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A Ni^{II} Complex Electrocatalyst for CO₂ Reduction and H₂ Evolution

Alyssa Sam

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Introduction

Carbon dioxide reduction and hydrogen evolution show promise in addressing increased green house gas emissions (especially CO₂) and energy shortage. This is accomplished by reducing carbon dioxide to fuel compounds, forming a system to recycle greenhouse gases, and by producing hydrogen gas from water with potential as an alternative fuel. Most common catalysts are made of expensive and precious metals as compared to cheap and abundant Ni. A N-tetradentate ligand dapbpy was synthesized and combined with Ni^{II} to get a Ni^{II}(dpabpy)(BF₄)₂ complex. The Ni^{II} complex was used as an electrocatalyst for selective CO₂ reduction and H_2 evolution.



Figure 1 – CV Curves, UV-vis Absorption

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v (m	0 •
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Inte	-50 -
rent	-75 -
Cul	-100 -

(A) CV curves of Ni^{II} complex with/without CO₂ and H₂O. (B) UV-vis absorption of Nⁱ complex in the absence (black)/presence (red) of CO₂.

Results and Discussion

The Ni^{II}(bpabpy) $(BF_4)_2$ complex was synthesized as shown in **Scheme 1**. The structures of the products were confirmed by NMR and single crystal X-ray diffraction. The electrochemical study of the Ni^{II} complex showed a reversible Ni^{II}/Ni^I redox peak at -1.09 V (vs. Fc^{+/0}) under N_2 .

In the presence of CO_2 , the Ni^{II}/Ni^I peak turned to irreversible. In the presence of H_2O , the typical CO_2 reduction peak, at -2.24 V (vs. Fc^{+/0}), signal was remarkably enhanced (Figure 1a). The UV-vis absorption shows the coordination of CO₂ to Ni¹ complex.

Scheme 1- Synthesis of Ni^{II}(bapbpy)(BF₄)₂



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GC and NMR were used to confirm that CO is the only product for the CO_2 reduction. In the presence of 5 mM of H_2O , CO_2 was selectively reduced to CO with 57% Faradaic efficiency, further increase of the concentration of H₂O showed a remarkable H₂ evolution reaction and the selectivity of CO formation was decreased. As shown in **Figure 2**, in the presence of acid, the proton reduction peaks were increased for more than 20 times. To our surprise, in the case of 2,4- $Cl_2PhNH_3^+$, there is a super-low overpotential for the H₂ evolution (only 0.04 V) with 239 s⁻¹ TOF.





 $Ni(MeCN)_6(BF_4)$ MeCN, rt





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Figure 2 – H₂ Evolution with Acids — 1.0 mM Potential (V, vs $Fc^{+/0}$) (a) -0.25 -

 $CV(a) PhNH_3BF_4$, (b) $CNPhNH_3BF_4$, (c) 2,6- $CI_2PhNH_3BF_4$, (d) 2,4- $Cl_2PhNH_3BF_{4.}$

Conclusion

In conclusion, a Ni^{II} complex with a N-tetradentate ligand bapbpy was prepared as a catalyst for CO_2 reduction and H_2 evolution. In the presence of 5 mM H₂O, the Ni^{II} complex showed good selectivity and efficiency for CO formation. The Ni^{II} complex also showed a very low overpotential and high efficiency for the H₂ evolution.

Table 1- H₂ Evolution Overpotential (OP) and Turnover Frequency (TOF) with Acid

Acid	OP (V)	TOF (s ⁻¹)
PhNH ₃ BF ₄	0.17	140
CNPhNH ₃ BF ₄	0.39	195
2,6-Cl ₂ PhNH ₃ BF ₄	0.36	179
2,4-Cl ₂ PhNH ₃ BF ₄	0.04	239





Ni(dpabpy)(MeCN)₂(BF₄)₂