

Material Design and Product Pathway Selection in CO₂ Photoelectrocatalysis

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Abstract. As global warming increases, excessive CO₂ emissions have become a major challenge to environmental sustainability. CO₂ reduction is regarded as a promising pathway toward carbon neutrality. This work reviews catalytic materials including metal-based, carbon-based, metal–organic frameworks (MOFs), and covalent organic frameworks (COFs), focusing on their structural features, catalytic performance, and photoelectrocatalysts. Studies have shown that Cu-based catalysts favor multi-carbon products, whereas Ag and Au primarily yield CO. Methanol is particularly attractive due to its low energy barrier, convenient storage and transport, and high chemical value. Overall, catalyst type and reaction conditions strongly influence product distribution, but achieving selective control remains a key challenge for efficient conversion. Future research should emphasize multifunctional catalyst design, interfacial electronic regulation, and the integration of product separation with utilization to advance practical CO₂ reduction technologies.

Keywords: Carbon dioxide reduction, photoelectrocatalysts, catalytic product

1. Introduction

In the context of global climate change, 1.1 In the context of global climate change, excessive emissions of carbon dioxide, the most significant greenhouse gas, have become a central driver of global warming and a major threat to ecological stability. Addressing this issue is a pressing global challenge. The United Nations Sustainable Development Goals (SDGs) identify “Climate Action” as Goal 13, underscoring the urgency of coordinated international efforts to combat the climate crisis [1]. In recent years, numerous studies and reviews have emphasized that reducing CO₂ emissions and promoting its resource utilization. They are essential pathways toward sustainable development [2,3]. Although photocatalysis and electrocatalysis have shown great potential for carbon dioxide reduction, these technologies still face several limitations. These limitation including low catalytic efficiency, poor stability, dependence on specific light sources, high cost, and limited operational lifetimes [4,5]. These shortcomings have seriously restricted their large-scale application. Therefore, improving the efficiency, stability, and practicality of photocatalytic and electrocatalytic systems remains a central challenge. 1.3 At present, countries worldwide are accelerating efforts toward achieving “carbon neutrality,” with carbon dioxide reduction technologies playing a central role in this process. These technologies not only help lower emissions through advances in materials

science [6] and chemical engineering but also enable the conversion of CO₂ into value-added chemical feedstocks. Tthereby aligning environmental benefits with economic gains. Among them, electrocatalysis and photocatalysis are the most widely studied. Photocatalysis harnesses solar energy to convert CO₂ into fuels or chemicals, reducing reliance on fossil resources [7]. Electrocatalysis utilizes electrochemical devices to drive CO₂ reduction on electrode surfaces under ambient conditions, producing value-added products such as CO, methanol, and methane [8]. In both cases, the choice of catalyst plays a decisive role in governing efficiency and selectivity. Collectively, these technologies offer promising strategies to address both energy shortages and environmental challenges.1.4 Although significant progress has been made in the design of catalytic materials and in understanding reaction mechanisms. The practical application of CO₂ reduction technologies is still hindered by two major challenges. First, the selective control of product pathways remains inadequate, hindering precise regulation toward desired products such as methanol, methane, or ethanol. Second, many photocatalysts—particularly semiconductor-based photocatalysts—suffer from rapid electron–hole recombination under illumination, which significantly limits their efficiency [9,10]. To address these issues, it is essential to deepen our understanding of how catalyst structures influence product formation pathways and to develop new strategies that enhance both selectivity and efficiency. Against this backdrop, this review aims to systematically examine how different catalytic materials regulate product distribution, highlight recent progress in improving selectivity and efficiency, and provide theoretical guidance for the design of high-performance and sustainable CO₂ conversion systems.The scope of this review mainly centers on representative catalytic materials and their regulation of product pathways. First, we compare the structural characteristics, synthetic approaches, and catalytic performance of several classes of materials. Next, we analyze the mechanisms governing the selective generation of key products, with particular emphasis on methane, methanol, and ethanol. Finally, we summarize and evaluate existing research results, pointing out both strengths and limitations, as well as unresolved challenges and future opportunities. This article not only reviews the current research landscape but also distills general principles of catalyst design for pathway regulation, offering useful references for the efficient and value-added utilization of CO₂.

2. Recent research and product control strategies

Recent advances in catalytic materials for CO₂ reduction have focused on four major categories: metal-based materials, metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and carbon-based systems. Metal-based catalysts, including single atoms and metal oxides, have demonstrated strong activity and tunable selectivity in CO₂ reduction reactions [11]. MOFs, composed of metal ions or clusters connected by organic ligands. And possess highly porous crystalline architectures that enable precise regulation of product pathways through modification of active metal nodes [12]. Similarly, COFs—was constructed from organic building blocks linked by covalent bonds. COFs can offer a versatile platform whose selectivity toward multi-carbon products can be enhanced by incorporating transition-metal sites such as Cu or Fe [13]. In addition, carbon-based materials exhibit advantages such as low density, high strength, thermal stability, and excellent electrical conductivity, while also being low-cost and chemically robust. However, their intrinsic limitation in C–C coupling often necessitates hybridization with metals or metal oxides. Thereby improving multi-carbon product formation, particularly ethanol. Collectively, these strategies highlight how structural design and compositional tuning across different material classes can effectively modulate product selectivity in CO₂ reduction.

3. Method

This study focused on four categories of catalysts—metal-based, MOFs, COFs, and carbon-based materials—selected for their extensive application in CO₂ reduction. To evaluate catalytic performance, three representative products (CO, CH₄, and CH₃OH) were selected for comparison. For product detection, in addition to commonly employed techniques such as gas chromatography (GC) and nuclear magnetic resonance (NMR). The rotating ring-disk electrode (RRDE) method was introduced to monitor short-lived intermediates and products formed during electroreduction in real time. Specifically, GC was employed for the quantitative analysis of gaseous products [14], NMR was used for structural identification and quantification of liquid-phase products [15], and RRDE enabled dynamic tracking of reaction intermediates by measuring current changes between the ring and disk electrodes, thereby providing insights into the reaction mechanism [16].

4. Result

Catalytic materials used in the carbon dioxide reduction reaction (CO₂RR) mainly include metal-based catalysts, metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and carbon-based materials. These materials effectively reduce the reaction energy barrier, thereby facilitating the conversion of CO₂ into high-value chemicals and fuels. Variations in active site structure, electronic properties, and the stability of adsorbed intermediates among different catalysts play a decisive role in determining product distribution and selectivity. Representative catalytic performances are summarized in Table 1.

Table 1. Catalyst product type and Faradaic efficiency

Catalyst	Product type	Faradaic efficiency
Metal-based	Ag: CO	Ag > 90%
	Cu: CH ₄ , C ₂ H ₄ , CH ₃ OH	Cu ~ 40%
Mofs	CO, CH ₃ OH	60 ~ 85%
Cofs	CO, CH ₃ OH	50 ~ 90%
Carbon-based	CO, HCOOH	60 ~85%

Notes:

1. Hydrophobic Ag nanoparticles can achieve a Faradaic efficiency (FE) exceeding 90% for CO₂ reduction by tuning the interfacial microenvironment, while effectively suppressing the competing hydrogen evolution reaction [17].

2. Cu supported on carbon black has been demonstrated as an efficient electrocatalyst for CO₂ electroreduction, exhibiting unexpectedly high selectivity toward methane, with a CH₄ FE of up to 42% [18].

3. Metal–organic frameworks (MOFs) have been employed as efficient CO₂ reduction catalysts for CO production, achieving a FE of 80.1% at –2.5 V (vs. Ag/Ag⁺) [19].

4. Covalent organic frameworks (COFs) exhibit excellent catalytic performance for the aqueous electrochemical reduction of CO₂ to CO, reaching a FE of 90% at pH 7 and an applied potential of –0.55 V [20].

5. Ni–N–C materials deliver a CO Faradaic efficiency of approximately 85% during CO₂ electroreduction [21].

5. Product pathway

Carbon monoxide (CO) is one of the most common products obtained during the CO₂ reduction reaction (CO₂RR). Its formation mainly involves sequential electron transfer steps coupled with oxygen removal from CO₂. The proposed pathway is summarized in Table 2 [22].

Table 2. Carbon monoxide production pathway

Pathway
CO ₂ +e ⁻ +**CO ₂ ⁻
*CO ₂ ⁻ +H ⁺ *CO ₂ H
*CO ₂ H+H ⁺ +e ⁻ *CO+H ₂ O

Notes: Carbon monoxide (CO) is the most obtained product in the CO₂ reduction reaction (CO₂RR). Its formation mainly involves electron transfer processes coupled with the removal of oxygen atoms from CO₂. The symbol “*” is typically used to denote an active site on the catalyst surface, which can stabilize adsorbed intermediates through chemical or physical interactions, thereby enabling subsequent reaction steps to occur. Methane (CH₄) formation in CO₂RR requires an eight-electron transfer process, making it more complex than CO or methanol generation. This multi-step pathway involves proton–electron coupling steps that are crucial for stabilizing intermediates and driving the reaction toward methane. The pathway is summarized in Table 3 [23].

Table 3. Methane production pathway

Pathway
CO ₂ *CO ₂ H*CO
*CO*COH
*COH+H ₂ O*OCH ₂
*OCH ₂ *OCH ₃
*OCH ₃ *O+CH ₄

Notes: The formation of methane (CH₄) in the CO₂ reduction reaction requires the transfer of eight electrons, making the process considerably more complex than the generation of CO or methanol. This pathway typically involves multiple proton–electron coupling steps, which play a crucial role in stabilizing intermediates and driving the reaction toward methane production. Methanol (CH₃OH) has received significant attention due to its high value and broad application potential. In CO₂RR, CO often acts as a key intermediate that undergoes further hydrogenation to form methanol. The proposed pathway is shown in Table 4 [24].

Table 4. Methanol production pathway

Pathway
CO ₂ *CO
*CO*COH
*COH*OCH ₃
*OCH ₃ CH ₃ OH

Notes: In CO₂ reduction, methanol has attracted considerable attention due to its high value and broad application potential. Carbon monoxide (CO), as a key intermediate, is industrially important for syngas production and as a chemical feedstock. Although methane possesses a high calorific value, it is typically a byproduct because of its high energy demand and low selectivity. Future efforts focusing on the precise tuning of catalyst surface active sites and electronic structures may enable controlled regulation of product pathways, thereby improving the efficiency of CO₂ conversion.

6. Conclusion

This research provided a comprehensive analysis of four major categories of catalysts applied in the carbon dioxide reduction reaction (CO₂RR), namely metal-based, carbon-based, metal–organic frameworks (MOFs), and covalent organic frameworks (COFs). It examined their structural features, synthesis approaches, and regulatory mechanisms that influence the formation of key products such as CO, CH₄, and CH₃OH. By evaluating electron transfer capabilities and intermediate stability across different catalysts, fundamental correlations between catalytic behavior and product selectivity were identified. Furthermore, commonly employed techniques for product detection and material characterization were summarized, highlighting the critical role of fast and sensitive analytical methods in advancing CO₂RR research.

In contrast to previous reviews that often focused on a single catalyst type or a specific product, this work established an integrated analytical framework encompassing multiple catalyst systems and product pathways. Such a multidimensional perspective provides a holistic reference for guiding future investigations in the field.

Looking forward, progress in CO₂RR is expected to be driven by several directions: the design of catalysts with enhanced stability and selectivity to lower energy consumption and improve conversion efficiency; the application of strategies such as heteroatom doping, single-atom dispersion, and interface engineering to strengthen catalytic activity and durability; and the refined control of reaction intermediates and transformation routes to achieve precise synthesis of target products. The integration of in situ spectroscopic techniques with computational modeling will further deepen understanding of critical intermediates and enable rational electronic structure design, thereby guiding the formation of desired products such as CO, methane, and methanol.

In summary, as photocatalysis and electrocatalysis technologies continue to evolve, CO₂ reduction is poised to overcome existing limitations in efficiency and selectivity, holding great promise as a pivotal strategy for future energy conversion systems and sustainable carbon management..

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