

EDITORIAL: Metal Hydrides as Catalytic Intermediates

Sarah R. Soltau, Ph.D.

Department of Chemical Sciences, Bridgewater State University, Bridgewater, MA 02325, United States
Email: ssoltau@bridgew.edu

Metal hydrides are essential intermediates for many important processes in alternative energy production such as hydrogen (H₂) production or H₂ oxidation, electrochemical reduction of carbon dioxide (CO₂) to carbon based fuels, and the hydrogenation of CO₂ and carbon monoxide. These processes are the future of the alternative energy landscape and necessary developments to combat global climate change. Development of catalysts that can be better tuned particular chemical reactions will increase the efficiency and success of the chemical processes necessarily for alternative energy production. The review by Drs. Taheri and Berben in this issue discusses the efforts to prepare catalysts that selectively perform CO₂ reduction rather than favoring H₂ production. In their [review](#), a selection of iron carbonyl cluster catalysts that vary in their ability to reduce CO₂ or produce H₂ based on their structure and hydricity are discussed (Taheri and Berben 2017).

Importance of Hydricity in Water

Hydricity is the thermodynamic parameter for the loss of a hydride (H⁻) and is defined by the Gibbs free energy for for the hydride transfer to solvent ($\Delta G^{\circ}_{H^-}$) (Wiedner, Chambers et al. 2016). Most hydricity measurements have been calculated in organic solvents such as acetonitrile, however, most hydride transfers in alternative energy reactions occur in water. The relative hydricity values change significantly in pure water as compared to the hydricity values in organic solvents. The hydricity value in water can provide insight to whether the reaction will favor H₂ production or CO₂ reduction. This review provides great insight for the use of this thermodynamic parameter as a measure to evaluate electrocatalyst function.

Metal Hydride Intermediates for H₂ or Formate Production

A series of different iron carbonyl cluster catalysts prepared, containing differing interstitial atoms (N or C). These catalysts exhibit different reactivity for H₂ production or CO₂ reduction based on the identity of the interstitial atom. The [HFe₄N(CO)₁₂]⁻ complex containing a nitrogen atom as the interstitial atom was found to favor CO₂ reduction to produce formate through catalytic experiments with cyclic voltammetry (HCOO⁻) (Taheri, Thompson et al. 2015). Alternatively, the [HFe₄C(CO)₁₂]²⁻ complex with a carbon atom as the interstitial atom was found to favor H₂ production (Taheri and Berben 2016). The reduced hydricity of the N containing complex was suggested to play a role in the selectivity of the complex for CO₂ reduction. The studies have further been extended to phosphine and hydroxyl substituted catalysts with nitrogen atoms as interstitial atoms and analysis of the hydricity parameters has been able to evaluate which catalysts are effective for H₂ production vs. CO₂ reduction (Loewen, Thompson et al. 2016). These results provide an opportunity to classify these catalysts for CO₂ reduction solely based on hydricity and help with the design of next generation catalysts that will increase catalytic efficiency and selectivity.

Bridging Hydride Intermediates

Bridging hydrides between two metal complexes have often been observed as side reactions or byproducts, because they are poorly reactive (Johnson, Nielsen et al. 2016). Future efforts to design CO₂ reduction catalysts could use the bridging hydride design a method to selectively tune the hydricity to conditions that minimize H₂ and maximize CO₂ reduction (Taheri and Berben

2017). These catalysts may have better overall catalytic function for CO₂ reduction as they react poorly and therefore are less susceptible to side reactions that form H₂. This strategy has the potential to redirect systems formerly seen as "failed" H₂ production catalysts to fully functional systems for selective CO₂ reduction.

The reduction of CO₂ into fuels such as formate is an important part of the alternative energy future. These types of multimetallic carbonyl clusters are one of the many ways we will develop more alternative fuel catalysts in the future.

References

Johnson, S. I., R. J. Nielsen and W. A. Goddard (2016). "Selectivity for HCO₂⁻ over H₂ in the Electrochemical Catalytic Reduction of CO₂ by (POCOP)IrH₂." ACS Catalysis 6(10): 6362-6371. <https://doi.org/10.1021/acscatal.6b01755>

Loewen, N. D., E. J. Thompson, M. Kagan, C. L. Banales, T. W. Myers, J. C. Fettinger and L. A. Berben (2016). "A pendant proton shuttle on [Fe₄N(CO)₁₂]- alters product selectivity in formate vs. H₂ production via the hydride [H-Fe₄N(CO)₁₂]." Chemical Science 7(4): 2728-2735. <https://doi.org/10.1039/C5SC03169A> PMCID:PMC5477009

Taheri, A. and L. A. Berben (2016). "Tailoring Electrocatalysts for Selective CO₂ or H⁺ Reduction: Iron Carbonyl Clusters as a Case Study." Inorganic Chemistry 55(2): 378-385. <https://doi.org/10.1021/acs.inorgchem.5b02293> PMid:26689238

Taheri, A. and L. A. Berben (2017). "Metal Hydrides as Catalytic Intermediates: The Curious Case of Iron Carbonyl Clusters." Journal of Postdoctoral Research 5(7) 3-8. <http://doi.org/b9sw>

Taheri, A., E. J. Thompson, J. C. Fettinger and L. A. Berben (2015). "An Iron Electrocatalyst for

Selective Reduction of CO₂ to Formate in Water: Including Thermochemical Insights." ACS Catalysis 5(12): 7140-7151. <https://doi.org/10.1021/acscatal.5b01708>

Wiedner, E. S., M. B. Chambers, C. L. Pitman, R. M. Bullock, A. J. M. Miller and A. M. Appel (2016). "Thermodynamic Hydrlicity of Transition Metal Hydrides." Chemical Reviews 116(15): 8655-8692. <https://doi.org/10.1021/acs.chemrev.6b00168> PMid:27483171