International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 14 Issue 5 ǁ May 2026 ǁ PP. 94-99

Development and Reaction Mechanism Introduction of Cu-Based Catalysts Applied to CO_2RR

Xichen Feng[a] *
[a] *School of Materials and Chemistry, University of Shanghai for Science & Technology, Shanghai, 200093, China*
Corresponding Author: Xichen Feng

Abstract: *Since the oil crisis, research on the synthesis of clean and renewable energy has received widespread attention. Electrochemical reduction has proven to be an effective approach for converting CO_2 into industrial chemicals and fuels needed by humans. Cu-based materials, as catalysts capable of converting CO_2 into various carbon products, play a crucial role in the industrialization of CO_2RR and have achieved remarkable results through the efforts of researchers. However, for true industrial application, Cu-based catalysts still face significant challenges, such as difficulty in achieving high selectivity for specific target products, catalyst reconstruction, and structural instability. In this regard, this paper introduces the mechanism of CO_2RR and the current development status of Cu-based catalysts, providing insights for future design.*

Date of Submission: 12-05-2026 Date of Acceptance: 26-05-2026

I. Introduction

Carbon dioxide (CO_2), as a widely present greenhouse gas, accounts for approximately 0.03% to 0.04% of the total atmospheric volume and plays a role in retaining heat on the ground[1-2]. However, since the Industrial Revolution, the large-scale use of fossil fuels has led to a sharp increase in atmospheric CO_2 levels. According to relevant reports, global CO_2 concentrations have risen from about 280 ppm at the end of the 18th century to 415 ppm in recent years, triggering a series of significant problems: global warming, rising sea levels, loss of biodiversity, acid rain, and more[3]. Moreover, as society develops, human demand for energy continues to rise, and the use of fossil fuels shows no sign of decreasing. Therefore, it is imperative to develop green, recyclable clean energy and to curb and reduce the current atmospheric CO_2 levels. Converting CO_2 into raw materials urgently needed for daily life and industrial production can not only address the issue of excessive CO_2 levels but also reduce the production costs of industrial raw materials. To this end, researchers are attempting to achieve this goal through various technological approaches[2, 4].

Among the various approaches, electrocatalysis can convert CO_2 into a variety of high-value carbon products (such as C_2H_4, C_2H_5OH, C_3H_8O, etc.)[5-7]. Compared to other methods, it offers advantages such as no restrictions on working environment, high energy conversion efficiency, and a wide range of achievable products. Additionally, it enables the effective utilization of wind and solar power, which are often unstable due to their dependence on production conditions and, in most cases, cannot be reliably integrated into the power grid for domestic and industrial use[8]. Electrocatalysis provides an excellent way to harness these renewable energy sources, enabling green production and green usage, thereby playing a significant role in protecting the global environment[9].

Given the above application demands and the existing research framework, this paper provides a detailed introduction to the reaction mechanism and current development status of electrocatalytic CO_2 reduction technology, with a focus on reviewing the advanced work and recent progress of Cu-based materials in the field of electrocatalytic CO_2 reduction.

1. Electrocatalytic CO_2 Reduction Mechanism

Electrocatalytic CO_2 reduction is a complex reaction involving multiple steps and intermediates. Depending on the product, the process involves the transfer of 2, 4, 8, or even more electrons[3]. Table 1 lists the number of electrons transferred and the standard reaction potentials for generating different products during the CO_2RR process[10-11]. Under conventional conditions, CO_2 molecules are in a chemically inert state[12-13], which means that breaking the bonds between C and O requires overcoming an energy barrier of approximately 750 $kJ \cdot mol^{-1}$. The thermodynamic and kinetic processes of the reaction play a dominant role in this context.

Table 1 Potentials required for the formation of reduction products at room temperature, atmospheric pressure, and pH 7[10-11].

Reaction Equation	Potential (V vs.RHE)
$CO_2 + e^- \rightarrow CO_2^-$	-0.197
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH^-$	-0.610
$CO_2 + 2H_2O + 2e^- \rightarrow HCOOH^- + OH^-$	-1.491
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.530
$CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$	-1.347
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	-0.913
$2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$	-1.003
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.480
$CO_2 + 3H_2O + 4e^- \rightarrow C + 4OH^-$	-1.311
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	-0.200
$CO_2 + 2H_2O + 4e^- \rightarrow C + 4OH^-$	-1.040
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.380
$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^-$	-1.225
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.240
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH-$	-1.072
$2CO_2 + 12H^+ 12e^- \rightarrow CH_4 + 4H_2O$	-0.349
$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	-1.177
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	-0.329
$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$	-1.157
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	-0.270
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + H_2O$	-0.310

The thermodynamic theory of E CO_2RR primarily involves the Gibbs free energy of the reactants and products. As shown by the data listed in Table 1, the activation of CO_2 molecules requires an overpotential of -1.9 V, which exceeds the formation potentials of many reduction products. Therefore, the introduction of catalysts is necessary to lower the energy barrier of the reaction[14]. With the aid of catalysts, CO_2^- (activated CO_2) formed through electron coupling plays an important role in the ECO_2RR system, as its presence can reduce the overpotential required for product formation. According to the formula $\Delta G = -nFE$ (where ΔG represents Gibbs free energy, n is the number of electrons transferred, F is Faraday's constant, and E is the onset potential), it can be observed that the reaction processes for generating hydrocarbons/alcohols are thermodynamically more favorable compared to CO and HCOOH[15]. However, due to the kinetic barrier imposed by the concentration of mobile protons in the electrolyte, these products are more difficult to obtain in practice. Additionally, as seen in Table 1.1, the potentials required for the formation of all products are lower than the standard potential of HER. Consequently, the competitive hydrogen evolution reaction inevitably occurs during the CO_2RR process[16].

The kinetics of E CO_2RR are directly related to product selectivity and reaction rate. During the CO_2RR process, CO_2 needs to be converted into final products through the following multiple steps[17-19]: 1) CO_2 molecules dissolve into the electrolyte; 2) CO_2 molecules are transferred from the electrolyte and adsorbed onto the catalyst surface; 3) CO_2 molecules undergo a series of steps to transform into final products; 4) The products desorb from the catalyst surface. Among these, step 3) involves multiple pathways, including C=O bond cleavage, C-C bond coupling, C-H/O-H bond formation, etc., ultimately leading to various carbon-containing products. To date, the CO_2RR products reported by researchers mainly include the following: 1) C1 products, including carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), formaldehyde (HCHO), methanol (CH_3OH), etc.; 2) C_2 products, including ethylene (C_2H_4), ethanol (C_2H_5OH), ethane (C_2H_6), etc.; 3) C_{3+} products, such as propanol (C_3H_7OH). Furthermore, improving proton transfer is an effective strategy for optimizing kinetic steps, with noticeable effects achieved by using suitable electrolytes (e.g., carbonates, bicarbonates) and electrolysis cells (e.g., flow cells). Electron transfer is another key point, as it not only controls the final product selectivity but is also closely related to the reaction rate. The electron transfer capability primarily depends on the conductivity of the catalyst and the electrolyte. Selecting highly conductive catalysts/substrates and electrolytes can effectively optimize the electron transfer capability.

The complete reaction pathway of E CO_2RR involves multiple processes, starting with the activation of CO_2 molecules adsorbed on the catalyst surface (i.e., the formation of CO_2^-) and the bending of the linear molecular structure[20-21]. Depending on the binding mode, CO_2^- interacts with the catalyst in the forms of $^*COOH$ and *OOCH (* represents the active site on the catalyst surface). If the active sites of the catalyst bind strongly with the C atom of CO_2^-, the *COOH configuration tends to form. Additionally, the binding strength of C-*/O-** can be tuned by electron-poor/electron-rich sites on the catalyst surface—due to electrostatic interactions, O tends to bind to electron-poor sites, while C atoms prefer electron-rich sites. As the reaction proceeds, the $^*OOCH$ intermediate gains e^- and H^+ to form HCOOH and desorbs, while $^*COOH$ converts to $^*CO$ and desorbs as CO. Among these, $^*CO$ is a key intermediate capable of generating a series of high-value-added products: For C_1 products, the process involves C–O bond cleavage, C–H and O–H bond formation, along with additional $2e^-$, $4e^-$, and $6e^-$ reactions, ultimately yielding HCHO, CH_3OH, and CH_4. For C_2 products, the dimerization of *CO, *CHO, and *COH is the rate-determining step, followed by the formation of *COCO, *COCHO, and *COCOH, leading to the final

products. For C_3 products, the reaction pathway is similar to that of C_2 products but involves an additional trimerization step. Based on the above brief description, the CO_2RR pathways for C_1, C_2, and C_3 products are illustrated in Figure 1[22].

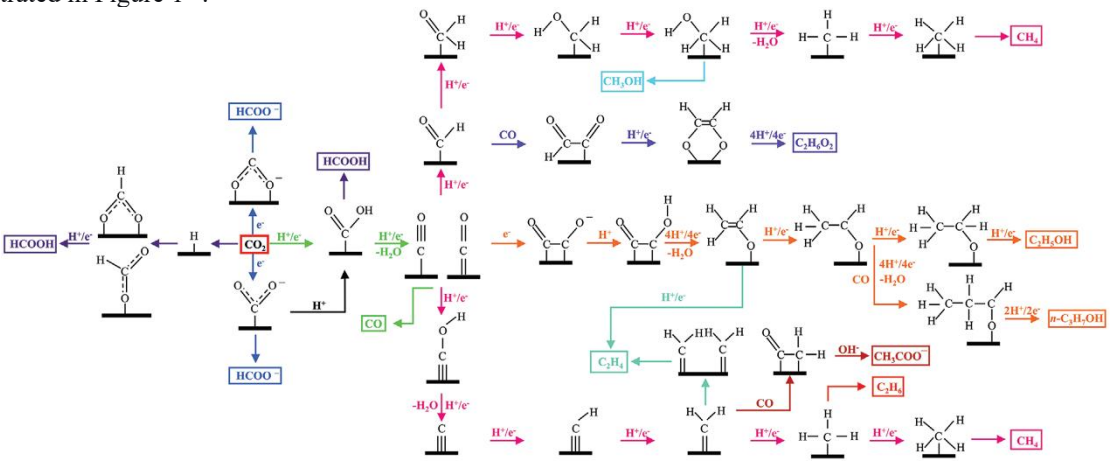

Figure 1. Schematic illustration of the reaction pathways for the formation of various compounds via CO_2RR[22].

2. Research Progress of Cu-Based Catalysts

Copper-based materials can reduce CO_2 to a variety of products (including C_1 and C_{2+}), and their wide selectivity range makes them ideal catalysts for electrocatalytic CO_2 reduction systems. Through continuous research, various different copper-based catalyst systems have been developed. This section provides an overview of the design strategies for CO_2RR electrocatalysts, including single-metal Cu, Cu alloys, Cu oxides, and Cu compounds.

Single-metal Cu catalysts: Single-metal Cu catalysts are the simplest and earliest studied Cu-based catalysts, with preparation methods including wet chemical reduction and electrodeposition[23-24]. The wet chemical reduction method typically uses strong reducing agents such as sodium borohydride ($NaBH_4$) or hydrazine hydrate ($N_2H_4 \cdot H_2O$) to reduce copper salts to metallic Cu. The electrochemical deposition strategy, on the other hand, employs a three-electrode working system to reduce and deposit copper species from the electrolyte onto a prepared substrate. By adjusting relevant parameters during the reaction process, such as applied voltage/current, deposition time, solution pH, type of copper salt, and electrolyte concentration, the structure and morphology of the Cu catalyst can be effectively controlled. Therefore, this method is more popular than the wet chemical reduction approach. Chen et al. prepared a Cu^0-rich catalyst grown on the surface of an Au working electrode using electrochemical deposition[25]. Electrochemical analysis showed that it possesses a significantly enhanced active surface area and reduced charge transfer resistance, while the Faradaic efficiency for C_2H_4 remained stable above 40%. Tu et al. developed an alkali-ion adsorption-controlled electrodeposition method to grow Cu nanocrystals with controllable morphology[26]. In flow cell reactor tests, the Cu nanocrystals achieved a Faradaic efficiency of over 80% for C_{2+} products. In situ attenuated total reflection Fourier-transform infrared spectroscopy and density functional theory calculations confirmed that alkali ions (Li^+, Na^+, K^+, Cs^+) added to the electrolyte play a regulatory role in the growth of the Cu nanocrystals.

Cu Alloy Catalysts: By incorporating additional metals into the system to form Cu-based alloys, the electronic structure of the catalytically active centers can be effectively tuned, thereby altering the adsorption strength of reaction intermediates, enhancing the selectivity for target products, while suppressing the competitive hydrogen evolution reaction. Xie et al. employed density functional theory to calculate the adsorption strength of intermediates on various metal-Cu alloys[27]. Their study showed that under acidic conditions, X-Cu (X = W, Cr, Mo, etc.) type alloys exhibit stronger adsorption for $^*CO_2$ and $^*CO$ than for $^*H$, favoring the formation of C^{2+} products. Research has indicated that the doping amount of the non-Cu metal in the alloy can influence product distribution. Li et al. prepared Cu-Pd alloys with different atomic ratios using wet chemical reduction and electrochemical replacement strategies[28]. The test results showed that at low Pd content (Cu/Pd-0.25%, Cu/Pd-0.5%), the selectivity for C_{2+} products was higher; however, when the Pd content increased (Pd > 1%), the FE_{CO} increased by 3-5 times. Using in situ Raman spectroscopy, the authors found that the $^*CO$ on the surface of Cu/Pd-1% mainly consists of low-frequency band $^*CO$, which is more favorable for the formation of C_{2+} products. DFT calculations confirmed that the bimetallic Cu-Pd catalyst enhances the adsorption of $^*CO$ and lowers the energy barrier for C-C coupling. Shang et al. prepared Cu-Sn alloy catalysts (Cu_xSn_y) with different ratios using electrodeposition[29]. Among them, low-entropy Cu_3Sn achieved a Faradaic efficiency of 64% for ethanol, while high-entropy Cu_6Sn_5 mainly produced formic acid. This difference is attributed to the enhanced adsorption of key intermediates for ethanol formation on low-entropy Cu_3Sn. To date, widely reported Cu alloy catalysts include Cu-Ag, Cu-Pd, Cu-Au, Cu-Sn, Cu-Gd, Cu-Mg, Cu-Zn, and Cu-Mo. These introduced atoms generally enhance

the adsorption capacity of $^*CO$ on the catalyst surface, making them suitable for the preparation of C_{2+} products. Hoang et al. used DAT as an inhibitor during electrodeposition to prepare high-surface-area Cu-Ag nanowire catalysts (CuAg-wire)[30]. Compared to single-metal Cu-wire, CuAg-wire increased the Faradaic efficiency of C_2H_4 from less than 40% to nearly 60%, while maintaining an FE_{C2H5OH} of about 25%. Subsequent electrochemical mechanism tests and in situ Raman spectroscopy indicated that the stable Cu oxide overlayer on the catalyst surface, together with Ag, promotes $^*CO$ dimerization, thereby facilitating the conversion to C_{2+} products. Furthermore, through structural tuning, Cu-based alloys can also achieve high selectivity for C_1 products. Ren et al. reported a Cu-Sn alloy ($Cu_{97}Sn_3$), in which isolated Sn sites exhibited an extremely high surface density (8%). Compared to Cu_{100} and $Cu_{70}Sn_{30}$, $Cu_{97}Sn_3$ achieved an FE_{CO} close to 100%. The authors stated that density functional theory demonstrates that the unique Cu-Sn local coordination environment of $Cu_{97}Sn_3$ plays a crucial role in modulating the types of reaction intermediates.

Cu Oxides: Cu oxide (OD-Cu) catalysts, primarily composed of CuO and Cu_2O, feature characteristics such as multiple grain boundaries, low coordination numbers, and specific oxygen content, demonstrating promising potential for the production of high-value multi-carbon compounds like C_2H_4, C_2H_5OH, and C_3H_8O[12, 31-32]. Extensive research has been conducted on the morphology and grain boundaries of OD-Cu catalysts. Mandal et al. attempted to elucidate the role of grain boundaries by preparing nanoneedles (NNs), nanocubes (NCs), and nanoparticles (NPs)[33]. XRD confirmed the corresponding crystal facets of the catalysts, including the Cu_2O (111) and (200) facets for NNs, the Cu_2O (200) facet for NCs, and the Cu_2O (111) facet for NPs. Theoretical calculations confirmed that after the initiation of the CO_2RR reaction, the reduction of Cu_2O to Cu is inevitable, leading to the formation of numerous defects and grain boundaries due to the stripping of oxygen atoms, thereby enhancing catalytic performance. Lei et al. investigated the difference in activity between pristine metallic Cu and Cu generated through in situ reduction during the reaction. They prepared HQ-Cu, containing Cu, CuO, and Cu_2O, via thermal quenching, as well as AN-Cu through anodization. HAADF-STEM and EELS observations revealed that Cu oxides were reduced to Cu^0 during the reaction, and the reduced HQ-Cu maintained a high Faradaic efficiency for C_2H_4, demonstrating that C_{2+} product selectivity is not directly related to a specific oxidation state of Cu. Although OD-Cu catalysts exhibit good selectivity for C_{2+} products, their unstable oxidation state makes them highly susceptible to reduction and reconstruction during the reaction. To address this, researchers have proposed various stabilization strategies. Jang et al. constructed Al-doped CuO materials (CuO-Al)[34]. SEM observations showed that the addition of Al caused CuO to reconstruct into a nanosheet structure during the reaction while maintaining high selectivity for C_{2+} products.

Cu-Based Compounds: Compared to single-metal Cu, alloys, and oxides, Cu-based compounds are the most widely reported category of catalysts, covering an extensive range. Based on the position of their anions in the periodic table, they include Group B (primarily B), Group C (primarily C), Group S (S, Se, etc.), and the halogens (F, Cl, Br, etc.)[35-36].

The electronic configuration of the B atom is $2s^2\ 2p^1$, possessing one occupied and five empty p orbitals, which allows it to effectively tune the valence state of Cu[35, 37]. Additionally, the Lewis acid nature of B enables it to accept electrons from Cu, making the local electronic structure of Cu more positive, thereby promoting the conversion of CO_2 to C_{2+} products. Sargent et al. reported that B doping can improve the stability of Cu^+ and effectively enhance the production of C_2 products (FE > 80%). Cu atoms located near B exhibit a raised d-band center and positively charged characteristics, which demonstrate stronger binding energy for CO and enhanced CO + CO dimerization.

Carbon (C) materials are widely used in the field of electrocatalysis due to their ability to serve as conductive platforms for active sites and active phases. In recent years, significant progress has been made in the study of CO_2 conversion to tunable carbonaceous products catalyzed by Cu modulated by C materials, mainly focusing on carbon-supported SACs and cluster materials. Similar to C, nitrogen (N) materials, with three unpaired electrons and diverse coordination forms, are particularly notable. N atoms tend to retain lone pair electrons when forming compounds, possess a small atomic radius, short coordination bond lengths, and strong interatomic bonding forces, making them ideal candidates for the development of coordination catalysts. The work by Yin et al. indicated that Cu_3N nanocubes prepared via a solvothermal method exhibit good CO_2RR selectivity and stability[38]. Theoretical calculations demonstrated that the exposed Cu_3N (100) facets can effectively promote CO–CHO coupling, while N vacancies also help stabilize Cu^+, thereby providing sustained reactivity.

Chalcogen elements, also known as Group O elements, generally refer to O, S, Se, Te, etc. Since Cu oxides have already been discussed separately in the OD-Cu section, the chalcogen elements reviewed in this section do not include O. Chalcogen elements are widely used to construct advanced copper-based catalytic materials due to their versatility and accessibility[39-41]. Among them, metal sulfides possess good electrical conductivity, tunable electronic structures, and flexible compositions, and have been widely applied in the field of catalysis—for example, MoS_2 is an ideal HER material. Copper-based sulfides (Cu_xS_y) offer low cost and high abundance. A series of studies have been conducted on the application of sulfur-doped thin films. Research has shown that the presence of S can alter the oxidation state of Cu centers, affecting the adsorption behavior of key intermediates.

Similar to OD-Cu, S in the catalyst is also leached during the CO_2RR process, facilitating the formation of abundant anion vacancies and active centers with tunable electronic and coordination structures. The outermost electronic configuration of Se is similar to that of S and O, but Se has a larger atomic radius and lower electronegativity, thus exhibiting unique characteristics in modulating the valence state of Cu and the reduction reaction pathway. Se coordination can increase the covalency of metal–anion bonds and the d-orbital occupancy of Cu, because Se has lower electronegativity than O[42]. Catalytically active Cu centers with modulated electron density can promote intermediate CO adsorption, prolong CO residence time, and lead to increased hydrogen adsorption in the vicinity through Lewis acid–base interactions, thereby facilitating the formation of more C_{2+} products. Research on tellurium-coordinated copper-based catalysts is relatively limited. Tellurium has low electronegativity and forms more covalent bonds with copper than sulfur and selenium. In chalcogen-modified copper systems, tellurium introduces low-basicity sites with weaker blocking effects on adjacent copper atoms, leading to poor formic acid selectivity. However, precise design can make copper telluride an efficient CO_2RR catalyst.

Halogen (F, Cl, Br, I) atoms, due to their unique electronic configurations, can readily combine with Cu atoms in catalysts (in the order $F^- < Cl^- < Br^- < I^-$)[32, 37]. F^- is typically used to promote electron transfer and charge redistribution in copper-based catalysts, while Cl-, Br-, and I- ions may introduce defects, owing to their different ionic radii (F^-: 0.136 nm, Cl^-: 0.181 nm, Br^-: 0.196 nm, I^-: 0.220 nm) and decreasing electronegativity ($F^- > Cl^- > Br^- > I^-$). Research has shown that the presence of halide ions, either in Cu-based catalysts or in the electrolyte, can influence surface reconstruction during electrochemical oxidation/reduction cycles, providing effective strategies for the development of highly stable copper-based catalysts.

II. Conclusion

Converting CO_2 into industrial chemicals and fuels needed by humans through electrochemical reduction has been proven to be an effective means of mitigating the greenhouse effect, offering advantages such as high energy efficiency, environmental friendliness, and low cost. Among these, Cu-based catalysts hold great promise due to their ability to convert CO_2 into a variety of C_{2+} products. However, although Cu-based compounds provide numerous solutions to meet the demands for various chemical feedstock productions and have achieved some success in practical industrial applications, there are still notable shortcomings that cannot be ignored, such as poor selectivity and insufficient stability. At the same time, the phase and structural changes of the catalysts during the reaction remain poorly understood. Therefore, there is an urgent need to develop low-cost, green electrocatalysts with high product selectivity, good stability, and a well-understood reaction mechanism.

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