

REVIEW

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Advancements in CO₂ conversion technologies: a comprehensive review on catalyst design strategies for high-performance CO₂ methanation

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The increasing levels of atmospheric carbon dioxide (CO₂) have raised significant environmental concerns, driving the development of innovative solutions to mitigate its impact. CO₂ methanation, a catalytic process that converts CO₂ into methane (CH₄), has emerged as a promising technology for carbon recycling and renewable energy storage. This review critically examines the advancements in catalyst design strategies aimed at enhancing the efficiency and stability of CO₂ methanation. The focus spans monometallic and multimetallic catalysts, elucidating their roles in optimizing catalytic performance. Additionally, the importance of support materials in stabilizing active sites and facilitating electron transfer is discussed in detail. Key mechanisms, such as the creation of oxygen vacancies, surface and interface engineering, and defect engineering, are highlighted for their contributions to improving reaction kinetics and resistance to deactivation. The interplay between these strategies and their impact on the catalytic properties is analyzed, providing insights into their underlying principles. The review further addresses current challenges, including scalability, energy efficiency, and environmental considerations, while exploring emerging trends such as the integration of renewable energy in methanation processes. By synthesizing recent developments and identifying future research directions, this study aims to serve as a comprehensive resource for researchers and industry stakeholders seeking to advance the field of CO₂ conversion and contribute to global efforts toward carbon neutrality.

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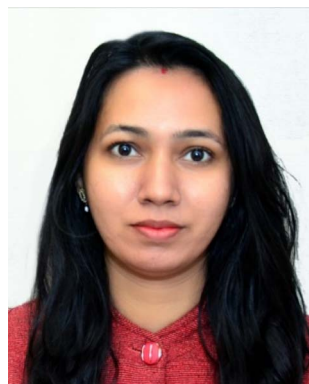
1. Introduction

The dual crisis of climate change and energy security have brought carbon dioxide (CO₂) to the forefront of scientific and industrial discourse. Anthropogenic CO₂ emissions, primarily driven by fossil fuel combustion, industrial processes, and

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deforestation, have escalated atmospheric concentrations of this greenhouse gas to unprecedented levels.¹ This surge in CO₂ is a significant driver of global warming, which manifests in rising temperatures, melting polar ice caps, and more frequent extreme weather events. Concurrently, the depletion of non-renewable energy resources necessitates a transition to sustainable energy systems, wherein CO₂ can serve as a valuable feedstock for chemical and fuel production.² Recycling atmospheric CO₂ into valuable fuels or chemicals offers a promising strategy for addressing climate change and resource sustainability. Transforming CO₂ into fuels not only integrates seamlessly with existing fuel infrastructure but also contributes to reducing global atmospheric CO₂ levels. Among various processes for CO₂ conversion, heterogeneous catalytic conversion of CO₂ into methane (CH₄), commonly referred to as CO₂ methanation, stands out as a promising method.³ This process, also known as the “Sabatier reaction,” involves the reaction between CO₂ and hydrogen (H₂) to yield CH₄ and water (H₂O). Given the challenges associated with hydrogen (H₂) storage, transportation, and large-scale utilization, alongside the established industrial applications of CH₄, the combination of CO₂ with H₂ to produce CH₄ through the CO₂ methanation reaction presents a practical and effective solution (Fig. 1).⁴ The significance of CO₂ methanation lies in its dual role of reducing CO₂ emissions and producing a renewable energy resource. It offers a sustainable approach to treating CO₂ not merely as

a waste product but as a valuable resource. Additionally, CH₄, as a clean-burning fuel, bridges the gap between conventional fossil fuels and renewable energy, thereby facilitating the transition towards a more sustainable energy ecosystem. More importantly, this process utilizes waste industrial heat to simultaneously reduce carbon and heat emissions while avoiding significant infrastructure costs. CO₂ methanation is an exothermic reaction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H^\circ_{298\text{ K}} = -164\text{ kJ mol}^{-1}$), but its efficiency is thermodynamically constrained at high temperatures.⁵ Despite its advantages, the CO₂ methanation process faces several challenges.⁶ Being an exothermic reaction, it is more effective at lower temperatures for achieving high CH₄ yields.⁶ However, the stability of the linear CO₂ molecule necessitates highly active catalysts to enable its activation at low temperatures.⁷ Furthermore, the competitive reverse water–gas shift (RWGS) reaction, which produces carbon monoxide (CO) and water, poses a significant challenge to achieving optimal CH₄ production under these conditions.⁸ Catalysts are central to the success of heterogeneous CO₂ methanation, as they facilitate the activation and transformation of CO₂ and H₂. Typically, these catalysts consist of metal nanoparticles supported on high-surface-area materials such as oxides, carbides, or nitrides.⁹ The choice of catalyst composition, structural properties, and morphology plays a pivotal role in determining the reaction kinetics, selectivity, and overall efficiency of the methanation process.



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applications including solar cells, fuel cells, and CO₂ conversion, water sensing with worldwide collaboration at the national rank research teams in Russia, USA, Italy, Japan (SPRING-8), and the UK. Hosting research projects from academic and industrial funds on physical chemistry research and environment sensing technologies. He heads a group of nanocrystal design and fabrication for energy conversion applications. The main work in his group is atomic cluster decoration techniques for modifying the redox performance of catalysts by incorporating interdisciplinary, and multi-scales mechanisms in heterogeneous catalysis. The work is strongly motivated by emerging real-life problems and their challenges in green energy. His group currently works with 3 domestic groups, 1 TW company, and 2 international groups (UK@UoL and SP-8@Japan).



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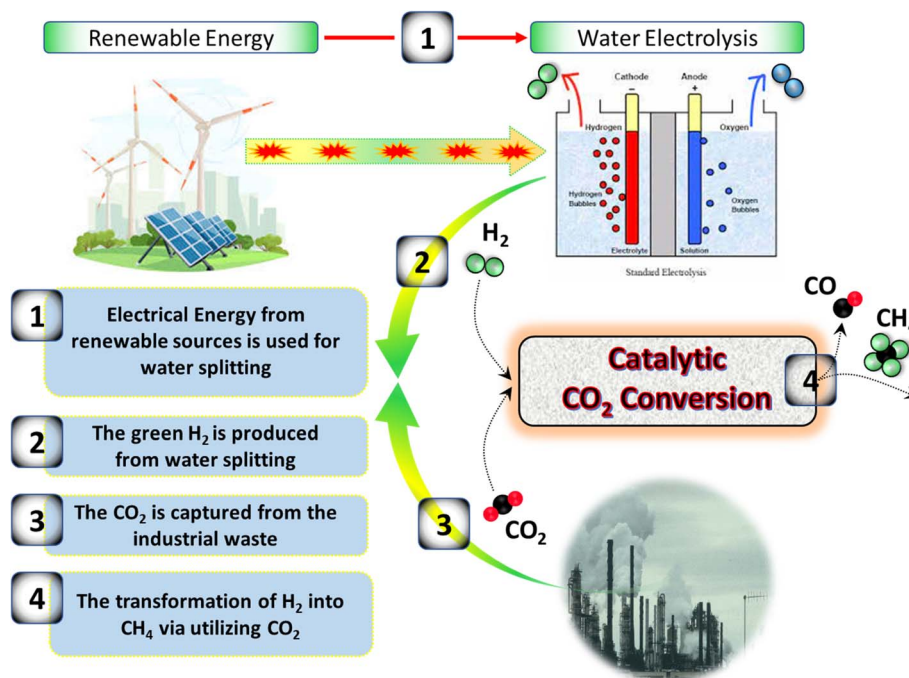


Fig. 1 Schematic representations of the closed carbon loop.

As shown in Fig. 2, heterogeneous CO₂ methanation typically proceeds through three key stages: (i) adsorption of reactants on the catalyst surface, (ii) formation of intermediate species, and (iii) desorption of the final products.¹⁰ According to Sabatier's principle, the adsorption energy of intermediates on the catalyst surface must be finely balanced to ensure optimal reaction kinetics.¹¹ If the adsorption energy is too low, the bond-breaking steps of the reactants may be inefficient. Conversely, if the adsorption energy is too high, it can hinder the desorption of the final products, affecting the overall efficiency of the process. In recent years, substantial research efforts have focused on overcoming these challenges and advancing the field of CO₂ methanation. Strategies such as designing and synthesizing advanced catalysts, optimizing reaction conditions, and enhancing the mechanistic understanding of the process have

been explored to improve catalyst performance.^{12,13} These efforts aim to increase reaction efficiency, reduce operational costs, and ensure the scalability of CO₂ methanation for industrial applications. This review provides a comprehensive analysis of recent advancements in catalyst design strategies for high-performance CO₂ methanation. Key topics include the development of monometallic and multimetallic catalysts, the role of support materials, the influence of oxygen vacancies, and the application of surface, interface and defect engineering techniques. By synthesizing current knowledge and identifying research gaps, this review aims to guide future developments in the field, contributing to the broader goals of sustainable energy and environmental remediation. These discussions encompass innovative approaches in catalyst design, enhanced understanding of reaction mechanisms, and the implementation of

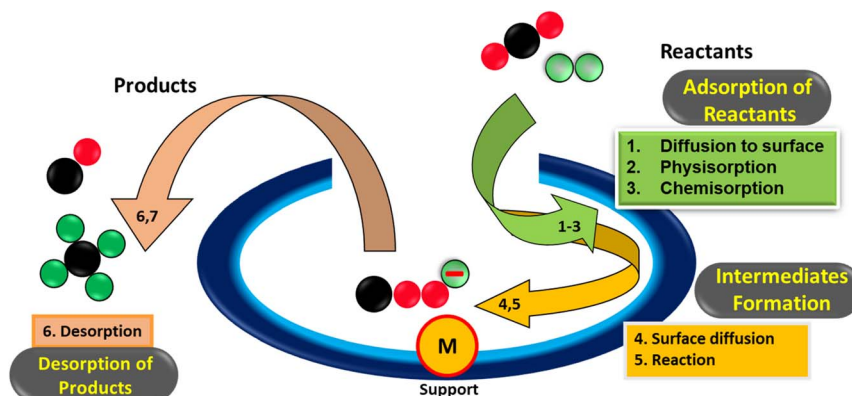


Fig. 2 The reaction pathways for heterogeneous catalytic CO₂ methanation.



optimized process parameters to achieve higher CH₄ yields and improved catalyst stability.

2. Reaction pathways for CO₂ methanation

Understanding the detailed mechanisms and identifying key intermediates in CO₂ methanation reactions is crucial for the development of high-performance catalysts. Extensive research has been conducted to elucidate the underlying mechanisms, employing both experimental approaches and theoretical modeling.^{14,15} While the specific intermediates and pathways leading to CH₄ formation remain subjects of scientific debate, two primary pathways have emerged as widely

accepted: the associative and dissociative mechanisms, illustrated in Fig. 3. In the associative mechanism, adsorbed CO₂ undergo a reaction with adsorbed hydrogen atoms (H^{*}), leading to the formation of intermediates such as formate (*HCOO) or carboxylate (*COOH). These intermediates are then progressively hydrogenated, resulting in CH₄ formation. This pathway can be further categorized into the formate route and the reverse water-gas shift (RWGS) route, depending on the specific intermediate involved in the reaction.^{16,17} Conversely, the dissociative pathway, often referred to as the CO pathway, involves the initial dissociation of chemisorbed CO₂ species into *CO and *O.¹⁸ The subsequent reaction steps then facilitate the hydrogenation of these species, ultimately yielding methane. These pathways offer insights into the reaction dynamics, highlighting the complexity of the processes involved. Further elaboration on the associative and dissociative pathways is provided in subsequent sections, shedding light on their unique characteristics and implications for catalyst design.

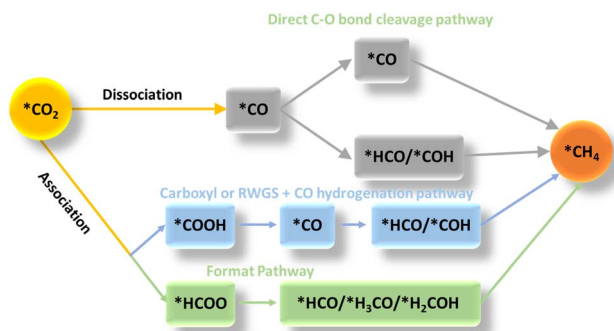


Fig. 3 Schematic representation of possible reaction pathways of CO₂ methanation.

2.1. Associative pathway

The associative pathways of CO₂ methanation involve the stepwise addition of hydrogen (H^{*}) atoms to adsorbed CO₂ molecules (*CO₂), culminating in the production of methane (CH₄) and potential by-products. These pathways are distinguished by their reliance on intermediate species formed during the reaction process, with subsequent hydrogenation steps leading to the final methane product. Unlike dissociative

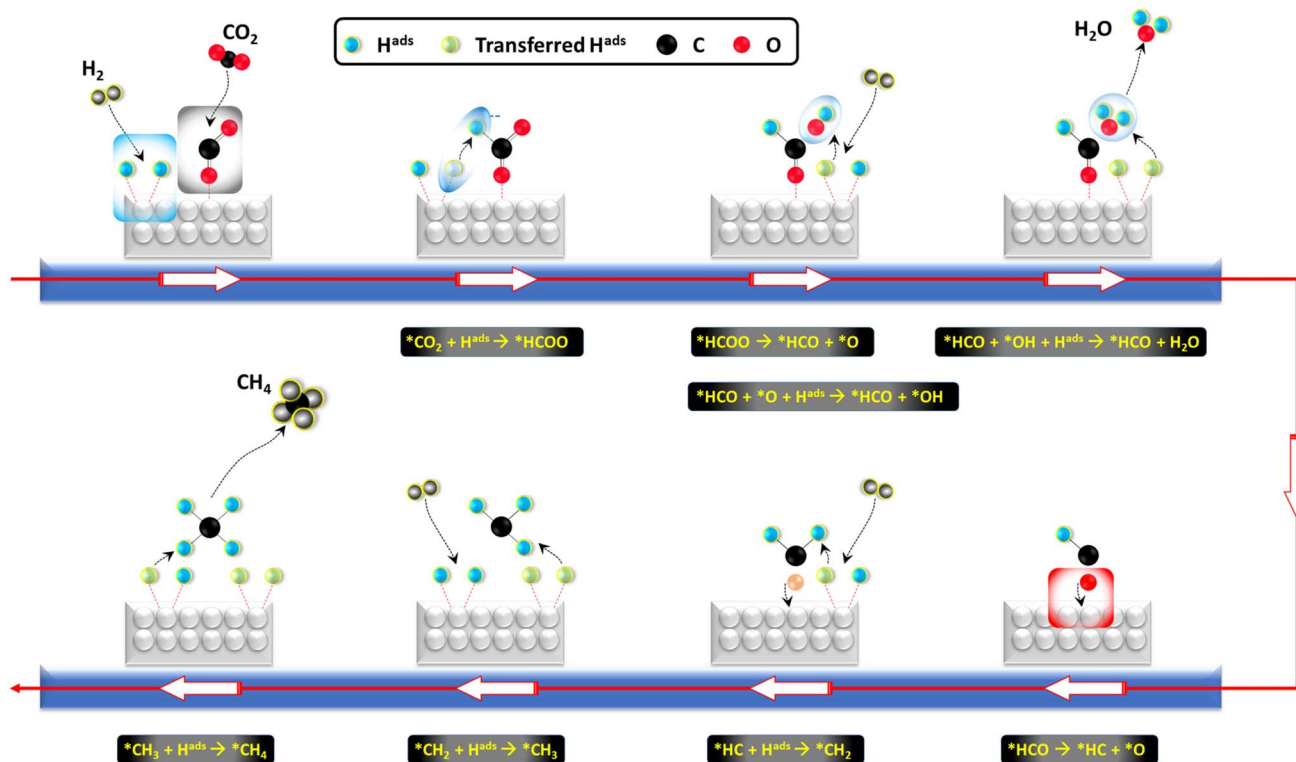


Fig. 4 The formate reaction pathway of CO₂ methanation.



pathways, the associative mechanism does not require the prior breakdown of CO₂ into carbon monoxide (CO) and oxygen (O) species. One of the most widely recognized associative mechanisms is the formate pathway, also referred to as CO₂ associative methanation.¹⁶ As illustrated in Fig. 4, this pathway begins with the chemisorption of CO₂ molecules onto the catalyst's surface, typically through interaction with the oxygen center. The adsorbed CO₂ is then converted into bidentate formates (HCOO*), which act as key intermediate species. These formates undergo a series of hydrogenation reactions, resulting in the formation of formic acid (HCOOH). In the final stages, formic acid is further hydrogenated to produce methane (CH₄). The formate pathway highlights the direct incorporation of CO₂ into reaction intermediates, streamlining its subsequent transformation into methane. This mechanism underscores the role of catalyst surface interactions, particularly the adsorption of CO₂ at oxygen sites, in driving the reaction toward efficient methane production.

Another notable associative pathway is the carboxyl pathway (Fig. 5), characterized by the direct involvement of CO₂ in the reaction process. In this mechanism, the chemisorbed CO₂ species are initially transformed into carboxyl intermediates (*COOH).¹⁷ These intermediates then undergo a series of hydrogenation steps, ultimately yielding CH₄ as the final

product. Similar to the formate pathway, the carboxyl pathway relies on the direct incorporation of CO₂ into intermediate species, facilitating the conversion process leading to methane production. However, a key distinction lies in the adsorption behavior of CO₂ molecules on the catalyst's surface. In this pathway, CO₂ interacts with the catalyst primarily through its carbon center and subsequently forms carbon monoxide (CO) as an intermediate product during the reaction.

In summary, associative pathways in CO₂ methanation involve the direct participation of CO₂ in forming intermediate species, which are subsequently hydrogenated to produce methane. These mechanisms are distinguished by the integration of CO₂ into the reaction process without its prior dissociation into CO and oxygen species. Gaining a comprehensive understanding of these pathways is crucial for refining catalyst designs and optimizing reaction parameters to improve the efficiency of methane production in CO₂ methanation processes.

2.2. Dissociative pathway

Dissociative pathways in CO₂ methanation are characterized by the initial decomposition of CO₂ into CO and oxygen species, which subsequently participate in methane formation. One of the most extensively investigated dissociative mechanisms is

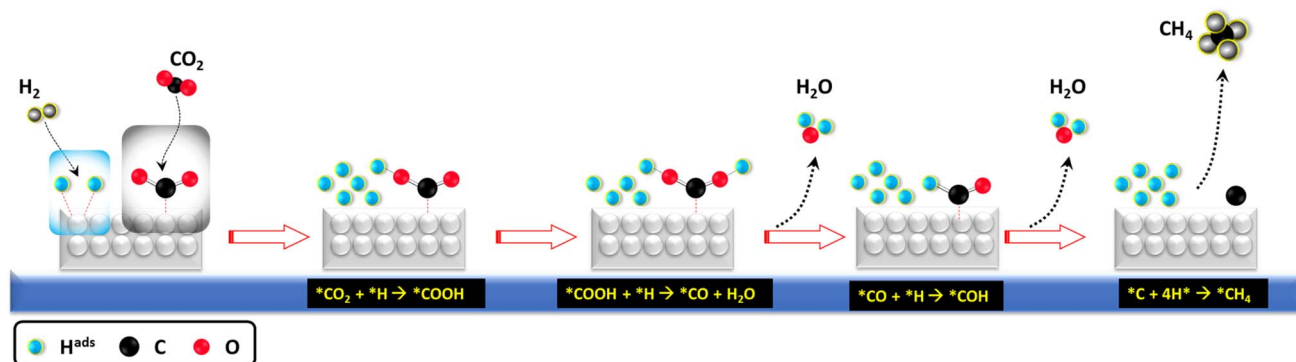


Fig. 5 The carboxyl pathway of CO₂ methanation.

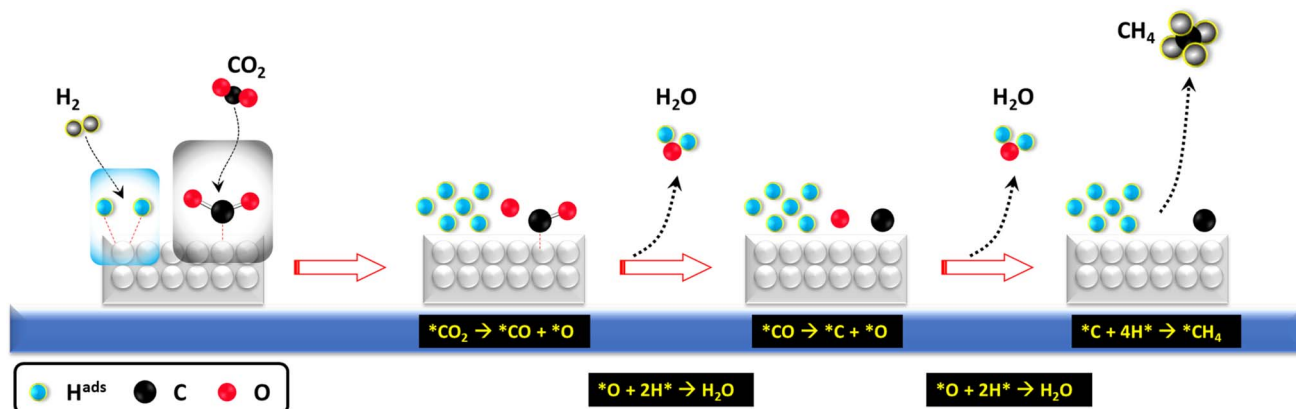


Fig. 6 The dissociative reaction pathway of CO₂ methanation.



the CO pathway, often referred to as CO₂ dissociative methanation. As illustrated in Fig. 6, this pathway involves the chemisorption of CO₂ molecules onto the catalyst's surface, where they break down into *CO and *O intermediates. The *CO species then undergo successive hydrogenation steps, forming carbon species (*C) that further react with hydrogen atoms to generate CH₄. Simultaneously, the *O species combine with hydrogen to form water (H₂O).¹⁸

3. Technical bottlenecks for implementation of CO₂ methanation

Implementing CO₂ methanation technology is accompanied by several technical challenges that must be addressed to enhance its efficiency and feasibility:

3.1. Catalyst performance

The development of highly active, selective, and stable catalysts is fundamental for the success of CO₂ methanation. A significant challenge lies in optimizing the composition, structure, and active sites of catalysts to achieve high CO₂ conversion rates while minimizing the formation of undesired by-products.¹⁹

3.2. Low-temperature efficiency

Achieving substantial CO₂ conversion at lower temperatures is vital for improving energy efficiency and reducing operational costs.²⁰ Enhancing catalytic performance under low-temperature conditions without compromising stability remains a critical issue.

3.3. Catalyst deactivation

Catalyst deactivation due to issues like carbon deposition, poisoning, or sintering can severely impact the efficiency and cost-effectiveness of the process.²¹ Strategies to prevent or mitigate these issues, thereby extending the catalyst's lifespan, are urgently needed.

3.4. Reaction kinetics

A deep understanding of the complex reaction kinetics involved in CO₂ methanation is necessary for optimizing both process parameters and reactor design.²² Identifying and characterizing intermediates and reaction pathways are key to enhancing reaction efficiency and selectivity.

3.5. Hydrogen source

Since CO₂ methanation relies on hydrogen, securing a sustainable and affordable hydrogen supply is paramount. Renewable hydrogen production methods, such as water electrolysis or biogas reforming, should be prioritized to support a viable process.²³

Addressing these challenges will be instrumental in overcoming these barriers and unlocking the full potential of CO₂ methanation as a solution for carbon capture and utilization.

4. Innovative approaches in catalyst design for CO₂ methanation

Designing catalysts for CO₂ methanation involves a comprehensive approach that integrates the selection of active metals, support materials, nanostructure engineering, active site optimization, reaction condition refinement, and a deep understanding of catalytic mechanisms.²⁴ These strategies focus on tailoring catalyst properties to enhance CO₂ activation, facilitate H₂ dissociation, and maximize CH₄ production, while simultaneously minimizing the formation of undesired by-products and mitigating catalyst deactivation. Significant progress has been made in developing optimal configurations for heterogeneous catalysts used in CO₂ methanation. These efforts emphasize fine-tuning various components, including active sites, support materials, promoters, and preparation techniques.²⁵ Among the most promising candidates are metal-oxide-supported catalysts that incorporate active metals, such as noble or transition metals, along with a variety of conventional and advanced support materials.^{26,27} In certain cases, interfacial layers or additional promoters, such as secondary metals, are employed to further enhance catalytic performance.^{28,29} In the following sections, we delve into the specific modifications and innovations applied to each component of catalytic materials, highlighting their roles in advancing the efficiency and durability of catalysts for CO₂ methanation.

4.1. Factors influencing the performance of heterogeneous catalysts

The efficiency of heterogeneous catalysts in CO₂ methanation is determined by a range of factors that significantly impact their catalytic behavior. A thorough understanding of these factors is crucial for refining catalyst design and improving their effectiveness in CO₂ methanation. As illustrated in Fig. 7, several elements influence the CO₂ methanation performance of metal-based catalysts. These factors are explored in detail in the following sections.

4.1.1. Selection of active metals. In the field of CO₂ methanation, it is essential to differentiate between a catalyst's activity and its selectivity. Earlier research has examined and categorized metal catalysts—primarily from groups 8 to 11 of the periodic table (Fig. 8)—based on their performance in terms of activity and selectivity.³⁰ These studies often present varying conclusions. However, a careful review and analysis of these studies reveal a consistent trend in the activity and selectivity profiles of different metals used in CO₂ methanation.

Activity:

Ru > Rh > Ni > Fe > Co > Os > Pt > Ir > Mo > Pd > Ag > Au.

Selectivity:

Pd > Pt > Ir > Ni > Rh > Co > Fe > Ru > Mo > Ag > Au.

Based on the published literature, noble metals, such as Ru and Rh, are known for their exceptional activity, while Pd, Pt, and Ir are recognized for their superior selectivity.^{31,32} However, their limited availability and high costs pose significant challenges for large-scale industrial use. As a result, there is an increasing focus on identifying cost-effective alternatives with



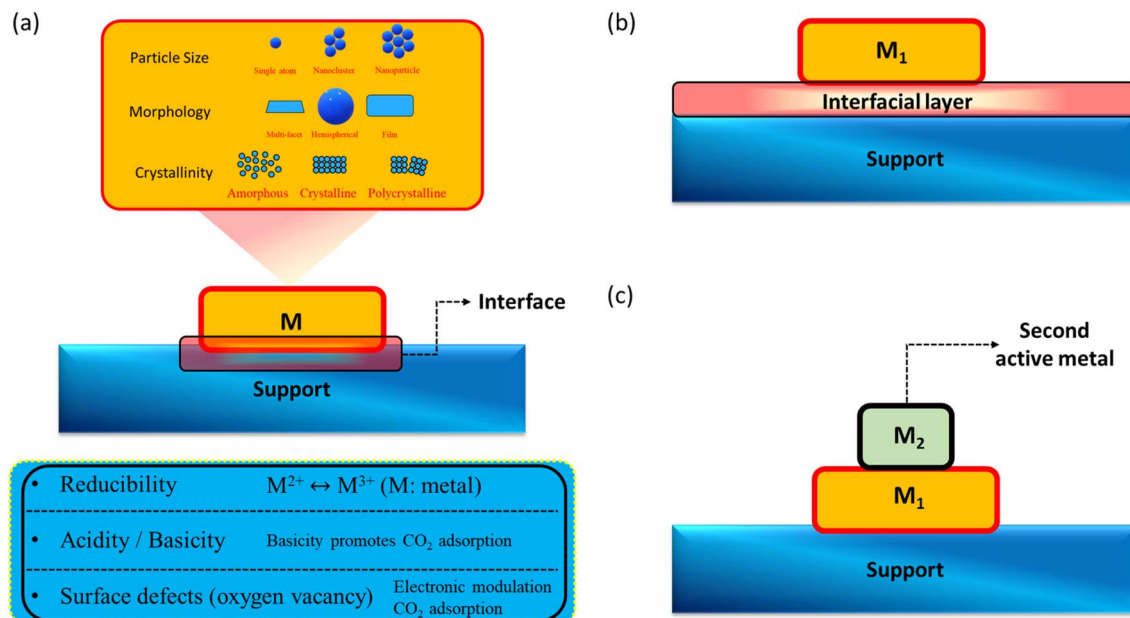


Fig. 7 The schematic representation of factors affecting the catalytic performance of heterogeneous catalysts in CO₂ methanation. Here “M” stands for the active metal. (a) The parameters of active metal affecting the catalytic performance, (b) the interfacial layer and (c) the additive of second metal.

VI	VII	VIII	IX	X	XI
24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Fig. 8 The elements with shaded portions in the periodic table are active metals for CO₂ methanation.

high catalytic activity. Among these, transition metal-based catalysts supported on metal oxides have gained substantial attention. Nickel (Ni)-based catalysts, in particular, are widely

studied for CO₂ methanation due to their excellent catalytic performance and abundant availability.^{33,34} Supported Ni nanoparticles, often dispersed on metal oxides, have demonstrated impressive efficiency in CO₂ methanation processes. Some of the Ni-based catalysts exhibited very high activity in the CO₂ methanation with nearly 100% CH₄ selectivity are summarized in Table 1.

While these catalysts have demonstrated significant potential for CO₂ methanation in practical applications, several challenges remain. Issues such as high activation temperatures, limited CH₄ productivity at lower temperatures, and catalyst deactivation due to sintering under reaction conditions pose barriers to their large-scale implementation. Cobalt (Co)-based catalysts exhibit methanation activity comparable to Ni-based catalysts; however, their higher cost makes them less favorable for industrial use. Similarly, iron (Fe)-based catalysts show reasonable activity for CO₂ methanation but suffer from low

Table 1 The CO₂ methanation performance of Ni-based catalysts on metal-oxide supports

Catalyst	Temp (°C)	CO ₂ conversion (%)	CH ₄ selectivity (%)	References
15 wt% Ni/TiO ₂	260	96	99	35
15 wt% Ni-La/SiC	360	85	100	36
10 wt% Ni/CeO ₂	350	93	100	37
70 wt% Ni/SBA-15	300–450	99.2	100	38
20 wt% Ni/H-Al ₂ O ₃	300	99	99	39
20 wt% Ni/nanocrystalline γ-Al ₂ O ₃	350	78	100	40
14 wt% Ni/USY	400	65.5	94.2	41
5 wt% Ni/2 wt% ceria/Al ₂ O ₃	300	70	100	42
10 wt% Ni/β-zeolite	360	97	N/A	43
10 wt% Ni/β-zeolite with plasma	240	94	N/A	
12 wt% Ni/ZrO ₂ -Al ₂ O ₃	360	69.8	100	44
5 wt% Ni-Ce _x Zr _{1-x} O ₂	350	80	98	45



Table 2 Summary of the optimized parameters of the active metals in Ni-based catalysts for enhanced CO₂ methanation

Factors	Catalyst type	Key findings	References
Different Ni-metal loadings	Ni/F-SBA-15	(1) CO ₂ methanation was highly influenced by Ni loadings (1–10%) onto F-SBA-15 (2) The CO ₂ methanation performance is progressively improved when Ni loading is increased from 1% to 5% Ni and suppressed after further raising the Ni to 10% (3) The XRD results show that the increasing Ni loading from 1 to 5% → NiO crystallite size slightly increased from 7.99 nm to 8.92 nm → representing homogenous dispersion of NiO crystallites. Besides for 10% Ni, a drastic enlargement of NiO crystallites size (17.73 nm) is observed → aggregation	47
Different sizes of Ni nanoparticles with the same metal loading	Ni/CeO ₂	(1) The effect of Ni particle size on CH ₄ production has been revealed on Ni/CeO ₂ catalysts (2) AP-XPS investigation shows that oxygen vacancies are insensitive to Ni particle size (3) The DRIFTS studies revealed that the larger Ni (8 nm particles) over CeO ₂ efficiently facilitated the hydrogenation of the surface formate intermediates	48
Different synthesis methods	Ni/Al ₂ O ₃	(1) Al ₂ O ₃ -supported Ni nanoparticles are prepared by impregnation method (NiAl ₂ O ₃ -I) and microwave-assisted (NiAl ₂ O ₃ -M) methods (2) Ni-Al ₂ O ₃ catalysts prepared by microwave-assisted method show better Ni dispersion and CO ₂ methanation performance	49

CH₄ selectivity, limiting their effectiveness.⁴⁶ Given these challenges, Ni-based catalysts are considered the most promising for practical and scalable applications. Overcoming the limitations associated with Ni-based catalysts is crucial to fully exploit their potential and support the widespread adoption of metal-oxide-supported Ni-transition metal catalysts in CO₂ utilization technologies. Table 2 provides a summary of key factors optimized in previous studies to enhance the performance of Ni-based catalysts for CO₂ methanation.

4.1.2. Synthesis methodologies. The synthesis method of Ni-based catalysts plays a critical role in determining their physicochemical properties, including surface area, metal dispersion, reducibility, and metal-support interactions, all of which directly impact catalytic performance in CO₂ methanation. For instance, Song *et al.* employed a microwave-assisted synthesis approach to fabricate Ni/Al₂O₃ catalysts (Ni20–Al₂O₃-M), leveraging the efficiency of microwave heating for achieving high dispersion of metal precursors on the support material.⁴⁹ To enhance the dispersibility of Ni nanoparticles on γ -Al₂O₃, polyvinyl pyrrolidone (PVP) was introduced as a surfactant, while distilled water acted as a microwave absorbent during the synthesis process. For comparison, a reference catalyst (Ni20–Al₂O₃-I) was prepared using the conventional impregnation method. Structural and morphological characterization techniques, including X-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM), confirmed that the microwave-assisted method led to superior Ni dispersion. Additionally, H₂-temperature programmed reduction (H₂-TPR) and CO₂-temperature programmed desorption (CO₂-TPD) analyses demonstrated that Ni20–Al₂O₃-M exhibited an increased number of active Ni sites under lower H₂ pretreatment temperatures and improved surface basicity. As a result, Ni20–Al₂O₃-M displayed

significantly enhanced catalytic activity for CO₂ methanation, particularly at lower reaction temperatures, while maintaining high CH₄ selectivity across the entire temperature range. Moreover, the catalyst exhibited excellent stability during a 72 hours continuous operation at 325 °C, demonstrating its potential for long-term application in CO₂ methanation processes. Several widely used techniques have been developed to prepare Ni-based catalysts, each offering distinct advantages in optimizing catalyst structure and activity.

Impregnation is one of the most common methods for synthesizing Ni-based catalysts due to its simplicity and scalability. In this method, a porous support material such as Al₂O₃, SiO₂, or CeO₂ is impregnated with a nickel precursor solution (*e.g.*, Ni(NO₃)₂·6H₂O) followed by drying and calcination.⁵⁰ The loading of Ni can be controlled by adjusting precursor concentration, while post-synthetic treatments such as reduction influence metal dispersion and catalyst stability.

Co-precipitation is another widely employed technique that enables uniform mixing of metal precursors and support materials. In this approach, Ni salts and support precursors are simultaneously precipitated from solution using a base such as NaOH or NH₄OH, followed by filtration, drying, and calcination.⁵¹ The advantage of co-precipitation lies in its ability to produce well-dispersed and homogeneously distributed metal nanoparticles, which enhance catalytic activity by providing more accessible active sites.

Sol-gel synthesis is a method that allows for the fine control of metal-support interactions at the molecular level. This process involves the formation of a colloidal solution (sol) that undergoes gelation, drying, and calcination to yield highly porous catalysts with uniform metal dispersion.⁵² The sol-gel technique is particularly beneficial for incorporating Ni into



mixed metal oxides, such as Ni–Al₂O₃ or Ni–CeO₂, which exhibit enhanced reducibility and oxygen mobility.

Hydrothermal and solvothermal methods have gained attention for synthesizing Ni-based catalysts with controlled morphology and crystallinity. These techniques involve the reaction of metal precursors in aqueous (hydrothermal) or organic (solvothermal) solutions at elevated temperatures and pressures, leading to the formation of nanostructured catalysts with tailored properties. The hydrothermal approach is particularly useful for preparing Ni catalysts supported on metal oxides with high surface area and strong metal–support interactions, thereby improving catalytic stability.⁵³

Deposition–precipitation is another synthesis method that enables precise control over Ni particle size and dispersion. In this technique, Ni precursors are deposited onto a support material through controlled precipitation, followed by washing, drying, and calcination. Compared to traditional impregnation methods, deposition–precipitation provides better metal dispersion and stronger metal–support interactions, which enhance catalytic performance in CO₂ methanation.⁵⁴

Each of these synthesis techniques influences the structural, textural, and electronic properties of Ni-based catalysts, ultimately affecting their efficiency in CO₂ methanation. By selecting an appropriate synthesis method and optimizing reaction conditions, researchers can develop catalysts with improved activity, stability, and resistance to deactivation, making Ni-based catalysts a promising choice for large-scale CO₂ conversion applications.

4.1.3. Selection of support materials. The selection of support materials is a critical factor influencing the performance of Ni-based catalysts in CO₂ methanation.⁵⁵ Support materials (*e.g.*, carbon-based materials, metal-oxides, mixed-metal oxides *etc.*) serve as a structural framework for anchoring active metal nanoparticles, aiding their dispersion and impacting the catalyst's surface characteristics. In addition, to conventional supports, zeolite-based nanomaterials have also been used as support material.⁵⁶ Several aspects highlight the importance of support materials in optimizing the performance of Ni-based catalysts for CO₂ methanation:

4.1.3.1. Surface area and dispersion. High-surface-area support materials promote uniform dispersion of Ni particles, enhancing interactions between the active metal species and CO₂ molecules. This results in improved catalytic activity and selectivity for methane production.⁵⁷

4.1.3.2. Redox properties. Supports with redox-active sites, such as CeO₂, ZrO₂, and TiO₂, facilitate CO₂ activation and subsequent hydrogenation. These properties enhance the reducibility of Ni species, improving CO₂ conversion efficiency.⁵⁸

4.1.3.3. Acid–base properties. Since CO₂ is acidic, basic support materials are advantageous for its activation, making the catalyst more effective.⁵⁹

4.1.3.4. Metal–support interaction (MSI). Metal–support interaction (MSI) plays a crucial role in determining the activity, stability, and selectivity of heterogeneous catalysts. In CO₂ methanation, MSI influences the electronic structure, dispersion, and oxidation state of the active metal sites, thereby

affecting their catalytic performance. Strong metal–support interactions (SMSI) can enhance catalytic activity by facilitating charge transfer between the metal and support, promoting the formation of active sites, and improving resistance to sintering and deactivation. For example, in Ni/CeO₂ catalysts, ceria provides oxygen vacancies that enhance CO₂ adsorption and activation, while Ru/TiO₂ systems benefit from electron transfer effects that modify reaction pathways.^{60,61} Understanding and optimizing MSI through advanced techniques such as Density Functional Theory (DFT) and *in situ* spectroscopy is essential for designing high-performance catalysts for thermal and photocatalytic CO₂ conversion. A strong interaction between the Ni species and the support material enhances catalyst stability by reducing metal sintering under reaction conditions. This interaction also affects the electronic structure of the active sites, thereby influencing the overall catalytic activity.⁶²

4.1.3.5. Surface oxygen vacancies. Certain support materials, like CeO₂ and TiO₂, contain surface oxygen vacancies that promote CO₂ activation. These vacancies facilitate the generation of reactive oxygen species, which play a key role in methane production.⁶³

Table 3 provides an overview of the support materials investigated in previous studies, along with their impact on the performance of Ni-based catalysts.

4.1.4. Interface engineering. Interface engineering in Ni-based catalysts for CO₂ methanation focuses on optimizing the interaction between the active Ni sites and the support material at their interface.⁷⁰ This approach aims to improve catalytic performance by regulating factors such as the electronic structure, surface morphology, and chemical environment. Several strategies are employed to achieve effective interface engineering:

4.1.4.1. Selection of support. The choice of an appropriate support material is fundamental for interface optimization. Materials like TiO₂, CeO₂, and Al₂O₃ are commonly used due to their ability to stabilize and disperse Ni nanoparticles, as well as their high surface area and excellent thermal stability.

4.1.4.2. Support modification. Modifying the surface of the support material introduces specific functionalities or defects that enhance the interaction between Ni and the support. Techniques include creating oxygen vacancies, adding dopants, or incorporating functional groups on the surface.

4.1.4.3. Nano-structuring. Designing the nanostructure of both the Ni catalyst and the support material increases the interfacial contact area and facilitates mass transport of reactants and products. Methods such as nanoscale alloying, deposition of nanostructures, or forming hierarchical structures can be employed for this purpose.

4.1.4.4. Tuning electronic properties. Adjusting the electronic properties at the catalyst–support interface can influence the adsorption and activation of CO₂ and H₂ molecules. This can involve modifying the oxidation state of Ni, introducing electron-rich species at the interface, or inducing metal–support interactions that alter the electronic structure of Ni.

4.1.4.5. Synergistic effects. Leveraging synergistic interactions between Ni and the support material can improve both catalytic activity and selectivity. Examples include facilitating



Table 3 Various support materials explored in the published literature

Factors	Catalyst type	Key findings	References
Single metal-oxide support	Ni-based catalysts supported on TiO ₂ , Al ₂ O ₃ , Y ₂ O ₃ , and CeO ₂	(1) Honeycomb-type Ni-based catalysts with different oxide supports were synthesized (2) 10 wt% Ni/CeO ₂ honeycomb catalyst showed the best CO ₂ methanation activity (80%)	64
	Ni/ZrO ₂	(1) The obtained Ni/ZrO ₂ catalyst shows high Ni dispersion with principally exposed Ni(111) lattice plane (2) An enhanced cooperation between Ni and interfacial active sites is achieved as well, which leads to rapid dissociative adsorption of H ₂ and hydrogen spillover (3) Sufficient H atoms are thereby generated for CO ₂ hydrogenation and helpful in creating oxygen vacancies on the ZrO ₂ surface	65
Composite metal-oxide supports	Ni-Ce _x Zr _{1-x} O ₂	(1) Carbon dioxide methanation was carried out over a series of Ni-Ce _x Zr _{1-x} O ₂ catalysts prepared by a pseudo sol-gel method (2) The influence of CeO ₂ /ZrO ₂ mass ratio and noble metal addition was investigated (3) The addition of ZrO ₂ to CeO ₂ increased the oxygen mobility in the lattice of cerium oxide and promoted the formation of vacancies, which in turn affected the consumption of H ₂ and the activation of CO ₂ rapidly	45
	NiO/ZrO ₂ /Al ₂ O ₃	(1) Promotion of the stability, anti-carbon deposition and anti-sintering performance of Ni/Al ₂ O ₃ catalyst modified by ZrO ₂ is obtained (2) Adding ZrO ₂ restrains the formation of NiAl ₂ O ₄ , weakens the Ni-Al ₂ O ₃ interaction, and makes the catalyst more easily reduced, enhancing significantly the activity of catalyst	66
Carbon supports	Ni/Ce-CNT	(1) The confinement effect of carbon nanotubes prevented the active phase migration and sintering (2) Catalytic performances exhibited that Ni/Ce-CNT catalyst possessed the highest activity with 83.8% conversion of CO ₂ and almost 100% selectivity of CH ₄ without obvious deactivation after a 100 h stability test under reaction conditions	67
	Ni-Ce/RGO	(1) The oxygen functional groups can act as anchoring sites to improve the dispersion of nickel nano-particles on RGO (2) The Ni-Ce/RGO works the best for CO ₂ methanation, which could reach the highest CO ₂ conversion of 84.5% and the highest methane yield of 83.0% at 350 °C with atmospheric pressure as compared to Al ₂ O ₃ support	68
Zeolite supports	Ni catalysts on ITQ-2 and ZSM-5 zeolites support	(1) The higher hydrophobicity of used zeolites favors the CO ₂ methanation	69

the spillover of reactive intermediates between Ni and the support or developing dual-function sites for CO₂ activation and hydrogenation.

One of the notable example of interface engineering has been reported by Zhou *et al.*, where they controlled the metal support interaction between Ru and TiO₂ via proper controlling the interfacial compatibility.⁷¹ Given that the nature of the support material significantly influences the catalytic activity, selectivity, and stability of metal nanoparticles, primarily through metal-support interactions (MSIs). However, the intricate mechanisms governing these interactions remain incompletely understood, as MSIs are affected by factors such as the composition, size, and crystallographic facets of both the metal and the support. Utilizing Ru/TiO₂ catalysts supported on rutile and anatase as model systems, it has been shown that interfacial compatibility plays a decisive role in controlling MSI modes and catalytic behavior in CO₂ hydrogenation. When Ru/

rutile-TiO₂ is annealed in air, the resulting improved interfacial coupling, driven by lattice matching between RuO_x and rutile-TiO₂, enhances the conversion of CO₂ to methane. Conversely, annealing Ru/anatase-TiO₂ leads to reduced CO₂ conversion and shifts the reaction product to CO, attributed to the formation of strong metal-support interactions (SMSIs). Despite having the same chemical composition, rutile and anatase exhibit distinct effects on interfacial coupling, demonstrating how compatibility at the interface can profoundly influence the coupling strength, surface morphology, atomic configurations, MSI modes, and overall catalytic performance of Ru/TiO₂ in heterogeneous catalysis. Furthermore, Kang *et al.* demonstrated the effect of interfacial layer between active metal and support for enhanced H-spillover during CO₂ conversion.⁷² It is frequently reported in the literature that the migration of reducible metal oxides, such as TiO₂, onto the surface of metal nanoparticles can help prevent sintering but often negatively



affects catalytic activity. However, a novel approach demonstrates the *in situ* formation of TiO_x patches on an MnO support, creating effective pathways for hydrogen spillover. These pathways facilitate the generation of highly active hydrogen species on the MnO surface, which are crucial for converting CO_2 to CO —a pivotal step in transforming CO_2 into valuable chemicals. The $\text{Ru}/(\text{TiO}_x)\text{MnO}$ ($\text{Ru}/\text{Ti}/\text{Mn}$) catalyst exhibits a 3.3-fold improvement in reverse water–gas shift (RWGS) performance compared to traditional Ru/MnO_x catalysts. Using a combination of advanced techniques, including *in situ* analyses, kinetic and catalytic evaluations, and theoretical modeling, it has been shown that the oxide–oxide interfaces, formed spontaneously during reductive treatment in H_2 , significantly enhance catalytic activity. This finding underscores the potential of designing innovative hydrogenation catalysts by leveraging *in situ* oxide–oxide interface creation as active transport channels for hydrogen species. Another interesting study on the importance of interface has been demonstrated by Xu *et al.*, where a highly efficient composite $\text{Ni}-\text{Y}_2\text{O}_3$ catalyst was developed, demonstrating exceptional performance by forming numerous active $\text{Ni}-\text{NiO}_x-\text{Y}_2\text{O}_3$ interfaces under water–gas shift (WGS) reaction conditions.⁷³ This catalyst achieved a remarkable

activity rate of $140.6 \mu\text{mol}_{\text{CO}} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$ at 300°C , marking it as the most active Ni-based catalyst to date. Through a combination of theoretical analysis and *ex/in situ* experimental studies, it was revealed that Y_2O_3 plays a crucial role in facilitating H_2O dissociation at the $\text{Ni}-\text{NiO}_x-\text{Y}_2\text{O}_3$ interfaces, effectively accelerating this rate-limiting step in the WGS reaction. The creation of such innovative interfacial structures for molecular activation highlights significant potential for advancing catalytic systems in various applications. In summary, interface engineering for Ni-based catalysts aims to finely tune the properties of both the active metal sites and the support material to create highly efficient and selective systems for converting CO_2 into methane. Table 4 highlights significant examples of interface engineering strategies applied to Ni-based catalysts for CO_2 methanation.

4.1.5. Addition of secondary metals. Researchers have extensively investigated the role of transition metal additives in improving the performance of Ni-based catalysts for CO_2 methanation. Among these, Fe and Co are frequently highlighted as effective secondary metals. The incorporation of such dopants into the Ni lattice can significantly alter the electronic properties of nickel and influence the methanation reaction

Table 4 Notable examples of interface engineering

Factors	Catalyst type	Key findings	References
Interface engineering	$\text{Ni}/\text{ZrO}_{2-x}$	(1) Zirconium dioxide-supported Ni catalysts toward low-temperature CO_2 methanation are obtained <i>via</i> structural topological transformation of NiZrAl -layered double hydroxide (LDH) precursors, which have the feature of an interfacial structure ($\text{Ni}-\text{O}-\text{Zr}^{3+}-\text{VO}$) between Ni nanoparticles and ZrO_{2-x} support ($0 < x < 1$) (2) The optimized catalyst ($\text{Ni}/\text{ZrO}_{2-x}\text{S}_2$) exhibits exceptional CO_2 conversion ($\sim 72\%$) at 230°C temperature with $\sim 100\%$ CH_4 selectivity	74
	Ni/mpCeO_2	(1) Ni nanoparticles were encapsulated in ordered mesoporous ceria, mpCeO_2 , for CO_2 methanation (2) At 225°C , TOF of Ni/mpCeO_2 catalyst (0.183 s^{-1}) is 3 times higher than Ni catalyst supported on conventional CeO_2 prepared by the same method (0.057 s^{-1}) (3) The encapsulated structure provides a rich Ni– CeO_2 interface with more oxygen vacancies, playing a key role in CO_2 activation (4) Small and highly dispersed Ni nanoparticles in channels of mpCeO_2 facilitate H_2 dissociation	75
	$\text{Ni}-\text{NiO}_x-\text{Y}_2\text{O}_3$	(1) The cross-referencing results of <i>ex/in situ</i> experimental study and theoretical calculations indicates that Y_2O_3 favors the H_2O dissociation at the $\text{Ni}-\text{NiO}_x-\text{Y}_2\text{O}_3$ interfaces	73
	Ru/TiO_2	(1) The results show that rutile and anatase TiO_2 supports can dramatically modify the morphology, surface atomic configuration, MSI mode, and catalytic performances of Ru catalysts for CO_2 hydrogenation reaction, although they share the same chemical compositions (2) $\text{Ru}/\text{R}-\text{TiO}_2-\text{H}_2$ and $\text{Ru}/\text{A}-\text{TiO}_2-\text{H}_2$ show similar CO_2 conversions between 120°C and 320°C , suggesting that R- TiO_2 and A- TiO_2 apply similar support effects on directly reduced Ru/TiO_2 catalysts (3) However, the CO_2 conversion efficiency dramatically differentiate by pre-annealing treatment in air at 400°C . $\text{Ru}/\text{R}-\text{TiO}_2-\text{air}-\text{H}_2$ displays an enhanced catalytic performance, with CO_2 conversion at 300°C increasing from 31.4% to 89.2% (4) $\text{Ru}/\text{A}-\text{TiO}_2-\text{air}-\text{H}_2$ shows a highly decreased activity, with CO_2 conversion at 300°C reducing from 29.4% to 1.7%. At each reaction temperature, $\text{Ru}/\text{R}-\text{TiO}_2-\text{air}-\text{H}_2$ shows the highest CO_2 conversions among four catalysts. The results indicate that R- TiO_2 and A- TiO_2 apply opposite support effects on the activity of Ru NPs	71



pathway. These modifications may enhance the catalyst's activity and stability or, in some cases, lead to deactivation, depending on several factors. Key considerations include the ratio of Ni to the dopant, the extent of intermixing between the metals, and the interaction of the metal additives with the support material. By strategically integrating transition metal

additives, the catalytic properties of Ni-based systems can be fine-tuned, resulting in improved CO₂ methanation performance. However, achieving the desired outcomes requires a careful balance of these parameters to prevent potential deactivation of the catalyst. Table 5 provides an overview of examples where secondary metal additives have been employed

Table 5 Notable examples of the second metal additives to Ni-based catalysts

Additive	Catalyst type	Key findings	References
Fe	Ni _x Fe _{1-x} /Al ₂ O ₃	(1) The maximum carbon conversion and CH ₄ selectivity are achieved on Ni _{0.7} Fe _{0.3} /Al ₂ O ₃ catalyst, outperforming the monometallic Ni/Al ₂ O ₃ (2) Further, increasing Fe content led to enhancing the water gas shift reaction and hydrocarbon formation	76
	Ni _x Fe _y /Al ₂ O ₃	(1) A systematic investigation on Fe promotion in Ni-based methanation catalysts reveals that catalysts comprising 75% Ni and 25% Fe exhibited optimal activity (2) Bimetallic NiFe alloy catalysts supported on alumina and silica displayed higher CH ₄ yields compared to their monometallic counterparts (Ni and Fe), with alumina-supported catalysts showing superior enhancement (3) This enhancement was attributed to the formation of a suitable alloy phase and increased CO ₂ chemisorption at unreduced Fe ₃ O ₄ sites	77
	NiFe alloy	(1) Fe promotes Al ₂ O ₃ , ZrO ₂ , TiO ₂ and SiO ₂ supported Ni during CO ₂ hydrogenation (2) Enhancement due to the formation of suitable Ni-Fe alloy on all supported catalysts	78
	Ni ₃ M/Al ₂ O ₃	(1) Ni ₃ M/Al ₂ O ₃ (M = Fe and Cu) possess different types (Ni ₃ Fe and Ni _{1-x} Cu _x) of alloys (2) Enhanced CO ₂ methanation performance over Ni ₃ Fe catalysts, attributed to favorable changes in the electronic properties of the active Ni phase (3) In contrast, Ni ₃ Cu alloy formation was found detrimental to CH ₄ production	79
	17 wt% Ni ₃ Fe/γ-Al ₂ O ₃	(1) A γ-Al ₂ O ₃ supported Ni ₃ Fe alloy catalyst with high dispersion was prepared (24%) (2) A high fraction of Ni and Fe formed the desired Ni ₃ Fe alloy within a size range of 4 nm (3) As-prepared material outperforms the monometallic counterparts	80
	Ni _{3.2} Fe/Al ₂ O ₃	(1) They investigated the deactivation of a Ni-based catalyst and unravelled the protective role of "sacrificial" iron in a Ni _{3.2} Fe catalyst during dynamic CO ₂ methanation (2) During the simulated H ₂ dropout, the monometallic Ni catalyst was prone to form surface oxygen species resulting in an irreversible formation of NiO leading to catalyst deactivation during the subsequent methanation step (3) In the presence of Fe, the active Ni ⁰ species was protected from oxidation during the simulated H ₂ dropout by preferential formation of FeO	81
Co	Ni-Fe/(Mg, Al)O _x	(1) The Fe/Ni ratio severely affects the product yield	82
	Co-modified Ni/SiO ₂	(1) Methanation activities of Ni-Co/SiO ₂ catalysts were significantly dependent on Co/Ni molar ratios (2) The increase of Co loading led to the remarkable increase of CO ₂ conversions at temperature range from 250 to 350 °C	83
	Co-Ni catalyst on ordered mesoporous Al ₂ O ₃	(1) The synergistic collaboration between Co-Ni decreased the activation energy of CO ₂ methanation (2) Ni and Co existed as adjacent monometallic phases on the mesoporous Al ₂ O ₃ structure, serving as active sites for H ₂ and CO ₂ chemisorption, respectively	84
	Ni-Co/Al ₂ O ₃	(1) The addition of cobalt improved the reducibility of nickel species	85
	Ni-x/CeO ₂ -ZrO ₂ (x = Fe, Co)	(1) Co is an excellent promoter to boost the activity and selectivity towards methane	86



to enhance the efficiency of Ni-based catalysts in CO₂ methanation. More specifically, the role of Fe and Co as promoters in Ni-based catalysts for CO₂ methanation is intricately linked to their influence on reaction pathways, active site modification, and overall catalytic performance. While Fe is known to facilitate CO₂ dissociation, favoring the dissociative pathway, Co is suggested to enhance H₂ activation, promoting the formate and carboxyl pathways. However, a comprehensive understanding of the dominant reaction mechanism and its governing factors remains critical. Systematic experimental validation of these pathways requires an in-depth investigation of the structural and electronic modifications induced by Fe and Co in Ni-based catalysts. Advanced characterization techniques such as *in situ* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can provide valuable insights into electronic interactions, oxidation states, and surface species

evolution during CO₂ methanation. Additionally, density functional theory (DFT) calculations coupled with kinetic modeling can aid in establishing a quantitative correlation between the nature of the promoter, CO₂ activation pathways, CO₂ conversion, and CH₄ selectivity. A holistic approach integrating experimental and computational findings is essential to unravel the mechanistic complexities of CO₂ methanation and to optimize catalyst design for enhanced efficiency and selectivity.

4.1.5.1. Promotion of Ni-based catalysts with Fe. Iron (Fe) has emerged as a widely studied secondary metal in bimetallic Ni-based catalysts for CO₂ methanation due to its cost-effectiveness, availability, and its ability to dissolve readily in the Ni lattice to form NiFe alloys (Fig. 9a).⁸⁷ Computational studies and experimental data suggest that alumina-supported, Ni-rich NiFe catalysts significantly enhance CO₂ conversion rates, with the ideal Ni/(Ni + Fe) ratio ranging from 0.7 to 0.9.^{88,89} Extensive research has been conducted on NiFe alloys

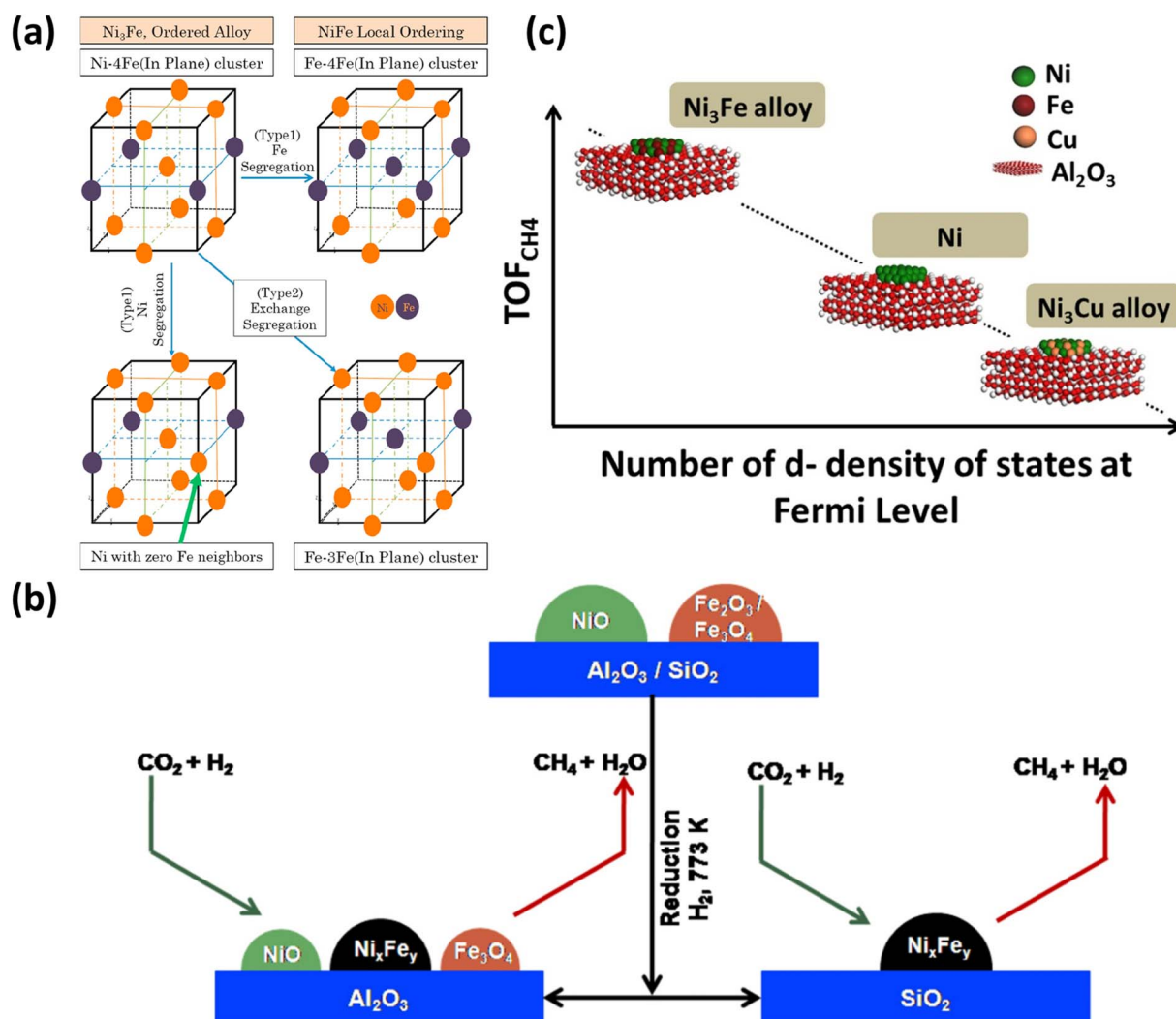


Fig. 9 (a) Solubility of Fe in Ni lattice (this figure has been reproduced from ref. 87 with permission from Elsevier, copyright 2018). (b) Promotional effects in alumina and silica-supported bimetallic Ni-Fe catalysts during CO₂ hydrogenation (this figure has been reproduced from ref. 78 with permission from Elsevier, copyright 2016). (c) Linear correlation between the turnover frequency for CH₄ production (TOF_{CH4}) and the number of d-density of states (d-DOS) at Fermi level (NEF) for Ni, Ni₃Fe and Ni₃Cu catalysts (this figure has been reproduced from ref. 79 with permission from Elsevier, copyright 2017).

synthesized through various techniques and supported on different metal oxides.⁷⁸ The Ni/Fe ratio and the reducibility of the support material have been identified as key factors determining whether Fe acts as a promoter or inhibitor for CO₂ methanation activity. In a notable study, Pandey *et al.* systematically explored Fe promotion in Ni-based catalysts, demonstrating that a composition of 75% Ni and 25% Fe delivered optimal catalytic performance.⁹⁰ Bimetallic NiFe alloy catalysts supported on alumina and silica exhibited higher methane yields compared to their monometallic counterparts, with alumina-supported catalysts showing the greatest improvement (Fig. 9b). This enhanced activity was attributed to the formation of favorable alloy phases and improved CO₂ chemisorption at unreduced Fe₃O₄ sites. Further investigation into Ni₃Fe catalysts on various supports identified alumina as the most effective due to its interaction with Fe, which enhanced alloy formation and catalytic performance.⁷⁸ In another study, Ray *et al.* developed a predictive model for CO₂ methanation performance in Ni₃M bimetallic catalysts, where M represents Fe or Cu. Using density functional theory (DFT) calculations, they correlated the turnover frequency for methane production (TOF-CH₄) with the density of d-states (d-DOS) at the Fermi level (Fig. 9c). This model confirmed enhanced methanation performance for Ni₃Fe catalysts due to favorable modifications in the electronic properties of the active Ni phase. Conversely, the formation of Ni₃Cu alloys was found to inhibit methane production.⁷⁹

The Grunwaldt group has significantly advanced the development of NiFe-based methanation catalysts, offering valuable insights into the role of Fe in enhancing catalytic performance. In one study, Mutz *et al.* synthesized Ni₃Fe catalysts supported on Al₂O₃ through a deposition–precipitation method.⁹¹ The resulting alloy nanoparticles were highly dispersed and exhibited small sizes, resulting in superior activity and stability at lower temperatures compared to monometallic Ni-based catalysts. Notably, these catalysts demonstrated stable performance over a 45 hours time-on-stream operation under industrially relevant conditions, with no evidence of carbon deposition under various gas feeds, as revealed by *operando* Raman spectroscopy. This finding underscored the durability and resistance to deactivation of the NiFe alloy catalysts. Farsi *et al.* investigated the kinetics of CO₂ methanation using Ni₃Fe catalysts under practical operational conditions. Their study found that shorter residence times and elevated temperatures led to increased CO selectivity over CH₄, with water concentration acting as a significant inhibiting factor.⁹² Furthering this work, Serrer *et al.* employed advanced *operando* spectroscopic techniques to explore Fe's role in CO₂ methanation.⁸¹ They discovered that Fe acts as a “sacrificial” dopant, particularly under H₂-dropout conditions during methanation (Fig. 10a). Unlike Ni-based catalysts, which undergo oxidation and fail to recover their initial activity when H₂ flow is restored, NiFe-based catalysts maintain reduced Ni⁰ sites due to Fe's preferential oxidation to FeO. Under normal operating conditions, Fe enhances the reducibility of Ni, leading to the formation of small FeO_x clusters on the surface of alloy nanoparticles. These clusters, exhibiting various oxidation states, are believed to

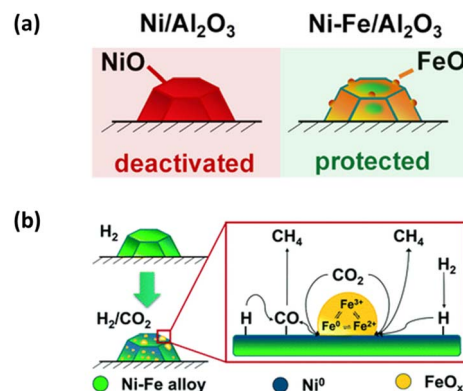


Fig. 10 (a) Deactivation of a monometallic Ni-based catalyst and the protective role of “sacrificial” iron in a NiFe catalyst during dynamic methanation of CO₂ (this figure has been reproduced from ref. 81 with permission from Wiley, copyright 2019). (b) Scheme representation of the CO₂ activation mechanism on Ni–Fe alloy-based catalysts during methanation reaction (this figure has been reproduced from ref. 93 with permission from RSC, copyright 2020).

promote CO₂ chemisorption and activation, potentially contributing to the increased methanation performance of NiFe alloy catalysts (Fig. 10b). This protective and enhancing role of Fe provides a mechanistic basis for the superior performance of NiFe-based systems in CO₂ methanation.⁹³

Mebrahtu *et al.* developed NiFe/(Mg, Al)O_x catalysts using hydrotalcite precursors with a tailored Fe/Ni ratio to achieve high metal dispersion and intermixing.⁸² The Fe/Ni ratio played a critical role in shaping the catalysts' physicochemical characteristics and catalytic performance. Notably, an Fe/(Ni + Fe) ratio of 0.1 was found to optimize key parameters, including nanoparticle size, metal dispersion, and the presence of surface basic sites. Catalysts with this composition demonstrated exceptional low-temperature performance, achieving high CO₂ conversion and CH₄ selectivity, outperforming those with higher Fe content, as depicted in Fig. 11. The study also highlighted a potential deactivation mechanism in monometallic Ni catalysts, wherein the *in situ* generation of water during the

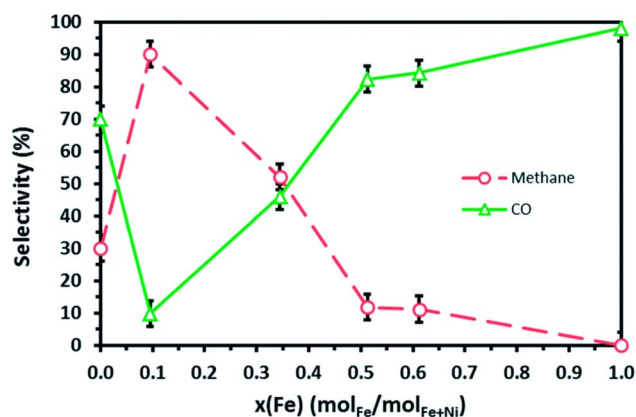


Fig. 11 Effect of Fe content on CH₄ and CO selectivity in comparison to sole metals (this figure has been reproduced from ref. 82 with permission from RSC, copyright 2018).



methanation process leads to the formation of Ni hydroxides. Mebrahtu *et al.* also observed that the inclusion of Fe mitigated this deactivation pathway by suppressing the formation of Ni-OH species, thereby enhancing the catalyst's stability and activity.⁹⁴ Additionally, it was proposed that Fe, instead of forming alloys with Ni, contributed to spinel phase formation on alumina nanosheets. This strategic incorporation of Fe not only prevented deactivation but also augmented the overall catalytic efficiency of the NiFe/(Mg, Al)O_x system. These findings underscore the significance of precise Fe/Ni ratio optimization in enhancing the performance of Ni-based catalysts for CO₂ methanation.

Furthermore, the research has explored the influence of Fe addition on the performance of Ni-based catalysts, revealing varied results depending on the catalyst composition, support material, and Fe loading. For instance, Li *et al.* reported that introducing 3% Fe to a 12% Ni/Al₂O₃ catalyst slightly improved CO₂ conversion and CH₄ selectivity. However, increasing the Fe content to 12% (Fe/Ni ≈ 1) resulted in reduced methanation efficiency (Fig. 12a).⁹⁵ Liang *et al.* investigated Fe-modified Ni/Al₂O₃ catalysts and observed an increase in oxygen vacancies, altering the reaction mechanism as confirmed by electron paramagnetic resonance (EPR).⁹⁶ Conversely, Daroughegi *et al.* found that a 25% Ni/Al₂O₃ catalyst with 5% Fe performed worse than its monometallic Ni counterpart in methanation activity.⁹⁷ The choice of support material also plays a significant role in the methanation performance of NiFe-based catalysts.⁹⁸ Ren *et al.* demonstrated that modifying a 30% Ni/ZrO₂ catalyst with 3% Fe improved its low-temperature activity.⁹⁹ However, higher Fe contents led to decreased performance due to the incomplete reduction of Fe species, which remained in the Fe(II) oxidation

state (Fig. 12b). These Fe(II) species enhanced Ni dispersion and reducibility and promoted the reduction of ZrO₂, creating oxygen vacancies that facilitated CO₂ chemisorption and dissociation (Fig. 12c). Yan *et al.* studied low-load Ni and Fe catalysts supported on ZrO₂ and identified distinct interfacial sites that influenced product selectivity during CO₂ hydrogenation.¹⁰⁰ Adding Fe in an equimolar ratio to Ni slightly improved CO₂ conversion and CH₄ selectivity by maintaining a methane-selective Ni-ZrO₂ interface. However, a high Fe/Ni ratio (Fe/Ni = 3) increased CO selectivity by favoring the reverse water-gas shift (RWGS) reaction through the formation of Ni-FeO_x interfaces. Other investigations highlighted the role of Fe promotion in enhancing the methanation performance of Ni-based catalysts supported on Al₂O₃ and mesoporous clay modified with ZrO₂.^{101,102} These findings underline the complex relationship between catalyst composition, support material properties, and operating conditions, which collectively dictate the effectiveness of CO₂ methanation.

4.1.5.2. Promotion of Ni-based catalysts with Co. Cobalt (Co), a transition metal similar to nickel (Ni), is widely utilized in bimetallic NiCo catalysts for CO₂ methanation. Its ability to integrate into the Ni lattice and transition between oxidation states (Co³⁺, Co²⁺, and Co⁰) enables modifications to the electronic properties of the catalyst.¹⁰³ Early investigations by Guo *et al.* examined SiO₂-supported NiCo catalysts with varying Co/Ni ratios, finding that higher Co content enhanced catalytic activity, with an optimal Co/Ni ratio of 0.4.⁴⁶ The formation of a uniform NiCo alloy facilitated CO dissociation and hydrogen spillover, improving methanation performance.⁸³ Subsequent research shifted focus to Al₂O₃-supported NiCo catalysts, employing methods like evaporation-induced self-assembly

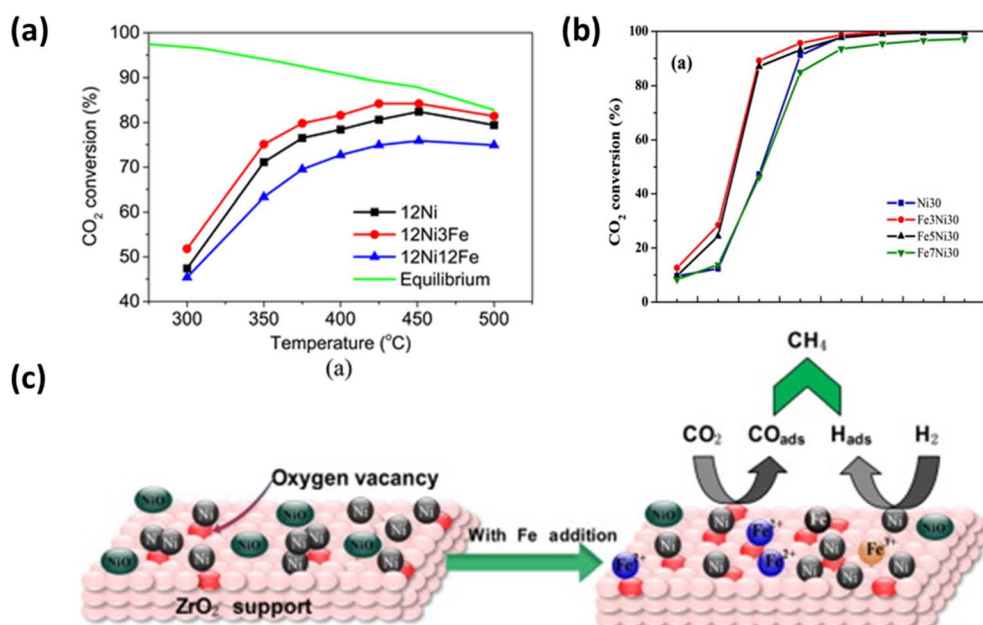


Fig. 12 (a) The CO₂ conversion performance of NiFe catalysts with different Fe content (this figure has been reproduced from ref. 95 with permission from Wiley, copyright 2018). (b) CO₂ conversion over Ni-Fe/ZrO₂ catalysts with various Fe content (this figure has been reproduced from ref. 99 with permission from Elsevier, copyright 2019), and (c) schematic representation of CO₂ methanation over Ni/ZrO₂ and NiFe/ZrO₂ (this figure has been reproduced from ref. 100 with permission from Elsevier, copyright 2015).



(EISA) to introduce ordered mesoporosity. Xu *et al.* demonstrated that a Co/(Ni + Co) ratio of 20% improved catalytic activity and stability, attributing the enhancement to the synergy between Ni and Co phases, which served as active sites for H₂ and CO₂ chemisorption, respectively (Fig. 13a and b). This interaction reduced the activation energy for CO₂ methanation.⁸⁴ Similarly, Liu *et al.* reported improved low-temperature activity and stability in ordered mesoporous NiCo/Al₂O₃ composites due to NiCo alloy formation and the confinement effect of the mesoporous structure.¹⁰⁴ Alrafei *et al.* studied Al₂O₃-supported NiCo catalysts and observed that a bimetallic catalyst with 10% Ni and 10% Co outperformed a monometallic 10% Ni catalyst, as Co enhanced the dispersion and reducibility of Ni.¹⁰⁵ However, a monometallic 20% Ni catalyst surpassed the performance of bimetallic catalysts with a total metal loading of 20%. All tested catalysts exhibited excellent stability over 200 hours of operation.⁴⁹ Conversely, Fatah *et al.* found that adding 5% Co to a 5% Ni/Al₂O₃ catalyst reduced CO₂ conversion and CH₄ selectivity by approximately 30%, likely due to the formation of larger particles and an increased presence of formate intermediates.¹⁰⁶ Beyond SiO₂ and Al₂O₃, research has focused on other supports like ZrO₂ and CeO₂-based materials. Ren *et al.* showed that modifying 30% Ni/ZrO₂ catalysts with Co enhanced CO₂ conversion but slightly reduced CH₄ selectivity compared to Fe-modified counterparts.⁹⁹ Razzaq *et al.* demonstrated that Co-modified Ni/CeO₂-ZrO₂ catalysts were particularly effective for CO and CO₂ co-methanation in CH₄-rich gas mixtures.¹⁰⁷ Zhu *et al.* confirmed that adding 5% Co to 15% Ni/CeO₂-ZrO₂ catalysts improved activity and stability for CO₂ methanation.¹⁰⁸ Pastor-Pérez *et al.* also reported that a 3% Co addition enhanced CO₂ conversion, CH₄ selectivity, long-term stability, and coke resistance.⁸⁶ In other studies, defect-rich supports like GDC did not show improved catalytic performance with Co

promotion. Jia *et al.* utilized TiO₂-coated silica spheres as supports, with the reducible TiO₂ layer improving metal dispersion and enhancing CO₂ and H₂ adsorption.¹⁰⁹ Zhang *et al.* incorporated Co into LaNiO₃ perovskite lattices supported on mesostructured cellular foam silica, yielding catalysts with enhanced activity and stability.¹¹⁰ In summary, cobalt's addition to Ni-based catalysts generally enhances CO₂ methanation performance by improving Ni reducibility, dispersion, and electronic properties. While the type of support material—whether inert or reducible—has a limited influence on the promotion mechanism, the Co/(Ni + Co) ratio plays a less critical role compared to similar NiFe systems. Overall, Ni-rich NiCo catalysts demonstrate consistently superior activity and stability for CO₂ methanation.

4.1.6. Role of oxygen vacancies for CO₂ methanation performance. Oxygen vacancies are critical in determining the effectiveness of catalysts used in the CO₂ methanation process. These vacancies, which represent defects within the lattice structure of materials like CeO₂, ZrO₂, and their derivatives, serve as active sites for CO₂ activation and subsequent conversion to methane.¹¹¹ A deeper understanding of these vacancies can inform strategies for optimizing catalyst design and enhancing performance.

4.1.6.1. CO₂ activation at oxygen vacancies. Oxygen vacancies function as adsorption and activation sites for CO₂ molecules due to their unique electronic characteristics. These defects facilitate the interaction of CO₂ with the catalyst surface, leading to its dissociation into reactive intermediates. This activation step is crucial for initiating the reaction pathway that eventually results in methane production.

4.1.6.2. Redox properties and catalytic cycle. Oxygen vacancies also influence the redox behavior of catalysts. By enabling the exchange of oxygen atoms between the catalyst surface and the reactants, they play an essential role in the methanation

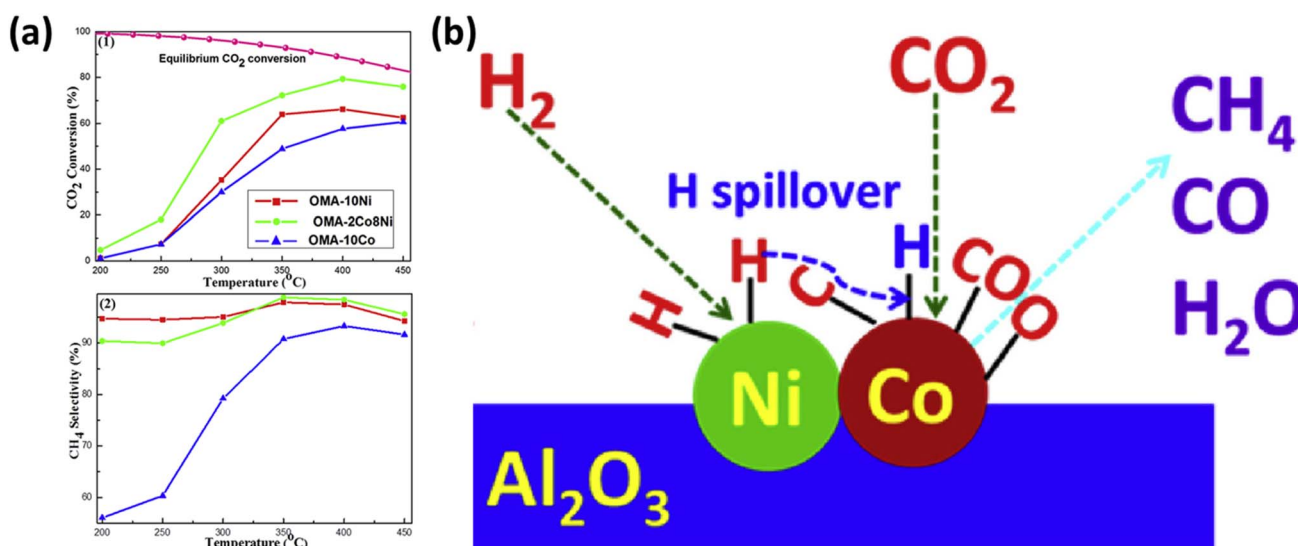


Fig. 13 (a) The CO₂ conversion and CH₄ selectivity versus reaction temperature over OMA-10Ni, OMA-2Co8Ni, and OMA-10Co catalysts. (b) The proposed synergistic mechanism between Co and Ni domains over the OMA-xCoNi catalysts toward CO₂ methanation (this figure has been reproduced from ref. 84 with permission from Elsevier, copyright 2018).

cycle. This activity promotes the efficient conversion of CO_2 and H_2 into methane and water.

4.1.6.3. Enhancing stability and longevity. The presence of oxygen vacancies contributes to the stability and durability of catalysts during extended reaction periods. These defects not only provide active sites for CO_2 conversion but also maintain the structural integrity of the catalyst, ensuring consistent performance over time. Stability and resistance to deactivation are essential for practical applications of CO_2 methanation catalysts.

4.1.6.4. Improved metal-support interactions. Oxygen vacancies also affect the dispersion and interaction of active metal sites, such as nickel or cobalt, supported on oxide surfaces. Strong interactions between the metal and the support, mediated by oxygen vacancies, enhance the accessibility and reactivity of the metal sites, thereby improving catalytic efficiency.

4.1.6.5. Case studies. Various researchers have demonstrated the importance of oxygen vacancies for CO_2 methanation. It is frequently reported in the literature that creating oxygen vacancies in metal oxide supports, especially CeO_2 , boosts the CO_2 methanation process. For instance, the mechanism of CO_2 methanation was examined for Ni/CeO_2 and $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts, with Ni/CeO_2 demonstrating superior activity and selectivity.¹¹² This is attributed to three key factors: (i) Ni/CeO_2 features two distinct active sites, where the $\text{NiO}-\text{CeO}_2$ interface facilitates efficient CO_2 dissociation, and Ni^0 particles enhance H_2 dissociation; (ii) water desorption, the rate-limiting step, is expedited by the high oxygen mobility

within the ceria lattice, preventing water molecules from occupying CO_2 adsorption sites; and (iii) the Ni/CeO_2 surface resists the buildup of carbon-containing species, enabling continuous CO_2 adsorption and dissociation. Conversely, $\text{Ni}/\text{Al}_2\text{O}_3$ faces challenges as all reaction steps occur on the same active sites, leading to delayed CO_2 adsorption due to slow water release and the accumulation of surface formats. The reaction pathways for CO_2 methanation on both supports are presented in Fig. 14a. Regardless of the well-explored role of oxygen vacancies in the metal oxide supports, Beniwal *et al.* revealed the merits of oxygen vacancies in the active metal for CO_2 methanation.¹⁴ A novel heterogeneous catalyst, $\text{NiFe}-\text{TiO}_2$, featuring oxygen vacancy-enriched atomic Fe-oxide clusters confined within TiO_2 -supported Ni-hydroxide, was developed using a wet chemical reduction method (Fig. 14b). This catalyst exhibited exceptional CH_4 productivity of $\sim 24\,358\text{ mmol g}^{-1}\text{ h}^{-1}$ at $300\text{ }^\circ\text{C}$, nearly doubling the performance of $\text{Ni}-\text{TiO}_2$ ($12\,481\text{ mmol g}^{-1}\text{ h}^{-1}$) by $\sim 95\%$. It also demonstrated remarkable durability, achieving a peak productivity of $\sim 36\,399\text{ mmol g}^{-1}\text{ h}^{-1}$ with 90.5% CH_4 selectivity after 116 cycles (155 hours) and maintaining stability over 220 cycles (330 hours). Mechanistic studies revealed that oxygen vacancies in Fe-oxide clusters and adjacent Ni-hydroxide domains synergistically enhance CO_2 activation and H_2 dissociation, enabling efficient methanation kinetics. These findings highlighted the critical role of oxygen vacancies in improving catalytic performance and pave the way for designing advanced catalysts for various applications.

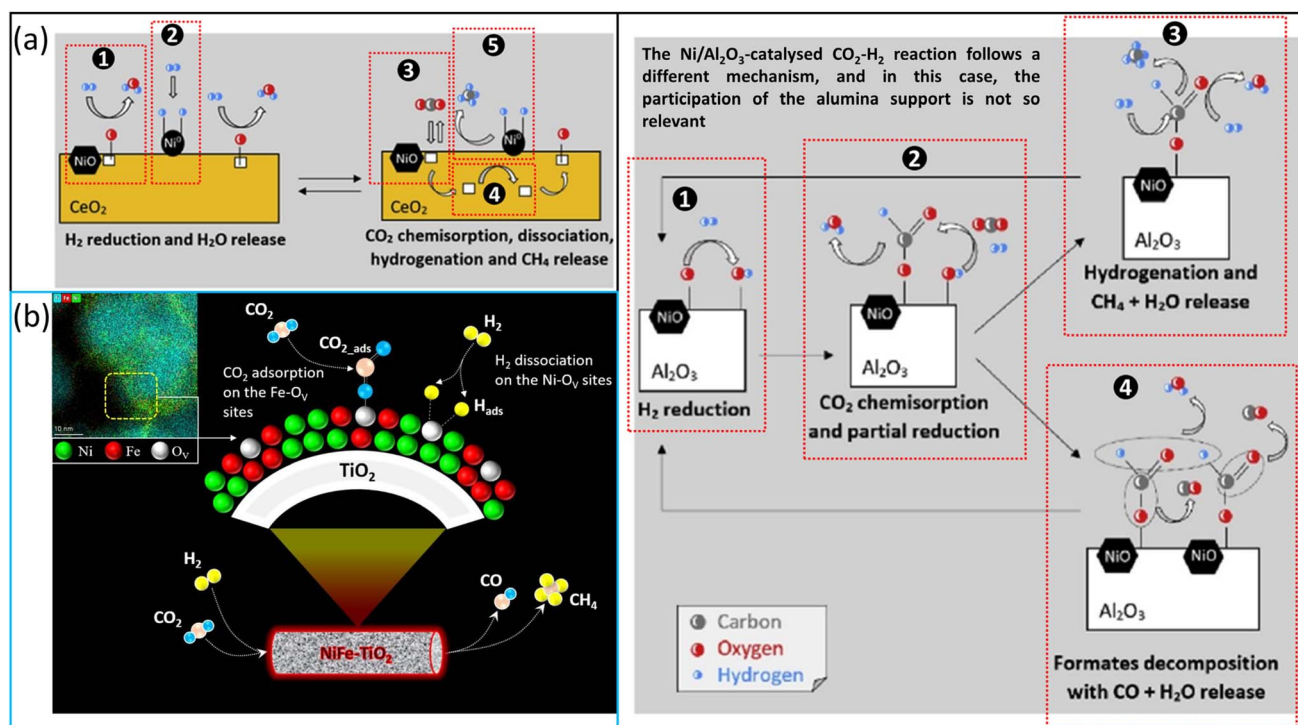


Fig. 14 The CO_2 methanation reaction pathways on (a) CeO_2 and Al_2O_3 support (this figure has been reproduced from ref. 112 with permission from Elsevier, copyright 2020). (b) The schematic representation of $\text{NiFe}-\text{TiO}_2$ catalyst (this figure has been reproduced from ref. 14 with permission from Elsevier, copyright 2024).



5. *In situ* characterization techniques for unveiling the CO₂ methanation reaction pathway

In situ characterization techniques play a pivotal role in uncovering the intricate reaction mechanisms of CO₂ methanation, providing real-time insights into the dynamic changes occurring on catalyst surfaces under reaction conditions. Advanced methods such as *in situ* X-ray absorption spectroscopy (XAS) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) enable the investigation of oxidation states and electronic structures of active sites. Additionally, techniques like diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) allow the identification of surface-adsorbed intermediates, revealing the sequential steps of CO₂ activation and hydrogenation. Combining these tools with *operando* setups further bridges the gap between experimental observations and catalytic performance, offering a comprehensive understanding of reaction pathways. This detailed knowledge is instrumental for rational catalyst design, enabling the optimization of activity, selectivity, and durability for efficient CO₂ conversion. The more details about aforementioned technologies are given in following section.

5.1. *In situ* X-ray absorption spectroscopy (XAS)

In situ XAS is a powerful tool for investigating the dynamic structural and electronic changes occurring in catalysts during CO₂ methanation. By providing element-specific insights into oxidation states, local atomic environments, and coordination changes under reaction conditions, *in situ* XAS enables a deeper understanding of the active sites and reaction intermediates.¹⁴ For instance, it can reveal the role of reducible metal oxides or metal-support interactions by tracking the evolution of oxidation states and structural transformations in real-time. This information is crucial for elucidating reaction mechanisms, identifying active phases, and optimizing catalyst design to enhance performance and durability in CO₂ methanation. Beniwal *et al.* used *in situ* XAS analysis to reveal the potential synergy between oxygen vacancies, Ni and Fe sites during CO₂ methanation.¹⁴ Insights gained from *in situ* XAS and ambient pressure X-ray photoelectron spectroscopy revealed critical performance descriptors and reaction pathways. These studies highlighted the synergistic role of oxygen vacancies within atomic Fe-oxide clusters and adjacent Ni-hydroxide domains in facilitating both CO₂ activation and H₂ dissociation. This synergy effectively supports the seamless progression of intermediate steps, significantly enhancing the kinetics of CO₂ methanation on the NiFe-TiO₂ catalyst surface.

5.2. Ambient pressure X-ray photoelectron spectroscopy (APXPS)

The APXPS is a powerful tool for probing surface chemistry and reaction mechanisms during CO₂ methanation under near-operational conditions. It provides real-time insights into the electronic states and chemical interactions at the catalyst

surface, enabling the identification of key intermediates and reaction pathways. APXPS helps elucidate how active sites, such as metal-support interfaces or oxygen vacancies, facilitate CO₂ activation and hydrogen dissociation. By tracking surface species and their evolution, this technique offers valuable information for optimizing catalyst design and improving overall methanation efficiency. For instance, Yan *et al.* used APXPS analysis to reveal the synergistic collaboration between adjacent reaction sites of Ni and Pd for CO₂ methanation.¹¹³ A hierarchically structured bimetallic nanocatalyst (NC), designated as NiOTPd-T, has been developed through a methodical process involving sequential metal ion adsorption followed by wet chemical reduction on a carbon nanotube support. This nanocatalyst features metallic Pd nanoclusters in proximity to locally tetrahedral symmetric Ni-oxide and is further modified with a thin tetramethyl orthosilicate (TMOS) layer. Utilizing a combination of structural characterization techniques, *in situ* ambient pressure X-ray photoelectron spectroscopy, and gas chromatography-mass spectrometry, the NiOTPd-T catalyst demonstrated a remarkable methane production yield of 1905.1 mmol g⁻¹ at 573 K, exceeding TMOS-decorated Pd-only catalysts (Pd-T) by over tenfold. This exceptional performance is attributed to the synergistic interaction between CO adsorption on Pd atoms and hydrogen dissociation on both Pd and Ni atoms at the interface. This collaboration activates a chain of reactions where the reduction of NiOT increases metallic Ni sites, further enhancing hydrogen splitting and optimizing methane production. Notably, the unique epitaxial arrangement of Pd and NiOT in the NiOTPd-T catalyst delivers an unparalleled methane production yield among comparable catalysts with similar compositions and loadings, making it a benchmark for catalytic efficiency in this domain. Furthermore, in another study, they revealed the interplay between oxygen vacancies and surface silicide using APXPS for enhanced CO₂ methanation.²⁰

5.3. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

The *in situ* DRIFTS plays a crucial role in studying CO₂ methanation by providing real-time insights into surface species and reaction intermediates.¹¹² By directly monitoring the catalyst surface during reaction, DRIFTS allows for the identification and characterization of key reaction intermediates, such as formates or carbonates, and the evolution of surface-bound species. This enhances the understanding of the reaction mechanism, facilitates the optimization of catalyst properties, and helps in improving the efficiency of CO₂ conversion to methane. The ability to perform *in situ* measurements under reaction conditions ensures more accurate, dynamic data compared to *ex situ* techniques, providing valuable information for catalyst design and process development.

5.4. *In situ* Raman spectroscopy

In situ Raman spectroscopy offers unique insights into the molecular transformations occurring on the catalyst surface during reaction conditions, providing real-time, non-



destructive analysis. The process involves the interaction of CO₂ with H₂ over a catalyst surface, typically transition metals or metal oxides, under controlled temperature and pressure conditions. Raman spectroscopy, through its ability to probe vibrational modes of molecules and surface intermediates, enables the identification of active sites, reaction intermediates, and the determination of reaction pathways. CO₂ methanation *via in situ* Raman spectroscopy involves several key steps and considerations.¹¹⁴ Firstly, during the initial adsorption of CO₂ and H₂ on the catalyst surface, Raman spectra can reveal changes in vibrational frequencies that indicate the formation of adsorbed species such as CO₂^{*}, CO^{*}, and H^{*}. These species act as precursors to subsequent reaction steps. As the reaction progresses, monitoring changes in these vibrational modes can elucidate the kinetics of surface reactions, including the formation of CH₄ and water. Moreover, *in situ* Raman spectroscopy provides invaluable information on catalyst stability and deactivation mechanisms. By continuously monitoring changes in spectra during prolonged reaction times, researchers can identify catalyst poisoning or structural changes that lead to reduced activity or selectivity. This capability is critical for designing more robust and efficient catalyst materials for CO₂ methanation processes. Several studies have utilized *in situ* Raman spectroscopy to investigate CO₂ methanation on various catalyst systems. For example, research by Mutz *et al.* demonstrated the use of *in situ* Raman spectroscopy to track the formation of CH₄ and CO intermediates on Ni-based catalysts.¹¹⁵ The study highlighted the role of surface morphology and metal-support interactions in influencing catalytic performance. Similarly, work by Gao *et al.* employed Raman spectroscopy to study the role of surface defects on ruthenium-based catalysts in the CO₂ methanation.¹¹⁶ In summary, *in situ* Raman spectroscopy serves as a powerful tool for advancing our understanding of CO₂ methanation processes by providing detailed molecular-level insights into catalyst behavior, reaction mechanisms, and kinetics. Its ability to monitor surface species and reaction intermediates in real time contributes significantly to the development of efficient catalysts for sustainable CO₂ conversion technologies. Future research directions may focus on further enhancing the sensitivity and spatial resolution of Raman spectroscopy techniques to explore complex catalyst systems and optimize process parameters for enhanced CO₂ utilization and methane production.

6. Photocatalytic CO₂ methanation: a sustainable alternative to thermal CO₂ methanation

6.1. Introduction

The conversion of CO₂ into CH₄ is a promising approach to mitigating greenhouse gas emissions and producing a renewable energy carrier. While thermal CO₂ methanation, commonly known as the Sabatier reaction, has been widely studied and industrially implemented, its reliance on high temperatures (200–500 °C) imposes significant energy and economic costs. In

contrast, photocatalytic CO₂ methanation offers a sustainable alternative by utilizing solar energy to drive the reaction under mild conditions, reducing the dependency on fossil fuel-derived heat sources.^{117–125} This section explores the mechanisms, catalysts, and recent advancements in photocatalytic CO₂ methanation and how it compares with its thermal counterpart.

6.2. Comparison between thermal and photocatalytic CO₂ methanation

Thermal CO₂ methanation, which was discussed in the previous section, typically employs transition-metal-based catalysts such as nickel (Ni), or cobalt (Co) supported on oxides (*e.g.*, Al₂O₃, TiO₂, CeO₂).^{126–131} These catalysts facilitate CO₂ activation and hydrogenation to methane *via* a surface-mediated reaction mechanism. *In situ* Raman spectroscopy has proven to be an essential tool in studying reaction intermediates, active sites, and catalyst stability under thermal conditions. In contrast, photocatalytic CO₂ methanation relies on the absorption of solar photons to generate electron-hole pairs in semiconductor catalysts, which subsequently drive CO₂ reduction and H₂ oxidation reactions. This process occurs at ambient temperatures and pressures, making it a greener and more energy-efficient alternative. However, the reaction efficiency and selectivity are often limited by issues such as low photon absorption, fast charge recombination, and insufficient catalyst stability.

6.3. Mechanism of photocatalytic CO₂ methanation

The mechanism of photocatalytic CO₂ methanation can be divided into the following key steps:

- (1) Photon absorption: a semiconductor photocatalyst absorbs light with energy equal to or greater than its bandgap, generating excited electron-hole pairs.
- (2) Charge separation and transfer: the photoexcited electrons migrate to the conduction band while the holes remain in the valence band. Effective charge separation is crucial for preventing recombination, which reduces photocatalytic efficiency.
- (3) Surface reactions: the excited electrons reduce CO₂ adsorbed on the catalyst surface through intermediate species such as CO₂^{•-}, CO, and HCOO⁻. Simultaneously, hydrogen oxidation or water splitting occurs *via* hole-mediated reactions.
- (4) Methane formation: successive proton-coupled electron transfer steps lead to the formation of CH₄ as the final product, along with possible by-products such as CO and H₂.

6.4. Catalyst development for photocatalytic CO₂ methanation

The choice of photocatalyst is critical for achieving high activity and selectivity in CO₂ methanation. Some of the most studied photocatalysts include:

6.4.1. TiO₂-based photocatalysts. Titanium dioxide (TiO₂) is one of the most widely explored photocatalysts due to its stability, non-toxicity, and abundance. However, its wide bandgap (~3.2 eV) limits its absorption to the UV region (~5%



of the solar spectrum). To enhance its performance, researchers have employed strategies such as:

(i) Doping with metals (*e.g.*, Ni, Cu, or Ru) and non-metals (*e.g.*, N, C, S) to extend light absorption into the visible region.

(ii) Coupling with plasmonic nanoparticles (*e.g.*, Au, Ag) to improve charge transfer and enhance localized surface plasmon resonance (LSPR).

(iii) Surface modification with oxygen vacancies and co-catalysts (*e.g.*, Pt, Ru) to enhance CO₂ activation.

6.4.2. Perovskite photocatalysts. Perovskite materials such as LaCoO₃ and SrTiO₃ have gained attention due to their tunable electronic properties and excellent charge transport characteristics. These materials exhibit strong visible light absorption and can be further optimized by:

(i) Substituting A- or B-site cations (*e.g.*, La → Ce, Co → Ni) to modulate electronic structure.

(ii) Incorporating heterojunctions with TiO₂ or g-C₃N₄ to enhance charge separation.

6.4.3. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). MOFs and COFs are emerging photocatalysts due to their high surface area, tunable porosity, and ability to anchor active metal sites. For example, Ru-based MOFs have shown high selectivity for methane formation under visible light irradiation. However, their stability remains a challenge, necessitating the development of hybrid structures with stable inorganic supports.

6.4.4. Graphitic carbon nitride (g-C₃N₄). Graphitic carbon nitride (g-C₃N₄) has attracted interest due to its narrow bandgap (~2.7 eV), allowing visible light absorption. It can be further modified through:

(i) Heterojunction formation with other semiconductors like TiO₂, ZnO, and MoS₂.

(ii) Doping with heteroatoms such as boron (B) or phosphorus (P) to enhance conductivity.

(iii) Loading with transition metal nanoparticles (*e.g.*, Ni, Ru) to improve catalytic activity.

6.5. Challenges and future perspectives

Despite the potential of photocatalytic CO₂ methanation, several challenges hinder its widespread implementation:¹³²

(i) Low quantum efficiency: due to rapid charge recombination and limited light absorption, photocatalytic efficiency remains lower than thermal processes.

(ii) Selectivity issues: competing side reactions such as CO₂-to-CO reduction or H₂ evolution can reduce methane selectivity.

(iii) Long-term stability: many photocatalysts suffer from degradation over time, necessitating durable materials with strong resistance to photodegradation.

(iv) Scale-up and integration: industrial-scale implementation requires efficient light management strategies, reactor design optimization, and integration with renewable hydrogen production.

To address these issues, future research should focus on:

(i) Developing multi-component heterojunctions to facilitate charge separation.

(ii) Engineering catalysts with controlled defect structures for enhanced CO₂ adsorption.

(iii) Designing photoreactors that optimize photon utilization and heat management.

(iv) Integrating photocatalytic methanation with electrochemical and bio-catalytic approaches for hybrid CO₂ conversion systems.

In summary, photocatalytic CO₂ methanation presents a promising alternative to conventional thermal CO₂ methanation by leveraging solar energy to drive the reaction under ambient conditions. While thermal CO₂ methanation remains the most industrially viable process due to its high efficiency and well-established technology, advancements in photocatalyst design and light-harvesting strategies are steadily improving the feasibility of photocatalytic routes. Bridging the gap between these two approaches through hybrid thermal-photocatalytic systems could offer a pathway toward scalable and sustainable CO₂-to-CH₄ conversion technologies. Continued research into material innovation, reaction engineering, and process integration will be essential for realizing the full potential of photocatalytic CO₂ methanation in future energy and carbon management systems.

7. Density functional theory (DFT) approach for designing high-performance CO₂ thermal and photocatalysts

The development of efficient catalysts for CO₂ conversion, whether through thermal or photocatalytic pathways, requires a fundamental understanding of reaction mechanisms, active sites, and electronic structures. Density Functional Theory (DFT) has emerged as a powerful computational tool for designing and optimizing catalysts by providing atomistic insights into catalytic activity, stability, and selectivity.¹³³ By modelling the electronic structure of materials and their interactions with CO₂ and reaction intermediates, DFT enables researchers to tailor catalyst compositions and structures for enhanced performance.¹³⁴ This section discusses the role of DFT in designing high-performance CO₂ methanation catalysts, bridging thermal and photocatalytic processes.

7.1. DFT in thermal CO₂ methanation catalyst design

Thermal CO₂ methanation, often facilitated by transition metal catalysts such as Ni, Ru, and Co, involves multiple adsorption, dissociation, and hydrogenation steps. DFT plays a crucial role in predicting:

(1) Catalyst surface reactivity: by calculating adsorption energies of CO₂ and intermediates (CO, HCOO⁻, CH₃O⁻), DFT helps identify the most active surface facets and sites for CO₂ conversion.

(2) Activation energy and reaction pathways: transition state analysis allows the estimation of energy barriers for key reaction steps, guiding catalyst modification to lower activation energies.



(3) Metal–support interactions: DFT studies on metal-oxide interfaces (e.g., Ni/CeO₂, Ru/TiO₂) reveal charge transfer mechanisms and oxygen vacancy roles in enhancing catalytic activity.

(4) Poisoning and stability: computational modeling of sulfur, carbon, and oxygen interactions on catalyst surfaces aids in designing more resistant and durable catalysts.

7.2. DFT in photocatalytic CO₂ methanation

For photocatalytic CO₂ methanation, DFT is instrumental in designing semiconductor-based catalysts by optimizing their electronic structures for efficient light absorption and charge separation. Key contributions of DFT include:

(1) Band structure engineering: DFT helps in calculating bandgap energies and band edge positions, ensuring suitable alignment for CO₂ reduction and H₂ oxidation.

(2) Defect engineering: the role of surface defects, oxygen vacancies, and dopants in modifying charge carrier dynamics and adsorption properties can be systematically studied using DFT.

(3) Heterojunction design: interface modeling between semiconductors (e.g., TiO₂/g-C₃N₄, ZnO/MoS₂) predicts charge transfer efficiency, guiding the selection of materials for enhanced photocatalytic activity.

(4) Surface adsorption and reaction kinetics: by determining adsorption energies and reaction pathways of CO₂-derived intermediates, DFT provides insights into selectivity control and product formation mechanisms.

The integration of DFT with experimental studies, machine learning, and *in situ* spectroscopy will further accelerate the discovery of novel CO₂ methanation catalysts. Advanced simulations incorporating solvation effects, dynamic charge redistribution, and large-scale reaction networks will improve the predictive power of DFT. Hybrid computational approaches combining DFT with microkinetic modeling can offer more accurate insights into real-world catalytic performance, paving the way for next-generation high-efficiency catalysts. DFT-based computational modeling has revolutionized catalyst design for CO₂ methanation by offering atomic-level insights into reaction mechanisms and material properties. Its application in both thermal and photocatalytic systems enables the development of tailored catalysts with improved activity, stability, and selectivity. As computational power and algorithms continue to evolve, DFT-driven catalyst design will play an increasingly vital role in advancing CO₂ conversion technologies toward sustainable energy solutions.

8. Industrial applications of CO₂ methanation

CO₂ methanation has gained significant industrial interest as a key process for carbon capture and utilization (CCU), energy storage, and synthetic fuel production.¹³⁵ One of the most promising applications is power-to-gas technology, where surplus renewable electricity is used to produce hydrogen *via* water electrolysis, which is then combined with captured CO₂ to generate methane.¹³⁶ This methane, also known as synthetic

natural gas (SNG), can be directly injected into existing natural gas grids, providing a scalable solution for long-term energy storage and grid balancing. Several industrial-scale PtG plants have been established in Europe, such as Audi's e-gas facility in Germany, which produces renewable methane for transportation applications.

Another critical application of CO₂ methanation is in biogas upgrading, where CO₂ present in raw biogas is converted into methane, increasing its calorific value and making it compatible with natural gas infrastructure.¹³⁷ This approach enhances the efficiency of biogas utilization by maximizing methane yield while simultaneously reducing greenhouse gas emissions. Industrial biogas upgrading systems employing catalytic methanation have been developed to produce high-purity biomethane, which can be used as a sustainable fuel for power generation and transportation. CO₂ methanation also plays a vital role in closed-loop carbon recycling for space and aerospace applications. For instance, the Sabatier process is integrated into the International Space Station (ISS) to convert astronaut-exhaled CO₂ into methane and water, with the latter being recycled for life-support systems. This concept is being explored for future Mars missions, where *in situ* resource utilization (ISRU) could enable methane production for rocket fuel using Martian CO₂ and hydrogen from water electrolysis. Additionally, methane production *via* CO₂ methanation is gaining traction in industrial sectors looking to decarbonize operations, particularly in steel, cement, and chemical manufacturing. By capturing CO₂ emissions from these industries and converting them into methane, companies can create a circular carbon economy while reducing reliance on fossil fuels. Furthermore, the synthesized methane can be utilized as a feedstock for further chemical synthesis, including the production of methanol and higher hydrocarbons *via* Fischer-Tropsch processes. In summary, CO₂ methanation is emerging as a pivotal technology in multiple industrial sectors, enabling sustainable energy storage, low-carbon fuel production, and carbon recycling. Continued advancements in catalyst development, reactor design, and integration with renewable energy sources will further enhance its commercial viability and environmental benefits.

9. Summary and outlook

The increasing concentration of CO₂ in the atmosphere and its role as a primary driver of climate change have underscored the urgent need for technologies that enable efficient CO₂ conversion and utilization. Among these, CO₂ methanation offers a promising route to produce methane, a clean and energy-dense fuel, while simultaneously reducing atmospheric CO₂ levels. Over the past decades, significant advancements have been made in designing catalysts to enhance the efficiency, selectivity, and stability of the CO₂ methanation process. Key developments in catalyst design strategies have revolved around optimizing active metal components, supports, and promoter elements to achieve superior catalytic performance. Nickel-based catalysts, owing to their cost-effectiveness and high activity, have been widely explored. The incorporation of



secondary metals, such as cobalt, iron, and noble metals (e.g., Ru, Rh, Pd), has led to the development of bimetallic and multimetallic catalysts that exhibit synergistic effects, including enhanced reducibility, better dispersion, and improved resistance to deactivation. The role of support materials, such as CeO_2 , Al_2O_3 , TiO_2 , ZrO_2 , and SiO_2 , has also been extensively studied. Supports contribute significantly to catalytic activity by influencing metal dispersion, providing structural stability, and facilitating the adsorption and activation of CO_2 and H_2 . Reducible oxides like CeO_2 and ZrO_2 have garnered particular attention due to their ability to generate oxygen vacancies, which act as active sites for CO_2 activation and intermediate stabilization. Furthermore, the interaction between active metals and support materials plays a crucial role in determining catalytic performance, as demonstrated in Ni/CeO_2 and $\text{Ni/Al}_2\text{O}_3$ systems. Promoters, such as alkali and alkaline earth metals, have been employed to fine-tune catalyst properties. These promoters enhance CO_2 adsorption, alter electronic properties, and improve the reducibility of active metal species, leading to better catalytic efficiency. For example, the addition of potassium and magnesium has been shown to boost CO_2 adsorption while suppressing undesirable side reactions. The development of novel synthesis techniques has further refined catalyst design. Methods such as co-precipitation, sol-gel synthesis, impregnation, and chemical vapor deposition have been utilized to control the morphology, particle size, and distribution of active metal species. Advanced strategies like the use of ordered mesoporous supports, core-shell structures, and atomically dispersed catalysts have yielded materials with enhanced catalytic activity, stability, and resistance to sintering and coking. Mechanistic insights gained through advanced characterization techniques, including *in situ* X-ray absorption spectroscopy (XAS), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and transmission electron microscopy (TEM), have deepened our understanding of the CO_2 methanation process. These studies have elucidated reaction pathways, identified key intermediates, and highlighted the importance of oxygen vacancies, metal-support interactions, and the role of formate and carbonate species in the reaction mechanism. Despite these advancements, several challenges remain. Catalyst deactivation due to sintering, carbon deposition, and sulfur poisoning poses significant barriers to long-term operation. Additionally, the optimization of reaction conditions, such as temperature, pressure, and H_2/CO_2 ratios, is crucial to maximize methane selectivity and yield.

The future of catalyst design for CO_2 methanation lies in addressing current challenges and leveraging emerging technologies to develop robust, efficient, and scalable catalytic systems. Below are key areas for future research and development:

(1) Advanced catalyst architectures:

○ The design of catalysts with hierarchical structures, such as core-shell and yolk-shell architectures, can enhance active site accessibility and prevent sintering and coking.

○ The use of atomically dispersed catalysts and single-atom alloys offers potential for achieving maximum atom efficiency and exceptional catalytic performance.

(2) Exploration of novel materials:

○ Beyond traditional supports, the exploration of materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hybrid systems can open new avenues for catalyst development.

○ Transition metal carbides and nitrides, with their unique electronic properties, represent promising alternatives to conventional catalysts.

(3) Tailored oxygen vacancy engineering:

○ Precise control over oxygen vacancy generation in reducible supports like CeO_2 and ZrO_2 can further enhance CO_2 activation and intermediate stabilization.

○ Strategies to stabilize oxygen vacancies under reaction conditions will be crucial for long-term catalyst durability.

(4) Integration of computational and experimental approaches:

○ The use of density functional theory (DFT) calculations and machine learning algorithms can accelerate the discovery of new catalyst compositions and optimize reaction conditions.

○ High-throughput screening techniques can complement computational studies, enabling rapid identification of promising candidates.

(5) Improved resistance to deactivation:

○ Developing catalysts with enhanced resistance to sintering, coking, and poisoning by sulfur and other impurities will be vital for industrial applications.

○ Coating active sites with protective layers or incorporating self-regenerative mechanisms can prolong catalyst lifespan.

(6) Mechanistic understanding and *operando* studies:

○ Advanced *in situ* and *operando* characterization techniques will continue to play a pivotal role in unraveling reaction mechanisms and identifying active sites.

○ The development of techniques that allow real-time monitoring of catalytic processes under industrially relevant conditions will bridge the gap between fundamental research and practical applications.

(7) Energy efficiency and sustainability:

○ Coupling CO_2 methanation with renewable hydrogen production (e.g., *via* water electrolysis powered by solar or wind energy) will enhance the sustainability of the process.

○ Exploring catalysts that operate efficiently at lower temperatures and pressures can reduce energy consumption and operational costs.

(8) Scale-up and industrial implementation:

○ Translating laboratory-scale findings to industrial-scale processes requires the development of robust catalysts that maintain performance under high space velocities and prolonged operation.

○ Collaboration between academia, industry, and policy-makers will be essential to overcome barriers to commercialization.

(9) Integration into carbon utilization pathways:

○ CO_2 methanation can be integrated into broader carbon utilization frameworks, such as synthetic natural gas (SNG) production, power-to-gas technologies, and carbon capture and utilization (CCU) systems.



○ Developing multi-functional catalysts capable of co-converting CO₂ with other waste streams (e.g., CO, syngas, or biomass-derived intermediates) can enhance process versatility.

(10) Environmental and economic assessment:

○ Life cycle assessment (LCA) and techno-economic analysis (TEA) will be crucial for evaluating the environmental and economic viability of CO₂ methanation technologies.

○ Identifying cost-effective and scalable synthesis methods for catalyst production will be key to enabling widespread adoption.

10. Conclusion

Catalyst design strategies for CO₂ methanation have made significant strides in recent years, offering promising solutions for both CO₂ utilization and methane production. CO₂ methanation, the process of converting carbon dioxide into methane (CH₄) through a reaction with hydrogen (H₂), is a key component in the broader quest for carbon-neutral energy solutions. Methane, as a natural gas, is an energy carrier with a relatively high energy density and can be used in a variety of applications, including power generation, transportation, and heating. However, the transition to a more sustainable energy system requires the efficient and scalable conversion of CO₂ into methane, and this depends largely on the development of advanced catalysts. Over the years, catalytic systems have evolved to improve both activity and selectivity in CO₂ methanation. Early catalysts, such as nickel-based and cobalt-based systems, were widely studied due to their low cost and relatively good performance. However, these catalysts often suffer from limitations such as deactivation over time, low resistance to sintering, and reduced efficiency under reaction conditions. Newer approaches have focused on improving catalyst stability, enhancing CO₂ adsorption properties, and fine-tuning the reaction mechanism to reduce side reactions like reverse water-gas shift (RWGS), which produces CO and limits the overall methane yield. One of the most promising strategies for next-generation catalyst development is the incorporation of bimetallic and alloy catalysts. These catalysts, which typically involve a combination of metals like nickel with transition metals such as copper, palladium, or platinum, offer enhanced performance by providing synergistic effects that improve the activation of CO₂ and H₂. By fine-tuning the electronic and geometric properties of the metal surfaces, these bimetallic systems can achieve higher CO₂ conversion rates while maintaining long-term stability. Additionally, advances in nanostructuring, such as the creation of smaller particle sizes or the development of core-shell structures, help maximize surface area and increase catalytic activity. Another exciting avenue for catalyst design lies in the use of metal-organic frameworks (MOFs) and other porous materials. These materials can be engineered to provide a high surface area for CO₂ adsorption and activation, making them excellent candidates for catalysis. MOFs, in particular, offer a high degree of tunability, with specific pore sizes and functional groups that can be tailored for optimal CO₂ interaction. *In situ* techniques such as Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) are critical in

understanding how these catalysts interact with CO₂ and H₂ at the atomic level, helping to refine their performance and ensure more efficient reactions. Furthermore, interdisciplinary approaches combining catalysis with advances in renewable energy and carbon capture technologies are helping to accelerate the development of CO₂ methanation as a commercially viable process. For example, integrating CO₂ methanation with renewable energy sources like solar, wind, or biomass-derived hydrogen creates a sustainable cycle in which excess renewable energy can be stored in the form of methane. This creates an effective energy storage solution, addressing the intermittency issues associated with renewable energy sources. Additionally, coupling CO₂ methanation with carbon capture systems allows for the direct utilization of CO₂ from industrial emissions, helping mitigate climate change by reducing atmospheric CO₂ concentrations. The integration of these advancements holds immense potential to transform CO₂ methanation into a cornerstone technology for a sustainable and circular carbon economy. With further research and innovation, these technologies could significantly reduce greenhouse gas emissions and provide a scalable pathway for mitigating climate change. The development of efficient and robust catalysts will enable the conversion of waste CO₂ into a valuable energy resource, contributing to a circular carbon economy where carbon is continuously recycled and utilized rather than emitted into the atmosphere. In conclusion, the continuous advancements in catalyst design, coupled with innovative interdisciplinary approaches, are creating a new era for CO₂ methanation. The synergy between CO₂ conversion, renewable energy, and carbon capture technologies will not only drive the development of more efficient and sustainable catalysts but also pave the way for a greener, more sustainable future where CO₂ can be captured, converted, and reused as a valuable resource. The path forward promises a significant step toward achieving a sustainable, low-carbon economy and addressing global climate challenges.

Data availability

No new data were generated or analysed as part of this review.

Conflicts of interest

The authors declare no conflict of interest.

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