Analysis of Selection Strategies for Electrocatalytic Reduction of Carbon Dioxide using Metal-based Catalysts

Zifeng Jin *

College of Chemistry and Chemical Engineering, Central South University, Changsha,410083, China

* Corresponding Author Email: jzf2005001@outlook.com

Abstract. Excessive consumption of fossil fuels has led to excessive emissions of carbon dioxide (CO_2), triggering serious environmental problems such as global warming. Electrocatalytic reduction of CO_2 (CO_2RR), a core technology for achieving CO_2 capture and high-value conversion under the "dual carbon" goals, can directionally convert CO_2 into high-value products, such as carbon monoxide (CO), multi-carbon fuels (C_2^+), and methanol, under mild conditions. The key to its technological breakthrough lies in the research and selection of efficient catalysts. Metal-based catalysts (represented by copper-based and silver-based ones) can significantly optimize catalytic activity, product selectivity and long-term stability through modification strategies such as crystal plane regulation, defect engineering and carrier composite, demonstrating potential for large-scale application. This paper systematically reviews the research progress of copper-based, silver-based and other metal-based catalysts, analyzes their modification mechanisms and performance advantages, sorts out the core challenges currently faced in industrialization, and looks forward to the future development direction, providing a reference for the selection optimization and industrial application of CO_2RR metal-based catalysts.

Keywords: CO_2RR, metal-based catalysts, Cu-based catalysts, Ag-based catalysts.

1. Introduction

The continuous advancement of global industrialization and the large-scale consumption of fossil energy have led to excessive emissions of greenhouse gases such as CO_2, and the resulting global warming has become one of the core environmental challenges restricting the sustainable development of human society [1]. To address this issue, driven by China's strategic goals of "carbon peak and carbon neutrality", researchers have conducted systematic studies on the capture, storage and conversion technologies of CO_2, aiming to build a closed-loop carbon cycle system [2].

Electrocatalytic reduction of CO_2 (CO_2RR) is one of the core technologies for achieving high-value conversion of CO_2. It can directly convert CO_2, which has extremely high chemical stability, into high-value chemicals or energy carriers such as dimethyl ether (DME), multi-carbon fuels (C_2^+), and carbon monoxide (CO) under mild conditions, providing a feasible path for the recycling of carbon resources. Due to the fact that CO_2RR needs to overcome a relatively high reaction activation energy barrier, the design and preparation of efficient catalysts have become the core bottleneck and key breakthrough for promoting this technology from laboratory research and development to industrial application.

In current research, metal-based catalysts have become the mainstream direction due to their clear active sites and regulatory potential: copper (Cu) -based catalysts, with their unique electronic structure, can achieve the directional conversion of CO_2 to C_2^+ products and are core candidate systems for preparing liquid fuels [1]; Silver (Ag) -based catalysts exhibit excellent CO selectivity in the low overpotential range, providing an efficient path for subsequent syngas preparation. [2] By regulating the crystal plane orientation, morphology and size, electronic state and carrier interaction of such catalysts, their catalytic activity, selectivity and long-term stability can be further optimized, laying the foundation for the large-scale application of CO_2RR.

This paper will study the main structures, advantages and modification strategies of copper-based, silver-based and other types of metal catalysts. Through the research of this article, highly efficient

catalysts for the electrocatalytic reduction of carbon dioxide have been identified, which are conducive to the capture and conversion of carbon dioxide, as well as the production of industrial products such as carbon monoxide and methanol. This is not only beneficial to environmental protection, but also of great significance and far-reaching influence on the entire chemical and energy industries.

2. Overview of Electrocatalytic Carbon Dioxide Reduction (CO2RR)

2.1. Reaction principle

CO_2RR is a complex electrochemical reaction process involving multi-electron transfer and multi-intermediate transformation. Its core lies in the adsorption of CO_2 molecules at active sites on the catalyst surface, gradually breaking the C=O bond and combining protons (H^+) and electrons (e^-), ultimately generating the target product. The entire process can be divided into three key stages: CO_2 adsorption and activation, proton-electron transfer and intermediate evolution, and product desorption. Moreover, the generation pathways of different products vary significantly.

2.2. Key performance indicators

The performance of CO_2RR catalysts needs to be comprehensively evaluated through multiple dimensions of indicators. The core indicators include initial potential, Faraday efficiency, current density, stability and turnover frequency.

The Onset Potential refers to the minimum applied voltage required when the target product is first detected on the catalyst surface and is usually expressed as the potential relative to the reversible hydrogen electrode (RHE). The closer the initial potential is to the thermodynamic equilibrium potential of CO_2RR (for example, the equilibrium potential for generating CO is -0.11 V vs RHE), the stronger the catalyst's ability to overcome the activation energy barrier of the reaction, the lower the required overpotential (actual potential - equilibrium potential), and the lower the energy consumption. For example, the initial potential of silver-based catalysts for generating CO is usually -0.2 to -0.3 V vs RHE, which is significantly better than that of most metal-based catalysts [2].

Faradaic Efficiency (FE) is a core indicator that measures the utilization of electrons in electrochemical reactions, defined as: "Percentage of the total input charge consumed to generate the target product." The closer the Faraday efficiency is to 100%, the more selective the catalyst is for the target product and the fewer side reactions (such as HER). For example, optimized silver-based catalysts can achieve a Faraday efficiency of more than 95% for CO generation, while the Faraday efficiency for unmodified copper-based catalysts for C_2^+ products is typically less than 50% [1][2].

Current Density (j) is a key indicator of the catalytic activity of a catalyst, which refers to the current passing through the electrode per unit area, usually in mA/cm^2 or A/cm^2. The higher the current density, the faster the CO_2 conversion rate and the higher the catalytic activity per unit time. In industrial applications, catalysts are often required to achieve high current densities (e.g., > 100 mA/cm^2) at lower overpotentials to meet capacity requirements [3].

Stability is an indicator that measures the long-term operational ability of catalysts, and there are two main evaluation methods. One method is the chronometric current method (I-t curve), which records the change of current density with time at a constant potential, and if the current density retention rate is > 80% within 100 h, the stability is considered to be excellent. Another method is cyclic voltammetry (CV cycle). After 1000~5000 cycles, if the starting potential shifts by < 50 mV and the Faraday efficiency decreases by < 10%, it indicates that the catalyst structure and active site are not significantly damaged. The main reasons for insufficient catalyst stability include metal particle agglomeration, oxidative dissolution of active sites, electrolyte corrosion, etc [4].

Turnover Frequency (TOF) is an indicator of the intrinsic catalytic efficiency of a single active site, defined as "the number of molecules catalyzing the production of a target product per unit time". The higher the TOF value, the higher the utilization efficiency of the active site, and the stronger the

intrinsic activity of the catalyst, which is one of the core indicators for screening efficient catalysts [3].

2.3. Product classification

The directional generation of CO_2RR mainly depends on the selection of catalysts: silver and gold-based catalysts tend to generate $CO(C_1)$, copper-based catalysts are the core system for the generation of C_{2+} products, and palladium, indium-based catalysts show advantages in formic acid, methanol and other C_1 products.

3. Research progress of metal-based catalysts

3.1. Copper-based catalysts

The active site of copper-based catalysts is mainly below the +2 valence Cu, and the lower the valence state of Cu, the higher the catalytic activity. Improving the dispersion of Cu species on the surface of the catalyst is also beneficial to improve catalytic activity. The addition of additives can change the oxidation state and aggregation degree of Cu, resulting in significant changes in product distribution and catalyst stability [1].

Copper-based catalysts are the most studied catalysts for the electrocatalytic reduction of carbon dioxide to methanol [4][5]. The Cu system has two characteristics: its activity and selectivity are greatly affected by structure, morphology, and composition, and it is inactivated relatively quickly during the process [6][7].

Cu/Zn oxide catalysts obtained by co-precipitation of copper and zinc oxide (the latter at a content of 5 – 20%) are selective for ethanol (Faraday efficiency >22%), but for methanol, this value does not exceed 10 – 12% at the optimal reaction potential (0.6 V) [8]. The use of copper-zinc nanoalloy particles of different composition even leads to the formation of acetone, while ZnO-supported Cu nanoparticles are conducive to the formation of methanol [9].

The Faraday efficiency of methanol was significantly improved by electrodeposition using an O_2 film containing ZnO, which increased the rate and selectivity. The specific indicator is that Faraday efficiency is as high as 45% in 1.14 M $KHCO_3$, and 315.656 $\mu mol \cdot cm^{-2}$ methanol is obtained at a formation rate of 52.609 $\mu mol \cdot cm^{-2} \cdot h^{-1}$. [10][11].

3.2. Silver-based catalysts

Silver-based catalysts are also an important type of carbon dioxide electrocatalytic reduction catalyst, which shows the outstanding characteristics of high selectivity through reasonable method modification.

Silver (Ag) atoms were introduced into the zeolite imidazole backbone (ZIF)-8 structure, co-precipitated to obtain Ag-ZIF-8 catalyst, and silver-supported nitrogen-doped carbon (Ag-NC) catalysts were prepared by high-temperature annealing. The catalyst uses the synergy between silver and nitrogen atoms to optimize the catalyst's electronic structure, making it efficient for CO_2ER performance. The results showed that the optimized Ag-NC catalyst had better CO_2ER performance than the nitrogen-doped carbon (NC) catalyst without Ag, and the selectivity of carbon monoxide (CO) in the gas phase reached 78.66%, and the current density per unit mass of the catalyst was 54 $mA/(cm^2 \cdot mg)$ [2].

3.3. Other catalysts

In addition to copper-based and silver-based metal-based catalysts, such as palladium (Pd), indium (In), and tin (Sn) also show specific advantages in CO_2RR and are mainly used for the directed generation of C1 products (formic acid, methanol) [1].

The Pd-based catalyst has excellent selectivity for formic acid (HCOOH), and its core mechanism is that the d-band center of Pd matches the adsorption energy of HCOO intermediates, which can

promote the conversion of CO_2 to HCOO and desorption to form formic acid. In-based catalysts such as In_2O_3 are important candidates for methanol (CH_3OH) synthesis, and the oxygen vacancy in In_2O_3 can serve as CO_2 adsorption and activation sites, promoting the conversion of CO_2 to HCOO* and further hydrogenation to methanol.

A series of Bi-Inx alloy catalysts was prepared by reducing metal salts with different mass ratios, such as Bi and in metal bimetallic catalysts. With the change in the amount of indium salt, Bi nanosheets are transformed into nanosheet assembly structures. At the addition of indium salt at a mass ratio of 6%, a Bi-In bimetallic catalyst (BiIn-0.06) was obtained in which microscopic nanosheets were assembled with a three-dimensional porous honeycomb structure, which facilitated the transport of electrons and reactants. The catalyst has more surface active sites, and the two metal elements work synergistically to optimize and accelerate the chemical reaction, improving the generation efficiency of the target product. At the electrode potential of -1.0 VRHE, BiIn-0.06 has a maximum Faraday efficiency (FE_{HCOOH}) of 96.97%, an HCOOH current density of 31.9mA/cm², and a FE_{HCOOH} of greater than 91% in the range of -0.8~-0.1 VRHE potential. Different doping contents can change the crystal structure and surface morphology of Bi-based catalysts, promote the adsorption of reaction intermediates, and greatly improve the activity of CO_2RR and product selectivity [12].

4. Modification strategies

4.1. Binding with inorganic substances

Inorganic substances (such as metal oxides, metal salts, and ceramic materials) have the advantages of structural stability and strong chemical inertness and can be combined with metal-based catalysts to optimize their performance through the following mechanisms. Some inorganic substances (e.g., Al_2O_3, SiO_2, ZrO_2) can act as "inert carriers" to inhibit metal particle agglomeration (sintering) through spatial confining effects, while protecting the active site from electrolyte corrosion. Metal oxides (such as ZnO, TiO_2, CeO_2) can form an "electron synergy effect" with metal-based catalysts through electron transfer, regulate the d-band center of metals, optimize the adsorption energy of intermediates, and improve product selectivity. In addition, some inorganic substances (such as CeO_2 and MgO) have strong alkaline sites, which can adsorb CO_2 molecules (CO_2 is acid gas) through electrostatic action, increase the CO_2 concentration on the surface of the catalyst, and accelerate the reaction rate.

The electrochemical performance tests showed that the Cl-Ag catalyst showed excellent catalytic activity and selectivity in the CO_2RR CO reaction, and its performance was significantly better than that of Br-Ag and E-Ag. In the traditional H-type electrolytic cell, Cl-Ag maintained a CO Faraday efficiency of more than 90% in the wide potential window of -0.7 V ~ -1.1 V vs. RHE. In the flow-type electrolytic cell, the Faraday efficiency of CO is always maintained at more than 97% in the wide current density range of -100 ~ -400 mA/cm2, especially at the current density of -200 mA/cm^2, which meets the requirements of industrialization, and can achieve stable operation for up to 20 hours. The CO_2 absorption-release chemical reaction system of DETA-MDEA was further introduced to achieve efficient capture and release of CO_2, which increased the CO_2 utilization rate to 89.1% during the reaction process, which was significantly higher than the existing literature reports, and reduced the process cost to a certain extent. [13]

4.2. Binding to organic matter

Organic materials (e.g., carbon materials, MOFs, polymers) have the advantages of high electrical conductivity, high specific surface area, and adjustable structure, and can be combined with metal-based catalysts to optimize their performance through the following mechanisms:

The use of carbon materials can increase the electron conduction rate. Carbon materials (such as graphene, carbon nanotubes, graphite carbon nitride g-C_3N_4) have excellent electrical conductivity (graphene conductivity > 10^4 S/m) and can be combined with metal-based catalysts to construct "efficient electron transport channels", reduce electron transfer resistance, and increase current

density. The C-modified Cu catalyst (Cu-C 6%) achieves high selectivity for C_2H_4 over a wide potential range and exhibits high amperage-level current density during the CO_2RR process. At 1.0 mol· The total current density of L−1 KOH electrolyte can reach 1.25 $A \cdot cm^{-2}$, with FE(C_2H_4)being 54.4% and FE (C_{2+}) being 80.2% [14].

The use of MOFs and polymers can regulate the dispersion of active sites. MOFs (metal-organic frameworks) and polymers have a porous structure (specific surface area is usually > 1000 m^2/g), which can be used as "molecular templates" to evenly disperse the active sites of metal-based catalysts in the pores and increase the number of active sites [3]. Figure 1 shows a schematic diagram of a Cu-THQ (tetrahydroxyquinone) catalyst, one of this type of catalyst.

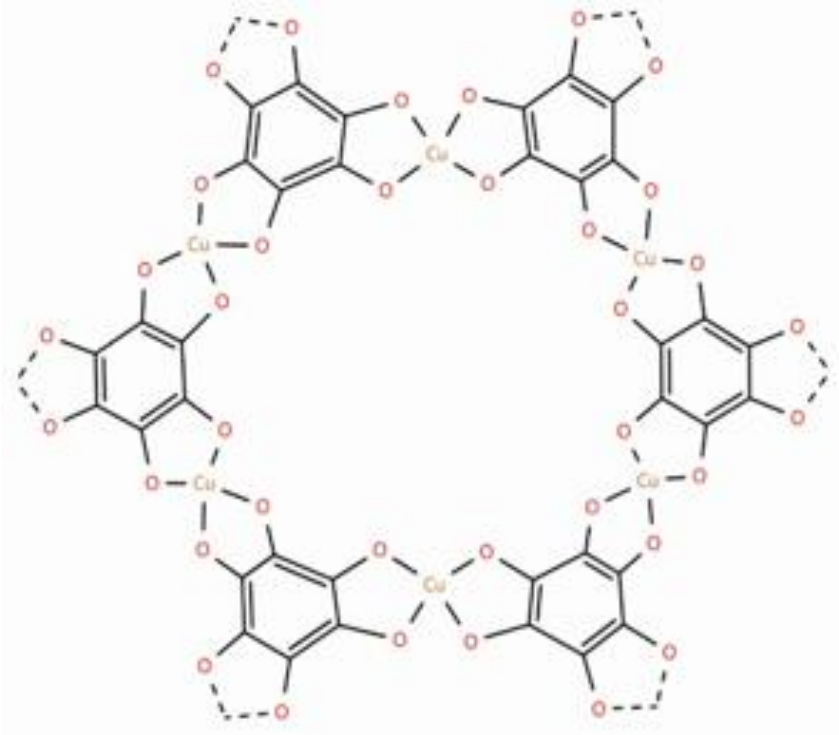

Fig 1. Schematic diagram of Cu-THQ (tetrahydroxyquinone) catalyst.

Some organic matter (e.g., fluoropolymers, N-doped carbon materials) have hydrophobic or specific functional groups, which can reduce H^+ adsorption on the catalyst surface and inhibit HER side reactions.

5. Industrialization challenges and future directions

5.1. Industrialization challenges

Some metal-based catalysts still have side reactions (such as HER and carbon deposition), resulting in insufficient selectivity of the target product. Industrial applications require catalysts to operate continuously for thousands of hours. However, most current metal-based catalysts are prone to problems such as metal particle agglomeration, oxidation and dissolution of active sites, and collapse of the carrier structure during long-term operation.

Some high-performance metal-based catalysts rely on precious metals (such as Pd, Au-doped Ag catalysts), which are scarce and expensive to be applied on a large scale. Even for non-precious metals such as copper and silver, high-purity nanoscale metal precursors are expensive to prepare.

5.2. Future directions

Scientists should develop different forms of catalysts that are both efficient and cost-effective. They can continue to study the reaction mechanism of electrocatalytic reduction of carbon dioxide on different catalysts, actively try the combination of different metals and various inorganic and organic

substances, improve and innovate the preparation methods of catalysts, change the composition ratio to make them exert different properties, and ultimately screen out the type of catalyst with the best performance and the lowest cost. It is recommended to give priority to metals with relatively lower costs such as copper. Modification is superior to directly using precious metal materials. The "series catalytic system" can combine the advantages of different catalysts to achieve multi-step reaction coordination [15]. Single-atom metal catalysts (such as single-atom Cu and Ag) have the advantages of a high atomic utilization rate (close to 100%) and uniform active sites, which can significantly reduce metal usage and costs.

6. Conclusion

Electrocatalytic reduction of CO_2 (CO_2RR) is a core technology for achieving the "dual carbon" goals and promoting the high-value conversion of CO_2, and the selection and optimization of metal-based catalysts are the key to breakthroughs in this technology. Three types of catalysts, namely copper-based catalysts, silver-based catalysts, and other metal-based catalysts such as palladium and indium, can meet the requirements of different products and provide support for the diversified applications of CO_2RR. Modification strategies are the key to performance improvement. Through the synergy of multiple strategies, a comprehensive enhancement of catalytic activity, selectivity, and stability can be achieved. The performance of some modified catalysts has approached industrial requirements. However, the industrialization development still faces some challenges. In the future, it needs to be optimized through the development of new catalysts, the optimization of green preparation processes, the design of efficient reactors, and in situ characterization.

Metal-based catalysts are an important type of electrocatalytic reduction catalysts for carbon dioxide, with copper-based and silver-based catalysts as representative types. Through continuous adjustment and optimization, they have demonstrated outstanding performance. In the future, with the continuous efforts of scientific workers, they will shine brightly in the resource utilization of carbon dioxide, making an indelible contribution to alleviating the greenhouse effect and achieving the "dual carbon" goals.

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