A Computational Exploration on CO_2 Reduction Mechanism via CO Dimerization on Copper Oxide Surface

Chun-Chih Chang, Elise Y. Li* and Ming-Kang Tsai*

National Taiwan Normal University, Taipei 11677, Taiwan
**Email: mktsai@ntnu.edu.tw and eliseytli@ntnu.edu.tw*

Abstract:
The CO••CO dimerization mechanism is investigated using Density Function Theory (DFT) calculations on CuO, Cu_4O_3 and Cu_2O surfaces in order to characterize the potential reaction pathway on the oxide-derived Cu catalysts for CO_2 reduction. With the presence of oxygen vacancy on CuO and Cu_4O_3 surfaces, CO could be adsorbed at the side-on orientation on these surfaces. The side-on adsorbed orientation of CO on Cu_2O 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-Cu_4O_3 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 $(OC)^{\delta+}(CO)^{\delta-}$ on Ov-Cu_4O_3 is assigned where the intrinsic mixed-valence nature of Cu interaction sits of Cu_4O_3 is responsible to stabilize such charge-separated OCCO species.

Keywords: CO_2 reduction, C-C coupling, Copper Oxide.

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