

Strategies and Mechanisms to Improve the Catalytic Performance of Cu-Based Catalyst for CO₂ Electrochemical Reduction Reaction to Methane

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Abstract. This article introduces three significant ways of producing methane by electrocatalytic reduction of carbon dioxide. Electrocatalytic reduction of carbon dioxide can efficiently convert CO₂ molecules into various high-energy fuels under ambient conditions. Methane gas, among them, stands out due to its relatively high calorific value, chemical stability, ease of storage and transportation. Therefore, research on electrocatalytic reduction of CO₂ to generate methane is crucial. Common methods include adjusting catalyst morphology to expose more active sites, building nanoscale catalysts results in smaller-sized nanostructured copper and combining copper with other metals to form alloys, creating multi-metal catalysts. By optimizing these catalysts, we can efficiently reduce carbon dioxide into methane.

Keywords: CO₂RR, Methane, Cu catalyst.

1. Introduction

The widespread use and burning of traditional fossil fuels not only degrade the environment and cause pollution, but the excessive CO₂ emissions during their combustion also exacerbate the greenhouse effect. The overabundance of greenhouse gases leads to worsening global warming, resulting in severe climate changes worldwide. To address this issue, countries around the world have begun taking action. The extensive consumption of primary energy sources undoubtedly worsens environmental issues, making urgent the international utilization of new and renewable energy sources. Currently, over 140 countries worldwide have committed to achieving carbon neutrality by around 2050, with more than 130 countries aiming for this goal by the mid-century. Reducing carbon emissions and vigorously developing clean, efficient, and environmentally friendly renewable energy sources will undoubtedly become crucial principles for future development.

Currently, there are two main large-scale methods for reducing CO₂ emissions: chemical absorption and physical sequestration. Chemical absorption is a relatively mature CO₂ capture technology that has been industrially applied since the 1930s. It primarily uses alkaline solvents to neutralize and react with acidic CO₂ gas during absorption. Industrial applications often use chemical reagents like organic amine solutions, known for their fast absorption rate, high efficiency, and low cost. However, these solvents are highly corrosive, cause significant environmental pollution, and consume high energy, leading to resource wastage, thereby limiting large-scale industrial CO₂ capture [1]. Physical sequestration of CO₂ using geological methods involves injecting CO₂ into suitable geological formations capable of permanent storage through physical burial. Unlike other CO₂ storage stages, each storage site possesses unique geological characteristics, posing risks related to risk management. Moreover, the amount of CO₂ stored depends heavily on site conditions, requiring thorough research and large-scale practical verification [2]. Despite their feasibility, both CO₂ emission reduction methods have significant flaws that cannot be ignored. Therefore, it is imperative to find a straightforward, effective, economically feasible, and environmentally non-polluting method for CO₂ reduction.

Through electrochemical reduction of carbon dioxide, renewable energy sources can facilitate electron transfer on catalysts, enabling easier conversion of stable CO₂ molecules at ambient temperatures into high-value industrial chemicals such as CO, HCOOH, CH₄, C₂H₄, C₂H₅OH, and others. Compared to other CO₂ conversion technologies, electrochemical reduction offers distinct

advantages: it utilizes renewable electricity for driving, is easily controllable, and operates under mild aqueous conditions for enhanced safety. Its use of renewable power also ensures environmental friendliness without secondary pollution concerns. The simplicity of its reaction setup further facilitates industrial production [3, 5].

Methane, as a crucial energy source, emits significantly less CO₂ upon combustion compared to petroleum (71.4%) and coal (5.7%), releasing only CO₂ and water. This makes methane a cleaner fossil fuel alternative widely utilized across industries, agriculture, and transportation. Methane gas stands out due to its relatively high calorific value, chemical stability, ease of storage and transportation [4]. Converting carbon dioxide into methane is an economically and environmentally friendly solution, therefore, research on electrocatalytic reduction of CO₂ to produce methane is crucial.

Copper metal catalysts uniquely possess the adsorption capability necessary for methane production in CO₂ electrochemical reduction. While pure copper catalysts yield limited methane, modification significantly enhances methane production. Methods to obtain more methane include: (I) adjusting catalyst morphology to expose more active sites, optimizing composition, and (II) building nanoscale catalysts results in smaller-sized nanostructured copper (III) by combining copper with other metals to form alloys, creating multi-metal catalysts.

2. Organization of the Text

2.1. Adjusting the sizes and shapes of catalysts

Adjusting the size and shape of copper-based catalysts is one of the most widely used methods to intensify catalyst performance. Among various approaches to improving catalyst performance, as one of the numerous cathode catalysts for electrochemical CO₂ reduction, single-atom catalysts (SACs) composed of isolated metal atoms supported on carriers have garnered special attention in heterogeneous catalysis. SACs boast high atomic efficiency, unsaturated coordination environments, and unique electronic states. These advantages make SACs particularly intriguing in the field. Large surface areas and unique geometries and electronic properties in two-dimensional materials allow directly exposed single atoms, providing SACs with more unsaturated coordination environments compared to bulk materials. Therefore, constructing SACs with CO₂ reduction activity using metal atoms confined in two-dimensional materials is expected to enhance their activity and selectivity.

The central metal atoms on SACs typically act as primary active sites, determining the catalyst's electrocatalytic activity and product selectivity. Modify the electronic structure of these central metal atoms, such as their oxidation state and charge density, can improve the electrocatalytic activity [6]. The coordination environment also significantly affects the catalytic activity and selectivity of SACs. The carrier material is crucial for SACs, influencing their catalytic activity and selectivity optimization. Due to their high atomic efficiency and catalytic activity, SACs confined in two-dimensional materials hold great promise for electrochemical CO₂ reduction. The electrocatalytic performance of SACs is influenced by the type of central metal atom and its electronic state [7-8]. Moreover, regulating the coordination number of central metal atoms or introducing heteroatom coordination can effectively optimize SACs' activity and selectivity. Defects in two-dimensional material carriers also notably impact SAC performance. Therefore, when designing efficient catalysts for CO₂ reduction reactions, the role of two-dimensional material-supported single atoms cannot be overlooked.

In practical applications, the construction of single-atom catalysts typically involves combining them with other materials, focusing on carbon-nitrogen-metal structures and using other organic materials as the catalyst's structural framework [9-10]. Materials commonly used as structural frameworks include graphite materials and organic metal frameworks. For instance, metal-organic frameworks (MOFs) are a novel type of porous material with exceptionally high surface area, extremely high porosity, and customizable organic structures. The multifunctional flexibility of MOF

materials allows us to alter their organizational structure at the molecular level and anchor and modify the enclosed metals. This enhances their ability to reduce CO₂ and produce methane [11].

2.2. Building nanoscale catalysts

Another method to augment the reduction of carbon dioxide to methane is to construct nanostructures of copper, obtaining smaller copper particles. The different nanostructures of nano-copper also affect catalytic performance, as different structures of nano-copper particles possess varying surface chemical adsorption, catalytic activity, and selectivity. Compared to conventional copper particle catalysts, nanostructured catalysts have numerous advantages such as larger surface area, a high density of low-coordination sites, and more active sites [12]. With the advancement of nano-catalyst technology, adjusting catalyst performance by precisely controlling catalyst size and shape at the molecular level is possible. Therefore, studying the effect of catalyst size on the electrocatalytic reduction performance of carbon dioxide is crucial. Typically, nano-copper structures are classified into nano-cubes and nano-octahedrons. Nano-copper octahedrons exhibit more facets, thus nano-cubic Cu favors the production of C₂H₄, while octahedrons favor CH₄ production. Research has shown significant differences in the catalytic performance of nano-copper octahedrons of different sizes. Among them, 75nm octahedral Cu nanocrystals exhibit optimal methane catalytic performance, achieving a Faraday efficiency of up to 77% in the reduction of carbon dioxide to methane. Other studies suggest that reducing the size of Cu nanocrystals not only adjusts inherent activity to favor CH₄ generation but also promotes overall CO₂ reduction based on geometric effects [13-14].

Further research has shown that compared to electrodes made from high-purity copper foil, spherical 7 nm copper particles uniformly distributed on glassy carbon carriers achieve methane production at extremely high current densities. The principle behind this is that the spherical shape of copper is more conducive to forming *CO₂•-, an intermediate in the reaction that significantly enhances the activity of carbon dioxide reduction to methane. The presence of glassy carbon with distributed spherical copper is crucial, as high-performance carbon carriers also promote the reaction. This is because carbon carriers possess active sites for generating intermediate carbon-hydrogen compounds, which facilitate CO₂ electroreduction to carbon-hydrogen compounds. Additionally, carbon-based carriers can prevent the aggregation of Cu atoms, maintaining a larger distance between adjacent clusters of copper atoms, which further enhances methane production. For instance, based on this principle, Cu-based catalysts supported on MOFs demonstrate excellent performance in the reduction of carbon dioxide to methane reactions [15].

Moreover, the distance between copper particles can also be adjusted by the loading amount of catalyst on the carrier. The loading amount significantly influences the diffusion of reactants between copper particles and diffusion gradients, as well as the adsorption process of intermediates in the reduction of carbon dioxide. Research has found that under conditions of large particle spacing, the adsorption process of reaction intermediates is influenced solely by one nanometer-sized particle, without involvement from adjacent nanometer particles. Therefore, under conditions of large particle spacing, product selectivity is solely influenced by the size of nanometer particles. For smaller nanometer particles, the formation of CO increases, but the formation of H₂ is inhibited. This is due to the presence of low-coordination sites or changes in the catalyst's electronic properties, thereby enhancing the binding energy between reactants and intermediates. Hence, increasing the size of copper nanometer particles can enhance the production of CH₄. Conversely, smaller particle spacing leads to diffusion transfer of intermediates between adjacent nanometer particles. Therefore, the catalytic performance of the catalyst is influenced not only by nanometer size but also by the spacing between copper nanometer particles. Additionally, with increasing coverage of Cu particles, the re-adsorption process of reaction intermediates such as CH₄ and C₂H₄ on adjacent nanometer particles is promoted, resulting in an increase in CH₄ production. However, due to increased consumption of carbon-hydrogen compounds, selectivity towards CO decreases [16].

2.3. Creating multi-metal catalysts

The third method to enhance methane selectivity involves mixing copper with other metals to jointly participate in the reduction reaction of carbon dioxide. Bimetallic combinations can effectively regulate the electronic properties of the main elements, which can manifest in the generation of intermediate products during CO₂ reduction. Therefore, forming bimetallic alloys can enhance the catalytic activity of copper and adjust the binding strength of intermediates, thereby improving CO₂ reduction performance. Bimetallic catalysts also provide numerous active sites on their surfaces, which facilitate the formation of crucial intermediates in CO₂ reduction reactions [17]. Common high-performance bimetallic catalysts include Cu-Pd alloys, Cu-Ag, Cu-Au, Cu-Pt alloys, among others, each exhibiting significant variations in catalytic performance.

Palladium (Pd) is a special metal catalyst that exhibits unique catalytic effects in electrochemical carbon dioxide reduction. At low overpotentials, it produces formic acid (HCOOH), while at higher overpotentials, it forms hydrocarbons. Alloying copper with palladium allows for the adjustment of the chemical adsorption extent of intermediates on the catalyst surface through geometric and electronic effects, thereby achieving optimal CO₂ reduction activity and selectivity. In pure palladium, the main products of CO₂ reduction are CO with a small amount of CH₄. The low methane yield is attributed to inhibited binding of reaction intermediates [18]. Alloying Pd with Cu enhances the formation of CH₄ from CO₂ due to the presence of Pd hydride sites in the bimetallic structure. The synergistic interaction between Pd-H sites and Cu-CO sites plays a crucial role in reducing CO₂ to hydrocarbons. Compared to copper nanoparticles, the selectivity towards CH₄ is significantly improved [19].

Silver (Ag) has a lower affinity for oxygen and hydrogen compared to copper (Cu), making CO the primary product in electrochemical CO₂ reduction. In Ag-Cu bimetallic catalysts, when Cu coverage is low, the alloy shows higher selectivity towards CO, whereas catalysts predominantly composed of copper exhibit greater selectivity towards hydrocarbons [20]. Research has shown that Ag-modified Cu nanowires as CO₂ electrocatalysts can produce a significant amount of CH₄. The nanowires undergo irreversible structural reconstruction from a bimetallic segregated phase to an alloyed phase. This transformation not only eliminates the reoxidation of copper but also optimizes catalyst performance by adjusting tensile strain, thereby enhancing the binding strength with *CHO intermediates, which is beneficial for producing CH₄ in large quantities.

3. Summary

This article introduces three of the most common methods for constructing catalysts that electrochemically reduce carbon dioxide to form methane. Firstly, by adjusting catalyst morphology to expose more active sites, optimizing composition, to enhance the selectivity for CH₄, typically achieved by constructing single-atom catalysts to improve catalyst atom efficiency and by building an organic framework to stabilize the catalyst. Researchers could also build nanoscale catalysts results in smaller-sized nanostructured copper, by adjusting the size of the nanoparticles to control the generation of reaction intermediates, methane selectivity can be further enhanced. Ultimately, by combining copper with other metals to form alloys, creating multi-metal catalysts, adjusting the overall catalyst performance by leveraging the unique chemical properties of other metals.

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