Computational Molecular Electrocatalysis: The Role of Proton Relays in H_2 Oxidation and Evolution Catalysts

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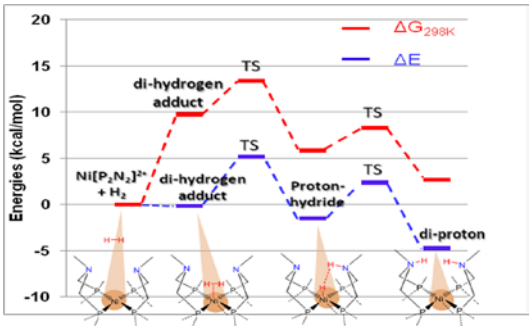
The rational design of improved molecular electrocatalysts for small molecule activation (for example H_2, O_2, N_2, H_2O, CO_2) requires a detailed molecular level understanding of the energetic and mechanistic factors controlling the movement of protons and electrons during the catalytic cycle. $Ni(P_2N_2)_2^{2+}$ complexes are a family of mononuclear nickel complexes with cyclic diphosphine ligands that incorporate amine bases, in a mimic of enzyme functionalities. The presence and positioning of the amine bases near the metal center is the critical, enzyme-mimicking structural feature for the activity[1] and the efficiency of these catalysts, as these bases facilitate the heterolytic cleavage or formation of the H-H bond while acting as proton relays in the management of the proton and electron movement during the catalytic cycle.

We will highlights computational studies (electronic structure and *ab initio* meta-dynamics calculations) of the catalytic cycles in $Ni(P_2N_2)_2^{2+}$ catalysts. Proton-hydride species are key intermediates. H_2 oxidation and evolution proceed via heterolytic bond cleavage or formation of the H-H bond. We will discuss what we have learned about these catalysts, the importance of the proton relays, their number, their active and inactive states, and the role of solvent and water molecules in giving rise to fast turnover rates. The concept of proton relays is being extended to O_2 and N_2 reductions reactions as well as H_2O oxidation.



Typical Potential Energy Maps for $Ni(P_2N_2)_2^{2+}$ Complexes Depicting the Role of Pendant Amine Relays in H_2 Oxidation or Evolution (shown here based on ΔG)

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