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Fundamental Insights into Aqueous Electrochemical Reduction of CO_2 on the Ligand-Protected Charged Au_{25} Clusters DOMINIC ALFONSO, DOUGLAS KAUFFMAN, CHRISTOPHER MATRANGA, National Energy Technology Laboratory - Department of Energy, MATERIALS FUNDAMENTAL TEAM — Recent breakthroughs in electrochemical studies in our group showed aqueous CO_2 reduction to CO on atomically precise, inherently charged Au_{25} clusters occurring at low overpotentials. Using first-principles density functional theory and continuum solvation models, the role of the cluster in the reduction process was examined. Free energies of species that were proposed as intermediates in its mechanism were determined. Contrary to previous assumptions, our results show that the fully ligand protected version of the cluster can be ruled out as an active participant. In particular, COOH species on the intact cluster should not be expected to form unless very high potentials are applied. Instead, the calculations suggest that the reduction process would likely occur on a dethiolated gold site. These findings point to the crucial role of such reaction center on the Au_{25} clusters in facilitating the CO_2 conversion via the formation of low energy COOH intermediates.

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