A Computational Exploration on CO₂ Reduction Mechanism via CO Dimerization on Copper Oxide Surface

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Abstract:
The CO••CO dimerization mechanism is investigated using Density Function Theory (DFT) calculations on CuO, Cu₃O₄ and Cu₂O surfaces in order to characterize the potential reaction pathway on the oxide-derived Cu catalysts for CO₂ reduction. With the presence of oxygen vacancy on CuO and Cu₃O₄ surfaces, CO could be adsorbed at the side-on orientation on these surfaces. The side-on adsorbed orientation of CO on Cu₂O surface could also be identified without oxygen vacancy. The transition states of CO••CO dimerization on these three surfaces are identified and the formation of OCCO as the final products are determined. The Ov-Cu₃O₄ surface, containing an oxygen vacancy, surface is found to outperform other two surfaces with the barrier predicted at 0.98 eV and thermodynamically favorable to the OCCO formation. The electronic structure of the adsorbed OCCO is analyzed by Bader charge analysis, electron localization functional and local density of state analysis. The C-C triple-bond and charge-separated character for (OC)δ+(CO)δ on Ov-Cu₃O₄ is assigned where the intrinsic mixed-valence nature of Cu interaction sits of Cu₃O₄ is responsible to stabilize such charge-separated OCCO species.

Keywords: CO₂ reduction, C-C coupling, Copper Oxide.

Reference: