Catalyst design for bidirectional CO_2 hydrogenation & formic acid dehydrogenation using Ir complexes

Glenn Blade Literature Seminar December 6, 2022

As carbon dioxide concentrations in the atmosphere continue to rise and climate change becomes an imminent threat, alternative fuels that do not contain carbon are important to study. Hydrogen (H_2) as a fuel has seen a renewed interest recently, but logistic issues still bar it from being a viable alternative to carbon-based fuels, including issues with safe storage and transport, high desorption energy, and low volumetric energy density. A potential solution for these problems could be the use of liquid hydrogen carriers (LHCs) as H_2 storage media.[1] By making use of a catalytic cycle by alternating between a hydrogen rich species and a hydrogen lean species, LHCs can be referred to rechargeable chemical hydrogen batteries (Fig. 2B).[2] As such, many have attempted to design catalysts that can efficiently perform this bidirectional hydrogenation-dehydrogenation (BHD) chemistry on various LHCs, including formic acid. As compared to other hydrogen storage media, FA has a high hydrogen density (4.4 wt %) and can be dehydrogenated with lower energy consumption due to the exergonic nature of the reaction (Fig. 2A).[3,4]

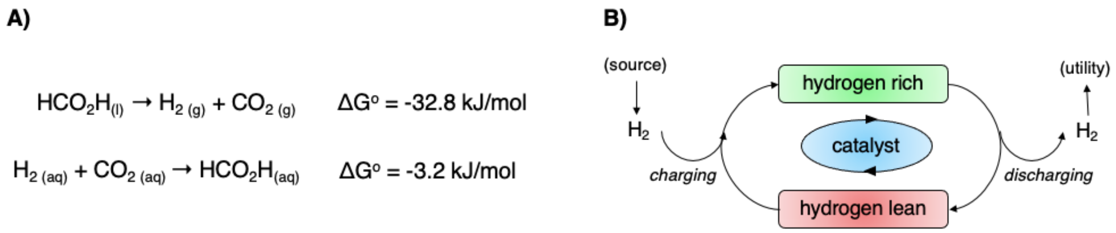

Figure 1. (A) Free energy for dehydrogenation of formic acid and aqueous hydrogenation of CO_2. (B) Liquid hydrogen carriers (LHCs) as chemical hydrogen batteries (adapted from Maji, et al.)

While many catalysts have been developed for BHD catalysis with FA, most still require the use of organic solvents, organic additives, or harsh conditions including high pressure and temperature.[4,-7] Designing effective catalysts for aqueous BHD of formic acid relies on several features of the ligands used, including: strong electron-donation, secondary coordination sphere effects, and water solubility. Strongly electron-donating ligands, particularly anionic donors like deprotonated amides have been shown to enhance catalytic activity of Ir complexes by increasing electron density on the metal center.[3] Electron-donation of the ligand can also be enhanced by adding proton-responsive substituents such as hydroxyl groups to the ligand backbone. Furthermore, secondary coordination sphere effects have been observed in Ir catalysts before, where certain substituents on the ligand can stabilize reactive intermediates in the catalytic cycle.[6]

Kanega and coworkers presented a series of Cp*Ir catalysts with various picolinamidate ligands that featured different substituents on both the amide-N and pyridine ring.[3] By analyzing the CO_2 hydrogenation ability of the various Ir catalysts under both pressurized (1.0 MPa) and ambient (0.1 MPa) conditions, the authors were able to ascertain the effects of ligand structure on catalytic activity. Across the board, the picolinamidate ligand-containg Ir complexes performed better than other complexes evaluated, including those with pyridiyl-imidizoline, picolinic acid, or

2-pyridinethioamide ligands. Catalytic activity was further enhanced by adding substituents like phenyl groups to the amide-N or hydroxyl groups to the pyridine ring in either the ortho- or para-positions, like in IrL12 (Fig. 2A). IrL12 also performed exceptionally well under ambient conditions, with a TOF of 198 h^{-1}. A number of five-membered N-heterocycles with amide moieties were also evaluated, where it was found that substituting a pyridine with an imidazole also gave high TOF values (IrL16, Fig. 2A). Mechanistic studies involving both DFT and experimental evidence were also performed. The authors asserted that the CO_2 hydrogenation goes through direct hydrolysis to form an Ir hydride intermediate. Experimental evidence supported this claim, as they were able observe the Ir-H intermediate both in the ^1H-NMR spectrum and characterizing it crystallographically.

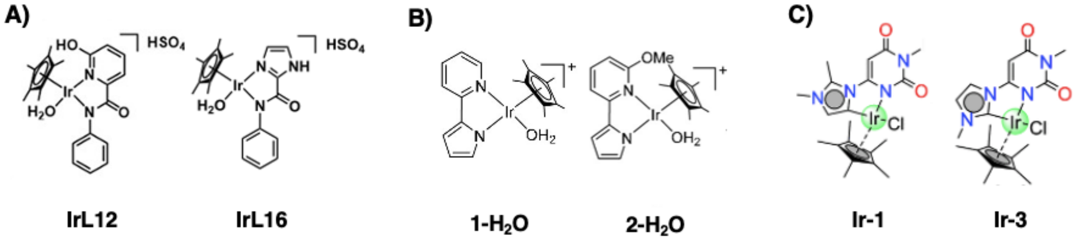

Figure 2. Representative catalysts from each group: (A) Picolinamidate Ir complexes from Kanega, et al.; (B) Pyridylpyrrole Ir complexes from Mo, et al.; (C) "Uracil-NHC" Ir complexes from Maji, et al.

Mo and coworkers reported a new family of Cp* Ir complexes bearing pyridylpyrrole ligands with either Cl or H_2O ligands.[8] They studied the performance of the complexes towards CO_2 dehydrogenation under ambient conditions and found that the H_2O bound Ir complex bearing a methoxy-substituted pyridine (2-H_2O, Fig. 2B) was most effective, with a TOF of 29 h^{-1}. The authors attributed the higher activity of the OMe complexes to the electron-donation effect of the ligand. As for FA dehydrogenation, the catalysts showed moderately good activity at 90°C, with TOF of up to 16300 h^{-1}. The authors sought to understand these reactions further, and therefore performed various mechanistic studies, including KIE experiments using D_2O and CDOOD. These studies revealed the metal-ligand cooperative effect of the C-H bond on the pyrrole group of the ligand, and how this plays a key role in the interconversion between CO_2/H_2 and FA/formate.

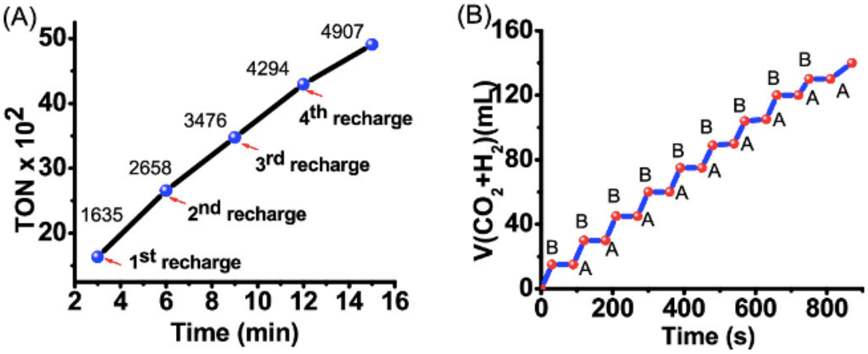

Figure 3. (A) Recharging experiment for formic acid dehydrogenation with Ir-1. (B) Switchable formic acid dehydrogenation with Ir-1.

Lastly, Maji and coworkers approached BHD catalysis by designing a series of Ir complexes bearing cyclic amide-NHC ('uracil-NHC') ligands (Figure 2C).[2] By including a uracil moiety in the ligand backbone, they were able to increase the water solubility of the complex and enhance the bifunctionality of the catalyst by exploiting its lactam-lactim tautomerism. The complexes in general showed high catalytic efficiency towards CO_2 hydrogenation, with TON of up to 3218, albeit with high pressures of up to 30:30 bar H_2/CO_2. The catalysts also showed highly efficient FA dehydrogenation at 80^oC, with TOF of up to 70674 h^{-1}.

Interestingly, the authors were also able to show that their catalyst was both rechargeable and on/off switchable. Running the FA dehydrogenation with Ir-1, the authors added more equivalents of formic acid/formate every 3 min and observed the catalyst remained active through several recharging cycles (Fig. 3A). Furthermore, they were able to demonstrate that the catalysts had the ability to be turned "on/off" by the addition of H^+/OH^- to the reaction mixture. Upon addition of the base into the reaction, the generation of H_2 and CO_2 is completely halted, due to the availability of the proton source being depleted. As soon as an equivalent amount of acid is added however, the reaction turns back on (Fig. 3B). Another interesting experiment was performed using Ir-1, in which the gases generated from the dehydrogenation of FA were utilized directly. The H_2 generated from the reaction was funneled to a reactor containing quinoxaline with Ir-1, and the hydrogenated product 1,2,3,4-tetrahydroquinoxaline was isolated in 88% yield. Likewise, the CO_2 generated from the reaction was captured in KOH and rehydrogenated to form formate again. These studies show that their catalysts have a high potential for being effective towards the application of rechargeable chemical hydrogen batteries.

References

1. Abe, J. O.; Popoola, A. P. I.; Ajenifuja, E.; Popoola, O. M. Hydrogen energy, economy and storage: Review and recommenda- tion. *Int. J. Hydrogen Energy* **2019**, *44*, 15072-15086.
2. Maji, B.; Kumar, A.; Bhattacherya, A.; Bera, J.K.; Choudhury, J. Cyclic Amide-Anchored NHC-Based Cp*Ir Catalysts for Bidirectional Hydrogenation–Dehydrogenation with CO_2/HCO_2H Couple. *Organometallics* **2022**, Articles ASAP.
3. Kanega, R.; Ertem, M.Z.; Onishi, N.; Szalda, D.J.; Fujita, E.; Himeda, Y. CO_2 Hydrogenation and Formic Acid Dehydrogenation Using Ir Catalysts with Amide-based Ligands. *Organometallics* **2020**, 39, 1519-1531.
4. Onishi, N.; Iguchi, M.; Yang, X.; Kanega, R.; Kawanami, H.; Xu, Q.; Himeda, Y. Development of Effective Catalysts for Hydrogen Storage Technology Using Formic Acid. *Adv. Energy Mater*. **2019**, 9, 1801275
5. Wang, W.; Wang, S. P.; Ma, X. B.; Gong, J. L. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem. Soc. Rev*. **2011**, 40, 3703−3727.
6. Wang, W. H.; Hull, J. F.; Muckerman, J. T.; Fujita, E.; Himeda, Y. Second-coordination-sphere and Electronic Effects Enhance Iridium- (III)-Catalyzed Homogeneous Hydrogenation of Carbon Dioxide in Water Near Ambient Temperature and Pressure. *Energy Environ. Sci*. **2012**, 5, 7923−7926
7. Filonenko, G. A.; van Putten, R.; Schulpen, E. N.; Hensen, E. J.; Pidko, E. A. Highly Efficient Reversible Hydrogenation of Carbon Dioxide to Formates Using a Ruthenium PNP-Pincer Catalyst. *ChemCatChem* **2014**, 6, 1526−1530.
8. Mo, X.; Liu, C.; Chen, Z.; Ma, F.; He, P.; Yi, X. Metal−Ligand Cooperation in Cp*Ir-Pyridylpyrrole Complexes: Rational Design and Catalytic Activity in Formic Acid Dehydrogenation and CO_2 Hydrogenation under Ambient Conditions. *Inorg. Chem*. **2021**, 60, 16584-16592.