



First-principles study of copper nanoclusters for enhanced electrochemical CO₂ reduction to CH₄



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ABSTRACT

The conversion of carbon dioxide (CO₂) into usable hydrocarbon fuels is important for recycling carbon resources and mitigating environmental problems. However, converting CO₂, which is a stable compound, requires a high additional energy. Therefore, it is essential to understand the electrochemical reduction mechanisms of CO₂ and develop more efficient catalysts. In this study, density functional theory calculations were performed to examine electrochemical CO₂ reduction on copper nanoclusters (NCs) (Cu₁₃ NCs and Cu₅₅ NCs) and the Cu(1 1 1) surface to verify the effect of the surface geometry and size of the NCs on the conversion of CO₂ into CH₄. The highest energy barriers to CO₂ reduction (i.e., the potential-limiting step) on the Cu₁₃ NCs (0.64 eV), Cu₅₅ NCs (0.83 eV), and Cu(1 1 1) surface (0.86 eV) lie in the CO* → CHO* step. The formation of an adsorbed CHO intermediate depending on the catalyst surface geometry may significantly influence the energy barrier, as demonstrated by analyses of the electronic properties, such as the density of states, charge density difference, and highest occupied molecular orbital and lowest unoccupied molecular orbital band gap.

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1. Introduction

The conversion of carbon dioxide (CO₂), which makes up the largest portion of greenhouse gases (GHGs), [1] into usable hydrocarbon compounds [e.g., methane (CH₄) and ethylene (C₂H₄)] is of great importance for solving the problem of global warming by reducing GHGs and recycling carbon resources. CO₂ can be directly converted into hydrocarbon compounds through electrochemical reduction on electrodes in solution. The electrochemical CO₂ reduction reaction requires external energy input and is competitive with the hydrogen evolution reaction (HER) that has the lowest energy barrier in CO₂ conversion into hydrocarbon compounds. Therefore, it is necessary to develop a catalyst capable of enhancing the reaction efficiency of a desired product while appropriately suppressing HER. A number of studies investigating the use of metal-based catalysts as the electrodes [2–12] have been conducted to solve this competitive reaction. In particular, Hori et al. [13–16] studied the conversion of CO₂ into various organic compounds such as CO, CH₄, C₂H₄, C₂H₅OH, and HCOOH using single-crystal Cu electrodes and confirmed that CH₄, which is generally used as a fuel, is produced mainly on the Cu(1 1 1) surface [16]. Nie et al. [17] proposed water-solved model (producing COH*)

and H-shuttling model (producing CHO*) considering water molecule directly (where “*” denotes an adsorbed species). This research reported that the COH pathway was more stable than CHO pathway and was able to produce C₂H₄ as well as CH₄. However, electrochemical CO₂ conversion into a large amount of hydrocarbon compounds using Cu catalysts still must overcome the relatively high overpotential for CO₂ reduction [18,19]. Thus, if the highest energy barrier of rate-limiting step where the overpotential is observed can be lowered effectively, we will save the energy for the reduction of CO₂ as well as have an enhanced selectivity for suppressing the by-products (i.e., the evolution of hydrogen). This study suggests important factors to design catalyst for fundamentally lowering the overpotential rather than alternative reaction pathways.

To decrease the high overpotential for CO₂ reduction, [20–22] the nanoclustering technique may be used to help solve the problem by creating Cu nanoclusters (NCs) that consist of more open structures than flat Cu surfaces. In particular, NCs function as both homogeneous and heterogeneous catalytic systems [23,24]. Homogeneous catalysts generally have excellent activity and selectivity, and heterogeneous catalysts in different phases from those of the reactants are considered more environmentally friendly owing to their high recoverability [24]. These properties were demonstrated by previous studies reporting CO₂ conversion into a variety of hydrocarbon compounds [25–27] and organic transformations by the Suzuki cross-coupling reaction [28,29]. In addition, it is known

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