

Computational Studies of CO₂ Activation using Transition Metal Catalysts

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CO₂ activation and conversion mediated by transition metal(TM) catalysts has been investigated. Homogeneous catalysis of the reverse water gas shift reaction $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$ was studied as a means to reduce CO₂. β -diketiminatometal models $\text{L}'\text{M}^I$ ($\text{L}' = \text{C}_3\text{N}_2\text{H}_5^-$; $\text{M} =$ first-row TMs) were considered as potential catalysts. The thermodynamics of prototypical reaction pathways were simulated using B3LYP/aug-cc-pVTZ. Results show that middle series metal complexes result in more thermodynamically favorable properties; therefore, more detailed thermodynamic and kinetic studies were carried out for Mn, Fe, and Co complexes. Calculations show favorable thermodynamics and reasonable reaction barriers. On the other hand, heterogeneous catalysis of the reduction of CO₂ to CO were carried out on Fe, Co, Ni, and Cu fcc (100) surfaces, using the PBE density functional. Reaction energies were calculated using generalized gradient approximation (GGA), and reaction barriers were calculated using the climbing image nudged elastic band method. Calculations show spontaneous activation of CO₂, and favorable thermodynamics for the CO₂ decomposition, on Fe, Co, and Ni surfaces. In summary, an interesting energetic trend was found for both homo- and heterogeneous catalysis, as a function of metal: earlier metals tend to have stronger interaction with CO₂ than the later metals.