

Study on the mechanism of low-temperature CO₂ methanation catalyzed by LaNiO₃/CeO₂

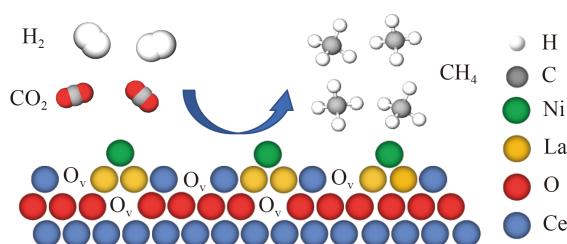
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Abstract: Perovskite-type catalysts have exhibited significant potential for CO₂ methanation. However, their efficacy at low temperatures and the underlying catalytic mechanisms remain inadequately understood. In this study, a perovskite catalyst LaNiO₃/CeO₂ was successfully constructed *via* the sol-gel method combined with an impregnation process. By comparing the physicochemical properties and catalytic activity of LaNiO₃, LaCeNiO₄, Ni/CeO₂ and La-Ni/CeO₂ catalysts, the underlying mechanism for the low-temperature CO₂ methanation catalyzed by LaNiO₃/CeO₂ was elucidated. During reduction, the LaNiO₃ perovskite structure *in situ* decomposed to generate highly dispersed and small-sized Ni⁰ particles with an average diameter of 12.6 nm. The CeO₂ support provided abundant oxygen vacancies (Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio of 9.2%) as well as weak and moderate basic sites, synergistically promoting CO₂ adsorption and activation. The interaction between the active phase and the CeO₂ support further stabilized the dispersion of Ni⁰ and optimized the surface basicity and oxygen vacancy concentration. Under catalytic conditions at 200–300 °C, LaNiO₃/CeO₂ exhibited nearly 100% selectivity toward CH₄, while CO₂ conversion increased monotonically to 23.6%. This study clarified the crucial role of the perovskite pre-structuration and *in situ* reduction strategy in regulating the dispersion of active metals and the catalyst structure, laying a theoretical foundation for the design of catalysts for low-temperature CO₂ methanation.

Key words: carbon dioxide hydrogenation; low-temperature methanation; Ni-based catalysts; perovskite-type oxide; CeO₂ support



Excessive carbon dioxide (CO₂) emissions have triggered severe environmental issues such as global warming and increased frequency of extreme weather events^[1–2]. It is urgently necessary to effectively curb the excessive CO₂ emissions and develop technologies for its resource utilization. CO₂ hydrogenation into methane (CH₄) is one of the key pathways for CO₂ resource utilization^[3]. Developing efficient catalysts is crucial to overcoming the kinetic limitations of the inert CO₂ methanation reaction. Ni-based catalysts demonstrate promising potential for CO₂ methanation due to their favorable catalytic performance and relatively low cost.

In practical applications for CO₂ methanation, Ni-based

catalysts commonly encounter issues such as agglomeration and sintering of Ni particles, which leads to catalyst deactivation. The incorporation of promoters (such as Ca^[4], Mg^[5], Ru^[6] and La^[7]) can optimize the metal dispersion, Ni-support interaction, and stability of Ni-based catalysts. Among them, La is an excellent promoter that can effectively improve the dispersion of Ni species, modify the electronic environment of Ni particles, and enhance the surface basicity of the catalyst, thereby facilitating the activation of CO₂. Garbarino et al.^[8] synthesized a La-doped Ni/ γ -Al₂O₃ catalyst, in which La notably improved the catalytic activity of Ni/ γ -Al₂O₃, while the catalyst maintained high selectivity toward CH₄ even at a reaction

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temperature of 400 °C. After H₂ reduction, this structure promoted the formation of Ni⁰ particles with smaller size and favorable dispersion, thereby enhancing the reaction efficiency. Notably, the perovskite-type oxide structure formed by La and Ni promoted the reaction, since it allowed Ni⁰ particles to attain smaller size and better dispersion after H₂ reduction^[9]. Alkhoori et al.^[10] reported that the LaNiRuO₃ perovskite-type catalyst achieved 67% CO₂ conversion and over 92% CH₄ selectivity in CO₂ methanation at 450 °C.

Selecting a suitable support is a key factor in enhancing the activity of Ni-based catalysts. CeO₂ is a basic oxide that can enhance CO₂ adsorption, thereby providing favorable conditions for CO₂ activation and exhibiting significant potential in CO₂ methanation^[11]. In addition, a strong electronic interaction between Ni and CeO₂ facilitates electron transfer from Ni to the CeO₂ 4f orbital, which promotes the reduction of Ce⁴⁺ to Ce³⁺ and forms non-stoichiometric CeO_{2-x} (0 ≤ x ≤ 0.5). This process generates abundant oxygen vacancies that are endowed with exceptional activity for activating CO₂^[12]. Consequently, CeO₂-supported Ni-based catalysts exhibit high CO₂ conversion and CH₄ selectivity in CO₂ methanation reactions. Perovskite-type oxides combined with CeO₂ supports, which possess excellent oxygen storage capacity, exhibit highly efficient methanation catalytic performance. Jon et al.^[13] synthesized a LaNiO₃/CeO₂ catalyst that demonstrated excellent catalytic activity. LaNiO₃ promoted the high dispersion of Ni nanoparticles and strong interfacial interactions, while the oxygen vacancies and surface basicity of CeO₂ further enhanced the activation efficiency of CO₂.

Although perovskite-type catalysts show significant potential for CO₂ methanation, current research has primarily focused on high-temperature reaction conditions, and the underlying mechanisms involving both the perovskite structure and the support in the methanation reaction remain to be further elucidated. Herein, a LaNiO₃/CeO₂ catalyst was prepared *via* the perovskite pre-structuration and *in situ* reduction strategy, with its low-temperature (≤300 °C) methanation activity as the focus. For comparison, four additional catalysts were also synthesized, namely LaNiO₃, LaCeNiO₄, Ni/CeO₂ and La-Ni/CeO₂. The perovskite structure, the Ni-La interaction, the CeO₂ support, and the active-component-support interaction were investigated *via* comparative activity evaluation and characterization. This work seeks to unravel their combined mechanistic contributions to the enhanced low-temperature methanation activity of LaNiO₃/CeO₂.

1 Experimental

1.1 Materials

All chemicals and reagents, including Ce(NO₃)₃·6H₂O (purity > 99.0%), La(NO₃)₃·6H₂O (purity > 99.0%), Ni(NO₃)₂·6H₂O (purity > 99.0%), citric acid (purity >

99.5%) and ethylene glycol (purity > 99.0%), were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd and used without further purification.

1.2 Preparation of catalysts

LaNiO₃ was synthesized as follows. 0.3680 g of La(NO₃)₃·6H₂O and 0.2477 g of Ni(NO₃)₂·6H₂O were dissolved in 40 mL of deionized water. To this solution, 0.3266 g of citric acid (CA) and 95 μL of ethylene glycol were added, corresponding to a molar ratio of ethylene glycol:CA:La:Ni = 2:2:1:1. The mixture was heated to 40 °C and vigorously stirred for 1 h. The temperature was then raised to 80 °C and maintained until the water was completely evaporated. The resulting gel was dried overnight in an oven at 80 °C. The dried gel was subsequently transferred to a muffle furnace and calcined at 200 °C for 1 h (heating rate: 5 °C/min), followed by further calcination at 650 °C for 2 h at the same heating rate.

LaCeNiO₄ was synthesized as follows. 0.3680 g of La(NO₃)₃·6H₂O, 0.2477 g of Ni(NO₃)₂·6H₂O and 0.3698 g of Ce(NO₃)₃·6H₂O were dissolved in 40 mL of deionized water. Then, 0.98 g of CA was added in a 2:1 molar ratio relative to the sum of metal cations. The solution was stirred and dried following the same procedure as described for LaNiO₃. The resulting gel was dried and then calcined in a muffle furnace: first at 200 °C for 1 h (heating rate 5 °C/min) and subsequently at 800 °C for 4 h using the same heating rate.

CeO₂ was synthesized as follows. A predetermined amount of Ce(NO₃)₃·6H₂O was placed in a crucible and transferred to a muffle furnace. The sample was then calcined at 450 °C for 2 h with a heating rate of 5 °C/min.

LaNiO₃/CeO₂ was synthesized *via* the following steps. The LaNiO₃ precursor solution was prepared as described above. Afterward, 0.5 g of CeO₂ was dispersed in 10 mL of deionized water *via* ultrasonication for a period of time. The LaNiO₃ precursor solution was then poured into this suspension. After stirring for 1 h, the mixture was evaporated to dryness at 80 °C to obtain a gel uniformly distributed over the CeO₂ support. The subsequent steps were identical to those used for the preparation of LaNiO₃.

Ni/CeO₂ was synthesized as follows. 0.1580 g of Ni(NO₃)₂·6H₂O was dissolved in 40 mL of deionized water. After complete dissolution, 0.5 g of CeO₂ was added to the solution. The mixture was stirred at 40 °C for 1 h, then the temperature was raised to 80 °C to evaporate the water to dryness. The obtained solid was dried overnight at 80 °C, followed by calcination at 600 °C for 4 h with a heating rate of 5 °C/min.

Ni-La/CeO₂ was synthesized as follows. 0.3680 g of La(NO₃)₃·6H₂O and 0.2477 g of Ni(NO₃)₂·6H₂O were dissolved in 40 mL of deionized water. Then, 0.5 g of CeO₂ was added to the solution, and the mixture was stirred at room temperature for 1 h. The subsequent drying and calcination conditions were identical to those employed in

the preparation of LaNiO₃.

1.3 Catalytic performance test

The CO₂ methanation activity of the catalysts was evaluated using a fixed-bed reactor operated at atmospheric pressure. The reactor tube had an inner diameter of 8 mm and a length of 450 mm. A precisely weighed amount of 0.1 g of catalyst was mixed with 0.2 g of quartz sand and loaded into the catalytic reactor tube. The catalyst bed was packed with a layer of quartz wool at both the top and bottom to secure its position. Subsequently, the reactor was heated to 600 °C under a continuous N₂ flow (50 mL/min). Upon reaching this temperature, the gas was switched to a mixture of 80% H₂ and 20% N₂ flowing at 35 mL/min for catalyst reduction, which lasted for 1 h. After reduction, the gas was switched back to N₂ and the reactor was cooled to the desired reaction temperature (200–300 °C). The reaction was then initiated by introducing the feed gas mixture (H₂/CO₂/N₂ = 72:18:10) at a gas hourly space velocity (GHSV) of 20000 mL/(g·h). The reaction products were analyzed online at 15 min intervals using a Fuli F80 gas chromatograph equipped with a thermal conductivity detector (GC-TCD). Ar served as the carrier gas and N₂ was used as the internal standard. The volumetric percentages and flow rates of each component in the feed and outlet gases were determined by applying the internal standard method. To ensure data reliability, the test results for each catalyst were verified through repeated experiments. In each run, after the reactor reached the set temperature and the feed gas was introduced, the system was allowed to stabilize for 3 h. The average value calculated from multiple data points collected during this stable period was taken as the final test result. The performance of the catalysts was evaluated based on CO₂ conversion (%), CH₄ selectivity s_{CH_4} (%), CH₄ yield y_{CH_4} (%), CO selectivity s_{CO} (%) and CO yield y_{CO} (%).

$$x_{CO_2} = \frac{F_{CO_2 in} - F_{CO_2 out}}{F_{CO_2 in}} \times 100\% \quad (1)$$

$$s_{CH_4} = \frac{F_{CH_4 out}}{F_{CH_4 out} + F_{CO out}} \times 100\% \quad (2)$$

$$s_{CO} = \frac{F_{CO out}}{F_{CH_4 out} + F_{CO out}} \times 100\% \quad (3)$$

$$y_{CH_4} = x_{CO_2} \times s_{CH_4} \quad (4)$$

$$y_{CO} = x_{CO_2} \times s_{CO} \quad (5)$$

where F denotes the gas flow rate of the feed gas and outlet gas, with the unit of mL/min.

1.4 Catalyst characterization

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$

radiation ($\lambda = 0.15406$ nm), between 5°–90° at a scanning speed of 5(°)/min.

H₂ temperature programmed reduction (H₂-TPR) was conducted on an AutoChemII 2920 chemisorption instrument. 60 mg of the catalyst (40–60 mesh) was loaded into a quartz tube and held in place with quartz wool plugs at both ends. The sample was purged with N₂ at 200 °C for 30 min and then cooled to room temperature under a N₂ flow before the test. The analysis was performed using a 10% H₂/Ar mixture at a flow rate of 30 mL/min. The temperature was ramped from room temperature to 700 °C at a rate of 10 °C/min and held at 700 °C for 2 min.

CO₂ temperature programmed desorption (CO₂-TPD) was conducted on an AutoChemII 2920 chemisorption instrument. The catalyst was first reduced in H₂ at a specified temperature for 1 h. The sample was swept with He (40 mL/min) while heating to 300 °C at 10 °C/min and holding for 1 h after reduction. Subsequently, the temperature was lowered to 50 °C. CO₂ was introduced and adsorbed for 1 h when the baseline stabilized. Physically adsorbed CO₂ was then removed by sweeping with He (40 mL/min) at 50 °C for 30 min. The desorption step was carried out under a He flow (50 mL/min) by heating from 50 to 800 °C at a rate of 10 °C/min. The desorbed CO₂ was monitored using a TCD, and the amount of CO₂ desorbed was quantified by calibration with a standard reference.

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo escalab 250Xi spectrometer equipped with a monochromatized Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV). All reduced samples were stored in sealed containers at room temperature to prevent oxidation before the test. All spectra were corrected by referring the binding energy of the C 1s neutral carbon peak at 284.8 eV to determine the binding energies.

The field emission transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analyses were performed on a JEOL JEM-F200 microscope operated at an accelerating voltage of 200 kV. The particle sizes of randomly selected NiO particles were measured using ImageJ software based on the TEM images.

Raman spectroscopy was performed on a Horiba Scientific LabRAM HR Evolution high-resolution spectrometer equipped with a 523 nm semiconductor laser excitation source.

2 Results and discussion

2.1 Phase composition and structure of the catalysts

The XRD patterns of the fresh LaNiO₃/CeO₂, LaNiO₃, LaCeNiO₄, Ni/CeO₂ and La-Ni/CeO₂ are presented in Figure 1(a). The XRD pattern of LaNiO₃/CeO₂ exhibited characteristic diffraction peaks corresponding to both LaNiO₃ (PDF#34-1028, $2\theta = 23.1^\circ, 32.8^\circ, 41.3^\circ, 47.4^\circ, 58.6^\circ, 68.8^\circ$ and 79.0°) and CeO₂ (PDF#34-0394, $2\theta = 28.5^\circ, 33.0^\circ, 47.4^\circ, 56.3^\circ, 59.0^\circ, 69.4^\circ, 76.7^\circ$ and 88.4°).

This confirmed the successful formation of the LaNiO₃ perovskite structure supported on CeO₂. LaCeNiO₄ belongs to a layered perovskite structure variant derived from La₂NiO₄, where La³⁺ is partially substituted by Ce³⁺. The difference in ionic radii between La³⁺ (1.03 Å) and Ce³⁺ (1.01 Å) induced lattice distortion and changes in interplanar spacing upon Ce incorporation^[14–15]. The main diffraction peaks observed for LaCeNiO₄ corresponded to La₂O₃ (PDF#71-5408) and NiO (PDF#47-1049), which showed a marked difference from the diffraction patterns of LaNiO₃/CeO₂. This indicated that LaCeNiO₄ was not formed during the preparation of LaNiO₃/CeO₂. This is because LaNiO₃ (ABO₃) and LaCeNiO₄ (A₂BO₄) belong to distinct crystal structures and follow different synthesis pathways. Research has shown that the formation of the LaCeNiO₄ phase generally required precise Ce doping and higher calcination temperatures, whereas the preparation conditions of LaNiO₃/CeO₂ (with CeO₂ serving as a pre-synthesized support and calcination at 650 °C) tended to favor the formation of the two phases (LaNiO₃ and CeO₂)^[15]. The XRD pattern of Ni/CeO₂ exhibited sharp diffraction peaks of CeO₂ alongside distinct NiO peaks at $2\theta = 37.2^\circ, 43.2^\circ, 62.8^\circ, 75.3^\circ$ and 79.3° . The XRD pattern of La-Ni/CeO₂ showed no characteristic peaks for LaNiO₃ or La₂O₃. Only diffraction peaks of CeO₂ and NiO were observed, indicating that Ni existed in the form of NiO. These results suggested that the formation of LaNiO₃ required the assistance of citric acid and ethylene glycol. The carboxyl groups (–COOH) of citric acid formed stable complexes with La³⁺ and Ni²⁺ ions, ensuring the homogeneous distribution of La and Ni. Meanwhile, the

hydroxyl groups (–OH) of ethylene glycol underwent an esterification reaction with the carboxyl groups of citric acid to link the metal ions to the citrate complexes, thereby guaranteeing uniform mixing of the metal ions and the formation of a stable structure^[16].

The XRD patterns of the reduced samples are presented in Figure 1(b) (reduction conditions: 600 °C, 80% H₂/20% N₂, 1 h). After reduction, the diffraction peaks of LaNiO₃ in LaNiO₃/CeO₂ disappeared, with the formation of La₂O₃ ($2\theta = 26.1^\circ, 27.7^\circ, 39.4^\circ$ and 46.0°), NiO and Ni⁰ (PDF#04-0850, $2\theta = 44.5^\circ$ and 51.7°). After reduction of LaCeNiO₄, diffraction peaks corresponding to La₂O₃ and Ni⁰ were observed. After reduction, the XRD pattern of the Ni/CeO₂ catalyst still showed diffraction peaks of CeO₂ and NiO, with partial reduction of NiO to Ni⁰. Similarly, reduction of La-Ni/CeO₂ led to the formation of Ni⁰, and the diffraction peaks of La₂O₃ were also observed.

The average crystallite sizes of NiO and Ni⁰ were calculated using the Debye-Scherrer equation, with the results presented in Table 1. The size relationship between NiO and Ni⁰ particles remained consistent in both the fresh and reduced samples. The Ni⁰ particle size of La-Ni/CeO₂ was significantly smaller than that of Ni/CeO₂ (15.2 vs. 35.1 nm). Similarly, the reduced LaNiO₃ perovskite displayed smaller Ni⁰ particles (13.9 nm). The Ni⁰ particle size was further reduced to 12.6 nm in LaNiO₃/CeO₂. These results demonstrated that the LaNiO₃ perovskite structure, the interaction between La and Ni, and the interaction between the active phase and the CeO₂ support were key factors promoting the dispersion of Ni species.

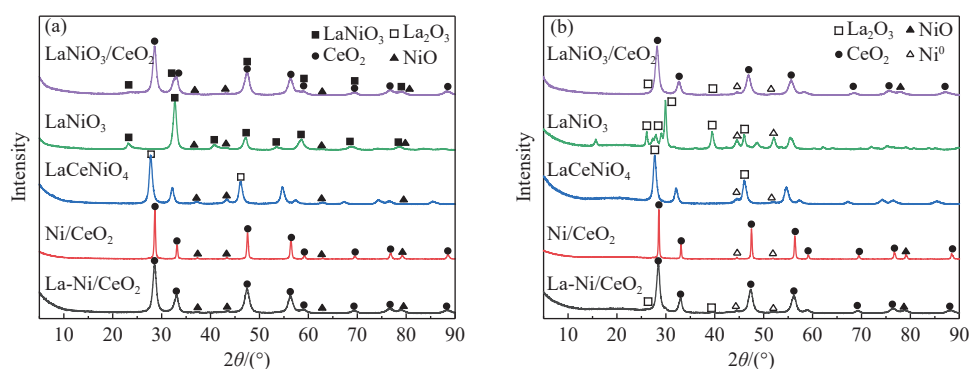


Fig. 1 XRD patterns of the fresh (a) and reduced (b) catalysts

Table 1 Physical and chemical properties of the catalysts

Catalyst	NiO crystallite size ^{a,b} /nm	Ni ⁰ crystallite size ^{a,c} /nm	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺) ^d /%
LaNiO ₃ /CeO ₂	10.9	12.6	9.2
LaNiO ₃	15.4	13.9	—
LaCeNiO ₄	11.5	15.5	9.9
Ni/CeO ₂	30.9	35.1	7.0
La-Ni/CeO ₂	11.5	15.2	7.3

^a: The crystallite size was estimated from the XRD patterns by using the Debye-Scherrer equation; ^b: Only determined for the fresh catalysts; ^c: Only determined for the reduced catalysts; ^d: Calculated by the fitted XPS spectra.

The synergistic effect of the aforementioned factors further endowed LaNiO₃/CeO₂ with smaller-sized and highly dispersed Ni⁰ particles. The TEM image of LaNiO₃/CeO₂ (Figure 2) further confirmed that the NiO particles possessed structural features of small size and high dispersion. The particle size distribution was concentrated in the range of 5–12 nm, with an average diameter of 8.55 nm. Meanwhile, EDX mapping revealed a homogeneous distribution of Ni, La and Ce elements across the catalyst region.

2.2 Reduction behavior of active species and distribution of surface basic sites

The reduction behavior of active species in the fresh catalysts was characterized by H₂-TPR. The reduction profiles and the corresponding hydrogen consumptions are shown in Figure 3(a) and Table 2, respectively. Both

LaNiO₃ and LaNiO₃/CeO₂ exhibited two reduction peaks in their H₂-TPR profiles. The low-temperature reduction peak at 350–400 °C was attributed to the destruction of the perovskite structure, where Ni³⁺ was reduced to Ni²⁺. The high-temperature reduction peak at 450–550 °C was ascribed to the reduction of Ni²⁺ to Ni⁰[17–18]. La-Ni/CeO₂ exhibited a prominent reduction peak in the range of 300–350 °C, which may be attributed to the predominant presence of Ni in the form of NiO rather than in a perovskite structure with La. The reduction peak is attributed to the direct reduction of Ni²⁺ to Ni⁰. The reduction peaks of Ni/CeO₂ at 280–310 and 310–340 °C were attributed to the reduction of oxygen species in the Ni–Ce–O solid solution. This solid solution was formed by the incorporation of Ni²⁺ into the CeO₂ lattice, which generated oxygen vacancies and created easily reducible oxygen species[19]. The reduction peak at 360–390 °C corresponded to the reduction of well-dispersed NiO species that exhibited strong interaction with the CeO₂ support[20].

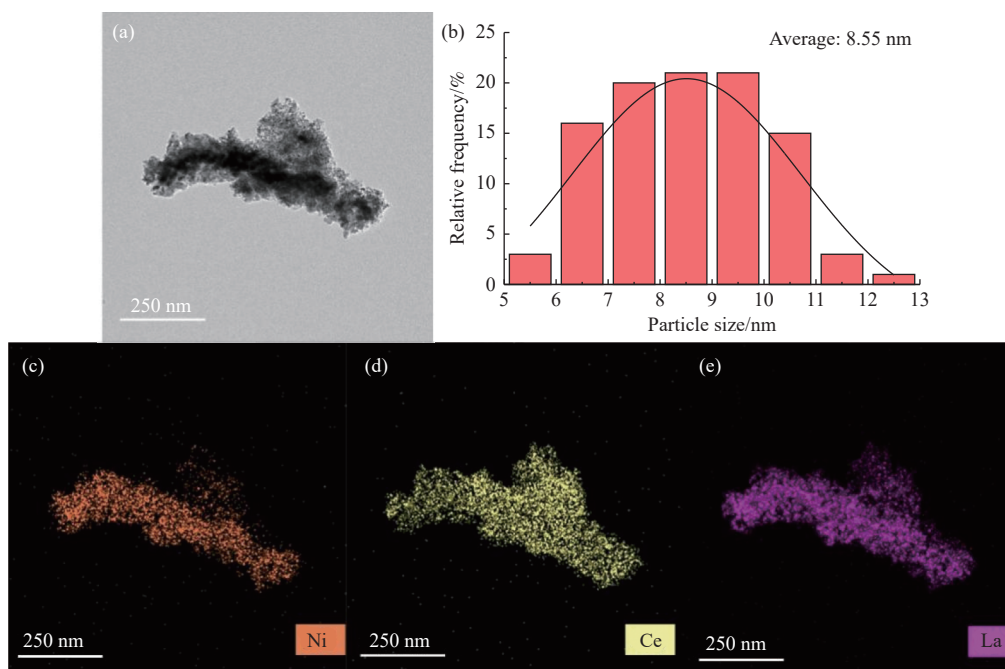


Fig. 2 TEM image of LaNiO₃/CeO₂ (a), the size distributions of NiO nanoparticles (b), as well as EDX images of Ni (c), Ce (d) and La (e)

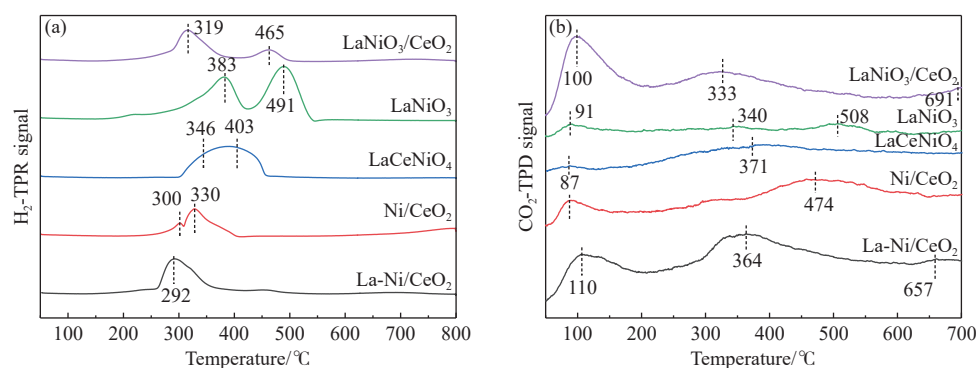


Fig. 3 H₂-TPR profiles (a) and CO₂-TPD profiles (b) of all the fresh catalysts

Table 2 H₂ consumptions for all the catalysts in TPR

Catalyst	Temperature at maximum/°C	Consumed H ₂ /(mmol·g ⁻¹)
LaNiO ₃ /CeO ₂	319	1.0491
	465	0.2862
LaNiO ₃	383	1.3274
	491	1.6957
LaCeNiO ₄	346	0.3467
	403	1.3872
Ni/CeO ₂	300	0.1430
	330	0.6659
La-Ni/CeO ₂	292	1.2542

LaCeNiO₄ exhibited a broad reduction peak in the range of 300–450 °C. The peak at 300–400 °C was ascribed to the reduction of surface NiO species, while the peak at 400–450 °C corresponded to the reduction of NiO species weakly interacting with the support^[21–22].

The surface basic sites of the fresh catalysts were determined by CO₂-TPD (Figure 3(b)), and the amount of CO₂ desorbed is presented in Table 3. The CO₂ adsorption capacity of the catalyst at low temperatures is directly governed by the strength and population of its surface basic sites, which furthermore play distinct roles in the reaction^[23–24]. CO₂ desorption peaks at 50–200 °C correspond to weak basic sites, which originate primarily from surface hydroxyl groups. Peaks at 200–400 °C are assigned to medium basic sites, whereas desorption peaks above 400 °C are attributed to strong basic sites, namely Lewis basic sites associated with anions^[25]. Weak and moderate basic sites improve CO₂ methanation performance, whereas strong basic sites show no promotional effect and can even suppress the hydrogenation reaction^[26]. LaNiO₃, LaNiO₃/CeO₂ and La-Ni/CeO₂ consisted of weak, moderate and strong basic sites; LaCeNiO₄ contained weak and moderate sites, and Ni/CeO₂ was composed of weak and strong basic sites. CO₂-TPD quantification revealed that LaNiO₃/CeO₂ exhibited considerably larger CO₂ uptake on its weak, moderate, and strong basic sites compared to LaNiO₃, while La-Ni/CeO₂ also showed higher adsorption on its weak and moderate sites relative to LaCeNiO₄. This improvement was largely because the CeO₂ support played a key role in enhancing the catalyst basicity^[27]. The higher CO₂ uptake observed on the weak and moderate basic sites of LaNiO₃/CeO₂ relative to La-Ni/CeO₂ further confirmed that the perovskite structure contributes to an improved basic property of the catalyst. Basic sites facilitated the adsorption and activation

of CO₂ at low and medium temperatures and are thus critical to improving catalytic activity^[28]. In contrast, Ni/CeO₂ showed inferior activity owing to its lack of weak and moderate basic sites and the resulting low CO₂ adsorption capacity. Nevertheless, the strength of basic sites on the catalyst did not exhibit a linear correlation with its catalytic performance. A comprehensive analysis that also considered properties such as oxygen vacancy concentration and dispersion of active sites was required to evaluate the catalytic activity, as discussed in Section 2.4.

2.3 Surface chemistry and oxygen defect density of the catalysts

The five catalysts were characterized by XPS, focusing on the Ni, La and Ce elements for surface composition and chemical state analysis. As shown in Figure 4(a), all four catalysts (LaNiO₃/CeO₂, LaNiO₃, LaCeNiO₄ and La-Ni/CeO₂) contained both La and Ni elements. However, the peaks of Ni 2p_{3/2} and La 3d_{3/2} overlapped, thus resulting in multiple split peaks. Two peaks with binding energies in the range of 848–850 and 855–857 eV corresponded to La 3d_{3/2}^[29]. The peaks located at 850–852 and 853–855 eV were assigned to Ni²⁺ in NiO and Ni³⁺ in LaNiO₃, respectively, while the satellite peak appearing at about 864 eV confirmed the coexistence of mixed Ni²⁺/Ni³⁺ valence states in the fresh catalysts. The binding energies of the corresponding peaks showed slight shifts, and their intensities varied across different catalysts. These differences could be attributed to variations in Ni dispersion and the metal-support interactions among Ni, La and Ce^[30]. Ni²⁺ peaks (854 eV) and Ni satellite peaks (860 eV) could be observed in the Ni 2p XPS spectrum of the Ni/CeO₂^[31].

 Table 3 The CO₂-TPD quantitative data of the catalysts

Catalyst	Basic sites/(mmol·g ⁻¹)		
	weak	moderate	strong
LaNiO ₃ /CeO ₂	0.38111	0.39340	0.18005
LaNiO ₃	0.03903	0.09144	0.02567
LaCeNiO ₄	0.00607	0.27197	—
Ni/CeO ₂	0.09759	—	0.32351
La-Ni/CeO ₂	0.28288	0.38255	0.38241

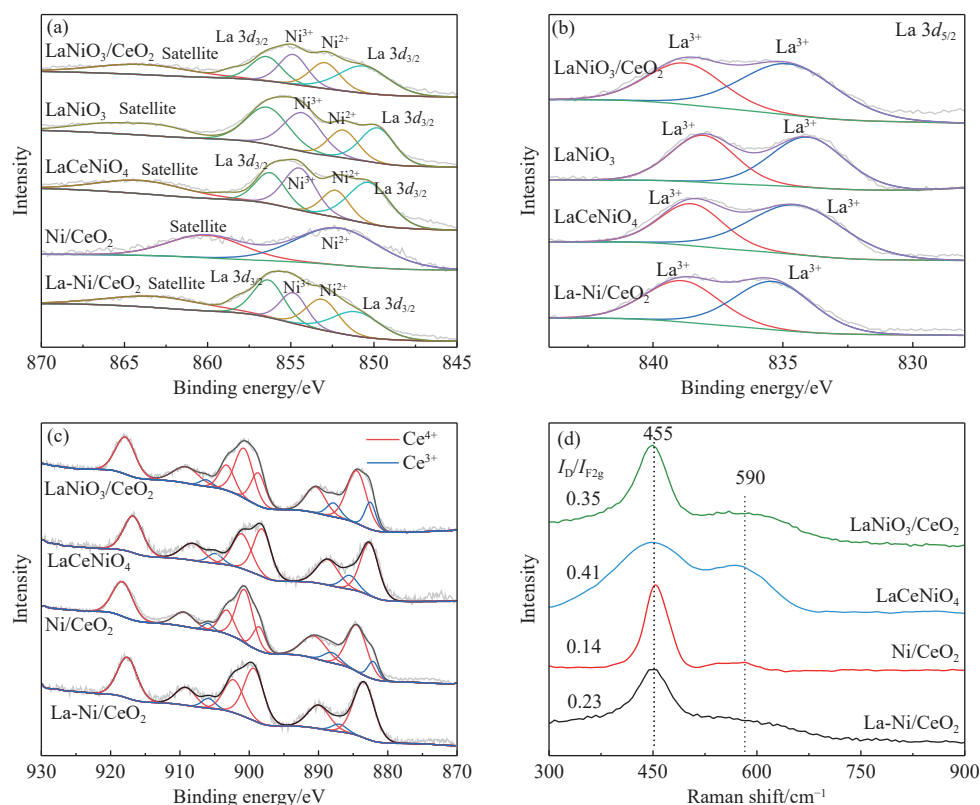


Fig. 4 XPS spectra (Ni 2p (a), La 3d_{5/2} (b), Ce 3d (c)) and Vis-Raman spectra (d) of fresh catalysts

Figure 4(b) shows the La 3d_{5/2} XPS spectra of the four catalysts. All four La-containing catalysts exhibited characteristic doublet peaks at approximately 835 and 837 eV binding energies, which were close to those of La₂O₃, indicating that La existed as stable La³⁺ in the four catalysts^[32]. Previous studies have indicated that La₂O₃ as a promoter can suppress the aggregation of Ni particles^[33]. This was corroborated by comparing the Ni particle sizes of Ni/CeO₂ with those of the other four catalysts (Table 1), clearly indicating that La₂O₃ effectively reduces the Ni particle size and improves its dispersion.

Figure 4(c) shows the Ce 3d spectra for all cerium-containing catalysts. The key advantage of CeO₂ lies in its ability to undergo reversible conversion between Ce⁴⁺ and Ce³⁺. This process is accompanied by the generation of oxygen vacancies. A higher proportion of Ce³⁺ indicates a greater concentration of oxygen vacancies in the catalysts^[34]. The ratios of Ce³⁺/(Ce³⁺+Ce⁴⁺) for the four catalysts are listed in Table 1.

The Raman spectra of the Ni/CeO₂, La-Ni/CeO₂, LaNiO₃/CeO₂ and LaCeNiO₄ are shown in Figure 4(d). All CeO₂-containing catalysts exhibited two vibrational bands at approximately 455 and 590 cm⁻¹, which were assigned to the F2g and defect-induced mode (D) of the cubic ceria fluoride phase, respectively^[35–36]. Oxygen vacancy concentrations in the CeO₂ phase could also be evaluated by the intensity ratio I_D/I_{F2g} , with a higher ratio indicating more abundant vacancies^[37–38]. The trend was consistent with the Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio derived from XPS.

Ni/CeO₂ showed the lowest conversion in the activity

tests (Section 2.4), which was attributed to its limited oxygen vacancies and poor CO₂ activation ability. The electronic interaction between the LaNiO₃ perovskite and the CeO₂ support in LaNiO₃/CeO₂ facilitated the reduction of Ce⁴⁺ to Ce³⁺, thereby increasing the number of oxygen vacancies (Ce³⁺/(Ce³⁺+Ce⁴⁺) = 9.2%). This high oxygen vacancy concentration enabled efficient adsorption and activation of CO₂ even at low temperatures (Section 2.4). Notably, catalytic performance was maximized only when oxygen vacancies worked in synergy with properly tuned active sites. This was exactly confirmed by LaCeNiO₄. Despite having the highest oxygen vacancy concentration, its conversion at 300 °C (16.5%) was lower than that of LaNiO₃/CeO₂ (Section 2.4). This inferior activity might be due to the low basicity (Table 3) and the lack of effective metal-support interaction in its perovskite-variant structure, which consequently failed to optimally regulate the dispersion and particle size of Ni⁰ active sites (Table 1).

2.4 Catalytic performance

The catalytic performance of the catalysts was investigated in the temperature range of 200–300 °C, as shown in Figure 5. A consistent increasing trend in CO₂ conversion was observed for each catalyst with increasing temperature. Ni/CeO₂ exhibited the lowest catalytic performance. The CO₂ conversion increased gradually from 3.4% at 200 °C to 8.6% at 300 °C, while the CH₄ selectivity remained around 80% within 200–275 °C and increased to 84% at 300 °C. The doping of La improved the catalytic

performance. For the La-Ni/CeO₂ catalyst, the CO₂ conversion increased progressively from 5.7% at 200 °C to 15.1% at 300 °C, while the CH₄ selectivity increased gradually from 87% at 200 °C to 91% at 300 °C. In contrast, the perovskite structure showed improved catalytic performance. For LaNiO₃, the CO₂ conversion increased gradually from 10.4% at 200 °C to 14.7% at 300 °C, while the CH₄ selectivity increased significantly from 200 to 275 °C and then stabilized at around 98% after 275 °C. LaCeNiO₄ exhibited a CO₂ conversion of 7.0% at 200 °C that increased progressively to 16.5% at 300 °C, with CH₄ selectivity consistently exceeding 98%. By combining the advantages of the perovskite structure and the CeO₂ support, LaNiO₃/CeO₂ exhibited significantly superior catalytic activity compared to the other four catalysts. Its CO₂ conversion increased progressively from 12.0% at 200 °C to 23.6% at 300 °C, while the CH₄ selectivity remained consistently close to 100%.

Based on the combined physicochemical characterization and catalytic activity evaluation results presented above, the mechanism of low-temperature CO₂ methanation over LaNiO₃/CeO₂ is schematically summarized in Figure 6.

First, the perovskite structure promoted the dispersion of active phase. As a promoter, La optimized the dispersion of Ni species in the catalyst while preventing the agglomeration of Ni⁰ particles. This effect was directly evidenced by the Ni⁰ crystallite sizes obtained from XRD (Table 1 and Figure 2), where LaNiO₃ and La-Ni/CeO₂

showed much smaller Ni⁰ particles than the La-free Ni/CeO₂. La played a key role in improving the dispersion of Ni species^[33], which consequently enabled La-Ni/CeO₂ to exhibit significantly higher CO₂ conversion and CH₄ selectivity than Ni/CeO₂. XRD characterization further revealed that the perovskite structure could generate more dispersed Ni⁰ particles after reduction, whereas La-Ni/CeO₂ showed poorer Ni dispersion because of the absence of the perovskite architecture. Therefore, LaNiO₃/CeO₂ achieved markedly higher CO₂ conversion and CH₄ selectivity than La-Ni/CeO₂, demonstrating that the perovskite structure was one of the core factors enabling high-performance, low-temperature CO₂ methanation.

Second, the type and population of basic sites on the catalyst were critical factors for CO₂ adsorption. The CO₂-TPD results (Table 3) showed that Ni/CeO₂ contained a comparatively large number of strong basic sites, owing to the lack of La modification and the absence of perovskite structure regulation. In contrast, LaCeNiO₄ mainly exhibited medium basic sites, which was attributed to the lattice distortion caused by Ce substitution. However, the desorption capacities of weak and medium basic sites over LaNiO₃/CeO₂ were significantly higher than those of the other catalysts. The CeO₂ support and perovskite structure synergistically optimize the distribution of basic sites^[39], which was crucial for the efficient activation of CO₂ over LaNiO₃/CeO₂ at low temperatures.

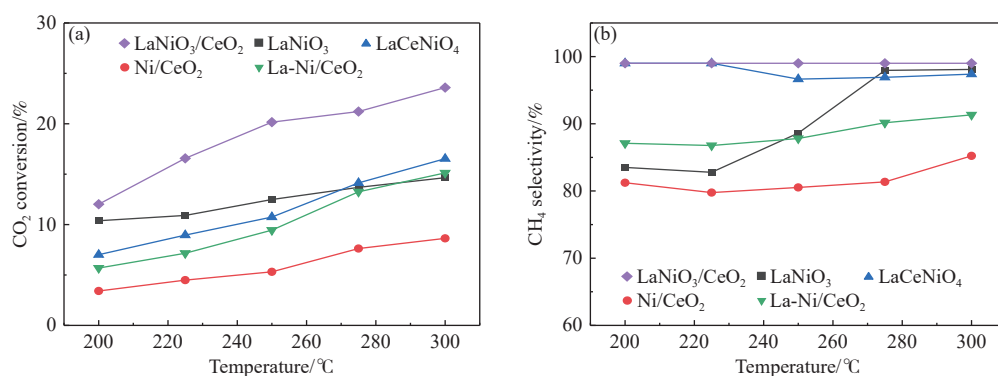


Fig. 5 Catalytic performance of all the catalysts: CO₂ conversion (a), CH₄ selectivity (b)

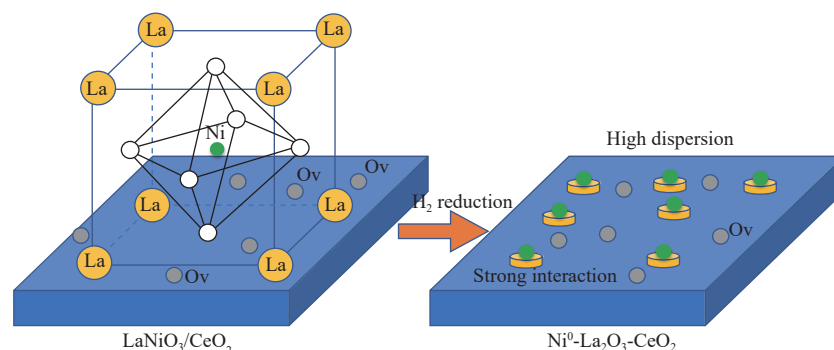


Fig. 6 Scheme of the mechanism of low-temperature CO₂ methanation catalyzed by LaNiO₃/CeO₂

Third, the oxygen vacancies in CeO₂ promoted CO₂ activation. Compared with the unsupported LaNiO₃, LaNiO₃/CeO₂ consistently exhibited higher CO₂ conversion, and its CH₄ selectivity remained close to 100%. In contrast, the CH₄ selectivity of LaNiO₃ was only 83.5% at 200 °C and stabilized at 98% by 275 °C. These results indicated that the oxygen vacancies provided by the CeO₂ support played a crucial role in enhancing the low-temperature methanation performance.

Finally, the interaction between the active phase and the support could further improve the performance of CO₂ methanation. A comparison between LaCeNiO₄ and LaNiO₃/CeO₂ showed that LaNiO₃/CeO₂ achieved a substantially higher CO₂ conversion. Although Raman and XPS results indicated that the Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio of LaCeNiO₄ (9.9%) was higher than that of LaNiO₃/CeO₂ (9.2%), LaCeNiO₄ exhibited a much weaker metal-support interaction. This demonstrated that when CeO₂ served as a support, it not only optimized the dispersion of Ni species but also, through interaction with Ni, promoted the reduction of Ce⁴⁺ and increased the oxygen vacancy concentration^[40]. In contrast, LaCeNiO₄ involved Ce substituting La sites, which only modified the perovskite lattice structure. These results confirmed that the active phase-support interaction was the key factor for enhancing catalytic performance.

3 Conclusion

In this study, the LaNiO₃/CeO₂ catalyst was prepared *via* a perovskite structure pre-structuration and *in situ* reduction strategy. Its low-temperature CO₂ methanation performance was investigated, and the underlying reaction mechanism was systematically explored by combining multiple characterizations, including XRD, TEM, XPS, H₂-TPR, CO₂-TPD and Raman spectroscopy. The main conclusions are as follows.

LaNiO₃/CeO₂ exhibited excellent catalytic activity at low temperatures, with CH₄ selectivity consistently approaching 100% and CO₂ conversion reaching 23.6% at 300 °C. After reduction, the LaNiO₃ perovskite yielded small-sized and highly dispersed Ni⁰ particles (average particle size: 12.6 nm), which provided abundant active sites for the reaction. The CeO₂ support not only significantly increased the number of basic sites on the catalyst surface, but also promoted the activation of CO₂ through its high concentration of oxygen vacancies (Ce³⁺/(Ce³⁺+Ce⁴⁺) = 9.2%, I_D/I_{F2g} = 0.35). The interactions among the active Ni species, La species and the CeO₂ support further enhanced the catalytic activity and additionally facilitated the generation of oxygen vacancies in CeO₂. The synergy of the above effects endowed the LaNiO₃/CeO₂ catalyst with outstanding performance for low-temperature CO₂ methanation. By systematically studying the physicochemical properties and catalytic activity of LaNiO₃/CeO₂, this work provides a theoretical reference for

the design and optimization of efficient catalysts for low-temperature CO₂ methanation.

Declaration of Competing Interest

The authors declare no conflict of interest.

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LaNiO₃/CeO₂ 催化 CO₂ 低温甲烷化的作用机制研究

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摘要: 钙钛矿型催化剂表现出优异的 CO₂ 甲烷化潜力, 然而其低温甲烷化性能及其催化作用机制尚不明晰。本工作通过溶胶-凝胶法结合浸渍法构建了钙钛矿型 LaNiO₃/CeO₂ 催化剂, 对比研究了 LaNiO₃、LaCeNiO₄、Ni/CeO₂ 和 La-Ni/CeO₂ 的物理化学性质与催化活性, 揭示了 LaNiO₃/CeO₂ 催化 CO₂ 低温甲烷化的作用机制。LaNiO₃ 钙钛矿结构在还原过程中原位分解生成高分散小尺寸 Ni⁰ 颗粒(平均粒径 12.6 nm); CeO₂ 载体提供丰富的氧空位 (Ce³⁺/(Ce³⁺+Ce⁴⁺) 比为 9.2%) 与弱/中碱性位点, 协同促进 CO₂ 吸附-活化; 活性相与 CeO₂ 载体相互作用进一步稳定 Ni⁰ 分散状态并优化表面碱性与氧空位。在 200–300 °C 催化条件下, LaNiO₃/CeO₂ 对 CH₄ 选择性始终接近 100%, CO₂ 转化率单调增加至 23.6%。本研究阐明了钙钛矿结构预置-原位还原策略对活性金属分散和催化剂结构调控的关键作用, 为 CO₂ 低温甲烷化催化剂设计奠定了理论基础。

关键词: CO₂ 加氢; 低温甲烷化; Ni 基催化剂; 钙钛矿型氧化物; CeO₂ 载体

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