

Exploration of heterobimetallic complexes for electrocatalytic CO₂ reduction

CO₂ emissions have led to serious greenhouse effects and climate change.^{1,2} In this regard, scientists have been working to convert CO₂ into value-added products as an abundant and inexpensive carbon source for the chemical industry.³ Although there are some classes of molecular catalysts known to convert CO₂, none rival the rate and catalytic efficiency for the reversible reduction to CO by the enzyme *Ch* Ni-CODH II (Figure 1),⁴⁻⁶ which consists of a Ni and a proximal Lewis acidic Fe. There is evidence that redox-inactive Lewis acidic metals proximal to a redox-active metal center can increase CO₂ reactivity by shifting reduction potentials to milder values.⁷⁻⁹ Additionally, excess alkali cations in solution are known to enhance catalytic processes by stabilizing electron-rich intermediates.¹⁰⁻¹⁴

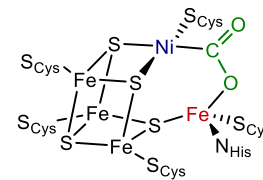


Figure 1. Active site of reduced *Ch* Ni-CODH II in the presence of CO₂. (Adapted from reference 5)

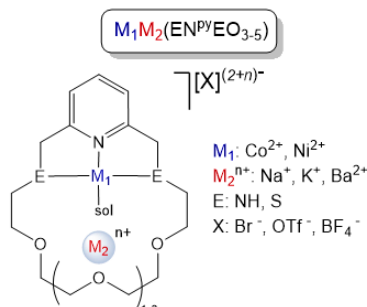


Figure 2. Proposed $M_1M_2(ENP^yEO_{3-5})$ heterobimetallic complexes.

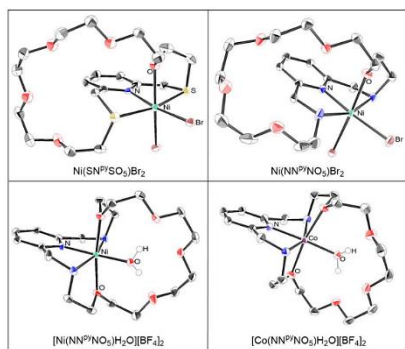


Figure 3. Solid state structure of **1, 2, 4** and **5**. Thermal ellipsoids are drawn to 80% probability. Hydrogen atoms (except for those bound to water) have been omitted for clarity.

To understand heterobimetallic systems for CO₂ activation, a modular ligand framework with crown ether moieties was explored, we report the synthesis and characterization of two ligands (Figure 2). It was possible the synthesis of a series of Co and Ni complexes [Ni(NNP^yNO₅)H₂O][BF₄]₂(**1**), [Co(NNP^yNO₅)H₂O][BF₄]₂(**2**), Ni(NNP^yNO₅)Br₂(**3**), [Ni(SNP^ySO₃)H₂O][BF₄]₂(**4**), [Ni(SNP^ySO₃)H₂O][BF₄]₂(**5**) and Ni(SNP^ySO₃)Br₂(**6**), as well as their characterization, including XRD (Figure 3). **1-6** were employed for CO₂ electroreduction in presence of Lewis acids; this study was held by using cyclic voltammetry, control potential electrolysis, and GC-MS⁺ to detect CO as a product, and determine overpotential, faradaic efficiency, and kinetics, (Figure 4).

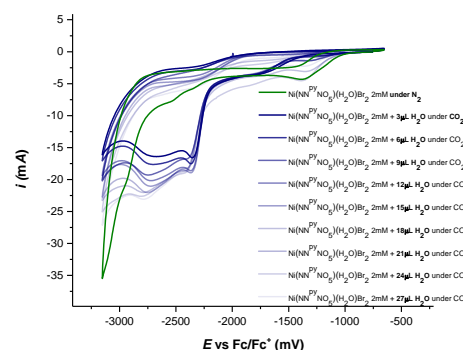


Figure 4. Cyclic voltammetry experiments for CO₂ reduction to CO, using 2 mM of **3**. Electrolyte TBAPF₆ 0.1 M, in acetonitrile, scan rate 100 mV s⁻¹.

References

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