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Research Progress in Copper-Based Catalysts for CO_2 Reduction

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Abstract. As carbon dioxide (CO_2) emissions increase and global warming intensifies, research and practical applications in the field of CO_2 reduction have gained significant prominence in modern society and drawn considerable global attention. Copper-based catalysts exhibit superior electrical conductivity and catalytic performance. Crucially, copper possesses distinctive carbon-carbon coupling capability, enabling the generation of high-value multi-carbon compounds. In the electrochemical CO_2 reduction reaction system, Cu as a catalyst exhibits excellent catalytic activity, efficiently driving the CO_2 electroreduction process and generating various C_{2+} products. This study aims to conduct a review and analysis of the existing literature to summarize the distinct C-C coupling ability inherent to copper-based catalysts, and to synthesize their pivotal roles and underlying reaction mechanisms in the electrochemical reduction of carbon dioxide (CO_2RR). Through this study, a more comprehensive understanding of copper-based catalysts for CO_2 reduction has been achieved. Future work is encouraged to extend and refine this foundation to propel the development and advancement of the field.

Keywords: copper-based catalyst, CO_2 reduction, electro-catalysis, C-C coupling

1. Introduction

In recent years, excessive dependence on fossil fuels has resulted in rising CO_2 emissions, intensifying the global warming crisis. Against this backdrop, the "dual carbon" goals of achieving carbon peak and carbon neutrality have emerged as a core global strategy for sustainable development, urgently requiring efficient CO_2 conversion technologies to drive the circular carbon economy. Currently, technologies such as electrocatalysis, thermocatalysis, photocatalysis, and biological conversion offer pathways for CO_2 resource utilization. Among these, the electrocatalytic CO_2 reduction reaction (eCO_2RR) stands out as a promising solution due to its distinctive advantages: This technology enables direct coupling with renewable electricity sources (e.g., solar, wind) to convert CO_2 into high-value chemicals or fuels—including carbon monoxide, formic acid, and ethylene—under ambient conditions [1]. Characterized by its green/low-carbon footprint, mild reaction requirements, and tunable product selectivity, it represents a cutting-edge strategy for achieving negative-carbon conversion. In the 1980s, Hori et al. discovered copper as an effective catalyst for the CO_2 reduction reaction to produce key hydrocarbon products, notably methane and ethylene [2]. Furthermore, copper-based catalysts exhibit robust operational stability, rendering them promising candidates for practical deployment.

In electrocatalytic CO_2 reduction, catalyst performance governs both reaction efficiency and product distribution. Metallic catalysts offer superior catalytic activity and electrical conductivity. Notably, copper exhibits intermediate *CO binding strength, rendering it the unique metallic catalyst capable of producing hydrocarbons [3]. Moreover, copper-based catalysts possess distinctive catalytic activity originating from their electronic structure. Compared to other metallic catalysts, copper exhibits distinctive capability for carbon-carbon coupling, enabling the production of high-value multi-carbon products. The product selectivity divergence (e.g., formate/ethylene/ethanol) on identical copper catalysts originates from their valence versatility, which mediates distinct CO_2 reduction pathways to govern product distribution. When CO_2 adsorbs at active sites on the copper electrode surface, it undergoes sequential proton-coupled electron transfer (PCET) at -0.8 V (vs. RHE), forming a bent H–C=O intermediate. This intermediate is progressively reduced through further PCET steps, ultimately evolving into methane or methanol [4]. However, copper-based catalysts face inherent limitations including poor selectivity, operational instability, and susceptibility to impurity-induced deactivation. To address these challenges, researchers employ hierarchical strategies—spanning size control, surface morphology engineering, and compositional tuning—to enhance their activity and product selectivity [1].

Building upon this foundation, this review synthesizes the pivotal roles and reaction mechanisms of copper-based catalysts in the electrochemical CO_2 reduction reaction, while projecting emerging trajectories for future development. Simultaneously, this review articulates critical research prospects addressing the inherent challenges of copper-based catalysts, thereby delineating prioritized research avenues for the scientific community.

2. Copper-based catalysts

2.1. Overview of copper-based catalysts

Copper-based catalysts fall under the category of metal-based catalysts. Metal-based catalysts generally exhibit good electrical conductivity and favorable catalytic performance; however, due to the high cost of certain noble metals, their application is subject to certain limitations [3].

Copper's indispensable role in electrocatalytic CO_2 reduction originates from its distinctive carbon-carbon coupling capability, which facilitates the evolution of multicarbon intermediates. Despite copper catalysts' capability to produce multicarbon products, they confront critical challenges including high overpotential, low selectivity toward target products, and poor operational stability. Notably, inadequate operational stability presents a predominant challenge, manifested by rapid activity decay during initial operation hours. This severely constrains the sustainable deployment potential of copper-based catalysts in scalable CO_2 electrolyzers.

2.2. Catalytic mechanism of copper-based catalysts

In the 1980s, Hori et al. identified copper as an effective catalyst for the CO_2 reduction reaction, demonstrating unique capability to generate key hydrocarbon products including methane and ethylene [2]. Subsequently, extensive experimental and computational investigations have been conducted to elucidate CO_2 reduction mechanisms across diverse catalytic surfaces, driving significant advancements in catalyst design.

In copper-based catalysts, electron transfer is mediated by valence transitions of copper from Cu^0 to Cu^+/Cu^{2+}. This facilitates the reduction of adsorbed CO_2 into key intermediates such as *COOH and *COO. The *COOH intermediate subsequently evolves toward C_1 products. For C_2 product formation, *CO dimerization generates the $*C_2O_2$ intermediate, which undergoes further reduction to form C-C coupled products [1]. From a thermodynamic perspective, the electrochemical CO_2 reduction reaction faces inherent constraints: the robust C=O bonds in CO_2 exhibit high stability, necessitating substantial overpotentials to initiate bond cleavage and resulting in kinetically sluggish processes. Furthermore, the hydrogen evolution reaction (HER) presents a dominant competing pathway during CO_2 reduction; kinetic analyses reveal that heterogeneous catalysis for carbon-chain product formation in eCO_2RR proceeds through multiple pathways, including distinct surface binding configurations such as chemisorption and physisorption on electrocatalysts.

2.3. Product list from CO_2 electroreduction

CO_2 reduction yields distinct products based on electron transfer stoichiometry, as summarized in Table 1. Similarly, Table 1 reveals that the equilibrium potentials for reduction half-reactions of different products are closely clustered [5].

Table 1. Electrode potentials and products of electrochemical CO_2 reduction half-reactions (25°C, pH=7)

Half-reaction	Electrode potential (V)	Product
$CO_2 + 2H_2 + 2e^- \rightarrow CO + H_2O$	-0.52	CO
$CO_2 + 2H_2 + 2e^- \rightarrow HCOOH$	-0.61	HCOOH
$CO_2 + 4H_2 + 4e^- \rightarrow HCHO + H_2O$	-0.51	HCHO
$CO_2 + 6H_2 + 6e^- \rightarrow CH_2OH + H_2O$	-0,38	CH_2OH
$CO_2 + 8H_2 + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24	CH_4
$2CO_2 + 12H_2 + 12e^- \rightarrow C_2H_2 + 4H_2O$	0.064	C_2H_4
$2CO_2 + 12H_2 + 12e^- \rightarrow C_2H_5OH + 3H_2O$	0.084	C_2H_5OH

3. State-of-the-art and mechanistic insights into copper-based catalysts

In recent years, to engineer high-performance copper-based reduction catalysts, researchers have developed a spectrum of advanced materials spanning monometallic Cu, copper oxides, copper compounds, bimetallic systems, single-atom copper, and copper-based metal-organic frameworks (MOFs) [3]. In the 1980s, Hori et al. identified copper as an effective catalyst for the CO_2 reduction reaction, demonstrating unique capability to generate key hydrocarbon products including methane and ethylene [2]. Copper's valence versatility enables mediation of distinct CO_2 reduction pathways, thereby governing catalyst-specific product distributions. This intrinsic multivalence constitutes the fundamental origin of divergent product generation on identical catalytic systems.

3.1. Metal copper catalysts: morphology and crystal facet control

Metallic copper catalysts with distinct morphologies require tailored design strategies: exposed crystallographic facets, nanodendritic architectures,rhombic dodecahedrons and particle size effect.

Firstly, regarding facet-exposure design strategies, Takahashi et al. demonstrated that for the (111) facets of face-centered cubic (fcc) copper crystals predominantly electrocatalyze CO_2

reduction to methane (CH_4), and its (100) facets selectively generate ethylene (C_2H_4) [6]. Copper nanocubes exposing {100} facets lower the *CO adsorption barrier, achieving 57% Faradaic efficiency (FE) for ethylene production in electrochemical CO_2 reduction. For crystal plane control, etching is commonly employed to treat the crystal surface, thereby exposing specific crystal planes (facets) [4].

For nanodendritic architectures, Wu et al. synthesized copper nanodendrites via wet-chemical synthesis and in situ electrochemical restructuring [7]. Compared to Cu nanoparticles, the Cu nanodendrites demonstrated: 70-120% enhancement in ethylene production rate and 60-220% increase in C_3 product yield (n-propanol and propane) with a lower onset potential of -0.55 V vs RHE. This is attributed to the porous structure between the nanodendrites, which increases the specific surface area of the catalyst. This enhancement facilitates the local enrichment of CO, thereby improving ethylene yield by approximately 70% to 120%.

For copper nanoparticles with a rhombic dodecahedral morphology, the shape can be tuned via crystal facet-selective etching. Here, specific binding agents (e.g., N,N-dimethylformamide, DMF) play a critical role in promoting the formation of such defined structures. The nanoparticles formed via selective etching exhibit a coating effect on the Cu (100) facets. This rhombic dodecahedral Cu nanostructure, possessing high-energy (110) facets, achieves significantly higher current densities than conventional counterparts [8]. These observations reveal that the high-energy (110) facets facilitate an approximately twofold enhancement in current density.

Regarding the particle size effect, Reske et al. found that in the electrochemical CO_2 reduction reaction [9], as the particle size of spherical Cu nanoparticles (Cu NPs) in the catalyst decreases, both their catalytic activity and the selectivity toward H_2 and CO in the reaction products gradually increase. This is because nanoparticles smaller than 5 nm exhibit an increased number of unsaturated coordination sites, which can strongly adsorb *H/*CO, thereby enhancing hydrogen evolution capability. Their stronger chemical adsorption capacity further facilitates the generation of H_2 and CO.

Furthermore, it is evident that the catalytic behavior of Cu-based catalysts—including reaction rate, selectivity, and activity—is strongly correlated with the crystal facet effects. The distinct atomic geometries and chemical properties inherent to different crystal facets constitute the critical factor responsible for the observed performance variations.

3.2. Copper oxide catalysts: valence synergy mechanisms

The material systems for copper oxide catalysts comprise three primary categories: Cu_2O/Cu interfaces, prismatic CuO nanostructures, Cu_2O@MOF core-shell configurations and SW-Cu_2O/Cu cubic structure.

Cu^+ species stabilize the chemical adsorption of CO_2 molecules and their reduction intermediates during CO_2 electroreduction. This promotes a reduction in the activation energy barrier for CO_2 molecular activation, thus facilitating more efficient reduction. For Cu_2O/Cu interfaces, Yang et al. engineered Cu/Cu_2O nanocrystals comprising CuO and Cu^+ species for electrocatalytic CO_2 reduction [10]. Their study revealed how catalyst architecture governs eCO_2RR selectivity. The innovation lies in the dynamic Cu^+/Cu^0 transformation, which stabilizes *CO_2^-intermediates while promoting *CO dimerization. This dual effect achieves a notable 75% Faradaic efficiency (FE) for C_2 products at -1.2 V vs. RHE.

For prismatic CuO, Li et al. synthesized CuO nanocatalysts via hydrothermal methods and applied them in the electrocatalytic CO_2 reduction reaction [11]. They observed a Faradaic efficiency (FE) of 65.1% for formate production at -0.9 V vs. RHE. This enhancement originates from highintensity electric fields localized at prism edges, which significantly reduce CO_2 adsorption energy, thereby boosting eCO_2RR activity.

For Cu_2O@MOF core-shell systems, Yang Chaoran et al. engineered a metal-organic framework (MOF) Cu-BTC protective layer over octahedral Cu_2O cores, successfully fabricating Cu_2O@Cu-BTC core-shell architectures [12]. The introduced Cu-BTC shell effectively stabilizes Cu^+ active sites, enabling the core-shell catalyst to outperform unmodified octahedral Cu_2O in CO_2-to-C_2^+ electroreduction. This configuration significantly elevates the ethylene-to-methane product ratio (C_2H_4/CH_4) by a factor of 2.5 at -1.1 V vs. RHE. Collectively, the MOF overlayer suppresses the reduction of Cu^+ species, preserving their active oxidation state during CO_2RR. This stabilization elevates the C_2H_4/CH_4 selectivity ratio by 30% relative to unmodified octahedral Cu_2O under continuous electrolysis.

For the SW-Cu_2O/Cu cubic structure, Wang et al. successfully prepared an SW-Cu_2O/Cu cubic catalyst with both Cu^+ and Cu^0 active sites using a square-wave potential modulation technique [13]. Experimental data reveal that this catalyst achieves a Faradaic efficiency ((FE) of 75% for C_{2+} product generation in the electrochemical CO_2 reduction reaction, exhibiting significantly enhanced catalytic performance compared to pristine Cu_2O cubes without square-wave potential treatment. Density functional theory (DFT) calculations further reveal that the interfacial synergistic effect between Cu^+ and Cu^0 at the catalyst interface effectively reduces the formation free energy of the key intermediate *COCO and lowers the energy barrier for water molecule dissociation. This interfacial synergistic mechanism is considered the core reason for the catalyst's high selectivity toward multi-carbon product generation in ECO_2RR. It follows that the Cu^+/Cu^0 interface constructed by square-wave potential reduces the formation energy of *COCO, enabling the catalyst to achieve a FE of 75% for C_{2+} product generation in the electrochemical CO_2 reduction reaction.

3.3. Bimetallic copper-based catalysts: synergistic effects

Bimetallic copper-based catalysts, as the nomenclature implies, incorporate a secondary metal into Cu-based systems, thereby allowing the copper catalyst matrix to achieve enhanced properties. Such synergistic effects modulate adsorption energetics of key intermediates on catalyst surfaces, facilitating C-C coupling in ECO_2RR and enhancing selectivity toward target products [1]. Bimetallic Cu-based systems feature diverse alloy architectures including: Au-Cu nanoparticles, Cu-Sn stepped surfaces, Cu-Zn porous alloys,and Ag/Cu_2O crystal plane interface.

For Au-Cu nanoparticles, Kim et al. synthesized bimetallic nanocatalysts that deliver exceptional performance in the electrocatalytic CO_2 reduction reaction, achieving >80% Faradaic efficiency for CO at industrially relevant current densities (>200 mA/cm^2) [14]. Studies have revealed that the synergistic effect between the two metals enhances the adsorption stability of key intermediates (*CO and *COOH) on the catalyst surface, while effectively inhibiting the competing hydrogen evolution reaction (HER), thereby collectively improving the overall activity of the catalyst and the selectivity toward target product formation. The team further discovered that inducing an atomic arrangement transformation in AuCu nanoparticles from a disordered alloy structure to an ordered intermetallic compound significantly elevates the Faradaic efficiency (FE) of CO_2 reduction to CO. Compared to disordered AuCu nanoparticles more susceptible to HER, the ordered structure achieves a Faradaic efficiency (FE_CO) of 80%. The performance enhancement is attributed to a three-atom-thick Au shell coating the core of the ordered AuCu intermetallic compound. It was further found that the underlying design principle lies in the compressive strain induced by the Au layer, which optimizes the electronic structure and thereby enhances CO_2adsorption.

For Cu-Sn stepped surfaces, Ye et al. fabricated Cu-Sn alloy catalysts via co-deposition for ECO_2RR [15]. These catalysts achieve 82.3% Faradaic efficiency (FE) for formate at -0.8 V vs. RHE. The design principle leverages Sn to suppress hydrogen evolution while stabilizing HCOO intermediates, ensuring exclusive formic acid pathway selectivity;The Cu-Zn porous alloy leverages its porous architecture to enhance the specific surface area and lower the *COOH formation energy barrier, which collectively elevates the Faradaic efficiency (FE) of CO generation to 90.69%; Liu Yi et al. prepared three Ag/Cu bimetallic catalysts with different exposed crystal planes of Cu_2O, specifically Ag/Cu_2O-(100) (exposing Cu_2O (100) crystal planes), Ag/Cu_2O-(111) (exposing Cu_2O (111) crystal planes), and Ag/Cu_2O-(100/111) (simultaneously exposing both Cu_2O (100) and Cu_2O (111) crystal planes) [16]. Studies have found that the Cu(100)/Cu(111) interface enhances the adsorption capacity of *CO, reduces the C-C coupling energy barrier, and ultimately achieves a Faradaic efficiency (FE) of 57.7% for C_{2+} product formation.

4. Conclusion

This paper primarily investigates issues related to copper-based catalysts for CO_2 reduction. Through a review and analysis of existing literature, it is revealed that copper-based catalysts exhibit excellent electrical conductivity and catalytic performance. Notably, copper possesses a unique C-C coupling capability, enabling the generation of high-value multi-carbon compounds. Conclusions regarding the design strategies for different copper-based catalysts are drawn, which are of significant importance for addressing current challenges and provide new insights and directions for future research. In subsequent studies, the adoption of more advanced research methodologies and techniques is recommended. Additionally, integrating findings from other disciplinary fields could broaden the scope and depth of research.

Collectively, this study advances nuanced comprehension of pertinent challenges in copper-based catalysts for CO_2 reduction. It is anticipated that subsequent research will extend and refine this foundation, propelling progress and innovation within the field.

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