

DFT mechanistic study on small molecule activation by homogeneous catalyst

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Catalysts capable efficiently activating and producing H₂ and catalysts that convert CO₂ to useful chemicals are in high demand. To design an efficient and selective catalyst, it is essential to elucidation the underlying mechanism. DFT calculations give the mechanistic insights that are difficult to be obtained by the experimental studies. In this seminar, I introduce the DFT mechanistic studies of (1) NiIr catalyzed H₂ and CO oxidations (2) Mn electrocatalyzed CO₂ reduction to CO.

(1) H₂ and CO oxidation by NiIr catalyst in aqueous solution

A problem with using hydrogen gas as a fuel is the suppression of H₂ oxidation by carbon monoxide that is mixed with industrially produced hydrogen sources. To overcome this problem, it is important to develop a catalyst that selectively oxidizes either CO or H₂, or a catalyst that co-oxidizes the mixture. Recently, a NiIr catalyst, [Ni^{II}Cl(X)Ir^{III}Cl(η⁵-C₅Me₅)](X=N,N'-dimethyl-3,7-diazanonane-1,9-dithiolate) has been developed that selectively oxidizes either H₂ or CO by controlling pH.¹ We performed DFT calculations to elucidate the reaction mechanism of H₂ and CO oxidations catalyzed by the NiIr catalyst. The DFT calculations showed that the H–H bond cleavage in H₂ oxidation catalyzed by Lewis pairs. The process of CO oxidation can be divided into two steps; (1) formation of metallocarboxylic acid and (2) conversion of metallocarboxylic acid to hydride complex. The formation of metallocarboxylic acid involves remarkable structural change with the cleavage of Ir–S bond and rotation of COOH group along NiIr axis. The metallocarboxylic acid is converted to the hydride complex by intramolecular proton transfer and subsequent CO₂ elimination. The revealed mechanism of CO oxidation is analogous to the that of water-gas shift reaction.

(2) CO₂ reduction to CO by Mn electrocatalyst in the presence of Lewis acid

The addition of a Lewis Acid (Mg²⁺) has been shown to improve the efficiency of CO₂ reductions by homogeneous electrocatalysts. Recently, a CO₂ reduction protocol involving a Mn electrocatalyst with a bulky bipyridine ligand [Mn(mesbpy)(CO)₃ MeCN] [mesbpy = 6,6'-dimesityl-2,2'-bipyridine] in the presence of Mg(OTf)₂ was reported (Sampson et al. *J. Am. Chem. Soc.* 2016, 138, 1386-1393). However, a detailed mechanistic understanding of this reaction is lacking. The DFT calculations demonstrate that the primary role of Mg(OTf)₂ is to stabilize a two-electron reduced Mn intermediate through Lewis pair binding. Furthermore, Mg(OTf)₂ makes the reaction thermodynamically and kinetically feasible. In our presented mechanism, two molecules of CO₂ and Mg(OTf)₂ contribute to the C–O bond cleavage reaction. The demonstrated roles of Mg(OTf)₂ in this catalytic process are important for informing the design of novel multimetallic catalysts for mild CO₂ conversion reaction.

(1) Ogo, S.; Mori, Y.; Ando, T.; Matsumoto, T.; Yatabe, T.; Yoon, K. S.; Hayashi, H.; Asano, M., One Model, Two Enzymes: Activation of Hydrogen and Carbon Monoxide. *Angew. Chem. Int. Ed.* **2017**, *56*, 9723-9726.

(2) Sampson, M. D.; Kubiak, C. P., Manganese Electrocatalysts with Bulky Bipyridine Ligands: Utilizing Lewis Acids To Promote Carbon Dioxide Reduction at Low Overpotentials. *J. Am. Chem. Soc.* **2016**, *138*, 1386-1393.