

A review of methane photocatalytic systems

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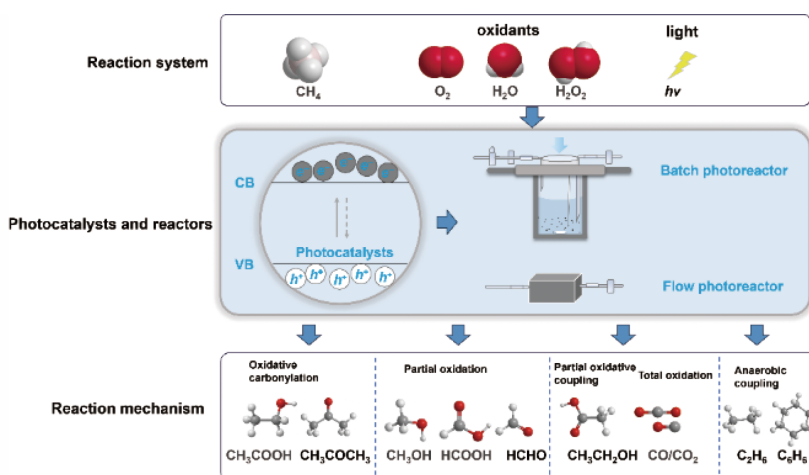
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Abstract: Methane (CH_4), the main component of natural gas, is regarded as an ideal feedstock for producing high-value-added chemicals and clean fuels due to its high hydrogen-to-carbon ratio. However, the CH_4 molecule is highly chemically inert, and traditional thermal catalytic reforming processes suffer from long reaction pathways and high energy consumption. In contrast, photocatalytic technology enables highly selective conversion of CH_4 under mild conditions, even



at room temperature, offering environmental benefits, economic advantages, and process efficiency, thereby facilitating the transition toward low-carbon chemical production. This review systematically summarizes recent advances in room temperature photocatalytic systems for direct CH_4 conversion. It begins by elucidating the mechanisms, product distributions, and inherent challenges of four key reaction pathways: partial oxidation, non-oxidative coupling, oxidative coupling and oxidative carbonylation of CH_4 . The discussion then shifts to the critical role of catalyst architecture, focusing on the design of semiconductor supports, the modulation of metal sites, and the integration of advanced porous frameworks. Furthermore, this review also addresses reactor design and process intensification strategies, including batch and continuous-flow reactors, novel structured reactors, as well as photo-electro and photo-thermo synergistic catalytic approaches. Finally, the reaction mechanisms of photocatalytic CH_4 conversion are summarized. Despite considerable progress, this field still faces challenges in fundamental understanding, performance evaluation, and technological integration. Future efforts should focus on in-depth mechanistic studies, standardization of evaluation protocols, development of non-noble metal catalysts, optimization of system processes, and comprehensive sustainability assessments.

Key words: methane; photocatalyst; reactor design; process intensification; photocatalytic system

Methane (CH_4) is a greenhouse gas with a global warming potential approximately 28 times higher than that of carbon dioxide (CO_2)^[1]. As such, controlling CH_4 emissions can significantly mitigate climate change. Currently, CH_4 emissions originate from a wide range of

sources, primarily distributed across energy extraction, agricultural activities, and waste management. Conventional treatment methods mostly employ direct combustion, converting CH_4 into CO_2 . While this approach avoids direct CH_4 emissions, it still generates substantial CO_2 , resulting in

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the limited overall abatement efficiency. Meanwhile, with continuous breakthroughs in the exploration and recovery technologies of unconventional natural gas such as shale gas and combustible ice, global natural gas reserves are becoming increasingly abundant, and extraction costs are relatively decreasing. As the main component of natural gas, CH₄ possesses a high hydrogen-to-carbon ratio, making it an ideal feedstock for producing high-value chemicals and clean fuels. Compared to traditional chemical processes based on coal or petroleum, CH₄ conversion routes generally entail lower energy consumption and reduced CO₂ emissions, thereby facilitating the transition of the chemical industry toward low-carbon practices. Therefore, developing efficient and low-energy CH₄ conversion technologies not only helps transform an environmental challenge into a resource opportunity but also holds significant importance for the sustainable development of global chemical production.

However, the CH₄ molecule possesses a highly symmetric tetrahedral structure (Figure 1(A)), with a C–H bond dissociation energy as high as 434 kJ/mol, rendering it chemically stable and challenging to activate^[2]. Consequently, CH₄ activation is thermodynamically non-spontaneous under ambient conditions and typically requires harsh environments such as high temperature and high pressure. Current CH₄ conversion technologies are broadly classified into indirect and direct routes. The conventional indirect approach primarily employs steam CH₄ reforming (SMR) to produce syngas (CO/H₂), which is subsequently converted into value-added chemicals through downstream processes such as Fischer-Tropsch synthesis or methanol synthesis^[3–4]. However, the SMR process is a reversible, endothermic reaction. Industrially, it is commonly conducted using mature nickel-based catalysts under high temperatures (>700 °C) and pressures (15–40 atm), often accompanied by significant carbon deposition, which can eventually lead to catalyst deactivation^[5]. In contrast, the direct conversion of CH₄ into oxygenates or multi-carbon hydrocarbons under mild conditions offers a promising alternative to circumvent the

high energy consumption and lengthy processes inherent to SMR. Early studies on direct CH₄ conversion predominantly focused on low-temperature thermocatalytic homogeneous systems. For instance, Pt-based (e.g., K₂PtCl₆) or Hg-based (e.g., HgSO₄) catalysts were employed in conjunction with strongly acidic media such as concentrated sulfuric acid or trifluoroacetic acid to promote the formation of ester products, thereby enhancing reactivity and selectivity. Nevertheless, the practical application of these routes has been hindered by high catalyst costs and the use of corrosive media^[6]. Since the early 2000s, several heterogeneous catalytic routes for direct CH₄ conversion have been reported. Prominent examples include the oxidative coupling of CH₄ (OCM) over alkali/alkaline earth metal (e.g., Li, Mg)-modified metal oxides (e.g., Mn₂O₃, La₂O₃)^[7], and the direct conversion of CH₄ to oxygenates driven by Fe- or Cu-modified zeolites^[8]. However, despite achieving direct conversion, these systems still require elevated temperatures (300–900 °C) and thus fail to fundamentally address the key issue of high energy consumption. Therefore, direct CH₄ conversion under mild conditions has gradually emerged as a research hotspot in heterogeneous catalysis in recent years. Beyond thermocatalysis, electrocatalytic CH₄ conversion has also shown promise, enabling the controlled transformation of CH₄ into various products by modulating the applied potential at room temperature and atmospheric pressure. However, current densities remain generally low, and the overall system energy efficiency, which is significantly influenced by the required electrolysis voltage, remains inadequate. In comparison, photocatalytic CH₄ conversion technology utilizes sunlight energy to drive the reaction, typically under ambient temperature without the need for external heating or high-voltage input, thereby substantially reducing the reaction energy consumption^[6].

In recent years, utilizing light energy to replace conventional thermal energy has enabled the selective conversion of inert molecules under relatively low or even ambient temperatures, demonstrating significant environmental, economic, and process advantages^[9–10].

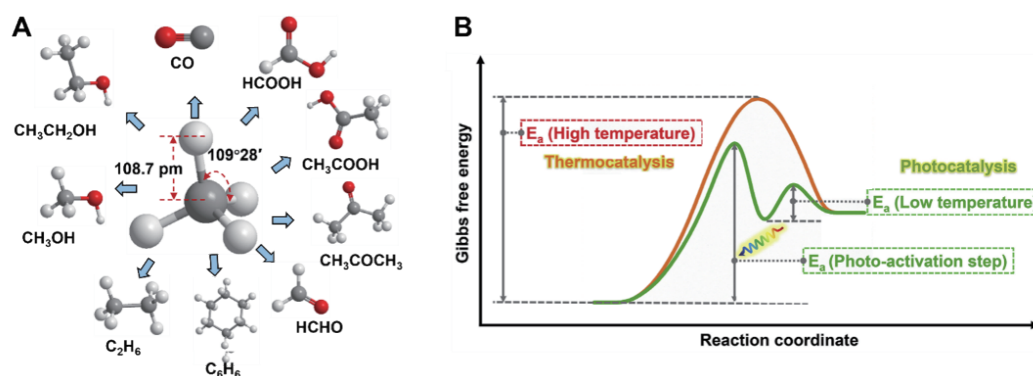


Fig. 1 (A) Structural diagram of CH₄ and its derivatives; (B) Thermal and photocatalytic CH₄ conversion thermodynamic energy barriers^[11] (with permission from Elsevier)

In photocatalytic processes, the photogenerated hole-electron pairs (h^+/e^-) possessing strong redox capabilities, along with highly reactive species such as superoxide radicals ($\cdot O_2^-$) and hydroxyl radicals ($\cdot OH$), can effectively promote the activation of C–H bonds in CH_4 (Figure 1(B))^[11]. This review systematically summarizes recent advancements in various room-temperature photocatalytic systems for the direct conversion of CH_4 , covering both oxidative and coupling reaction pathways, with particular focuses on analyzing and discussing progress in catalyst structure and design, oxidant selection, and the electron transfer mechanisms.

1 Photocatalytic methane conversion systems

Clarifying the reaction systems and conversion pathways for CH_4 transformation is of paramount importance for advancing the directed regulation of photocatalytic CH_4 conversion. Based on the different reaction pathways and target products, photocatalytic CH_4 conversion systems can be categorized into several technical routes. Typically, depending on whether O_2 is introduced into the reaction system and the chemical mechanisms it drives. Accordingly, these systems can be summarized into three representative categories: the partial oxidation of CH_4 (POM) aimed at generating liquid oxygenates^[12–14]; the non-oxidative coupling of CH_4 (NOCM) for constructing C–C bonds under anaerobic conditions^[15–16]; and the oxidative coupling of CH_4 (OCM) along with oxidative carbonylation of CH_4 , both of which achieve C–H bond activation and C–C bond formation in aerobic environments^[17–18]. These systems exhibit distinct thermodynamic behavior, reaction mechanisms, target products, and technical challenges, collectively forming the main framework of current research on photocatalytic CH_4 conversion.

1.1 Photocatalytic partial oxidation of methane

Photocatalytic POM enables the direct conversion of CH_4 into high-value liquid oxygenates, such as CH_3OH ^[19], $HCHO$ ^[20] and CH_3OOH ^[21]. The reaction mechanism typically involves C–H bond activation by photogenerated active species like holes (h^+) or $\cdot OH$, generating the key methyl radical ($\cdot CH_3$) intermediate. Subsequently, $\cdot CH_3$ species react with various reactive oxygen species (ROS) to progressively transform into different types of liquid oxygenates. POM is inherently a thermodynamically spontaneous cascade reaction ($CH_4 \rightarrow CH_3OH \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2$), wherein the target products are metastable intermediates along the reaction pathway. Furthermore, due to the typically strong polarity of liquid oxygenates, they tend to adsorb strongly onto catalyst surfaces, particularly hydrophilic ones. This strong adsorption makes desorption difficult and renders the products highly susceptible to over-oxidation, ultimately leading to CO_2 formation. Therefore, the core challenge in

achieving high selectivity and yield in POM lies in promoting the rapid desorption of target products while effectively suppressing their over-oxidation^[22].

To address these challenges, researchers have developed various catalyst and reaction system design strategies. Among them, precisely tailoring the micro-physical structure of catalysts *via* efficient heterojunction interface construction to promote charge separation and enhance target product selectivity has become a significant research direction. For instance, Zhao et al.^[23] constructed a series of MOF composites with tunable interface coverage by epitaxially growing ZIF-8 on the surface of MIL-125-NH₂. Through a two-step thermal treatment, these composites were converted into ZnO/TiO_x heterojunctions for photocatalytic CH_4 oxidation. The resulting heterojunction interface plays a crucial role in charge separation. The loaded Au and CoO_x species, situated on TiO₂ and ZnO respectively, synergistically promote O_2 activation and charge separation, ultimately achieving a product yield of 1723.5 $\mu mol/(g \cdot h)$ with 99% selectivity in POM reactions. In another study, Yan et al.^[24] reported a ReO₂@TiO₂ catalyst that achieved a total liquid oxygenate yield of 11581.2 $\mu mol/(g \cdot h)$ with 94.5% selectivity under Xe lamp irradiation. Its superior performance is attributed to the ReO₂@TiO₂ heterojunction, which promotes the migration of photogenerated electrons (e^-), thereby enhancing charge separation efficiency and subsequently strengthening the conversion of O_2 to $\cdot OH$ radicals. Similarly, Cao et al.^[25] effectively suppressed the ultrafast recombination of photogenerated carriers by constructing a BiOI/BN heterojunction interface. This interface facilitates the rapid transport of photo-induced charges and carbon-containing intermediates, increasing the CH_4 conversion rate to 15.5% while maintaining 86.4% selectivity for CH_3OH over 24 h (Figure 2(A))^[25].

Furthermore, precise regulation of the type and generation pathways of ROS during the reaction can effectively suppress over-oxidation. Zhou et al.^[21] achieved directed control over ROS generation pathways by precisely tailoring the size and exposed crystal facets of Au nanoparticles on Au/ZnO catalysts. On the optimized 1.0% Au/ZnO-9.6 catalyst (with 1% Au loaded on ZnO, featuring a (111) surface and a size of 9.6 nm), $\cdot OOH$ emerged as the primary ROS. Leveraging its mild oxidizing properties, this system achieved an exceptionally high CH_3OOH yield of 36.4 $mmol/(g \cdot h)$ with nearly 100% selectivity. The team further accomplished precise modulation of $\cdot OH$ generation by adjusting the Pd/Au loading ratio on In₂O₃, resulting in a CH_3OH yield of 2187 $\mu mol/(g \cdot h)$ with 94% selectivity from CH_4 conversion^[28]. Finally, reactor engineering serves as an effective strategy to inhibit product over-oxidation. For example, employing continuous-flow reactors enables the timely removal of generated liquid products from highly active reaction zones, fundamentally preventing their prolonged contact with photogenerated h^+ and ROS, thereby enhancing selectivity toward target products^[29].

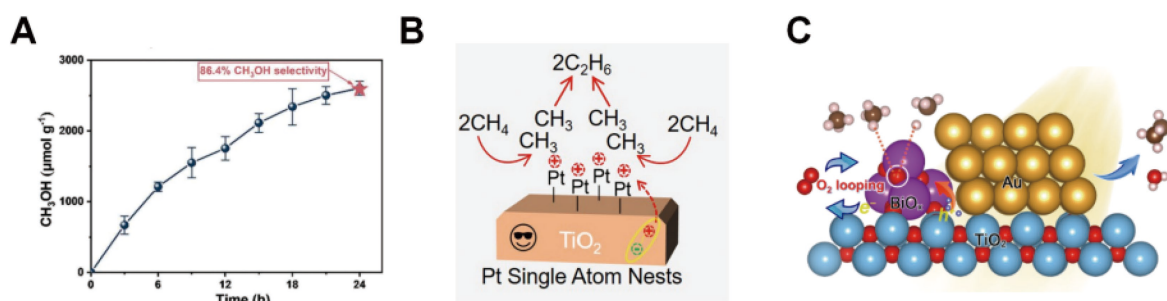


Fig. 2 (A) Photocatalytic performance of BiOI/BN-1:0.5; (B) Photocatalytic CH₄ coupling mechanism on Pt single-atom nest in T-PtSAs-N; (C) Photocatalytic OCM reaction mechanism on Au/BiO_x-TiO₂^[25–27] (with permission from Wiley Publications, ACS Publications and AAAS Publications)

In summary, although photocatalytic POM holds thermodynamic advantages, its industrial application still faces the challenge of over-oxidation. Current research primarily focuses on designing alloy catalysts, utilizing supports with oxygen buffering capacity, and developing novel reactor configurations to precisely regulate active oxygen species, thereby improving selectivity and stability. However, key bottlenecks remain, including achieving long-term catalyst stability while maintaining high activity and selectivity, and developing cost-effective, highly efficient non-noble metal catalyst systems.

1.2 Photocatalytic non-oxidative coupling of methane

Photocatalytic NOCM refers to the process that directly converts CH₄ into C₂ and higher hydrocarbons (such as C₂H₆^[30] and C₂H₄^[31]) while co-producing H₂ under anaerobic conditions^[32]. Unlike the POM pathway, NOCM avoids the introduction of oxidants, thereby eliminating the possibility of product over-oxidation to CO₂. Its typical reaction mechanism involves: photogenerated h⁺ activating CH₄ to generate methyl radicals (·CH₃), two of which couple on the catalyst surface to form ethane (C₂H₆); C₂H₆ can further dehydrogenate to ethylene (C₂H₄), while protons (H⁺) are reduced by photogenerated e⁻ to produce H₂.

Despite the clarity of its mechanism, achieving an efficient NOCM process faces several key challenges. First, the reaction is non-spontaneous with a positive Gibbs free energy change ($\Delta G > 0$) and is highly reliant on photon energy input to overcome the reaction barrier. This necessitates catalysts with superior light absorption and utilization capabilities. Second, a delicate balance is required between the surface coverage and desorption kinetics of ·CH₃ radicals: sufficient surface coverage is a prerequisite for C–C coupling, but excessively strong adsorption can hinder the regeneration of active sites and impede gas-phase coupling. Therefore, the adsorption energy of ·CH₃ must be tuned to an optimal range to balance its generation and desorption. Furthermore, reverse and side reactions pose significant challenges. The produced H₂ may induce the reverse reaction (C₂H₆ + H₂ → 2CH₄), reducing C₂ hydrocarbon yield; concurrently, intermediates like ·CH₃ may undergo excessive dehydrogenation or polymerization, leading to carbon

deposition and catalyst deactivation^[33].

To address these challenges, extensive research has been conducted on promoting CH₄ activation, optimizing intermediate adsorption behavior, accelerating product desorption, and inhibiting reverse reactions. For instance, introducing single-atom sites of metals such as Ag, Pt, Pd, or Cu can tune the electronic structure to optimize the adsorption strength of ·CH₃ intermediates, endowing them with both high activity and moderate desorption capability. Wang et al.^[30] co-dispersed Ag and Pd species on TiO₂ to construct a composite photocatalyst with synergistic effects, achieving selective conversion of CH₄ to C₂H₆ (yield ~250 μmol/g, selectivity > 92%). Mechanism studies indicated that Ag⁺ species facilitated CH₄ activation, while Pd primarily governed the ·CH₃ coupling step.

Introducing heterogeneous metal centers to construct asymmetric dual-site structures can break the symmetry of local charge distribution and modulate the electron cloud structure of active sites, thereby synergistically enhancing CH₄ activation and coupling selectivity. For example, Li et al.^[34] constructed a Mo-WO_{3-x} catalyst with dual active sites by substituting W with Mo⁶⁺ in WO₃. This structure not only accelerated the C–H bond cleavage process but also significantly lowered the desorption energy barrier for C₂H₄, ultimately achieving a C₂H₄ production rate of 152.19 μmol/(g·h) with 95% selectivity.

Constructing active sites with high intrinsic activity that can alleviate the steric hindrance of intermediates is another key strategy for improving NOCM performance. Zhang et al.^[26] developed a catalyst featuring Pt single-atom nest structures anchored on TiO₂, which achieved a CH₄ conversion rate of 251.6 μmol/(g·h), 3.2 times higher than that of conventional Pt single-atom catalysts. Theoretical calculations revealed that this Pt-nest structure significantly lowered the activation energy barrier for CH₄ molecules and alleviated their spatial resistance, thereby efficiently promoting the generation of C₂H₆ (Figure 2(B)).

In summary, the core challenges of the photocatalytic NOCM process stem from its stringent thermodynamic constraints and the high reactivity of its products. This leads to low single-pass CH₄ conversion, and the target products are prone to excessive dehydrogenation, causing carbon deposition and rapid catalyst deactivation. Currently, strategies focus on developing bifunctional catalysts to

synergistically catalyze C–H bond activation and C–C bond coupling, often employing “reaction-regeneration” cyclic processes to manage carbon deposition. Nevertheless, significant hurdles remain for the industrialization of this system. First, the single-pass CH_4 yield is far below economically viable requirements. Second, the frequent regeneration operations severely limit process continuity and economic feasibility. Additionally, an insufficient understanding of the micro-mechanisms governing highly selective C–C coupling constrains the rational design of catalysts. Future research hinges on achieving precise control over the microscopic “activation-adsorption-desorption” processes on catalyst surfaces, aiming to collaboratively overcome the thermodynamic and kinetic bottlenecks through integrated applications of electronic structure design, interface/surface engineering, and advanced reactor technologies.

1.3 Photocatalytic oxidative coupling of methane

OCM aims to directly convert CH_4 into C_{2+} hydrocarbons via C–C coupling in the presence of O_2 . Compared to NOCM, the OCM reaction offers advantages of stronger thermodynamic feasibility, faster reaction rates, and higher single-pass conversion, positioning it as one of the CH_4 conversion pathways closest to industrial application. However, since the reaction activity of the products (e.g. C_2H_6 and C_2H_4) is higher than that of CH_4 , they are highly susceptible to over-oxidation to CO_2 in the presence of O_2 . Furthermore, the reaction is highly exothermic, which can easily lead to localized overheating in the reactor. This not only induces catalyst sintering and deactivation but also exacerbates deep oxidation processes. Consequently, the core challenges of the OCM process lie in low product selectivity and the difficulty in effectively managing the reaction heat^[35].

Photocatalytic OCM effectively circumvents the challenges of high-temperature environments and heat management faced by conventional thermocatalytic OCM, owing to its distinct reaction mechanism. Nevertheless, the selectivity in photocatalytic OCM typically follows a “volcano-shaped” trend, necessitating a trade-off between activity and selectivity during the process. On one hand, achieving high reactivity often relies on strong oxidizing species (e.g., $\cdot\text{O}_2$, $\cdot\text{OH}$) to achieve efficient C–H bond cleavage in CH_4 . On the other hand, these species can indiscriminately attack the already formed C_{2+} products, leading to their over-oxidation to CO_2 ^[36]. Additionally, the OCM reaction requires precise regulation of the competition between gas-phase radical reactions and catalyst surface reactions. The key step for generating C_2 products is the coupling of $\cdot\text{CH}_3$ radicals in the gas phase. If these radicals become overly stabilized and adsorbed on the catalyst surface, they are prone to complete oxidation by surface lattice oxygen or h^+ . Therefore, the design of photocatalytic OCM systems is centered on achieving precise control over

ROS and optimizing the adsorption/desorption behavior of key intermediates on the catalyst surface.

In 2024, Zhai et al.^[27] constructed composite catalytic sites comprising BiO_x and Au on a TiO_2 substrate, achieving photocatalytic OCM with high conversion rates, high selectivity, and good stability. The study indicated that lattice oxygen in BiO_x could be activated as a localized oxidant to promote CH_4 activation, while the Au sites regulated the transfer process of $\cdot\text{CH}_3$ radicals, promoting C–C coupling and inhibiting product over-oxidation. Other research has pointed out that using zeolites or MOFs with suitable pore sizes as catalyst supports can leverage their nanoconfinement effects to stabilize the transition state of $\cdot\text{CH}_3$ radicals and promote dimerization reactions. Simultaneously, the pore size can restrict the diffusion of oxidants, thereby protecting the generated C_2 hydrocarbons from over-oxidation (Figure 2(C)).

Concurrently, membrane reactor technology demonstrates unique advantages in enhancing OCM efficiency. Employing a dense oxygen separation membrane reactor allows O_2 to permeate to the reaction side slowly and controllably in the form of lattice oxygen, achieving on-demand supply of the oxidant. This fundamentally avoids the over-oxidation issues caused by locally high O_2 concentrations, providing an effective engineering solution for selectivity control in the OCM process^[37].

In summary, the core challenge in photocatalytic OCM research lies in surpassing the thermodynamic-kinetic upper limit of C_2 product yield. This is intrinsically because that the target products are more reactive than CH_4 and thus more susceptible to over-oxidation, leading to an inherent trade-off between selectivity and conversion. To address this challenge, future research will focus on two levels. At the catalytic material level, it is essential to precisely regulate the reactivity of oxygen species by adjusting the electronic structure and coordination environment of active sites. This should be combined with carriers possessing confinement effects to jointly construct a unique reaction microenvironment that favors C–H bond activation while protecting C–C bonds from cleavage. At the reaction engineering level, advanced technologies such as membrane reactors should be integrated to optimize the reaction process. The ultimate goal is to achieve efficient and highly selective conversion of CH_4 to high-value olefins driven by light. However, it must be acknowledged that fundamentally breaking the trade-off between selectivity and conversion, and developing cost-effective catalyst systems capable of long-term stable operation, remain ultimate challenges yet to be overcome in this field.

1.4 Photocatalytic oxidative carbonylation of methane

Photocatalytic oxidative carbonylation of CH_4 aims to utilize photoexcitation to drive C–C coupling between CH_4 and other carbon sources such as CO, enabling the direct synthesis of C_{2+} oxygenates, including acetic acid

(CH₃COOH), ethanol (CH₃CH₂OH), acetone (CH₃COCH₃), etc. Compared with coupling pathways that yield C₂ hydrocarbons, this reaction route offers superior atom economy and yields products that are easier to separate and transport, making it a highly promising route for CH₄ valorization. However, this system involves gas-liquid-solid multiphase interfacial reactions, requiring the cooperative activation of inert small molecules like CH₄ and CO. Core challenges include complex reaction pathways, limited mass transfer efficiency, and the susceptibility of intermediates to over-oxidation.

In terms of reaction mechanism, photocatalytic CH₄ oxidative carbonylation diverges from traditional thermocatalytic processes that rely on noble metals (e.g., Rh, Ir) and strong acidic media, establishing a mild conversion pathway based on radical-metal synergy. The key to its reaction network lies in the precise regulation on the generation and transformation of key intermediates. On one hand, the strong oxidizing radicals (e.g., ·OH) generated in the system must preferentially activate CH₄ rather than the carbonylating agent CO to efficiently produce ·CH₃ radicals. On the other hand, CO molecule must effectively collide with ·CH₃ and be captured by metal centers to complete the carbonyl insertion step. The pathways for different products share similar initial stages: CH₄ is attacked by photo-generated active species (e.g., h⁺, ·OH) to form ·CH₃, which subsequently forms a methyl-metal intermediate (M-CH₃) with a metal center (M). Thereafter, the formation of CH₃COOH requires CO insertion into the M-CH₃ bond, forming an acetyl-metal species (M-COCH₃), followed by hydrolysis. The formation of CH₃CH₂OH can proceed *via* direct hydrogenation of M-CH₃, or through the hydrogenation of M-COCH₃ to a CH₃CHO intermediate followed by further hydrogenation; this pathway necessitates efficient proton/hydrogen source supply and hydrogenation sites on the catalyst surface. The formation of CH₃COCH₃ involves either the coupling of two M-COCH₃ molecules or the combination of one M-COCH₃ with a surface-adsorbed ·CH₃.

Therefore, the core of selectivity control in this reaction lies in precisely guiding the transformation pathways of key intermediates (M-CH₃, M-COCH₃), which is critical for achieving efficient sequential coupling and spatial synergy across the three-step reactions: radical generation, ·CH₃ capture and CO insertion. In 2025, Li et al.^[38] reported a catalyst based on MoS₂-confined Rh-Zn atomic pairs supported on TiO₂, which efficiently drives the photocatalytic oxidative carbonylation of CH₄ to CH₃COOH achieving a yield of 152.0 μmol/(g·h) with 96.5% selectivity. Theoretical calculations and experimental results indicated that the Rh-Zn atomic pair effectively synergizes to promote the photoreduction of O₂, generating highly active Zn-OH species at the Zn sites, which can efficiently activate CH₄ to form ·CH₃ species. These ·CH₃ species then

couple with CO on adjacent Rh sites, forming the crucial -COCH₃ intermediate and ultimately leading to the production of CH₃COOH (Figure 3(A))^[38]. Concurrently, Fei et al.^[39] constructed a photothermal synergistic reaction system using TiO₂ as the photoactive substrate and Pd nanoparticles as a co-catalyst, successfully achieving the one-step coupling of CH₄ and CO to produce CH₃COCH₃ with a selectivity as high as 80% at 150 °C under light irradiation. Isotope labeling experiments confirmed that CH₃COCH₃ originates from the direct coupling of two CH₄ molecules with one CO molecule. The study further highlighted that the appropriate adsorption strength between Pd nanoparticles and reaction intermediates is key to forming the C₃ product: Pd can effectively adsorb and activate CO, promoting its reaction with CH₄; in the absence of Pd, CO tends to form COO intermediates on the TiO₂ surface, leading instead to CH₃COOH. Hao et al.^[40] designed a hollow multilayer CeO₂@PdO@FeO_x nanosphere catalyst with asymmetric interfaces, in which the PdO/FeO_x and CeO₂/PdO catalytic interfaces selectively activate CH₄ and CO, respectively. The hollow multilayer structure further promotes the directional transport and coupling of ·CH₃ and CO, thereby enabling efficient synthesis of CH₃CH₂OH (Figure 3(B)). Under a light intensity of 100 mW/cm² at room temperature and without using photosensitizers or sacrificial agents, this catalyst achieved a maximum CH₃CH₂OH yield of 728 μmol/(g·h).

Mass transfer efficiency is a critical bottleneck constraining the performance of photocatalytic CH₄ oxidative carbonylation reactions. As a typical gas-liquid-solid triphasic catalytic system, its reaction pathway is limited by the dissolution-diffusion kinetics of gaseous reactants (CH₄ and CO) in the liquid phase and their migration efficiency to the catalyst active sites. To overcome the mass transfer barriers inherent in conventional heterogeneous catalysis, the academic community has proposed various strategies, including the design of homogeneous catalytic systems, reconstruction of the reaction microenvironment, and innovation in reactor structures.

In the realm of homogeneous catalysis, Pan et al.^[41] developed a homogeneous system based on a terpyridine iron catalyst utilizing ligand-to-metal charge transfer (LMCT) mechanism in 2025. By establishing a molecular-scale homogeneous reaction environment, this approach fundamentally eliminates mass transfer barriers at gas-liquid-solid interfaces, achieving excellent performance with a CH₃COOH yield of 327 μmol and a C₂/C₁ selectivity exceeding 20/1. Mechanism studies indicate that Fe(II) and Fe-carbonyl complexes can circumvent the over-oxidation of ·CH₃ radicals *via* a pathway akin to a radical rebound mechanism, thereby attaining exceptionally high reaction efficiency in CH₄ carbonylation.

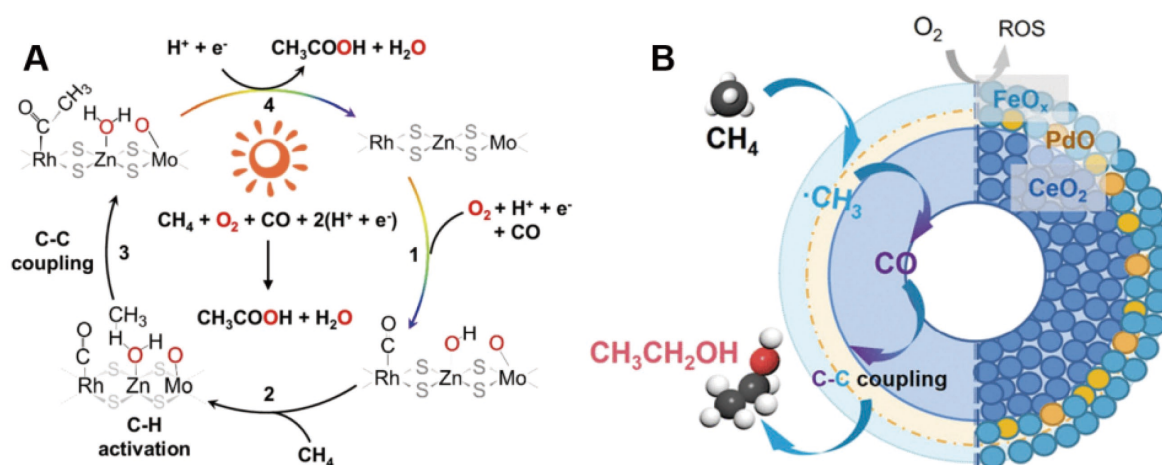


Fig. 3 (A) The catalytic cycle of CH_4 , CO and O_2 generating CH_3COOH on $\text{RhZn-MoS}_2/\text{TiO}_2$ catalyst^[38]; (B) Photocatalytic mechanism of $\text{CeO}_2@\text{PdO}@\text{FeO}_x$ ^[40] (with permission from Springer Nature, ACS Publications)

In terms of reaction microenvironment reconstruction, He et al.^[42] proposed an innovative triphasic interface floating membrane strategy. They constructed a Fe(III)-crosslinked macroporous alginate hydrogel membrane encapsulating C_3N_4 ($\text{Fe(III)}@\text{ACN}$). Leveraging its lightweight macroporous structure, this material stably floats at the gas-water interface, forming a unique gas-solid-liquid triphasic reaction zone. By substantially shortening the gas diffusion pathway, it effectively promotes the contact between CH_4 molecules and active species within the pores under ambient pressure, ultimately achieving a $\text{CH}_3\text{CH}_2\text{OH}$ production rate of $171.7 \mu\text{mol}/(\text{g}\cdot\text{h})$ with excellent selectivity of 90%.

In the field of reactor engineering, enhancing reaction efficiency through structural innovations to optimize mass transfer pathways has proven to be an effective strategy. For instance, Zhang et al.^[43] designed a flow-type photochemical reaction device that optimizes reactant mass transfer, achieving a CH_3COOH yield of $1.5 \text{ mmol}/(\text{g}\cdot\text{h})$ with 91.6% selectivity on a $\text{PdO}/\text{Pd-WO}_3$ heterointerface composite material. This photochemical flow reactor features an arc-shaped channel design where the catalyst sample is deposited. CH_4 and H_2O are pre-mixed and then introduced into the channel to contact the catalyst, creating a triphasic interface that enhances CH_4 mass transfer rates and improves the utilization of $\cdot\text{CH}_3$ and carbonyl intermediates.

Based on the above, future research on photocatalytic CH_4 oxidative carbonylation will focus on the following directions: designing catalytic materials that combine efficient photogenerated charge separation capability with well-defined active sites for C-C coupling; optimizing CO insertion selectivity by regulating the structure of active centers at the molecular scale; and developing hierarchical mass transfer channels through reactor engineering and interface regulation strategies to overcome diffusion limitations. The ultimate goal is to achieve efficient and highly selective synthesis of high-value oxygenates from CH_4 . In summary, Table 1 systematically organizes the

chemical equations, Gibbs free energies^[44–45] and pros-and-cons of various photocatalytic CH_4 conversion systems, aiming to provide a clear comparative basis for selecting suitable reaction pathways aligned with different research objectives, such as high-value product selectivity, reaction rate, or system stability.

2 Design of photocatalysts for methane conversion

Across diverse photocatalytic CH_4 conversion systems, achieving selective and efficient transformation from C-H bond activation to target products relies on the rational design of catalyst materials. Consequently, the systematic development of high-performance photocatalysts constitutes a core task for advancing this field. In traditional photocatalytic systems, semiconductor materials dominate due to their unique electronic structures. However, intrinsic semiconductors commonly face challenges such as a limited light absorption range, rapid charge carrier recombination rates, and insufficient surface active sites, which severely constrain the further enhancement of their photocatalytic performance. To overcome these bottlenecks, research focus has gradually shifted toward the precise engineering of semiconductor substrates. Strategies like elemental doping, defect engineering, and the construction of heterojunctions are employed to optimize their photoelectronic properties and surface reactivity. Simultaneously, the introduction of metal sites, which can modulate charge carrier dynamics and facilitate C-H bond activation, has emerged as a pivotal strategy for boosting photocatalytic performance. In recent years, novel porous crystalline materials such as Metal-Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) have rapidly gained prominence in the field of photocatalytic CH_4 conversion, owing to their advantages such as high specific surface area, tailorable pore structures and well-defined tunable active sites.

Table 1 Advantages and disadvantages of different photocatalytic CH₄ conversion systems

System	Chemical equation	$\Delta G_0(298\text{ K})$ /(kJ·mol ⁻¹)	Advantage	Disadvantage
POM	2CH ₄ + O ₂ → 2CH ₃ OH	-233	Well-defined active sites; Tunable oxidizing capacity; Excellent stability	Typically requires a sacrificial agent, resulting in low atom economy; Risk of over-oxidation; Limited light absorption
	2CH ₄ + O ₂ → 2CO + 4H ₂	-173		
	2CH ₄ + O ₂ → 2HCHO + 2H ₂	-104		
NOCM	2CH ₄ → C ₂ H ₆ + H ₂	68.6	No over-oxidation; Co-production of high-value H ₂ ; Mild conditions	Thermodynamically challenging, with low quantum efficiency; Slow kinetics, leading to low space- time yield; Prone to catalyst deactivation
	6CH ₄ → C ₆ H ₆ + 9H ₂	434		
	2CH ₄ → C ₂ H ₄ + 2H ₂	169.6		
OCM	4CH ₄ + O ₂ → 2C ₂ H ₆ + 2H ₂ O	-320	Thermodynamically favorable; Kinetically competent; Operationally mild	Prone to over-oxidation; Requires precise oxygen control; Complex catalyst design
	2CH ₄ + O ₂ → C ₂ H ₄ + 2H ₂ O	-288		
Oxidative Carbonylation of CH ₄	CH ₄ + CO ₂ → CH ₃ COOH	71.1	High-value and selective products; Mild conditions; High atom economy; Novel mechanism	Complex reaction system; Low quantum efficiency and slow kinetics; Challenging catalyst recovery in homogeneous systems
	2CH ₄ + CO ₂ → CH ₃ COCH ₃ + H ₂ O	115		

2.1 Design of semiconductor substrates

Among numerous traditional photocatalytic materials, semiconductors such as titanium dioxide (TiO₂), zinc oxide (ZnO), and tungsten trioxide (WO₃) have served as primary catalyst substrates in early research on photocatalytic CH₄ conversion due to their excellent chemical stability, non-toxic nature, and suitable band structures^[46]. In recent years, significant progress has been made in optimizing their photocatalytic performance through strategies such as crystal phase engineering and defect regulation.

In 2022, Jiang et al.^[47] modulated the crystal phase composition of commercial anatase-phase TiO₂ via a thermal annealing process, constructing a biphasic anatase-rutile TiO₂ catalyst with an optimal phase ratio (90% anatase-TiO₂) for the photocatalytic partial oxidation of CH₄ to HCHO. Mechanism studies revealed that crystal phase engineering of TiO₂ effectively promotes the separation and migration of photogenerated charge carriers, thereby extending their lifetime. Concurrently, CH₄ is readily activated via lattice oxygen on the rutile phase surface, generating an OCH₃ intermediate that is subsequently oxidized to HCHO. Experimental results demonstrated an HCHO yield as high as 24.27 mmol/g with 97.4% selectivity under ambient temperature. In 2023, Tang et al.^[48] further constructed a biphasic TiO₂ catalyst with an anatase/rutile heterojunction (P25-800/2, A/R ≈ 3:1) by high-temperature calcination of commercial P25 TiO₂. In the presence of CH₄ and H₂O₂, this catalyst exhibited a total yield of C₁ liquid oxygenates of 9.94 mmol/(g·h) with 99.42% selectivity. Mechanism investigations indicated that the anatase/rutile heterojunction interface not only promotes charge separation but also significantly lowers the activation energy barrier for CH₄ → ·CH₃ through enhanced polarization of the CH₄ molecule by interfacial oxygen atoms. During the reaction, ·OH and ·OOH served as key reactive oxygen species, facilitating the efficient conversion

of CH₃OH to HCHO via a ·CH₂OH intermediate.

ZnO is also widely adopted as a catalyst for the photocatalytic conversion of CH₄. Xiao et al.^[49] prepared a ZnO photocatalyst rich in interstitial zinc (Zn_i) defects (ZnO(Zn_i)-350) via thermal decomposition of a ZnO₂ precursor, achieving efficient photocatalytic partial oxidation of CH₄ to liquid oxygenates. Studies showed that O₂ adopts a special terminal adsorption configuration on Zn sites and is selectively converted to ·OOH rather than ·OH, thus suppressing over-oxidation. Under conditions of 30 °C, 1.9 MPa CH₄ and 0.2 MPa O₂, this catalyst achieved a liquid oxygenate yield of up to 6080 μmol/g with 98.6% selectivity, with CO₂ byproduct formation being only one-tenth that of conventional Au/ZnO catalysts.

Additionally, beyond in-depth studies on TiO₂ and ZnO, research on WO₃ has also achieved certain breakthroughs. In 2024, Fan et al.^[50] systematically investigated the influence of different crystal facets on the photocatalytic CH₄ oxidation pathways over WO₃. The study found that the (001) facet enables the direct oxidation of CH₄ by lattice oxygen to produce HCHO, achieving 100% HCHO selectivity even in a pure CH₄ atmosphere. In contrast, the (110) facet preferentially adsorbs H₂O and generates radicals like ·OH, leading to a reaction pathway involving intermediates such as CH₃OOH and CH₃OH, which results in lower HCHO selectivity. This research clearly reveals the intrinsic relationship between surface atomic structure, O₂ activation pathways, and CH₄ oxidation selectivity.

In addition to the aforementioned traditional metal oxides, perovskite oxides (ABO₃), as a class of functional materials with flexible composition and tunable structures, have also found widespread application in the field of photocatalytic CH₄ conversion. The replaceability of A- and B-site elements and the tunability of oxygen vacancy concentration allow for the flexible design of perovskite oxides in terms of band structure, oxygen species activity, and charge carrier transport properties. This provides an

ideal research platform for understanding the participation mechanism of lattice oxygen in photocatalysis and constructing efficient photothermal/photoelectrochemical synergistic systems.

For example, Dong et al.^[51] developed a Z-scheme heterojunction engineering strategy, constructing a composite photocatalyst of manganese-doped halide perovskite (CsPbBr₃) and bismuth vanadate (BiVO₄) (Mn@CsPbBr₃/BiVO₄) via an *in situ* growth method. This approach effectively modulates the interfacial charge transfer pathway, significantly enhancing the separation efficiency of photogenerated carriers and strengthening the system's reduction capability, thereby achieving highly selective photocatalytic CH₄ conversion using air as the oxidant under mild conditions. The research utilized the Z-scheme heterojunction formed between CsPbBr₃ and BiVO₄ to enrich photogenerated h⁺ in the valence band of BiVO₄, effectively oxidizing H₂O to generate ·OH radicals. These radicals then efficiently activate the C–H bond of CH₄, producing ·CH₃ intermediates that are ultimately converted into liquid oxygenates (CH₃OH and HCHO). Experimental results confirmed that this catalyst achieved a total liquid oxygenate yield of 533.5 μmol/(g·h) with 94.8% selectivity in a cyclic flow reaction system. Mechanism studies further indicated that ·OH radicals are the key species for CH₄ activation, with oxygen atoms in the products primarily originating from O₂ and partially from H₂O.

In 2024, Nie et al.^[52] developed a high-entropy LaMnO₃-type perovskite (HELMO) sub-nanowire heterostructure strategy, achieving highly selective photocatalytic conversion of CH₄ to CH₃COOH under ambient temperature and pressure without external oxidants. The yield reached 4.45 mmol/(g·h) with selectivity exceeding 99%, accompanied by excellent cycling stability. Mechanism studies showed that photogenerated h⁺ oxidized H₂O at phosphotungstic acid (PTA) sites to generate ·OH radicals, which then activate CH₄ to form ·CH₃ intermediates. The sub-nanoscale heterojunction formed between HELMO and PTA effectively promotes the separation and migration of photogenerated h⁺/e⁻ pairs while enhancing the stability of the key intermediate COOH, facilitating the smooth C–C coupling between ·CH₃ intermediates and COOH. The electron buffering effect of PTA can effectively suppress the over-oxidation of intermediates, improving the selectivity of the photocatalytic reaction.

In 2025, Li et al.^[53] developed a lattice oxygen activation strategy by partially substituting Fe sites with Mn in LaFeO₃ and loading Ru nanoparticles to construct a Ru/LaMnFeO photothermal catalyst. This significantly enhanced the performance of light-driven dry reforming of CH₄ (DRM), achieving H₂ and CO production rates of 42.89 and 54.92 mol/(g·h), respectively, with stable operation for 150 h. Mechanism studies revealed that Mn doping induces charge transfer from La to Mn. This process acts synergistically with photogenerated electrons to reconstruct

the perovskite's electronic structure and weaken the La–O–Mn bond, thereby significantly promoting lattice oxygen migration. Under light irradiation, CH₄ dissociates into ·CH₃ at Ru sites, which are then oxidized by activated lattice oxygen to CH₃O, effectively suppressing carbon deposition and ensuring good catalyst stability. CO₂ splits into CO at oxygen vacancies, replenishing the lattice oxygen and completing the catalytic cycle.

The aforementioned research provides valuable experience and new insights for overcoming the trade-off between activity and selectivity in photocatalytic CH₄ conversion, guiding the design of photocatalysts with high activity and selectivity.

2.2 Design of metal sites

In the early research on photocatalytic CH₄ conversion, introducing metal co-catalysts onto the catalyst surface emerged as a common and effective strategy to enhance selective conversion of CH₄ under mild conditions. However, the practical application of this approach was often constrained by several factors. Firstly, the catalytic process depended on externally added H₂O₂, which increased both costs and process complexity. Second, the inherent wide bandgap of the semiconductor materials limited their absorption of visible light, while rapid recombination of photogenerated charge carriers resulted in low overall photocatalytic efficiency^[54–55]. To overcome these limitations, subsequent research has focused on developing various modification strategies, including metal cluster loading, alloy modified, coordination environment regulation, and single-atom site engineering, aiming to broaden the spectral response, promote charge separation, and optimize surface reaction pathways^[56].

In 2019, Song et al.^[9] proposed using the more economical and environmentally friendly O₂ as an alternative oxidant. By loading trace amounts (0.1%) of noble metal co-catalysts (Pt, Pd, Au, Ag) onto ZnO surfaces via a NaBH₄ reduction method. This study achieved the selective photocatalytic oxidation of CH₄ to liquid oxygenates (CH₃OOH, CH₃OH, HCHO) under ambient temperature in an aqueous phase, using O₂ as the sole oxidant. Among the optimized systems, 0.1% Au/ZnO exhibited the optimal performance, with a liquid oxygenate yield as high as 125 μmol/h with selectivity exceeding 95% (Figure 4(A)). Mechanism studies revealed that photogenerated h⁺ on the ZnO surface efficiently activate the C–H bond of CH₄, to generate ·CH₃ radicals, while Au co-catalysts promote the reduction of O₂ to form the key intermediate ·OOH. These two species further couple to form CH₃OOH as the primary product, which subsequently transforms stepwise into CH₃OH or HCHO (Figure 4(B)). This work pioneered the highly selective photocatalytic oxidation of CH₄ under mild conditions using O₂ as the oxidant and H₂O as the medium, providing a new pathway for the valorization of low-carbon alkanes.

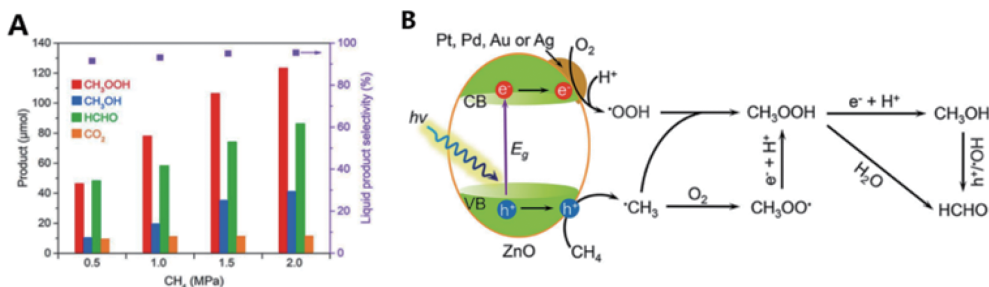


Fig. 4 (A) photocatalytic POM performance of 0.1% Au/ZnO and (B) reaction mechanism^[9] (with permission from ACS Publications)

Subsequently, to achieve the leap from C_1 to C_{2+} products, the research focuses gradually shifted towards the precise structural engineering of semiconductor materials. In 2022, Zhang et al.^[32] proposed a heteroatom engineering strategy, which involved constructing a Pd- O_4 coordination structure on the TiO_2 surface to effectively modulate its valence band electron distribution, thereby significantly enhancing the NOCM of CH_4 (Figure 5(A)). Such single-atom Pd modified TiO_2 (Pd_1/TiO_2) promoted the concentration of photogenerated h^+ at the Pd sites, accelerating the C-H bond cleavage of CH_4 as well as the generation and coupling of $\cdot CH_3$ intermediates. An ethane (C_2H_6) production rate of 0.91 mmol/(g·h) with a selectivity as high as 94.3% was achieved.

Compared to C_2H_6 , propane (C_3H_8) is easier to liquefy, significantly reducing storage and transportation costs. To achieve the directed conversion of CH_4 to C_3H_8 , Nie et al.^[37]

developed a novel photocatalyst featuring Au nanoparticles encapsulated within porous TiO_2 (Au/ TiO_2). After a water vapor activation post-treatment, this material induced lattice tensile strain in the Au nanoparticles, which in turn modulated their local electronic structure, enhancing the adsorption capacity for reaction intermediates and promoting the deep coupling of CH_4 to form C_3H_8 . Furthermore, the nanoconfinement environment created by the porous TiO_2 framework effectively prolonged the residence time of reaction intermediates, thereby increasing the probability of C-C coupling and reaction efficiency. Under simulated sunlight and continuous flow conditions, this catalyst achieved a C_3H_8 selectivity of 91.3% with a production rate of 1.4 mmol/(g·h). The apparent quantum efficiency (AQE) at 365 nm reached a remarkable value of 39.7%, and the catalyst exhibited excellent stability for over 200 h, providing a new perspective for improving the economic viability of CH_4 conversion products.

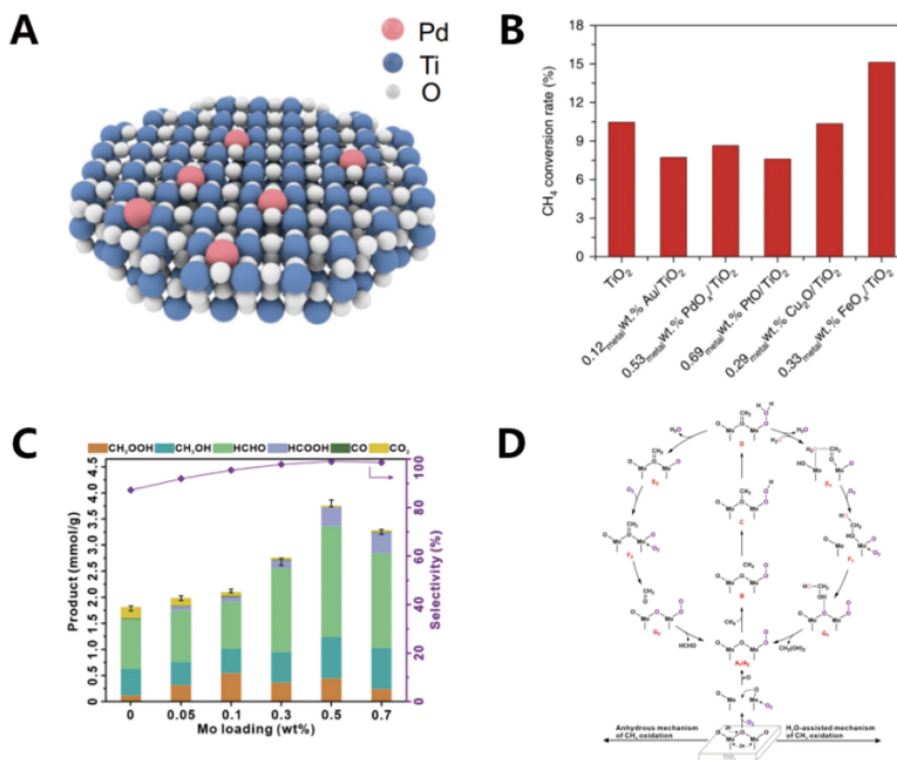


Fig. 5 (A) Schematic illustration for Pd_1/TiO_2 (001)-based models; (B) Photocatalytic CH_4 oxidation performance of TiO_2 modified by different metals; (C) Photocatalytic POM performance of MoO_x-TiO_2 and (D) reaction mechanism^[10,32,57] (with permission from Springer Nature)

It is noteworthy that non-noble metal materials show significant application potential in photocatalytic CH_4 conversion owing to their advantages of low cost and abundant reserves. For instance, in 2018, Xie et al.^[10] reported a photocatalyst consisting of highly dispersed iron oxide nanoclusters (primarily FeOOH and Fe_2O_3) supported on anatase TiO_2 ($\text{FeO}_x/\text{TiO}_2$) for the selective photocatalytic oxidation of CH_4 to CH_3OH at ambient temperature and pressure. Under optimized conditions, the 0.33% $\text{FeO}_x/\text{TiO}_2$ catalyst achieved a CH_4 conversion rate of 15%, with CH_3OH selectivity exceeding 90%. Its performance significantly surpassed that of noble metal-based photocatalysts reported at the time (Figure 5(B)). Mechanism studies revealed that TiO_2 acted as the light-absorbing unit generating e^-/h^+ pairs, while the highly dispersed Fe^{3+} species served as electron acceptors, greatly enhancing charge separation efficiency. More importantly, the Fe species could effectively lower the overpotential of H_2O_2 reduction to generate $\cdot\text{OH}$ radicals, promoting the formation of key active intermediates. Simultaneously, they could suppress the generation of superoxide radicals ($\cdot\text{O}_2^-$), preventing the further over-oxidation of CH_3OH to CO_2 , thus fundamentally ensuring the high selectivity.

Additionally, Wu et al.^[57] reported a sub-nanometer MoO_x cluster composite catalyst ($\text{MoO}_x\text{-TiO}_2$), which was constructed *via* a simple impregnation method using anatase

TiO_2 nanosheets exposing (001) facets as the support. $\text{MoO}_x\text{-TiO}_2$ exhibited excellent catalytic activity and stability using O_2 as the oxidant. Under optimized conditions, the optimal sample achieved a C_1 oxygenate (including CH_3OOH , CH_3OH , HCHO , HCOOH) production rate of 3.8 mmol/g with selectivity approaching 100% (Figure 5(C)), along with good cycling stability. Mechanism investigations indicated that the MoO_x clusters efficiently captured photogenerated e^- from TiO_2 , forming reduced-state active sites ($\text{Mo}^{5+}/\text{Mo}^{4+}$). These sites then combined with adsorbed O_2 to generate Mo-OO species, significantly inhibiting the formation of radicals like $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ to effectively avoid product over-oxidation (Figure 5(D)).

In addition to using co-catalysts, a key strategy is to design semiconductor composite interfaces. This builds synergistic multi-component systems that enhance light absorption, charge separation, and surface reactivity. For instance, in 2021, Song et al.^[46] reported a ZnO/TiO_2 composite photocatalyst loaded with Au nanoparticles, which exhibited excellent OCM performance with a C_2H_6 yield exceeding 5000 $\mu\text{mol}/(\text{g}\cdot\text{h})$ and a stability of 12 h continuous reaction maintaining 91% selectivity (Figure 6(A)). Mechanism studies revealed that the ZnO/TiO_2 heterojunction effectively promoted the spatial separation of photogenerated charge carriers.

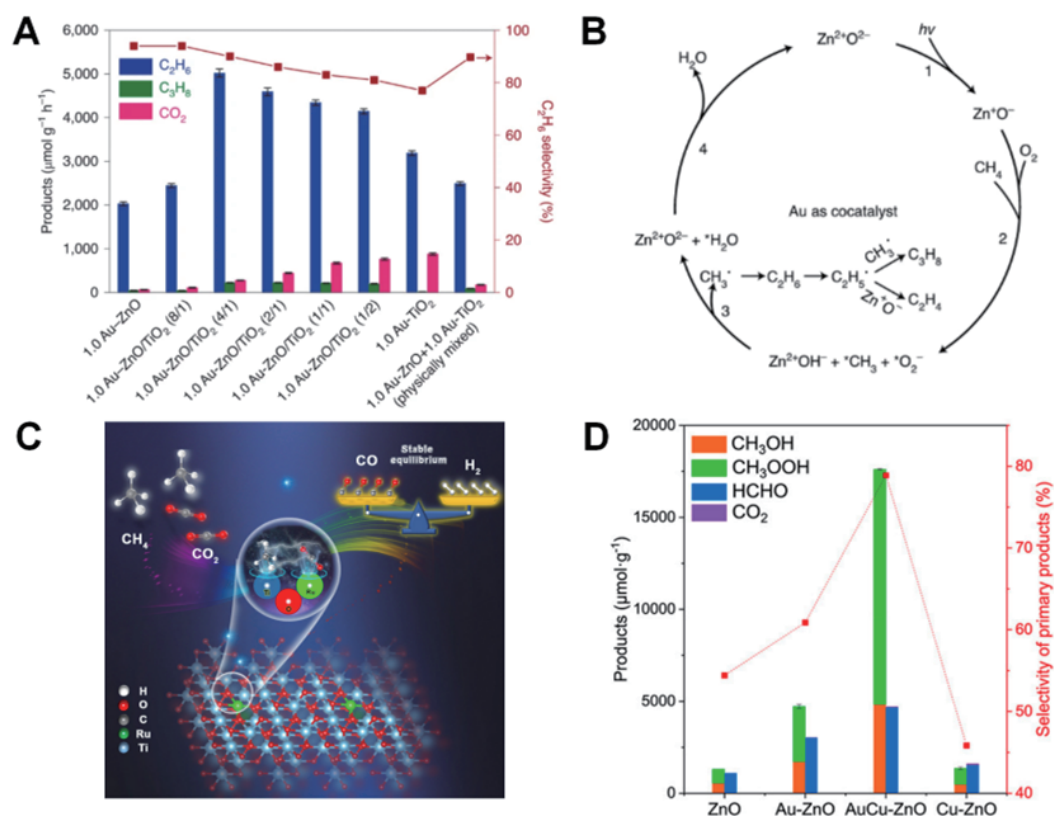


Fig. 6 (A) Photocatalytic activity of OCM over a 1.0 Au-ZnO/TiO₂; (B) Reaction mechanism of 1.0 Au-ZnO/TiO₂; (C) Reaction mechanism of 1.0 Ru-TS; (D) Photocatalytic POM performance of Au₄Cu₄-ZnO^[46,58-59] (with permission from Springer Nature, Elsevier, ACS Publications)

The Au nanoparticles not only enhanced O_2 adsorption and activation but also significantly lowered the desorption energy barrier for $\cdot CH_3$ intermediates. The synergistic interplay among ZnO, TiO_2 and Au overcame the trade-off high activity and selectivity in photocatalytic CH_4 oxidation, providing a new catalyst design concept and mechanism insight for efficient CH_4 conversion under mild conditions (Figure 6(B)). He et al.^[58] reported an atomically dispersed ruthenium (Ru)-modified hierarchical porous TiO_2 - SiO_2 composite catalyst (Ru-TS), achieving a significant breakthrough in the photocatalytic dry reforming of CH_4 (Figure 6(C)). This catalyst was prepared using an evaporation-induced self-assembly strategy, where Ru single atoms were precisely anchored on the TiO_2 surface, forming active centers with a Ru- O_v -Ti local coordination structure (O_v represents an oxygen vacancy). In this structure, the Ru sites are responsible for CO_2 adsorption and activation, while the Ti sites are dedicated to CH_4 activation. The presence of O_v effectively alleviates steric hindrance, enabling CO and H_2 production rates achieving 98.5 and 96.5 mmol/(g·h), respectively. The H_2/CO ratio is close to 1:1, meeting the feedstock requirement for Fischer-Tropsch synthesis. The catalyst showed no activity decay during 20 h of continuous operation in a flow reactor, and its activity was significantly superior to pure TiO_2 - SiO_2 , Ru nanoparticles modified TiO_2 - SiO_2 , and contrast samples modified with other metals (e.g., Co, Ni). Mechanism studies indicate that the well-matched dual active sites effectively promoted C–O coupling while suppressing side reactions such as the reverse water-gas shift reaction and CH_4 cracking. This significantly reduced carbon deposition, thereby enhancing the reaction stability.

To further enhance the activity of photocatalytic CH_4 conversion, constructing binary or multi-component co-catalyst systems with complementary functions on the catalyst surface has become an effective strategy. Based on this concept, Luo et al.^[59] developed a ZnO catalyst co-modified with highly dispersed Au and CuO_x (Au_xCu_y -ZnO). This system achieved efficient and highly selective conversion of CH_4 to C_1 oxygenates under ambient temperature using O_2 as the oxidizer. In this system, Au served as a h^+ acceptor, promoting the oxidation of H_2O to generate $\cdot OH$, while Cu acted as an e^- acceptor, promoting the reduction of O_2 to generate $\cdot OOH$. Their synergy significantly enhanced the efficiency of C–H bond activation. This catalyst achieved a total yield of CH_3OH , $HCHO$ and CH_3OOH of 11225 $\mu mol/(g \cdot h)$, with selectivity close to 100%, and its performance significantly surpassed that of other reported photocatalytic CH_4 systems at the time (Figure 6(D)).

Another crucial approach for enhancing the added value of photocatalytic CH_4 conversion products and achieving the targeted synthesis of C_{2+} products is the regulation of the support material's electronic structure *via* elemental doping. In 2022, Ma et al.^[60] synthesized ultrathin TiO_2 nanosheets co-doped with Cu and Si *via* a solvothermal method (Figure 7(A)). The introduction of Cu and Si formed

Ti–O–Cu and Ti–O–Si bonds, effectively modulated the electronic structure of TiO_2 and optimized the distribution of ROS, thereby significantly improved photocatalytic CH_4 coupling for C_2H_6 synthesis. This catalyst achieved a C_2H_6 production rate of 33.8 $\mu mol/(g \cdot h)$ with a selectivity of 88.4% and maintained excellent stability after five consecutive cycles (4 h each) (Figure 7(B)). In 2023, Li et al.^[61] developed a TiO_2 photocatalyst modified with PdCu nano-alloys (approximately 2.3 nm), achieving efficient and stable photocatalytic OCM in a room-temperature flow reaction system. In this system, Pd served as the key site for CH_4 activation. On one hand, it promoted CH_4 activation through strong interaction with the C–H bond; on the other hand, it acted as a h^+ acceptor, facilitating h^+ transfer from TiO_2 to Pd and suppressing e^-/h^+ recombination. Cu, meanwhile, promoted the desorption of C_2 products by weakening their adsorption energy on the catalyst surface, preventing their further dehydrogenation to form carbon deposits, while also enhancing charge separation efficiency as a synergistic h^+ acceptor. This catalyst achieved a C_2H_6 production rate of 2480.0 $\mu mol/(g \cdot h)$, significantly higher than previously reported room-temperature photocatalytic processes ($\lambda > 300$ nm), and could operate stably for 112 h. In 2024, Sun et al.^[62] proposed a strategy based on electronic asymmetry of lattice oxygen. Using ZnO as the support, they constructed electronically asymmetric lattice oxygen sites *via* Ce doping and loaded Au as a C–C coupling co-catalyst, successfully preparing the Ce0.6%-AZnO photocatalyst (Figure 7(C)). In the reaction for converting CH_4 to C_2H_6 , Ce0.6%-AZnO achieved a yield of C_2H_6 exceeding 16000.0 $\mu mol/(g \cdot h)$ under optimal conditions, with a multi-carbon product selectivity of 94.9% (Figure 7(D)). Mechanism studies revealed that Ce doping not only promoted ROS generation but also influenced lattice oxygen activity by modulating metal-oxygen bond strength. This facilitated $\cdot CH_3$ desorption to form C_2H_6 and accelerated H_2O desorption to free up active sites, thereby enabling efficient conversion of CH_4 to C_2H_6 under aerobic conditions.

In summary, the design strategies for photocatalytic CH_4 conversion systems have evolved from early reliance on single noble metal loading to the synergistic application of diverse modification techniques. Through the deep integration of advanced characterization techniques and theoretical simulations, researchers have achieved more precise control over key aspects such as the identification of active sites, elucidation of reaction pathways, and the synergistic effects of crystal structure, surface properties, and multi-component systems. These systematic advancements have significantly enhanced the overall performance of photocatalytic CH_4 conversion in terms of efficiency, selectivity, and stability. They provide a solid scientific foundation and viable technological pathways for the future development of efficient catalytic systems, promoting the resourceful and clean utilization of CH_4 , and contributing to the achievement of carbon neutrality goals.

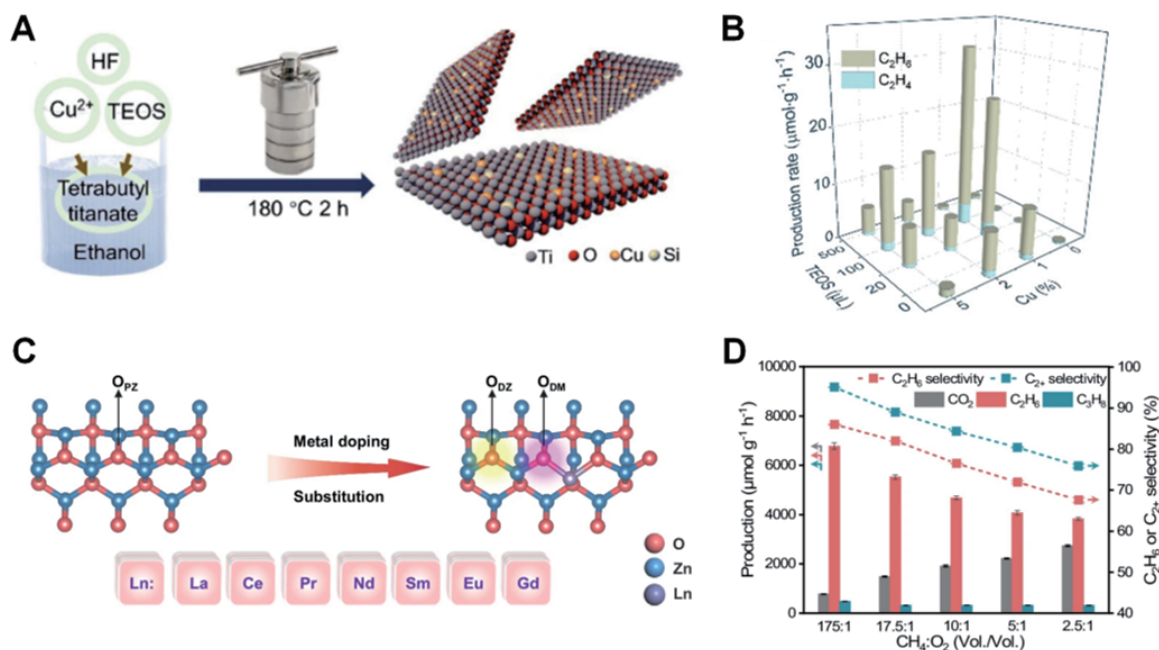


Fig. 7 (A) Schematic illustration of the preparation of $\text{TiO}_2(\text{Si})-x\%\text{Cu}$ and (B) photocatalytic performance; (C) The chemical environment of localized O_L atoms in $\text{Ce}_{0.6}\%\text{-AZnO}$ and (D) photocatalytic performance^[60,62] (with permission from RSC Publications, Springer Nature)

2.3 Design of novel photocatalytic materials

Covalent organic frameworks (COFs) and metal-organic frameworks (MOFs), as two emerging classes of porous materials, exhibit broad application prospects in multiple cutting-edge fields due to their high specific surface area, precisely tunable structures, excellent photophysical properties, and outstanding compositional diversity. Compared to traditional metal oxide semiconductors (e.g., TiO_2 , ZnO), COFs/MOFs possess unique advantages in light absorption performance and bandgap regulation. The bandgap tuning of traditional metal oxide semiconductors typically relies on elemental doping or heterojunction construction, but the rigidity of their crystal structures limits the precision of this control. In contrast, COF/MOF materials enable precise bandgap modulation through strategies like ligand engineering, framework topology control, and post-synthetic modification, demonstrating far greater flexibility and precision than conventional metal oxide semiconductors. Their light absorption characteristics not only encompass interband transitions common in inorganic semiconductors but can also achieve efficient capture of visible light through molecular-level design of the catalysts. In recent years, rational design of their electronic structures has allowed such materials to exhibit typical semiconductor behavior, garnering widespread attention in photo-electrocatalytic reactions^[63–64]. Their core advantage lies in the precise integration of photosensitizing units, catalytically active sites, and mass transport channels at the molecular level, thereby providing an ideal platform for the efficient separation of photogenerated charge carriers, highly selective regulation of reaction pathways,

and effective enrichment of products.

In COF materials, the highly ordered π -conjugated skeletons formed by strong covalent bonds not only promote cross-dimensional transport of photogenerated charges but also create favorable conditions for complex multi-step catalytic reactions^[65]. In 2023, Huang et al.^[63] prepared a series of $\text{CdS}@\text{COF}$ (CCF) composite photocatalysts with different CdS loading mass *via* a hydrothermal method for the dry reforming of CH_4 to produce syngas. Among them, the optimal catalyst, $\text{CdS}@\text{COF}$ (5/5) exhibited excellent catalytic performance under ambient conditions, achieving a CO production rate of $640 \mu\text{mol/g}$ and an H_2 production rate of $113.24 \mu\text{mol/g}$ (Figure 8(A)). This composite material effectively promoted the separation of photogenerated h^+/e^- pairs by constructing a Z-scheme heterojunction, while simultaneously lowering the activation energy barriers for the C–H bond in CH_4 and the C=O bond in CO_2 , thereby significantly enhancing the overall catalytic efficiency of CH_4 dry reforming.

MOF materials, owing to the high tunability of their metal nodes and organic linkers, show great potential in constructing synergistic catalytic active sites. In 2024, Feng et al.^[64] synthesized a MOF-based Cu single-atom catalyst *via* a solvothermal method, achieving the highly selective photocatalytic oxidation of CH_4 to HCHO . Using a Zr-based MOF (UIO-66-NH_2) as the support, the $\mu_3\text{-OH}$ sites in its $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$ clusters were deprotonated with *n*-butyllithium (*n*-BuLi). This was followed by sequential reactions with CuCl_2 and reduction/hydration with NaEt_3BH , ultimately constructing the Cu single-atom catalyst $\text{UION-Cu}(\text{OH})$ with a well-defined tetra-oxygen coordination environment (Figure 8(B)).

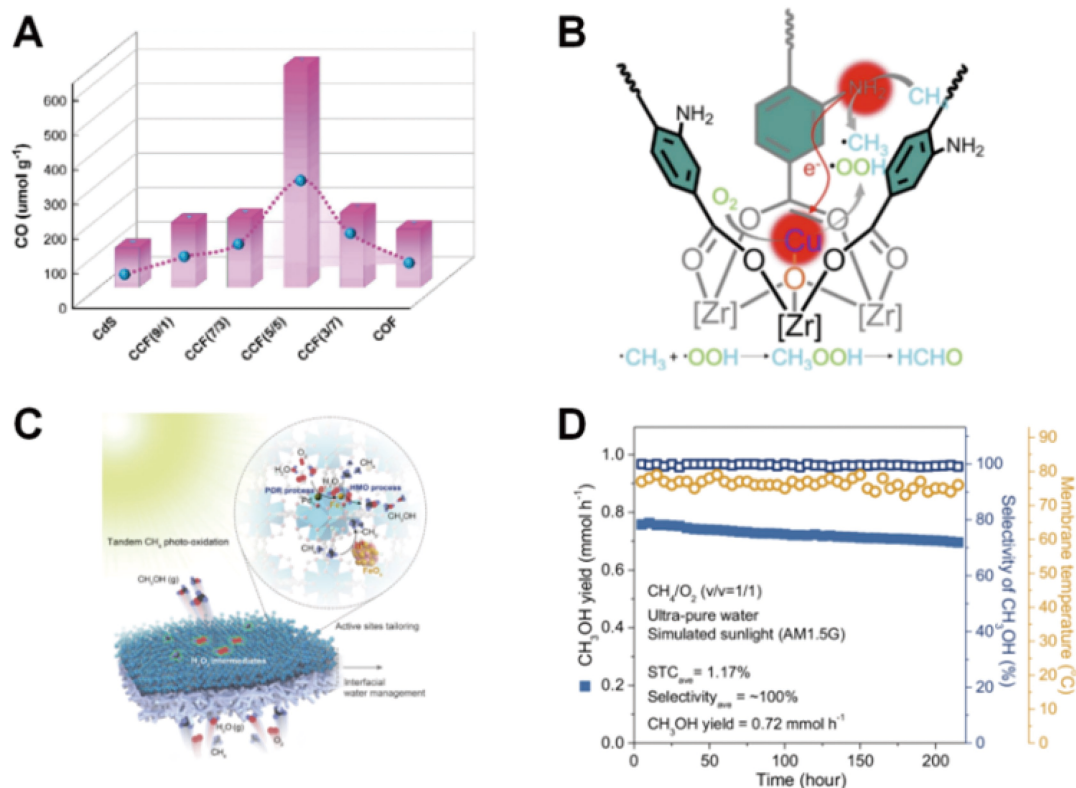


Fig. 8 (A) CdS@COF(5/5) CO rate of the photocatalytic DRM; (B) The mechanism of UION-Cu(OH) photocatalytic reaction; (C) The reaction mechanism and (D) photocatalytic performance of Pd₁FeO_x/aUiO(H) membranes^[63–64,66] (with permission from Elsevier, Springer Nature)

Under reaction conditions of 20 °C, 9 bar CH₄ and 1 bar O₂, UION-Cu(OH) demonstrated excellent performance in the photocatalytic oxidation of CH₄, with a maximum HCHO yield reaching 13.76 mmol/g and selectivity approaching 100%. After five consecutive reaction cycles (totaling 25 h), the catalyst's crystal structure, Cu valence state, and coordination environment showed no significant changes, indicating good structural stability. Mechanism studies suggest that the Cu single-atom sites can directionally activate O₂ via an end-on adsorption mode to generate $\cdot\text{OOH}$ intermediates. The rapid combination of these intermediates with $\cdot\text{CH}_3$ radicals, followed by stepwise conversion to HCHO, is the key to the high selectivity.

In 2025, Hao et al.^[66] designed and constructed an atomically modified NH₂-UiO-66 membrane nanoreactor. This system enables the efficient and continuous photocatalytic oxidation of CH₄ to CH₃OH at the gas-solid interface under gas-solid interface conditions. Through a two-step strategy, the adjacent Pd₁ and Fe₁ single-atom sites with a synergistic catalytic effect on the Zr-O nodes of the MOF were spatially constructed in the reactor. This design allows for the efficient *in situ* generation and utilization of H₂O₂ even in the absence of liquid water. Coupled with the unique gas transport and interface enrichment capabilities inherent to MOFs, this system successfully achieves the direct photocatalytic oxidation of CH₄ to CH₃OH within its open framework structure (Figure 8(C)). The membrane reactor demonstrated stable continuous operation for 210 h

under simulated sunlight, achieving a CH₃OH production rate of 14.4 mmol/(g·h) with selectivity close to 100%. The average solar-to-chemical energy conversion efficiency was 1.17%. Remarkably, even under natural sunlight and using air as the oxidant and tap water as the proton source, the system maintained a high production rate of 11.8 mmol/(g·h) and excellent selectivity (Figure 8(D)).

Therefore, COFs and MOFs, as a new generation of semiconductor catalytic materials, provide an ideal catalytic platform for photocatalytic CH₄ conversion. This is attributed to their tunable pore environments, high specific surface area, precisely integrated active sites, and the ability for precise bandgap modulation achieved through molecular-level design. These characteristics endow COF/MOF materials with advantages over traditional metal oxide semiconductors in terms of light absorption range, charge separation efficiency, and the designability of active sites. Through the rational functional design of the material's structure, fine control over the reaction pathway and product distribution can be achieved, thereby enabling the synergistic enhancement of both high activity and high selectivity.

In summary, the field of photocatalytic CH₄ conversion has developed a variety of efficient catalytic systems encompassing traditional metal oxide semiconductors, metal/non-metal modified materials, single-atom catalysts, and emerging porous framework materials (MOFs/COFs). Through strategies such as band structure engineering, defect engineering, crystal facet control, interface structure

construction, and active site design, significant progress has been made in improving CH₄ conversion efficiency, product selectivity, and reaction stability. When evaluating photocatalytic performance, commonly used metrics include product type, yield, selectivity, and the Apparent Quantum Yield (AQY). AQY is defined as the ratio of the number of electrons involved in the reaction to the total number of incident photons under irradiation with specific monochromatic light. Unlike the photocatalytic Quantum Yield (QY), which is calculated based on the number of absorbed photons, AQY uses the number of incident photons as the denominator. This effectively circumvents the difficulty in accurately determining the number of photons actually absorbed by the catalyst during the reaction in heterogeneous systems due to factors such as light scattering and reflection, providing a feasible basis for performance comparison across different studies^[67]. Regarding the AQY data compiled in Table 2, most involve UV-absorbing semiconductor photocatalysts, their bandgap structures are better matched to the ultraviolet region. This allows for efficient absorption of incident photons and excitation of charge carriers, resulting in higher AQY values under 365 nm UV light irradiation. In contrast, in the visible light region, the light absorption capability of the materials is more limited, and the excitation and separation efficiency of charge carriers are significantly reduced, leading to generally lower AQY values. Additionally, there remains an order-of-magnitude gap between the current energy efficiency of light-driven CH₄ conversion and the level required for industrialization; in most photocatalytic systems, it falls far below the basic requirements for energy economy in chemical processes. Low AQY not only reflects the insufficient utilization of light energy but also highlights core challenges such as severe recombination of photogenerated charge carriers and slow reaction kinetics. Therefore, developing novel photocatalytic materials with broad spectral response and high charge carrier separation efficiency, and further optimizing the reaction systems and process conditions, are key to enhancing the energy utilization efficiency of catalysts and advancing photocatalytic CH₄ conversion technology toward industrialization in the future. Based on this, this review systematically summarizes the structural characteristics, reaction pathways, and key performance metrics of representative catalysts in Table 2, aiming to provide a reference for the subsequent rational design of catalysts and optimization of processes.

3 Design of photocatalytic reactors and process intensification

On the basis of systematically reviewing various reaction pathways and catalyst designs for photocatalytic CH₄ conversion, it is essential to highlight that macroscopic performance metrics, such as conversion rate, product selectivity, and space-time yield, are not solely determined by the intrinsic activity of the catalyst. They are also

significantly influenced by multiple engineering factors such as mass transport, photon flux distribution, thermal management, and reactant/product residence time. Particularly, these factors are also governed by the structural design of the reactor. Therefore, in the transition from laboratory research to industrial application, the collaborative optimization of reactor engineering serves as the crucial bridge for achieving efficient scale-up. As operational modes and design concepts have evolved, photocatalytic reactors have primarily progressed from batch-stirred tank reactors to continuous flow systems, and further towards novel structured reactors customized for specific photochemical processes. It is worth emphasizing that process intensification strategies are becoming important directions for the design of a new generation of reactors, which is exemplified by photoelectrochemical and photothermal synergistic catalysis. Coupling multiple energy fields and integrating multipronged approaches hold the potential to overcome the bottlenecks in reaction efficiency and product selectivity inherent in single-mode photocatalysis, paving broader technical pathways for the utilization of CH₄.

3.1 Design of photocatalytic reactors

3.1.1 Batch reactors

Batch reactors are the most widely used type in photocatalytic CH₄ conversion research, offering advantages such as simple structure, low cost, operational flexibility, and good pressure resistance. They provide an ideal experimental platform for catalyst screening and reaction mechanism studies. A typical setup usually consists of a quartz or glass vessel with good light transmittance, an external light source (Xenon lamp or LED array), and an internal magnetic stirring system, forming a gas-liquid-solid triphasic reaction system. During operation, the catalyst is uniformly dispersed in a solvent (usually water). After evacuation and replacement with CH₄ (or a gas mixture), the reaction is initiated under controlled temperature and pressure with light irradiation and stirring. Liquid samples can be collected in real-time during the process *via* a sampling needle for analysis (Figure 9(A))^[72].

In a batch reactor, the light penetration depth is a decisive factor for reaction efficiency, regulated by factors such as catalyst color, concentration, and solution composition. Suspensions of dark-colored or high-concentration catalysts have poor light transmittance, significantly reducing the light penetration depth and leaving a large number of catalyst particles ineffectively excited^[73]. Certain components in the solution (e.g., nitrite ions, NO₂⁻) can also selectively absorb specific wavelengths of light radiation, further weakening the effectiveness of light propagation^[74]. Therefore, rationally designing reactor structures with shorter optical paths helps mitigate the light-shielding effect and improves irradiation uniformity.

Table 2 Summary of representative catalysts for photocatalytic CH₄ conversion and their performance

Catalyst	Experimental conditions	CH ₄ conversion rate	Products	Yield	Selectivity	AQY	Reference
P25-800/2	300 W Xe lamp, 5 mg, 165 μ L H ₂ O ₂ + 80 mL H ₂ O, 2 MPa CH ₄ , 30 °C, 2 h	—	CH ₃ OOH; CH ₃ OH; HCHO; HCOOH	9.94 mmol/(g·h)	99.42%	—	[48]
A/R-TiO ₂	300 W Xe lamp, 2 mg, 180 mL H ₂ O, 2.0 MPa CH ₄ , 0.5 MPa O ₂ , 30 °C, 3 h	—	CH ₃ OH; HCHO	11.6 mmol/g	97.4%	3.28% (365 nm)	[47]
Au/TiO ₂	AM 1.5G, 50 mg, 10 mL/min CH ₄ , 1.5 mL/min Air, 200 °C, 220 h	—	C ₃ H ₈	1.4 mmol/(g·h)	91.3%	39.7% (365 nm)	[37]
Au60s/TiO ₂	100W LED, 20 mg, 320 mL/min CH ₄ + 12 mL/min Air, 200 °C	—	C ₂ H ₆ ; C ₂ H ₄	1.1 mmol/h	86% 93%	10.3±0.6% (365 nm)	[68]
Pd ₁ /TiO ₂	300 W Xe lamp, 0.1 MPa CH ₄ , RT, 3 h	—	C ₂ H ₆	0.91 mmol/(g·h)	94.3%	3.05% (365 nm)	[32]
FeO _x /TiO ₂	300 W Xe lamp, 10 mg, Ar, H ₂ O ₂ , 70 μ mol CH ₄ , RT, 3 h	15%	CH ₃ OH	1056 μ mol/g	90%	—	[10]
MoO _x -TiO ₂	300 W Xe lamp, 10 mg, 100 mL H ₂ O, 2 MPa CH ₄ , 0.1 MPa O ₂ , 25 °C, 2 h	—	CH ₃ OOH; CH ₃ OH; HCHO; HCOOH	3.8 mmol/g	~100%	13.3% (365 nm)	[57]
0.1% Au/ZnO	AM 1.5G, 10 mg, 100 mL H ₂ O, 2 MPa CH ₄ , 0.1 MPa O ₂ , 25±2 °C, 2 h	—	CH ₃ OOH; CH ₃ OH; HCHO	125 μ mol/h	95%	—	[9]
Au- ZnO/TiO ₂	300 W Xe lamp, 20 mg, 70 mL/min CH ₄ , 20% O ₂ /N ₂ , 140 °C, ≈1 s	1.43%	C ₂ H ₆	5000 μ mol/(g·h)	90%	7.2% (365 nm)	[46]
Ru-TS	300 W Xe lamp, 30 mg, 10 mL H ₂ O, 0.1 MPa CH ₄ :CO ₂ :N ₂ = 20:20:60, RT, 2 h	—	CO; H ₂	98.5 mmol/(g·h) 96.5 mmol/(g·h)	~100%	1.64% (365 nm)	[58]
(Pt/NPW)/Ti O ₂	400 W Xe lamp, 50 mg, 0.1 MPa CO, 1.0 MPa CH ₄ , 20 °C, 60 h	0.15%	CH ₃ COOH	1166 μ mol/g	>90%	2.55% (360 nm)	[69]
TiO ₂ (Si)- 1%Cu	300 W Xe lamp, 20 mg, CH ₄ , room temperature and pressure, 4 h	—	C ₂ H ₆	33.8 μ mol/(g·h)	88.4%	—	[60]
Au _x Cu _y -ZnO	300 W Xe lamp, 20 mg, 100 mL H ₂ O, 1.9 MPa CH ₄ + 0.1 MPa O ₂ , 25 °C, 2 h	—	CH ₃ OH; HCHO; CH ₃ OOH	11225.0 μ mol/(g·h)	~100%	14.1% (365 nm)	[59]
Ce _{0.6%} -AZnO	300 W Xe lamp, 5 mg, CH ₄ : O ₂ =175:1(50 mL/min), 120 °C, 1 h	—	C ₂ H ₆	34000 μ mol/(g·h)	95.6%	33.7% (365 nm)	[62]
CdS@COF (CCF)	Xe lamp, CO ₂ + CH ₄ , 4 h	—	CO; H ₂	640 μ mol/g 113.24 μ mol/g	~100%	—	[63]
Rh ₁ /pMOF	AM 1.5G, 20 mg, 20 mL H ₂ O, 1.5 MPa CH ₄ + 0.5 MPa CO + 4 MPa O ₂ , 150 °C, 3 h	5.22%	CH ₃ COOH	23.62 mmol/(g·h)	66.4%	—	[70]
UION- Cu(OH)	Xe lamp, 5 mg, 20 mL H ₂ O, 0.9 MPa CH ₄ + 0.1 MPa O ₂ , 20 °C, 5 h	—	HCHO	2.75 mmol/(g·h)	~100%	3.52% (375 nm) 1.26% (400 nm) 0.83% (420 nm) 0.22% (450 nm)	[64]
Pd ₁ FeO ₄ /aUi O(H)	AM 1.5G, 50 mg, CH ₄ /O ₂ (V/V = 1:1), 75 °C, 2 h	—	CH ₃ OH	14.4 mmol/(g·h)	~100%	1.2%	[66]
PtO _x /CTF-1	100 W Xe lamp, 1 g, CH ₄ :O ₂ = 16:1, 20% CH ₄ /Ar, 25 °C, 4 h	2.33%	C ₂ H ₅ OH	167.6 μ mol/h	79.6%	9.4% (365 nm)	[71]

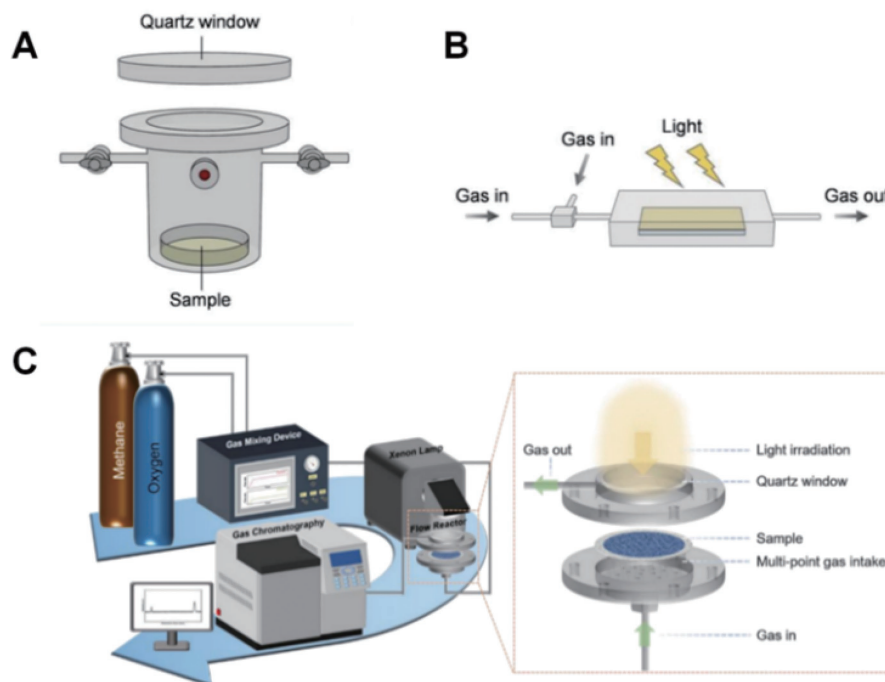


Fig. 9 (A) Batch reactor; (B) Flow reactor; (C) Schematic diagram of the continuous flow reaction system and multi-point gas injection flow reactor^[72,80]
(with permission from Wiley Publications, ACS Publications)

The illumination method is another key factor affecting light distribution and utilization efficiency within the reactor. Common irradiation methods include side, top, and internal illumination. In side illumination, light is prone to reflection loss at the curved surface of the reactor, causing uneven lighting; bilateral symmetric irradiation can be used to improve uniformity. Top illumination is currently a commonly used mode where light enters from the liquid surface and penetrates the slurry, reflecting at the reactor bottom, offering relatively high photon utilization efficiency. However, its irradiation area is limited, and dark catalyst suspensions severely restrict light penetration capability. Internal illumination places the lamp inside the reactor, offering advantages such as a large irradiation area and short optical path length. But the system design is more complex, and internal components (e.g., thermocouples, stir bars, lamp tubes) may interfere with the uniform distribution of the catalyst, affecting reaction efficiency.

The batch reactors are suitable for the systematic optimization of a wide range of reaction parameters (e.g., pressure, temperature, light source conditions) and is more commonly used in studies of photocatalytic POM for producing liquid oxygenates. For example, in our previous research based on a high-pressure batch reaction system, we systematically evaluated the performance of ZnO and TiO₂ catalysts modified with metals such as Fe, Ag and Rh. Under optimized conditions using an Ag-ZnO catalyst, a liquid oxygenate yield of 29 mmol/(g·h) with nearly 100% selectivity was achieved^[75–78].

However, batch reactors have several apparent limitations in photocatalytic CH₄ conversion: (1) The solubility of CH₄ in water is extremely low (approximately 1.3 mmol/L at

25 °C, 1 atm), making its mass transfer process a major factor limiting the reaction rate and hindering the improvement of apparent activity; (2) Severe light attenuation and inter-particle “shadow effects” exist within the reaction solution, resulting in low photon utilization efficiency; (3) Reaction products continuously accumulate in the closed system, making it difficult to avoid their further over-oxidation to CO₂. They also compete for active sites and reactive species, leading to decreased selectivity; (4) Limited by light penetration capability in the liquid phase, batch reactors are difficult to scale up effectively and cannot be directly used for industrial-scale applications^[79].

In summary, batch reactors are important tools in the fundamental research stage of photocatalytic CH₄ conversion. However, their inherent limitations in mass transfer, low photon utilization efficiency, and product inhibition constrain their further application. To achieve efficient and highly selective CH₄ conversion, there is an urgent need to develop continuous flow reaction systems capable of real-time product removal, thereby fully unleashing the performance potential of the catalysts.

3.1.2 Flow reactors

Continuous flow reactors are a crucial engineering platform bridging laboratory research and industrial applications. Compared to batch systems, they maintain a dynamic steady state in the reaction system through continuous feeding of reactants and simultaneous output of products, effectively avoiding issues of product inhibition and over-oxidation. This characteristic not only

significantly enhances the selectivity of photocatalytic CH₄ conversion but also lays a technical foundation for process scale-up and industrial implementation. In a typical photocatalytic flow reactor, reactants are pumped at a constant flow rate into a reaction chamber containing immobilized catalysts. After conversion under light irradiation, the fluid continuously exits and enters an online analysis or collection system (Figure 9(B))^[72]. Since target products are rapidly carried away from the catalyst active sites and the irradiation zone once formed, their residence time in the reaction zone is substantially reduced. It is effectively to suppress the side reaction of product over-oxidation to CO₂, providing a key engineering means for achieving highly selective partial oxidation. Currently, flow reactor is primarily applied in NOCM and OCM systems using CH₄ or CH₄/O₂ as reactants, and its application has also been extended to POM processes involving CH₄, H₂O, and O₂^[81].

In 2020, Li et al.^[82] first reported the co-deposition of Pt nanoparticles and CuO_x clusters on TiO₂ (PC/50) photocatalyst to drive an OCM reaction within a room-temperature and atmospheric-pressure flow reactor. This reactor enabled flexible adjustment of the CH₄ to O₂ ratio, ensuring the uniform gas passage through the catalyst bed and the precise online product analysis. Under optimized conditions using the Cu_{0.1}Pt_{0.5}/PC-50 sample and at a gas hourly space velocity (GHSV) of 2400 h⁻¹, the maximum C₂ product yield reached 6.8 μmol/h. In 2021, Singh et al.^[83] investigated gallium oxide (Ga₂O₃) for photocatalytic NOCM in a similar flow system, achieving continuous generation of C₂H₆ and H₂ from CH₄ feed. The C₂H₆ selectivity can be enhanced by increasing the gas flow rate to promote the rapid migration and coupling of ·CH₃ radicals, benefiting from the restraint of side reactions such as carbon deposition and further coupling. Wang et al.^[84] further reported the use of an Ag-AgBr/TiO₂ catalyst in a pressurized flow reactor for photocatalytic OCM, achieving a C₂H₆ production rate of 35.4 μmol/(g·h) and C₂₊ selectivity of 79%. In this system, the heterojunction formed between AgBr and TiO₂ promoted charge separation and migration, while the pressurized flow reactor effectively inhibited over-oxidation, demonstrating that the synergistic design of both catalyst and reactor system collectively determines the overall performance.

Continuous flow reactors can also significantly improve mass transfer efficiency through internal structural designs such as microchannels or fixed beds. These designs enable ordered fluid flow, shorten diffusion paths, and enhance the transport of reactants to the catalyst surface, thereby alleviating mass transfer limitations caused by the low solubility of CH₄. For example, Chen et al.^[80] loaded the Au/TiO₂ photocatalyst in a self-designed 3D-printed flow reactor, achieved a C₂₊ hydrocarbon yield of 218.2 μmol/h with approximately 90% selectivity and maintained good stability over 240 h (Figure 9(C)). This study provided a foundation for achieving mass transfer enhancement, reactant activation, and over-oxidation suppression through

the synergistic design of reactors and catalysts, advancing the development of high-performance photocatalytic OCM flow systems. Furthermore, continuous flow reactors offer stable and easily controllable processes, allowing operation under steady-state conditions with constant temperature, pressure, concentration, and residence time, resulting in good experimental reproducibility. This makes them more conducive to kinetic studies and process optimization^[61].

In summary, continuous flow reactors, characterized by dynamic and continuous operational, provide a fundamental engineering solution to the challenges of selectivity and reactor scale-up in photocatalytic CH₄ conversion. Future research and development will focus on three keys: developing novel, highly stable structured catalyst supports; designing new reaction chambers that achieve high synergy among light, flow, and solid phases; and exploring synergistic mechanisms that integrate processes such as membrane separation and photothermal catalysis with continuous flow photoreactors.

3.1.3 Novel reactors

While continuous flow reactors have demonstrated significant effectiveness in overcoming the drawbacks of batch systems, traditional fixed-bed and fluidized-bed configurations still face considerable challenges in achieving synergistic integration of photon and mass transfer. To break through these bottlenecks, a series of novel reactors featuring new structures, materials, and principles is continuously emerging. These innovative designs proactively regulate the synergistic processes of light, mass, and heat transfer through structural optimization, and even enable *in situ* coupling of reaction and separation units, representing the future direction of photocatalytic reactor engineering.

(1) Membrane Reactors: These reactors integrate separation membranes with photocatalytic processes. The core component typically consists of microfiltration/ultrafiltration membranes, porous ceramic membranes, or organic framework membranes loaded with nanocatalysts. In terms of reactor design, the light source is placed on one side of the membrane module, while the reactant fluid flows over the membrane surface or through its channels, where catalytic reactions occur under illumination. The primary advantage lies in the ability to achieve *in situ* and immediate separation of reactants, catalysts, and products (particularly small and high-value-added products). This effectively prevents product over-oxidation or catalyst loss, while maintaining stable exposure of active sites and continuous renewal of the reaction interface, thereby significantly enhancing reaction selectivity and process continuity^[85–86].

(2) Optical Fiber Reactors: This configuration consists of bundles of quartz optical fibers (hundreds to thousands) whose surfaces are roughened or coated with catalysts. Light is introduced from one end, transmitted within the fibers *via* total internal reflection, and uniformly leaked

through the sidewalls, providing homogeneous illumination along the entire length of the catalyst coating. The reactant fluid flows through the gaps between the fibers where the reaction occurs. Its core advantage lies in providing an extremely high illuminated surface area per unit volume and excellent photon transfer efficiency, essentially eliminating internal light limitations within the system and ensuring uniform irradiation of the catalyst bed^[87].

(3) Microchannel Reactors: As a typical example of process intensification, these reactors feature networks of channels with dimensions ranging from tens to hundreds of micrometers, etched onto substrates such as silicon, glass, or metal. The channel walls are coated with thin-film catalysts. Reactants flow through in a laminar regime and undergo conversion under light irradiation. Their unique advantages include: extremely high surface-area-to-volume ratios enabling rapid mass transfer and nearly eliminating mass transfer limitations; narrow residence time distributions and uniform temperature/concentration fields providing excellent parameter control precision and reproducibility; and channel depths designed to match the light penetration depth, ensuring efficient irradiation of the catalyst layer^[88–89].

It is important to note that the practical application of these novel reactor designs in the field of photocatalytic CH₄ conversion remains in the exploratory stage. In the foreseeable future, batch reactors will continue to serve as an important platform for fundamental research, while the optimization and development of continuous flow reactors will remain the focus for scale-up studies. Future reactor engineering will move beyond simple structural improvements toward targeted and functionalized design grounded in a deep understanding of the multi-scale

mechanisms underlying photocatalytic processes. By integrating advanced concepts like optical fibers and microchannels as well as combining these with technologies such as 3D printing, smart coatings, and sensing, it is promising to achieve customized reactor design, functional integration, and intelligent control, thereby advancing photocatalytic CH₄ conversion technology from the laboratory toward industrial application.

In summary, this section systematically reviews the advantages and limitations of batch, continuous flow, and selected emerging reactor types in photocatalytic CH₄ conversion (as summarized in Table 3). The aim is to provide a reference for selecting suitable reactor types for different research objectives and reaction systems, and to indicate directions for the future optimization and innovation of reactor engineering.

3.2 Process intensification strategies

3.2.1 Photothermal synergistic catalysis

Photothermal synergistic catalysis is a highly promising direction for process intensification. Its core principle lies in the conversion of light energy into thermal energy by the catalysts under illumination through mechanisms such as non-radiative relaxation, creating localized high-temperature zones that work in concert with photogenerated e^-/h^+ to drive the reaction. This strategy effectively overcomes the limitations of slow reaction kinetics and difficult product desorption in traditional photocatalysis, offering a new pathway for the efficient conversion of CH₄^[90].

Table 3 Advantages and disadvantages of different photocatalytic CH₄ conversion reactors

Reactor type	Advantage	Disadvantage
Batch reactors	Simple device and low cost; Flexible operation, suitable for initial reaction condition screening; No need for continuous feeding and precision pumping system, easy to operate; Good compatibility with slow kinetics reactions	Low mass transfer efficiency; Uneven illumination; Unable to produce continuously, with low spatiotemporal efficiency; During the reaction process, the concentration of reactants continues to decrease while the concentration of products continues to increase, making it prone to peroxidation
Flow reactors	Extremely high mass transfer and mixing efficiency; High and uniform illumination efficiency; Accurate control of reaction parameters, easy to optimize and amplify; Can operate continuously and stably, with high spatiotemporal productivity	The initial equipment is complex and the cost is high; Special requirements for catalysts; Poor compatibility with slow response
Novel reactors	Membrane reactor: achieves synergistic efficiency of reaction and separation, with continuous process and high product selectivity, effectively suppressing excessive oxidation. Optical fiber reactor: has high light efficiency, uniform and strong light intensity, flexible structure. Microchannel reactor: has extremely high specific surface area, precise light control, excellent heat transfer performance, safe and easy to scale up	Membrane reactor: membrane fouling, long-term stability challenges, high cost, and risk of membrane pore blockage. Optical fiber reactor: complex catalyst immobilization process, high cost, and potential for light attenuation. Microchannel reactor: complex manufacturing, high cost, easy channel blockage, and complex catalyst immobilization process

Photothermal conversion is the foundation of this strategy, which is primarily achieved through the following three mechanisms:

(1) Localized Surface Plasmon Resonance (LSPR): When light irradiates metal nanoparticles (e.g., Au, Ag, Cu), collective oscillations of their conduction band electrons occur, leading to strong light absorption at specific wavelengths. These oscillating electrons dissipate energy as heat into the surrounding environment *via* electron-phonon scattering, resulting in high temperatures both on the particles and in their vicinity^[91].

(2) Non-Radiative Relaxation: After photons absorption, the excited e^-/h^+ pairs in semiconductor materials undergo non-radiative transitions through defect energy levels upon recombination, converting energy into lattice vibrations and thereby raising the overall temperature of the material^[92]. In addition to semiconductor materials, sp^2 carbon-based nanomaterials (e.g., graphene, carbon nanotubes) can absorb photons, inducing $\pi \rightarrow \pi^*$ electronic transitions that produce high-energy excited-state electrons. These electrons undergo ultrafast (femtosecond to picosecond timescale) intrinsic electron-phonon scattering for non-radiative relaxation, converting energy into high-frequency phonon vibrations of the carbon lattice and generating localized heating^[93].

(3) Hot Electron Injection: The high-energy “hot electrons” generated during LSPR can be injected into the conduction band of adjacent semiconductors to participate in reduction reactions, while their residual energy is converted into a thermal effect. For example, Zhang et al.^[94] created an oxygen vacancy-rich CuSeO_{3-x} plasmonic photocatalyst, achieving the conversion of CH_4 to CH_3OH with an apparent quantum yield of 1.5% and nearly 100% selectivity. This excellent performance is attributed to plasmon-induced hot electrons reducing O_2 to $\cdot\text{OH}$ radicals, thereby providing a favorable kinetic pathway for CH_4 activation.

The localized high temperatures generated during photothermal conversion significantly enhance the photocatalytic CH_4 conversion process in the following key aspects:

(1) Markedly lowering the activation energy barrier for C–H bonds: The local high temperature provides additional thermal kinetic energy for the cleavage of C–H bonds in CH_4 molecules. Synergizing with the chemical oxidation by photogenerated h^+ , it substantially reduces the apparent activation energy and increases the reaction rate. For instance, Xue et al.^[95] achieved the selective oxidation of CH_4 to $\text{CH}_3\text{CH}_2\text{OH}$ on Cu_9S_5 nanoparticles and Cu single-atom modified crystalline carbon nitride ($\text{Cu}_9\text{S}_5/\text{Cu-CCN}$). The photothermal effect of Cu_9S_5 created localized hot spots which promoted CH_4 activation, and under the synergy of photothermal and photocatalytic effects, a $\text{CH}_3\text{CH}_2\text{OH}$ production rate of $549.7 \mu\text{mol}/(\text{g}\cdot\text{h})$ with 94.8% selectivity was achieved.

(2) Promoting target product desorption and inhibiting over-oxidation: The photothermal effect can accelerate the

desorption of intermediates and products, reducing their contact time with reactive oxygen species, thereby enhancing the selectivity for the target product. On an $\text{Au}/\text{ZnO}/\text{TiO}_2$ composite catalyst, Song et al.^[46] found that the photothermal effect promoted the desorption of $\cdot\text{CH}_3$ intermediates from the Au surface, significantly improved C_2H_6 efficiency and effectively suppressing CO_2 formation.

(3) Accelerating surface reactions and mass transfer processes: Heat can significantly increase the mobility and reaction rates of adsorbed species on the catalyst surface, while also enhancing the mass transfer efficiency of gaseous reactants to the active sites. Sun et al.^[96] developed a $\text{NiO}/\text{ZnO-CoNi}$ solid solution catalyst achieving 88% CH_4 conversion at ambient temperature. Its excellent performance is attributed to the photothermal effect-driven significant increase in lattice oxygen mobility on the surface of NiO nanocrystals and the overall enhancement of reaction kinetics.

3.2.2 Photoelectrochemical synergistic catalysis

Photoelectrochemical synergistic catalysis (PEC) integrates photocatalysis with electrochemical processes by applying an external bias to a semiconductor electrode. This utilizes the electric field to drive the directional separation and migration of photogenerated e^-/h^+ , addressing the critical issue of severe charge carrier recombination in traditional photocatalytic systems. This “photo-generated charge-electric field synergistic separation” mechanism not only significantly enhances quantum efficiency but also provides unique advantages for achieving highly selective CH_4 conversion^[97].

A typical PEC system consists of a working electrode (photoanode/photocathode), a counter electrode, and a reference electrode, immersed in an electrolyte solution. When the semiconductor electrode is photoexcited to generate e^-/h^+ pairs, the spatial electric field formed by the applied bias strongly drives h^+ towards the electrode surface to participate in CH_4 oxidation reactions, while e^- flow through the external circuit to the counter electrode to participate in reduction reactions (such as H_2 evolution or O_2 reduction), thereby achieving efficient spatial separation of charge carriers^[98].

The enhancement of the CH_4 conversion process by the external electric field is mainly reflected in two aspects:

(1) Significantly Suppressing Charge Recombination and Enhancing Quantum Efficiency: The driving force provided by the external bias is far greater than the band bending of the semiconductor itself, enabling the forced separation of photogenerated carriers and reducing their recombination rate by orders of magnitude. Consequently, more h^+ and e^- participate in surface reactions, significantly improving the AQE and reaction rate of CH_4 conversion. For example, Ma et al.^[99] optimized the reactivity of $\cdot\text{OH}$ on WO_3 through crystal facet engineering. The study found that increasing the anodic potential promoted the transfer of photogenerated e^- on the WO_3 photoanode surface,

inhibited surface charge recombination, and thereby enhanced the generation efficiency of $\cdot\text{OH}$, achieving efficient photoelectrochemical CH_4 conversion to ethylene glycol.

(2) Precisely Regulating Redox Potentials: By adjusting the magnitude of the external bias, the oxidation potential of photogenerated h^+ can be regulated to a certain extent, enabling precise guidance of the reaction pathway. Nie et al.^[52] reported that high-entropy LaMnO_3 -polyoxometalate sub-nanowires exhibited excellent performance for the photoelectrochemical coupling of CH_4 to CH_3COOH under mild conditions (1 bar, 25 °C), achieving a yield as high as 4.45 mmol/(g·h) with selectivity exceeding 99%.

As two advanced process intensification strategies, photothermal and photoelectrochemical synergistic catalysis provide innovative pathways to overcome the limitations of traditional photocatalytic CH_4 conversion (Table 4). Photothermal synergistic catalysis utilizes light-to-heat conversion to create localized high-temperature fields on the catalyst surface. Through the synergy of thermal and photochemical effects, it effectively lowers the activation energy barrier for C–H bonds and promotes the rapid desorption of intermediates, thereby simultaneously enhancing reaction rate and product selectivity. In contrast, photoelectrochemical synergistic catalysis drives the directional separation of photogenerated carriers by applying an external bias, fundamentally suppressing e^-/h^+ recombination. This approach not only significantly increases quantum efficiency but also enables precise control over the reaction pathway through electric field regulation. These two strategies advance the development of photocatalytic CH_4 conversion technology from two key dimensions: reaction kinetics and charge separation efficiency. They demonstrate the great potential of multi-energy field coupling in catalytic processes and provide important directions for designing efficient CH_4 conversion systems in the future.

4 Mechanism of photocatalytic methane conversion reaction

Photocatalytic CH_4 conversion is a complex multi-step process. Its reaction pathway and final product distribution are jointly governed by the reaction conditions and catalyst

properties. Although the target products may differ, the overall reaction process can be summarized into four core stages: the excitation and separation of photogenerated charge carriers, the generation of key active species, the activation of C–H bonds in CH_4 and the formation of $\cdot\text{CH}_3$, and finally, the transformation of intermediates and the selective formation of target products.

Stage I: Excitation and separation of photogenerated charge carriers:

In the initial stage of photocatalytic CH_4 conversion, the excitation and efficient separation of photogenerated charge carriers form the critical foundation determining the subsequent reaction efficiency. When the incident photon energy is no less than the bandgap of the semiconductor catalyst (e.g., TiO_2 , ZnO , WO_3), an e^- in the valence band (VB) is excited and jumps to the conduction band (CB), simultaneously leaving behind a h^+ in the VB. Subsequently, driven by mechanisms such as the built-in electric field, band bending, or defect sites, the photogenerated e^-/h^+ pairs must migrate rapidly to the catalyst surface to participate in reactions. If the charge carrier migration rate is lower than their recombination rate, bulk or surface recombination occurs, dissipating energy as heat or light and leading to a significant decrease in quantum efficiency^[100]. Therefore, the performance of catalysts in different reaction systems, such as POM, NOCM and OCM, fundamentally depends on their light absorption capability and charge separation efficiency. Evidence for this stage primarily relies on the following characterization methods:

(1) Spectroscopic Characterization: Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) is utilized to evaluate the material's light absorption capability and bandgap width. Steady-state/transient photoluminescence spectroscopy (PL/TRPL) probes the separation and recombination efficiency of photogenerated carriers; typically, weaker fluorescence intensity and shorter lifetime indicate higher separation efficiency.

(2) Photoelectrochemical Tests: Techniques such as surface photovoltage spectroscopy (SPS), transient photocurrent response (TPC), and electrochemical impedance spectroscopy (EIS) can directly or indirectly characterize the charge carrier separation efficiency and migration ability under an electric field.

Table 4 Characteristics of enhancement strategies for different photocatalytic CH_4 conversion processes

Reaction type	Mechanism	Advantage	Disadvantage
Photothermal reaction	Utilizing light energy to generate local high temperatures to drive catalytic reactions, usually in conjunction with photochemical effects	Fast reaction rate; Strong activation ability; Broad spectrum light response; Potential high selectivity	Thermal management challenges; Energy efficiency issues; High requirements for catalyst design; Complex mechanism
Photoelectric reaction	Using semiconductor photoelectrodes to absorb light and generate e^-/h^+ pairs, driven by external bias or chemical bias	The charge separation efficiency is extremely high; Strong controllability of the reaction; The product is easy to separate	The system is complex and costly; Electrolytes must be used; Electrode stability challenge; Large scale difficulty

(3) Theoretical Calculations: Density functional theory (DFT) calculations can simulate the local distribution of electronic structures and predict the migration pathways of photogenerated h^+/e^- , providing theoretical support for separation efficiency^[101].

Stage II: Generation of key active species:

After the successful separation and migration of photogenerated charge carriers on the catalyst surface, the interfacial redox reactions between them and surface adsorbates constitute the core step for generating key active species. This step directly determines the pathway, efficiency, and product selectivity of the subsequent CH_4 activation. The h^+ migrating to the catalyst surface possesses strong oxidizing ability and can directly oxidize adsorbed H_2O or surface hydroxyl groups ($[OH]$) to generate highly active $\cdot OH$ or metal-coordinated vacancies ($\square$) (Equations (1), (2)). Simultaneously, the conduction band e^- can reduce adsorbed O_2 to generate ROS such as $\cdot O_2^-$ and its protonated products ($HOO\cdot/H_2O_2$) (Equations (3)–(5)). In NOCM reaction systems, e^- can directly reduce the catalyst own metal sites (e.g., W^{6+}/W^{5+}) or activate lattice oxygen, forming variable valence state cycles and active oxygen vacancies. These generated active species (e.g., $\cdot OH$, $\cdot O_2^-$, H_2O_2 , $[O]$) directly participate in the activation of CH_4 and the subsequent transformation of intermediates. Their type, concentration, and distribution dictate whether the reaction tends towards deep oxidation or the selective formation of high-value-added products^[102]. Therefore, precisely guiding the flow of e^- and h^+ by tuning the catalyst surface properties and reaction system to directionally generate the target ROS is a key strategy for achieving efficient and highly selective CH_4 conversion. Evidence for this stage primarily relies on the following characterization methods:

(1) Radical trapping and spectral identification: Using electron paramagnetic resonance (EPR) technology with specific spin trapping agents (e.g., DMPO, TEMP) allows for the direct detection and identification of short-lived radical intermediates such as $\cdot OH$, $\cdot O_2^-$ and $^1O_2$, providing the most direct evidence for the existence of active species.

(2) Isotope labeling and mass spectrometry (MS) analysis: Isotope labeling experiments using $^{18}O_2$ or $H_2^{18}O$, combined with online MS or gas chromatography-mass spectrometry (GC-MS), can accurately trace the source of oxygen atoms in the products, clearly distinguishing whether oxygen from $[O]$, gaseous oxygen, or water participates in the reaction, thereby revealing the generation pathways of active species.

(3) Surface-sensitive spectroscopy and chemical probes: *In situ* infrared spectroscopy (FT-IR) or Raman spectroscopy can be used to monitor the dynamic changes of adsorbed species on the catalyst surface and the formation of intermediates during the reaction. Additionally, comparative photocatalytic activity experiments using radical scavengers (e.g., sodium oxalate to quench h^+ , benzoquinone to quench $\cdot O_2^-$) can indirectly assess the roles of different active species in the reaction^[103].

Stage III: C–H bond activation of CH_4 and formation of

$\cdot CH_3$ radical:

The activation of the C–H bond in CH_4 and the generation of the $\cdot CH_3$ radical, is widely considered the rate-determining step of the entire reaction. The C–H bond cleavage mechanism exhibits significant differences and intrinsic connections across different reaction systems. In NOCM systems, the strictly anaerobic environment limits the pathway for $\cdot OH$ generation, making direct oxidation by h^+ (Equation (6)) and activation by lattice oxygen $[O]$ (Equation (7)) the two main mechanisms for CH_4 conversion. The former requires the catalyst's valence band position to have a sufficiently high oxidation potential to provide the thermodynamic driving force, while the latter relies on the catalyst's own mobile and reactive lattice oxygen to achieve selective oxidation of CH_4 . In POM systems, the aqueous environment rich in H_2O molecules and OH^- promotes the $\cdot OH$ activation pathway for CH_4 (Equation (8)) as the primary activation mechanism. Although its high reactivity helps increase the reaction rate, it also more easily leads to product over-oxidation. In OCM systems, the presence of O_2 enriches the reaction pathways; besides the $\cdot OH$ radical attack pathway, other ROS generated from O_2 can also participate in C–H bond activation (Equations (9), (10))^[79]. Evidence for this stage primarily relies on the following characterization methods:

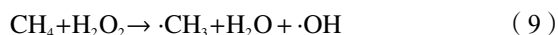
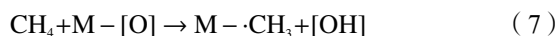
(1) Radical trapping and spectral identification: Using EPR technology with the DMPO spin trap allows for the direct detection and identification of the $\cdot CH_3$ radical intermediate.

(2) Isotope labeling and MS analysis: Using $^{13}CH_4$ as the reactant, combined with online MS or GC-MS technology, clearly tracks the flow of ^{13}C in intermediates and final products, providing the most direct evidence for the reaction pathway.

(3) *In situ* spectroscopy: *In situ* FT-IR can be used to detect characteristic vibrational peaks of intermediate species adsorbed on the catalyst surface, such as methyl ($-CH_3$) and methylene ($-CH_2-$), in real-time. *In situ* Raman is sensitive to low-frequency vibrations like M–C bonds, helping to confirm the formation of metal-carbon bonded intermediates.

(4) Theoretical calculation and simulation: DFT calculations can simulate the adsorption configuration of CH_4 on the catalyst's active site, the energy barrier for C–H bond cleavage, and compare the reaction thermodynamics and kinetics of different pathways such as direct oxidation by h^+ and attack by $\cdot OH$, revealing the nature of the rate-determining step at the atomic scale^[13].

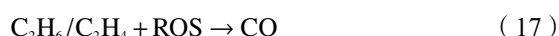




Stage IV: Intermediate transformation and selective formation of target products:

This stage is the key determining the final product selectivity, and several reaction systems exhibit distinctly divergent pathway characteristics at this point: In NOCM systems, the anaerobic environment restricts the subsequent reaction pathways of the $\cdot\text{CH}_3$ radical. It primarily undergoes homonuclear coupling of two $\cdot\text{CH}_3$ radicals on the catalyst surface or in the gas phase to form C_2H_6 (Equation (11)), which can further dehydrogenate to C_2H_4 (Equation (12)). In POM systems, the reaction pathway involves the stepwise combination of the $\cdot\text{CH}_3$ radical with ROS species, undergoing a multi-step oxidation process (Equations (13)–(15)). In OCM systems, the reaction pathway exhibits both coupling and oxidative characteristics: $\cdot\text{CH}_3$ can either couple to form C_2H_6 (Equation (11)) or be further oxidized to liquid oxygenates (Equation (16)). The primary challenge of this pathway lies in precisely regulating the dynamic balance between coupling and oxidation, effectively suppressing over-oxidation side reactions (Equation (17)) to achieve the highly selective synthesis of C_2 hydrocarbons. In CH_4 carbonylation systems, by introducing external CO, a novel coupling pathway is provided for the $\cdot\text{CH}_3$ radical. The surface $\cdot\text{CH}_3$ reacts with adsorbed CO *via* an insertion mechanism, leading to the formation of high-value-added C_2 oxygenates (using CH_3COOH as an example, Equations (18), (19))^[104]. Evidence for this stage primarily relies on the following characterization methods: (1) *In situ* spectroscopy: *In situ* FT-IR can directly detect characteristic vibrational peaks of key intermediates such as methoxy, carbonyl, and acetyl groups (e.g., the C=O stretching vibration at $\sim 1700\text{--}1650\text{ cm}^{-1}$ in $\text{M}-\text{C}(\text{O})\text{CH}_3$)^[105], providing direct evidence for the stepwise oxidation mechanism in POM and the insertion mechanism in carbonylation. (2) Isotope labeling and MS analysis: Labeling experiments using isotopes like $^{13}\text{CH}_4$, D_2O , or ^{13}CO , followed by MS analysis of the products' isotopic composition, clearly trace the flow of C and H atoms, distinctly differentiating between pathways such as NOCM, POM, and carbonylation. (3) Synchrotron radiation X-ray techniques: Utilizing synchrotron-based X-ray absorption fine structure spectroscopy, particularly *in situ* XANES and EXAFS, allows precise probing of the oxidation state and local coordination environment evolution of the catalyst's active metal centers under reaction conditions. This provides the most direct structural evidence for the formation of key intermediates such as $\text{M}-\text{CH}_3$ or

$\text{M}-\text{C}(\text{O})\text{CH}_3$. (4) Theoretical calculation and simulation: DFT calculations can simulate the complete pathways and energy barriers for elementary reactions like $\cdot\text{CH}_3$ coupling, oxidation, and CO insertion, providing energy barriers for each step along the $\text{M}-\text{CH}_3$ bond reaction pathway, which uncovers the competitive relationships between different reaction paths at the atomic scale. This provides mechanism explanations and predictions for experimental observations, guiding the design of highly selective catalysts^[72].



In summary, the pathways of photocatalytic CH_4 conversion form a network branching from common initial steps (photogenerated charge separation, C–H bond activation) to different product outcomes (C_2 hydrocarbons, oxygenates). The $\cdot\text{CH}_3$ radical serves as the pivotal hub determining the reaction direction. The success of NOCM relies on the rate of coupling reactions relative to reverse reactions; the selectivity in POM depends on the competition between oxidation and desorption; OCM requires finding the optimal balance among activation, coupling, and oxidation; the core of the CH_4 oxidative carbonylation pathway lies in whether the catalyst can efficiently promote the key step $\text{M}-\text{CH}_3 + \text{CO} \rightarrow \text{M}-\text{C}(\text{O})\text{CH}_3$ and make it kinetically favored over the coupling or oxidation pathways of $\cdot\text{CH}_3$. A profound understanding of the competition and synergy among these pathways forms the foundation for the rational design of catalysts and the control of reaction outcomes.

5 Summary and outlook

Photocatalytic CH_4 conversion technology has achieved systematic progress in four key aspects through long-term accumulation and development: catalyst design, reaction pathway regulation, reactor engineering, and mechanism studies. In terms of catalyst design, the research focus has shifted from merely enhancing activity to a comprehensive consideration of stability and cost. Developing non-noble metal catalysts and improving catalyst durability under continuous operation have become urgent tasks. Concurrently, catalyst systems have expanded from

traditional semiconductors to include single-atom catalysts, heterojunctions, and porous materials like MOFs/COFs. Band structure engineering and interface design have significantly improved charge carrier separation and CH₄ activation efficiency. At the level of reaction pathway regulation, efforts are primarily dedicated to improving target product selectivity and reaction atom economy. Multiple technical routes have been established, covering C₁ and C₂ liquid oxygenates to C₂₊ hydrocarbons, including POM, NOCM, and OCM. Among these, POM directly converts CH₄ into high-value liquid oxygenates, demonstrating a promising yet highly challenging research direction. Future work requires synergistic innovation across catalyst design, reaction medium optimization, and reactor engineering to ultimately achieve highly selective synthesis of liquid oxygenates through precise regulation of reaction pathways. Meanwhile, the OCM reaction offers advantages such as strong thermodynamic feasibility, fast reaction rates, and high single-pass conversion, positioning it as one of the photocatalytic CH₄ conversion pathways closest to industrial application. In reactor engineering, addressing mass transfer limitations and low photon utilization efficiency has become a consensus. Reactor configurations have evolved from batch systems through continuous flow designs to structured systems such as microchannel and optical fiber reactors. These novel reactors demonstrate significant advantages in increasing surface area and optimizing light field distribution. In mechanism studies, the integration of *in situ* characterization techniques and theoretical calculations has progressively revealed the evolution pathways of active species, the dynamic behavior of intermediates, and the structure-performance relationships of catalysts during reactions, laying a solid foundation for the rational design of catalysts.

However, this technology still faces numerous challenges on its path toward industrialization. In fundamental research, understanding remains insufficient regarding the dynamic evolution of key active sites, competition mechanisms between radicals and surface-adsorbed species, and precise regulation mechanisms of multi-step reaction networks. In performance evaluation, significant difficulties exist in comparing results across different research systems due to the lack of unified testing standards and systematic literature benchmarks. At the technology integration level, issues such as catalyst stability, noble metal replacement strategies, and reactor scale-up effects have not been fundamentally resolved.

Looking ahead, research should focus on the following directions: In fundamental research, developing *in situ/operando* characterization methods with higher spatiotemporal resolution and establishing multi-scale theoretical models encompassing electronic structure, surface processes, and mass transfer effects are essential to achieve precise analysis and regulation of reaction networks. For example, for the POM pathway, the key is to address the mechanism of over-oxidation of oxygenated

intermediates to CO₂; for the NOCM pathway, the critical challenge lies in promoting C–C coupling while inhibiting deep dehydrogenation and coking; and for the OCM pathway, it is necessary to balance C–H activation capability with the desorption rates of C₂H₄/C₂H₆ products. In performance evaluation, establishing unified performance assessment standards and databases is crucial. Priority should be given to developing broadband light-responsive material systems suitable for full-spectrum solar energy utilization. There is also an urgent need to enhance the apparent quantum efficiency by constructing charge transfer channels or employing crystal facet engineering to suppress carrier recombination. At the technology integration level, a multi-scale synergistic design encompassing “material-reactor-process” should be adopted to build a complete technology chain from the molecular scale to the system level. To meet industrial scale-up demands, priority should be given to developing modular reactors with high throughput and low pressure drop to address scaling effects in light, mass, and heat transfer. Simultaneously, technologies for direct solar energy utilization integrated with concentrating systems should be explored, and performance evaluation systems based on real solar irradiation conditions should be established. From an industrialization perspective, a complete innovation chain from laboratory-based fundamental research to engineering demonstration needs to be established. In the near term, POM for producing liquid chemicals like CH₃OH shows relatively good feasibility; in the medium to long term, the NOCM route for C₂₊ hydrocarbons hold greater development potential due to its high product value and ease of separation. Furthermore, during the industrialization process, it is necessary to strengthen carbon footprint accounting and lifecycle analysis to systematically evaluate energy consumption and environmental impacts from catalyst preparation to the reaction process. Only solutions that are both technologically feasible and economically competitive can truly achieve the large-scale application and sustainable development of photocatalytic CH₄ conversion technology.

Declaration of Competing Interest

The authors declare no conflict of interest.

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甲烷光催化体系的研究进展

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摘 要: 甲烷是天然气的主要组分, 因其较高的氢碳比而被视为制备高附加值化学品与清洁燃料的理想原料。然而, 甲烷分子具有高度化学惰性, 传统热催化重整过程存在反应路径长、能耗高等问题。相比之下, 光催化技术可在温和条件下实现甲烷的高选择性转化, 兼具环境友好性与工艺经济性, 有助于推动化工过程低碳化转型。本工作系统综述了近年来发展的室温光催化甲烷直接转化体系: 首先解析了四种典型反应体系-甲烷部分氧化、甲烷无氧偶联、甲烷氧化偶联以及氧化羰基化的反应机制、产物分布与技术难点; 重点介绍了催化剂的设计与结构, 涵盖半导体载体、金属位点及新型光催化材料; 阐述了反应器设计及过程强化策略, 包括间歇式与连续流动式反应器、新型结构化反应器, 以及光电、光热协同催化等强化路径; 概括了光催化甲烷转化的反应机理。目前该领域在基础研究、性能评估与技术集成等方面仍面临挑战, 未来应注重反应机理深入探索、评估标准统一、非贵金属催化剂开发、系统工艺优化, 并加强全流程可持续性分析。

关键词: 甲烷; 光催化剂; 反应器设计; 过程强化; 光催化系统

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