

Mechanistic Studies on CO₂ Reduction to Formate by Ni-NHC Catalysts

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Formic acid formation (HCOOH) by the reduction of CO₂ is highly desirable as it constitutes a pathway to convert the greenhouse gas to the valuable products for synthesis, hydrogen storage and other industrial uses. However, carbon monoxide (CO) rather than formic acid often tends to be given as a major CO₂ reduction product by various earth-abundant-metal based catalysts.

Recently, Albrecht and coworkers reported on a series of nickel-based molecular CO₂ reduction catalysts which shows high selectivity in HCOOH formation versus CO formation.¹ Nevertheless, the reason for the high selectivity remains unexplored. Inspired by this work, we attempted to clarify the mechanism of CO₂ reduction to HCOOH by DFT calculations. Here we focus on the mechanism of catalysis by **Ni-NHC**,¹ corresponding to one of the catalysts in their report. The computational approach allows us to give an insight into the interactions between the **Ni-NHC** catalyst and CO₂. Furthermore, the free energy changes while forming several reaction intermediates can also be evaluated, leading to help us better understand the reason for the unexceptionally high selectivity for HCOOH formation.



Our calculations reveal that the one-electron-reduced species ²[Ni^IL₂]⁻ is initially formed and then the concerted proton electron transfer (CPET) to this species proceeds to give a metal-hydride intermediate ¹[Ni^{II}(H)L₂]⁻, which plays a key role in the formation of Ni-formate complex ¹[Ni^{II}(OCOH)L₂]⁻ (see **Figure 1**). This CPET step is found to be the sole route to the hydride because neither protonation nor one-electron reduction of ²[Ni^IL₂]⁻ is energetically feasible. Our study also clarify that the hydride atom can attack the carbon center of CO₂, leading to form a H-C bond in the transition state. In the presentation, the energy diagram and proposed mechanism of CO₂ reduction to formate will be discussed in detail.

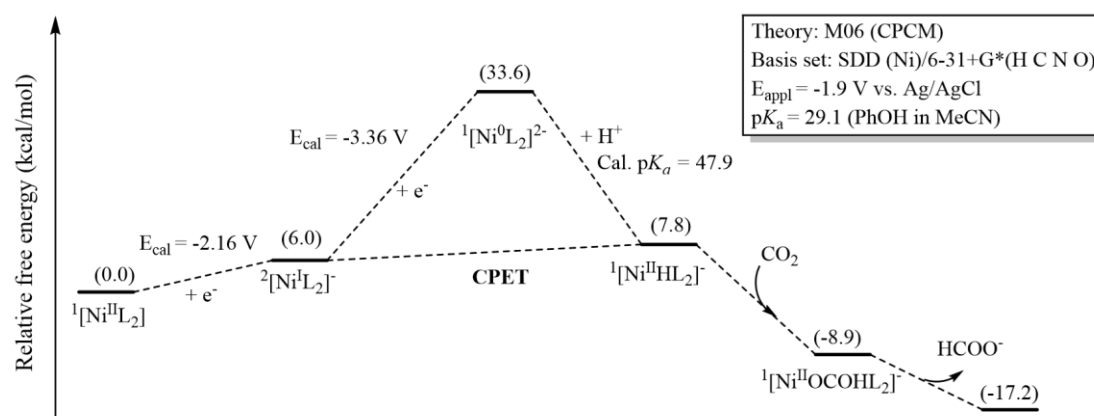


Figure 1. Energy diagram computed by DFT for CO₂ reduction to formate by **Ni-NHC**.

1. S. Bertini, M. Rahaman, A. Dutta, P. Schollhammer, A. Rudnev, F. Gloaguen, P. Broekmann and M. Albrecht, *Green Chem.*, **2021**, 23, 3365-3373.