

Rationalizing the Reactivity of Bimetallic Molecular Catalysts for CO₂ Hydrogenation

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We have recently reported the heterobimetallic nickel-gallium complex,^[1] NiGaL (where L represents the tris(phosphinoamido)amine ligand, $[\text{N}(o\text{-}(\text{NCH}_2\text{P}i\text{-Pr}_2)\text{C}_6\text{H}_4)_3]^{3-}$), which is the most active Ni-based molecular catalyst for CO₂ hydrogenation to date. Understanding the reaction mechanism of this catalytic system and identifying the factors that govern its catalytic activity are important toward designing even more efficient base metal catalysts. I will present the results of a computational study of possible reaction pathways for CO₂ hydrogenation catalyzed by NiGaL. The most favorable pathway for formate production has four elementary steps: (1) H₂ binding to the Ni center, (2) deprotonation of the H₂ adduct, (3) hydride transfer to CO₂ to form formate adduct, and (4) formate release to regenerate NiGaL. The reaction mechanism identified by the calculations agrees well with several key experimental observations. For hydride transfer to CO₂, the free energy of activation was found to depend linearly on the thermodynamic hydricity for a series of bimetallic HM₁M₂L⁻ complexes. This linear relationship provides a simple and efficient strategy for screening other bimetallic catalysts by predicting the free energies of activation for the hydride-transfer step based on experimental or computed thermodynamic hydricity data, rather than by calculating the entire reaction mechanism. The predicted trends and structure-activity relationships arising from these computational calculations provide tools for the rational design of more efficient catalysts for CO₂ hydrogenation and other hydride transfer processes for which reactive M–H species are generated in the presence of a Lewis base.

[1] Ryan C. Cammarota; Vollmer, M. V.; Xie, J.; Ye, J.; Linehan, J. C.; Burgess, S. A.; Appel, A. M.; Gagliardi, L.; Lu, C. C. *J. Am. Chem. Soc.* **2017**, *139* (40), 14244–14250.

