

The Importance of CO Attack on the Formation of C₂₊ Products over Fe-phthalocyanine Single Atom Catalysts

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Electroreduction of CO₂ to value-added products with more than one carbon atom (C₂₊) is an advantageous route for direct synthesis of value-added products. CO₂ reduction reaction (CO₂RR) to C₂₊ products has traditionally been dominated by solid state heterogeneous electrocatalysts, such as copper (Cu) [1]. In contrast to this, single atom catalysts (SACs) are used primarily to convert CO₂ into C₁ products, such as carbon monoxide, formate, methanol and methane [2-3]. However, certain experimental data suggests that iron phthalocyanine (FePc) as a single-atom catalyst (SAC), can produce limited quantities of compounds containing two or more carbon atoms, such as ethylene (C₂H₄), ethane (C₂H₆), propene (C₃H₆), and propane (C₃H₈) [4, 5]. A comprehensive understanding of the underlying mechanism behind this significant advancement is still lacking. Indeed, uncovering such a mechanism could pave the way for the development of SACs utilizing transition metal-doped graphene. In this research, our goal is to explore and analyze various reaction mechanisms that could result in the formation of post-CO and C₂₊ products over FePc, employing density functional theory (DFT) calculations. Our computational results demonstrate that at a negative applied potential, CO binds more firmly to the Fe-CO intermediate, making it kinetically more challenging to be released. Consequently, the formation of post-CO via proton attack on Fe-CO becomes more feasible. After surpassing the CO step, the reaction progresses smoothly without encountering significant thermodynamic or kinetic barriers towards forming a Schrock-type carbene (Fe=CH₂). Our findings indicate that although methanol formation is thermodynamically feasible, it is impeded by a high activation barrier. Subsequently, C₂₊ products are generated through CO direct attack at the carbene. Our analysis indicates that this reaction encounters only minor thermodynamic and kinetic barriers.

References

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