Insight into the Mechanism of Plasma-Catalytic CO_2 Hydrogenation into Methanol over Supported Cu and Cu/Zn Catalysts

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ABSTRACT

While interest in plasma-catalytic CO_2 hydrogenation for the synthesis of methanol is growing rapidly, the fundamental understanding of the reaction process is still lacking. We report a combined experimental/computational analysis of plasma CO_2 hydrogenation into CH_3OH over Cu/SiO_2 and $Cu\text{-}Zn/SiO_2$ catalysts. Our experimental results reveal a synergistic effect between the Cu/SiO_2 catalyst and the CO_2/H_2 plasma, with a CO_2 conversion of 27.5% over the Cu/SiO_2 catalyst and a CH_3OH selectivity of 22.8%, which rises to 34.5% when the Zn promoter is introduced. Furthermore, the energy consumption for CH_3OH generation was around 20 times less than that for the plasma alone system. We performed density functional theory (DFT) calculations on a Cu and Cu/Zn alloy model and discovered that the Cu and Zn promoter's interfacial sites have a dual function synergy: they not only activate the CO_2 molecules but also significantly adsorb critical intermediates, thereby promoting further hydrogenation of CO_2 molecules. Reactive plasma species can control the catalyst surface reactions via the Eley-Rideal (E-R) mechanism, accelerating the hydrogenation process and promoting the formation of critical intermediates. Through competitive adsorption on the Cu/Zn surface, plasma gas-phase radicals induce CH_3OH desorption. This study offers new insights into CO_2 hydrogenation via plasma catalysis and provides inspiration for the plasma-catalytic conversion of virous other small molecules (CH_4, N_2, CO, etc.) using Cu-based catalysts.

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