Chem Catalysis

CellPress

Preview

Leveraging intramolecular electrostatics to boost electrocatalytic CO_2 reduction

David S. Tresp[1] and Demyan E. Prokopchuk[1,*]

In a recent issue of *Chem Catalysis*, McCrory et al. present bimetallic CO_2 reduction reaction (CO_2RR) electrocatalysts. They demonstrate that a heterometallic molecular Co-Zn catalyst, with each metal nestled into a separate pyridyldiimine ligand pocket, operates faster and more efficiently than the Co-Co analogue, emphasizing the importance of electrostatics in multimetallic electrocatalysts.

The conversion of CO_2 to value-added products is a thriving field, especially as greenhouse gases continue to build up in our atmosphere and raise the average global temperature. A particularly promising direction to address this challenge is by using Earth-abundant metal electrocatalysis to reduce CO_2 into valuable C_n products. For instance, the heterogeneous reduction of CO_2 directly on copper metal in aqueous solutions can result in the formation of important commodity chemicals like ethylene and ethanol, but product selectivity is an ongoing challenge. (Figure 1A)[1,2]

Moving from heterogeneous to homogeneous organometallic electrocatalysts allows for increased selectivity toward value-added products such as carbon monoxide (CO) and formic acid (HCO_2H), the formation of which is highly pH dependent.[5–8] Homogeneous catalysts are not often industrially relevant and are more frequently used as models to parse mechanistic minutiae of heterogeneous catalyst systems, allowing for the rational design of nanomaterials as well as multilayer assemblies of catalysts upon electrode surfaces.[9,10] Thus, the study of molecular electrocatalysts represents a promising way forward for bulk reduction of CO_2 to synthesize useful feedstock chemicals such as CO. Thus, this preview describes high-performance bimetallic molecular electrocatalyst systems for the reduction of CO_2 to CO, as found in a recent issue of *Chem Catalysis* (Figure 1A).[3]

To contextualize the findings in the article by McCrory et al., it is helpful to examine Nie, Tarnopol, and McCrory's previous work on modifying a mono-cobalt pyridyldiimine (Co(PDI)) electrocatalyst framework (Figure 1B).[3,4] In their previous work, McCrory and co-workers expanded the conjugation of the PDI ligand by attaching a phenyl group in the *para* position on the pyridine donor. Moreover, they attached a *para*-pyridyl group to expand conjugation and explore how electron withdrawing effects influence electrocatalysis (Co(PDI-Py)). Finally, they synthesized an analogue with a N-methylpyridinium moiety that adds an electrostatic component to the system (Co(PDI-PyMe$^+$I$^-$). Comparing each complex as CO_2RR electrocatalysts, the order of activity is as follows: Co(PDI) < Co(PDI-Ph) < Co(PDI-Py) < Co(PDI-PyMe$^+$I$^-$). For Co(PDI-PyMe$^+$I$^-$), the observed rate constant (k_{obs}) is 9.4×10^4 s^{-1} for the electrocatalytic reduction of CO_2 to CO in acetonitrile/water, making it one of the most active CO_2RR electrocatalysts at the time of publication.[4] This elegant study showed that increased ligand conjugation, electron withdrawing groups, and addition of a positive charge to the ligand scaffold collectively increase the electrocatalytic activity for CO_2RR.

In a recent issue of *Chem Catalysis*, McCrory et al. synthesize the dicobalt complex Co(PDI)-(PDI)Co and heteto-bimetallic complex [Zn(PDI)-(PDI)Co], which are tethered together through a rigid aryl-aryl bond on the pyridyl ring (Figure 1C). They go on to study these molecules via cyclic voltammetry (CV), observing that [Co(PDI)-(PDI)Co] shows sequential reduction events at each Co center, suggestive of electronic coupling between the two cobalt centers facilitated by the conjugated pyridines. They show that there is no such electronic coupling in the [Zn(PDI)-(PDI)Co] complex, rationalizing that the Zn(PDI) moiety adds a new dimension of electrostatic control to the system.

Examining CVs of their monometallic, homobimetallic, and heterobimetallic complexes in the cathodic direction under N_2, they report sequential redox processes assigned to $Co^{3+/2+}$, $Co^{2+/+}$, and PDI/PDI$^{\bullet-}$ in acetonitrile solvent. When the complexes are placed under CO_2 with no proton sources present, they see current enhancement at or beyond the electrochemical event assigned to the PDI ligand, indicating that the final ligand-based reduction event initiates a catalytic reaction with CO_2.[4] The peak catalytic current under CO_2 dramatically increases for each complex, with the Zn-Co complex exhibiting the greatest response. To measure kinetics under a concentration-independent

[1]Department of Chemistry, Rutgers University-Newark, 73 Warren St, Newark, NJ 07102, USA

*Correspondence: demyan.prokopchuk@rutgers.edu

https://doi.org/10.1016/j.checat.2024.101053

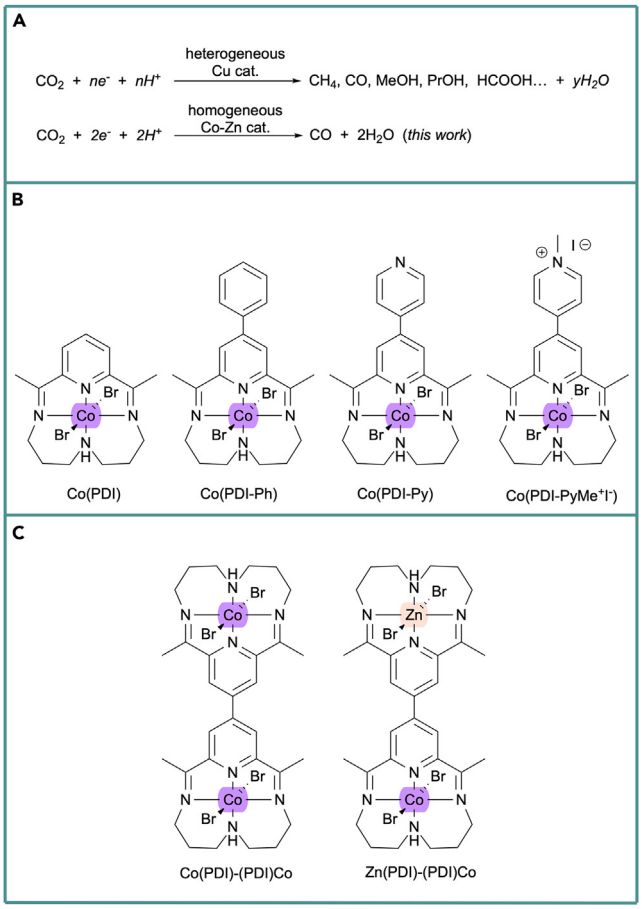

Figure 1. CO_2 reduction electrocatalysis

(A) Catalysis with heterogeneous copper catalysts and a homogeneous Cu-Zn system for the reduction of CO_2 to CO described in this preview.[3]

(B) Previously published Co electrocatalysts with *para*-pyridyl modification.[4]

(C) Covalently linked homobimetallic and heterobimetallic electrocatalysts synthesized by McCrory et al. in a recent issue of *Chem Catalysis*.[3]

proton regime, they use an 11-mol/L concentration of water as their standard conditions for catalysis. The kinetic parameters for each complex are impressive, with the fastest being the Zn-Co bimetallic complex (k_{obs} of 3.3 × 10^5 s^{-1}), nearly an order of magnitude larger when compared to the previously reported Co(PDI-PyMe$^+$I$^-$) system.[4] To examine catalyst stability, controlled potential electrolysis (CPE) experiments are performed with each complex, enabling them to measure the volume of gaseous products evolved and determine the Faradaic efficiency of these electrocatalysts. Each system evolves CO gas, with Zn(PDI)-(PDI)Co exhibiting the highest Faradaic efficiency (95.2% ± 3.0%) under a CO_2 atmosphere.

The authors also performed several experiments to elucidate the speciation of their electrocatalysts. After CPE experiments, the electrode surface was examined by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) to determine the elemental composition of any deposits formed on the electrode surface throughout the experiment. In concert, dynamic light scattering was used on the electrolyte solution to examine the size and presence of any nanoparticle suspensions. Both experiments confirmed that some degree of degradation occurred, with the most Co deposition and the largest nanoparticles forming during CPE with the monometallic Co(PDI) complex. Reusing electrodes from previous CPE experiments without the addition of exogenous Co complexes resulted in no CO_2RR, confirming that electrocatalysis is indeed being performed by solution-phase species and not electrodeposited product(s) on the electrode surface.

To ensure that their electrocatalytic activity depends on the presence of cobalt, the authors synthesized the monozinc analogue, Zn(PDI), and the homometallic Zn(PDI)-(PDI)Zn. Both complexes are inactive for CO_2RR, and equimolar mixtures of Zn(PDI) and Co(PDI) were not as active as the Zn(PDI)-(PDI)Co. Similarly, a mixture of the Zn(PDI)-(PDI)Zn and the Co(PDI)-(PDI)Co was also not as active as the Zn(PDI)-(PDI)Co, cementing the fact that proximal Zn^{2+} is essential to improve catalytic activity.

This methodical analysis of synergistic electrostatic effects in molecular electrocatalysis by McCrory et al. has broad implications in the field of CO_2RR with Earth-abundant metals, suggesting that inclusion of proximal redox-inert moieties into multidimensional heterogeneous catalyst architectures such as COFs and MOFs might dramatically enhance their electrocatalytic performance.

ACKNOWLEDGMENTS

This work was generously funded by the National Science Foundation (2055097) and a startup grant from Rutgers University-Newark.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Nitopi, S., Bertheussen, E., Scott, S.B., Liu, X., Engstfeld, A.K., Horch, S., Seger, B., Stephens, I.E.L., Chan, K., Hahn, C., et al. (2019). Progress and Perspectives of

Electrochemical CO2 Reduction on Copper in Aqueous Electrolyte. Chem. Rev. *119*, 7610–7672. https://doi.org/10.1021/acs.chemrev.8b00705.

2. Savéant, J.M. (2008). Molecular Catalysis of Electrochemical Reactions. Mechanistic Aspects. Chem. Rev. *108*, 2348–2378. https://doi.org/10.1021/cr068079z.

3. Zhou, J., Nie, W., Tarnopol, D.E., and McCrory, C.C.L. (2024). Co-Co and Co-Zn Bimetallic Complexes for Electrocatalytic CO2 Reduction: The Role of Interrelated Intramolecular Effects on Activity. Chem Catalysis *4*, 101006.

4. Nie, W., Tarnopol, D.E., and McCrory, C.C.L. (2021). Enhancing a Molecular Electrocatalyst's Activity for CO2 Reduction by Simultaneously Modulating Three Substituent Effects. J. Am. Chem. Soc. *143*, 3764–3778. https://doi.org/10.1021/jacs.0c09357.

5. Kinzel, N.W., Werlé, C., and Leitner, W. (2021). Transition Metal Complexes as Catalysts for the Electroconversion of CO2: An Organometallic Perspective. Angew. Chem. Int. Ed. *60*, 11628–11686. https://doi.org/10.1002/anie.202006988(acccessed2024/06/09.

6. Saha, P., Amanullah, S., and Dey, A. (2022). Selectivity in Electrochemical CO2 Reduction. Acc. Chem. Res. *55*, 134–144. https://doi.org/10.1021/acs.accounts.1c00678.

7. Gonell, S., and Miller, A.J.M. (2018). In Advances in Organometallic Chemistry, *70*, P.J. Pérez, F.G.A. Stone, and R. West, eds., Advances in Organometallic Chemistry (Academic Press), pp. 1–69.

8. Barlow, J.M., and Yang, J.Y. (2019). Thermodynamic Considerations for Optimizing Selective CO2 Reduction by Molecular Catalysts. ACS Cent. Sci. *5*, 580–588. https://doi.org/10.1021/acscentsci.9b00095.

9. Franco, F., Rettenmaier, C., Jeon, H.S., and Roldan Cuenya, B. (2020). Transition metal-based catalysts for the electrochemical CO2 reduction: from atoms and molecules to nanostructured materials. Chem. Soc. Rev. *49*, 6884–6946. https://doi.org/10.1039/D0CS00835D.

10. Lei, K., and Yu Xia, B. (2022). Electrocatalytic CO2 Reduction: from Discrete Molecular Catalysts to Their Integrated Catalytic Materials. Chemistry – A European Journal *28*, e202200141. https://doi.org/10.1002/chem.202200141.