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Types of Carbon Dioxide Reactions and Current Advances

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ABSTRACT

Carbon dioxide (CO2) conversion has attracted increasing attention as a promising strategy for both carbon mitigation and the production of value-added chemicals. However, the high thermodynamic stability and kinetic inertness of CO2 make its efficient transformation challenging. In this review, CO2 conversion is classified according to whether the oxidation state of the central carbon atom changes during the reaction process, dividing it into reductive and non-reductive pathways. Reductive conversion mainly produces CO, CH4, and multicarbon (C2+) products, while non-reductive conversion mainly yields carbonates, carbamates, and urea derivatives through direct functionalization. The characteristics, representative pathways, and major challenges of these product systems are briefly discussed. Overall, reductive pathways are more suitable for fuel production and carbon upgrading, whereas non-reductive pathways show advantages in the selective synthesis of fine chemicals. This review provides a concise framework for understanding CO2 conversion routes and highlights key challenges and future directions for their sustainable development.

KEYWORDS

Carbon dioxide utilization; Catalytic conversion; Product classification.

1. INTRODUCTION

Carbon dioxide (CO_2) is one of the major greenhouse gases, and its continuous accumulation in the atmosphere has been widely recognized as a key contributor to global warming, climate anomalies, and broader ecological and environmental changes. With the large-scale consumption of fossil resources and the ongoing advancement of industrialization, CO_2 emissions have continued to increase, making the effective reduction of carbon emissions and the resource utilization of CO_2 a central concern in the fields of energy, environment, and chemistry. As an abundant, inexpensive, non-toxic, and renewable C_1 feedstock, CO_2 can be converted into value-added fuels and chemicals through chemical transformation, which not only helps mitigate the greenhouse effect and environmental pressure, but also provides an important pathway toward the development of a low-carbon and sustainable chemical industry.

However, the CO_2 molecule possesses a highly symmetric linear structure and high chemical stability, with its carbon center in the highest oxidation state. As a result, CO_2 exhibits remarkable thermodynamic stability and kinetic inertness. These intrinsic properties mean that the chemical conversion of CO_2 usually involves high reaction energy barriers and often requires relatively harsh reaction conditions. Meanwhile, in practical reaction systems, mass transfer limitations are commonly encountered, and the complexity of reaction pathways often makes it difficult to simultaneously achieve high conversion efficiency and product selectivity. In addition, competing reactions and side reactions frequently reduce the yield of target products. Collectively, these factors make the

synergistic optimization of high activity, high selectivity, high stability, and low energy consumption a significant challenge in CO_2 conversion.

To more clearly summarize the fundamental features of CO_2 conversion reactions and establish a systematic framework for the following discussion, this review classifies CO_2 chemical transformations according to whether the oxidation state of the central carbon atom changes during the reaction process. Based on this criterion, CO_2 conversion can generally be divided into two categories. One is **reductive transformation**, in which the oxidation state of the carbon center is lowered through the introduction of electrons and/or hydrogen, leading to products such as carbon monoxide, methane, methanol, and higher-carbon compounds. The other is **non-reductive transformation**, in which the oxidation state of the carbon center remains essentially unchanged, and CO_2 is mainly converted through the construction of C-O, C-N, or related bonds to realize carbon fixation and functionalization, such as the cycloaddition of CO_2 with epoxides to produce cyclic carbonates and the reaction of CO_2 with amines to form carbamates or urea derivatives. On this basis, the various CO_2 conversion reactions discussed in this review will be further categorized according to the target products, and their current research status, major challenges, and future development directions will be systematically evaluated.

2. CO_2 REDUCTION REACTION

The diversity of CO_2 reduction products fundamentally arises from the fact that reduction reactions usually involve multi-electron/multi-proton transfer processes and multiple parallel reaction pathways. Meanwhile, the formation and subsequent fate of key intermediates (e.g., *CO, *CHO, and *OCHO) are jointly governed by surface adsorption strength, the local microenvironment, and competing reactions, thereby giving rise to a product distribution pattern in which synergy and competition coexist [1]. Based on differences in reaction mechanisms and product formation pathways, the products of CO_2 reduction can be broadly classified into two categories: C_1 products and multicarbon products. In general, the formation of C_1 products does not involve C–C bond construction, and the reaction process is mainly limited by CO_2 activation, the generation of key intermediates, and the subsequent proton-coupled electron transfer steps, resulting in relatively well-defined pathways [2]. In contrast, the synthesis of multicarbon products must overcome the crucial bottleneck of stepwise C–C coupling (e.g., *CO–*CO coupling or other chain-growth pathways), while simultaneously maintaining sufficient *CO coverage and moderate intermediate stability on the catalyst surface [3]. As the carbon chain extends, the reaction network becomes rapidly more complex, imposing higher demands on the synergy among active-site structure, interfacial microenvironment, and mass transfer conditions. Therefore, current multicarbon product systems still generally face challenges such as insufficient overall selectivity, broad product distributions, and limited long-term stability.

2.1. Carbon monoxide(CO)

The section headings are in boldface capital and lowercase letters. Second level headings are typed as part of the succeeding paragraph (like the subsection heading of this paragraph). Carbon monoxide (CO) is a key platform molecule in syngas chemistry and C_1 chemical manufacturing. The conversion of CO_2 into CO not only enables carbon resource utilization, but also provides an important feedstock for downstream processes such as methanol synthesis and Fischer–Tropsch synthesis. Therefore, CO production is regarded as one of the most fundamental and industrially relevant routes in CO_2 chemical conversion.

From a thermocatalytic perspective, CO_2-to-CO conversion is mainly achieved through the reverse water–gas shift reaction (RWGS, $CO_2 + H_2 \rightleftharpoons CO + H_2O$) and dry reforming of methane (DRM, CO_2

+ CH_4 ⇌ 2CO + $2H_2$). Although both routes can produce CO or syngas, they differ significantly in reactant systems, product distributions, and engineering constraints.

In the RWGS reaction, H_2 serves as the reductant to convert CO_2 into CO, and elevated temperatures are generally required to shift the equilibrium toward CO formation. The reaction usually involves CO_2 adsorption and activation on metal sites or defective oxide surfaces, followed by deoxygenation steps, and its performance is strongly influenced by the nature of active sites and the adsorption strength of surface intermediates (Fig.1a). The main challenge of RWGS lies in developing catalysts with high activity and long-term stability under harsh reaction conditions [4].

In contrast, DRM enables the co-conversion of CO_2 and CH4 into syngas with an H_2/CO ratio close to 1, offering a promising route for the simultaneous utilization of two major greenhouse gases [5]. However, because DRM is highly endothermic and typically operated at high temperatures, it commonly suffers from severe carbon deposition caused by methane cracking and the Boudouard reaction, as well as metal sintering. These issues reduce the availability of active sites, leading to catalyst deactivation and even reactor blockage. Accordingly, resistance to coking and high-temperature stability are considered key criteria in DRM catalyst design (Fig. 1b).

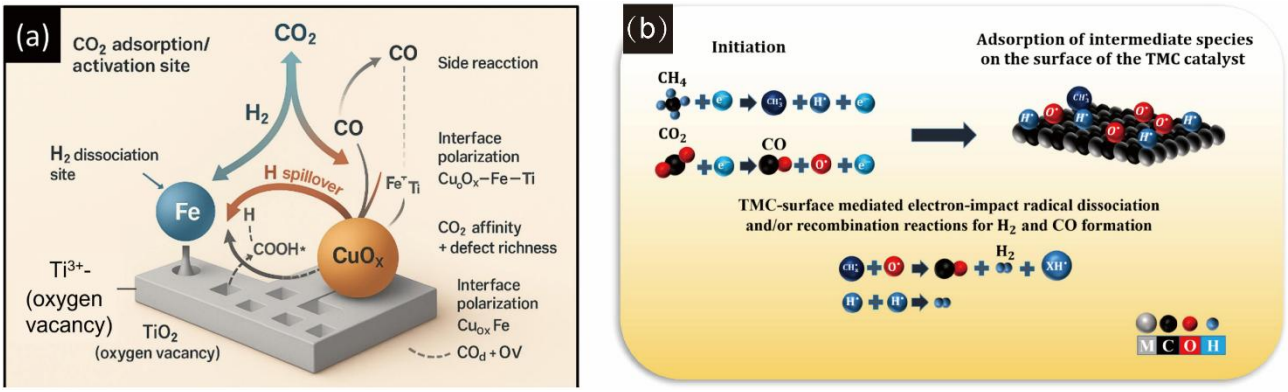

Fig 1. (a) Schematic diagram of the mechanism for CuOX-Fe_3O_4-X-TiO_2 catalysed RWGS [6]; (b) Schematic diagram of the mechanism for DBD plasma-assisted DRM reaction on TMC catalyst [7].

2.2. Methane(CH_4)

CO_2 + $4H_2$ ⇌ CH_4 + $2H_2O$. This process has attracted considerable attention because it integrates several key elements of future carbon-neutral energy systems, including carbon capture and utilization, renewable energy storage, and synthetic fuel production. In particular, surplus renewable electricity can be used to generate H_2 via water electrolysis, which then reacts with captured CO_2 to produce CH_4, a storable and dispatchable fuel compatible with existing natural gas infrastructure. Compared with many conventional energy storage technologies, CO_2 methanation offers the advantage of long-term chemical energy storage, thereby enhancing grid reliability and system flexibility (Fig. 2)[8].

Mechanistically, CO_2 methanation generally proceeds through two classical pathways. One involves formate intermediates, in which CO_2 is first adsorbed on basic or defective sites of the support and then hydrogenated stepwise to surface formate species before further conversion to CH_4. The other proceeds through a CO intermediate, where CO_2 is initially converted to *CO via an RWGS-like step, followed by successive hydrogenation on metal sites to form CH_4. These pathways are strongly dependent on catalyst composition, metal–support interfacial properties, and surface hydrogen coverage, highlighting the synergistic roles of metal sites for H_2 activation and support/defect sites for CO_2 adsorption and activation.

Despite its advantages, CO_2 methanation is highly exothermic and highly sensitive to the operating window. Under high-conversion conditions, significant temperature rise and hotspot formation may occur, leading to catalyst sintering, deactivation, and selectivity fluctuations. Therefore, the major

challenges of this reaction lie in thermal management, reactor intensification, catalyst stability, and the simultaneous achievement of high activity and high selectivity under relatively mild conditions.

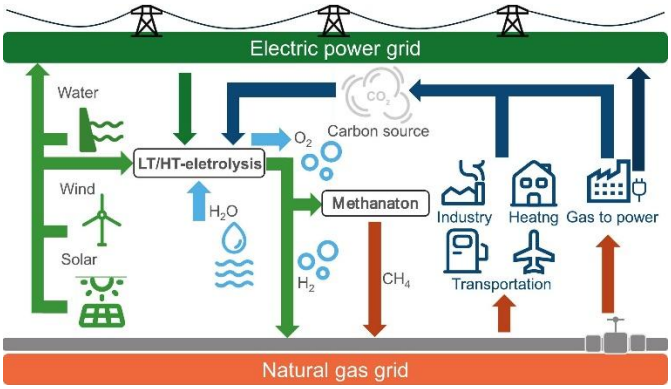

Fig 2. Schematic of Industrial Carbon Dioxide Methane Conversion and Conceptual Diagram of Power-to-Gas

2.3. Polycarbonate products (C_{2+})

The conversion of CO_2 into multicarbon (C_{2+}) products is one of the most value-added yet most challenging directions in CO_2 utilization. Typical C_{2+} products include ethylene, ethanol, acetate, propanol, and higher oxygenates or hydrocarbons (Fig. 3). Their high value mainly arises from the increased molecular complexity enabled by C-C bond formation. However, the formation of C_{2+} products generally requires complex multi-electron and multi-proton transfer processes, and the kinetics of C-C coupling, especially for longer-chain products, are often sluggish [9].

For thermocatalytic routes, the synthesis of high-value C_{2+} products from CO_2 typically begins with heterogeneous catalytic steps that generate key intermediates such as CO, methanol, or light olefins. Among the most extensively studied pathways are the tandem reverse water–gas shift/Fischer–Tropsch synthesis (RWGS–FTS) route and the methanol-mediated methanol-to-olefins (MTO) route. These pathways involve distinct intermediates and carbon-coupling mechanisms, leading to different C_{2+} product distributions. In particular, the production of heavier hydrocarbons (e.g., C_{5+}) generally relies on the prior formation of light olefins, which can subsequently undergo oligomerization, cyclization, and aromatization over acidic zeolite phases to yield longer-chain and structurally diverse hydrocarbons[10].

Overall, the major advantage of CO_2-to-C_{2+} conversion lies in its high product value and strong potential for carbon upgrading. However, its limitations remain significant, including complicated reaction networks, insufficient selectivity, and the need for precise control over multifunctional catalysts and tandem reaction environments.

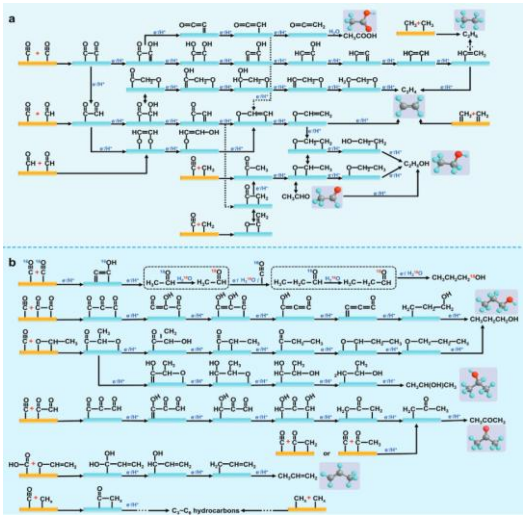

Fig 3. The pathway for producing (a) C_2 and (b) C_3 products via carbon dioxide reduction.

3. NON-REDUCTION REACTIONS OF CO2

As discussed above, reductive CO_2 conversion generally involves coupled multi-electron/multi-proton transfer processes and multiple parallel reaction pathways. When C–C coupling and chain growth are further involved, the number of intermediates and the complexity of the reaction network increase substantially, often leading to stronger competition from side reactions and lower product selectivity. These factors significantly limit the directed synthesis of target products and the overall reaction efficiency.

Since the construction of valuable chemical frameworks does not necessarily require deep reduction of the carbon center, increasing attention has been directed toward non-reductive CO_2 conversion strategies in recent years. In these pathways, the oxidation state of the central carbon atom remains essentially unchanged, while target molecular frameworks are directly constructed through functionalization or cyclization reactions. As a result, the reaction mechanism can be simplified and the probability of side reactions arising from the accumulation of multiple intermediates can be reduced. At present, research in this area mainly focuses on two classes of high-value products: carbonates and their derivatives, and nitrogen-containing fine chemicals such as carbamates and urea derivatives.

3.1. Carbonates and Their Derivatives

The synthesis of carbonates and their derivatives from CO_2 is a typical non-reductive CO_2 conversion route. Without significantly changing the oxidation state of the carbon center, CO_2 can be selectively fixed through the formation of C-O bonds, giving this pathway the advantages of relatively simple reaction processes, well-defined products, and high selectivity. At present, the main high-value products in this area include cyclic carbonates, dialkyl carbonates, and carbonate-derived monomers.

Among these, the cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates is widely recognized as one of the most representative routes. This reaction features high atom economy and minimal theoretical by-products, while the products can be used as green solvents, battery electrolyte components, and intermediates for fine chemical synthesis. Recent studies have increasingly shifted from simple feasibility toward greener and more scalable processes, including the direct synthesis of cyclic carbonates from flue gas or under low-pressure conditions [11].

In comparison, the synthesis of dialkyl carbonates from CO_2 and alcohols also has significant industrial value, but this route is more strongly constrained by thermodynamic equilibrium and process conditions. As a result, current research often focuses on process coupling and condition

optimization, such as water-removal strategies to shift the equilibrium, together with catalyst design based on surface acid-base properties and defect structures[12].Overall, carbonate-related routes combine high product value with excellent selectivity, but their broader application still requires further improvements in reaction efficiency under mild conditions, reduced dependence on cocatalysts or additional process units, broader substrate scope, and better catalyst recyclability and long-term stability.

3.2. Carbamates and Urea Derivatives

The conversion of CO_2 into carbamates and urea derivatives is another important non-reductive route for producing nitrogen-containing fine chemicals. In this pathway, CO_2 is incorporated into target molecules through C-N bond formation while the oxidation state of the carbon center remains essentially unchanged. Owing to its direct functionalization nature, this route generally offers clear product structures and relatively high atom efficiency.

Carbamates and urea derivatives are typically synthesized from CO_2 with amines, alcohols, or ammonia-related substrates, and they are widely used in pharmaceuticals, polymers, and organic synthesis. Despite these advantages, their synthesis still faces challenges such as the low intrinsic reactivity of CO_2, competing side reactions, and in some cases equilibrium limitations or reliance on additional activating agents. Therefore, further progress depends on developing more efficient catalytic systems and achieving high conversion and selectivity under milder and greener conditions.

4. SUMMARY

In conclusion, CO_2 conversion is an important strategy for both carbon management and the production of value-added chemicals. Based on whether the oxidation state of the central carbon atom changes, CO_2 transformation can be broadly divided into reductive and non-reductive pathways. Reductive conversion mainly yields CO, CH_4, and multicarbon products, but generally involves complex multi-electron/multi-proton transfer, competing pathways, and limited selectivity, especially for C_{2+} products. By contrast, non-reductive conversion enables the synthesis of carbonates, carbamates, urea derivatives, and related products through direct functionalization, often with clearer reaction pathways and higher selectivity.

Despite substantial progress, major challenges remain in catalyst design, reaction efficiency, product selectivity, and long-term stability under practical operating conditions. Future research should focus on developing more efficient and robust catalytic systems, clarifying structure–activity relationships and reaction mechanisms, and integrating catalytic processes with sustainable energy and carbon-management technologies. These efforts will be crucial for advancing CO_2 conversion toward scalable and practical applications.

CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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