Photocatalytic carbon dioxide to methane Energy Closed-Loop System: Carbon Neutrality Potential and Cutting-Edge Advances

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Abstract. The photocatalytic conversion of carbon dioxide to methane represents a promising strategy for achieving carbon neutrality by integrating renewable solar energy with chemical fuel production and utilization.This review systematically examines recent advances in catalyst design,reaction mechanisms,and system integration for constructing efficient carbon dioxide to methane energy closed-loop systems.Key breakthroughs include the development of high-performance catalysts such as single-atom Ru/Niobium pentoxide (96% methane selectivity) and interface-engineered heterostructures (93% selectivity), which address the kinetic challenges of the 8-electron reduction pathway through precise active site control and oxygen vacancy engineering. Mechanistic studies reveal the critical role of proton-coupled electron transfer (PCET) processes and intermediate stabilization in determining reaction selectivity. The integration of photocatalytic carbon dioxide reduction with methane combustion enables complete carbon cycling, where methane serves as both an energy carrier and a carbon vector, while combustion-derived heat can be recycled to enhance overall energy efficiency. However, challenges remain in scaling these technologies, including improving catalyst stability, optimizing system-level energy efficiency,and reducing gas separation costs. Future research should focus on developing robust hybrid photothermal-photocatalytic systems and integrating them with renewable energy infrastructure to realize practical deployment. This work provides a comprehensive framework for advancing carbon dioxide to methane conversion technologies and their role in sustainable energy systems.

Keywords: Carbon dioxide hotoreduction; methane production; carbon neutrality; photocatalysis; energy closed-loop system.

1. Introduction

Global climate change and energy crisis have become one of the most serious challenges facing mankind in the 21st century. As the concentration of carbon dioxide continues to rise, it is urgent to develop efficient and sustainable carbon neutralization technologies [1]. Among the many carbon dioxide conversion pathways, photocatalytic reduction of carbon dioxide to methane has attracted much attention because of its unique advantages: methane has high energy density(55.5 MJ/kg), which is compatible with existing natural gas infrastructure, and can achieve true carbon neutralization through the closed-loop cycle of "carbon dioxide convert to methane and back to carbon dioxide again" [2, 3]. This process simulates natural photosynthesis and converts carbon dioxide and water into storable chemical energy using solar energy, which provides innovative ideas for solving the problem of intermittence of renewable energy [4].

However, photocatalytic reduction of carbon dioxide to methane faces a number of great challenges, mainly due to its complex 8-electron transfer process and multi-step proton coupling reaction [1]. Traditional catalysts generally have some problems, such as low selectivity (mainly carbon monoxide formation), poor quantum efficiency and lack of stability. In recent years, remarkable breakthroughs have been made in this field through advanced catalyst design and reaction mechanism research. For example, monatomic catalysts (such as Ru/Nb_2O_5) achieve 96% methane selectivity [5], while double interface structures (such as In_2S_3-CdS/Zn) increase the selectivity to 93% by directional electron transfer [6]. These developments have laid the foundation for the construction of efficient photocatalysis system [7].

Understanding the reaction mechanism of carbon dioxide reduction to methane is the key to optimize the design of the catalyst.Studies have shown that this process usually follows the proton-coupled electron transfer (PCET) mechanism, involving key intermediates such as COOH, CHO and CH_3 transition [8, 9]. Through the combination of in-situ characterization techniques (such as DRIFTS, XPS) and theoretical calculations, researchers have been able to visualize the reaction path and identify the speed steps [8]. At the same time, oxygen vacancy engineering has been proved to effectively promote the adsorption and activation of carbon dioxide, thus enhancing the reaction kinetics [5, 9].

The construction of a complete energy closed-loop system requires the combination of photocatalytic carbon dioxide reduction and methane combustion. Literature 11 points out that the theoretical light energy conversion efficiency of this "artificial photosynthesis-combustion" cycle can reach 11.4%, but the actual system efficiency is limited by a number of factors, including the loss of light capture, electron transfer and product separation. The latest photothermal synergy strategies, such as the efficient operation of the Pt/CeO_2 catalyst at 600°C and 30x sunlight, provide a new direction for addressing these challenges [10].

This paper systematically reviews the latest research progress of photocatalytic carbon dioxide reduction to methane, focusing on: The design principle and structure-activity relationship of high efficiency catalyst and the mechanism and path regulation of multi-electron transfer reaction. Additionally, the construction and optimization strategy of energy closed-loop system. By integrating the multidisciplinary perspectives of material chemistry, catalytic mechanism and systems engineering, we aim to provide theoretical guidance and technical roadmap for the development of feasible carbon-neutral energy technologies.

2. Synergistic components

In artificial photosynthetic systems, the photocatalytic conversion of carbon dioxide to methane relies on three synergistic components: light-harvesting units that capture solar energy, charge separation networks that transport photogenerated carriers, and catalytic active sites that drive molecular transformations [7]. These three elements collectively form the fundamental architecture of an efficient catalytic system.

2.1. Single-Atom Catalysts

The catalyst of Ru single atom supported on Niobium pentoxide nano-sticks was reported in reference 5, and 96% methane selectivity was achieved. In this study, it was confirmed by EXAFS and AC-STEM that the isolated Ru atoms formed a Ru-O-Nb coordination structure with the Niobium pentoxide carrier. This unique geometry promoted the adsorption and activation of carbon dioxide atoms and optimized the multi-electron transfer process by regulating the degree of electron localization. Density functional theory (DFT) calculations show that the single atomic site of Ru significantly reduces the energy barrier (rate-determining step) of COOH formation, thus accelerating the whole reaction kinetics.

2.2. Dual-Active Site Systems

Synergistic catalysis of double active sites is another effective strategy. Literature 1 studied the blue TiO modified by Ag/W(Ag.W-BTO), and found that the spatially separated Ag site (specializing in carbon dioxide reduction) and W site (specializing in Methoxy group oxidation) achieved 92.08% dimethoxy methane (DMM) selectivity through synergism.

2.3. Oxygen Vacancy Engineering

Oxygen vacancy engineering plays a key role in regulating the electronic structure of catalysts. It is found that the oxygen vacancy in bismuth oxycarbonate can activate the linear carbon dioxide molecule into a curved state, which reduces the energy barrier of subsequent hydrogenation.

2.4. Interface Architecture

The Indium trisulfide-CdS/Zn (SCZ) double heterojunction structure was designed in reference 6. The directional flow of photogenerated electrons was induced by the double Schottky junction formed by the Indium trisulfide/CdS and CdS/Zn interface, and 93% methane selectivity was achieved.

3. Reaction Mechanism and Pathway Optimization

The photocatalytic reduction of carbon dioxide to methane involves a complex multi-step mechanism that has been extensively studied using advanced characterization techniques. Through in-situ DRIFTS and XPS analyses, researchers have identified key intermediates in the reaction pathway, including COOH (observed at 1716 cm^{-1}), CHO (1580cm^{-1}) and CH_3 (1450cm^{-1}). These studies reveal that the formation of COOH serves as the rate-determining step, with DFT calculations showing an energy barrier of ΔG is 0.53 eV [5,8]. The reaction predominantly follows a proton-coupled electron transfer (PCET) mechanism, where initial steps ($CO_2 \rightarrow$ COOH) involve concerted proton-electron transfer, while later stages (CHO$\rightarrow CH_3O$) proceed through sequential transfers [2]. Recent work has significantly improved our understanding of how to optimize this challenging reaction. A major breakthrough came from studies of Ni@CeO_2 catalysts, where the electronic back-donation effect was found to enhance CHO coverage by 2-3 times, effectively suppressing unwanted CO desorption [8]. Similarly, oxygen vacancy engineering in Bi-O-C systems has been shown to extend intermediate lifetimes by 3-5 times [9]. Charge transfer limitations, another critical challenge, have been addressed through innovative interface designs. For instance, the In_2S_3-CdS/Zn dual heterojunction demonstrates remarkably fast electron transfer (τ = 12 ps), eight times faster than conventional CdS (τ=102 ps), leading to significantly improved CH4selectivity (93% at -0.4 V vs RHE) [6]. The thermodynamic challenges of coupling endothermic water splitting with exothermic carbon dioxide reduction have been mitigated through several approaches. Spatial decoupling strategies, as exemplified by the Ag/W-BTO system, separate oxidation and reduction sites to optimize energy matching [2]. Additionally, Zn-doped CeO_2 catalysts maintain stable performance under combined light-thermal conditions, demonstrating the potential for practical applications [10]. These optimizations are summarized in the following table 1, highlighting the remarkable progress achieved in recent years:

Table 1. Four optimizations

Challenge	Traditional Performance	Optimized Solution	Improvement
Intermediate stability	low CHO coverage	Ni@CeO_2 back-donation	2-3 times increase
Charge transfer	Slow (τ = 102 ps)	In2S3-CdS/Zn heterojunction	8 times faster
Selectivity control	~50% CH_4	Single atom Ru/Nb_2O_5	96% CH_4
System stability	Rapid deactivation	Zn-doped CeO_2	100+hours operation

These advances collectively represent significant progress in photocatalytic carbon dioxide methanation, providing clear design principles for future catalyst development. The integration of atomic-level active sites, interface engineering, and dynamic control has pushed the boundaries of what's achievable in this field[5,6,7]. Looking ahead, the focus will likely shift toward scaling these advanced materials while maintaining their exceptional performance under industrially relevant conditions.

4. Optimization of methane combustion technology

Methane combustion is a key step of energy release in a closed-loop system, and its core goal is to achieve efficient energy conversion, while ensuring complete oxidation to carbon dioxide methane to avoid carbon emissions.

The results show that the selectivity of methane combustion is significantly affected by catalysts and reaction conditions. It is pointed out in reference 10 that under high temperature (> 800 °C) and oxygen-rich conditions, methane can be completely oxidized to carbon dioxide, while low temperature or reducing environment may lead to carbon monoxide formation [10]. Moreover, catalytic combustion technology (such as $Pd/Al2O_3$ combustion) can reduce the reaction temperature, improve the combustion efficiency, and reduce the by-products such as NOx [10].

For energy recovery and utilization, the combustion calorific value of methane is up to 55.5 MJ/kg, which can be used efficiently through cogeneration (CHP) system [11]. Additionally, the heat released from combustion can be partially supplied to the photocatalytic carbon dioxide reduction module to form an energy closed loop [4].

5. System Integration and Optimization Strategies for Closed-Loop Operation

The effective integration of system components represents a critical aspect of closed-loop operation, requiring sophisticated coordination between catalytic conversion, energy management, and material cycling. Rather than simply selecting optimal individual components, the system demands careful optimization of interfacial connections and energy/material flow pathways.

5.1. Catalyst-Reactor Integration

The integration of high-performance catalysts with reactor design requires consideration of both molecular-level interactions and macroscopic transport phenomena. While advanced catalysts like single-atom Ru/Niobium pentoxide (96%.methane selectivity) and $Co@C-TiO_2$ core-shell structures (94% selectivity) provide excellent active sites, their effectiveness depends on proper integration within the reactor architecture to ensure efficient mass and heat transfer. The optimization involves matching catalyst distribution with light penetration profiles and reactant flow patterns to maximize active site utilization.

5.2. Energy Cascade Utilization

The system employs a hierarchical energy management approach where high-grade solar energy drives the photocatalytic reaction, while lower-grade thermal energy from combustion is recovered for auxiliary processes. This energy cascade strategy significantly improves overall energy efficiency by utilizing energy at appropriate quality levels for different processes. The integration requires careful thermal management to minimize exergy losses during energy conversion and transfer between subsystems.

5.3. Material Flow Coordination

The closed-loop material flow necessitates precise coordination between carbon dioxide capture, conversion, and recycling processes. The integration of selective adsorbents like PECONFs with catalytic systems requires optimization of adsorption-desorption kinetics to match the reaction rates, ensuring continuous operation without bottlenecks. This involves tuning the operational parameters to maintain synchronisation between the comparatively fast combustion process and the slower photocatalytic conversion.

5.4. Interface Optimization

The interfaces between different functional units require special attention to minimize energy and material losses. This includes optimizing the heat exchange between combustion and photocatalytic

units, developing efficient gas separation membranes between reaction and capture units, and designing effective light-transmitting interfaces for photothermal integration. These interfacial optimizations often yield more significant improvements than individual component enhancements.

5.5. System-Level Dynamic Control and Multi-scale Integration

The operation stability relies on advanced control strategies that can accommodate fluctuations in solar input, variable reaction rates, and changing energy demands. The integration of real-time monitoring with adaptive control algorithms enables dynamic adjustment of operational parameters to maintain optimal performance under varying conditions.

This represents a crucial optimization approach that transcendsn individual component performance. The system integration spans multiple scales, from nanoscale catalyst design to macroscopic reactor engineering. The optimization requires simultaneous consideration of molecular-level reaction kinetics, microscale transport phenomena, and macroscale system thermodynamics. This holistic approach ensures that improvements at one scale do not compromise performance at other scales.

6. Conclusion

The photocatalytic carbon dioxide to methane conversion system represents a promising pathway toward achieving carbon neutrality by integrating renewable solar energy with chemical fuel production and utilization. This review has systematically examined the fundamental mechanisms, advanced catalyst designs, and system integration strategies that enable the construction of efficient energy closed-loop systems. Several key conclusions can be drawn from the current state of research:

First, remarkable progress has been made in catalyst design, with single-atom catalysts (e.g., Ru/Niobium pentoxide achieving 96% methane selectivity) and interface-engineered heterostructures (e.g. Indium trisulfide-CdS/Zn reaching 93% selectivity) demonstrating exceptional performance in addressing the kinetic challenges of the 8-electron reduction pathway. These advancements are underpinned by precise control of active sites, oxygen vacancy engineering, and sophisticated interface architecture that collectively enhance carbon dioxide activation and intermediate stabilization.

Second, mechanistic studies utilizing in situ characterization techniques and theoretical calculations have elucidated the proton-coupled electron transfer (PCET) mechanism as the dominant pathway, with COOH formation identified as the rate-determining step. This fundamental understanding has enabled targeted optimization strategies, such as electronic back-donation effects in Ni@CeO_2 catalysts that enhance CHO coverage by 2-3 times, and oxygen vacancy engineering in Bi-O-C systems that extend intermediate lifetimes by 3-5 times

Third, the integration of photocatalytic carbon dioxide reduction with methane combustion creates a complete carbon cycle where methane serves as both an energy carrier and carbon vector. This closed-loop system demonstrates the potential for true carbon neutrality when combined with efficient energy recovery systems, such as cogeneration (CHP) that utilizes combustion-derived heat to drive photocatalytic processes.

However, significant challenges remain in scaling these technologies for practical implementation. The overall system efficiency is currently limited by several factors: light capture efficiency (~85%), electron transfer losses (~40-60%), and gas separation requirements (~ 15-20% energy penalty). Future research should focus on developing robust hybrid photothermal-photocatalytic systems that can maintain stability under operational conditions exceeding 100 hours, while achieving solar-to-fuel conversion efficiencies compatible with industrial requirements.

Looking ahead, several research directions appear particularly promising: The development of multi-functional catalysts that integrate light harvesting, charge separation, and catalytic functions within unified architectures and the optimization of reactor designs that enable efficient mass and heat transfer while maintaining optimal light distribution. Moreover, the implementation of advanced

process control strategies that can dynamically adapt to varying solar input and reaction conditions; and the integration of carbon dioxide capture and conversion technologies with existing energy infrastructure to facilitate practical deployment.

The realization of commercially viable photocatalytic carbon to methane systems will require continued interdisciplinary collaboration between materials scientists, chemical engineers, and energy specialists. By addressing the current limitations in catalyst stability, system efficiency, and scalability, this technology has the potential to play a significant role in the global transition to sustainable energy systems and the achievement of carbon neutrality goals.

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