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Review

Recent Progress in Electrochemical CO_2 Reduction at Different Electrocatalyst Materials

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Abstract: Given the environmental problems caused by burning fossil fuels, it is believed that converting carbon dioxide (CO_2) into chemical inputs is a great ally to generating clean energy. In this way, investigative studies related to electrochemical CO_2 reduction (CO_2RE) concerning the behavior of metal catalysts have received attention about the processes involved. CO_2RE can be an important tool to mitigate the presence of this gas in the Earth's atmosphere. Given these considerations, in this review, we report the main catalysts used to act as CO_2RE. Among them, we emphasize catalysts based on Ni, Zn, and Cu, which encompass the main properties related to the electrochemical conversion of CO_2. Regarding the Cu-based catalyst, it presents high conversion efficiency but low selectivity. Furthermore, we also describe the main mechanisms related to the electrochemical conversion of CO_2.

Keywords: carbon dioxide; electroreduction of CO_2; electrocatalysts; copper; zinc; nickel

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1. Introduction

1.1. General Perspectives

Over the years, there has been an increase in the use of fossil fuels (oil, natural gas, and coal), which are responsible for the greenhouse effect [1–3]. Recent research, presented by Mikkelsen, Jørgensen, and Krebs, points out that the atmospheric concentration of greenhouse gases, including CO_2, nitrous oxide (N_2O), methane (CH_4), and chlorofluorocarbons (CFCs), reveals an excess of approximately 3.9% in relation to the natural cycle carbon [4].

CO_2 is naturally present in the atmosphere in quantities less than 0.035%, being essential to the life of the planet as it is one of the fundamental elements for carrying out photosynthesis, the process in which photosynthetic organisms transform solar energy into chemical energy, absorbing atmospheric CO_2 and transforming it into glucose and releasing oxygen (O_2), thus contributing to the chemical energy of living beings [5].

From the second half of the 20th century, after the Second World War, the amount of CO_2 in the atmosphere began to increase [6]. Since then, some environmental issues relating to the emission of greenhouse gases (GHG) have been discussed. Faced with this concern, in 1997, the United Nations (UN) proposed an agreement (called the Kyoto Protocol) for developing countries to commit to reducing GHG emissions. This agreement was implemented between 2008 and 2012 to reduce the greenhouse effect by 5.2% and so that annual temperatures would not exceed 1.5 °C of pre-industrial levels [7]. To maintain control over CO_2 and other GHG emissions, this protocol was extended to the Paris Agreement in 2015. In this new agreement, the countries involved, such as Australia, the United Kingdom, Norway, Switzerland, Ukraine, and the European Union, presented their commitments, following what each government considers viable based on the local social and economic scenario [8]. Bearing in mind that UN member countries are concerned about GHG emissions and their respective consequences, the 2030 agenda was then signed in the

Paris Agreement, where 17 objectives for sustainable development (SDG) were established. The Sustainable Development Goals constitute a global call to eradicate poverty, preserve the environment and climate, and ensure the opportunity for all people, regardless of location, to achieve peace and prosperity. Within these objectives, the main focus is on Objective 13, which aims to combat climate change [9].

Against this problem, the objective of this review is to present studies produced by the scientific community focused on the capture and use of CO_2 through the development of different electrocatalysts, aiming at a more sustainable approach to obtaining less polluting chemical products.

1.2. Alternatives to Mitigate CO_2 Emissions

CO_2 can be captured directly from industrial sources through three methods: post-combustion capture, pre-combustion capture, and combustion of fossil fuels in a pure oxygen environment. Post-combustion capture, which uses chemical solvents such as monoethanolamine, separates CO_2 from the exhaust gas, which is composed mainly of a mixture of N_2 and CO_2 [10]. Researchers are directing efforts to reduce costs and improve the efficiency of post-combustion capture. This involves exploring more effective chemical solvents and membranes for separating CO_2 from N_2. At the same time, materials are being developed to reduce investment costs in large separation equipment required for industrial-scale capture. Research also focuses on the development of new materials capable of resisting higher temperatures and pressures, aiming to improve efficiency in energy generation with CO_2 capture [10].

One of the alternatives for reducing CO_2 emissions into the atmosphere is the conversion of atmospheric CO_2 into low-carbon fuels. It can be used as an energy storage carrier, demonstrating great importance in alleviating energy shortages and global environmental pollution [11]. Currently, several methods for CO_2 conversion are being investigated, such as photocatalytic reduction, electrocatalytic reduction, and photoelectrocatalytic CO_2 reduction. Photocatalytic reduction of CO_2, similar to the photosynthetic process in plants, seeks to convert atmospheric CO_2 into oxygen, a function performed by green plants and photosynthetic bacteria. Over the years, scientists have developed and designed several types of photocatalysts, covering metal oxides, metal nitrides, metal phosphides, and semiconductors, among other materials [11]. Although there are a variety of photocatalytic materials, their practical efficiency has not yet reached an ideal level. Given this, researchers have explored techniques to improve photocatalytic performance, involving control of morphology and size, manipulation of the crystalline face, doping, application of noble metals, recombination of semiconductors, sensitization by dyes, and introduction of defects, among other approaches [11].

The other two methods to reduce carbon dioxide emissions are electrocatalytic reduction of CO_2 and photoelectrocatalytic reduction of CO_2. The first method is the process that uses the external electric field as the main source of energy to induce the redox reaction in the electrodes and the photoelectrocatalytic reduction of CO_2, as the two previous techniques present limitations for their application. Another method is the photoelectrocatalytic reduction of CO_2, which refers to the process in which the semiconductor photoelectrode generates electrons by photoexcitation, and then electrons migrate to the electrode surface under the guidance of an external voltage to carry out the catalytic reduction of CO_2 [11].

Concerning other processes that involve CO_2 capture, it is adsorption, because a good adsorbent should present high selectivity, high adsorption capacity at low pressure, fast adsorption/desorption kinetics, good mechanical properties, high hydrothermal and chemical stability, high regeneration capacity, and low synthesis costs. Some examples that have been studied are zeolites, metal-organic frameworks (MOFs), and carbon-based adsorbents [12].

CO_2 captured from various sources can be reused in a process known as carbon capture and utilization. This not only reduces the CO_2 concentration in the atmosphere but also reduces dependence on fossil fuel raw materials. Research focuses on CO_2 storage and capture techniques, particularly the effective and long-term use of catalysts in various CO_2 conversion reactions. Transforming this pollutant into value-added products represents a significant challenge, but it also offers many opportunities to reduce CO_2 emissions [12].

Furthermore, other approaches to dealing with CO_2 include capturing and storing it or converting it into valuable chemicals. Another method that is being extensively studied and researched is the recycling of the CO_2 molecules by electrochemical reduction [13]. The electrochemical route is the most promising of the alternatives available for CO_2 reduction, as it does not require high temperatures or high pressures for efficient reduction, uses water as a source of protons, and allows greater product selectivity than that obtained with other reduction methods. In addition to having greater operational flexibility, it can be easily installed in places with difficult access and/or the availability of cheap energy [14–16].

2. Electrochemical CO_2 Reduction (CO_2RE)

In electrochemical reduction, catalysts have the function of accelerating CO_2 reduction reactions, thereby improving the electrochemical efficiency of the process and playing an important role in facilitating electrons during CO_2 reduction, which promotes the selective formation of desired products. Specific catalysts facilitate electron transfer, promoting the selective formation of desired products. This form of approach offers your ability to operate continuously and be able to maintain precise control of the products formed [17].

Some approaches in the literature are interesting to correlate with electrochemical CO_2 reduction (CO_2RE), which is the photocatalytic reduction of CO_2. The methods are complementary to converting carbon dioxide into value-added products. In CO_2RE, the application of electric current to a catalytic electrode promotes the selective reduction of CO_2, generating products such as CO, methane, and ethanol with precise control of the reaction kinetics. In photocatalytic reduction, photoactive catalysts are used under sunlight to convert CO_2 into organic products, offering a more sustainable path. Both methods aim to mitigate CO_2 emissions and explore sustainable sources. The synergy between these strategies promotes a sustainable transformation of CO_2, with implications for climate change mitigation and clean technologies [17,18].

When correlating, another method that can be compared with electrochemical CO_2 reduction is electrocatalytic CO_2 reduction. This method involves the direct intervention of catalysts, accelerating reduction reactions, and improving electrochemical efficiency. The relationship between electrochemical CO_2 reduction and electrocatalytic reduction highlights a promising approach for the sustainable transformation of CO_2, highlighting the crucial role of catalysts in improving the overall efficiency of electrochemical processes [19–21].

Finally, photoelectrocatalytic reduction incorporates light as an energy source, using semiconductor materials to generate photoinduced charge carriers. These charge carriers then participate in light-driven CO_2 reduction reactions. The presence of specific catalysts during this photoelectrocatalytic process is essential to increasing the conversion efficiency and enabling the selective formation of desired products. This approach stands out for its dependence on solar energy, which makes it especially attractive in scenarios where the availability of renewable energy is high [22,23].

The three methods mentioned correlate with the electrochemical reduction of CO_2 and represent an integrated approach to the sustainable transformation of CO_2. With the use of catalysts, all strategies can be explored in complementary ways, seeking to improve the overall efficiency of the process, maximizing selectivity, and accelerating reaction rates. This integration is crucial to moving towards more effective technologies for climate change mitigation and the sustainable production of chemicals from CO_2, representing a significant step towards a more sustainable future [24].

CO_2RE is an electrochemical process in which the CO_2 molecule is converted into hydrocarbons or other organic compounds with added economic value. The electrochemical system for the electroreduction of CO_2 consists of three electrodes: a cathode, where the reduction half-reaction occurs; an anode, where the oxidation half-reaction occurs; and a reference electrode, where the applied potential is monitored. In general, the electrolyte used is an aqueous solution saturated with CO_2, and organic solvents saturated with CO_2 are also used. The oxygen evolution reaction (OER) occurs in the anode compartment, and the hydrogen evolution reaction (HER) and the CO_2 reduction reaction occur in the cathode compartment. The industrial application prototype of CO_2 electroreduction is carried out in electrolyzers. The system has a two-electrode configuration: a working electrode that acts as a cathode and a counter electrode that acts as an anode and reference electrode. For large-scale applications, energy and economic viability parameters are evaluated. Because of this, the energy required for CO_2 conversion must derive from sustainable, low-carbon sources, e.g., solar, wind, tidal energy, etc. [14,15,25,26].

Electrochemical reactions occur at the electrolyte-electrode interface, where species are transported by diffusion, migration, or convection phenomena. The electrochemical reduction of CO_2 involves four steps [27]:

(1) CO_2 chemisorption on the surface of the electrocatalyst, in which CO_2 species are adsorbed at the electrode interface by chemical phenomena;
(2) Cleavage of the C=O bond through electron transfer and/or proton coupling;
(3) Formation of C-C and C-H bonds to form hydrocarbons;
(4) Rearrangement of the configuration and desorption of products into the electrolyte.

The presence of water in the electrolyte makes CO_2 reduction even more challenging due to the HER, in which hydrogen becomes the main product and competes with the CO_2 reduction reaction [28].

Depending on the number of electrons and protons transferred in the reaction, CO_2 can be converted into up to 16 distinct products, which include CO, oxalic acid ($H_2C_2O_4$) ($C_2O_4{}^{2-}$, basic medium), formic acid (HCOOH) (HCOO, basic medium), formaldehyde (HCHO), methanol (CH_3OH), methane (CH_4), ethylene (C_2H_4), ethanol (C_2H_5OH), ethane (C_2H_6), and n-propanol (C_3H_7OH) (Equations (2)–(21)); CO_2 reduction potentials concerning RHE at pH 7 [29,30]. Table 1 presents the CO_2 reduction reactions to different products and the thermodynamic potential measured under standard conditions. Through multiple steps of proton and electron transfers, a series of products can be obtained. These products can be classified according to the protonation of the CO_2 molecule and the amount of carbon [29,30].

Table 1. CO_2 reduction reactions to different products and standard thermodynamic potential [29,30].

Reaction	E°/V vs. RHE	Equation
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH^-$	−0.610	(1)
$CO_2 + 2H_2O + 2e^- \rightarrow HCOOH^-$	−1.491	(2)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.530	(3)
$CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$	−1.347	(4)
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.913	(5)
$2CO_2 + 2e^- \rightarrow C_2O_4{}^{2-}$	−1.003	(6)
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.480	(7)
$CO_2 + 3H_2O + 4e^- \rightarrow HCHO + 4OH^-$	−1.311	(8)
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	−0.200	(9)
$CO_2 + 2H_2O + 4e^- \rightarrow C + 4OH^-$	−1.040	(10)
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.380	(11)
$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^-$	−1.225	(12)
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.240	(13)
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$	−1.072	(14)
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−0.349	(15)

Table 1. *Cont.*

Reaction	E°/V vs. RHE	Equation
$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	−1.177	(16)
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.329	(17)
$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$	−1.157	(18)
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−0.270	(19)
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + H_2O$	−0.310	(20)
$2H^+ + 2e^- \rightarrow H_2$	0.000	(21)

However, the experimental potential of the reactions is higher than the thermodynamic one due to resistance to charge transfer and ohmic drop. To ensure an efficient CO_2 catalytic reaction, it is important to promote both the cathodic half-reaction and the anodic half-reaction (OER), making use of a highly active catalyst and creating reaction conditions that minimize resistance ohmic, allow adequate mass transport [31], and kinetically inhibit the formation of H_2 as much as possible, while at the same time promoting the reduction of CO_2 to increase the production of desired products [28].

The main challenge is to manufacture an electrocatalyst with high conversion efficiency, high selectivity of the product formed, and a low overpotential barrier [15,25]. Some important parameters are evaluated in the electrochemical reduction of CO_2 to determine the efficiency of the process, such as faradaic efficiency (FE) and energy efficiency [16,25].

In the literature, researchers [31–33] have emphasized that the main challenge in CO_2RE is the manufacture of electrocatalysts with high conversion efficiency, high selectivity of the product formed, and low overpotential [15,25]. Thus, this theme continues to be widely discussed, with investigative studies related to overpotential parameters, current density (j), faradaic efficiency, and catalyst stability [25,34,35]. Furthermore, there is also concern related to the cost of CO_2RE, which can be reduced through the use of electrocatalysts based on non-noble metals [36], such as Sn, Ni, Fe, Co, Zn, and Cu [36,37].

From this perspective, we highlight the studies by Du et al., where they mention that Sn and its oxides have been widely used as cathode materials for CO_2RE to obtain formate/formic acid [38]. Rende et al. investigated a Sn/SnOx-based catalyst in a 0.1 M $KHCO_3$ aqueous solution saturated with CO_2 and observed the best performance at a potential of 1.8 V vs. Ag/AgCl, reaching an FE of 74.7%. Furthermore, the authors observed that Sn/SnOx exhibited greater catalytic stability and electrochemically active surface area (2.08 cm^2) than the Sn plate (0.82 cm^2) [39]. The use of Ni and Fe electrocatalysts in CO_2RE has been reported in the literature with carbon doped with nitrogen [40,41], as proposed by Cheng et al., in which they emphasized the development of single-atom catalysts (SAC) at low cost that can be produced through the pyrolysis process. In this way, they developed Ni SAC electrocatalysts doped with nitrogen and carbon nanotubes (NiSAC-N-CNTs), where the Ni (20% weight) exhibited good activity and selectivity for CO_2 reduction under j = 23.5 mA cm^{-2}, at 0.70 V vs. RHE, with an FE of 91.3% [42]. According to Mustapha et al., Fe electrocatalysts have high activities for RHE that compete with CO_2 reduction [40]. In studies by Liang et al., metallic Fe was incorporated into N-doped carbon (Fe-NC) structures and exhibited high catalytic activity in the conversion of CO_2 to CO, reaching an FE of 94% at a current density of 5 mA cm^{-2} [41]. Aljabour et al. produced a cobalt oxide (Co_3O_4) nanofiber electrocatalyst for the Co electrocatalyst under fluorine-doped tin oxide (FTO) electrodes. In this study, the experiments were carried out in a type H electrochemical cell with CO_2 and N_2 purge at configuration three electrodes: Pt-reference, cobalt oxide nanofiber (Co_3O_4)-work, and counter electrode–Ag/AgCl in medium 0.1 M hexafluorophosphate of tetrabutylammonium (TBAPF6) in acetonitrile at 1% vol. H_2O, making it possible to convert CO_2 into CO with FE of ~90% under potential of −1.56 V vs. RHE during 8 h [43]. Zn-based catalysts compete with RHE; therefore, they have low selectivity in CO_2RE. According to Wu et al., to overcome this limitation, it would be interesting for research to be explored using the methods of electrodeposition, anodization, or oxide reduction [44], as proposed by Luo et al., Quan et al., and Xiao et al., respectively [45,46]. In these studies, Luo et al. employed the electrodeposition method for the porous Zn electrocatalyst, applying a potential of −0.95 V vs. RHE in 0.1 M $KHCO_3$ medium, where it was possible to convert CO_2 into CO with FE of ~95% and j = 27 mA cm^{-2} during 6 h [45]. Quan et al. used Zn nanoplates adopting the anodization and electroreduction methods under a potential of −1.10 vs. RHE in 0.5 M NaCl medium, identifying the conversion of CO_2 to CO with FE of 93% and j = 15 mA cm^{-2} for 10 h [46]. Xiao et al. investigated the behavior of the hexagonal Zn nanoplate via electrodeposition and reduction in the potential of −0.96 vs. RHE in 0.1 M $KHCO_3$ medium, where they noted the conversion of CO_2 to CO with FE of 94.2% and j = 5.3 mA cm^{-2} for 12 h [47]. Finally, the Cu electrocatalyst stands out in the field of CO_2RE, as reported by Choi et al., in which they used Cu nanowire to reduce CO_2 to C_2H_4 with a FE of 77.4% for more than 200 h [48]. Wang et al. used a nanodiamond electrocatalyst doped with nitrogen and Cu nanoparticles to reduce CO_2 to oxygen C2 with FE 63% at a potential of 0.5 V vs. RHE for 120 h [49]. Xu et al. produced a carbon-supported Cu catalyst aimed at converting CO_2 into ethanol; thus, the authors obtained an EF of 91% at −0.7 V vs. RHE for 16 h [50].

Given the above, electrochemical CO_2 reduction emerges as a promising approach to promoting artificial carbon recycling, a fundamental step in the search for solutions to global energy and sustainability challenges. The first step towards advancing research lies in the development of highly efficient electrocatalysts, which can increase the selectivity of CO_2 and valuable products at low overpotentials [51].

3. Electrocatalysts for CO_2 Reduction

An electrocatalyst participates in an electron transfer reaction (at an electrode) and facilitates the acceleration of a chemical reaction [26,52]. Electron transfer reactions are the most important processes at electrochemical interfaces. They are determined by the interaction between the interaction of the reagent with the solvent and the electronic levels of the electrode surface. Both electron transfer and kinetic chemistry must be fast for an efficient electrocatalyst [51]. Furthermore, an ideal electrocatalyst must present a good thermodynamic correspondence between the redox potential for the electron transfer reaction and the chemical reaction being catalyzed (e.g., reduction of CO_2 to CO) [26,52].

The effectiveness of the electrochemical reduction of CO_2 is directly linked to the electrocatalyst, making it possible to adjust its activity and selectivity by modifying its structure. To improve electrocatalysts, two engineering protocols are widely employed: (1) increase the number of active sites on an electrode, exposing more active sites per gram through optimization of the catalyst structure; and (2) improve the intrinsic activity of each active site. These strategies are not mutually exclusive and can be combined to achieve significant improvements. Several approaches, such as nanostructures, the use of supports, modeling, alloy formation, and doping with heteroatoms, among others, are used in the manufacture of high-performance catalysts [53].

The electrocatalyst used and the applied potential electrode have a great influence on the final reduction products [14,15,25]. Metallic electrodes, such as Cu, Au, and Sn, have been extensively explored in recent decades for CO_2 reduction. The generation of intermediate CO_2 is crucial to the rate of CO_2 reduction in most cases. Therefore, the main function of these electrocatalysts is to stabilize this intermediate to achieve high energy efficiency in reducing CO_2. Metal electrodes can be classified into three groups, depending on the binding tendency of intermediates and final products, as shown in Figure 1. Group I has difficulty binding to the CO_2 intermediate, resulting in the formation of formate or formic acid by an outer sphere mechanism. Group II, the intermediate *CO obtained, is weakly bound to the metal surface, being easily dissolved and emerging as the predominant product. Group III, represented only by Cu, is capable of binding and converting the *CO intermediate into higher value-added products, such as hydrocarbons and alcohols, through *COH or *CHO intermediates [54].

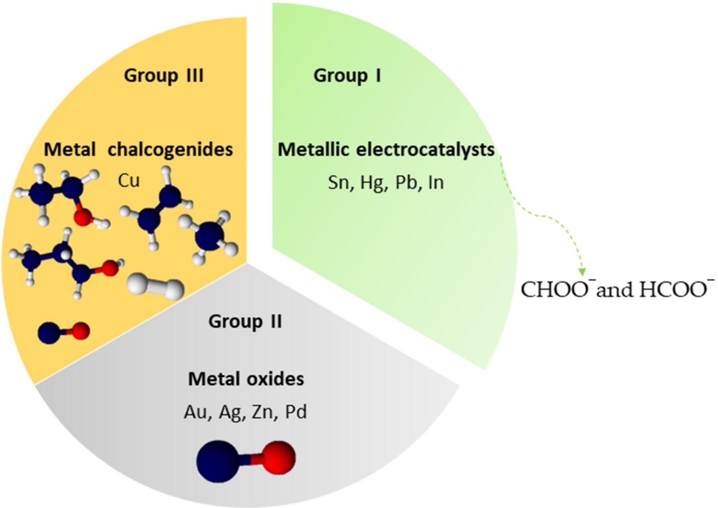

Figure 1. Classification of metal electrodes with their respective products.

To implement practical applications in the electrochemical reduction of CO_2, it is necessary to develop electrocatalysts efficient in electron transfer that operate close to the thermodynamic potential of the reaction to be conducted. Therefore, it is essential to choose a catalyst that contributes to accelerating the reaction of interest as well as the supporting electrolyte that favors the processes [7,55].

Electrocatalysts can be classified into three types, such as metallic, non-metallic, and molecular. The materials used in the preparation of the catalysts are what designate their characteristics. Therefore, metallic catalysts can have a metal in their composition or a combination of two metals, termed monometallic or bimetallic. For non-metallic catalysts, the most commonly used materials are carbon nanofiber, nitrogen-doped carbon, metal-organic structure, known as MOF, and covalent-organic structure, Covalent-Organic Framework (COF). On the other hand, molecular catalysts present in their composition the formation of macrocyclic complexes linked to some metals [56,57]. The electrocatalyst material involves the conversion of CO_2 into various products, as listed in Table 2.

Table 2. Main electrocatalysts described in the literature with their respective Faradaic efficiency, stability, and final products.

Electrocatalyst	Electrolyte	Main Product	Faradaic Efficiency	Stability	Ref.
$FeF_{20}TPP$/CNT-CF/CC	0.5 M $NaHCO_3$	HCOOH	95%	50 h	[58]
CuSn-4	0.5 M $KHCO_3$	HCOOH	93.7%	-	[59]
Ni@HNC	0.1 M $KHCO_3$	CO	98.7%	-	[60]
Ag-NP	2 M KOH	CO	99.9%	-	[61]
Cu-polyamine	1 M KOH	C_2H_4	72%	3 h	[62]
Cu/PTFE	0.1M $KHCO_3$	C_{2+}	80%	24 h	[63]
Cu-12	0.1M $KHCO_3$	C_2H_4	64%	190 h	[64]
Cu/Ni(OH)	0.5 M $NaHCO_3$	CO	92%	22 h	[65]
4H/fcc Au-MMT	1.0 M $KHCO_3$	HCOOH	92.3%	12 h	[66]
CNT@mC/Ni	0.5 M $KHCO_3$	CO	98%	24 h	[67]
Ag_{75}/C	1 M KOH	CO, H_2, and HCOOH	90.1%	30 h	[68]
Pd/PdOx	0.5 M $KHCO_3$	CO	90%	24 h	[69]
ZnO	1 M KOH	CO	91.6%	18 h	[70]
Ni-N_2-C	0.5 M $KHCO_3$	HCOOH	98%	10 h	[71]

Table 2. *Cont.*

Electrocatalyst	Electrolyte	Main Product	Faradaic Efficiency	Stability	Ref.
Bi-N_4	0.1 M $NaHCO_3$	CO	97%	4 h	[72]
CuNNs	5 M NaOH	C_2H_4	52%	6 h	[73]
Sn	0.1 M Na_2SO_4	HCOOH	95%	10 h	[74]
Cu–In	0.1 M $KHCO_3$	CO	55%	24 h	[75]
CuO–Sn	0.1 M $KHCO_3$	CO	90%	14 h	[76]
Cu nanowire	0.1 M $KHCO_3$	CO, HCOOH, C_2H_4	17.5%	5 h	[77]
Cu (dendrite)	[EMIM](BF_4)/H_2O (85/15 *v*/*v*)	HCOOH	87%	8 h	[78]
Ag	0.5 M $KHCO_3$	CO	30–80%	285 min	[79]
Sn	0.5 M $KHCO_3$ + 2 M KCl	HCOOH	70%	4 h	[80]
Cu-based metal–organic porous materials	0.5 M $KHCO_3$	CH_3OH, C_2H_5OH	56%	90 min	[81]
Cu_2O/ZnO	0.5 M $KHCO_3$	CH_4 C_2H_4	31.4%	90 min	[82]

Analyzing the work presented in Table 2, we can observe that several types of electrocatalysts enable the reduction of CO_2 with high efficiency. Furthermore, it is noted that the most enterprising venture is metallic [57,83], with copper being used. This factor is related to its characteristic of continuing the reduction of CO_2 into aldehydes, hydrocarbons, and alcohol with high efficiency [84].

In previous publications regarding CO_2, Hori et al. studied the intermediate products by reducing CO at Cu electrodes, which is subsequently reduced to hydrocarbons and alcohols. CO is also formed on Ni and Pt electrodes and subsequently adsorbed on the electrode. And in this way, the adsorbed CO prevents further reduction of CO_2 in Ni and Pt. These points lead the metal electrodes to be classified into two groups: CO formation metals (Cu, Au, Ag, Zn, Pd, Ga, Ni, and Pt) and $HCOO^-$ (Pb, Hg, In, Sn, Cd, and Tl) [85–87].

In 2019, Zhou and collaborators [88] highlighted the need to recycle CO_2 in the atmosphere due to the greenhouse effect and the energy crisis. It addresses electrocatalytic CO_2 reduction as a viable solution but highlights the challenge of developing electrocatalysts with high activity, selectivity, and durability for this reaction. Explores recent advances in nanostructures of different dimensions as promising catalysts to accelerate CO_2 conversion, discussing the challenges and prospects for achieving high efficiency in this process.

Moreover, in 2020, Tang and collaborators [89] discussed the carbon dioxide reduction electrochemistry along transition metals, addressing a complex network of reactions. The study combines experimental observations from the literature with theoretical analysis to explain that not all intermediates in CO_2 reduction are formed by direct protonation steps. A selectivity map for two-electron products (carbon monoxide and formate) on pure metal surfaces is derived, using only the CO and OH binding energies as descriptors. The analysis rationalizes the experimentally observed product distributions in CO_2RE in pure metal systems, highlighting the need for additional descriptors for screening materials in CO_2 reduction and the importance of considering the competition in the elementary steps of the hydrogen evolution reaction.

Johnson and collaborators [90] highlighted the significant role of carbon dioxide in global warming, with the burning of fossil fuels being the main source of pollution. The capture and reduction of CO_2 for the production of valuable chemicals using renewable energy sources is an important area of research. Catalysts, support structures, and electrolytes are key factors affecting the electrochemistry of CO_2 reduction for the production of value-added chemicals and fuels. The review covers the field of CO_2RE electrocatalysis, focusing on non-precious transition metal-based catalysts and highlighting design, synthesis, characterization, and mechanisms. Advanced catalyst design, including two-dimensional metal carbide and nitride materials, and state-of-the-art in situ/operando spectroelectrochemical techniques are emphasized. The text concludes by highlighting the remaining challenges and perspectives for future research and opportunities.

In 2022, Jiang and collaborators [91] highlighted the electrochemistry of CO reduction as a promising approach to address the energy crisis and reduce carbon emissions. Cu-based electrocatalysts have been considered to generate hydrocarbons and alcohols in CO_2RE, but face challenges of high initial potential and low selectivity. The study proposes a series of Cu-based single-atom alloy catalysts (SAACs), TM1/Cu (111), designed by isolated doping of transition metal (TM) atoms on the Cu (111) surface. TM1/Cu (111) demonstrated, theoretically, greater stability and efficiency in the hydrogenation of CO_2, avoiding hydrogen evolution. Theoretical calculations suggest that the initial hydrogenation of CO_2 in SAACs would form the *CO intermediate, which could be subsequently hydrogenated to produce methane. The bond angle of adsorbed *CO_2 and the binding energy of *OH were identified as important descriptors of the activity and activation capacity of TM1/Cu (111) in CO_2RE. It is speculated that V/Cu (111) may present the best activity and selectivity among all TM1/Cu doped with 3d-TM (111). The study provides rational guidance for the efficient design of new single-atom catalysts for CO_2RE.

Clark and collaborators [92] address electrosynthesis, such as CO_2 reduction, which involves the formation of dipolar and polarizable transition states during the rate determination step. Highlights the need for systematic and independent control of surface reactivity and electric field strength to accelerate the discovery of highly active electrocatalysts. The study shows that intermetallic alloys allow independent control over the d-band energetics and work function by varying the alloy composition and the identity of the oxophilic constituent. Identifies intermetallic phases with the potential for greater intrinsic activity in CO reduction compared to conventional Cu-based electrocatalysts. However, it highlights the propensity of these alloys to segregate in the air as a significant challenge for investigating their electrocatalytic activity.

4. Mechanisms of Formation of C_1 and C_2 Compounds

Through successive stages of electron and proton transfer, different organic products are formed through the electrochemical reduction of CO_2. According to the carbon number, the products formed in the reaction can be classified into two groups (C_1 compounds: methane, methanol, and formate) [93] or two carbon atoms (C_2 compounds: ethylene, ethanol, and acetic acid). The selectivity in the formation of a major product depends on a series of factors related to the structural properties of the electrocatalyst, morphology, intermediate formation from the CO_2 molecule adsorbed at the catalyst interface, and the strengths of adsorbed/catalyst interactions. Given this, research has focused on developing theoretical models to understand the reaction mechanisms for the different products in the C_1 and C_2 groups.

4.1. Copper Electrocatalysts

Copper-based electrocatalysts have received notable attention at CO_2RE due to their properties and effectiveness in the electrochemical conversion of CO_2 into value-added chemical products. Therefore, Cu-based catalysts are extraordinary at converting CO_2 into various forms of liquid and gaseous products [40].

The Cu electrodes developed to date cover several categories, including bulk Cu electrodes, Cu electrodeposited GCE, and in situ electrodeposited Cu electrodes. In addition to the production of low hydrocarbons, such as CH_4, C_2H_4, CO, HCOOH, alcohols (methanol, CH_3CH_2OH, and $CH_3CH_2CH_2OH$), and esters, the ability of these electrodes to generate relatively more complex hydrocarbons, such as paraffins and olefins with up to six carbon atoms, is observed in carbon [94].

Optimizing catalysts for CO_2 reduction involves exploring different compositions, materials, and morphologies. The relevance of copper-based catalysts lies in their ability to generate the main CO_2 reduction products (ethylene and ethanol), which are essential for the chemical and fuel industries. The present critical analysis examines the mechanistic pathways of CO_2RE for C_1 and C_2 products in copper-based materials [95].

The formation of C1 compounds, methanol and methane, shown in Figure 2, can occur through two possible mechanistic pathways, discussed in the work of Peterson and collaborators [96] and Nie and collaborators [97]. Peterson's work proposes that methane is formed via the *CHO intermediate through multiple proton coupling steps. In step 1 (Equation (22)), the CO_2 molecule adsorbed at the electrode interface is hydrogenated, forming an intermediate *CHOOH. Next, the intermediate *CO is formed from *CHOOH. Then, four stages of proton coupling occur, forming the $*CH_4O^+$ intermediate [96]. From the $*CH_4O^+$ intermediate, methanol can be formed via hydrogenation of the intermediate or methane via hydrogenation of methanol with the elimination of water [96].

$$CO_2 + H^+ + e^- \rightarrow *COOH \tag{22}$$

$$COOH + H^+ + e^- \rightarrow *CO + H_2O \tag{23}$$

$$*CO + H^+ + e^- \rightarrow *CHO \tag{24}$$

$$*CHO + H^+ + e^- \rightarrow CH_2O \tag{25}$$

$$CH_2O + H^+ + e^- \rightarrow *CH_3O \tag{26}$$

$$*CH_3O + H^+ + e^- \rightarrow *CH_4O^+ \tag{27}$$

$$*CH_4O^+ + H^+ + e^- \rightarrow CH_4OH \tag{28}$$

$$CH_4OH + H^+ + e^- \rightarrow CH_4 + H_2O \tag{29}$$

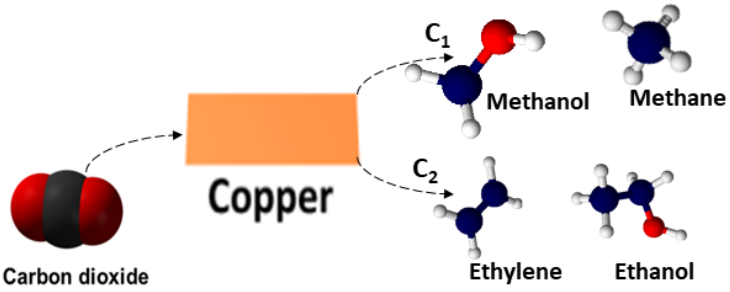

Figure 2. Representation of products formed at CO_2RE for copper electrocatalysts.

The work of Nie and colleagues reports another mechanistic route for the formation of methanol to methane [97]. From the hydrogenation of the intermediate *CO, *COH is formed. In the second mechanistic route, the formation of a reduced species *C via hydrogenation and water elimination is considered. Finally, four proton coupling steps occur, leading to the formation of CH_4 [97]. The formation of C_2 compounds in copper electrocatalysts occurs in multiple electron and proton transfer steps. Ren and collaborators demonstrated the mechanisms of ethanol and ethylene formation via the electrochemical reduction of CO_2. Equations (30) and (31) present the global reactions of ethylene and ethanol, respectively [98].

$$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^- \tag{30}$$

$$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^- \tag{31}$$

The CO_2 reduction mechanism involves multiple steps of proton-electron transfers to form reaction intermediates. In step 1 (Equation (32)), CO_2 is reduced via the transfer of an electron and coupling of a proton (hydrogenation), forming an intermediate COOH* adsorbed at the interface of the Cu electrocatalyst. Step 2 (Equation (33)) involves the possible formation of three intermediates: CO*, CH*, or CH_2O*. In step 3 (Equation (34)), the intermediates undergo coupling to form the C-C bond. Montoya and collaborators carried out DFT (density functional theory) studies to evaluate the kinetics of the C-C bond coupling (step 3) from the different intermediates formed in step 2. The dimerization of *CO is an unfeasible process at room temperature due to the high energy, with the remaining allowed reactions leading to the formation of the intermediate $C_2H_xO_2$ (x = 1, 2, 3, 4) [99].

$$2{*}CO \rightarrow O{*}C{*}CO \tag{32}$$

$$CO + {*}CHO \rightarrow O{*}C{*}CO \tag{33}$$

$$2{*}CHO \rightarrow {*}OCHCHO \tag{34}$$

$$*CHO + {*}CH_2O \rightarrow {*}OCH_2CHO \tag{35}$$

$$2{*}CH_2O \rightarrow {*}OCH_2CH_2O \tag{36}$$

The intermediate $*C_2HO_2$ is formed by the coupling reactions *CO and *CHO. The intermediate $*C_2H_2O_2$ is formed via dimerization of *CHO. The $*C_2H_3O_2$ intermediate is formed by the coupling of *CHO and $*CH_2O$. When x = 4, an intermediate $*CH_2H_4O_2$ is formed via dimerization of $*CH_2O$. Finally, in step 4 (Equation (40)), the intermediate $*C_2H_xO_2$ is reduced, leading to the formation of ethanol or ethylene.

$$CO_2 + H^+ + e^- \rightarrow {*}COOH \tag{37}$$

$$*COOH + H^+ + e^- \rightarrow {*}CO \text{ or } {*}CHO \text{ or } {*}CH_2O \tag{38}$$

$$*CO + H^+ + e^- \rightarrow {*}C_2H_xO_2 \tag{39}$$

$$*C_2H_xO_2 + H^+ + e^- \rightarrow C_2H_4 \text{ or } C_2H_5OH \tag{40}$$

4.2. Nickel Electrocatalysts

Nickel, an abundant transition metal with diverse applications in catalysis, faces significant limitations in its electrocatalysis for the reduction of CO_2 in aqueous media due to conflicts with the HER and surface poisoning by intermediates such as CO, among other factors. To overcome these challenges, several strategies have been implemented to tune the catalytic performance of Ni toward electrochemical CO_2 reduction [40].

In aqueous solutions under ambient conditions, Ni demonstrates the ability to produce H_2, CO, or other hydrocarbons. However, it is worth highlighting that these metals exhibit high activity in the hydrogenation of CO and/or CO_2 in heterogeneous catalytic reactions. In electrochemical CO_2 reduction experiments on Ni electrodes in an aqueous medium, the production of H_2 was observed, as well as some smaller hydrocarbons, such as CH_4, C_2H_4, and C_2H_6. Under elevated CO_2 pressure, it was possible to increase the Faradaic efficiency for CO_2 reduction in Ni electrodes by increasing the CO_2 pressure, reducing the temperature, and polarizing the electrode potential to more negative values [94].

Nickel electrocatalysts are selective for the formation of carbon monoxide (CO), as shown in Figure 3. According to Yadav and collaborators [100], the CO formation mechanism occurs in three stages. The CO_2 adsorption occurs at the interface of the electrocatalyst, forming proton coupling and electron transfer to form Ni species (COOH)* (Equation (41)). In Equation (42), through a second stage of proton transfer in the electron, the formation of the adsorbed CO radical Ni (CO)* occurs with the elimination of water. In the last stage, CO undergoes adsorption in the CO release reaction [100].

$$Ni^* + CO_2 + H^+ + e^- \rightarrow Ni\ (COOH)^* \tag{41}$$

$$Ni^* + CO_2 + H^+ + e^- \rightarrow Ni\ (CO)^* + H_2O \tag{42}$$

$$Ni\ (CO)^* \rightarrow Ni + CO \tag{43}$$

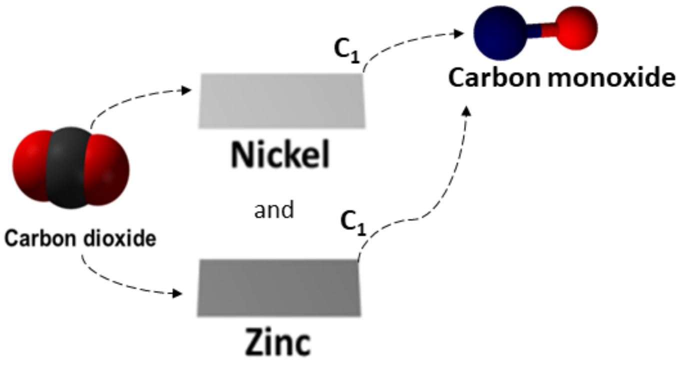

Figure 3. Representation of products formed at CO_2RE for nickel and zinc electrocatalysts.

According to Ishiki et al. [26], nickel favors the formation of molecular H_2 via the hydrogen evolution reaction through the water reduction process (a reaction parallel to the CO_2 reduction reaction). The HER depends on the pH of the medium [26,101].

4.3. Zinc Electrocatalysts

Zinc is widely investigated as a catalyst for CO_2 reduction electrochemistry due to its intrinsic advantages, such as abundance on Earth, economic viability, and high selectivity for CO production. However, bulk Zn electrodes demonstrate poor performance in CO_2RE, as they generally exhibit low CO partial current density and have considerable overpotentials [102]. Zn-based catalysts, as non-precious metals, are promising for transforming CO_2RE into value-added chemical products. However, this abundant metal faces challenge related to low selectivity due to competition with the hydrogen evolution reaction [94].

A similar mechanism was proposed by Zhao et al. for the formation of CO on metallic zinc electrocatalysts. The mechanism occurs in three stages, with stage I being the proton and electron transfer for the adsorption of CO_2 on the electrode surface, stage II being the formation of the adsorbed Zn(CO)* intermediate, and stage III being the desorption of carbon monoxide, as shown by the equations. Zinc tends to form carbon monoxide via the transfer mechanism of two protons and two electrons, as presented in Equations (44)–(46) [102].

$$Zn^* + CO_2 + H^+ + e^- \rightarrow Zn\ (COOH)^* \tag{44}$$

$$Zn\ (COOH)^* + H^+ + e^- \rightarrow Zn\ (CO)^* + H_2O \tag{45}$$

$$Zn\ (CO)^* \rightarrow Zn + CO \tag{46}$$

The competing hydrogen release reaction can occur at the Zn electrode interface, resulting in a decrease in the efficiency of the CO_2 reduction reaction. Zhao and collaborators inhibited the HER by adding chloride ions to the electrolyte. Research has demonstrated that chloride ions form a Zn-Cl layer at the electrode interface due to the action of chloride ions, removing the solvation layer and forming Zn-Cl bonds that block HER and facilitate electron transfer for CO_2 reduction. Competition stages of the hydrogen release reaction at the zinc electrode interface to reduce CO_2 reduction efficiency are presented in Equations (47)–(50) [103,104].

$$Zn + Cl^- \rightarrow Zn\text{-}Cl + e^- \tag{47}$$

$$Zn\text{-}Cl + e^- + CO_2 \rightarrow Zn\text{-}Cl\text{-}CO^{2-} \tag{48}$$

$$CO_2{}^- + H^+\ {}^* \rightarrow COOH^* \tag{49}$$

$$COOH^* + H^+ + e^- \rightarrow CO^* + H_2O \tag{50}$$

5. Conclusions and Future Perspectives

The carbon cycle is fundamental to regulating the climate. However, energy demand has led to excessive fossil fuel consumption, impacting the carbon cycle's natural balance. Given this, we highlight the importance of CO_2RE, as it represents an alternative to mitigate CO_2 emissions, offering environmental, economic, and sustainable benefits.

Recent studies presented in the literature investigate the behavior of various electrocatalysts in CO_2RE. Thus, this review provides a perspective related to CO_2RE covering different types of electrocatalysts, such as metallic, MOF, COF, and molecular. Taking into account the challenge of manufacturing an electrocatalyst with high conversion efficiency, selectivity, and low cost, we emphasize metallic electrocatalysts reported by several researchers, with an emphasis on copper, as it can reduce CO_2 and even more reduced species, such as molecular hydrogen, formate, ethanol, and propanol, which are important for technologies used in fuel cells, in the industrial sector, and in the food industry.

Given the above, the challenges involved in the practical application of electrocatalysts in CO_2RE require more in-depth studies into mechanisms for a better understanding of the process. Therefore, further research must continue to be explored to identify ideal system conditions regarding catalytic activity, selectivity, stability, and mass transport for the reactor reliably that contributes to the scientific community as well as society.

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