

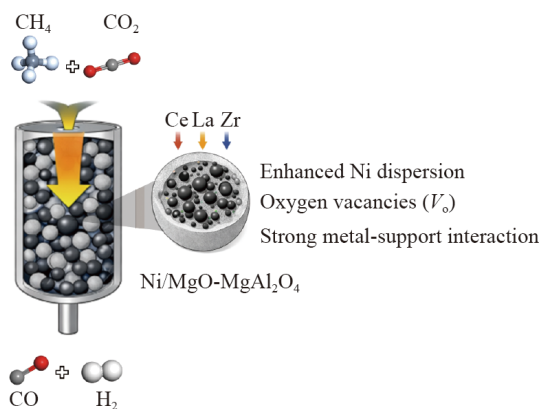
Mechanism of Ce/La/Zr doping on the structure and anti-coking performance of Ni/MgO-MgAl₂O₄ catalyst

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Abstract: Dry reforming of methane (DRM), which simultaneously converts CH₄ and CO₂ into syngas, represents a promising strategy for greenhouse gas mitigation and carbon-neutral feedstock production. However, Ni-based catalysts commonly suffer from severe sintering and carbon deposition under high-temperature, leading to rapid deactivation. In this work, MgO-MgAl₂O₄ composite supports are employed to regulate Ni loading. Ce, La and Zr are introduced as promoters to investigate their effects on DRM activity, structural stability, and surface oxygen species. The results show that an optimal Ni loading of 12.5% offers highest CH₄ and CO₂ conversions. Although the introduction of promoters slightly suppresses catalytic activity in the low-temperature region, they substantially modify the local structural order of the support and the metal-support interfacial environment, thereby improving NiO dispersion and increasing the concentration of surface oxygen vacancies (O_p). These changes enhance CO₂ adsorption-activation and effectively suppress carbon deposition. After 20 h of DRM reaction, the Ce-promoted catalyst exhibits the smallest Ni particle growth (6.23→8.07 nm) and the lowest carbon deposition, demonstrating superior structural stability and anti-coking capability. This study elucidates how Ce, La and Zr promoters enhance the resistance to sintering and coking through interfacial electronic modulation and improved oxygen storage/release capacity, offering valuable guidelines for the rational design of highly stable Ni-based DRM catalysts.



Key words: dry reforming of methane (DRM); Ni-based catalysts; promoter modification (Ce, La, Zr); oxygen vacancies; anti-coking performance

Dry reforming of methane (DRM) has attracted extensive attention because it enables the simultaneous conversion of two major greenhouse gases, methane (CH₄) and carbon dioxide (CO₂), into valuable synthesis gas (CO and H₂) which serve as a feedstock for methanol and Fischer-Tropsch synthesis. Consequently, DRM plays an important role in clean energy utilization and carbon neutrality strategies. Although DRM offers dual benefits in terms of carbon emission reduction and carbon capture and utilization (CCU)^[1–4], its strongly endothermic nature requires high reaction temperatures, typically in the range of 600–1000 °C, to overcome the high dissociation energies of CH₄ (435 kJ/mol) and CO₂ (526 kJ/mol)^[5]. Such harsh

reaction conditions readily induce side reactions, including methane decomposition and the Boudouard reaction. This would accelerate carbon deposition, coverage of active sites, pore blockage, and sintering of metal particles, ultimately resulting in rapid catalyst deactivation^[6–8]. Therefore, the development of catalysts with high activity, strong sintering resistance, and excellent coke resistance has become a critical in the research^[9–10].

Nickel (Ni)-based catalysts have long been regarded as the most industrially promising materials for DRM owing to their low cost and strong CH₄ activation capability^[11–12]. However, conventional Ni-based catalysts supported on Al₂O₃, SiO₂ or MgO still suffer from severe Ni particle

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sintering, excessive carbon deposition, and rapid deactivating under high-temperature^[13–15], which restrict their long-term stable operation. To overcome these limitations, extensive efforts have been devoted to optimizing support structures, introducing redox-active materials, and constructing bi- or multimetallic systems^[16–20]. By improving Ni dispersion, tuning electronic properties, and enhancing oxygen mobility, the catalytic activity and coke resistance of Ni-based catalysts have been effectively improved^[21–24]. Among various supports, magnesium aluminate spinel (MgAl_2O_4) has been widely employed for constructing thermally stable Ni-based systems due to its high melting point, excellent structural stability, and strong resistance to sintering^[25–26]. Nevertheless, single-component Ni/ MgAl_2O_4 and Ni/MgO systems still suffer from Ni particle agglomeration and carbon-induced deactivation at elevated temperatures.

To further enhance the durability and stability of Ni-based MgAl_2O_4 catalysts, considerable attention has recently been focused on the introduction of transition metals or rare-earth promoters to strengthen the redox properties, oxygen storage/migration capacity, and structural stability of the catalysts^[27–29]. Among these, Ce, La and Zr have attracted particular interest because of their outstanding promotional effects in Ni-based catalysts^[30–32]. It has been reported that CeO_2 incorporation can suppress surface CH_4 cracking, increase basicity and CO_2 adsorption capacity, and thereby facilitate the oxidative removal of carbon deposits^[33]. The introduction of La_2O_3 promotes the formation of lanthanum oxycarbonate species and favors the generation of predominantly amorphous carbon, thus enhancing carbon elimination ability^[34]. As a promoter, ZrO_2 facilitates the formation of small Ni crystallites and suppresses carbon-forming side reactions, such as CO disproportionation and methane decomposition^[35]. Although studies have reported the beneficial effects of Ce, La and Zr promoters on the performance of Ni-based DRM catalysts, a systematic understanding of their structural regulation when doped into $\text{MgO-MgAl}_2\text{O}_4$ composite supports, as well as their independent contributions to Ni dispersion, oxygen vacancy formation, and coke resistance, remains lacking. Establishing a clear correlation among “promoter type-support structure modification-Ni stability-coking behavior” is of great significance for the rational design of Ni-based catalysts.

In this study, Ce, La and Zr structural promoters are introduced into $\text{MgO-MgAl}_2\text{O}_4$ composite supports to investigate their effects on the structure and performance of Ni-based catalysts. By combining X-ray powder diffraction (XRD), H_2 temperature-programmed reduction (H_2 -TPR), CO_2 temperature-programmed desorption (CO_2 -TPD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) characterizations, the dispersion of Ni species, surface oxygen vacancy, metal-support interactions, and carbon formation pathways are comprehensively examined to reveal the synergistic regulation mechanisms induced by promoter incorporation.

The novelty of this work lies in the construction of a structure-performance relationship model linking “promoter doping-structural regulation-coke resistance”, which clarifies the roles of Ce, La and Zr in enhancing DRM activity, suppressing Ni sintering, and reducing carbon deposition. The findings provide new insights and a theoretical basis for the rational design of efficient and durable Ni-based DRM catalysts.

1 Experimental

1.1 Catalysts preparation

Ce-, La- and Zr-modified Ni/ $\text{MgO-MgAl}_2\text{O}_4$ catalysts were synthesized *via* sol-gel method. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were used as precursors for the Ni component and the MgO and MgAl_2O_4 supports, respectively. Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and zirconium nitrate pentahydrate ($\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$) served as precursors for the Ce, La and Zr promoters, respectively. While citric acid ($\text{C}_6\text{H}_{10}\text{O}_8$) was employed as the chelating agent.

The theoretical loading of the active metal Ni in the catalysts was optimized based on DRM performance tests, with Ni contents of 5.0%, 7.5%, 10.0%, 12.5% and 15.0%. During the preparation process, the molar ratio of (Ni + Mg) to Al was fixed at 3:1. At room temperature, the nitrate salts were successively dissolved in 20 mL of deionized water under continuous stirring, followed by the dropwise addition of 10 drops of 6 mol/L nitric acid. Citric acid was then added at a molar ratio of 1.5 relative to the total metal ions. The resulting solution was ultrasonicated for 30 min at a power of 50 W and subsequently stirred at 60 °C until a sol-like state was formed. The obtained sol was sealed and aged at room temperature for 72 h, followed by calcination at 750 °C for 4 h in air with a heating rate of 2 °C/min. The catalysts were denoted according to the type and loading of the promoter. For example, 12.5%Ni-7.0%(Ce/La/Zr) indicated a catalyst with theoretical Ni loading of 12.5% and a promoter (Ce, La or Zr) content of 7.0%.

1.2 Evaluation of DRM reaction performance

The CH_4 - CO_2 dry reforming reaction was carried out in a vertical fixed-bed quartz reactor under atmospheric pressure. The catalyst particles were sieved to 40–60 mesh (0.25–0.42 mm). A total of 300 mg of catalyst was loaded into the constant-temperature zone at the center of the reactor using two quartz wool plugs. A thermocouple was placed near the catalyst bed to monitor the bed temperature. Prior to reaction, the catalyst was *in situ* reduced in high-purity hydrogen at 650 °C for 120 min. After reduction, pure Ar was introduced to purge the system for 10 min.

Subsequently, the reaction was initiated at the desired reaction temperature by feeding a gas mixture of CH₄, CO₂ and Ar with volume ratio of 1:1:2. The gas flow rates were controlled using mass flow controllers, and the total flow rate was maintained at 120 mL/min.

The outlet gas composition was analyzed online using a gas chromatograph (GC9790 II, Zhejiang Fuli Analytical Instruments Co., Ltd.) equipped with a thermal conductivity detector (TCD). A silica gel tube was installed between the reactor outlet and the six-port valve of the gas chromatograph to remove water vapor generated during the reaction. The CH₄ and CO₂ conversions (CH₄ conv., CO₂ conv.) and the H₂/CO molar ratio (H₂/CO ratio) were calculated according to the following equations:

$$\text{CH}_4 \text{ conv.} = \frac{F_{\text{CH}_4, \text{in}} - F_{\text{CH}_4, \text{out}}}{F_{\text{CH}_4, \text{in}}} \times 100\% \quad (1)$$

$$\text{CO}_2 \text{ conv.} = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \times 100\% \quad (2)$$

$$\text{H}_2/\text{CO ratio} = \frac{F_{\text{H}_2, \text{out}}}{F_{\text{CO}, \text{out}}} \quad (3)$$

where $F_{\text{CH}_4, \text{in}}$ and $F_{\text{CO}_2, \text{in}}$ represented the inlet flow rates of CH₄ and CO₂ in the feed gas, respectively (mL/min); $F_{\text{CH}_4, \text{out}}$ and $F_{\text{CO}_2, \text{out}}$ denoted the outlet flow rates of CH₄ and CO₂ in the product stream, respectively (mL/min); $F_{\text{H}_2, \text{out}}$ and $F_{\text{CO}, \text{out}}$ corresponded to the outlet flow rates of H₂ and CO in the product stream, respectively (mL/min).

1.3 Catalysts characterization

The actual Ni content in the samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110). The crystalline phases and crystal structures of the catalysts after calcination, reduction, and reaction were characterized by X-ray powder diffraction (XRD, Rigaku Ultima IV). N₂ physisorption adsorption-desorption measurements were conducted on an automatic surface area analyzer (ASAP 2020, Micromeritics) to obtain the textural properties of the calcined catalysts.

The surface morphology and metal dispersion of the catalysts were examined using a field-emission scanning electron microscope (FE-SEM, Hitachi S4800). Elemental distribution on the catalyst surface was further analyzed by coupling SEM with energy-dispersive X-ray spectroscopy (EDS). The microstructure, particle size, and morphology of the catalysts were investigated by field-emission transmission electron microscopy (TEM, FEI Tecnai G2 F20).

X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi) was employed to analyze the surface elemental chemical states and electronic structures of the catalysts. Both survey and high-resolution spectra were recorded. All binding energies were calibrated using the adventitious carbon C 1s peak at 281.7 eV. Thermogravimetric analysis (TG, HITACHI STA200) was performed to quantify the amount of carbon deposition on

the spent catalysts.

The reduction behavior of the calcined catalysts was investigated by H₂ temperature-programmed reduction (H₂-TPR) using a Micromeritics AutoChem II 2920 instrument, and the H₂ consumption was monitored by a thermal conductivity detector (TCD). Approximately 50 mg of catalyst was loaded into a U-shaped quartz tube and pretreated at 200 °C for 30 min under an Ar flow of 30 mL/min. The sample was then cooled to 50 °C, followed by heating to 800 °C at a ramp rate of 5 °C/min under a 10% H₂-Ar atmosphere with a total flow rate of 30 mL/min. The H₂ consumption was calibrated using CuO as standard.

CO₂ temperature-programmed desorption (CO₂-TPD) measurements were conducted on the same instrument to analyze the density and strength of basic sites on the surface of the reduced catalysts. Approximately 50 mg of catalyst was placed in a U-shaped quartz tube and reduced at 650 °C for 120 min under a 10% H₂-Ar flow (30 mL/min). After reduction, the sample was purged with Ar for 30 min and then cooled to 50 °C. High-purity CO₂ was subsequently introduced for 1 h to achieve saturation. The catalyst was purged with He for 120 min to remove physically adsorbed CO₂. The CO₂ desorption profile was recorded under a He atmosphere by heating the sample to 800 °C at a rate of 5 °C/min. The amount of desorbed CO₂ was calibrated using basic zinc carbonate as standard.

2 Results and discussion

2.1 Catalytic performance

To determine the optimal Ni loading in the Ni/MgO-MgAl₂O₄ catalysts, catalysts with different Ni mass fractions (5.0%–15.0%) were prepared and evaluated for the CH₄-CO₂ dry reforming (DRM) at 650 and 750 °C, respectively (Figure 1). The experimental results show that, at both reaction temperatures, the catalytic activity initially increases and then decreases with increasing Ni loading. When the Ni content increases from 5.0% to 12.5%, the number of active metallic Ni sites increases accordingly, leading to a significant enhancement in CH₄ and CO₂ conversions. This behavior indicates that well-dispersed Ni particles are favorable for the reaction. However, when the Ni loading is further increased to 15.0%, excessive Ni aggregation occurs, which not only reduces the dispersion of active metal species but also partially destroys the pore structure, resulting in a decline in catalytic activity.

The CH₄-CO₂ dry reforming reaction is a strongly endothermic process ($\text{CH}_4(\text{g}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g}) + 2\text{H}_2(\text{g})$, $\Delta H = 247 \text{ kJ/mol}$). Therefore, increasing the reaction temperature markedly enhances both CH₄ and CO₂ conversions. In addition, for all samples, the CO₂ conversion is slightly higher than that of CH₄, which is mainly attributed to the occurrence of the reverse water-gas shift (RWGS) reaction ($\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$, $\Delta H = +41 \text{ kJ/mol}$), leading to further consumption of CO₂.

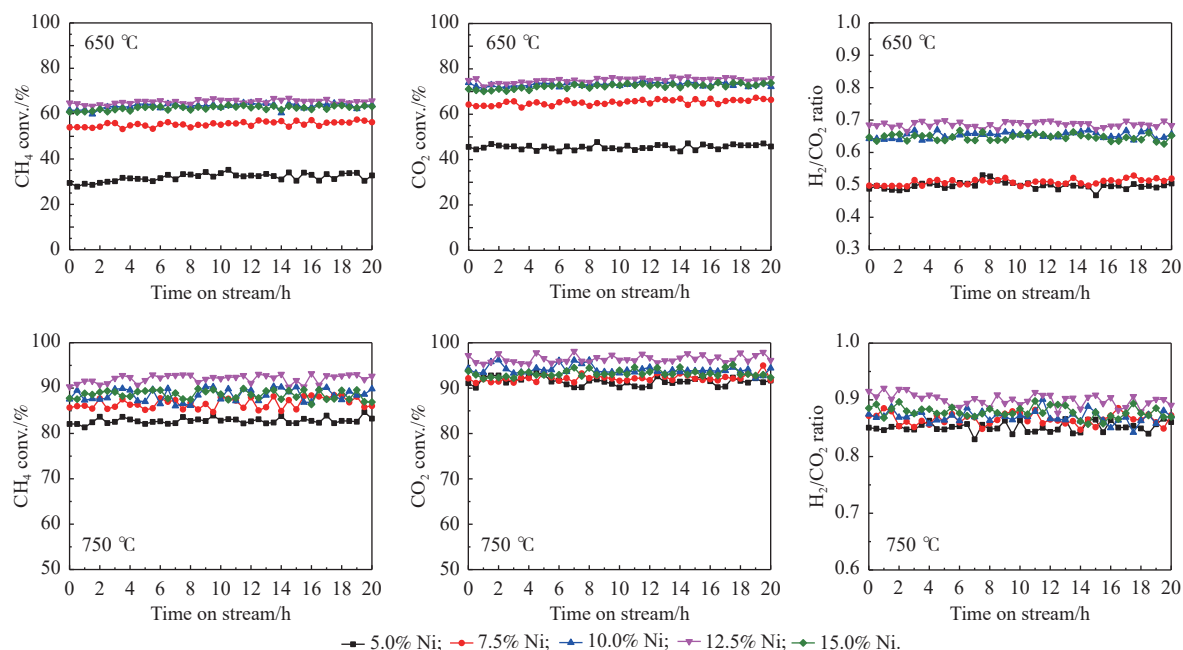


Fig. 1 Effect of Ni loading on CH_4 - CO_2 dry reforming performance (650 and 750 °C; CH_4 conversion, CO_2 conversion, H_2/CO ratio)

Reaction conditions: $\text{CH}_4/\text{CO}_2=1:1$, pressure 0.1 MPa, total flow rate 120 mL/min, catalyst weight 0.3 g;
All catalysts were pre-reduced under H_2 at 650 °C for 120 min.

In the temperature range of 650–800 °C, the CH_4 and CO_2 conversions over all four catalysts increase with increasing temperature (Figure 2). This trend mainly arises from the strongly endothermic nature of the DRM reaction and the gradual alleviation of thermodynamic limitations at elevated temperatures. In the range of 650–750 °C, the conversions over the Ce-, La- and Zr-modified catalysts are overall lower than those of the unmodified 12.5%Ni sample. When the temperature is further increased to 800 °C, the differences in catalytic activity among the catalysts become markedly reduced and tend to converge, indicating that the reaction gradually approaches thermodynamic equilibrium, under which the kinetic differences among the catalysts are significantly weakened.

It should be noted that the slight decrease in activity observed for the Ce-, La- and Zr-modified catalysts in the low- and medium-temperature regions does not imply a

deterioration of catalyst structure or a reduction in the number of active sites. Instead, it more likely reflects changes in the overall reaction behavior induced by promoter incorporation. On the one hand, the introduction of promoters may alter the electronic environment and reaction selectivity of Ni surface active centers, thereby partially suppressing CH_4 activation. On the other hand, the enhancement of surface oxygen-related reaction pathways may, to some extent, compete with the DRM reaction, leading to lower apparent conversions. Such behavior is commonly observed in Ni-based catalysts modified with rare-earth or transition metal oxides and highlights the “dual effect” of promoters in regulating the reaction pathways, rather than a simple promotion or inhibition of catalytic activity. This conclusion is further supported by the characterization results of the catalysts before and after reaction.

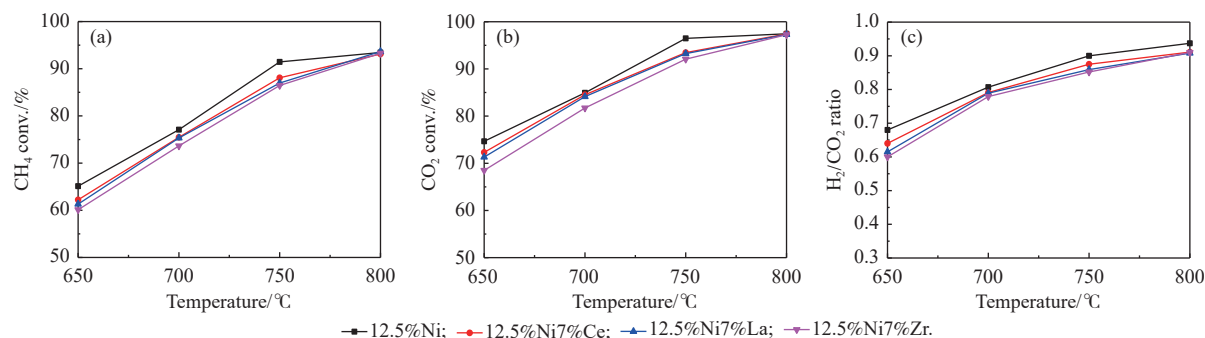


Fig. 2 Catalytic performance of Ce-, La- and Zr-modified Ni/MgO-MgAl₂O₄ catalysts in CH_4 - CO_2 dry reforming at different temperatures

Reaction conditions: $\text{CH}_4/\text{CO}_2=1:1$, pressure 0.1 MPa, total flow rate 120 mL/min, catalyst weight 0.3 g;
All catalysts were pre-reduced under H_2 at 650 °C for 120 min.

Considering that Ni-based catalysts are prone to form inert carbon deposits at relatively low temperatures, whereas higher temperatures are more favorable for suppressing carbon deposition and promoting H_2 production, a 20 h continuous reaction test was conducted at 750 °C for all four catalysts (Figure 3). Thermodynamic equilibrium conversions of CH_4 and CO_2 (See Figures 3(a) and 3(b)) in the absence of carbon formation were calculated using HSC Chemistry software based on the Gibbs free energy minimization method, yielding values of approximately 95% and 94%, respectively. The results indicate that all catalysts maintain relatively stable CH_4 and CO_2 conversions throughout the reaction period, with no obvious activity decay observed. This suggests that, within the investigated temperature and time scale, the catalysts do not enter a rapid deactivation stage dominated by severe carbon deposition or degradation of metal structures.

However, the stability of DRM catalysts cannot be simply equated with differences in short-term conversion decay rates. Instead, it is more closely associated with the structural evolution of metal particles during reaction, the nature of the formed carbon species, and the extent to which these carbon deposits disrupt the active interfaces.

2.2 Catalyst characterization before and after reaction

2.2.1 Crystal phase composition, pore structure, and morphology

Figure 4 presents the XRD patterns of the modified Ni/MgO-MgAl₂O₄ catalysts before and after reduction as well as after the reaction. All samples exhibit characteristic diffraction peaks associated with Ni-, Mg- and Al-containing phases. Strong diffraction peaks at 42.9° and 62.4° can be assigned to the MgO crystalline phase (JCPDS 45-0946), while the weak peaks located at 36.8°, 44.9°, 59.7° and 65.2° correspond to the MgAl₂O₄ spinel phase (JCPDS 21-1152). In addition, diffraction peaks at 31.4°, 37.0°, 45.0°, 59.7° and 66.5° are attributable to the NiAl₂O₄ phase (JCPDS 10-0339). As shown in Figure 4(a), characteristic peaks of cubic NiO appear at 37.2°, 43.3° and 62.9°, partially overlapping with those of MgO. The Ce-, La- and Zr-modified catalysts exhibit similar diffraction features to the unmodified 12.5%Ni sample, while no distinct diffraction peaks corresponding to CeO₂, La₂O₃ or ZrO₂ are detected, indicating that these promoter oxides are either highly dispersed or present in an amorphous state.

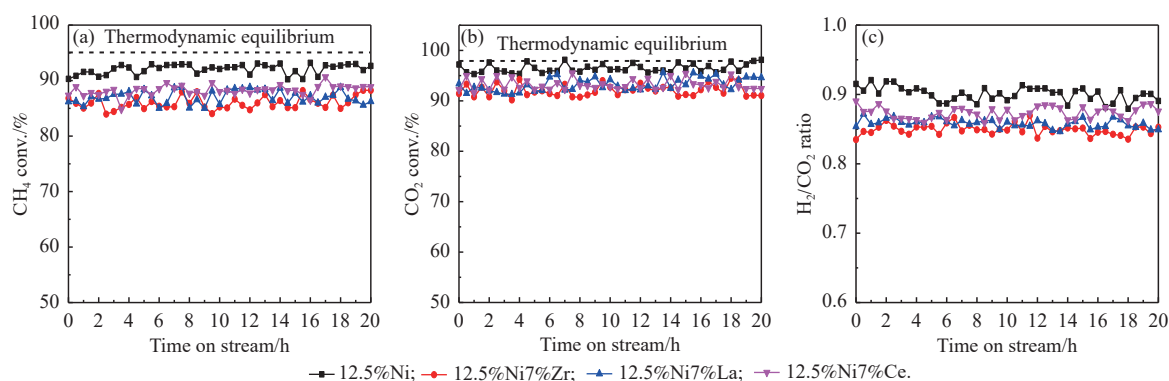


Fig. 3 Stability tests of Ce-, La- and Zr-modified Ni/MgO-MgAl₂O₄ catalysts in CH_4 - CO_2 dry reforming ((a) CH_4 conversion; (b) CO_2 conversion; (c) H_2/CO_2 ratio)

Reaction conditions: 750 °C, $CH_4/CO_2=1:1$, pressure 0.1 MPa, total flow rate 120 mL/min, catalyst weight 0.3 g;
All catalysts were pre-reduced under H_2 at 650 °C for 120 min.

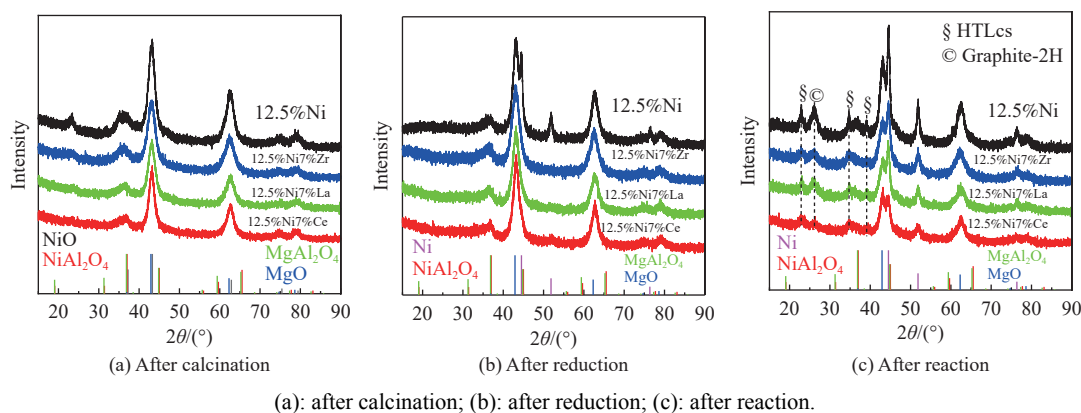


Fig. 4 XRD patterns of Ce-, La- and Zr-modified Ni/MgO-MgAl₂O₄ catalysts

Notably, the diffraction peak intensities of both MgO and MgAl_2O_4 phases reduce after promoter incorporation, suggesting that Ce, La and Zr doping decreases the crystallinity of the support. Meanwhile, the decreased intensity of NiO diffraction peaks implies enhanced dispersion of Ni species and reduced Ni particle size, which is beneficial for achieving a more uniform distribution of Ni.

Figure 4(b) shows the XRD patterns of the reduced catalysts. All samples retain the mixed MgO- MgAl_2O_4 support structure, whereas the diffraction peaks of NiO disappear and those of NiAl_2O_4 significantly weaken. Meanwhile, characteristic peaks of metallic Ni appear at 44.5° and 51.8° (JCPDS 04-0850). Among them, the unmodified 12.5%Ni sample exhibits markedly stronger Ni⁰ diffraction peaks than the three modified catalysts. It should be emphasized that although improved metal dispersion is generally favorable for catalytic activity, the activity decrease observed in DRM is not attributable to a reduction in the amount of Ni, but is more likely related to promoter-induced regulation of reaction pathways or the promotion of side reactions. Figure 4(c) presents the XRD patterns of the catalysts after 20 h of reaction. All samples display diffraction peaks corresponding to Ni, MgO, NiAl_2O_4 and MgAl_2O_4 phases. The diffraction intensity of metallic Ni is significantly enhanced compared with the reduced state, indicating that Ni particles undergo sintering to varying extents during the reaction. Notably, the increase in Ni peak intensity for the modified catalysts is much less pronounced than that for the 12.5% Ni-loaded sample, suggesting that interactions between Ce, La, Zr and Ni effectively inhibit the metal sintering. In addition, new diffraction peaks appearing at 22.9° , 34.8° and 39.2° can be assigned to hydrotalcite-like carbonates (HTLcs, JCPDS 70-2151), which are probably formed *via* surface hydration-carbonation-induced structural reconstruction of metal oxides under the combined influence of water generated from the RWGS reaction and CO_2 ^[36]. Furthermore, a diffraction peak at 25.9° corresponding to Graphite-2H is detected, originating from graphitic carbon formed during the DRM process^[37]. Compared with the 12.5%Ni catalyst, the modified catalysts exhibit much weaker Graphite-2H diffraction peaks. For the 12.5%Ni7%Ce sample, this peak is nearly invisible, further demonstrating the significant suppression effect of the promoters on carbon deposition.

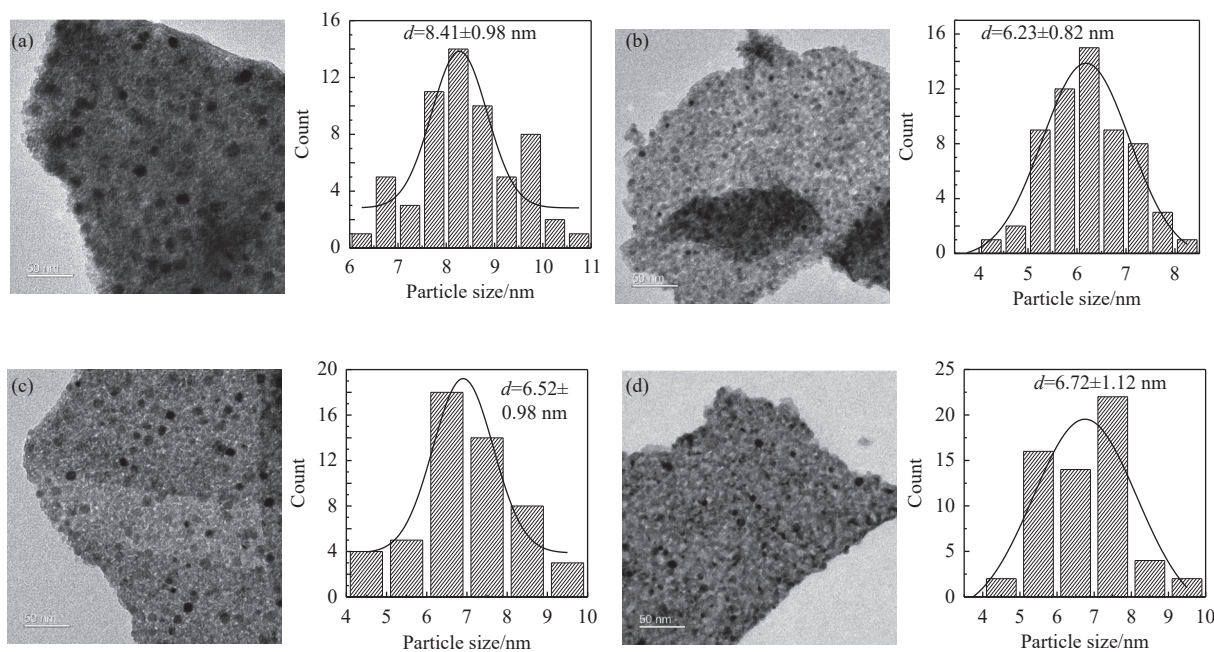
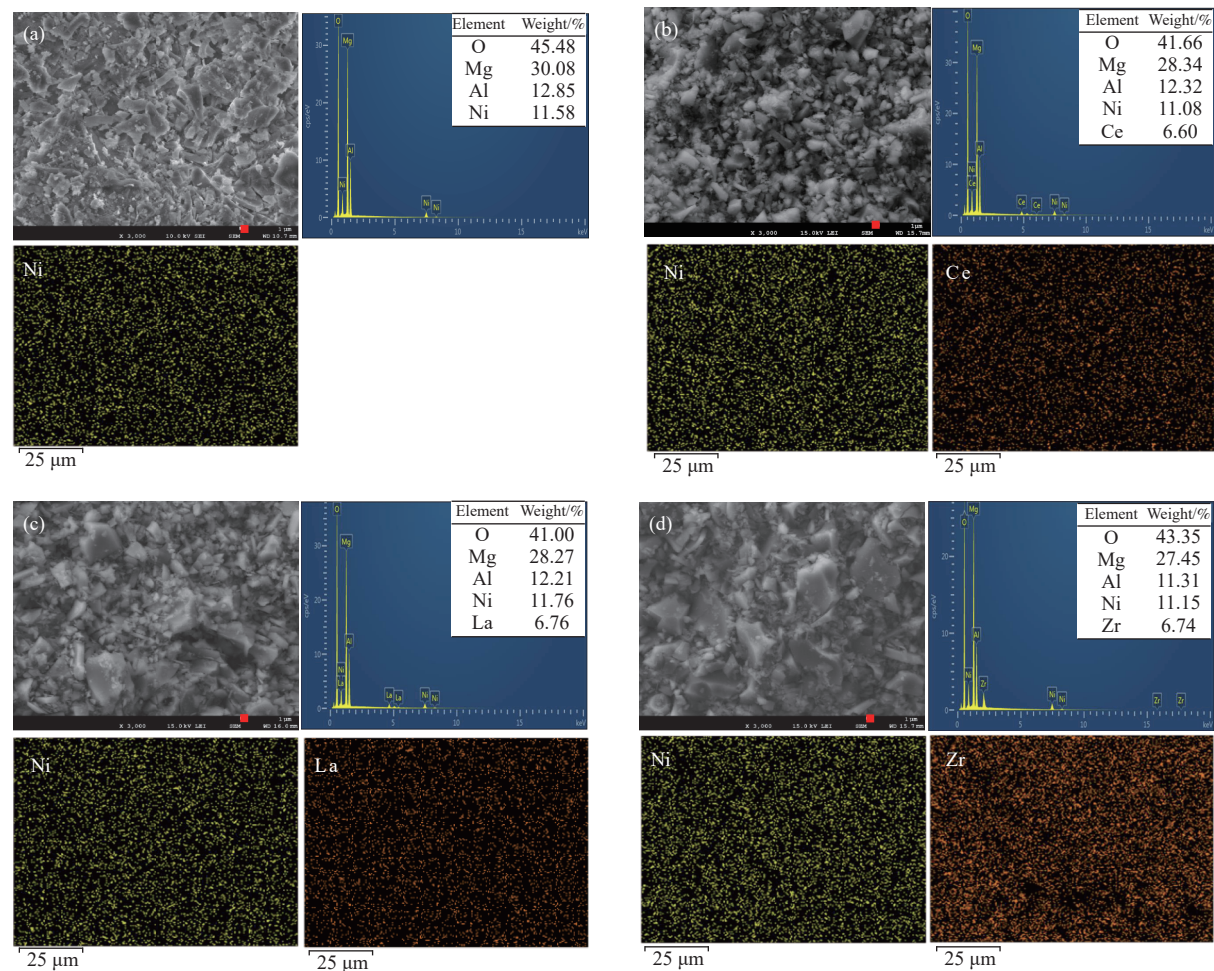
Table 1 summarizes the key elemental contents and pore structure parameters of the four catalysts after calcination. The actual Ni loadings were determined to be 10.25% for 12.5%Ni, 10.56% for 12.5%Ni7%Zr, 10.68% for 12.5%Ni7%La and 10.25% for 12.5%Ni7%Ce. While the actual contents of the Zr, La and Ce promoters were 5.58%, 5.67% and 5.67%, respectively. All measured values are slightly lower than their corresponding theoretical values (Ni: 12.5%; promoters: 7%), which is mainly attributed to the partial incorporation of Ni^{2+} and promoter cations into the MgO or MgAl_2O_4 lattices during calcination at 750°C , leading to the formation of stable NiO-MgO solid solutions and NiAl_2O_4 spinel phases. The introduction of promoters effectively regulates the dispersion of the active metal and the interfacial structure. The specific surface areas of the 12.5%Ni, 12.5%Ni7%Zr, 12.5%Ni7%La and 12.5%Ni7%Ce catalysts are 57.46, 60.62, 60.49 and $61.98\text{ m}^2/\text{g}$, respectively. Figure 5 presents the SEM-EDS images and elemental mapping of the calcined catalysts. As can be observed, the unmodified 12.5%Ni catalyst exhibits a relatively dense surface with small crystallites and a limited number of pores, whereas the Zr-, La- and Ce-modified catalysts display uniformly distributed particles with clear grain boundaries and well-developed porous structure. EDS and elemental mapping analyses further reveal the compositional distribution characteristics of the catalysts: Ni species in the unmodified catalyst appear relatively aggregated, while those in the Zr-, La- and Ce-modified samples are uniformly dispersed and form embedded interfacial structures with the promoters on the support surface, thereby constructing abundant and homogeneous Ni-*X* (*X* = Zr, La, Ce) interfaces. This structural feature is in good agreement with the XRD results, confirming that the incorporation of Zr, La and Ce effectively enhances the Ni dispersion.

To further elucidate the morphology and dispersion of metal particles in the reduced catalysts, transmission electron microscopy (TEM) images are recorded (Figure 6). Dark particles composed of Ni or Ni-*X* (*X* = Zr, La, Ce) species can be clearly observed in the reduced catalysts. Particle size distributions obtained using Nano Measurer 1.2 software reveal that the sizes of Ni or Ni-*X* particles follow a normal distribution and exhibit systematic variations depending on the type of the promoter introduced.

Table 1 Elemental analysis and texture properties of the catalysts after calcination

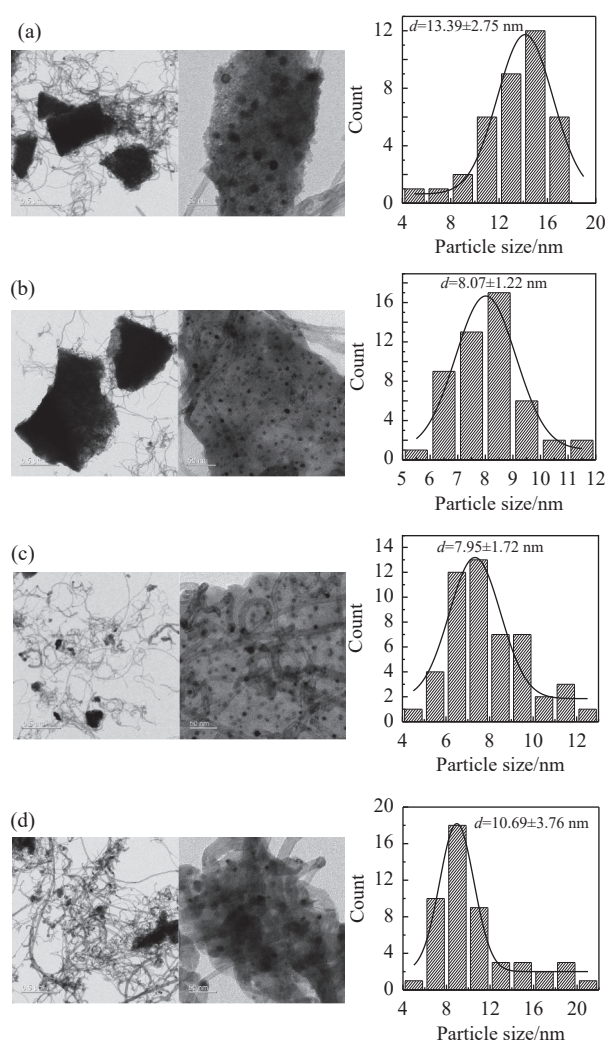
Sample	Element content w/%				$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_p/(\text{cm}^3 \cdot \text{g}^{-1})$
	Ni ^a		Zr/La/Ce			
	A	B	A	B		
12.5%Ni	10.25	11.58			57.46	0.06
12.5%Ni7%Zr	10.56	11.04	5.58	6.78	60.62	0.05
12.5%Ni7%La	10.68	11.76	5.67	6.76	60.49	0.07
12.5%Ni7%Ce	10.25	11.15	5.67	6.60	61.98	0.07

^a: The data obtained from ICP-OES and SEM-EDS are denoted as A and B, respectively.



The unmodified catalyst exhibits an average particle size of 8.41 ± 0.98 nm, whereas the average particle sizes of the 12.5%Ni7%Ce, 12.5%Ni7%La, and 12.5%Ni7%Zr catalysts decrease to 6.23 ± 0.82 , 6.52 ± 0.98 and 6.72 ± 1.12 nm, respectively. These results indicate that the promoters can form stable interfaces with Ni, effectively restricting metal migration and aggregation during the calcination and reduction.

Furthermore, the carbon deposition morphology and changes in metal particle size of the spent catalysts are investigated by TEM analysis (Figure 7). After 20 h of reaction, both filamentous carbon and encapsulating carbon are observed on the catalyst surfaces. Filamentous carbon has relatively minor impact on catalytic activity, whereas encapsulating carbon blocks metal active sites and leads to catalyst deactivation. The unmodified 12.5%Ni catalyst generated significantly larger amounts of filamentous and encapsulating carbon than the Zr-, La- and Ce-modified catalysts, indicating that the construction of Ni-*X* (*X* = Zr, La, Ce) interfaces effectively suppresses carbon deposition, which is consistent with the XRD results.



(a): 12.5%Ni; (b): 12.5%Ni7%Ce; (c): 12.5%Ni7%La;
(d): 12.5%Ni7%Zr.

Fig. 7 TEM images of catalysts after reaction

Statistical analysis of the metal particle sizes after reaction reveals that they still follow a normal distribution. After 20 h of reaction, the average particle sizes increase to 13.39 ± 2.75 , 8.07 ± 1.22 , 7.95 ± 1.72 and 10.69 ± 3.76 nm, respectively, representing an increase of 1.43–4.98 nm compared with those of the reduced catalysts. The results indicate that varying degrees of metal migration, aggregation, and sintering occur during the DRM process, with the unmodified catalyst exhibiting the most severe sintering. In contrast, the Ni-*X* interfaces can partially inhibit excessive growth of metal particles during reaction, thereby enhancing the structural stability of the catalysts.

2.2.2 Electronic coordination environment of surface elements

Figure 8 presents the O 1s XPS spectra of the reduced 12.5%Ni catalyst and its Ce-, La- and Zr-modified counterparts. The O 1s peak can be deconvoluted into lattice oxygen (O_a , 530.0–530.5 eV) and adsorbed oxygen/surface –OH species (O_b , 531.8–532.0 eV)^[38]. Because O_b species exhibit higher mobility and reactivity, their relative abundance is generally positively correlated with the concentration of surface oxygen vacancies, thereby influencing the adsorption and activation of CO₂ during the DRM reaction^[39]. Based on the integrated peak areas, the unmodified 12.5%Ni catalyst shows the lowest O_b content of 46.5%, while the Ce-modified sample exhibits the highest content of 67.6%. The La- and Zr-modified catalysts display the O_b contents of approximately 60%. The results indicate that the introduction of Ce, La and Zr effectively regulates the structure and reactivity of surface oxygen species.

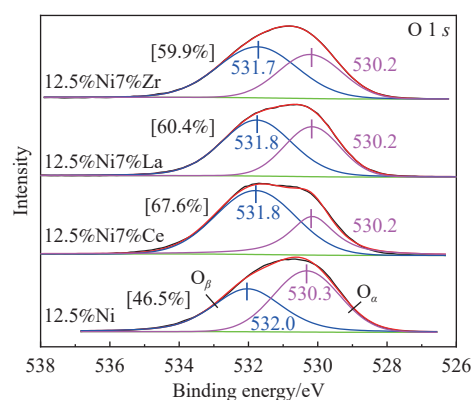


Fig. 8 O 1s spectra of catalyst surfaces after reduction

Figure 9 presents the Ni 2p_{3/2} XPS spectra of the calcined, reduced, and spent catalysts. In the calcined samples (Figure 9(a)), the characteristic peak at ~856.0 eV accompanied by satellite features is assigned to Ni²⁺ species, mainly originating from NiO and Ni²⁺ strongly interacting with the MgO-MgAl₂O₄ support. Upon modification, the Ni 2p_{3/2} binding energies shift overall toward higher values, indicating that Ce, La and Zr possess high oxygen affinity and can induce the formation of oxygen vacancies and

redistribution of oxygen charge density. This effect strengthens the Ni-support interaction and places Ni in a more electropositive environment.

In the reduced catalysts (Figure 9(b)), the 12.5%Ni sample exhibits a typical metallic Ni^0 peak at ~ 852.0 eV, while residual Ni^{2+} signals associated with hardly reducible Ni species in the NiAl_2O_4 structure are still observed. In contrast, no distinct peak appears in the Ni^0 region for the Ce- and Zr-modified samples. This phenomenon is not due to stronger anchoring effects that hinder NiO reduction, but is more plausibly attributed to two other reasons: (i) Ce/Zr modification enhances NiO dispersion, leading to extremely finely divided Ni^0 particles with weakened XPS signals; and (ii) strong electronic interactions between Ni and Ce (or Zr) alter the electron density of Ni^0 , shifting its characteristic peak toward higher binding energies (approximately 853.5–855 eV). This interpretation is corroborated by the weak Ni^0 diffraction peaks observed in the XRD patterns of reduced samples.

Figure 9(c) shows the Ni $2p_{3/2}$ spectra of the spent samples. For all catalysts, both Ni^0 and Ni^{2+} signals are markedly attenuated, mainly due to: (i) high-temperature-induced Ni sintering or inward migration, which decreases the surface Ni concentration; and (ii) coverage by carbon deposits that limits XPS detection. Nevertheless, the intensified Ni^0 peaks in XRD indicates the growth of bulk Ni^0 particles and increased reduction degree, revealing surface-bulk structural reconstruction under prolonged reaction conditions. Notably, the Ce- and La-modified

catalysts retain relatively higher Ni $2p_{3/2}$ intensities, suggesting that the modifiers more effectively suppress Ni sintering and carbon deposition, thereby imparting superior structural stability. For the La-modified catalyst (Figure 9(d)), the peak at ~ 851.5 eV in the calcined sample arises from overlap between the Ni $2p_{3/2}$ and La $3d_{3/2}$ signals. After reduction, the peak shifts to ~ 852.5 eV, which can be attributed to the combined contribution of metallic Ni^0 formation and La $3d$ signals.

2.2.3 Reducibility and basic site properties of the catalysts

The reducibility of Ni^{2+} species in the calcined catalysts was investigated by H_2 -TPR (Figure 10(a)). All samples exhibit two characteristic reduction features. The weak peak in the range of 450–500 °C can be attributed to NiO species with moderate interaction with the support, whereas the broad high-temperature peak between 550 and 850 °C arises from the sequential reduction of highly dispersed NiO (600–620 °C) and NiAl_2O_4 spinel (710–740 °C). The introduction of Ce and La have limited influence on the reduction peak positions, while Zr modification markedly shifts the high-temperature reduction peak to lower temperatures by approximately 15 °C. This indicates that the superior oxygen ion mobility of ZrO_2 and its ability to modulate the Ni-support interaction facilitate the reduction of NiO .

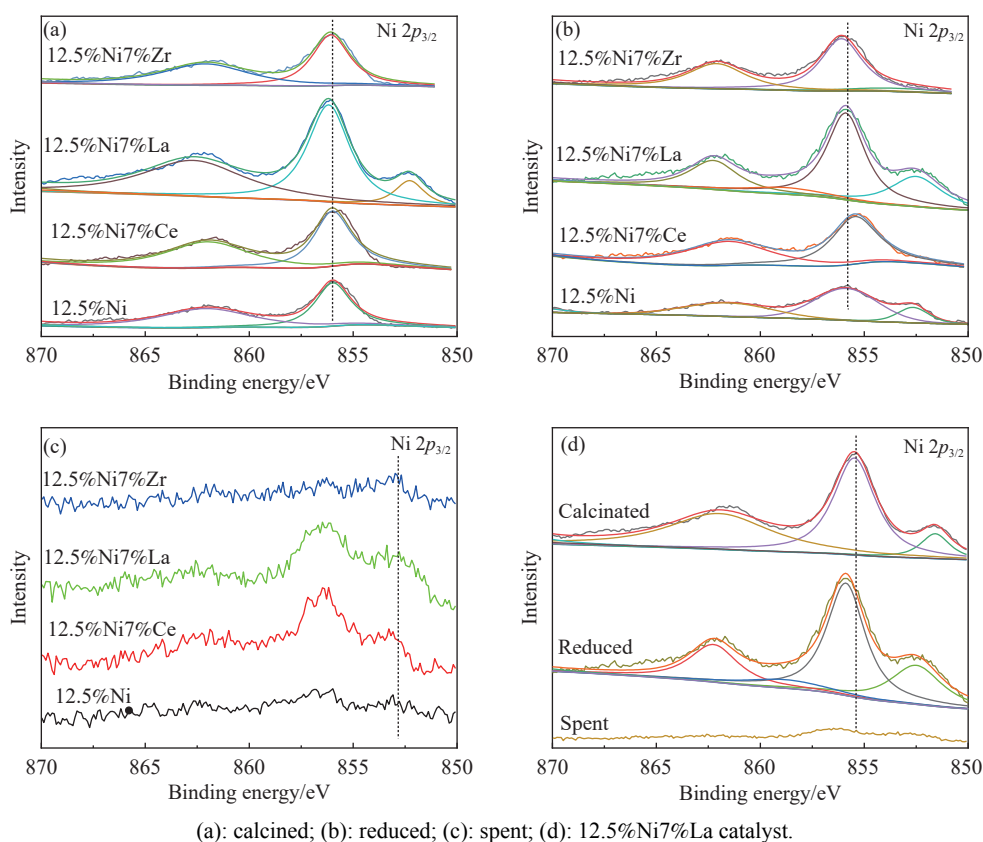


Fig. 9 Ni $2p_{3/2}$ XPS spectra of the catalysts

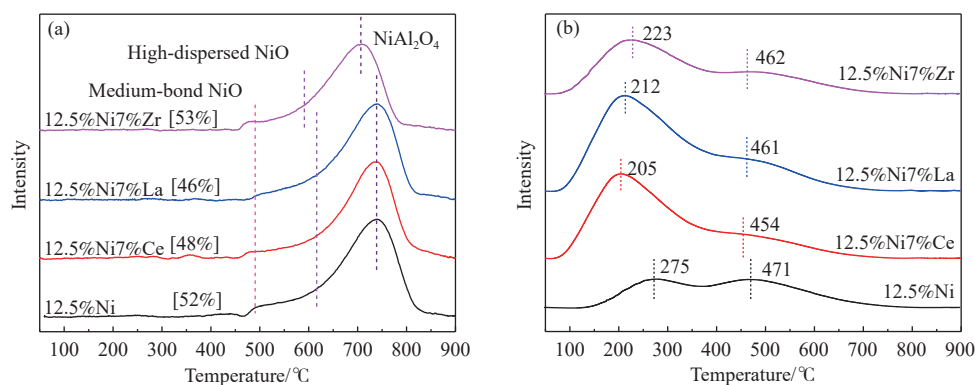


Fig. 10 (a) H₂-TPR profiles of catalysts after calcination; (b) CO₂-TPD profiles of catalysts after reduction

Based on H₂ consumption, the reduction degrees of the catalysts range from 45% to 55%, with the Ce- and La-modified samples exhibiting the lowest values, suggesting incomplete reduction of Ni²⁺ species. This is mainly attributed to the relatively low reduction temperature employed (650 °C) and the presence of the hardly reducible NiAl₂O₄ phase.

The basic properties of the catalysts are characterized by CO₂-TPD (Figure 10(b)). All samples display two CO₂ desorption peaks: the peak at 200–300 °C corresponds to medium-strength basic sites, primarily associated with metal-O²⁻ groups, while the peak at 450–480 °C is assigned to strong basic sites related to low-coordinated lattice oxygen. Compared with the unmodified 12.5%Ni catalyst, Ce-, La- and Zr-modified samples show desorption peaks shifted to lower temperatures to varying extents, particularly for the medium-strength basic sites, indicating that the promoters reduce the surface basic strength and modify the distribution of basic sites. It has been reported that rare-earth oxides can enhance the basic characteristics of MgO or MgAl₂O₄ supports by increasing oxygen coordination and surface oxygen vacancy concentration, which is consistent with the results in this study^[40]. Table 2 summarizes the desorption peak positions, basic site contents, and their relative proportions for the reduced catalysts.

Table 2 CO₂-TPD parameters of catalysts after reduction

Catalyst	Desorption peak position/°C	Relative contents ^a /%	Basicity ^b /(mmol·g ⁻¹)
12.5%Ni	275	37.3	0.465
	471	62.7	0.547
12.5%Ni7%Ce	205	71.5	0.916
	454	28.5	0.365
12.5%Ni7%La	212	66.4	1.093
	461	33.6	0.554
12.5%Ni7%Zr	223	65.0	0.604
	462	35.0	0.326

^a: The relative content was calculated from the peak areas obtained from the CO₂-TPD measurements; ^b: The basicity was calculated based on the CO₂-TPD profiles.

In the 12.5%Ni sample, strong basic sites dominate (62.7%), with a total basicity of 1.012 mmol/g. The incorporation of Ce, La or Zr significantly increases the proportion of medium-strength basic sites and further shifts the desorption peaks to lower temperatures. Specifically, for 12.5%Ni7%Ce, the proportion of medium-strength basic sites increases to 71.5%, the peak temperature decreases by approximately 70 °C, and the total basicity rises to 1.281 mmol/g. The 12.5%Ni7%La catalyst exhibits the most pronounced increase in total basicity (1.647 mmol/g), with the medium-strength basic site content reaching 1.093 mmol/g. In contrast, 12.5%Ni7%Zr shows a slightly lower total basicity (0.930 mmol/g), while the proportion of medium-strength basic sites increases to 65.0%, indicating that Zr modification mainly enhances CO₂ adsorption by improving oxygen mobility and Ni dispersion rather than increasing the total number of basic sites. Overall, the introduction of Ce, La and Zr favors the formation of a higher fraction of medium-strength basic sites, which is closely related to promoter-induced oxygen vacancy formation and local structural modulation. The oxygen storage capacity of CeO₂ and the intrinsically strong basicity of La₂O₃ further enhance the total surface basicity, whereas Zr doping predominantly strengthens CO₂ adsorption and activation through regulation of oxygen mobility and Ni-support interactions.

2.2.4 Analysis of carbon deposition behavior of catalysts

Although the four catalysts exhibit similar macroscopic deactivation behaviors during 20 h of reaction at 750 °C, their microscopic structural stability and carbon deposition characteristics may differ significantly. To verify this assumption, the carbon deposition behavior of the spent catalysts was systematically analyzed (Figure 11). The TG curves of all catalysts show three typical regions: the low-temperature weight loss below 200 °C is mainly attributed to the desorption of physically adsorbed water and gases; the intermediate-temperature weight gain at 300–400 °C originates from the oxidation of Ni⁰; and the high-temperature weight loss between 400 and 700 °C corresponds to the oxidative decomposition of surface

carbon species. Therefore, the weight loss in the high-temperature region is used to quantitatively evaluate the amount of carbon deposition.

Within the investigated temperature range, the 12.5%Ni catalyst exhibits the most severe carbon deposition, with the carbon content reaching as high as 32% at 650 °C. As the reaction temperature increased, carbon deposition decreased markedly, dropping to 14.62% at 750 °C. The suppression of carbon deposition at elevated temperatures can mainly be attributed to: (i) higher temperatures promoting the DRM reaction while thermodynamically suppressing side reactions such as CH₄ cracking and the Boudouard reaction; and (ii) accelerated oxidation gasification and surface migration of carbon species at high temperatures, which kinetically reduce the carbon formation rate. Compared with the benchmark catalyst, the 12.5%Ni7%Ce catalyst exhibits the best resistance to carbon deposition in the temperature range of 650–750 °C, with carbon contents maintained at 10%–12%. This behavior is primarily attributed to the excellent redox properties and abundant oxygen vacancies of CeO₂, which continuously promote the oxidation of carbon species. However, at 800 °C, the anti-coking performance of the catalyst declines, possibly due to the sintering or phase evolution of CeO₂, leading to reduced oxygen mobility, together with further sintering of Ni particles that promotes the CH₄ cracking and thus enhances carbon formation. The carbon content of the 12.5%Ni7%La

catalyst is maintained at 15%–18% after reaction, exhibiting an overall moderate anti-coking performance, with the lowest carbon deposition observed at 750 °C. The optimal performance may originate from the La promoter enhancing surface basicity and improving CO₂ adsorption, while the synergistic conversion efficiency of CH₄ and CO₂ and the oxidation rate of carbon species reach an optimal balance. For the 12.5%Ni7%Zr catalyst, the carbon content continuously decreases with increasing temperature, from 19.37% at 650 °C to 10.85% at 800 °C. This trend is closely related to the enhanced oxygen mobility and oxygen storage capacity of ZrO₂ at high temperatures, which promote CO₂ activation and *in situ* oxidation of surface carbon species. In addition, elevated temperatures can accelerate the carbon-oxygen cycle on Ni sites, further improving the overall resistance to carbon deposition.

Raman analysis is conducted to identify the surface carbon species on the catalysts after 20 h of reaction at 750 °C (Figure 12). All samples exhibited a D band at approximately 1350 cm⁻¹ (disordered carbon) and a G band at approximately 1580 cm⁻¹ (graphitic carbon). The D/G intensity ratio (I_D/I_G) is commonly used to characterize the degree of graphitization of carbon species, with higher values indicating more disordered carbon that is easier to oxidize and remove. The I_D/I_G values of the four catalysts follow the order: 12.5%Ni7%La (1.21) > 12.5%Ni7%Ce (1.20) > 12.5%Ni7%Zr (1.17) > 12.5%Ni (1.06).

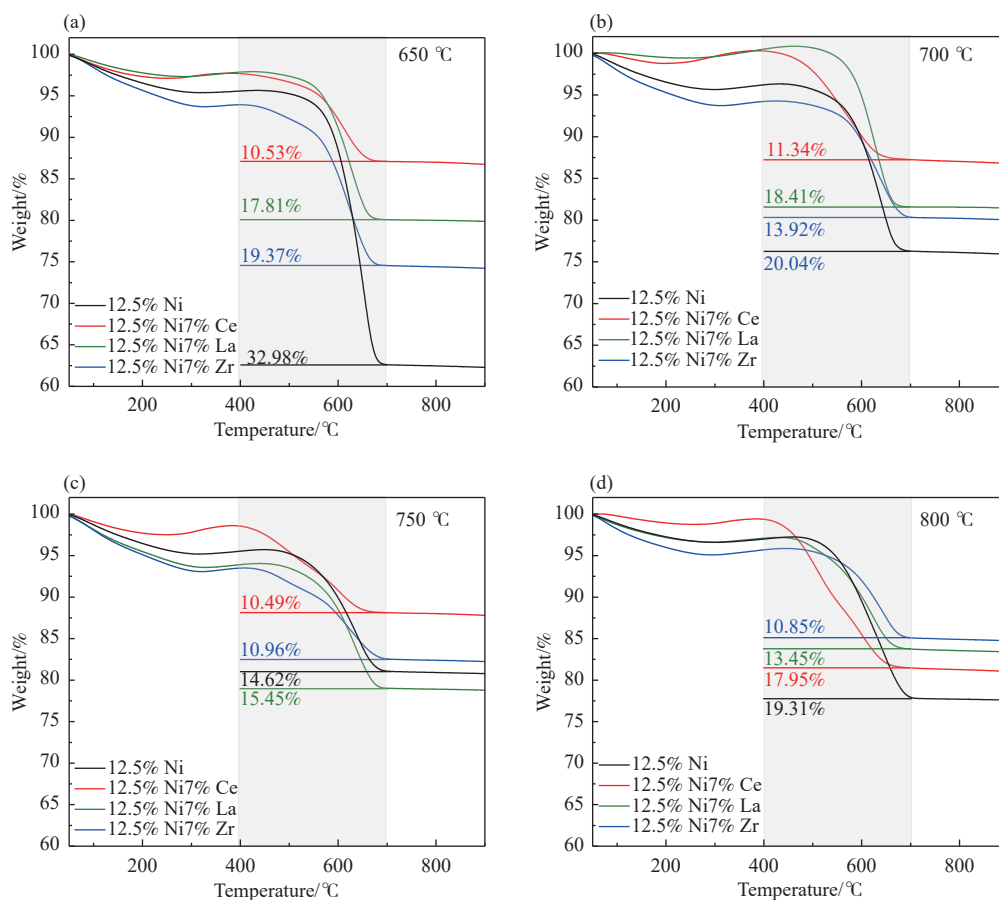


Fig. 11 TG curves of catalysts after reaction at different temperatures

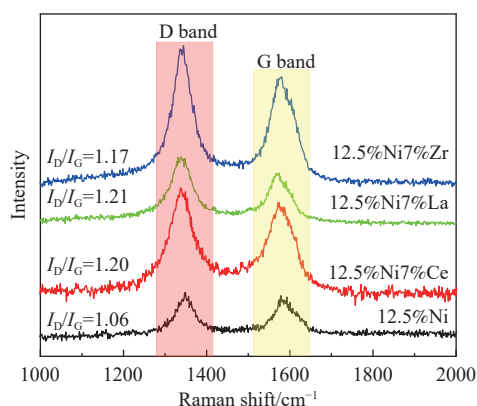


Fig. 12 Raman spectra of catalysts after 20 h reaction at 750 °C

The unmodified Ni catalyst exhibits the lowest I_D/I_G value, indicating the highest degree of carbon graphitization, which is consistent with its most severe carbon deposition observed in the TG analysis. In contrast, the La- and Ce-modified samples possess the most disordered carbon structures, further explaining their superior anti-coking performance. Combined with SEM/TEM observations, fibrous carbon is identified as the dominant carbon species formed on the catalyst surface after reaction. Such carbon readily covers active sites and destroys the pore structure, constituting one of the main causes of catalyst deactivation.

Overall, the results demonstrate that Ce, La and Zr modification alters the dynamic balance between carbon formation and removal, enabling carbon to exist in a more dispersed and readily oxidizable form, while effectively suppressing excessive growth of Ni particles during reaction. From a structural perspective, this significantly reduces the potential risk of catalyst deactivation.

2.2.5 Analysis of carbon deposition behavior of catalysts

Figure 13 presents the XPS spectra of Ce 3d, La 3d_{5/2}, and Zr 3d on the catalyst surfaces before and after reduction. Overall, after 20 h of reaction, the XPS signals of the elements are significantly weakened and exhibit a certain degree of spectral roughness. This is mainly attributed to carbon deposition, migration of metal or promoter species, surface structural reconstruction, and charge accumulation during the reaction, which collectively reduce the effective surface concentration of the elements and increase the heterogeneity of the chemical environment, thereby deteriorating the quality of the photoelectron signals.

Figure 13(a) shows the Ce 3d XPS spectra of the catalysts after reduction and reaction. Typical Ce⁴⁺ features (3d_{5/2}: V, V2, V3; 3d_{3/2}: U, U2, U3) and Ce³⁺ features (V1, U1) can be clearly identified. Deconvolution analysis indicates that the Ce⁴⁺/(Ce⁴⁺+Ce³⁺) fraction decreases from

0.774 in the reduced sample to 0.686 after reaction, indicating a decrease in the proportion of Ce⁴⁺ and a corresponding increase in Ce³⁺. This variation suggests that CeO_x participates in O²⁻ migration and release during the reaction. The reversible Ce⁴⁺/Ce³⁺ redox cycle provides surface active oxygen species, which are beneficial for *in situ* oxidation and removal of carbon deposits. Moreover, the Ce 3d spectra shift toward higher binding energy after reaction, further implying changes in the surface electronic environment, possibly associated with an increased concentration of oxygen vacancies and reduced electron density.

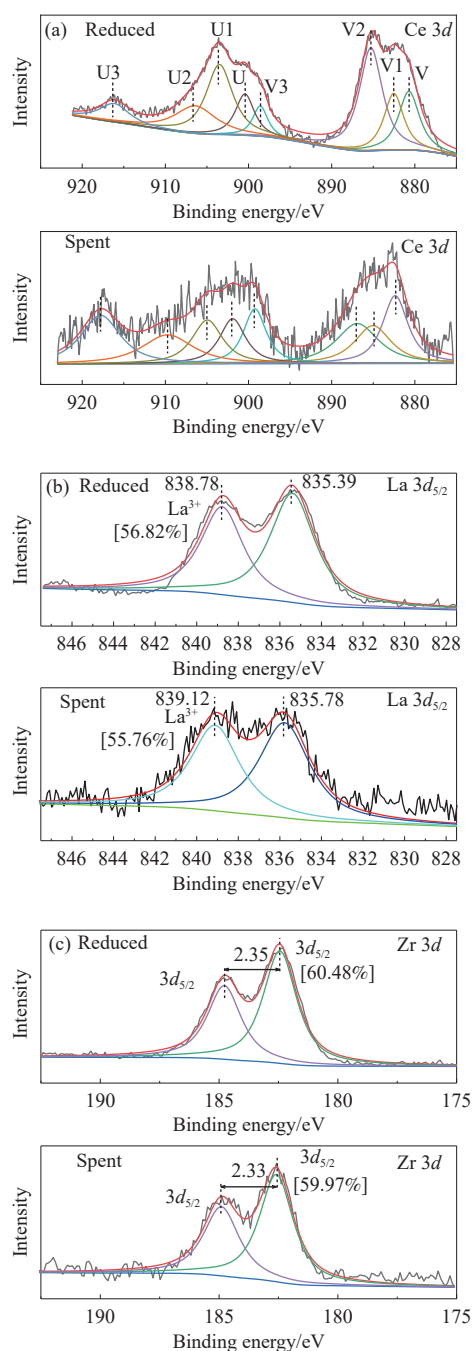


Fig. 13 XPS spectra of Ce 3d (a), La 3d_{5/2} (b) and Zr 3d (c) of the catalysts after reduction and reaction

Combined with the CO₂-TPD results, it can be inferred that Ce incorporation increases the number of medium-strength basic sites and enhances oxygen storage-release capability, thereby significantly promoting CO₂ activation and carbon-oxygen reactions, which accounts for the excellent anti-coking performance of the 12.5%Ni7%Ce catalyst.

Figure 13(b) and 13(c) display the La 3d_{5/2} and Zr 3d spectra of the catalysts before and after reaction, respectively. The peaks located at 838.8±0.5 and 835.5±0.5 eV correspond to the characteristic signals of La³⁺. Peak fitting results show that the relative content of La³⁺ is 56.82% after reduction and 55.76% after reaction, indicating only a slight change and suggesting that La maintains a relatively stable chemical valence during the reaction. Similarly, both the binding energies and peak areas of Zr 3d_{3/2} and 3d_{5/2} exhibit negligible changes before and after reaction, confirming that Zr species are chemically stable. The results demonstrate that La and Zr mainly act as structural modifiers, with their oxidation states remaining essentially unchanged under reaction conditions. Although XPS indicates stable chemical states for La and Zr, the CO₂-TPD results reveal that their incorporation significantly increases the proportion of medium-strength basic sites and shifts the desorption peaks toward lower temperatures, indicating enhanced CO₂ adsorption and activation. This enhancement may originate from lattice distortion of the support induced by La or Zr incorporation, leading to the formation of new surface defects or oxide interfacial structures, which optimize CO₂ adsorption-conversion behavior. The increased basic sites and improved CO₂ activation capability are conducive to promoting the oxidation and removal of carbon deposits.

3 Conclusion

This study elucidates the synergistic effects of Ni loading and Ce, La and Zr promoters on the structure and dry reforming performance of Ni/MgO-MgAl₂O₄ catalysts. An optimal Ni loading of 12.5% maximizes CH₄ and CO₂ conversions, whereas excessive loading (15.0%) causes activity loss due to Ni agglomeration and pore structure degradation. 750 °C is identified as a key temperature for distinguishing catalytic performance. Although promoter modification does not significantly enhance low- to intermediate-temperature DRM activity, Ce, La and Zr markedly strengthen Ni-support interactions and interfacial stability, effectively suppressing Ni migration and sintering. Promoter incorporation increases the proportion of surface active oxygen species (O_p, ~60%–68%) and induces a positive shift in Ni 2p binding energy, thereby enhancing CO₂ adsorption/activation and modulating DRM reaction pathways. More importantly, Ce-, La- and Zr-modified catalysts exhibit substantially reduced carbon deposition, lower carbon graphitization, and inhibited Ni particle growth. After 20 h of reaction, Ni particle size increases by

only 1–3 nm, compared with >5 nm for the unmodified catalyst. Overall, promoter-induced regulation of metal-support interactions, oxygen species distribution, and interfacial electronic structure significantly improves the catalyst stability and coke resistance, providing a rational design strategy for durable Ni-based DRM catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Ni/MgO-MgAl₂O₄ 催化剂掺杂 Ce/La/Zr 对其催化剂结构与抗积炭性能影响机理研究

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摘 要: 干重整甲烷(DRM)作为同时转化 CH₄ 与 CO₂ 的关键技术, 为温室气体减排与合成气制备提供了重要途径, 但 Ni 基催化剂在高温条件下易发生烧结与积炭, 严重限制其长期稳定性。本研究以 MgO-MgAl₂O₄ 复合载体为基础, 调控 Ni 负载量并分别引入 Ce、La、Zr 助剂, 考察其对 DRM 催化性能、结构稳定性及表面氧物种的影响。结果表明, 适中的 Ni 含量(12.5%)可获得较高的 CH₄ 与 CO₂ 转化率。助剂的引入在低温区间对催化活性存在一定抑制作用, 但通过改变载体局部结构序与金属-载体界面, 可以显著提高 NiO 的分散性并增加表面氧空位与活性氧(O_p)比例, 从而增强 CO₂ 的吸附-活化能力并有效抑制碳沉积。经 20 h DRM 稳定性测试后, Ce 修饰样品的 Ni 粒径增长最小(6.23→8.07 nm)且积炭最少, 表现出最佳的结构稳定性与抗积炭性能。研究揭示了 Ce、La、Zr 助剂通过界面电子结构调控与氧储放能力提升来增强 Ni 基催化剂抗烧结与抗积炭性的机理, 为构筑高稳定性 DRM 催化剂提供了可行的材料设计策略。

关键词: 干重整甲烷 (DRM); Ni 基催化剂; 助剂调控 (Ce、La、Zr); 氧空位; 抗积炭性能

中图分类号: TQ426

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