

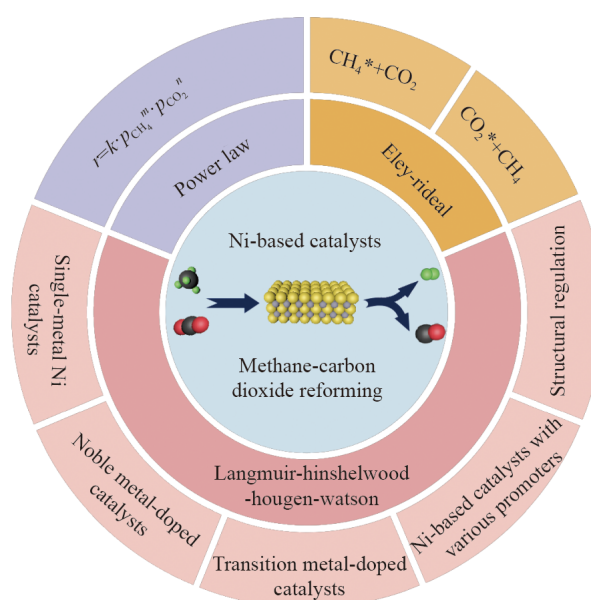
Research progress on the kinetics of methane-carbon dioxide reforming catalyzed by nickel-based catalysts

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Abstract: Under the backdrop of “Carbon Peak and Carbon Neutrality” (dual carbon) goal in China, the methane-carbon dioxide reforming reaction has attracted considerable attention due to its environmental benefits of converting two greenhouse gases (methane and carbon dioxide) into syngas and its promising industrial applications. Nickel (Ni)-based catalysts, with high catalytic activity, low cost, and abundant resources, are considered ideal candidates for industrial applications. In this article, three reaction kinetic models were briefly introduced, namely the Power-Law (PL) model, the Eley-Rideal (ER) model, and the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Based on the LHHW model, the reaction kinetics and mechanisms of different catalytic systems were systematically discussed, including the properties of supports, the doping of noble metals and transition metals, the role of promoters, and the influence of the geometric and electronic structures of Ni on the reaction mechanism. Furthermore, the kinetics of carbon deposition and elimination on various catalysts were analyzed. Based on the reaction rate expressions for carbon elimination, the reasons for the high activity of transition metal iron (Fe)-doped catalysts and core-shell structured catalysts in carbon elimination were explained. Based on the detailed collation and comparative analysis of the reaction mechanisms and kinetic characteristics across diverse Ni-based catalytic systems, a theoretical guidance for the designing of high-performance catalysts was provided in this work.

Key words: carbon dioxide reforming of methane; catalyst; model; kinetics; carbon deposit



As the economy grows, the consumption of fossil fuels continues to rise across countries, leading to a steady annual increase in global carbon dioxide (CO₂) emissions. Such intensive carbon emissions not only disrupt the natural equilibrium of the Earth's carbon cycle but also exacerbate the greenhouse effect, triggering systemic environmental crises like frequent extreme weather events and glacier

melting^[1-3]. With the ongoing implementation of the "dual carbon" strategic goals in China, carbon reduction has become a central focus in restructuring energy systems and transforming industries. In particular, the resource utilization of CO₂ has developed into a relatively mature application system, primarily used in the production of products such as urea^[4], methanol^[5], ethanol^[6] and dimethyl

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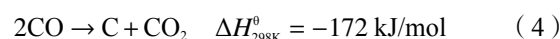
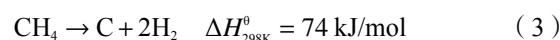
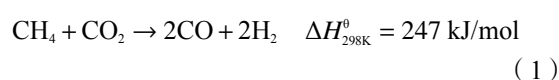
carbonate^[7]. These applications not only facilitate the recovery and utilization of CO₂ but also offer a sustainable raw material pathway for related chemical industries. Notably, among various CO₂ conversion technologies, the methane-carbon dioxide reforming reaction has gradually become a research hotspot due to its unique advantages^[8]. This reaction can convert CH₄ and CO₂ into synthesis gas (H₂/CO = 1), which serves as an excellent raw material for producing liquid fuels and low-carbon olefins through Fischer-Tropsch synthesis^[9–12].

The screening and design of catalysts are of vital importance in the methane-carbon dioxide reforming reaction. Among these catalysts, noble metals such as Pt, Rh and Ru demonstrate exceptional activity and stability; however, their scarcity and high costs significantly hinder their widespread industrial application^[13–15]. Ni-based catalysts, as prominent non-noble metal catalysts, are preferred for industrial use due to their high activity, low cost, and abundant availability. However, Ni-based catalysts face challenges such as carbon deposition and sintering during the methane-carbon dioxide reforming reaction, which can degrade their activity and stability^[16–19]. To address these challenges, strategies such as preparing bimetallic catalysts, using novel supports, or adding promoters have been employed to enhance the carbon resistance and catalytic activity of Ni-based catalysts^[20–21].

The derivation of rate expressions based on reaction mechanisms is the initial step in designing industrial reactors. Studies have revealed that variations in active metals, supports, and co-catalysts can lead to distinct reaction mechanisms and rate expressions^[22]. Therefore, this study systematically investigated the reaction mechanisms and rate equations over different catalysts, based on the three most commonly employed kinetic models for the methane-carbon dioxide reforming reaction. Additionally, it conducted a kinetic analysis of carbon deposition and elimination, aiming to provide a theoretical foundation for catalyst design and facilitate the industrialization of the methane-carbon dioxide reforming reaction.

1 Overview of methane-carbon dioxide reforming

The reactions for methane-carbon dioxide reforming and the main side reactions are presented in Equations (1) to (4). The main reaction is strongly endothermic which needs a high temperature to achieve a high reaction rate and conversion^[23–25]. The side reaction of reverse water gas shift (RWGS, Equation (2)) results in a high conversion of reactant CO₂ than CH₄, reducing the molar ratio of H₂ to CO in the syngas product. The methane decomposition reaction (Equation (3)) and CO disproportionation reaction (Equation (4)) produce carbon deposits on the catalyst surface, which will cover the active sites on the catalyst and block the pore structure, leading to catalyst deactivation.



Ni-based catalysts display high catalytic activity, somewhat close to that of noble metals such as Pt and Rh at high temperatures (700–900 °C), and have advantages such as abundant resources and low prices, making them more suitable for large-scale industrial applications. However, the Ni-based catalysts also suffer from problems such as easy sintering and severe carbon deposition in the methane-carbon dioxide reforming reaction. To address this issue, researchers have developed various modification strategies for Ni-based catalysts, such as introducing metal oxides as co-supports, constructing bimetallic catalysts, and adding promoters.

Figure 1 shows the catalytic activity of various Ni-based catalysts^[26–49]. Due to the occurrence of side reaction RWGS, the conversion of CO₂ on most catalysts was higher than that of CH₄. The core-shell structured Ni@SBA-15^[35] catalyst exhibited high reactant conversion at 700 °C, where the conversion of CO₂ was almost equal to that of CH₄, indicating that the dry reforming reaction of Equation (1) dominated the reaction process whereas the side reactions were greatly suppressed. The core-shell structured catalysts (Ni@SBA-15^[35], CeO₂@Ni-PsYS^[33] and Ni@SiO₂^[34]) showed high conversion, as the core-shell structure could inhibit the sintering of the catalyst through physical isolation and the shell porous structure could regulate the adsorption of reactants and the desorption path of products and then promote the reaction.

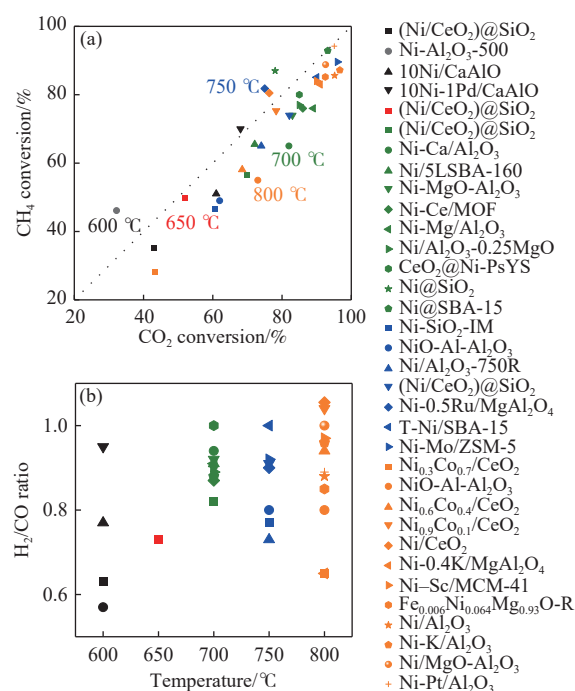


Fig. 1 Performance of different Ni-based catalysts in the methane-carbon dioxide reforming reaction: (a) reactant conversion and (b) H₂/CO ratio in the product

The addition of noble metals can optimize the electronic structure of Ni. In this temperature range, both 10Ni-1Pd/CaAlO₂^[27] and Ni-Pt/Al₂O₃^[49] showed excellent catalytic activity, and the conversions of two reactants were maintained at a similar high level. Such balanced catalytic performance can effectively inhibit the formation of carbon deposits and the occurrence of other side reactions. In contrast, over the Ni-Al₂O₃-500 catalyst^[26], two reactants were very different in their conversions, due to the large Ni particles (9.7 nm) which promoted the methane decomposition (Equation (3)).

As a core indicator of syngas, the H₂/CO ratio directly determines the adaptability of syngas in downstream chemical applications. The regulation of H₂/CO ratio in methane-carbon dioxide reforming can be achieved through the optimization of reaction conditions and catalyst design. In terms of reaction conditions, raising the temperature will significantly change the reaction path equilibrium. At a low temperature (< 700 °C), the H₂/CO ratio decreases due to the high reaction rate of the reverse water gas shift. Han et al.^[50] reported that the H₂/CO ratio over the (Ni/CeO₂)@SiO₂ catalyst was only 0.63 at 600 °C. At a high temperature (> 700 °C), the main reaction rate increases, while the reverse water gas shift is relatively inhibited^[51] and the methane decomposition reaction rate gradually accelerates, raising the H₂/CO ratio to 0.91 (at 750 °C). The feed ratio (CH₄/CO₂ ratio) also exerts a significant influence on the H₂/CO ratio in the product. Yoo et al.^[52] confirmed on the Ni/Al₂O₃ catalyst that when the CH₄/CO₂ ratio increased from 0.5 to 1.25, the H₂/CO ratio would rise from 0.72 to 0.9. When the CH₄/CO₂ ratio is relatively low, excessive CO₂ promotes the reverse water gas shift to consume H₂ and simultaneously accelerates the dissociation of CO₂ to form CO. In contrast, a relatively high CH₄/CO₂ ratio increases the cracking rate of CH₄.

In terms of catalyst design, the doping of noble metals can effectively suppress the side reactions^[27,53–54]. Taking the 10Ni-1Pd/CaAlO₂^[27] catalyst as an example, the introduction of Pd increases the H₂/CO ratio in the product from 0.77 to 0.95, owing to the formation of Ni-Pd solid solution, which effectively reduces the activation energy of methane-carbon dioxide reforming reaction, promotes the main reaction while reducing the rate of reverse water gas shift reaction, thereby avoiding excessive consumption of H₂. In addition, Pd can promote the reaction between CH₄ and CaCO₃, and maintain stable catalytic activity by inhibiting Ni sintering, thereby effectively improving the H₂/CO ratio.

Li et al.^[43] tried to regulate the H₂/CO ratio for the methane-carbon dioxide reforming by doping Co in the Ni/CeO₂ catalysts. A small amount of Co (Ni_{0.9}Co_{0.1}/CeO₂) produced a bimetallic synergistic effect with Ni, strengthened CO₂ adsorption and activation, so that CO₂ mainly participated in the main reaction, thereby inhibiting the reverse water gas shift reaction and making the H₂/CO ratio basically unchanged. However, excessive Co (e.g., Ni_{0.6}Co_{0.4}, Ni_{0.3}Co_{0.7}) could cover the active Ni sites to

inhibit CH₄ decomposition and H₂ production. Meanwhile, excessive CO₂ adsorption accelerated the consumption of H₂ via the reverse water gas shift reaction, thereby reducing the H₂/CO ratio in the product.

2 Reaction kinetics model

In the kinetic study of methane-carbon dioxide reforming reaction, the quantitative relationship between reactant partial pressure and reaction rate is mainly analyzed by the power law (PL) model, Eley-Rideal (ER) model, and Langmuir-Hinshelwood-Hougen-Watson (LHHW) model, and the reaction activation energy is obtained by the Arrhenius equation (Equation (5)). Among them, the LHHW model is the most commonly used model when exploring the reaction mechanism.

$$\ln k = -\frac{E_a}{RT} + \ln k_0 \quad (5)$$

where k is the reaction rate constant, E_a is the reaction activation energy, R is the gas constant (8.314 J/(mol·K)), T is the Kelvin temperature, and k_0 is the initial rate constant.

2.1 Power law (PL) model

The PL model is based on the power-function relationship between the partial pressure of reactants and the reaction rate observed by experiments. Its core hypothesis is that at a constant temperature, the reaction rate depends only on the partial pressure of reactants. In the methane-carbon dioxide reforming reaction, the reaction rate expression is expressed as:

$$r = k \cdot p_{\text{CH}_4}^m \cdot p_{\text{CO}_2}^n \quad (6)$$

where r is the consumption rate of the reactant or the production rate of the product, k is the reaction rate constant, and m and n are the reaction orders of CH₄ and CO₂, respectively.

The kinetic parameters of the PL model and activation energy data for methane-carbon dioxide reforming over different Ni-based catalysts are summarized in Table 1. Since side reactions (mainly the reverse water gas shift reaction, Equation (2)) will significantly affect the instantaneous concentration and apparent reaction rate of CO₂, CO and H₂, the PL model is usually fitted based on the CH₄ consumption rate. The results showed that for most catalysts, when fitting the PL model at the CH₄ consumption rate, the reaction order of CH₄ was higher than that of CO₂, indicating that the partial pressure of CH₄ plays a dominant role in the reaction rate, while the effect of CO₂ partial pressure was relatively small. The higher reaction order of CH₄ indicated that the reforming reaction rate was more sensitive to the change in the concentration of CH₄, implying that the adsorption or dissociation of CH₄ involved a higher energy barrier, so methane activation may be a rate control step of the reaction.

Table 1 Kinetic parameters of the power-law (PL) model for methane-carbon dioxide reforming over various Ni-based catalysts

Catalyst	Reaction temperature /°C	Activation energy/(kJ·mol ⁻¹)	r_{CH_4}		r_{CO_2}		r_{CO}		r_{H_2}		Ref.
			m	n	m	n	m	n	m	n	
Fe _{0.006} Ni _{0.064} Mg _{0.93} O-R	500–700	106.15	1.00	0	–	–	–	–	–	–	[47]
Ni-Ce/MOF	550–700	59.42	0.85	–0.39	–	–	–	–	–	–	[31]
Ni/CeO ₂	580–680	97.61	0.60	0.17	–	–	–	–	–	–	[44]
0.3Pt-10Ni/Al ₂ O ₃	580–620	23.60	1.00	0.87	–	–	–	–	–	–	[55]
0.2Pt-15Ni/Al ₂ O ₃	580–620	26.60	1.09	1.40	–	–	–	–	–	–	[55]
Ni-Pt/Al ₂ O ₃	600–700	66.00	0.43	0.31	0.33	0.60	0.25	0.45	0.37	0.25	[49]
β-Mo ₂ C-Ni/γ-Al ₂ O ₃	650–850	50.76	–	–	–	–	0.58	0.44	0.79	0	[56]
2D-β-Mo ₂ C-Ni/γ-Al ₂ O ₃	650–850	79.63	–	–	–	–	0.58	0.53	0.73	0	[56]
Ni/MgO-Al ₂ O ₃	600–700	70.50	0.41	0.35	0.34	0.58	0.23	0.46	0.34	0.19	[49]
Ni-Co/Al-Mg-O	650–750	63.30	0.48	0.29	–	–	–	–	–	–	[57]
Ni _{0.9} Co _{0.1} /CeO ₂	550–610	155.47	0.77	0.20	–	–	–	–	–	–	[43]
Ce _{0.7} La _{0.2} Ni _{0.1} O _{2-δ}	650–750	91.5	0.50	0.20	0.29	0.31	0.26	0.28	0.54	0.15	[39]

In contrast, the lower reaction order of CO₂ (partially close to 0 or negative) indicated a faster activation rate and a lesser effect of changes in the CO₂ concentration on the reaction rate. Therefore, the core characteristics of conventional catalysts are: the active site has weak activation ability of CH₄ and relatively strong conversion ability of CO₂. When designing and optimizing catalysts, focus should be on enhancing the activation of C–H bonds to reduce the dependence of the reaction on the CH₄ concentration.

The CO₂ reaction order on the Ni-Ce/MOF^[31] catalyst was negative, attributed to the strong adsorption of CO₂ by the CeO₂ support in the MOF-derived Ni-Ce catalyst, which significantly altered the reaction pathway. Stable carbonate species formed on the catalyst surface occupy the basic sites, which inhibits the CH₄ activation due to the steric hindrance effects and results in a negative CO₂ reaction order. For the 0.2Pt-15Ni/Al₂O₃ and 0.3Pt-10Ni/Al₂O₃^[55] catalysts, the former exhibits a significantly higher CO₂ reaction order ($n = 1.40$), because the reduced Pt content and diluting effect of Ni on Pt can jointly weaken the promotion of Pt in the oxygen transfer capacity. Consequently, the efficiency of CO₂ dissociation to generate reactive oxygen species is decreased. The reforming reaction then requires an increased CO₂ partial pressure to promote coke gasification and maintain active sites, ultimately leading to a significantly higher CO₂ reaction order.

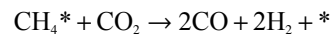
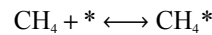
The PL model is relatively simple in application and parameter estimation, facilitating preliminary estimates of reaction parameters and providing fundamental information on the reactant concentrations and reaction rates. It is a widely applied kinetic model in methane-carbon dioxide reforming reactions^[58–59]. However, it cannot fully explain the mechanistic steps of surface reactions on catalysts. Therefore, other mechanism-based models need to be investigated to fit the kinetics of methane-carbon dioxide reforming reactions.

2.2 Eley-Rideal (ER) model

The Eley-Rideal (ER) model assumes that one molecule of the reactant (e.g., CH₄) preferentially adsorbs onto the catalyst surface. Subsequently, another gas-phase molecule (e.g., CO₂) reacts directly with this adsorbed species on the surface, forming a product that then desorbs. A relatively slow elementary step exists within the reaction process, which governs the overall reaction rate and is termed the rate-determining step (RDS). The ER model posits that the adsorption process rapidly reaches equilibrium, whereas the interaction between the gas-phase molecule and the adsorbed species is the reaction's rate-determining step.

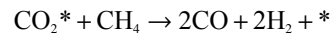
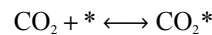
Since both CH₄ and CO₂ can serve as adsorbates in the methane-carbon dioxide reforming reaction, two models exist (ER I and ER II). The ER I model describes the reaction of adsorbed CH₄ with gas-phase CO₂, whereas the ER II model depicts the reaction of adsorbed CO₂ with gas-phase CH₄. As shown below, Mark et al.^[60] provided the reaction mechanisms and rate expressions for each model, where * denotes the active sites on the catalyst surface.

ER I



$$r_{CH_4} = \frac{k_{ref}K_{CH_4} \left(p_{CH_4}p_{CO_2} - \frac{p_{CO}^2p_{H_2}^2}{k_{ref}} \right)}{1 + K_{CH_4}p_{CH_4}}$$

ER II



$$r_{CH_4} = \frac{k_{ref}K_{CO_2} \left(p_{CH_4}p_{CO_2} - \frac{p_{CO}^2p_{H_2}^2}{k_{ref}} \right)}{1 + K_{CO_2}p_{CO_2}}$$

Sun et al.^[61] investigated the methane-carbon dioxide reforming reaction under the synergistic action of plasma

and Ni/SiO₂ catalysts. Under plasma promotion, CH₄ first dissociated and adsorbed on the active Ni metal sites to form CH₃* and H* species. Gaseous CO₂ reacted with H* species to generate COOH* or HCOO* species. Subsequently, COOH* and HCOO* species dissociated on the catalyst surface to produce CO* and OH*, with CO* desorbing to form CO. The reaction primarily followed the ERI mechanism, as the reactant molecules partially achieved vibrational states under plasma conditions, which enhanced the reactions between H* species and CO₂, O radicals and CH₃* species, and H radicals and HCOO* species, thereby conferring high activity to the ER reaction.

The ER model considers only reactions between adsorbed species and gas-phase molecules, effectively reducing the model complexity. However, in the actual methane-carbon dioxide reforming reaction process, the reaction mechanisms on the catalyst surface are more complex, typically involving interactions among multiple adsorbed species. The ER model fails to account for surface reactions between adsorbed species and other potential reaction pathways, which may limit its ability to accurately describe the actual reaction processes in certain catalyst systems. Consequently, the application of the ER model in current kinetic studies has become relatively uncommon.

2.3 Langmuir-Hinshelwood-Hougen-Watson model

The Langmuir-Hinshelwood-Hougen-Watson (LHHW) model assumes that the reactants (CH₄ and CO₂) first adsorb onto the catalyst surface, forming adsorbed species. Subsequently, surface reactions occur between adjacent adsorbed species, ultimately leading to the desorption of the generated products. In this process, any elementary step, no matter adsorption, surface reaction, or product desorption, as long as its kinetic resistance significantly exceeds that of other steps, can become the rate-determining step. In contrast, the steps not in the rate-determining position is assumed in a quasi-equilibrium state.

The LHHW model derives corresponding rate equations by analyzing the kinetic equilibrium of each step in the adsorption-surface reaction-desorption process. It enables more precise elucidation of the nature of surface reactions on catalysts, thereby providing guidance for the catalyst design, reaction condition optimization, and reactor design.

Numerous researchers have conducted in-depth studies on the kinetics of methane-carbon dioxide reforming based on the LHHW model. Results indicated that catalyst characteristics, such as active metal components, support properties, and additive modifications, could significantly influence the reaction mechanism, rate equations, rate-determining steps, and apparent activation energies. Therefore, subsequent sections of this study will primarily utilize the LHHW model to investigate the reaction mechanisms of methane-carbon dioxide reforming on different catalyst types. The aim is to provide theoretical guidance for optimizing catalyst design strategies, effectively promoting the activation of reactants CH₄ and

CO₂, and thereby enhancing the overall reaction rate.

3 Reaction kinetics and mechanism of Ni-based catalysts based on the LHHW model

3.1 Effect of support on the Ni-based catalysts

The properties of support for the Ni-based catalysts significantly influence the kinetics of methane-carbon dioxide reforming reactions. Commonly used supports include Al₂O₃, alkaline-earth metal oxides, transition metal oxides, and rare earth metal oxides. Doping of the support alters the metal-support interaction (MSI) within the catalyst. MSI modifies the reduction difficulty of the metal oxide, where hydrogen-temperature-programmed reduction (H₂-TPR) characterization can give an indirect assessment of the MSI strength. Strong metal-support interactions (SMSI) enable more stable dispersion of Ni nanoparticles on the support surface and the support's enveloping effect on Ni (induced by SMSI) can physically hinder the agglomeration of Ni particles. Additionally, support doping can adjust reactant adsorption by altering the concentration and strength of alkaline sites on the catalyst, thereby accelerating reaction rates or promoting coke gasification. The primary effects of different supports on catalyst performance are summarized in Table 2^[32,62–66].

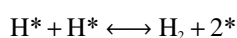
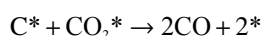
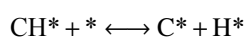
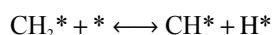
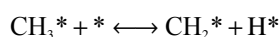
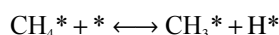
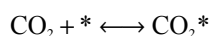
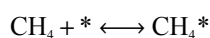
3.1.1 Al₂O₃

When the active metal Ni was loaded on an Al₂O₃ support, Silva et al.^[62] obtained two reduction peaks for Ni/Al₂O₃ by H₂-TPR analysis: the low-temperature region (259 °C) corresponded to the reduction of NiO with weak metal-support interactions, with an H₂ consumption of 13.3 cm³/g, and the high-temperature region (479 °C) corresponded to the reduction of the moderately strong metal-support interaction of NiAl₂O₄ phase with H₂ consumption of 35.65 cm³/g. The high dispersion of Ni promoted the activation of CH₄, but the catalyst adsorbed CO₂ weakly and was unable to eliminate the surface carbon accumulation in time, so the catalyst activity was decreased by 10.4% after 12 h of reaction.

Wang et al.^[67] investigated the kinetics of methane-carbon dioxide reforming reaction over Ni/γ-Al₂O₃ catalysts at 500–700 °C. CH₄ was progressively dehydrogenated at the Ni active site to form C* species and H* species, CO₂ was adsorbed and activated with CH₄ at the same active site, and the C* species reacted with surface adsorbed CO₂* to form CO, and the two molecules of H* species were desorbed to form hydrogen, wherein the formation of CO is the rate-determining step of the reaction. Over this catalyst, Ni particles, reduced NiAl₂O₄ and Ni-C intermediates were the active sites for the reaction. The reaction mechanism and rate expression are as follows^[67].

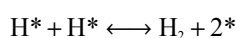
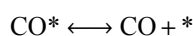
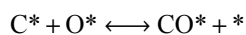
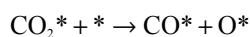
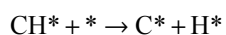
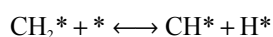
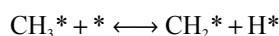
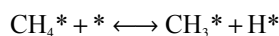
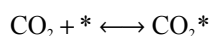
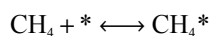
Table 2 Effects of the supports on the performance of Ni-based catalysts in the methane-carbon dioxide reforming

Metal oxide	H ₂ -TPR characteristics	CO ₂ -TPD characteristics	Key mechanisms	Ref.
Al ₂ O ₃	Reduction peak temperatures: 259 and 479 °C, with medium-strength MSI	–	NiAl ₂ O ₄ promotes Ni dispersion	[62]
MgO	Reduction peak temperatures: 410→770 °C, SMSI	Basic site concentration: 10.25→20.99 μmol/g, significant increase in the amount of strong basic sites	SMSI and enhanced basicity	[32]
MnO _x	Reduction peak temperatures: 255 and 321 °C →268 and 340 °C	Basic site concentration: 230→336 μmol/g	Increase in basic sites and oxygen vacancies due to lattice substitution	[63]
ZrO ₂	ZrO ₂ doping promotes the reduction of the catalyst, and the reduction peak temperature slightly decreases at 400 °C	–	Increase in oxygen vacancy concentration, CO pulse chemisorption indicates significant enhancement of MSI, promoting the migration of lattice oxygen	[64]
La ₂ O ₃	Reduction peak temperatures: 350→376 °C	Increase in basic site concentration	La ₂ O ₃ promoted CO ₂ adsorption, accelerated elimination of deposited carbon, MSI promoted Ni dispersion, and increased the reaction interface	[65]
CeO ₂	Reduction peak temperatures: 543→537 °C	Enhancement of basic site strength	Increase in oxygen vacancy concentration, enhanced basicity	[66]



$$r_{\text{CH}_4} = \frac{k_1 p_{\text{CH}_4} p_{\text{CO}_2}}{(1 + K_1 p_{\text{CH}_4})(1 + K_2 p_{\text{CO}_2})}$$

Dehimi et al.^[68] studied the reaction path over the Ni/Al₂O₃ catalyst (as shown below), CH₄ adsorbed and dissociated on Ni active sites to produce C* species and H* species, CO₂ dissociated and adsorbed on Ni active sites to produce CO* and O* species, and O* species oxidized C* species to produce CO*. In this case, the dissociation of the C–H bond in CH₄ and the dissociation of CO₂ were the rate-determining steps of the reaction.



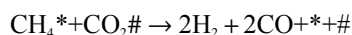
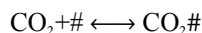
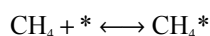
3.1.2 Alkaline-earth metal oxide

The doping of magnesium oxide (MgO) contributes multidimensionally to the performance enhancement of Ni/Al₂O₃ catalysts. Feng et al.^[32] revealed the critical role of MgO on alkaline sites through carbon dioxide programmed thermal desorption (CO₂-TPD) characterization: a moderate amount of doping ($x = 0.5$) increased the CO₂ adsorption of Ni_{0.5}/xMgO-Al₂O₃ from 10.25 to 20.99 μmol/g, attributed to the formation of NiAl₂O₄ spinel by MgO and Al₂O₃ which synergistically constructed a strongly alkaline surface with MgO, promoted CO₂ activation and accelerated the gasification of carbon deposits^[69–71].

The enhancement of metal-support interactions is another key mechanism^[72]. H₂-TPR analysis shows that the reduction peaks of NiO species gradually disappeared after MgO doping, while the reduction peaks of NiAl₂O₄ migrated to high temperatures above 800 °C. The doping of moderate amount of MgO ($x = 0.5$) enhanced the metal-support interactions by forming NiAl₂O₄ and Ni_xMg_{1-x}O solid solutions, which brought about no significant deactivation of Ni_{0.5}/0.5MgO-Al₂O₃ within 100 h, with a carbon accumulation of only 0.8%, much lower than that of 47.2% in the undoped case, and effectively maintained the stability of the active sites^[32].

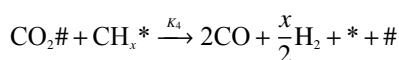
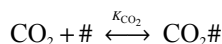
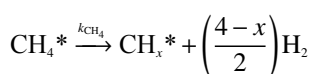
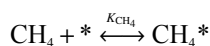
For the optimization of reaction path, the kinetic model developed by Karemire et al.^[49] confirmed that the reforming reaction over Ni/MgO-Al₂O₃ catalyst followed a bifunctional mechanism after MgO doping, CH₄ and CO₂ were adsorbed *via* molecular adsorption on two distinct active sites of the catalyst and the rate-determining step was identified as a surface reaction step. This mechanism enabled the catalyst to operate at 800 °C for 30 h without

carbon accumulation, indicating that the addition of MgO in the catalyst enhanced the basic sites and inhibited carbon deposition. The reaction mechanism and reaction rate equation are as follows^[49].



$$r_{\text{CH}_4} = \frac{k p_{\text{CH}_4} p_{\text{CO}_2}}{(1 + K_{\text{CH}_4} p_{\text{CH}_4})(1 + K_{\text{CO}_2} p_{\text{CO}_2})}$$

The modulation of the catalytic system by CaO focused on the enhancement of the basic sites. For the Ni-CaO-ZrO₂ catalysts, Wang et al.^[73] observed that CaO promoted CO₂ adsorption to form the CaCO₃ species by elevating the support's basicity but did not significantly alter the strength of the metal-support interaction. Unlike MgO doping, no enhancement of metal-support interactions was found in either CaO-doped Al₂O₃ or ZrO₂ supports^[74–75]. For the ZrO₂ support, its oxygen vacancies synergistically promoted CO₂ activation with CaO, which maintained a high catalytic activity for 100 h. Regarding the reaction mechanism, the CaO-modified system also followed a bifunctional mechanism: CH₄ was dehydrogenated on the Ni active site to generate CH_x* species and H₂, while CO₂ was adsorbed on the support to form CO₂#. These adsorbed species subsequently reacted to generate CO and H₂. The methane dissociation step and the surface reaction between CH_x* and CO₂# were jointly rate-controlling, and the reaction rate is expressed as follows^[73].



$$r_{\text{CH}_4} = \frac{K_{\text{CH}_4} k_{\text{CH}_4} K_{\text{CO}_2} K_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_{\text{CH}_4} k_{\text{CH}_4} K_{\text{CO}_2} p_{\text{CH}_4} p_{\text{CO}_2} + K_{\text{CH}_4} k_{\text{CH}_4} p_{\text{CH}_4} + K_{\text{CO}_2} K_4 p_{\text{CO}_2}}$$

3.1.3 Transition metal oxide

Transition metal oxide supports influence the methane-carbon dioxide reforming reaction pathways by modulating the electronic structure of metal active sites and the oxygen vacancy concentration in the catalysts through doping-induced metal-support interactions (MSI).

He et al.^[76] reported that the TiO_x layer (non-stoichiometric titanium oxide) in the Ni-TiO_x catalysts transferred electrons to Ni nanoparticles via metal-support interactions, forming electron-rich Ni-O_v-Ti³⁺ interface sites. The electron-rich Ni led to an upshift of its *d*-band center, promoting the cleavage of CH₄. The electron transfer schematic diagram on the Ni-TiO_x catalysts is illustrated in Figure 2. Concurrently, the strong metal-support interactions facilitated the formation of oxygen vacancies.

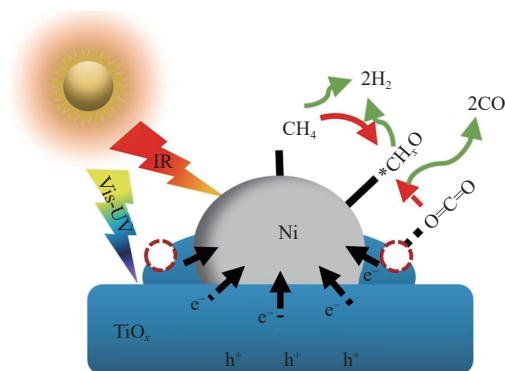


Fig. 2 Schematic diagram of electron transfer over the Ni/TiO_x catalyst^[76]
(with permission from Elsevier)

These vacancies serve as active sites for the adsorption and activation of CO₂, accelerating the oxidative removal of CH_x intermediates and thereby mitigating the formation of carbon deposits.

MnO_x doping modifies the catalyst properties through lattice substitution. Using the CO₂-TPD analysis, Sagar et al.^[63] found that the substitution of Ce⁴⁺ by Mn³⁺/Mn⁴⁺ increased the total basicity of the support from 0.2302 to 0.3361 mmol/g, while also elevating the oxygen vacancy concentration, which promoted the adsorption of CO₂ and the generation of reactive oxygen species, accelerating carbon deposit oxidation. H₂-TPR analysis revealed that the reduction peak shifted to higher temperatures and hydrogen consumption decreased after MnO_x doping, indicating that MnO_x doping could enhance the metal-support interaction between NiO and MnO_x-CeO₂, which suppressed Ni particle sintering and improved catalyst stability^[77].

The reaction mechanism of methane-carbon dioxide reforming on the Ni/MnO_x-CeO₂ catalysts is illustrated in Figure 3. MnO_x promotes the direct dissociation of CO₂ into the reactive oxygen species by increasing oxygen vacancies concentration within the catalyst. The resulting reactive oxygen species accelerate the oxidation of methane dissociation intermediates, thereby enhancing the reaction rates and suppressing the catalyst coking^[63].

ZrO₂ doping enhances catalyst reducibility through lattice distortion and increase of oxygen vacancy concentration, while boosts the reaction activity and stability by strengthening the metal-support interactions. Using H₂-TPR characterization, Das et al.^[64] demonstrated that when the Ni-PS@Ce_{1-x}Zr_xO₂ catalysts were doped with moderate amounts of ZrO₂ (*x* = 0.05–0.1), the reduction peaks of NiO and CeO₂ shifted toward lower temperatures, indicating that ZrO₂ doping promoted the synergistic reduction of NiO and CeO₂. The incorporation of Zr⁴⁺ into the CeO₂ lattice induces lattice distortion, facilitating the formation of oxygen vacancies. Furthermore, after doping 10% ZrO₂, the CO pulse chemisorption capacity decreased from 211 to 106 μmol/g_{Ni}, suggesting that the CeO₂-ZrO₂ support could enhance the metal-support interactions, increase the Ni particle coverage, and promote the migration of oxygen species from the support to the Ni metal surface through an enlarged interfacial contact area, thereby accelerating the reaction rate.

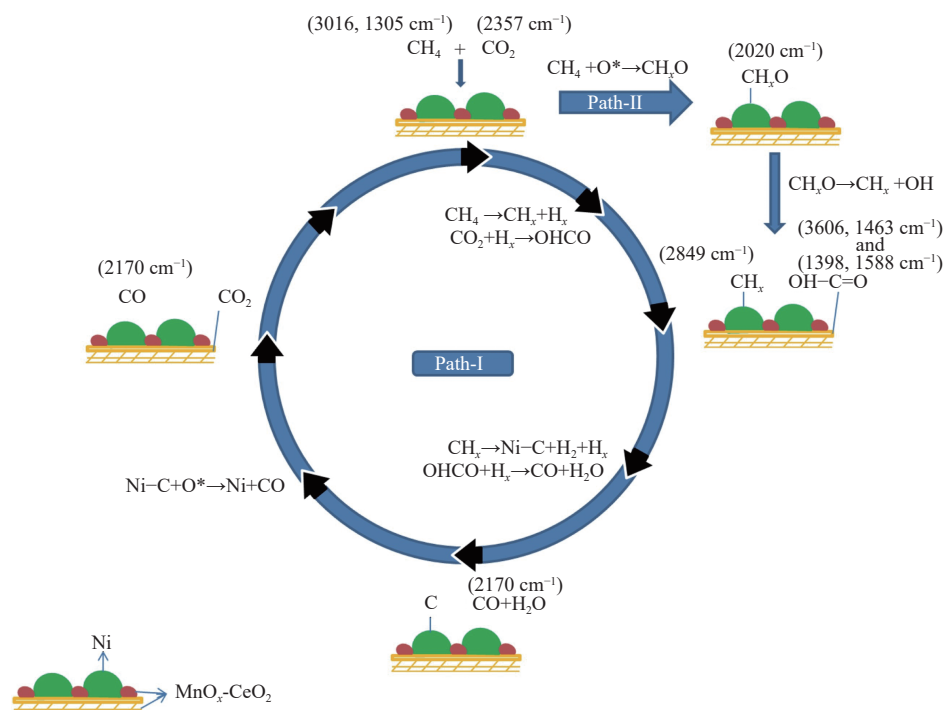
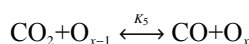
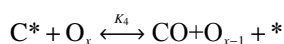
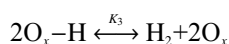
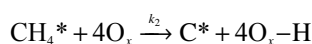
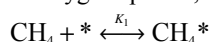


Fig. 3 Mechanism of methane-carbon dioxide reforming reaction on Ni/6MnO_x-CeO₂ catalyst^[63] (with permission from Elsevier)

Das et al.^[64] investigated the reaction pathway over the Ni-PS@Ce_{0.9}Zr_{0.1}O₂ catalysts between 600 and 675 °C and found that CH₄ reacted with reactive oxygen species to form C* species and hydroxyl species, which is considered as the rate-determining step. Hydrogen was produced via dehydrogenation of hydroxyl species, which subsequently regenerated the reactive oxygen species. These reactive oxygen species can further oxidize C* species derived from the dissociation of CH₄, producing CO and oxygen vacancies. Finally, CO₂ was dissociated at the oxygen vacancies to form CO and regenerate reactive oxygen species. The reaction steps and rate expressions are given as follows^[64], where * denotes Ni active sites, O_x represents reactive oxygen species, and O_{x-1} denotes oxygen vacancies.



$$r_{\text{CH}_4} = \frac{k_2 p_{\text{CH}_4} \left(1 - \frac{p_{\text{H}_2}^2 p_{\text{CO}}^2}{K_{\text{eq}} p_{\text{CH}_4} p_{\text{CO}_2}} \right)}{\left(1 + K_a \frac{p_{\text{CO}}}{p_{\text{CO}_2}} + K_b p_{\text{H}_2}^{0.5} \right)^4 \left(1 + K_c p_{\text{CH}_4} + K_d \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \right)}$$

$$\text{where } K_a = \frac{1}{K_5}, K_b = \frac{1}{K_3}, K_c = K_1, K_d = \frac{1}{K_4 K_5}$$

3.1.4 Rare earth metal oxide

In the methane-carbon dioxide reforming reactions, the

rare earth metal oxide La₂O₃ has demonstrated significant advantages as a catalyst support. Its core function lies in promoting CO₂ adsorption and activation, yielding the reaction intermediate La₂O₂CO₃, which effectively eliminates surface coking on the catalyst, thus forming a cyclic system of “La₂O₃→La₂O₂CO₃→La₂O₃”^[9,78–79]. This process significantly enhances catalytic efficiency and stability through metal-support interactions. The addition of CeO₂ is primarily aimed at optimizing the methane-carbon dioxide reforming reaction by increasing the oxygen vacancy concentration and the number of basic sites in the catalyst^[80].

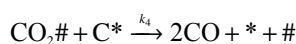
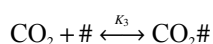
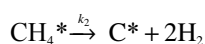
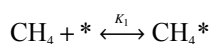
Regulating the metal-support interactions is crucial for optimizing the catalytic performance of rare-earth metal oxides. Li et al.^[81] prepared the Ni/La₂O₃ catalysts via different methods and found that stronger metal-support interactions promote the dispersion of Ni particles, significantly increasing the catalyst's metal-support interface area. This feature ensures that La₂O₂CO₃ can promptly react with coke deposits on the adjacent metal-support interfaces, effectively preventing coke accumulation and the excessive buildup of the reaction intermediate La₂O₂CO₃, which can not only accelerate the reaction rate but also enhance the catalyst stability.

Xu et al.^[65] investigated the effect of La₂O₃ doping on Ni/CeO₂ catalysts. H₂-TPR characterization revealed that La₂O₃ doping shifted the reduction peak of NiO from 350 to 376 °C, indicating significantly enhanced metal-support interactions. This enhancement resulted in a narrower Ni particle size distribution, with sizes refined from 9.4–22.8 to 4–10 nm. Concurrently, CO₂-TPD results revealed a substantial increase in the intensity of basic sites on the

catalyst surface, significantly promoting CO₂ activation. Ding et al.^[82] observed that in the CeO₂-incorporated Ni/MgCe_{0.12}O₃ catalysts, the proportion of oxygen vacancies increased to 40% from 15% in Ni/MgO, which was also proved by the Raman spectroscopy. CO₂-TPD test revealed that CeO₂ introduction strengthened the catalyst's basic sites, thereby enhancing CO₂ adsorption capacity. In-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) results indicated that surface CO₂ was primarily adsorbed as stable bicarbonate species, with minimal shifts in characteristic peak intensity at elevated temperatures, which further corroborated the enhanced CO₂ adsorption strength. In summary, CeO₂ can enhance the catalyst reactivity by increasing oxygen vacancy concentration and strengthening alkaline sites to activate CO₂. Kinetic data show a decrease of the activation energy from 65.9 to 52.9 kJ/mol, providing evidence of a lowered energy barrier for the improvement of catalyst performance through CeO₂ doping.

Regarding the reaction mechanism, Li et al.^[81] compared 5Ni/ La₂O₃-C (C denotes conventional preparation) with 5Ni/ La₂O₃-LOC (LOC indicates La₂O₃ derived from La₂O₂CO₃). They found that the methane-carbon dioxide reforming reaction on both catalysts followed a bifunctional mechanism and the dissociation of CH₄ on the Ni nanoparticle surface was the rate-determining step, which yielded H₂ and an active carbon intermediate. Subsequently, CO₂ adsorbed on the La₂O₃ surface formed La₂O₂CO₃, which reacted with the active carbon intermediate to produce CO and H₂, completing the La₂O₂CO₃-La₂O₃ cycle. Furthermore, Gao et al.^[83] confirmed that the oxygen vacancies provided by La₂O₃ could synergistically promote CO₂ conversion and carbon species oxidation, enhancing this cyclic process.

Gallego et al.^[84] investigated the reaction kinetics on the Ni/La₂O₃ catalysts and concluded that the complete dissociation of CH₄ at Ni active sites constituted the rate-determining step. The resulting carbon species can react with La₂O₂CO₃ generated from La₂O₃-activated CO₂ to produce CO. A rate expression for the reaction was derived based on the reaction mechanism^[84], where the symbol * denotes active sites on metallic Ni and # denotes active sites on the La₂O₃ support.



$$r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_3 k_4 p_{\text{CO}_2} + K_1 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2} + K_1 k_2 p_{\text{CH}_4} + K_1 k_2 K_3 p_{\text{CO}_2}}$$

Pino et al.^[39] investigated the methane-carbon dioxide reforming reaction catalyzed by Ce_{0.7}La_{0.2}Ni_{0.1}O_{2-δ} at a temperature between 650 and 750 °C. CeO₂ could form a solid solution with La₂O₃, increasing the concentration of oxygen vacancies within the catalyst and promoting the

adsorption and dissociation of CO₂. The specific reaction pathway involved the rapid dissociation of CH₄ at Ni active sites to generate carbon species. Subsequently, Ce₂O₂CO₃ and La₂O₂CO₃, formed by CO₂ reacting with Ce₂O₃ and La₂O₃, can interact with these carbon species to eliminate surface carbon deposition. The elimination of carbon species could maintain the catalyst stability and constitutes the rate-determining step. This reaction mechanism aligns with the findings of Gallego et al.^[84], demonstrating high fitting accuracy when kinetic data were modeled against their proposed rate expression. Wang et al.^[85] observed that CeO₂ in the catalyst promotes the activation of both CH₄ and CO₂ through a redox cycling, with the reaction pathway illustrated in Figure 4.

Table 3 gives a comparative summary of kinetic characteristics of methane-carbon dioxide reforming over the Ni-based catalysts with various supports, which demonstrates that the physicochemical properties of the support can significantly influence the reaction kinetics by altering active sites and reaction pathways. In particular, the Al₂O₃ support enables highly dispersed Ni active sites, allowing methane to undergo stepwise dehydrogenation on the catalyst, resulting in coking (CH₄→CH_x→C). However, due to the neutral nature of the Al₂O₃ support, its adsorption capacity for CO₂ is relatively weak, which hinders the elimination of deposited carbon. The rate-determining step for this system is either the dissociation of CH_x* species or the reaction between surface C* species and adsorbed CO₂.

In contrast, alkaline-earth metal oxide such as MgO strengthens the metal-support interaction (SMI) by forming Ni_xMg_yO solid solutions, promoting active metal dispersion. Both MgO and CaO enhance the catalyst's basicity, driving simultaneous activation of CH₄ and CO₂ at spatially separated active sites (* and #). This not only facilitates oxidation of CH_x* species but also suppresses the direct cracking of CH₄ that leads to coking. The rate-determining step here is the interaction between CH_x* and CO₂# species.

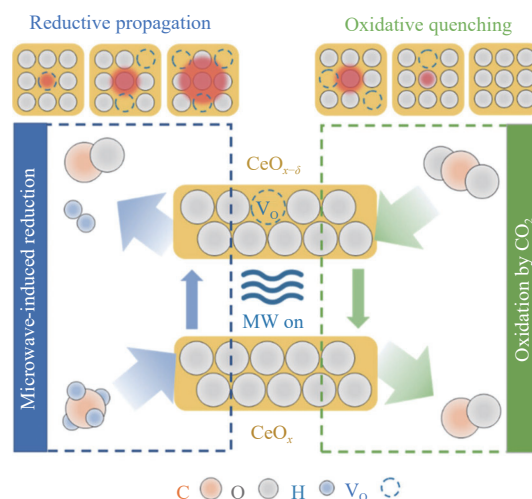


Fig. 4 Schematic diagram of CeO₂ redox cycling promoting methane-carbon dioxide reforming reaction^[85] (with permission from ACS Publications)

Table 3 Comparative analysis of reaction kinetics of methane-carbon dioxide reforming over the Ni-based catalysts with various supports

Support	Characteristics	Influence on kinetics	Rate determining step
Al ₂ O ₃	Ni active sites with high dispersion, neutral support	CH ₄ gradually dissociates to produce C* species, which leads to the gradual formation of carbon deposits	C* + CO ₂ * → 2CO + 2*
Alkaline-earth metal oxides	Enhance the basicity of the support, promote CO ₂ adsorption, and inhibit carbon deposition	CH ₄ and CO ₂ are activated at different active sites, promoting the reaction of CH _x * species	CO ₂ # + CH _x * $\xrightarrow{K_4}$ 2CO + $\frac{x}{2}$ H ₂ + * + #
Transition metal oxides	Increase the oxygen vacancy concentration of the support	Promote the oxidation of CH _x species	CH ₄ * + 4O _x $\xrightarrow{k_2}$ C* + 4O _x -H
Rare earth metal oxides	MSI promotes Ni dispersion, and increases the concentrations of oxygen vacancies and basic sites	La ₂ O ₃ reacts with CO ₂ to form La ₂ O ₂ CO ₃ , accelerating the gasification of carbon at the interface	CO ₂ # + C* $\xrightarrow{k_4}$ 2CO + * + #

Transition metal oxides primarily promote CO₂ adsorption and accelerate CH_x species oxidation by enhancing the oxygen vacancy concentration in the catalysts. Specifically, TiO_x doping creates electron-rich Ni-O_v-Ti³⁺ interface sites via MSI, effectively promoting CH₄ cracking while also facilitating CO₂ adsorption through oxygen vacancy formation, thereby accelerating CH_x oxidation. MnO_x increases catalyst basicity and oxygen vacancy concentration through lattice substitution; ZrO₂ enhances oxygen vacancies *via* lattice contraction and promotes oxygen species migration through MSI. The rate-determining step primarily involves the reaction between CH₄ and reactive oxygen species.

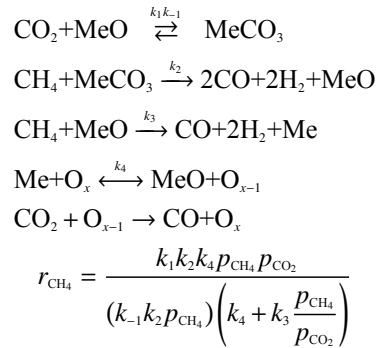
Doping of the rare earth metal oxide La₂O₃ effectively promotes the dispersion of active metal Ni and enlarges the metal-support interface *via* MSI, thereby facilitating the reaction between La₂O₂CO₃ and carbon deposits at the interface, which is the rate-determining step. Meanwhile, CeO₂ enhances the reaction by increasing the concentration of strongly basic sites and oxygen vacancies.

3.2 Noble metal-doped catalysts

Noble metal catalysts (such as Pt, Rh, Ru, etc.) are widely used in methane-carbon dioxide reforming reactions due to their high catalytic activity and strong anti-coking properties^[86–90]. However, their scarcity and high cost hinder widespread industrial application^[91–92]. One effective strategy to address this challenge is to incorporate trace amounts of noble metals into the Ni-based catalysts, which modulates the electronic structure of active sites, increases the concentration of surface oxygen species, and enhances coke resistance.

Bobrova et al.^[93] proposed the reaction mechanism over the Pt+Ni/Pr_{0.15}Sm_{0.15}Ce_{0.35}Zr_{0.35}O_x/YSZ catalyst at 650–850 °C, where Pt and Ni formed alloyed nanoparticles, enhancing the catalyst's capacity for CH₄ dissociation via strong metal-support interactions (SMSI), which altered the surface electron density of Ni. Concurrently, Pt synergistically promoted the formation of oxygen vacancies on the support surface with rare earth elements (Pr, Sm)^[94–95], significantly enhancing oxygen species migration.

CO₂ activation occurred simultaneously on the support's MeO and oxygen vacancy sites (O_{x-1}), while the enhanced oxygen migration further accelerated oxygen species cycling, promoting methane activation. Methane activation served as the rate-limiting step in the reaction, and the rate expression for methane conversion was derived through reaction pathway analysis^[93].



By combining the density functional theory with kinetic studies, Niu et al.^[96] demonstrated that Pt in Pt-Ni bimetallic catalysts significantly reduced the activation energy for CH₄ and CO₂ dissociation, thereby enhancing the surface concentration and reactivity of O* species generated from CO₂ dissociation. This promoted the oxidation of hydrocarbon species on the Pt-Ni catalyst surface rather than their cracking into surface carbon deposits, effectively enhancing catalyst stability. The incorporation of Pt also suppressed the reverse water-gas shift reaction by promoting hydrogen formation, thereby improving the H₂/CO ratio in the product.

By doping the noble metal Rh into the Ni₉/h-BN catalyst, Zhang et al.^[97] observed that the reduction of electronegativity by Rh minimized the electron transfer between the catalyst and hydrocarbon species, which significantly lowered the adsorption energy of CH_x (x = 1–4), thereby suppressing the presence of carbon deposit precursors. Additionally, by promoting the CO₂ activation, the coverage of oxygen species on the catalyst surface was enhanced, which facilitated the oxidation of CH* species. Concurrently, Rh doping increased the activation energy for C–C bond formation from 0.57 to 0.87 eV, significantly inhibiting the formation of carbon deposits.

In terms of reaction kinetics, the reaction pathways over the Ni₉/h-BN and Ni₈Rh₁/h-BN catalysts are shown in Figure 5, as reported by Zhang et al.^[97]; however, they did not further investigate whether there are differences in the kinetic expressions over different catalysts. On the Ni₉/h-BN catalyst, CH₄ underwent stepwise dissociation at active sites to form C* and CH* species, both of which were oxidized by the O* species. CO₂ dissociation was the rate-determining step for the reaction on the Ni₉/h-BN catalyst. For the Ni₈Rh₁/h-BN catalyst, the addition of the noble metal Rh increased the concentration of O* species on the catalyst surface, establishing the oxidation of CH* species as the primary pathway for converting the CH₄ dissociation intermediates. The breaking of the first C–H bond in CH₄ was the rate-determining step. Mao et al.^[98] also confirmed through the *in situ* DRIFTS studies that CH_x* species generated from CH₄ cracking on the RhNi-MgAl₂O₄ catalyst surface were preferentially oxidized by O* species rather than undergoing further dehydrogenation to form C*.

Zhou et al.^[99] investigated the kinetics of methane-carbon dioxide reforming on the Ru-Ni-MgO catalysts. X-ray photoelectron spectroscopy (XPS) analysis revealed that the oxygen affinity of Ru promoted the enrichment of oxygen species on the catalyst surface^[100]; these oxygen species preferentially reacted with carbon intermediates (e.g., CH* species) generated from CH₄ dissociation, preventing their polymerization into refractory graphitic carbon^[101]. Thermogravimetric analysis of the catalyst after 100 h of reaction at 760 °C revealed that the content of refractory graphitic carbon decreased from 5.1% to 2.5% upon Ru addition.

From a reaction kinetics perspective, the addition of Ru increased the CH₄ dissociation activation energy from 84 to 92 kJ/mol, making the dehydrogenation of CH₂* be the rate-determining step and suppressing the catalyst surface coking^[99]. Simultaneously, the elevated oxygen species concentration not only accelerated the direct oxidation of CH* species generated from CH₄ dissociation, thereby promoting the reforming reaction, but also enhanced the carbon gasification reaction rate, raising the pre-exponential factor from 19.2 to 18360 s⁻¹.

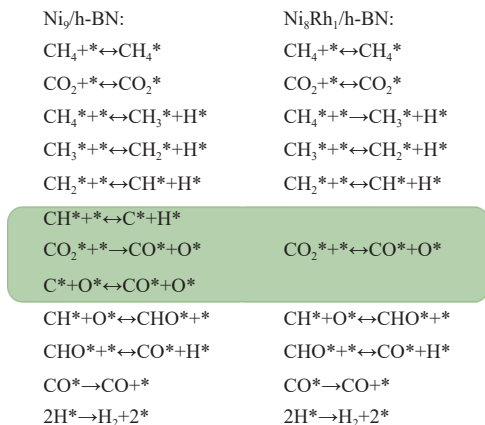
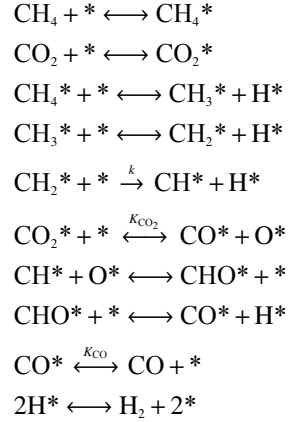


Fig. 5 Comparison of methane-carbon dioxide reforming reaction pathways on the Ni₉/h-BN and Ni₈Rh₁/h-BN catalysts^[97]



$$r_{\text{CH}_4} = k p_{\text{CH}_4} \left(\frac{1}{1 + \frac{K_{\text{CO}_2} p_{\text{CO}_2}}{K_{\text{CO}} p_{\text{CO}}}} \right)$$

The effects of noble metal (Pt, Rh, Ru) doping on the reaction kinetics of Ni-based catalysts are comparatively analyzed in Table 4. Noble metals primarily optimize the reaction kinetics by regulating the electronic structure and surface properties of Ni-based catalysts. Pt forms Pt-Ni alloys and induces SMSI with the support, enhancing CH₄ activation while promoting the formation of oxygen vacancies on the support, which accelerates CO₂ activation and reduces surface coking. The enhanced mobility of oxygen species makes methane activation be the rate-determining step. Rh, leveraging its low electronegativity, weakens the adsorption of CH_x species and promotes CO₂ dissociation, thereby increasing the coverage of oxygen species. It shifts the reaction pathway toward direct oxidation of CH*, which not only reduces the activation energy but also inhibits C–C bond formation, significantly suppressing carbon deposition. Although the addition of Ru increases the activation energy for CH₄ dissociation, its oxygen affinity promotes the CO₂ adsorption and enriches the surface oxygen species, which can accelerate the CH* oxidation and suppress the formation of difficult-to-gasify graphitic carbon. Concurrently, the pre-factor for carbon gasification reactions is substantially enhanced, accelerating carbon deposit gasification rates through a kinetic compensation effect.

3.3 Transition metal-doped catalysts

Among various transition metal catalysts, the Ni-based catalysts exhibit high catalytic activity and low cost, but they also face issues of carbon deposition and sintering. To address these challenges, the incorporation of other transition metals into Ni-based catalysts can modulate the electronic structure of Ni, enhance the dispersion of active metals, and improve resistance to carbon deposition, thereby maintaining catalytic stability.

Li et al.^[102] investigated the effect of Co addition on the reaction activity of Ni/Al₂O₃ catalysts.

Table 4 Effect of noble metal doping on the reaction kinetics of methane-carbon dioxide reforming over the Ni-based catalysts

Doped metal	Characteristics	Kinetic influence	Rate determining step
Pt	SMSI regulates Ni electron density, promotes oxygen vacancy formation, and increases oxygen migration rate.	CH ₄ activation is promoted and activation energy is reduced	CH ₄ + MeCO ₃ $\xrightarrow{k_2}$ 2CO + 2H ₂ + MeO CH ₄ + MeO $\xrightarrow{k_3}$ CO + 2H ₂ + Me
Rh	Electronegativity inhibits CH _x adsorption, promotes CO ₂ dissociation, and inhibits C–C bond formation	CH* oxidation is promoted by oxygen species and activation energy is reduced	CH ₄ * + * $\rightarrow$ CH ₃ * + H*
Ru	Oxygen affinity promotes O* enrichment and inhibits graphite carbon formation	Carbon deposition gasification is accelerated, and the dissociation E _a of CH ₄ increases (84→92 kJ/mol)	CH ₂ * + * $\xrightarrow{k}$ CH* + H*

H₂-TPR revealed that Co promoted the formation of NiAl₂O₄/CoAl₂O₄ spinel, enhancing the catalyst's MSI, which resulted in only a 7% increase in active metal particle size after 9 h of reaction at 750 °C (compared to a 29% increase for the undoped catalyst). Electron transfer weakened the catalyst's ability to crack CH₄, making CH₄ activation the rate-determining step of the reaction. The activation energy increased from 51.7 to 66.1 kJ/mol, whereas the coke formation was suppressed (decreasing from 9.1% to 3%).

Fan et al.^[103] investigated the kinetics of methane-carbon dioxide reforming over Ni-Co/MgO-ZrO₂ catalysts at 700–800 °C. The Ni-Co alloy effectively enhanced the sintering resistance of the catalyst, reducing the active metal dispersion from 21.3% to only 20.6% after 40 h of reaction at 750 °C. The reaction mechanism involved the reversible adsorption of CH₄ on the metal active sites before slowly dissociating into hydrogen and C* species. CO₂ was adsorbed on the basic support and reacted with carbon species released from CH₄ dissociation to form CO, effectively removing carbon deposits from the catalyst surface. The Ni-Co alloy reduces the catalyst's activation capacity for CH₄, making CH₄ cracking be the primary rate-determining step. The reaction rate expression derived from this step is as follows^[103].

$$\begin{aligned}
 &\text{CH}_4 + * \xrightleftharpoons{K_1} \text{CH}_4^* \\
 &\text{CH}_4^* \xrightarrow{k_2} \text{C}^* + 2\text{H}_2 \\
 &\text{CO}_2 + \# \xrightleftharpoons{K_3} \text{CO}_2\# \\
 &\text{CO}_2\# + \text{C}^* \xrightarrow{k_4} 2\text{CO} + * + \# \\
 &r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_1 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2} + K_1 k_2 p_{\text{CH}_4} + K_3 k_4 p_{\text{CO}_2}}
 \end{aligned}$$

De Coster et al.^[104] investigated the 8Ni5Fe/MgAl₂O₄ catalyst in methane-carbon dioxide reforming using *in situ* quick X-ray absorption spectroscopy (QXAS) and ⁵⁷Fe Mössbauer spectroscopy. Fe formed a stable spinel structure through lattice substitution with the MgAl₂O₄ support. The presence of NiO and MgFe_x²⁺Al_{2-x}O₄ in the reduced catalyst indicated the enhanced MSI, which could improve the active metal dispersion and sintering resistance^[104]. In the fresh catalyst, Fe existed as NiFe₂O₄ and MgFe_x²⁺Al_{2-x}O₄;

upon hydrogen reduction, the catalyst formed Ni-Fe alloy with trace amounts of MgFe_x²⁺Al_{2-x}O₄. Based on research by Theofanidis et al.^[105] in the methane-carbon dioxide reforming reactions, active metal Ni promoted CH₄ dissociation to generate C species, while Ni-Fe alloys and MgFe_x²⁺Al_{2-x}O₄ facilitated CO₂ adsorption which were oxidized to FeO_x and MgFe_x³⁺Al_{2-x}O₄. Finally, the latter was reduced by C, CH_x, or H species, enabling a redox cycling over the catalyst. The schematic diagram of the methane-carbon dioxide reforming reaction pathway over the 8Ni5Fe/MgAl₂O₄ catalyst is shown in Figure 6. Furthermore, when the feed ratio of CH₄/CO₂ ratio < 1, the FeO_x formation rate accelerated, establishing a stable FeO_x-alloy interface that maintained a steady-state rate, allowing the catalyst to adapt to varying feed conditions.

Zhang et al.^[47] investigated the promoting effect of Fe in the Fe_xNi_yMg_{1-x-y}O-R catalysts on methane-carbon dioxide reforming. Kinetic studies revealed that Fe doping enhanced CO₂ adsorption, increased the coverage of O* on the catalyst surface, and accelerated the gasification of surface carbon deposits^[106–107]. The incorporation of Fe altered the electron density on the Ni surface, weakening the Ni's ability to activate CH₄ and slowing the rate of carbon deposition. After 100 h of reaction at 750 °C, the carbon deposition was only 0.1%, demonstrating a significant improvement in catalyst stability^[47]. Concurrently, the activation energy increased from 87 to 101 kJ/mol for the Fe_{0.009}Ni_{0.061}Mg_{0.93}O-R catalyst, with cleavage of the C–H bond in CH₄ becoming the rate-determining step upon Fe doping^[108]. The elementary steps and rate expressions for methane-carbon dioxide reforming are presented below^[47].

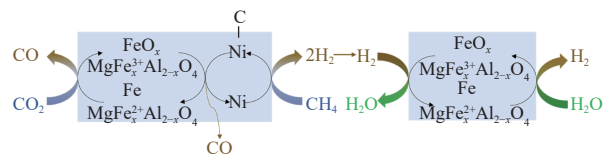
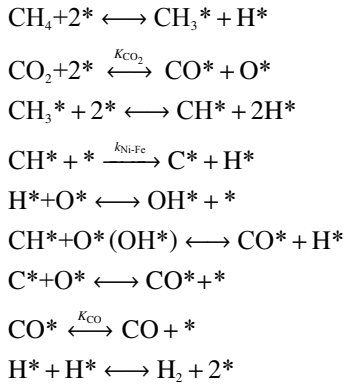


Fig. 6 Schematic diagram of methane-carbon dioxide reforming reaction over 8Ni5Fe/MgAl₂O₄ catalyst^[104] (with permission from Elsevier)

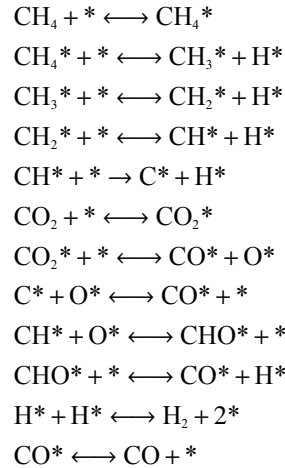


$$r_{\text{CH}_4} = k_{\text{Ni-Fe}} p_{\text{CH}_4} \left(\frac{1}{1 + \frac{K_{\text{CO}_2} K_{\text{CO}} p_{\text{CO}_2}}{p_{\text{CO}}}} \right)^2$$

Song et al.^[109] observed via XPS that Cu was enriched on the surface of Ni-Cu/Mg(Al)O catalysts (surface Cu⁰/Ni⁰ ratio of 0.8 at a catalyst composition of Cu/Ni ratio = 0.25) and the Cu-rich surfaces preferentially occupied the Ni step and edge sites to suppress excessive CH₄ cleavage. The electron transfer within the Cu-Ni alloy increased the energy barrier for C-H bond dissociation. The combined effects of Cu enrichment and electron interaction elevated the reaction activation energy from 51.8 to 62.7 kJ/mol. Cu also lowered the activation barrier for CO₂ activation, promoting its dissociation into oxygen species and accelerating carbon gasification rates on the catalyst surface^[110-111]. At Cu/Ni ratio = 0.25, the catalyst exhibited only 1.4% carbon deposition after 25 h of reaction at 600 °C (compared to 66.7% for the undoped catalyst). When Cu/Ni ratio > 0.25, excess Cu gradually reduced the number of exposed Ni active sites, thereby diminishing the catalytic activity^[110,112-114]. At a low reaction temperature of 450 °C, the Cu sites provided oxygen species that promoted CH₄ activation and carbon gasification, maintaining a conversion close to equilibrium and demonstrating excellent low-temperature adaptability^[115].

Boualouache et al.^[111] investigated the mechanism of methane-carbon dioxide reforming on Cu-Ni bimetallic surfaces using density functional theory (DFT). XPS

characterization revealed that Cu doping shifted the Ni *d*-band center from -1.33 eV in pure Ni to -1.49 eV in Cu₃Ni, weakening the hybridization between the C-H bonds of CH₄ and metallic *d* orbitals and inhibiting CH₄ cleavage. The reaction pathway involved stepwise dehydrogenation of CH₄ at Ni active sites to form C* and H* species. Cu promoted direct dissociation of CO₂, while abundant surface oxygen species reacted with CH*—the intermediate formed from CH₄ dehydrogenation—and C* to generate adsorbed CHO* species, ultimately converting to CO and H₂. Dissociation of CH* is the rate-determining step.



The effects of transition metal (Co, Fe, Cu) doping on the reaction kinetics of Ni-based catalysts are compared in Table 5. All three metals reduce the electron density of Ni, increase the energy barrier for CH₄ dissociation, significantly raise the reaction activation energy and effectively suppress the carbon deposition. Co doping further enhances MSI by forming NiAl₂O₄/CoAl₂O₄ spinel phases, improving the catalyst's sintering resistance. Under these conditions, CH₄ cracking becomes the rate-determining step. Fe doping enhances CO₂ adsorption and carbon removal capacity by forming a NiFe_xAl_{2-x}O₄ spinel phase and facilitating redox cycles involving iron oxides. This enables the catalyst to adapt to varying CH₄/CO₂ ratio feed ratios, with CH* cracking as the rate-determining step.

Table 5 Effect of transition metal doping on the reaction kinetics of methane-carbon dioxide reforming over the Ni-based catalysts

Doped metal	Characteristics	Kinetic influence	Rate determining step
Co	Electron transfer reduces Ni electron density and NiAl ₂ O ₄ /CoAl ₂ O ₄ spinel enhances MSI. Ni-Co promotes dispersion	CH ₄ dissociation energy barrier is increased, with <i>E_a</i> increasing (51.7→66.1 kJ/mol), and carbon deposition formation is inhibited (9.1%→3%)	CH ₄ * $\xrightarrow{k_2}$ C* + 2H ₂
Fe	NiFe _x Al _{2-x} O ₄ enhances MSI, promotes CO ₂ adsorption. Fe oxide realizes redox cycle, changing Ni electron density	CH ₄ dissociation energy barrier is increased, with <i>E_a</i> increasing (87→101 kJ/mol), reaction and dynamic carbon elimination are promoted by redox (carbon deposition is only 0.1%), adapting to feeds with different CH ₄ /CO ₂ ratios	CH* + * $\xrightarrow{k_2}$ C* + H*
Cu	Electron transfer occurs, and Cu occupies Ni active sites, Cu promotes CO ₂ dissociation and provides sufficient oxygen species	CH ₄ dissociation energy barrier is increased, with <i>E_a</i> increasing (51.8→62.7 kJ/mol), carbon deposition gasification is promoted by oxygen species (carbon deposition: 66.7%→1.4%), with excellent low - temperature adaptability	CH* + * → C* + H*

Cu doping enriches at the catalyst surface and occupies some Ni active sites, thereby reducing the activity of CH₄ dissociation. It also promotes the CO₂ dissociation and accelerates carbon gasification, with CH* cracking again being the rate-determining step. The advantage of Cu doping lies in maintaining high conversion at a low temperature (450 °C), demonstrating excellent low-temperature activity.

3.4 Addition of promoters

The addition of promoters to the Ni-based catalysts can improve their oxygen vacancy concentration, electron density, and acidity/basicity, thereby promoting the adsorption and activation of reactants, which can then enhance the reaction rates, catalyst stability, and resistance to carbon deposition. Commonly used promoters include CeO₂, K₂O and CaO.

Zhang et al.^[66] investigated the effect of CeO₂ addition on the catalytic activity of Ni/MSS (mesoporous silica). The results indicated that the CeO₂ promoter generated oxygen vacancies through the redox cycle of Ce³⁺ and Ce⁴⁺, increasing the catalyst's oxygen vacancy concentration ratio (expressed as $Q_s/(Q_s+Q_L)$, where Q_s represents surface-adsorbed oxygen or surface hydroxyl species and Q_L is lattice oxygen) from 0.51 to 0.6; meanwhile, the concentration of strong basic sites was simultaneously increased from 0 to 0.26 mmol/g. The synergistic effect between oxygen vacancy concentration and basic site concentration enhanced the CO₂ activation.

XPS analysis revealed that after adding CeO₂, the signals of Ni⁰ and Ni²⁺ shifted toward lower binding energies, indicating electron transfer from Ce to Ni. Electron-rich Ni accelerated the adsorption and activation of CH₄^[116]. The synergistic effects of oxygen vacancies, catalyst basicity, and electronic modulation collectively enhanced the reaction, reducing the activation energy from 44.5 to 39.7 kJ/mol. Figure 7 shows the schematic diagram of the reaction pathway and mechanism over the Ce-promoted Ni catalysts.

Nandini et al.^[117] proposed a mechanism for methane-carbon dioxide reforming on the Ni-K/CeO₂-Al₂O₃ catalysts. The K₂O promoter significantly optimized methane-carbon dioxide reforming performance through both basicity and electronic effects. Specifically, K₂O facilitated electron transfer from the CeO₂-Al₂O₃ support to the active Ni sites, while the electron-rich Ni promoted CH₄ activation and H₂ dissociation into adsorbed hydrogen (H*)^[117–118]. Concurrently, the redox properties of CeO₂ synergized with K₂O could further enhance electron transfer efficiency. Moreover, the alkalinity of K₂O enhanced CO₂ adsorption and reduced its activation energy barrier. This effectively promoted H*-induced CO₂ dissociation, yielding CO* and OH*, where the generated OH* reacted with CH_x* species from methane dissociation to form the CH_xO* intermediates.

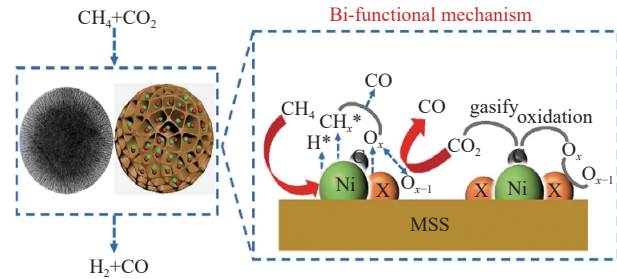
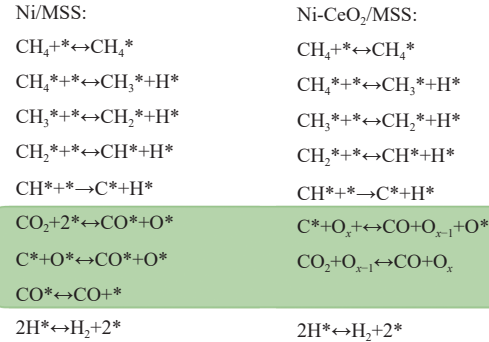
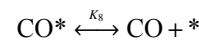
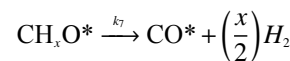
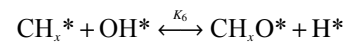
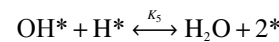
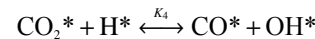
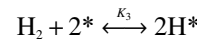
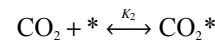
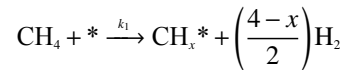


Fig. 7 Schematic diagram of reaction mechanism of methane-carbon dioxide reforming over the 5Ni2Ce/MSS catalyst^[66] (with permission from Elsevier)

Methane dissociation and CH_xO* species decomposition jointly constituted the rate-determining steps of the reforming reaction. Research by Azancot et al.^[119] indicated that when the K loading reached 3%, volatilized amorphous carbon preferentially formed on the catalytic surface rather than difficult-to-remove graphitic carbon, effectively extending the catalyst lifetime.



$$r_{\text{CH}_4} = \frac{k_{1L}p_{\text{CH}_4}}{\left[\left(\frac{k_{1L}p_{\text{CH}_4}p_{\text{CO}}}{k_{7L}K_a p_{\text{CO}_2}}\right) + \left(\frac{K_b p_{\text{CO}_2} p_{\text{H}_2}^{\frac{1}{2}}}{p_{\text{CO}}}\right) + \left(\frac{k_{1L}p_{\text{CH}_4}}{k_{7L}}\right) + 1\right]}$$

CaO promoters primarily enhanced the catalyst anti-coking performance by promoting CO₂ adsorption. Bachiller-Baeza et al.^[120] demonstrated that doping with a strongly basic CaO promoter facilitated CO₂ molecular adsorption to form carbonate species, which subsequently decomposed to generate surface hydroxyls, accelerating C* species elimination. Sun et al.^[121] further observed that CaO doping could suppress the methane cracking, reducing the

formation of coking precursors. In contrast, undoped Ni/ZrO₂-La₂O₃ exhibited slower CO₂ dissociation than CH₄ cracking, leading to C* accumulation and subsequent deactivation. CO₂ dissociation was the rate-limiting step for the reaction without CaO doping. After adding CaO, the rate-limiting steps shifted to the decomposition of carbonate species and the reaction between OH* and C*. The reaction mechanisms on both catalysts are illustrated in Figure 8^[120].

The doping effects of different promoters (CeO₂, K₂O, CaO) on the reaction kinetics of Ni-based catalysts are compared in Table 6. All three promoters can enhance carbon oxidation by promoting CO₂ adsorption. CeO₂ enhances oxygen vacancy concentration through Ce³⁺/Ce⁴⁺ redox cycling and strengthens the basic sites to activate CO₂. It also facilitates the CH₄ activation via electron transfer from CeO₂ to Ni, with CH* cleavage being the rate-determining step. K₂O enhances CO₂ adsorption through its basicity and accelerates H-induced CO₂ dissociation through electron transfer (from the support to Ni). Methane dissociation and CH_xO* species decomposition together constitute the rate-determining steps of the reaction. The K loading of 3% selectively generates easily gasified amorphous carbon. The rate-determining steps are the decomposition of carbonate species and the reaction between OH* and C*. CaO promotes carbon oxidation solely by forming carbonates with CO₂, with the rate-determining steps being the decomposition of carbonate species and the reaction between OH* and C*.

3.5 Effect of Ni active site structural regulation on the reaction mechanism

The geometric structure of Ni-based catalysts—ranging from nanoparticles and sub-nanoclusters to single atoms—is a core factor governing their performance in the methane-carbon dioxide reforming. It directly influences the number of exposed active sites, reaction pathway selectivity, and high-temperature stability. For nanoparticles (NPs), size effects are pivotal in the performance regulation. Reducing particle size significantly increases the proportion of exposed active sites, enhancing both CH₄ and CO₂ adsorption/activation.

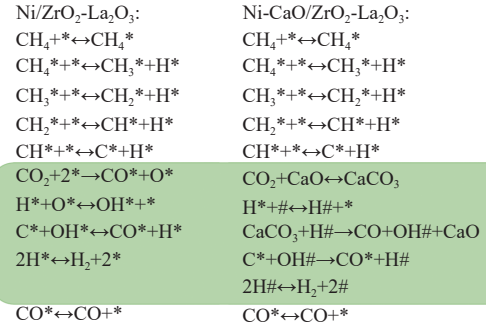


Fig. 8 Comparison of methane-carbon dioxide reforming reaction pathways on the Ni/ZrO₂-La₂O₃ and Ni-CaO/ZrO₂-La₂O₃ catalysts^[120]

This also suppresses the carbon deposition on Ni species by controlling reaction pathways, thereby improving reforming conversion rates. However, this approach faces challenges of sintering and deactivation at elevated temperatures. To resolve this contradiction, researchers typically enhance metal-support interactions (MSI) or increase the affinity between metal and support surface groups, leveraging the support's anchoring effect on active metals to suppress agglomeration.

Subnanoclusters exhibit distinct performance advantages over nanoparticles due to their unique geometric structure. Their exceptionally high specific surface area and abundant low-coordination sites confer outstanding intrinsic catalytic activity, while the support confinement further addresses stability concerns. Hu et al.^[122] reported a monolayer Ni cluster catalyst (hm-Ni/Al₂O₃), where Ni atoms were dispersed as monolayer clusters on the Al₂O₃ surface, achieving 100% atomic utilization. The H₂ and CO production rates reached 8572.96 and 9614.26 mmol/(min·g), respectively—an order of magnitude higher than those over conventional Ni nanoparticles—demonstrating the immense potential of sub-nanoclusters in providing highly active sites. More importantly, strong interactions exist between the clusters and the Al₂O₃ support. Density functional theory (DFT) calculations reveal a formation energy as low as -20.06 eV. This robust interaction effectively suppresses cluster migration and agglomeration, offering an effective approach to addressing the high-temperature stability issue of sub-nanoscale catalysts.

Table 6 Effect of transition metal doping on the reaction kinetics of methane-carbon dioxide reforming over the Ni-based catalyst

Doped metal	Characteristics	Kinetic influence	Rate determining step
CeO ₂	Oxygen vacancy concentration increases, strong basic site concentration increases, and CeO ₂ transfers electrons to Ni	the activation of CO ₂ and CH ₄ is promoted and E _a decreases (44.5→39.7 kJ/mol), following a dual-function mechanism	CH*+*→C*+H*
K ₂ O	Basicity regulation, electronic effect	the H*-induced dissociation of CO ₂ is promoted, improving the type of carbon deposition	$\text{CH}_4 + * \xrightarrow{k_1} \text{CH}_x^* + \left(\frac{4-x}{2}\right)\text{H}_2$ $\text{CH}_x\text{O}^* \xrightarrow{k_7} \text{CO}^* + \left(\frac{x}{2}\right)\text{H}_2$
CaO	Basic site concentration increases	the formation of carbonates is promoted, accelerating the oxidation of carbon deposition	$\text{CaCO}_3 + \text{H}\# \rightarrow \text{CO} + \text{OH}\# + \text{CaO}$ $\text{C}^* + \text{OH}\# \rightarrow \text{CO}^* + \text{H}\#$

Single-Atom Catalysts (SACs) achieve atomic-level dispersion and maximum utilization of active sites by anchoring the metal atoms in isolated form on the support surface. Isolated Ni atoms cannot provide multiple adjacent active sites to complete carbon chain growth or graphitization processes, thereby mechanistically inhibiting carbon buildup.

Akri et al.^[123] synthesized an atomically dispersed $2\text{Ni}_1/\text{HAP-Ce}$ catalyst (where Ni_1 denotes atomically dispersed Ni and HAP represents hydroxyapatite). The formation of coke was negligible upon continuous reaction at 750 °C for 65 h. Isolated Ni atoms could efficiently activate only the first C–H bond of CH_4 (activation energy 0.63 eV, significantly lower than the 0.9 eV on $\text{Ni}(111)$ surfaces), while the resulting CH_3^* intermediate resisted further dissociation (the activation energy for second C–H bond cleavage reached 1.54 eV). Subsequently, CH_3^* combined with O species provided by CeO_x to form the CH_3O^* intermediate, ultimately undergoing dehydrogenation to produce CO. This catalyst kinetically blocked the formation of coking precursors, demonstrating intrinsic anti-coking properties. To address the sintering susceptibility of single-atom catalysts, Ce-doped HAP supports were employed. By forming Ni-Ce coordination structures with Ni atoms (confirmed by EXAFS), the MSI was significantly enhanced, enabling atomic-level dispersion of Ni atoms under 750 °C^[123]. Akri et al.^[124] further proposed a complementary strategy: introducing the surfactant polyvinylpyrrolidone (PVP) during strong electrostatic adsorption synthesis. Leveraging the steric hindrance effect between its hydrophilic pyrrolidone groups and hydrophobic polyethylene backbone, this approach further improved Ni single-atom dispersion on the HAP support while simultaneously enhancing Ni-support interactions, significantly boosting catalyst stability.

The electronic structure of Ni-based catalysts directly determines their adsorption strength and activation pathways for the reaction intermediates, profoundly influencing the activity, selectivity, and anti-coking performance of DRM. Hu et al.^[122] reported that the electronic structure of the $\text{hm-Ni}/\text{Al}_2\text{O}_3$ catalyst significantly altered the energy barriers of the reforming reaction: the C^* oxidation barrier on the Ni cluster decreased from 1.61 to 1.49 eV, while the energy barrier for C polymerization forming coke increased from 0.67 to 1.63 eV. This shift facilitated the oxidation removal of C^* rather than its polymerization into coke, effectively and kinetically inhibiting the coke formation. In the $2\text{Ni}_1/\text{HAP-Ce}$ catalyst, Ce doping significantly stabilized the Ni valence state by forming SMSI with Ni single atoms^[123]. X-ray photoelectron spectroscopy (XPS) and H_2 -TPR results indicated that Ce introduction made Ni species more resistant to reduction. Even in H_2 atmosphere under 500 °C, Ni predominantly existed in highly oxidized states (e.g., Ni^{2+} , manifested as Ni-O coordination). This electronic structural modification not only enhanced the Ni single

atom's ability to activate the first C–H bond of CH_4 but also suppressed the migration and agglomeration by stabilizing the high oxidation state of Ni, achieving both high stability and anti-coking properties. PVP modification enhanced the strong interaction between Ni and the HAP support, stabilizing the high oxidation state of Ni (XANES spectra showed that the electronic state of Ni after modification approached that of NiO). The highly oxidized Ni significantly enhanced activation of CO_2 , effectively suppressing carbon deposition (thermogravimetric analysis showed negligible carbon accumulation)^[124].

The kinetic parameters of the methane dry reforming reaction over different Ni-based catalysts described earlier are summarized in Table 7, including catalyst composition, kinetic study temperature range, rate expression, rate-determining step, and apparent activation energy. Both the activation energy and rate-determining step of a catalyst are influenced by support properties (such as acidity/basicity and oxygen vacancy concentration) and the type of active sites. Specifically, the species such as MgO and CeO_2 can optimize the surface adsorption/dissociation kinetics, alter reaction pathways, and thereby affect reaction activation energies.

4 Kinetics of carbon deposition and elimination

Carbon deposition is a core bottleneck that limits the long-term stability of catalysts in the methane-carbon dioxide reforming reaction. It primarily originates from two sources: CH_4 decomposition and CO disproportionation. Hussien et al.^[125] compared the coking behavior of Ni/Ce-La-Cu-O and Ni/Ce-Sm-Cu-O catalysts at 750 °C, confirming that CH_4 decomposition was the dominant pathway for carbon deposition under these high-temperature conditions. In contrast, Makri et al.^[126] demonstrated through temperature programmed oxidation (TPO) and isotope labeling experiments that at 550 °C, carbon deposition on the catalyst was minimal and primarily resulted from the disproportionation of CO species generated by CO_2 activation.

Xu et al.^[127] proposed an expression for the coking rate on $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts based on the PL model (Equation (7)). Fitting reaction conditions with the coking rate r_D revealed that when temperature increased from 700 to 800 °C, the pre-exponential factor A for coking rose from 24.89 to 25.27, while activation energy E_a decreased from 52.8 to 46.3 kJ/mol. Concurrently, the reaction exponents α and β for CH_4 and CO_2 decreased from 0.94 to 0.7 and -0.09 to -0.1 , respectively. This indicated that the influence of CH_4 partial pressure on the carbon deposition rate gradually diminished during heating.

The rapid increase in the carbon deposition rate resulted from the synergistic effect of decreased activation energy and increased pre-exponential factor.

Table 7 Summary of reaction models of methane-carbon dioxide reforming on different Ni-based catalysts

Catalyst	Reaction temperature/°C	Reaction rate expression	Rate determining step	Activation energy / (kJ·mol ⁻¹)	Ref.
Ni/γ-Al ₂ O ₃	500–700	$r_{\text{CH}_4} = \frac{k_1 p_{\text{CH}_4} p_{\text{CO}_2}}{(1 + K_1 p_{\text{CH}_4}) \left(1 + K_2 p_{\text{CO}_2} \right)}$	$\text{C}^* + \text{CO}_2^* \rightarrow 2\text{CO} + 2^*$	80	[67]
NiMg/Al	600–800	$r_{\text{CH}_4} = \frac{k_1 p_{\text{CH}_4} p_{\text{CO}_2} \left(1 - \frac{p_{\text{CO}}^2 p_{\text{H}_2}}{K_{\text{Eq}} p_{\text{CH}_4} p_{\text{CO}_2}} \right)}{(1 + K_1 p_{\text{CH}_4} + K_4 p_{\text{H}_2}) (1 + K_2 p_{\text{CO}_2} + K_3 p_{\text{CO}})}$	$\text{CH}_4^* + \text{CO}_2^* \rightarrow 2\text{H}_2 + 2\text{CO} + ^* + ^*$	117	[72]
Ni/MgO-Al ₂ O ₃	600–700	$r_{\text{CH}_4} = \frac{k p_{\text{CH}_4} p_{\text{CO}_2}}{(1 + K_{\text{CH}_4} p_{\text{CH}_4}) (1 + K_{\text{CO}_2} p_{\text{CO}_2})}$	$\text{CH}_4^* + \text{CO}_2^* \rightarrow 2\text{H}_2 \uparrow + 2\text{CO} \uparrow + ^* + ^*$	75	[49]
Ni-CaO-ZrO ₂	630–720	$r_{\text{CH}_4} = \frac{K_{\text{CH}_4} k_{\text{CH}_4} K_{\text{CO}_2} K_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_{\text{CH}_4} k_{\text{CH}_4} K_{\text{CO}_2} p_{\text{CH}_4} p_{\text{CO}_2} + K_{\text{CH}_4} k_{\text{CH}_4} p_{\text{CH}_4} + K_{\text{CO}_2} K_4 p_{\text{CO}_2}}$	$\text{CH}_4^* \xrightarrow{k_{\text{CH}_4}} \text{CH}_x^* + \left(\frac{4-x}{2} \right) \text{H}_2$ $\text{CO}_2^* + \text{CH}_x^* \xrightarrow{k_4} 2\text{CO} + \frac{x}{2} \text{H}_2 + ^* + ^*$	122.4	[73]
Ni-PS@Ce _{1-x} Zr _x O ₂	600–675	$r_{\text{CH}_4} = \frac{k_2 p_{\text{CH}_4} \left(1 - \frac{p_{\text{H}_2}^2 p_{\text{CO}}^2}{K_{\text{eq}} p_{\text{CH}_4} p_{\text{CO}_2}} \right)}{\left(1 + K_a \frac{p_{\text{CO}}}{p_{\text{CO}_2}} + K_b p_{\text{H}_2}^{0.5} \right)^4 \left(1 + K_c p_{\text{CH}_4} + K_d \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \right)}$	$\text{CH}_4^* + 4\text{O}_x \xrightarrow{k_2} \text{C}^* + 4\text{O}_x - \text{H}$	54.2	[64]
Ni/La ₂ O ₃	500–700	$r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_3 k_4 p_{\text{CO}_2} + K_1 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2} + K_1 k_2 p_{\text{CH}_4} + K_1 k_2 K_3 p_{\text{CO}_2}}$	$\text{CH}_4^* \xrightarrow{k_2} \text{C}^* + 2\text{H}_2$ $\text{La}_2\text{O}_3 \text{CO}_3 + \text{C}^* \xrightarrow{k_4} \text{La}_2\text{O}_3 + 2\text{CO} + ^*$	68	[84]
Ce _{0.7} La _{0.2} Ni _{0.1} O _{2-δ}	650–750	$r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_3 k_4 p_{\text{CO}_2} + K_1 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2} + K_1 k_2 p_{\text{CH}_4} + K_1 k_2 K_3 p_{\text{CO}_2}}$	$\text{CH}_4^* \xrightarrow{k_2} \text{C}^* + 2\text{H}_2$ $\text{La}_2\text{O}_3 \text{CO}_3 + \text{C}^* \xrightarrow{k_4} \text{La}_2\text{O}_3 + 2\text{CO} + ^*$	136.9	[39]
Pt+Ni/PtSmCeZrO/YSZ	650–750	$r_{\text{CH}_4} = \frac{k_1 k_2 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{(k_{-1} k_2 p_{\text{CH}_4}) \left(k_4 + k_3 \frac{p_{\text{CH}_4}}{p_{\text{CO}_2}} \right)}$	$\text{CH}_4 + [\text{MeCO}_3] \xrightarrow{k_2} 2\text{CO} + 2\text{H}_2 + [\text{MeO}]$	61	[93]
Pt+Ni/PtSmCeZrO/YSZ	750–850	$r_{\text{CH}_4} = \frac{k_1 k_2 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{(k_{-1} k_2 p_{\text{CH}_4}) \left(k_4 + k_3 \frac{p_{\text{CH}_4}}{p_{\text{CO}_2}} \right)}$	$\text{CH}_4 + [\text{MeO}] \xrightarrow{k_3} \text{CO} + 2\text{H}_2 + [\text{Me}]$	29.8	[93]
Ru-Ni-MgO	500–700	$r_{\text{CH}_4} = k p_{\text{CH}_4} \left(\frac{K_{\text{CO}_2} p_{\text{CO}_2}}{1 + \frac{K_{\text{CO}} p_{\text{CO}}}{K_{\text{CO}} p_{\text{CO}_2}}} \right)$	$\text{CH}_4 + ^* \rightarrow \text{CH}_x^* + \left(\frac{4-x}{2} \right) \text{H}_2$	92	[99]
Ni-Co/MgO-ZrO ₂	700–800	$r_{\text{CH}_4} = \frac{K_1 k_2 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2}}{K_1 K_3 k_4 p_{\text{CH}_4} p_{\text{CO}_2} + K_1 k_2 p_{\text{CH}_4} + K_3 k_4 p_{\text{CO}_2}}$	$\text{CO}_2^* + \text{C}^* \xrightarrow{k_4} 2\text{CO} + ^* + ^*$	52.9	[103]
Fe _x Ni _y Mg _{1-x-y} O-R	500–700	$r_{\text{CH}_4} = k_{\text{Ni-Fe}} p_{\text{CH}_4} \left(\frac{1}{1 + \frac{K_{\text{CO}_2} K_{\text{CO}} p_{\text{CO}_2}}{p_{\text{CO}}}} \right) \frac{1}{k_{\text{IL}} p_{\text{CH}_4}}$	$\text{CH}_4 + 2^* \xrightarrow{k_1} \text{CH}_3^* + \text{H}^*$	101	[47]
Ni-K/CeO ₂ -Al ₂ O ₃	650–750	$r_{\text{CH}_4} = \frac{\left(\frac{k_{\text{IL}} p_{\text{CH}_4} p_{\text{CO}}}{k_{\text{TL}} K_4 p_{\text{CO}_2}} \right) + \left(\frac{k_{\text{IL}} p_{\text{CH}_4}}{k_{\text{TL}}} \right) + 1}{p_{\text{CO}}}$	$\text{CH}_4 + ^* \xrightarrow{k_1} \text{CH}_x^* + \left(\frac{4-x}{2} \right) \text{H}_2$ $\text{CH}_x\text{O}^* \xrightarrow{k_7} \text{CO}^* + \left(\frac{x}{2} \right) \text{H}_2$	107.2	[117]

Furthermore, the negative reaction order of CO₂ further confirmed that CO₂ can inhibit carbon deposition by accelerating the oxidation of surface C* species, highlighting its crucial role in regulating carbon deposition.

$$r_D = A \exp\left(-\frac{E_a}{RT}\right) p_{\text{CH}_4}^\alpha p_{\text{CO}_2}^\beta \quad (7)$$

Nayak et al.^[128] demonstrated the inhibitory effect of CO₂ on a 15Ni/Al₂O₃ catalyst: under 600 °C for 3 h; increasing the CO₂/CH₄ ratio from 1 to 1.5 significantly reduced catalyst coking from 23.5% to 7%. Regarding the mechanism, excess CO₂ activates oxygen species generated at Ni active sites, accelerating the removal of existing carbon deposits through carbon gasification reactions. Concurrently, CO₂ competitive adsorption reduces the frequency of CH₄ contact with active sites, thereby decreasing the formation rate of carbon deposits precursors.

Studying the elimination of deposited carbon could provide crucial guidance for catalyst design and process optimization, yet research on rate expressions for carbon removal reactions remains limited. Zhang et al.^[47] investigated the coke gasification behavior of Ni-Fe-MgO catalysts using CO₂-TPO technology and proposed a carbon removal rate expression:

$$r_g = A p_{\text{CO}_2}^n \theta^* \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

In the equation, r_g is the carbon removal rate, θ^* denotes the surface carbon coverage, E_a is the activation energy for carbon removal, and n is the reaction order of CO₂. Through CO₂-TPO experiments, catalysts with coke deposits were heated at a series of different heating rates (β). The temperature T_M corresponding to the maximum surface carbon volatilization rate was recorded. The reaction order of CO₂, the activation energy of the decarbonization reaction, and the pre-exponential factor were obtained by fitting Equation (9).

$$2\ln T_M - \ln \beta = \frac{E_a}{RT_M} + \ln\left(\frac{E_a}{A p_{\text{CO}_2}^n R}\right) \quad (9)$$

The derivation of this model is based on the following assumptions: (1) Pseudo-zero-order reaction kinetics, with negligible dependence on CO₂ partial pressure (i.e., reaction order $n \approx 0$); (2) Constant or slowly varying surface carbon coverage (θ^*); (3) All carbon species follow a single activation energy pathway. Although surface carbon coverage θ^* is difficult to quantify directly, the catalyst's carbon deposition resistance can be indirectly evaluated by analyzing kinetic parameters of the carbon removal reaction (activation energy, pre-exponential factor, and reaction order).

Taking the Ni-Fe-MgO catalyst as an example, Zhang et al.^[47] observed that although the introduction of Fe increased the de-carbonation activation energy from 98.1 to 168 kJ/mol, the pre-exponential factor significantly improved from 24.1 to $6.51 \times 10^5 \text{ s}^{-1}$, and the CO₂ reaction order increased from 0.43 to 0.57. This shift in kinetic parameters stems from Fe's enhanced affinity for the surface oxygen. Atomically dispersed Fe doping (Figure 9)

substantially increased the surface oxygen coverage, accelerating oxidation of surface carbon deposits and thereby increasing the pre-exponential factor in Equation (8). Fe also promoted the direct oxidation of CH*, making the reaction rate more sensitive to CO₂ partial pressure and increasing the reaction order. The increase in the pre-exponential factor and reaction order counteracted the effect of increased activation energy, enhancing the carbon removal rate.

Core-shell structured catalysts also exhibit high resistance to coking^[129]. Kosari et al.^[130] found that by controlling the shell thickness, coke primarily formed near the thicker shell adjacent to larger Ni particles. This partially prevented the active site blockage, maintained catalyst activity, and achieved partial carbon coverage (θ^*). The porous structure of the shell layer also enhanced CO₂ adsorption and activation on the catalyst, maintaining the pre-exponential factor (A) of the carbon elimination reaction at a high level, which significantly increased the carbon removal rate.

The rate expressions for carbon deposition and elimination provide references for process optimization and catalyst design, but they present certain limitations in practical applications. Regarding the carbon deposition model (Equation (7)), its reaction pathways are not comprehensively covered, as it only accounts for the direct cracking pathway of CH₄ without incorporating the contribution from CO disproportionation reactions. It also disregards the influence of surface carbon coverage θ^* . As θ^* increases, the reduction in available active sites inhibits CH₄ dissociation, leading to an overestimated carbon deposition rate. Furthermore, the model ignores the impact of H₂ product concentration, which at high temperatures can affect deposition rates through reverse water gas shift reactions or direct hydrogenation gasification of C*. Therefore, it is necessary to derive a more accurate coking rate expression based on the LHHW model, incorporating factors such as surface carbon coverage θ^* and H₂ concentration to enhance the predictive reliability. On the other hand, the carbon elimination model (Equation (9)) was established by fitting the apparent activation energy E_a and pre-exponential factor A , but its fundamental assumptions were deviated from the actual system. Raman spectroscopy and temperature programmed oxidation (TPO) results indicated that coke comprises three distinct species with significantly different reactivity: amorphous carbon, filamentous carbon, and graphitic carbon.

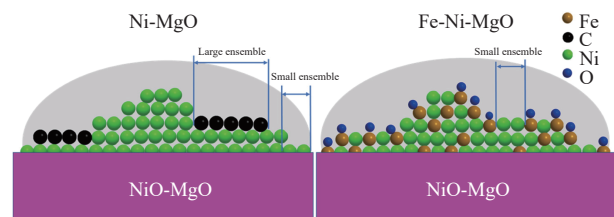


Fig. 9 Schematic diagram of atomic structure on Ni-Fe-MgO catalyst^[47]
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Among these, graphitic carbon, due to its high crystallinity, is difficult to gasify with CO_2 , resulting in a reaction order n significantly deviating from zero-order and invalidating the pseudo-zero-order kinetic assumption. Furthermore, the activation energy for graphitic carbon vaporization is substantially higher than that for amorphous carbon. As the reaction progresses and the proportion of graphitic carbon increases, the peak temperature (T_M) of the CO_2 -TPO curve rises and may even exhibit a double peak. This indicates that the single activation energy pathway is no longer valid, limiting the applicability of Equation (9) in describing such systems. Further research is needed, including establishing a carbon deposition kinetics model that encompasses multiple pathways, developing a carbon elimination kinetics theory based on multiple carbon species, and systematically validating the model's validity through a combination of experiments and simulations.

5 Conclusion and outlook

In the methane-carbon dioxide reforming, various types of catalysts are significantly different in the reaction pathways and kinetic characteristics, which can be modulated through regulating the key properties such as MSI, electronic effects, basicity, and oxygen species migration.

For monometallic Ni catalysts, supports enhance the dispersion of active Ni species via MSI: alkaline-earth metal oxides (e.g., MgO , CaO) increase catalyst basicity, whereas transition metal oxides (e.g., TiO_x , MnO_x , ZrO_2) elevate oxygen vacancy concentration through MSI; both effects promote the activation of CO_2 . Rare earth metal oxides (e.g., La_2O_3 , CeO_2) further enhance Ni dispersion and oxygen species migration at the metal-support interface via MSI; these synergistic effects drive the oxidation of CH_4 dissociation products on the Ni surfaces by oxygen species at the metal-support interface, establishing this oxidation process as the rate-determining step (RDS).

In the noble metal-doped catalysts, Pt enables efficient oxygen species migration via SMSI, Rh enhances CO_2 dissociation through its electron-accepting capacity, whereas Ru promotes the enrichment of surface oxygen species due to its high oxygen affinity. All three noble metals increase the concentration of surface oxygen species, rendering the oxidation of CH_4/CH^* species the RDS.

When transition metals (Co, Fe, Cu) form alloys with Ni, electron transfer shifts the d -band center of Ni downward, which weakens the ability of Ni to dissociate C–H bonds and elevates the reaction activation energy. For such Ni-alloy catalysts, the dissociation of CH_4/CH^* species becomes the primary RDS.

Promoters (CeO_2 , K_2O , CaO) enhance CO_2 activation primarily by increasing catalyst basicity: CeO_2 synergistically boosts reactant activation via oxygen vacancies and electron transfer, with CH^* dissociation serving as the RDS; K_2O facilitates hydrogen-induced CO_2

activation through electron donation, where both CH_4 dissociation and CH_xO^* decomposition act as RDS; CaO modulates the reaction rate by decomposing carbonate species and promoting the interaction between OH^- and C^* .

In the structural regulation of Ni active sites: geometrically clustered or atomically dispersed Ni activates reactants via high atomic utilization, inhibits Ni agglomeration through SMSI, and suppresses carbon deposition by restraining the deep dehydrogenation of CH_4 . Electronically, single-atom Ni efficiently activates the first C–H bond of CH_4 ; meanwhile, doping or modification modulates the electronic state of Ni to optimize reaction energy barriers and facilitate carbon elimination.

Furthermore, the analysis of carbon deposition kinetics revealed that CO_2 suppresses carbon deposition by competing for active sites. Decarbonization rates are dependent on catalyst regulation: doping with the transition metal Fe increases the pre-exponential factor and the reaction order with respect to CO_2 ; core-shell structures promote CO_2 activation via physical isolation and porous shell architectures. These two strategies significantly enhance decarbonization rates, providing a kinetic basis for the design of anti-carbon deposition Ni-based catalysts for methane-carbon dioxide reforming.

Future research on the Ni-based catalysts for methane-carbon dioxide reforming should focus on rational design, guided by composition-performance relationships and kinetic models. Three key directions are highlighted:

First, optimize catalyst components targeting rate-determining step (e.g., CH_4 dissociation, oxygen migration, carbon elimination). For instance, CeO_2 promoters enhance the dissociation of CH_4 on Ni via electron transfer, whereas ZrO_2 strengthens MSI to boost interfacial oxygen migration, suppressing carbon deposition and sintering.

Second, integrate main reaction kinetics with carbon deposition and elimination kinetics. Quantify how temperature and pressure affect competition between main and side reactions. Modulating kinetic parameters of carbon deposition (e.g., pre-exponential factors) can selectively inhibit carbon deposition, enabling long-term catalyst stability.

Third, leverage AI to transform catalyst design. Machine learning can build “component-structure-performance” databases, predicting bimetallic synergies and MSI. This shifts design from “trial-and-error” to “rational design,” accelerating industrialization of efficient, stable methane-carbon dioxide reforming technology.

Declaration of Competing Interest

The authors declare no conflict of interest.

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镍基催化剂上甲烷二氧化碳重整动力学研究进展

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摘 要: 在“双碳”背景下, 甲烷二氧化碳重整反应能够同时将甲烷和二氧化碳转化为合成气, 因其具有较高的环境效益与应用前景而备受瞩目。镍(Ni)基催化剂活性较高、成本低廉且资源丰富, 被视为工业化应用的理想候选材料。本工作介绍了用于甲烷二氧化碳重整的幂律(PL)、Eley-Rideal(ER)和Langmuir-Hinshelwood-Hougen-Watson(LHHW)三种反应动力学模型, 并重点基于 LHHW 模型, 讨论了不同催化体系的反应动力学特征与机理, 包括载体特性、贵金属掺杂、过渡金属掺杂、助催化剂的作用以及 Ni 的几何与电子结构对反应机理的影响。分析了催化剂上的积炭与消炭动力学, 并根据消炭反应速率表达式, 分析了过渡金属铁(Fe)掺杂催化剂和核壳结构催化剂具有较高消炭反应速率的原因。通过分析不同 Ni 基催化体系的反应机理与动力学特征, 为高性能催化剂开发提供了理论指导。

关键词: 甲烷二氧化碳重整; 催化剂; 模型; 动力学; 积炭

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