

Recent Advances in Electrocatalysts for Carbon Dioxide Reduction

Xiaojie Deng¹, Ziying Huang^{2,*}, and Xuheng Wu³

¹Guangzhou No.1 High School, Guangzhou, 510610, China

²School of Energy and Power Engineering, Changsha University of Science and Technology, Changsha, 410114, China

³Shanghai Hongwen School, Shanghai, 201399, China

Abstract. With the progress of science and technology and the economy, realizing "sustainable development" has become the common development goal of many countries and regions in the world today. Carbon dioxide (CO₂) is widely used as an important carbon resource, which aggravates the problem of global warming. electrocatalytic Carbon Dioxide reduction reaction (ECO₂RR) is a key technology for converting CO₂ into useful carbon-based products (such as C₂H₄, CO, CH₃OH). Thereby increasing the economic and commercial value of clean energy worldwide. In this paper, different electrocatalysts commonly used in ECO₂RR reactions were studied. By summarizing the definition, characteristics, deficiencies, and modification strategies of different electrocatalysts, different effects of different electrocatalysts on ECO₂RR reaction were studied. This paper helps to make up for the shortage of different electrocatalysts in the literature review of ECO₂RR reaction, promote the development of ECO₂RR reaction electrocatalysts, and promote the progress of ECO₂RR reaction. Let the ECO₂RR reaction enable energy conservation and emission reduction, and provide more effective measures for the early realization of the "double carbon goal". Due to the limited literature on electrocatalysts, the current research is not comprehensive. Future studies should summarize the characteristics of different electrocatalysts in ECO₂RR reactions more comprehensively.

1 Introduction

With the rapid development of global science and technology and economy, "sustainable development" has become a common development trend in many countries and regions in the world today, and the rise of new energy vehicles with renewable energy as the main energy and the widespread use of various fuel cells are important contents of sustainable development strategy. In the development process, carbon dioxide (CO₂) is recognized as a key carbon resource [1]. CO₂, crucial for maintaining life and ecological balance, has historically remained stable. However, in the last century, human activities, particularly fossil

* Corresponding author: 201931331019@stu.qhnu.edu.cn

fuel use, have led to CO₂ levels surpassing natural absorption capacities, contributing to global warming [2].

In this context, the electrocatalytic conversion of CO₂ into useful carbon-based products (such as C₂H₄, CO, and CH₃OH) offers a promising approach to reducing carbon emissions and advancing sustainable development [1,3]. As a key technology for electrocatalytic CO₂ reduction, Electrochemical Carbon Dioxide Reduction Reaction (ECO₂RR) technology holds potential for optimizing CO₂ and supporting clean energy growth. If ECO₂RR is widely adopted, it could increase the economic and commercial value of clean energy globally. Consequently, research on CO₂ reduction electrocatalysts has surged, with ongoing updates on various materials and structures [4].

Despite its promise, ECO₂RR still lacks the refined reaction mechanisms and conditions seen in other renewable technologies like solar, wind, geothermal, and tidal energy. How these gaps are closed is critical to advancing the technology. Multi-carbon products, due to their high market value and energy density, are particularly attractive but face significant barriers to large-scale application [5,6].

Numerous scientific studies have shown that ECO₂RR (electrochemical CO₂ reduction reaction) can efficiently couple protons and electrons with various catalysts. Given that this coupling process plays a crucial role in driving technological progress, further exploration in this area is essential. Several strategies have been proposed to enhance ECO₂RR's efficiency. These include developing new acid-resistant and highly efficient catalysts and improving the catalyst's micro-environment through structural engineering and surface modification [7].

This essay aims to define ECO₂RR and elucidate its reaction mechanism. It will compare major electrocatalysts--such as alloys, metal oxides, metal complexes, and metal polymers--and suggest viable approaches for advancing ECO₂RR to some extent. By analyzing catalyst adoption and reaction prerequisites, this paper will offer insights into selecting appropriate carbon dioxide reduction electrocatalysts, thus promoting further progress in this field.

2 Reaction mechanism of ECO₂RR

Electrochemical carbon dioxide reduction (ECO₂RR) holds significant promise for achieving carbon neutrality by converting CO₂ into high-energy chemicals or fuels using renewable energy sources. Copper-based catalysts, in particular, are highly promising due to their cost advantages and excellent catalytic activity. Among the various products of ECO₂RR, formic acid stands out for its potential in industrial production, given its applications as a hydrogen storage material and a fuel for internal combustion engines. Typically, ECO₂RR is conducted with a liquid electrolyte, but this setup has limitations. The solubility of CO₂ in the electrolyte is often low, and the electrolyte can fill the pores of the catalyst, confining the reaction to the catalyst's surface and thus limiting catalytic efficiency [8].

Heterogeneous catalysis generally involves several key steps: diffusion of the reactant from the bulk phase to the catalyst surface, adsorption of the reactant on the surface, reaction of the reactant with protons and electrons to produce the product, desorption of the product from the catalyst surface, and diffusion of the product back into the bulk phase. The steps of adsorption, surface reaction, and desorption involve chemical or physico-chemical changes in the adsorption mode and strength of the reaction species on the catalyst surface. These changes reflect the reaction path and mechanism, including the formation of formic acid from CO₂.

Specifically, formic acid formation involves the intermediate step of *OCHO, which is formed after proton-electron transfer from CO₂. This intermediate is reduced to form formic acid. Alternatively, CO₂ can gain an electron to form *CO²⁻, which then reacts with protons to form the OCHO or OCHO intermediates, eventually coupling with protons and electrons to produce formic acid. Recent studies emphasize the importance of optimizing the activation

energy of CO₂ on the catalyst surface to minimize overreaction potential and enhance energy efficiency. Additionally, optimizing the adsorption of intermediates like *OCHO or OCHO can improve the electronic structure of the catalyst surface, reducing the formation of undesired *COOH intermediates and facilitating higher yields of formic acid. Given the critical role of ECO₂RR and the importance of electrocatalysts in this process, this study focuses on investigating the electrocatalysts used in ECO₂RR [9].

3 Electrocatalysts for carbon dioxide reduction

3.1 Alloy electrocatalyst

Alloy electrocatalysts consist of an active metal and an inert metal. Despite the term "alloy," these catalysts may not always be in a true alloy form under reaction conditions; they can exhibit different metal phases. The combination of active and inert metals in an alloy catalyst can create a "ligand" effect, where one metal influences the behavior of the other through electronic interactions or a collective effect.

For instance, adding iridium (Ir) to Pt facilitates naphtha reforming at lower pressures, leading to an increased production of heavier distillates. Similarly, alloying nickel (Ni) with copper (Cu) does not alter the dehydrogenation activity of cyclohexane but significantly reduces the hydrogenolysis activity of ethane.

Alloy catalysts can also improve the active site density of single atoms. While individual metal atoms can exhibit high intrinsic activity (as measured by the turnover frequency, TOF), their mass or volume activity is often limited, restricting their practical applications. Therefore, enhancing the active site density of single atoms is crucial for improving catalyst performance.

Single-atom catalysts offer notable advantages in selective reaction control. They excel in selective hydrogenation of nitro compounds, alkynes/diolefins, carbon dioxide reduction in thermal or electrocatalytic processes, and selective hydrogen peroxide formation in electrochemical oxygen reduction reactions. This selectivity arises from their unique MO_x (MN_x, MS_x, etc.) structures and electronic properties, including partial positive charges on the single-atom centers [10].

Regarding stability, there is a common misconception that single-atom catalysts are less stable than nanocatalysts. However, recent research indicates that single atoms can be more stable than their nanocatalyst counterparts. This increased stability is due to the strong covalent bonds formed between the metal single atoms and the non-metal atoms on the support surface.

3.2 Metal oxide electrocatalyst

Metal oxide catalysts such as ZnO, CeO₂, WO₃, and In₂O₃ have demonstrated strong performance in photothermal catalytic CO₂ hydrogenation reactions. Among these, ZnO is particularly favored due to its high CO₂ adsorption capacity and catalytic efficiency. CeO₂ (Fig. 1) is notable for its excellent REDOX and hydrogen storage properties, allowing it to release additional oxygen without altering its structure. The oxygen vacancies on CeO₂'s surface also enhance CO₂ catalytic reactions [11].

Researchers have focused on improving CO₂ reaction efficiency and product selectivity through the preparation and modification of copper-based materials. This includes surface modifications and nano-structural engineering. Additionally, complex oxides, which consist of multi-component oxides or transition metals like V₂O₅-MoO₃ and V₂O₅-MoO₃-Al₂O₃, are

utilized. These alloys often feature interactions between their metallic components, where some act as primary catalysts while others serve as supports or carriers [12].

Due to their unique energy band structures, chemical properties, stability, and environmental benefits, metal oxides are widely used in photothermal catalytic hydrogenation. However, studies indicate that under electrocatalytic conditions, copper-based catalysts may exhibit instability in their subsurface, with minimal impact on the activity of oxide-derived copper catalysts.

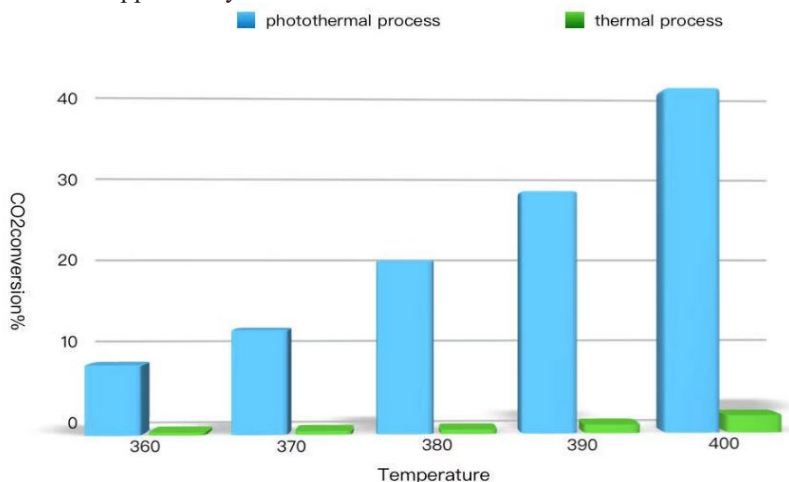


Fig. 1. Catalytic performance on Au/CeO₂ during different situations [11].

These catalysts exhibit defects that significantly impact their effectiveness in CO₂ reduction reactions (ECO₂RR). Defects in metal oxides can be categorized as point defects, line defects, surface defects, and bulk defects. Specifically, "introduced defects," such as point and surface defects, directly influence catalytic performance [13].

Adding oxygen defects to metal oxides boosts CO₂ reduction performance. These defects expose metal cations on the surface, increasing the contact area with CO₂ and reducing the activation energy of C=O bonds, thereby improving reduction efficiency.

3.3 Metal complex electrocatalyst

Metal complex catalysts have a wide range of applications in the pharmaceutical, medical, and carbon dioxide fields. Gold catalysts are mainly used in cyclic reactions to synthesize various heterocycles and thick rings with high resistance. Metal N-heterocyclic carbene complexes are widely used in the fields of medicine, materials, and catalysis, and have high activity and stability. The antibody-nail catalyst conjugate can be used for tumor-targeted therapy, and the metal nail catalyst can be delivered to the tumor cell surface through the antibody fragment to achieve collaborative therapy.

Metal complex catalysts are crucial for carbon dioxide reduction. Advances in supporting ligands have significantly influenced the reactivity and stability of these catalysts within their coordination spheres. Common ligands include organic compounds such as ethers, amines, carbonyl groups, and phosphines, which stabilize metal complexes. Recently, metal-like catalysts have demonstrated superior catalytic activity and selectivity due to their unique electronic and spatial environments, opening new avenues in synthetic chemistry and CO₂ reduction [14]. These catalysts often face challenges related to electrochemical operating conditions, leading to difficulties in formation within aqueous electrolytes and instability in molecular structure. Weak electronic communication between the fixed metal complex and

the substrate causes aggregation, which reduces electrical conductivity and overall reaction activity. Thus, metal complex catalysts are most effective when uniformly distributed on a substrate or electrically attached to an electrode surface, limiting their practical application. To enhance stability, multi-toothed ligands can act as scaffolds for stable metal complexes. Incorporating the main group of metal-like elements into transition metal complexes and optimizing their design improves stability. Additionally, integrating molecular catalysts with conductive carriers and using polymer-catalyst composites enhance stability, charge transfer, and active site exposure [15].

3.4 Colour illustrations

Metal polymers are essential for stabilizing metal nanoparticles in electrochemical CO₂ reduction reactions (ECO₂RR). They offer high catalytic performance and Faraday efficiency. The development of metal-polymer cathodes falls into two categories: polymer encapsulation and polymer binding. Polymer encapsulation enhances metal-catalyst interaction and activity but involves complex synthesis and stringent conditions. Polymer binding, on the other hand, simplifies material design and allows flexible configuration of ECO₂RR systems. Polymers can be tailored in terms of chemical function, molecular weight, and crystallinity, enabling precise control over metal-polymer interactions and catalytic properties [16]. Electropolymerized films can further improve catalyst stability and reactivity. The understanding of cathode activity with metal-polymer catalysts, the surface reaction process in ECO₂RR, and the role of surface charge and polymer interactions remains incomplete. The lack of detailed mass and charge transfer spectra at complex metal-polymer interfaces poses a significant challenge. Additionally, the significantly lower dielectric constant of polymer coatings on metal surfaces leads to inconsistent surface polarity compared to pure metal cathodes, an aspect that has been inadequately addressed in previous studies. Recent research shows that hybrid metal polymers improve ECO₂RR performance. A new multi-scale model (Fig. 2) offers insights into metal-polymer interactions. Increasing polytetrafluoroethylene (PTFE) content and adjusting the contact angle can alter the surface charge, with PTFE enhancing the availability of active sites in Cu nanoparticle catalysis.

Recent research has demonstrated that hybrid metal-polymers significantly enhance the catalytic performance of electrochemical CO₂ reduction reactions (ECO₂RR). A new multi-scale model (see Fig. 2) can understand the interaction of metal polymers. By analyzing this multi-scale model, it can show that by increasing the content of polytetrafluoroethylene (PTFE), and thus changing the contact Angle, it can change the surface charge of the cathode. In the case of copper nanoparticles catalyzing ECO₂RR, PTFE acts as a bridge to connect the less accessible active sites, which improves the overall catalytic efficiency [17].

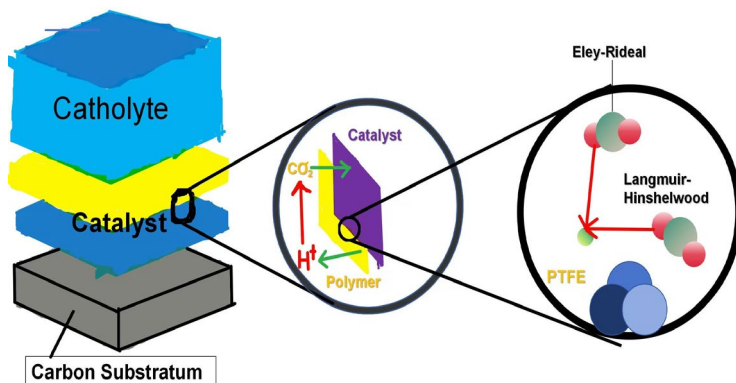


Fig. 2. New Multi-scale Model [17].

4 Conclusion

This paper provides a comprehensive analysis of electrocatalysts used in the electrochemical carbon dioxide reduction reaction (ECO₂RR). By reviewing their definitions, characteristics, limitations, and modification strategies, this article has highlighted the diverse effects these electrocatalysts have on ECO₂RR performance. Despite extensive research, literature summarizing the advantages and disadvantages of various electrocatalysts in ECO₂RR remains sparse. This gap is addressed by the study, which aims to simplify the selection process for researchers working in the field of carbon dioxide reduction. By offering a clearer overview of electrocatalysts, the paper supports the advancement of ECO₂RR technology and its role in energy conservation and emission reduction. This, in turn, contributes to the achievement of global "double carbon" goals. However, due to the limited existing literature, this review is not exhaustive.

Future studies should focus on a more detailed and comprehensive evaluation of the characteristics and performance of different electrocatalysts in ECO₂RR reaction, so as to highlight the importance of electrocatalysts in ECO₂RR reaction, further promote the development of electrocatalysts and carbon dioxide reduction industry, enable energy conservation and emission reduction, and promote the future process of "dual carbon plan".

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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