Quantum Mechanical Modeling of Electrocatalytic Carbon Dioxide Reduction Reactions on Copper-Doped Two-Dimensional Materials

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Our world is facing global warming and feedstock shortage, both of which can be potentially solvable through carbon dioxide reduction reaction (CO_2RR). Electrocatalysis is one strategy to overcome the potential energy barrier. The most common catalytic metal is copper. However, although copper nanocatalysts with different morphologies have been synthesized, their catalytic performance is limited to the exposed crystal surface, and its catalytic mechanism is difficult to be studied due to the complex structure. Monatomic catalysis solves this problem. As compared to the single-atom catalysts, using a few metal atoms as active sites was revealed to possess improved catalytic performance because of the synergistic effect of two adjacent adsorption sites. As the base material of the loaded metal, nitrogen-doped graphene two-dimensional planar material is considered as the best candidate due to its excellent thermal stability, good electrical conductivity and low preparation cost. Hence, “Electrocatalytic Carbon Dioxide Reduction Reactions on Copper-Doped Two-Dimensional Materials” is a very promising research topic. However, there are few experimental and theoretical studies on this system so far. For the experimenter, due to the short half-life and low abundance of intermediates and transition states, in-situ experimental measurements are not feasible. First-principles quantum mechanical modeling is an indispensable tool to explain the details of atomic level structure and energy as well as the distribution of final products. In this work, we proposed a Cu-doped two-dimensional material as such an alternative electrocatalyst which shows a very different selectivity. Combining quantum mechanics and statistical mechanics, we modeled reaction pathways leading to important one-carbon (C_1) and two-carbon (C_2) products, including methanol (CH_3OH), methane (CH_4), ethanol (CH_3CH_2OH), and ethylene ($CH_2=CH_2$), and demonstrated Gibbs free energy profiles for corresponding intermediates and transition states. Our results will provide the community with important hints for measurable C_1 and C_2 intermediates and products on the two-dimensional electrocatalyst in question, as well as new ideas to design and optimize alternative electrocatalysts.

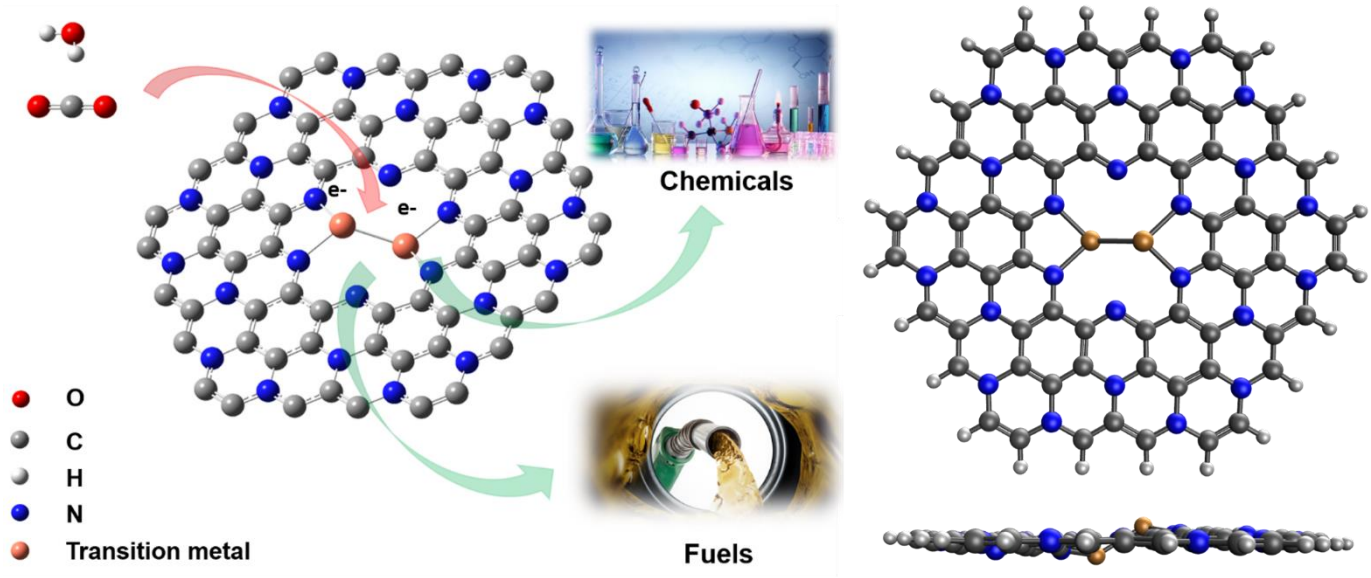

Figure 1. Schematic diagram of CO_2RR.