

Research progress on special structure catalysts for dry reforming of methane with carbon dioxide

LI Pengyang^{1,3}, TIAN Jinglei^{2,3}, HAN Xing^{1,3}, LIU Hongqiang^{1,3,*}

¹ HBIS Materials Technology Research Institute, Shijiazhuang 050023, China;

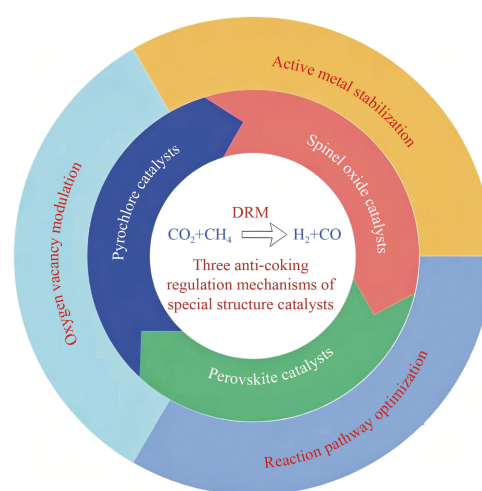
² HBIS Group Co., Ltd., Shijiazhuang 050000, China;

³ China-Serbia "Belt and Road" Joint Laboratory of Green Steel Manufacturing, Shijiazhuang 050023, China

Abstract: The continuous increase in greenhouse gas emissions is seriously threatening the human living environment. Dry reforming of methane (DRM) can convert carbon dioxide and methane into syngas which can be further used to produce value-added chemicals, providing an excellent solution for greenhouse gas mitigation. At present, dry reforming of methane confronts with issues such as carbon deposition and sintering of active sites, etc. Therefore, ideal catalysts should possess the dual advantages of inhibiting carbon deposition and maintaining high stability at high temperatures, which is the core challenge in catalyst design. Complex oxide materials with special structures have received extensive attention due to the excellent thermal stability, adjustable surface properties and the ability to incorporate metal cations into the lattice structure. In this review, the thermodynamic characteristics, reaction mechanisms and catalyst deactivation mechanisms of methane dry reforming are summarized.

Subsequently, the features of special-structured pyrochlore, spinel oxide and perovskite catalysts, as well as their research progress are systematically reviewed. Meanwhile, centered on the three regulation mechanisms of active metal stabilization, oxygen vacancy modulation and reaction pathway optimization, the structure-activity relationships between crystal structure, strong metal-support interaction (SMSI), oxygen vacancies and other factors and the anti-coking and anti-sintering properties of catalysts are elaborated. Finally, future research directions of special structure catalysts for DRM are prospected.

Key words: dry reforming of methane; reaction mechanisms; deactivation mechanism; anti-coking regulation; special structure catalysts



The rapid development of industry and the surging demand for fossil fuels have led to continuous rise in atmospheric CO₂ concentration, posing a serious threat to the environment^[1-2]. To address this challenge, 195 countries signed the Paris Agreement in 2025 to restrict the greenhouse gas emissions, marking an imminent major transformation in the energy sector^[3]. CCUS technologies and the synthesis processes of value-added chemicals have thus become the focus of attention in the low-carbon field^[4].

CO₂ and CH₄ are the primary greenhouse gases driving global climate change^[5]. DRM technology serves as an optimal approach that could convert CO₂ and CH₄ into syngas with H₂/CO molar ratio close to 1:1, particularly

suitable for producing value-added chemicals through Fischer-Tropsch synthesis^[6-7]. The technology was firstly proposed by Fisher et al.^[8] in 1928. Since then, researchers have successively developed a variety of high-performance catalyst systems based on metals including Pt, Ir, Ru, Rh and Co. However, the high cost limits the industrial application and the carbon deposition caused by methane decomposition during the reaction seriously impairs the catalyst activity. The DRM reaction requires high-temperature to achieve completely conversion which further aggravates the carbon deposition as well as the sintering of active sites^[9]. Hence, a desirable catalyst is required to possess two key merits: suppressing carbon deposition from

Received: 2026-03-16; Revised: 2026-04-29

Foundation items: Supported by the National Key Research and Development Program (2024YFE0215000).

* Corresponding author. Tel: 15128191032, E-mail: liuhongqiang@hbisco.com.

DOI: 10.3724/2097-213X.2026.JFCT.0010 CSTR: 32157.14.2097-213X.2026.JFCT.0130

the thermodynamic perspective and retaining long-term durability at high temperatures, which are the central challenges in catalyst design. At present, complex oxide materials with unique structures, such as pyrochlores, spinel oxides and perovskites, also referred to reduced solid solution catalysts, have attracted extensive attention due to the excellent catalytic performance. Therefore, the thermodynamic characteristics, reaction mechanisms and catalyst deactivation mechanisms, as well as the recent research progress of pyrochlore, spinel oxide and perovskite catalysts for DRM reaction are summarized in this review. In addition, focusing on three core regulation mechanisms including active metal stabilization, oxygen vacancy modulation and reaction pathway optimization, the effects of crystal structure, SMSI and oxygen vacancies of special structure catalysts on their anti-coking performance are systematically analyzed to provide theoretical guidance for the design and development of novel high-efficiency anti-coking catalysts.

1 Investigation of DRM

1.1 Thermodynamic analysis

The DRM reaction is relatively slow that requires a great quantity of energy in the form of heat to break the CO₂ and CH₄ molecules with decomposition energies of 439 and 750 kJ/mol, respectively^[10]. The main reactions are presented in Table 1. It can be seen that except for CO disproportionation (Eq. 4) and CO₂ hydrogenation (Eq. 5), the remaining are highly endothermic, suggesting that the DRM reaction proceeds effectively only under high-temperature. The ideal H₂/CO molar ratio of 1:1 fits with downstream processes such as Fischer-Tropsch synthesis and methanol production while supporting carbon utilization and economic viability. However, the reverse water-gas shift (RWGS) reaction (Eq. 2) promotes the CO₂ conversion and lowers the molar ratio to less than 1^[11–12]. Equally, a ratio higher than 1 specifies a quicker methane decomposition than coke gasification which leads to catalyst deactivation^[13]. CO disproportionation (Eq. 4) and methane cracking (Eq. 6) are the main causes of carbon deposition, which occurs at 550–700 °C. Meanwhile, CO₂

hydrogenation (Eq. 5) can also induce coking^[14]. Accordingly, the reaction temperature should be maintained above 700 °C, at which the occurrence probabilities of CO disproportionation, methane cracking and RWGS reactions decrease remarkably^[15]. As displayed in the thermodynamic equilibrium plot of DRM reaction (Figure 1), the H₂/CO molar ratio approaches 1 at above 625 °C. Complete conversion of CH₄ and CO₂ along with an H₂/CO molar ratio close to 1 can be realized at temperatures over 900 °C, demonstrating that elevated temperature inhibits the side reactions and carbon deposition. Since the DRM reaction features an increase in total molecular moles, low pressure favors high conversion of CH₄ and CO₂ with 1 atm being the optimal, whereas elevated pressure promotes the RWGS reaction and lowers the H₂/CO molar ratio^[16].

Owing to the complexity of the DRM reaction, the H₂/CO molar ratio is also correlated with the CO₂/CH₄ molar ratio and their distinct activation rates. The ideal H₂/CO molar ratio of 1 can only be achieved when the CH₄/CO₂ molar ratio is approximately 1^[15,17]. Slow activation of CO₂ leads to a higher H₂/CO molar ratio. While accelerated CO₂ activation reduces this ratio, and residual oxygen atoms tend to form water as by-product^[18].

1.2 DRM reaction mechanisms

DRM is a complex reaction with multiple pathways. So, an in-depth understanding of the reaction mechanisms and structure-activity relationship are crucial for designing high-efficiency catalysts. The reaction pathways are closely associated with the surface microenvironment of catalysts. Differences in catalyst surface properties and reaction conditions can alter the involved intermediates, and thus no general mechanism is applicable to all catalytic systems. Methane activation undergoes four consecutive dehydrogenation steps. CH₄ is adsorbed on the catalyst surface, where the C–H bonds are broken sequentially to generate CH_x* species (x=0–3)^[19]. Because of the high bond energy of C–H bonds, methane activation is difficult. Furthermore, the dissociation rate increases with increasing temperature, with methane activation representing the rate-controlling step of the reaction^[10,20].

Table 1 Main reactions in methane dry reforming

No.	Reactions	Reaction equation	$\Delta H_{298K}/(\text{kJ} \cdot \text{mol}^{-1})$
1	Dry reforming of methane	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{H}_2 + 2\text{CO}$	247.0
2	Reverse water gas shift	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$	41.0
3	CO Hydrogenation	$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	284.0
4	CO disproportionation	$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	–172.4
5	CO ₂ Hydrogenation	$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	–90.0
6	Methane cracking	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	75.0

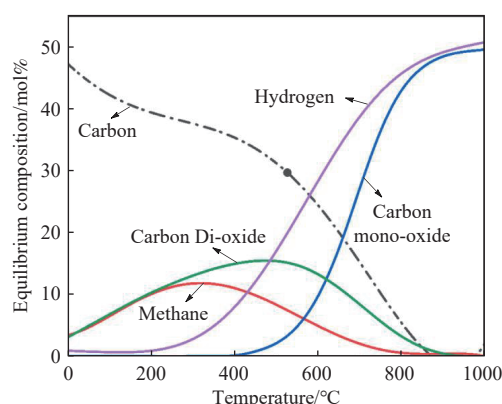


Fig. 1 Thermodynamic equilibrium plot for DRM at 1 bar using stoichiometric feeds^[9] (with permission from Elsevier)

The high C=O bond energy in CO₂ leads to activation difficulty compared with methane dissociation. However, given the inherent acidity of CO₂ molecules, catalysts constructed with basic supports can efficiently realize its adsorption and activation. Consequently, CO₂ activation is more facile than methane activation on the catalysts with specific physicochemical properties. Currently, there are three identified pathways for CO₂ dissociation (pathway 1–3). Pathway 1 shows direct dissociation of CO₂ adsorbed on the catalyst into CO and O. The other two are H-induced activation, which induced by adsorbed hydrogen species, namely CO₂*+H*→COOH*+*→CO*+OH* (pathway 2) and CO₂*+H*→HCOO*+*→CHO*+O* (pathway 3)^[20–22]. Subsequently, the CH₃*, CH₂* and CH* intermediates generated from CH₄ dissociation can be oxidized by adsorbed oxygen radicals (O*) or hydroxyl radicals (OH*) to form CHO_x* species, which further decompose into CO and H₂^[19,23–24]. Reaction steps of DRM process are illustrated in Figure 2 which involves several key steps: (1) the chemical adsorption and dissociation of CH₄ at the interface between the metal and support, (2) the chemical adsorption and dissociation of CO₂ at the interface between the metal and support, (3) the spillover of hydrogen and oxygen to form surface hydroxyls and (4) the oxidation of CH_x* species by surface hydroxyls and oxygens to generate CH_xO* followed by decomposition into H₂ and CO.

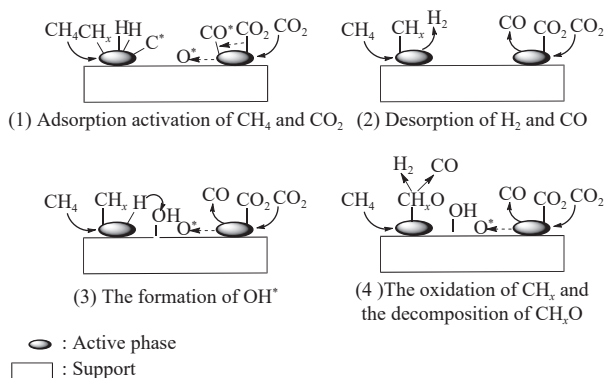


Fig. 2 Reaction steps of DRM process

1.3 Catalyst deactivation mechanisms

Except for mechanical damage, DRM catalysts deactivation can be categorized into three types: carbon deposition, sintering and poisoning^[28]. Among these, carbon deposition and high-temperature sintering are the core factors restricting the long-term operation of the catalysts.

The main sources of carbon deposition in DRM include CH₄ cracking, CO disproportionation, and CO₂ hydrogenation etc. Side reactions can lead to the accumulation of carbon on the surface of catalyst, which gradually covers and poisons the active sites and degrades the catalytic performance. Severe carbon deposition can block the reaction tubes and increase the pressure of the catalyst bed^[29]. In the temperature range of 550–700 °C, CH₄ cracking and CO disproportionation proceed simultaneously, resulting in severe carbon deposition. By contrast, CH₄ cracking dominates carbon formation at temperatures above 700 °C^[30]. Table 2 summarizes the types of carbon materials and their formation temperatures during the reactions. Generally, according to the differences in the activity of carbon species, carbon deposition can be classified into three types: (1) adsorbed atomic carbon (highly active carbon, C_α) which can be removed by reacting with oxygen or hydrogen or subsequent CO₂ oxidation (CO₂+C→2CO); (2) polycarbon(C_β) with high activity, which forms *via* the aggregation of dehydrogenated C_α species on the catalyst surface, and serves as an intermediate for the formation of inert carbon (C_γ); (3) C_γ (whisker carbon and graphitic carbon) with low activity which is resistant to oxidative removal, and the deposited carbon layers may block the active sites and induce catalyst deactivation.

Metal sintering originates from high temperature, which causes surface lattice particles to vibrate and migrate, followed by agglomeration to form relatively stable large metal particles. There are two mechanisms of sintering: migratory aggregation of particles and Ostwald ripening. The latter involves the dissolution of smaller particles and the redeposition onto larger particles, leading to growth of the larger particles and the disappearance of the smaller ones^[31]. The routes to inhibit the sintering mainly include strengthening the metal-support interaction^[32] and limiting the metal migration through space confinement^[33]. In addition, sulfur-containing compounds, particularly hydrogen sulfide, also contribute to catalyst poisoning and deactivation^[34].

Table 2 Carbon types and formation temperature on the catalyst surface

Carbon type	Appellation	Generation temperature/°C
Adsorbed atomic carbon	C _α	200–400
Polycarbon	C _β	250–500
Whisker carbon	C _γ	300–1000
Graphitic carbon		500–550

Therefore, when evaluating the stability of catalysts, it is also necessary to focus on the practical applicability in industrial conditions, especially the performance under harsh atmospheres containing sulfur species.

2 Special structure catalysts

Complex oxide materials with special structures possess exceptional thermal stability, tunable surface properties, and the ability to accommodate metal cations within their robust lattice structures. Active metals can exist either on the material surface or inside the support. Such distribution effectively strengthens the interfacial interaction between active phases and reactants, thereby improving the catalytic activity and stability^[35–36]. Meanwhile, the materials not only offer superior resistance to sintering and carbon deposition but also enable the fine-tuning of catalytic activity through structural modifications. According to the differences in general formula structures, special structure materials are classified into pyrochlores, spinel oxides and perovskites.

2.1 Pyrochlore catalysts

Pyrochlore catalysts include a group of materials with the general formula $A_2B_2O_7$, where A is a larger cation mostly a rare earth metal ion and B is a smaller cation mainly a transition metal ion. Such materials have high structural versatility, which means that various metal ions can be incorporated into both A and B positions, showing large impact on the catalytic activity^[37–39]. In addition, the precise regulation of metal compositions and the resultant electronic properties of pyrochlore structures are crucial for achieving high-efficiency performance. Table 3 summarizes the recent applications of pyrochlore catalysts in the DRM reaction.

2.2 Spinel oxide catalysts

Spinel oxides are a class of compounds with the general formula AB_2O_4 , in which A and B represent metal cations. These compounds crystallize in a cubic close-packed structure, where the cations occupy specific interstitial positions i.e. tetrahedral sites are occupied by A cations whereas octahedral sites are occupied by B cations^[46–48]. Owing to the robust crystal structure, excellent thermal stability and distinctive electronic properties, carbon deposition can be suppressed. In addition, abundant oxygen vacancies endow the materials with extremely high oxygen mobility, which enables continuous replenishment of oxygen on the catalyst surface. The dynamic oxygen exchange helps remove the carbon deposits and maintain the catalytic activity. Table 4 summarizes the recent applications of spinel oxide catalysts in the DRM reaction.

2.3 Perovskite catalysts

Perovskite materials have the chemical formula of ABO_3 , in which A is a large cation (typically a rare earth or alkaline earth metal), and B is a smaller cation (usually a transition metal). While the Ruddlesden-Popper structured perovskites follow the formula of A_2BO_4 consisted of alternating perovskite layers and A cation layers^[57]. The catalytic performance of perovskites is closely correlated with their atomic geometric structures and the electronic properties. The arrangement of octahedral B cations induces unique *d*-orbital splitting to modulate the adsorption energy. These cations can also form multiple electronic states by adjusting oxidation states, which not only reduces the reaction barriers but also accelerates the activation of CH_4 and CO_2 ^[58–59]. Furthermore, the distribution pattern of internal oxygen vacancies directly affects the carbon gasification rate. The ordered vacancy distribution at A sites markedly improve the oxygen mobility. Table 5 summarizes the recent applications of perovskite catalysts in the DRM reaction.

Table 3 The application of pyrochlore catalysts in DRM reaction

Catalyst	Reaction conditions			Reactant concentration	CH ₄ conversion/%	CO ₂ conversion/%	References
	space velocity (mL·g ⁻¹ ·h ⁻¹)	temperature /°C	time /h				
La _{1.95} Sr _{0.05} Zr _{1.904} Ni _{0.096} O ₇	24000 ^①	900	45	CH ₄ /CO ₂ =1:1	97.5	96.8	[37]
La _{1.95} Sr _{0.05} Zr _{1.44} Ni _{0.56} O ₇		900	45		53.7	73.5	
Ni-La ₂ Zr ₂ O ₇	30000	700	350	CH ₄ /CO ₂ =1:1	~ 80	~ 85	[40]
Ce ₂ Zr _{1.96} Pt _{0.04} O _{7-δ}	38120 ^②	650	24	CH ₄ /CO ₂ =1:1	97.6	95	[41]
La ₂ (CeZrNi) ₂ O ₇	60000	800	40	CH ₄ /CO ₂ /N ₂ =3:3:4	75	82	[42]
Ni-Gd ₂ Ti ₂ O ₇	—	800	200	—	70.8	86.6	[43]
La _{1.95} Sr _{0.05} Zr _{1.44} Ni _{0.56} O _{7-d}	18000	800	100	—	~ 50	~ 85	[44]
10%Ni/Y ₂ Zr ₂ O ₇	72000	800	8	CH ₄ /CO ₂ =1:1	91.6	93.2	[45]

① The unit is scc/(g⁻¹·h⁻¹); ② The unit is h⁻¹.

Table 4 The application of spinel oxide catalysts in DRM reaction

Catalyst	Reaction conditions			Reactant concentration	CH ₄ conversion/%	CO ₂ conversion/%	References
	space velocity (/mL·g ⁻¹ ·h ⁻¹)	temperature /°C	time /h				
Ni _{0.375} Co _{0.375} Mg _{0.25} Al ₂ O ₄	60000 ^①	850	—	CH ₄ /CO ₂ =1:1	92	~ 70	[49]
Ni ₄ Co ₁ /MgAl ₂ O ₄	—	800	—	—	90	>95	[50]
Ni _{0.05} Al ₁ O _{2-δ}	36000	800	50	CH ₄ /CO ₂ /Ar=1.5:1.5:7	~ 92	~ 97	[51]
NiAl ₂ O ₄	—	850	200	—	90	99	[52]
Rh/MgAl ₂ O ₄	520800	750	1	CH ₄ /CO ₂ =1:1	43.2	51.9	[53]
Ni-MgAl ₂ O ₄ -800	120000	750	300	CH ₄ /CO ₂ =1:1	90	~ 90	[54]
Ni-Mg _{1.5} AlO _x	120000	627	20	CH ₄ /CO ₂ /N ₂ =4.5:4.5:1	30.4	—	[55]
Co-Mg-Al-O _x	1200000	750	15	—	83	80	[56]

① The unit is h⁻¹.

Table 5 The application of Perovskite catalysts in DRM reaction

Catalyst	Reaction conditions			CH ₄ conversion/%	CO ₂ conversion/%	References
	space velocity (/mL·g ⁻¹ ·h ⁻¹)	temperature /°C	reactant concentration			
La(Co _{0.3} Ni _{0.7}) _{0.5} Fe _{0.5} O ₃	12000	750	CH ₄ /CO ₂ /N ₂ =1:1:1	63.5	80	[60]
LaNi _{0.34} Co _{0.33} Mn _{0.33} O ₃	12000	800	CH ₄ /CO ₂ /N ₂ =1:1.05:1	94	91	[61]
Sm _{1.5} Sr _{0.5} NiO ₄	60000	800	CH ₄ /CO ₂ /He=1:1:3	90	88	[62]
La _{0.9} Ce _{0.1} NiO ₃	18000	700	—	80	70.8	[63]
LaNi _{0.8} Mn _{0.2} O ₃	15000	750	CH ₄ /CO ₂ =1:1	>90	>90	[64]
40LaNi _{0.75} Fe _{0.25} O ₃ /SiO ₂	—	700	CH ₄ /CO ₂ /N ₂ =1:1:2	90	95	[65]
La ₂ NiMnO ₆	30000 ^①	800	CH ₄ /CO ₂ /He=1:1:3.6	>95	>95	[66]
La ₂ Ni _{0.8} Cu _{0.2} O ₄	12000	750	CH ₄ /CO ₂ /N ₂ =1:1:2	86	91	[67]
Ni _{0.8} Co _{0.2} /TiO ₂	—	700	CH ₄ /CO ₂ =1:1	35	50	[68]
PrBaMn _{1.7} Ni _{0.2} Fe _{0.08} Rh _{0.02} O _{6-δ}	36000	750	CH ₄ /CO ₂ /N ₂ =33:34:33	72	84	[69]
Co-La _{0.2} Ca _{0.8} NiO ₃ -ZrO ₂	42000 ^①	700	CH ₄ /CO ₂ /N ₂ =1:1:1	88	90	[70]
La _{0.8} Sm _{0.2} NiO ₃	200000	750	CH ₄ /CO ₂ /N ₂ =3:2:5	42	76	[71]
La _{0.8} Pr _{0.2} NiO ₃				25	56	
LaNi _{0.8} Zr _{0.2} O ₃	28800 ^①	800	CH ₄ /CO ₂ /N ₂ =1:1:1	50	37	[72]
LaNi _{0.6} Mn _{0.4} O ₃	15000	700	CH ₄ /CO ₂ /N ₂ =2:2:1	84	—	[73]
La ₂ NiO ₄	24000	750	—	91	91	[74]
Ni-Fe ₂ O ₃ /La _{0.8} Sr _{0.2} FeO ₃	—	800	—	99	99 ^②	[75]
PrBaMn _{1.6} Ni _{0.15} Fe _{0.05} O _{5+δ}	30000	800	CH ₄ /CO ₂ /N ₂ =33:34:33	~ 52	~ 54	[76]

① The unit is h⁻¹; ② The value refers to CO selectivity.

3 Anti-coking regulation mechanisms

In DRM, carbon deposition is the core bottleneck causing catalyst deactivation. Complex oxide catalysts with special structures have become a key research direction owing to their tunable crystal structures, strong SMSI effects and excellent dispersion of metallic active sites^[35–36]. Through precise structural modulation, the catalysts fundamentally

suppress the carbon deposition and accelerate the carbon removal, achieving synergistically enhanced activity and stability. The core regulation mechanisms mainly include active metal stabilization, oxygen vacancy modulation and reaction pathway optimization. So, the anti-coking strategies and relevant research progress for pyrochlores, spinel oxides, and perovskites are summarized.

3.1 Active metal stabilization

Sintering of active metal particles accelerate the carbon deposition *via* methane dissociation. Therefore, anchoring active metals through specific structures to suppress particle agglomeration represents a pivotal strategy for suppressing carbon deposition. The core of the strategy relies on lattice spatial confinement: doping active metal cations into the lattice or constructing SMSI by structural modulation can retain the active metals at ultrasmall sizes with homogeneous dispersion, thereby fundamentally suppressing the carbon deposition.

Pyrochlore materials serve as typical supports owing to the excellent structural flexibility^[37–38]. Active metals doped into A or B sites and anchored by the lattice structure can efficiently inhibit the agglomeration. Le Sache et al.^[40] found that when Ni was doped into $\text{La}_2\text{Zr}_2\text{O}_7$, Ni species could be stabilized by the pyrochlore lattice. During the reaction, Ni precipitated from the lattice to form well-dispersed metallic Ni^0 particles below 5 nm, which effectively prevented the formation of large Ni clusters prone to carbon deposition. As a result, the catalyst possesses better stability than impregnated Ni catalysts^[77]. Substitution of La with Sr in $\text{La}_2\text{Zr}_{1.44}\text{Ni}_{0.56}\text{O}_{7-\delta}$ could also markedly enhance the catalytic activity, since Sr doping increased the surface Ni content, reduced the particle size and improved the metal dispersion, which endowed the catalyst with superior sintering resistance and led to nearly no obvious growth of Ni particles in the stability tests^[44]. Fang et al.^[45] discovered that dielectric barrier discharge plasma treatment of $\text{Ni}/\text{Y}_2\text{Zr}_2\text{O}_7$ under H_2/Ar mixed atmosphere could further reduce the grain sizes of NiO and Ni, strengthen the interaction between Ni particles and pyrochlore, and thus further enhance the anti-sintering and anti-coking performance.

Spinel oxides realize the stable dispersion of active metals *via* cation modulation at crystal interstitial sites. Zhang et al.^[51] synthesized the $\text{Ni}_x\text{Al}_1\text{O}_{2-\delta}$ catalyst, where x stand for the Ni/Al molar ratio and δ represented the oxygen vacancy concentration. The structural evolution of the NiAl_2O_4 spinel phase in the catalyst before and after calcination and reduction is shown in Figure 3. After calcination, the Ni^{2+} species in $\text{Ni}_x\text{Al}_1\text{O}_{2-\delta}$ could not be completely reduced even at high temperatures. While partial reduction of the NiAl_2O_4 spinel phase yielded ultrafine Ni^0 nanoparticles, which enhanced the SMSI and optimized the dispersion of active sites, thus efficiently suppressing the carbon deposition. In addition, a coexisting phase of metallic Ni^0 and NiAl_2O_4 formed on the catalyst surface after the reaction. The interfacial structure between the two phases and the favorable SMSI effect endowed the catalyst with excellent anti-sintering and anti-coking performance^[52]. Anchoring single-layer Rh clusters on spinel MgAl_2O_4 nanosheets achieves 100% Rh atom utilization. The SMSI not only stabilized the Rh cluster structure but also lowered the activation energy for the oxidation of C^* and CH^* species in the rate-determining step, thereby synchronously improving the catalytic activity

and anti-coking performance^[53]. Wen et al.^[54] synthesized the $\text{Ni-MgAl}_2\text{O}_4-t$ catalysts (t represented calcination temperature) *via* evaporation-induced self-assembly strategy. It was found that the ordered mesoporous structure of $\text{Ni-MgAl}_2\text{O}_4-800$ had a strong confinement effect on Ni nanoparticles, which constructed robust SMSI and effectively suppressed the carbon deposition. In addition, the catalyst kept the conversion of CO_2 and CH_4 at approximately 90% during the 300 h stability test.

CO_2 could oxidize elemental Fe into FeO_x during the DRM and the formed FeO_x promoted the oxidation of deposited carbon, which was responsible for the excellent stability of NiFe catalysts^[78]. To explore the effect of Fe on the catalytic performance of spinel oxides, De Coster et al.^[79] doped Fe into $\text{Ni/MgAl}_2\text{O}_4$, where Fe existed on the catalyst surface in the form of NiFe_2O_4 . The results demonstrated that NiFe_2O_4 could be reduced to NiFe alloys by hydrogen dissociated from CH_4 during the DRM. The schematic diagram of DRM reaction on $\text{FeNi/MgAl}_2\text{O}_4$ catalyst is shown in Figure 4. CH_4 was activated and dissociated over Ni active sites to produce H_2 and carbon species. The generated surface carbon was further re-oxidized into CO by lattice oxygen derived from FeO_x . H_2 was capable of reducing iron oxides. Subsequently, the Fe species in the NiFe alloys could be oxidized into FeO_x by CO_2 or H_2O produced from the RWGS reaction, thus forming a continuous cycling. However, the above redox cycle could only be achieved when the CH_4/CO_2 molar ratio was no less than 1 because that adequate hydrogen suppressed the iron oxidation and sustained continuous NiFe alloy formation.

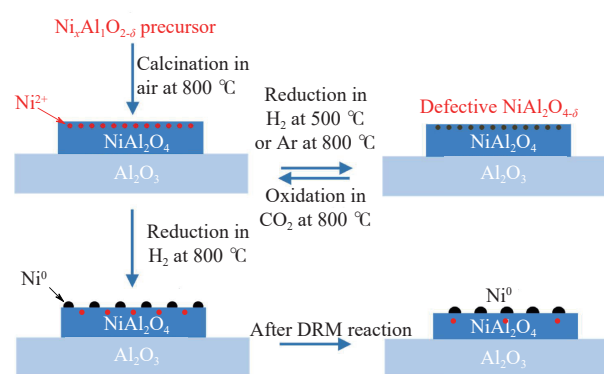


Fig. 3 The structure evolution of the $\text{Ni}_x\text{Al1O}_{2-\delta}$ catalyst before and after DRM reaction^[51]
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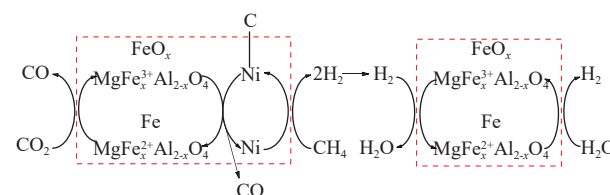


Fig. 4 Schematic diagram of DRM reaction on $\text{FeNi/MgAl}_2\text{O}_4$ catalyst^[79]
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Stable dispersion of active sites can also be realized for perovskite catalysts *via in situ* exsolution of active metals during reduction. As one of the most extensively investigated catalysts for DRM reaction, LaNiO_3 exhibited a reduced specific surface area after high-temperature calcination. Nevertheless, activation treatment before or during the reaction could generate highly dispersed small metallic Ni nanoparticles on the LaNiO_3 framework, which remarkably enhanced the catalytic activity^[80–82]. Sagar et al.^[72] reported that tuning the Ni/Zr molar ratio of $\text{LaNi}_x\text{Zr}_{1-x}\text{O}_3$ ($0 \leq x \leq 1$) catalysts could modulate the generation of La-Zr pyrochlore and La-Ni perovskite phases. In other words, higher Ni content promoted the phase transformation from La-Zr pyrochlore to La-Ni perovskite, yielding more uniform dispersion of Ni active sites and thus greatly enhancing the high-temperature stability and anti-coking performance of the catalysts. Yao et al.^[76] synthesized $\text{PrBaMn}_{1.6}\text{Ni}_{0.15}\text{Fe}_{0.05}\text{O}_{5+\delta}$ double perovskite catalysts. Upon reduction, NiFe alloy nanoparticles could be *in situ* exsolved from the lattice. Such alloy structure could effectively suppress the agglomeration of monometallic Ni. Compared with monometallic Ni-based catalysts, the materials delivered a distinct enhancement in anti-coking performance. Density functional theory (DFT) calculations were employed to investigate the carbon removal performance of alloy catalysts and monometallic Ni catalysts, as well as the differences in adsorption energies of key intermediates over the $\text{Ni}_4\text{Fe}_1(111)$ and monometallic Ni(111) crystal facets. The results revealed that although monometallic Ni formed slightly more oxygen vacancies than NiFe alloys, NiFe alloys showed better anti-coking performance, indicating that oxygen vacancies were not the main factor for carbon removal (Figure 5). The $\text{Ni}_4\text{Fe}_1(111)$ crystal plane exhibited stronger dissociation intensity for carbon-containing intermediates (CH_x^*) than Ni(111).

Meanwhile, Ni(111) had a higher adsorption energy for C^* , which facilitated coke formation on the surface^[83]. In addition, $\text{Ni}_4\text{Fe}_1(111)$ possessed a lower CO_2 dissociation energy than Ni(111) and Fe was oxyphilic. Therefore, addition of Fe to Ni-based catalysts could enhance the adsorption capacity for O^* species and reduced the CO_2 dissociation energy. The O^* species reacted more strongly with deposited carbon, thereby effectively reducing the coking rate.

3.2 Oxygen vacancy modulation

In the DRM reaction, the efficient elimination of coke relies on the continuous supply of oxygen species on the catalyst surface. Oxides with unique structures can generate abundant oxygen vacancies through lattice structure regulation, which markedly improves the oxygen mobility and realizes the dynamic replenishment of oxygen species. This further accelerates the reaction between deposited carbon and oxygen species, thereby achieving high-efficiency anti-coking performance. Oxygen vacancy regulation is primarily achieved by cation doping and phase transformation. Obvious differences exist in vacancy modulation routes among catalysts with diverse structures.

Regulating the oxygen vacancy concentration of pyrochlore catalysts *via* cation doping can effectively enhance their coke removal capacity^[41]. Bai et al.^[42] adjusted the Zr/Ce ratio in the $\text{La}_2(\text{CeZrNi})_2\text{O}_7$ catalyst to induce the transformation from pyrochlore phase ($\text{La}_2\text{Zr}_2\text{O}_7$) to defective fluorite phase ($\text{La}_2\text{Ce}_2\text{O}_7$). As the Zr/Ce ratio decreased, the structural ordering degree declined while the oxygen vacancy concentration increased remarkably. When the Zr/Ce ratio was 3, the catalyst possessed the maximum number of oxygen vacancies.

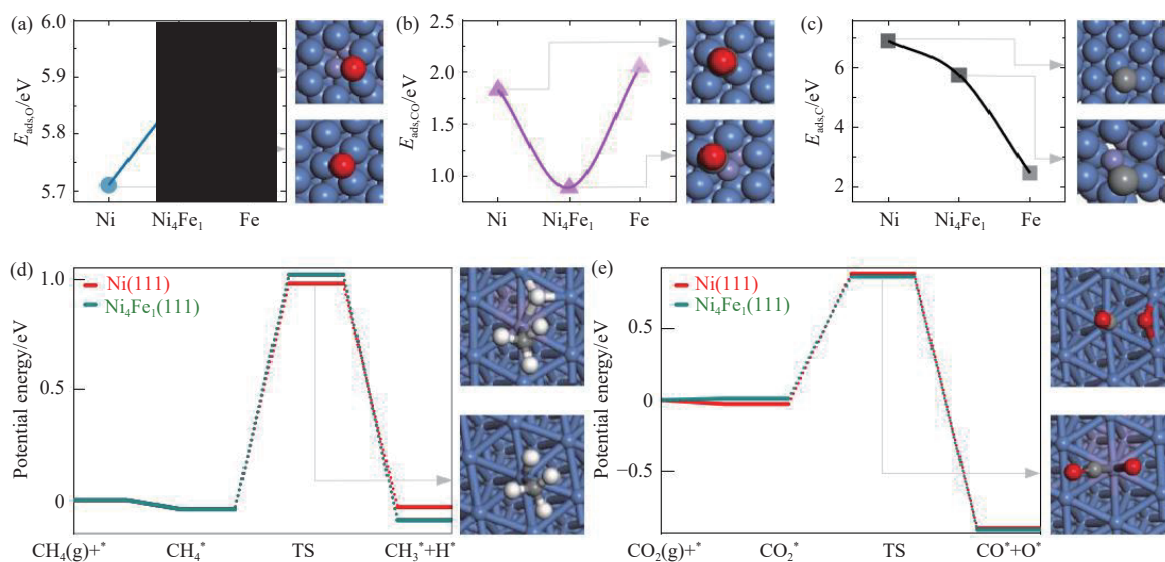


Fig. 5 Density function theory (DFT) calculation results, (a)–(c) O, CO and C adsorption energies on pure Ni(111), $\text{Ni}_4\text{Fe}_1(111)$ and Fe(111) surfaces; (d), (e) Potential energy profile for CH_4 and CO_2 dissociation on Ni(111) and $\text{Ni}_4\text{Fe}_1(111)$ ^[76] (with permission from Elsevier)

Meanwhile, the SMSI between Ni species and the support was strongest, accompanied by the optimal size distribution of Ni nanoparticles. The catalyst exhibited best anti-coking performance and catalytic activity. A-site doping can also increase the concentration of oxygen vacancies. Liu et al.^[43] synthesized Ni-modified $\text{Gd}_2\text{Ti}_2\text{O}_7$ catalysts and found that doping with 2% Gd could generate more oxygen vacancies and surface adsorbed oxygen in the $\text{A}_2\text{Ti}_2\text{O}_7$ lattice. This not only accelerated the oxidative removal of deposited carbon, but also strengthened the C–H bond activation capability of CH_4 and the adsorption capacity of CO_2 , thereby endowing the catalyst with outstanding stability.

Oxygen vacancies in spinel oxides mainly stem from cation doping and phase transformation whose high oxygen mobility facilitates efficient oxidative removal of deposited carbon. Doping Mg into Ni-Al-O_x and Co-Al-O_x catalysts induced transformation from spinel phases (NiAl_2O_4 and CoAl_2O_4) to periclase MgO , reduced the spinel phase ratio from 100% to 45% and regulated the coordination numbers of Mg and Al, thus enabling mutual substitution between Mg^{2+} and Al^{3+} sites. Specifically, partial Al^{3+} ions occupied the octahedral sites while Mg^{2+} ions took up the tetrahedral sites. Such structural evolution homogenized active site distribution, reduced particle size, improved metal reducibility and increased oxygen vacancy concentration, thereby accelerating the oxidative removal of deposited carbon^[56]. Nguyen-Phu et al.^[55] demonstrated that the performance of $\text{Ni-MgAl}_2\text{O}_4$ catalysts was closely correlated with the Mg/Al molar ratio i.e. increasing the ratio from 0.375 to 1.5 led to partial conversion of the spinel phase into periclase Ni-MgO phase, increased lattice defects and oxygen vacancy content, and exposed more moderate-strength basic sites, which effectively promoted the adsorption and activation of CO_2 and accelerated the oxidative removal of coke. However, excessively high Mg content ($\text{Mg/Al} = 4$) facilitated the incorporation of Ni into MgO to form stable NiO-MgO solid solutions, namely, the fully encapsulated Mg(Ni)O phase^[84–85]. Compared with Ni^{2+} species dispersed on the surface of MgO crystals, lattice-confined Ni^{2+} possessed lower reducibility with reduction temperature above 900 °C, which hindered the oxygen vacancy formation.

The distribution of oxygen vacancies in perovskite catalysts directly affects the carbon gasification rate. The elemental substitution at B sites can remarkably enhance the oxygen mobility. Georgiadis et al.^[71] demonstrated that the partial substitution of Ni in LaNiO_3 with Sm and Pr could reduce the crystallinity of deposited carbon, strengthen the SMSI, boost the oxygen mobility, and facilitate the gasification and removal of coke, thereby improving the structural stability and anti-coking performance of the catalyst. In $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ catalysts, partial substitution of Ni by Mn not only stabilized the perovskite structure but also increased the number of oxygen vacancies and basic sites. Meanwhile, lattice oxygen could directly react with coke. Almost no carbon deposition was detected on the catalyst surface after 20 h of reaction at 700 °C. In addition,

the catalyst synthesized *via* glycine-assisted ultrasonic spray pyrolysis (USP) might change the morphology from submicron solid spherical particles to hollow or shell-like particles, which remarkably increased the specific surface area and further enhanced the exposure degree of oxygen vacancies as well as coke removal efficiency^[73].

Furthermore, previous studies have confirmed that La_2NiO_4 possessed a unique carbon removal mechanism during the DRM reaction, as illustrated in Figure 6^[88]. The R denoted the pathways of carbon formation and removal, while D represented carbon transport. At the initial stage of the reaction, La_2NiO_4 decomposed into La_2O_3 and metallic Ni^0 under reducing atmosphere. The resultant Ni^0 nanoparticles were uniformly anchored on the perovskite matrix surface. The novel metal oxide bonding structure originating from crystal structural reconstruction not only stabilized active sites, but also provided distinctive binding sites for reaction intermediates. As shown in Figure 6(a), methane was activated at metallic Ni sites, where C–H bonds broke to produce hydrogen and coke (R1). The resultant solid carbon migrated across the Ni surface (D) and reacted directly with CO_2 to form CO (R2). Additionally, La_2O_3 interacted with CO_2 to yield $\text{La}_2\text{O}_2\text{CO}_3$. The released oxygen atoms facilitated the conversion of carbon into CO (R3)^[89]. When the carbon formation rate exceeded its elimination rate in local regions, accumulated carbon caused partial metallic Ni particles to detach from the La_2O_3 support (Figure 6(b)). The solid carbon beneath Ni particles could not be consumed by $\text{La}_2\text{O}_2\text{CO}_3$ and thus continuously accumulated. Nevertheless, the surface of accumulated carbon could still react with CO_2 to generate CO (R4).

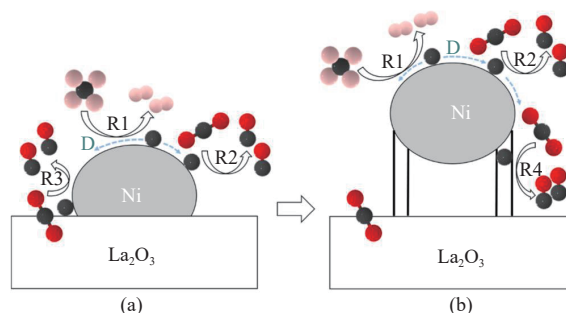


Fig. 6 Schematic diagram of carbon deposition and removal of La_2NiO_4 during DRM reaction^[88] (with permission from Elsevier)

3.3 Reaction pathway optimization

Regulating the conversion pathways of the intermediates to inhibit excessive carbon deposition from methane dissociation and promote CO_2 activation for reactive oxygen species generation serves as an important anti-coking strategy. Special structure catalysts can optimize the adsorption and conversion of intermediates and alter the reaction pathways *via* metal doping and electronic property

modulation, thereby reducing the carbon deposition fundamentally.

Spinel oxide catalysts primarily modulate the reaction pathways through metal doping to inhibit excessive dissociation of methane. Kim et al.^[50] synthesized a series of $\text{Ni}_x\text{Co}_y/\text{MgAl}_2\text{O}_4$ catalysts with different Ni/Co ratios. The Co content was fixed at 4% and the Ni doping amount was adjusted. Characterization results revealed that Co incorporation enhanced the oxygen affinity of catalysts. This enabled CH_x^* species to preferentially react with more O^* rather than directly dissociating into C^* . Meanwhile, it strengthened the interaction between CO_2 and Ni_4Co_1 , and elevated the density of moderately strong basic sites. Accordingly, CO_2 tended to form readily decomposable bidentate carbonates (OCOO^*) instead of monodentate species. The bidentate carbonate decomposed and reacted with H^* derived from methane dissociation to form formate (HCOO^*) which rapidly converted into CO and H_2 via dehydration, thereby suppressing the coke formation. Hence, formate content could serve as an indicator of anti-coking performance. Among all catalysts, Ni_4Co_1 showed the best catalytic activity and anti-coking performance, retained the alloy active sites after 100 h of reaction with coking rate of only 0.34% compared with monometallic Ni catalyst.

Perovskite catalysts modulate the electronic properties via cation substitution to optimize DRM reaction pathways. Cao et al.^[67] substituted the B sites of La_2NiO_4 perovskite with transition metals including Mn, Fe, Co and Cu. It was found that Co-substituted samples exhibited reduced catalytic activity and increased carbon deposition. While both activity and carbon deposition declined for Mn- and Fe-substituted samples. Although Cu-substituted samples showed a slight drop in CH_4 conversion and gradually declining in catalytic activity with the increase of Cu substitution ratio, their anti-coking performance was enhanced for more than 90 times compared with La_2NiO_4 . This phenomenon could be attributed to the formation of Ni-Cu alloy, which effectively inhibited methane cracking and reduced the generation rate of solid carbon. DFT calculations further revealed that partial Cu substitution could elevate the energy barrier of CH^* dehydrogenation step, thus kinetically slowing down the formation rate of solid carbon.

4 Conclusion and outlook

CO_2 dry reforming of methane technology can convert CO_2 and CH_4 into syngas for value-added chemical production, which serves as an effective way to alleviate the greenhouse gas emissions. Current catalysts commonly suffer from rapid deactivation caused by high-temperature sintering and carbon deposition. Three structurally distinctive oxides including pyrochlore, spinel oxide and perovskite are ideal systems to break the bottlenecks of anti-coking and anti-sintering performance, owing to superior

thermal stability, tunable lattice structure and SMSI. This review systematically elaborates the thermodynamic characteristics and multi-path reaction mechanisms of DRM, as well as catalyst deactivation mechanisms including carbon deposition, sintering and poisoning. The structural features and recent research progress of pyrochlore, spinel oxide and perovskite catalysts are summarized. In addition, focusing on three core regulation mechanisms including active metal stabilization, oxygen vacancy modulation and reaction pathway optimization, the effects of crystal structure, SMSI and oxygen vacancies of structurally specialized catalysts on their anti-coking performance are analyzed. Active metal stabilization suppresses agglomeration via crystal structure anchoring or SMSI to disperse uniformly with small particle sizes, thereby reducing the carbon deposition and sintering. Oxygen vacancy modulation generates abundant oxygen vacancies through lattice regulation to greatly improve oxygen mobility and dynamically supplement oxygen species, thus accelerating the carbon removal. Reaction pathway optimization adjusts the conversion routes of intermediates to restrain excessive dissociation of methane, thereby reducing the carbon formation. To facilitate industrial application of DRM technology, the following aspects deserve further exploration.

Catalysts should be developed with a clear understanding of reaction mechanism. Discrepancies in the microenvironment of catalyst surfaces can alter the reaction mechanisms. Sufficient *in situ* quantitative evidence is still lacking for the interfacial behavior, structural evolution and carbon species transformation under practical working conditions. Therefore, multiple advanced *in situ* characterization techniques should be adopted. Scanning tunneling microscopy (STM) can be employed to observe the atomic-scale structural features of the active interfaces, while ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) can be utilized to elucidate the dynamic structural evolution of the catalysts during the reaction. *In situ* Fourier transform infrared spectroscopy (FT-IR) and *in situ* X-ray absorption spectroscopy (XAS) can be applied to identify the state and reaction path of the intermediates on the active sites. Meanwhile, combined with DFT calculations, atomic-scale mechanistic models should be constructed to clarify the active sites and rate-determining steps on distinct structural systems, thereby guiding the targeted design of catalysts with high activity and stability from the mechanistic perspective.

Research results on anti-coking and stability show that specially structured catalysts gain enhanced performance through lattice confinement, *in situ* phase separation, SMSI and oxygen vacancy modulation. However, issues of inert carbon elimination, high-temperature sintering and sulfur poisoning persisted in long-term operation. Subsequent research can focus on three aspects. First, precise A/B-site doping, optimized phase transition ratio and elaborate design of *in situ* phase separation structure can strengthen the lattice anchoring and SMSI effect, stabilize particle size

and dispersion of active metals, inhibit high-temperature agglomeration and sintering, and reduce the formation of coking precursors fundamentally. Second, controllable synthesis strategies to construct oxygen vacancies with high concentration and mobility, enhance the dynamic cycle of lattice and adsorbed oxygen, improve carbon gasification efficiency, balance the carbon generation and elimination rates, and realize sustained and efficient carbon oxidative removal. Third, enhance catalyst adaptability to industrial conditions and long-term stability to secure favorable sulfur poisoning resistance.

Despite remarkable advances have been achieved in DRM catalysts with special structures, substantial gaps persist in industrialization. The fabrication of catalysts with high activity and stability remains the major bottleneck. Catalyst development shall focus on active interface modulation in the future. Integrating theoretical simulation with experimental verification, high-precision interfacial models can be established to systematically investigate how metal dispersion, particle size, crystal structure and oxygen vacancies regulate the interfacial configuration and catalytic properties. Furthermore, it is necessary to specify the standards of evaluating catalytic activity. For example, the conversion of CO₂ and CH₄ are affected by parameters such as reactant gas ratio, space velocity, bed length and catalyst dosage. Experimental conditions should remain constant in all catalyst tests, thereby realizing objective comparison and reliable verification of catalytic performance, and offering solid data support for catalyst screening, scale-up and subsequent industrial application. Besides, developing catalysts with specific interfacial structures should also take preparation cost and large-scale production feasibility into account.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] Wang J, Azam W. Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries[J]. *Geosci Front*, 2024, 15(2): 101757.
- [2] Nikoo M K, Amin N A. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation[J]. *Fuel Processing Technol*, 2011, 92(3): 678–691.
- [3] Rogelj J, Den Elzen M, Hohne N, et al. Paris Agreement climate proposals need a boost to keep warming well below 2 °C[J]. *Nature*, 2016, 534(7609): 631–639.
- [4] Li P Y, Wang G R, Niu J X, et al. Research progress on mechanism and catalysts for reverse water-gas shift reaction[J]. *J Fuel Chem Technol*, 2025, 53(1): 1–14.
- [5] Jeffry L, Ong M Y, Nomanbhay S, et al. Greenhouse gases utilization: a review[J]. *Fuel*, 2021, 301: 121017.
- [6] Song X W, Chen Z M, Long T, et al. Research progress on catalysts for dry reforming of methane with carbon dioxide[J]. *Modern Chemical Industry*, 2024, 44(10): 70–75.
- [7] Tian X, Wang F. A review on catalyst advances for photothermal dry reforming of methane reaction[J]. *Sep Purif Technol*, 2025, 354: 128799.
- [8] Fisher F, Tropsch H. Conversion of methane into hydrogen and carbon monoxide[J]. *Brennst-Chem*, 1928, 3(9): 9–46.
- [9] Wang Y, Li R, Zeng C Y, et al. Recent research progress of methane dry reforming to syngas[J]. *Fuel*, 2025, 398: 135535.
- [10] Li M J, Sun Z X, Hu Y H. Catalysts for CO₂ reforming of CH₄: A review[J]. *J Mater Chem A*, 2021, 9(21): 12495–12520.
- [11] Wang S, Lu G Q, Millar G J. Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: state of the art[J]. *Energy Fuels*, 1996, 10(4): 896–904.
- [12] Franke R, Selent D, Borner A. Applied hydroformylation[J]. *Chem Rev*, 2012, 112(11): 5675–5732.
- [13] Feng X, Du Z, Saenello E, et al. Syngas production at a near-unity H₂/CO ratio from photo-thermo-chemical dry reforming of methane on a Pt decorated Al₂O₃-CeO₂ catalyst[J]. *J Mater Chem A*, 2022, 10(14): 7896–7910.
- [14] Ginsburg J M, Pina J, El-solh T, et al. Coke formation over a nickel catalyst under methane dry reforming conditions: thermodynamic and kinetic models[J]. *Ind Eng Chem Res*, 2005, 44(14): 4846–4854.
- [15] Bao Z, Lu Y, Han J, et al. Highly active and stable Ni-based bimodal pore catalyst for dry reforming of methane[J]. *Appl Catal A-Gen*, 2015, 491: 116–126.
- [16] Rakhi G V, Mauss F. Insights into dry reforming of methane over nickel catalyst using a thermodynamic model[J]. *React Kinet Mech Catal*, 2023, 136(3): 1197–1210.
- [17] Gopaul S G, Dutta A. Dry reforming of multiple biogas types for syngas production simulated using Aspen Plus: the use of partial oxidation and hydrogen combustion to achieve thermo-neutrality[J]. *J Phys Chem C*, 2015, 40(19): 6307–6318.
- [18] He C X, Wu S Q, Li Q X, et al. Constructing matched active sites for robust photocatalytic dry reforming of methane[J]. *Chem*, 2023, 9(11): 3224–3244.
- [19] Huang H Y, Yu Y Z, Zhang M H. Mechanistic insight into methane dry reforming over cobalt: a density functional theory study[J]. *Phys Chem Chem Phys*, 2020, 22(46): 27320–27331.
- [20] Anil C, Modak J M, Madras G. Syngas production via CO₂ reforming of methane over noble metal (Ru, Pt, and Pd) doped LaAlO₃ perovskite catalyst[J]. *Mol Catal*, 2020, 484: 110805.
- [21] Cao D B, Li Y W, Wang J, et al. CO₂ dissociation on Ni(211)[J]. *Surf Sci*, 2009, 603(19): 2991–2998.
- [22] Niu J T, Du X S, Ran J Y, et al. Dry (CO₂) reforming of methane over Pt catalysts studied by DFT and kinetic modeling[J]. *Appl Surf Sci*, 2016, 376: 79–90.
- [23] Yuan B, Zhu T, Han Y W, et al. Deactivation mechanism and anti-deactivation measures of metal catalyst in the dry reforming of methane: a review[J]. *Atmosphere*, 2023, 14(5): 770.
- [24] Lyu Y, Xu R, Williams O, et al. Reaction paths of methane

- activation and oxidation of surface intermediates over NiO on Ceria-Zirconia catalysts studied by In-situ FTIR spectroscopy[J]. *J Catal*, 2021, 404: 334–347.
- [25] Aramouni N A, Touma J G, Tarboush B A, et al. Catalyst design for dry reforming of methane: analysis review[J]. *Renew Sust Energ Rev*, 2018, 82: 2570–2585.
- [26] Muraza O, Galadima A. A review on coke management during dry reforming of methane[J]. *Int J Energ Res*, 2015, 39(9): 1196–1216.
- [27] Ranjekar A M, Yadav G D. Dry reforming of methane for syngas production: a review and assessment of catalyst development and efficacy[J]. *J Indian Chem Soc*, 2021, 98(1): 100002.
- [28] Zhang Q, Akri M, Yang Y W, et al. Atomically dispersed metals as potential coke-resistant catalysts for dry reforming of methane[J]. *Cell Reports Phys Sci*, 2023, 4(3): 101310.
- [29] Abdulrasheed A, Jalil A A, Gambo Y, et al. A review on catalyst development for dry reforming of methane to syngas: recent advances[J]. *Renew Sust Energ Rev*, 2019, 108: 175–193.
- [30] Kawi S, Kathiraser Y, Ni J, et al. Progress in synthesis of highly active and stable nickel-based catalysts for carbon dioxide reforming of methane[J]. *ChemSusChem*, 2015, 8(21): 3556–3575.
- [31] Chen C C, Wei J J, Lu Y, et al. Confinement effects over Ni-based catalysts for methane dry reforming[J]. *Catal Sci Technol*, 2023, 13(21): 6089–6101.
- [32] Dong J H, Fu Q, Li H B, et al. Reaction-induced strong metal-support interactions between metals and inert boron nitride nanosheets[J]. *J Am Chem Soc*, 2020, 142(40): 17167–17174.
- [33] Yin P, Hu S L, Qian K, et al. Quantification of critical particle distance for mitigating catalyst sintering[J]. *Nat Commun*, 2021, 12(1): 4865.
- [34] Audasso E, Kim Y, Cha J, et al. In situ exsolution of Rh nanoparticles on a perovskite oxide surface: efficient Rh catalysts for dry reforming[J]. *Korean J Chem Eng*, 2020, 37(8): 1401–1410.
- [35] Binti-Rosdin R D, Yusu M, Abdullah B. Dry reforming of methane over Ni-based catalysts: effect of ZrO₂ and MgO addition as support[J]. *Mater Lett*, 2021, 12: 100095.
- [36] Zhong J W, Lin W T, Huang X Y, et al. Research progress of hydrotalcite-derived Ni-based catalysts in methane dry reforming to syngas[J]. *Low-Carbon Chem Eng*, 2025, 50(5): 60–68.
- [37] Bhattar S, Krishnakumar A, Kanitkar S, et al. 110th Anniversary: dry reforming of methane over Ni-and Sr-substituted lanthanum zirconate pyrochlore catalysts: effect of Ni loading[J]. *Ind Eng Chem Res*, 2019, 58(42): 19386–19396.
- [38] Pakhare D, Haynes D, Shekhawat D, et al. Role of metal substitution in lanthanum zirconate pyrochlores (La₂Zr₂O₇) for dry (CO₂) reforming of methane (DRM)[J]. *Appl Petrochem Res*, 2012, 2(1): 27–35.
- [39] Polo-Grahn F, Pakhara D, Spivey J J, et al. Dry reforming of methane on Rh-doped pyrochlore catalysts: a steady-state isotopic transient kinetic study[J]. *ACS Catal*, 2016, 6(6): 3826–3833.
- [40] Le Sache E, Pastor-Perez L, Watson D, et al. Ni stabilised on inorganic complex structures: superior catalysts for chemical CO₂ recycling via dry reforming of methane[J]. *Appl Catal B-Environ*, 2018, 236: 458–465.
- [41] Disha J, Saha S. Spectroscopic and kinetic insights into the methane reforming over Ce-pyrochlores[J]. *Mol Catal*, 2020, 492: 110964.
- [42] Bai J R, Fu Y, Kong W B, et al. Design of Ni-substituted La₂(CeZrNi)₂O₇ pyrochlore catalysts for methane dry reforming[J]. *ChemNanoMat*, 2022, 8(3): e202100422.
- [43] Liu Z, Qiao L Y, Zhou Z F, et al. High coking resistance of Ni/A₂Ti₂O₇ catalysts via modulating the A site of A₂Ti₂O₇(A=La, Gd) for dry reforming of methane[J]. *Fuel*, 2024, 368: 131639.
- [44] Bhattar S, Abedin M A, Shekhawat D, et al. The effect of La substitution by Sr-and Ca-in Ni substituted Lanthanum Zirconate pyrochlore catalysts for dry reforming of methane[J]. *Appl Catal A-Gen*, 2020, 602: 117721.
- [45] Fang X Z, Lian J, Nie K W, et al. Dry reforming of methane on active and coke resistant Ni/Y₂Zr₂O₇ catalysts treated by dielectric barrier discharge plasma[J]. *J Energ Chem*, 2016, 25(5): 825–831.
- [46] Farokhi G, Saidi M. Catalytic activity of bimetallic spinel magnetic catalysts (NiZnFe₂O₄, CoZnFe₂O₄ and CuZnFe₂O₄) in biodiesel production process from neem oil: process evaluation and optimization[J]. *Chem Eng Process*, 2022, 181: 109170.
- [47] Farokhi G, Saidi M, Najafabadi A T. Application of spinel type Ni_xZn_{1-x}Fe₂O₄ magnetic nanocatalysts for biodiesel production from neem seed oil: catalytic performance evaluation and optimization[J]. *Ind Crop Prod*, 2023, 192: 116035.
- [48] Dong L S, Wang Z G, Li Y Y, et al. Spinel-structured, multi-component transition metal oxide (Ni, Co, Mn) Fe₂O_{4-x} as long-life lithium-ion battery anode material[J]. *Batteries*, 2023, 9(1): 54.
- [49] Misture S T, Mcdevitt K M, Glass K C, et al. Sulfur-resistant and regenerable Ni/Co spinel-based catalysts for methane dry reforming[J]. *Catal Sci Technol*, 2015, 5(9): 4565–4574.
- [50] Kim D H, Seo J C, Kim Y J, et al. Ni-Co alloy catalyst derived from Ni₃Co₃/MgAl₂O₄ via exsolution method for high coke resistance toward dry reforming of methane[J]. *Catal Today*, 2024, 425: 114337.
- [51] Zhang S S, Ying M, Yu J, et al. Ni_xAl_{3-x}O_{2.6} mesoporous catalysts for dry reforming of methane: The special role of NiAl₂O₄ spinel phase and its reaction mechanism[J]. *Appl Catal B-Environ*, 2021, 291: 120074.
- [52] Abbas M, Sikander U, Mehran M T, et al. Exceptional stability of hydrotalcite derived spinel Mg (Ni)Al₂O₄ catalyst for dry reforming of methane[J]. *Catal Today*, 2022, 403: 74–85.
- [53] Zhang Y D, Wu S W, Li Y Z, et al. Quasi-monolayer Rh nanoclusters stabilized on spinel MgAl₂O₄ nanosheets for catalytic CO₂ reforming of methane[J]. *ACS Appl Nano Mater*, 2021, 4(9): 9866–9875.
- [54] Wen F L, Xu C, Huang N G, et al. Exceptional stability of spinel Ni-MgAl₂O₄ catalyst with ordered mesoporous

- structure for dry reforming of methane[J]. *Int J Hydro Energ*, 2024, 69: 1481–1491.
- [55] Nguyen-Phu H, Kim T, Kim Y, et al. Role of phase in NiMgAl mixed oxide catalysts for CO₂ dry methane reforming (DRM)[J]. *Cataly Today*, 2023, 411: 113894.
- [56] Alabi W O, Sulaiman K O, Wang H, et al. Effect of spinel inversion and metal-support interaction on the site activity of Mg-Al-O_x supported Co catalyst for CO₂ reforming of CH₄[J]. *J CO₂ Util*, 2020, 37: 180–187.
- [57] Safaripour M, Saidi M, Jahangiri A. Application of samarium doped lanthanum nickel oxide perovskite nanocatalyst for biodiesel production[J]. *Energ Conver Manage*, 2023, 296: 117667.
- [58] Bartel C J, Sutton C, Goldsmith B R, et al. New tolerance factor to predict the stability of perovskite oxides and halides[J]. *Sci Adv*, 2019, 5(2): eaav0693.
- [59] Ansari A A, Adil S F, Alam M, et al. Catalytic performance of the Ce-doped LaCoO₃ perovskite nanoparticles[J]. *Sci Rep*, 2020, 10(1): 15012.
- [60] Wang H Q, Dong X L, Zhao T T, et al. Dry reforming of methane over bimetallic Ni-Co catalyst prepared from La(Co_xNi_{1-x})_{0.5}Fe_{0.5}O₃ perovskite precursor: catalytic activity and coking resistance[J]. *Appl Catal B-Environ*, 2019, 245: 302–313.
- [61] Kim W Y, Jang J S, Ra E C, et al. Reduced perovskite LaNiO₃ catalysts modified with Co and Mn for low coke formation in dry reforming of methane[J]. *Appl Catal A-Gen*, 2019, 575: 198–203.
- [62] Nezhad P D, Bekheet M F, Bonmassar N, et al. Elucidating the role of earth alkaline doping in perovskite-based methane dry reforming catalysts[J]. *Catal Sci Technol*, 2022, 12(4): 1229–1244.
- [63] Du Z C, Petru C, Yang X, et al. Development of stable La_{0.9}Ce_{0.1}NiO₃ perovskite catalyst for enhanced photothermochemical dry reforming of methane[J]. *J CO₂ Util*, 2023, 67: 102317.
- [64] Valderrama G, Kiennemann A, De Navarro C U, et al. LaNi_{1-x}Mn_xO₃ perovskite-type oxides as catalysts precursors for dry reforming of methane[J]. *Appl Catal A-Gen*, 2018, 565: 26–33.
- [65] Yadv P K, Das T. Production of syngas from carbon dioxide reforming of methane by using LaNi_{1-x}Fe_xO₃ perovskite type catalysts[J]. *Int J Hydro Energ*, 2019, 44(3): 1659–1670.
- [66] Hossain A, Bhattacharjee M, Ghorai K, et al. High activity in the dry reforming of methane using a thermally switchable double perovskite and in situ generated molecular level nanocomposite[J]. *Phys Chem Chem Phys*, 2024, 26(6): 5447–5465.
- [67] Cao D S, Luo C, Luo T, et al. Dry reforming of methane by La₂NiO₄ perovskite oxide: B-site substitution improving reactivity and stability[J]. *Chem Eng J*, 2024, 482: 148701.
- [68] Qiu L, Ning Y N, Kang Y X, et al. TiO₂-supported perovskite-induced bimetallic Ni-Co nanoparticles for the dry reforming of methane[J]. *Ind Eng Chem Res*, 2024, 63(22): 9732–9739.
- [69] Yao X L, Chang Q P, Bai X Q, et al. Enlarging the three-phase boundary to raise CO₂/CH₄ conversions on exsolved Ni-Fe alloy perovskite catalysts by minimal Rh doping[J]. *ACS Catal*, 2024, 14(8): 5639–5653.
- [70] Oni B A, Tomomewo O S, Sanni S E, et al. Dry reforming of methane with CO₂ over Co-La_{1-x}Ca_xNiO₃ perovskite-type oxides supported on ZrO₂[J]. *Mater Today Commun*, 2023, 36: 106802.
- [71] Georgiadis A G, Tsiotsias A I, Siakavelas G I, et al. An experimental and theoretical approach for the biogas dry reforming reaction using perovskite-derived La_{0.8}X_{0.2}NiO_{3-δ} catalysts (X=Sm, Pr, Ce)[J]. *Renew Energ*, 2024, 227: 120511.
- [72] Sagar T V, Lingaiah N, Sai Prasad P S, et al. Phase transformation of Zr-modified LaNiO₃ perovskite materials: effect of CO₂ reforming of methane to syngas[J]. *Catalysts*, 2024, 14(1): 91.
- [73] Shahnazi A, Firoozi S. Mesoporous LaNi_{1-x}Mn_xO₃ perovskite with enhanced catalytic performance and coke resistance synthesized via glycine-assisted spray pyrolysis for methane dry reforming[J]. *Mol Catal*, 2023, 547: 113320.
- [74] Cao D S, Luo C, Tan Z Q, et al. Carbon deposition properties and regeneration performance of La₂NiO₄ perovskite oxide for dry reforming of methane[J]. *J Environ Chem Eng*, 2023, 11(5): 111022.
- [75] Rao Q, Zhang J R, Yang T L, et al. A nickel-modified perovskite-supported iron oxide oxygen carrier for chemical looping dry reforming of methane for syngas production[J]. *Chem Eng J*, 2024, 485: 150033.
- [76] Yao X L, Cheng Q P, Attada Y, et al. A typical stability of exsolved Ni-Fe alloy nanoparticles on double layered perovskite for CO₂ dry reforming of methane[J]. *Appl Catal B-Environ*, 2023, 328: 122479.
- [77] Le S E, Alvarez M A, Reina T R. Biogas conversion to syngas using advanced Ni-promoted pyrochlore catalysts: effect of the CH₄/CO₂ ratio[J]. *Front Chem*, 2021, 9: 672419.
- [78] Theofanidis S A, Galvita V V, Poelman H, et al. Enhanced carbon-resistant dry reforming Fe-Ni catalyst: role of Fe[J]. *ACS Catal*, 2015, 5(5): 3028–3039.
- [79] De C V, Srinath N V, Theofanidis S A, et al. Looking inside a Ni-Fe/MgAl₂O₄ catalyst for methane dry reforming via mossbauer spectroscopy and in situ QXAS[J]. *Appl Catal B-Environ*, 2022, 300: 120720.
- [80] Pereniguez R, Gonzalez-Delacruz V M, Caballero A, et al. LaNiO₃ as a precursor of Ni/La₂O₃ for CO₂ reforming of CH₄: effect of the presence of an amorphous NiO phase[J]. *Appl Catal B-Environ*, 2012, 123: 324–332.
- [81] Chawl S K, George M, Patel F, et al. Production of synthesis gas by carbon dioxide reforming of methane over nickel based and perovskite catalysts[J]. *Procedia Eng*, 2013, 51: 461–466.
- [82] Bhattar S, Abedin M A, Kanitkar S, et al. A review on dry reforming of methane over perovskite derived catalysts[J]. *Catal Today*, 2021, 365: 2–23.
- [83] Wang Z, Cao X M, Zhu J, et al. Activity and coke formation of nickel and nickel carbide in dry reforming: a deactivation scheme from density functional theory[J]. *J Catal*, 2014, 311: 469–480.
- [84] Arena F, Frusteri E F, Parmaliana A, et al. Effect of calcination on the structure of Ni/MgO catalyst: an X-ray diffraction study[J]. *J Chem Soc*, 1996, 92(3): 469–471.

- [85] Villa R, Cristiani C, Groppi G, et al. Ni based mixed oxide materials for CH₄ oxidation under redox cycle conditions[J]. *J Mol Catal A-Chem*, 2003, 204: 637–646.
- [86] Gili A, Schlicker L, Bekheet M F, et al. Revealing the mechanism of multiwalled carbon nanotube growth on supported nickel nanoparticles by in situ synchrotron X-ray diffraction, density functional theory, and molecular dynamics simulations[J]. *ACS Catal*, 2019, 9(8): 6999–7011.
- [87] Li K, Chang X, Pei C L, et al. Ordered mesoporous Ni/La₂O₃ catalysts with interfacial synergism towards CO₂ activation in dry reforming of methane[J]. *Appl Catal B-Environ*, 2019, 259: 118092.
- [88] Bhaskaran A, Singh S A, Da C P, et al. Unveiling the catalytic behaviour of LaNiO₃ and La₂NiO₄ for dry reforming of methane[J]. *Int J Hydro Energ*, 2024, 68: 623–634.
- [89] Bonmassar N, Bekheet M F, Schlicker L, et al. In situ-determined catalytically active state of LaNiO₃ in methane dry reforming[J]. *ACS Catal*, 2019, 10(2): 1102–1112.

CO₂ 甲烷干重整特殊结构催化剂研究进展

李鹏阳^{1,3}, 田京雷^{2,3}, 韩 星^{1,3}, 刘宏强^{1,3,*}

(1. 河钢材料技术研究院有限公司, 河北 石家庄 050023; 2. 河钢集团有限公司, 河北 石家庄 050000;
3. 中国-塞尔维亚钢铁绿色制造“一带一路”联合实验室, 河北 石家庄 050023)

摘 要: 温室气体排放量的持续增长, 严重危机人类生存环境。甲烷干重整技术可将二氧化碳和甲烷转化为高经济价值的合成气, 并用于生产高附加值化学品, 为限制温室气体排放提供了绝佳的解决工艺。当前甲烷干重整反应存在催化剂碳沉积、活性位点烧结等核心问题, 兼具抑制碳沉积和具备高热稳定性的催化剂是关键, 同时这也是未来催化剂设计的核心挑战。特殊结构的复杂氧化物材料因具备优异的热稳定性、可调表面特性以及可在晶格结构中掺杂金属阳离子等能力, 受到了广泛的研究。本综述概述了甲烷干重整反应的热力学特性、反应机理及催化剂失活机制, 梳理了特殊结构烧绿石、尖晶石氧化物和钙钛矿型催化剂的结构特点, 以及在甲烷干重整反应中的应用研究进展, 围绕“活性金属稳定、氧空位调控、反应路径优化”三大核心调控机制开展分析, 揭示晶体结构、金属载体强相互作用及氧空位等因素与催化剂抗积炭和抗烧结间的构效关系。针对特殊结构催化剂的未来研究方向进行了展望。

关键词: 甲烷干重整; 反应机理; 失活机制; 抗积炭调控; 特殊结构催化剂

中图分类号: X701; O643.36

文献标识码: A

作者简介:



李鹏阳(1994), 硕士, 工程师, 研究方向为绿色减污降碳及碳资源利用技术研究, 1146001241@qq.com。



刘宏强(1974), 工学博士, 正高级工程师, 研究方向钢铁新材料的研发、冶金工艺优化、低碳绿色技术研发及推广, liuhongqiang@hbisco.com。