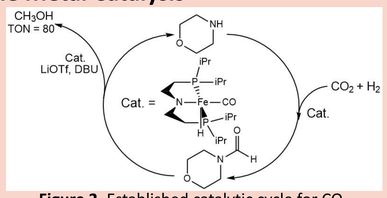


Figure 2. Established catalytic cycle for CO_2 reduction using non noble metal.[3]

Photochemical Reduction

Pros: Low toxicity and high abundance
Cons: Low efficiency and poor scalability

$$CO_2 + 2\,H^+ \xrightarrow[\text{Photoactivated}\ TiO_2/Ti_{(s)}]{H_2O} CH_3OH + O_2$$

Figure 3. Established photochemical CO_2 reduction.[4]

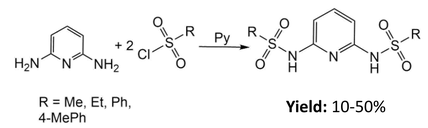
Electrochemical Reduction

Pros: Can achieve high specificity and energy efficiency
Cons: Specificity and efficiency are low unless noble metal catalysts are used at cathode

$$\text{Anode: } 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$
$$\text{Cathode: } CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$

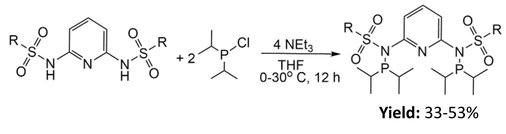
Figure 4. Half reactions for electrochemical CO_2 reduction.[5]

Ligand Synthesis



Yield: 10-50%

Scheme 1. Synthesis of pyridyl sulfonamide precursors.[6]



Yield: 33-53%

Scheme 2. Synthesis of PNP ligand derivatives.[7]

PNP Ligand Characterization

Increasing Electron Donation

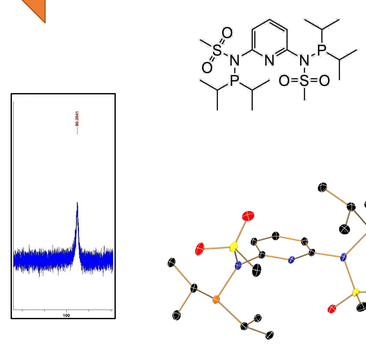


Figure 5. Synthesized PNP ligand (R=Me). Crystal structure, Chem Drawing depiction, and ^{31}P-NMR spectral data.

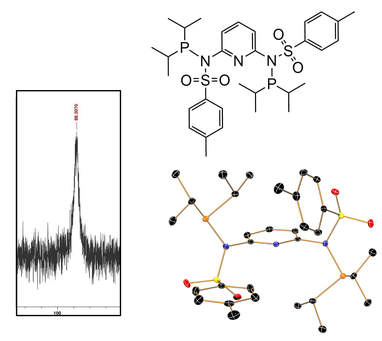
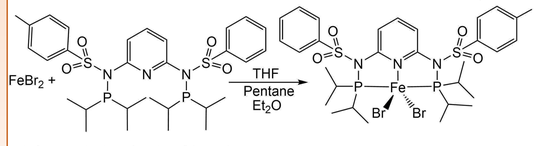


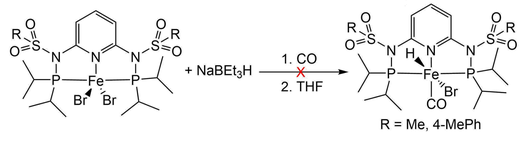
Figure 6. Synthesized PNP ligand (R=Tol). Crystal structure, Chem Drawing depiction, and ^{31}P-NMR spectral data.

- Broad ^{31}P-NMR signal indicates slow exchange barrier on NMR timescale
- Different rotamers indicate hindered rotation about N-P bonds
- Future work will include variable temperature NMR spectroscopy to determine rotation barrier value

Metalation to Iron



Scheme 3. Synthesis of (PNP)$FeBr_2$.



Scheme 4. Attempted synthesis of (PNP)FeBrHCO complex.

- Yellow solid obtained, consistent with similar examples from Kirchner group
- ^{1}H NMR spectral data supports a paramagnetic Fe(II) complex
- Future work will include synthesis of (PNP)Fe(H)(Br)(CO) complex and comparison of catalytic properties with literature complexes

Conclusions

- Synthesized and characterized pyridyl sulfonamide precursors and PNP ligands with electron donating and withdrawing groups
- Synthesized and characterized new (PNP)$FeBr_2$ complex

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