

Article

Ni/CeO₂ Catalyst Prepared via Microimpinging Stream Reactor with High Catalytic Performance for CO₂ Dry Reforming Methane

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Abstract: Methane reforming with carbon dioxide (DRM) is one promising way to achieve carbon neutrality and convert methane to syngas for high-value chemical production. Catalyst development with better performance is the key to its potential large-scale industrial application due to its deactivation caused by carbon deposition and metal sintering. Hence, a Ni/CeO₂ catalyst (Ni/CeO₂-M) with higher CO₂ conversion and better stability is prepared, supported on CeO₂ precipitated via a novel microimpinging stream reactor. A series of ex-situ or in-situ characterizations, such as CO titration measurements, two-step transient surface reaction (two-step TSR), CO₂ and CH₄ temperature-programmed surface reaction (CO₂-TPSR and CH₄-TPSR), X-ray absorption fine structure (XAFS), and in-situ Raman spectroscopy study, were used to investigate its structure and mechanism. In contrast to Ni supported on commercial CeO₂ (Ni/CeO₂-C), the Ni/CeO₂-M catalyst with stronger lattice oxygen mobility and higher oxygen storage capacity enhances its CO₂ activation ability and carbon deposition. The Ni particle size of the Ni/CeO₂-M catalyst decreased, and a higher oxidation state was obtained due to the strong metal-support interaction. Besides the reaction performance improvement of the Ni/CeO₂-M catalyst, the novel microimpinging stream reactor could achieve catalyst continuous production with a high preparation efficiency. This work provides a novel method for the high-performance catalyst preparation for DRM reaction and its mechanism study gives a deep insight into high-performance catalyst development via bottom-up study.

Keywords: dry reforming of methane; oxygen vacancy; Ni/CeO₂ catalyst



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1. Introduction

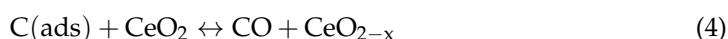
The high concentration of CO₂ and CH₄, which are identified as the world's most abundant greenhouse gases (GHG), have caused severe global climate change and ocean acidification [1]. The dry reforming of methane (DRM, Equation (1)) is regarded as one of the most promising routes to mitigate the environmental challenges associated with GHG emissions [2,3]. On one hand, DRM could utilize CO₂ and CH₄ to reduce GHG emissions. On the other hand, the syngas produced from DRM is the platform chemical for subsequent products via Fischer–Tropsch (FT) synthesis, methanol synthesis [4,5], et al.



Despite its considerable environmental potential, DRM is not an industrially mature process. The rapid deactivation of catalysts owing to carbon deposition and metal sintering hinders its potential large-scale industrial application [6–8]. Therefore, the catalysts' development with high performance is still a great challenge for their commercial and industrial

implementation. It is generally accepted that CO and H₂ are produced via two steps: (i) the C–H bond of CH₄ is directly dissociated to form surface carbon intermediates on metal active sites; (ii) the carbon intermediates are oxidized [9,10]. In the process, the oxygen vacancy in the catalyst could effectively assist the CO₂ activation and carbon intermediates removal via reversible redox cycling [11–13]. Furthermore, the metal particles tend to stabilize with oxygen vacancy to reduce the sintering [14]. Thus, developing a catalyst with abundant oxygen vacancies for better catalytic performance is a logical direction.

CeO₂ with high concentrations of oxygen vacancy has been extensively applied to the catalyst support for the dry reforming of methane [15–20] and Ni-based catalysts are a promising substitute for precious metal catalysts for DRM. The Ni supported on CeO₂ is believed to involve the steps shown in Equations (2)–(4) [21], where the oxygen vacancy involves activating CO₂, forming absorbed oxygen species, which could improve the elimination of coke deposition with the assistance of Ni species:



Thus, the increase in the concentration of oxygen vacancies over the Ni/CeO₂ catalyst could greatly enhance the catalytic performance. Previous studies have devoted a lot of efforts to the oxygen vacancy density increasing, such as modification of ceria with aliovalent cations [22–24], morphology control [25,26], and solid solutions [12,27], et al. However, most of the strategies are focused on mechanism studies over model catalysts without large-scale application potential. Thus, a simple method is still desired for preparing the high-performance Ni/CeO₂ catalyst with a higher density of oxygen vacancies at a large scale for the industrial DRM process.

The microimpinging stream reactor could significantly enhance the micromixing efficiency [28–30], easily controlling the crystallization process for the physical and chemical properties modification of the CeO₂ support. Hence, the Ni/CeO₂ catalyst (labeled as Ni/CeO₂-M) prepared supported on CeO₂ precipitated via a novel microimpinging stream reactor with higher CO₂ conversion and better stability is prepared in this work. A series of characterizations, including X-ray diffraction (XRD), transmission electron microscope (TEM), and CO titration measurements, are carried out for its structural investigation. The CO₂ and CH₄ temperature-programmed surface reaction (CO₂-TPSR and CH₄-TPSR), two-step transient surface reaction (two-step TSR), X-ray absorption fine structure (XAFS), and in-situ Raman spectroscopy study, are used to establish the “structure–catalytic performance–reaction mechanism” relationship. This work provides a novel method for high-performance catalyst preparation for DRM reaction and its mechanism study gives a deep insight into high-performance catalyst development via bottom-up study.

2. Results and Discussion

2.1. Structural Characterizations of the Ni/CeO₂ Catalysts

The structures of Ni/CeO₂ catalysts prepared by different methods are shown in Figure 1a and some structure characterizations of CeO₂ (CeO₂-M and CeO₂-C), including XRD and Raman, are shown in Figure S1. The main diffraction peaks at 2θ = 28.55, 33.08, 47.48, 56.33, 59.09, 69.40, 76.70, and 79.07°, corresponding to (111), (200), (220), (311), (222), (400), (331) and (420) crystal planes, clearly indicate the presence of cubic CeO₂ crystal phase (Joint Committee on Powder Diffraction File No. 34-0394). Besides the patterns of CeO₂ support, diffractions of NiO appear at 37.29° and 43.28° in the Ni/CeO₂ catalysts, indicating that Ni is successfully supported on the CeO₂ support. Compared to the Ni/CeO₂-C catalyst, the intensity of the CeO₂ diffraction peaks of the Ni/CeO₂-M catalyst is attenuated, indicating that the CeO₂ prepared via the microimpinging stream reactor tends to have a smaller particle size of the CeO₂ support and lattice disorder. Figure 1b shows the particle size of Ni/CeO₂-C and Ni/CeO₂-M catalysts calculated via

the Scherrer equation [31]. The average particle size of Ni/CeO₂-M catalysts is 109 nm, which is significantly smaller than that of Ni/CeO₂-C catalysts (210 nm). Furthermore, the BET specific surface areas of Ni/CeO₂-M catalysts are 112 m²/g, increasing 3.1-times more than that of Ni/CeO₂-C catalysts (36 m²/g), as shown in Table 1. The high surface area would contribute to the catalytic performance. Generally, the surface area would increase its active site and, consequently, lead to higher activity [32]. Previous researchers found that the high surface area would enhance the oxygen mobility and vacancies generation [33,34]. Compared with the commercial CeO₂ support, the microimpinging stream reactor provides a relatively uniform and rapid path for the formation of CeO₂ with a larger surface area due to its strong mixing efficiency and high mass transfer performance.

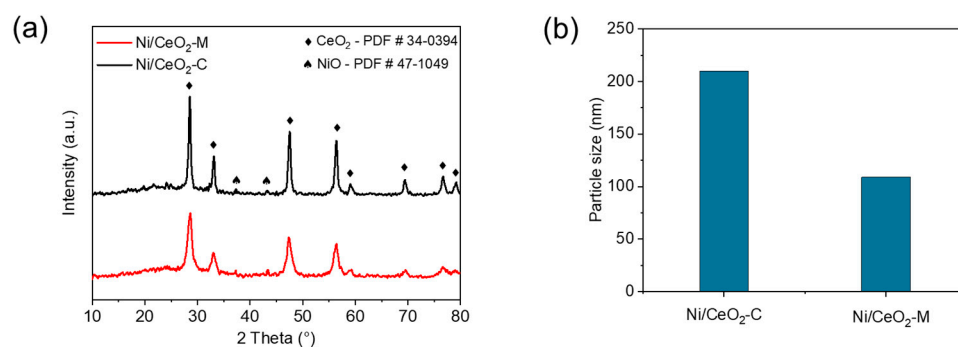


Figure 1. (a) XRD patterns and (b) particle size of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

Table 1. Characteristics of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

Catalysts	Ni Loading (wt%) ^a	S _{BET} (m ² /g) ^b	Ni Dispersion (D _{Ni}) (%) ^c	Ni Particle Size (d _{Ni}) (nm) ^d
Ni/CeO ₂ -C	4.96	36	4.8	19.7
Ni/CeO ₂ -M	4.92	112	8.9	11.3

^a Determined via ICP. ^b Determined via N₂ adsorption. ^{c,d} Determined via the CO chemisorption method.

The TEM and EDX characterizations of Ni/CeO₂-C and Ni/CeO₂-M catalysts are shown in Figure 2. From the TEM images, the Ni/CeO₂-M catalyst has a smaller grain size, whereas larger and aggregated particles were obtained in the reduced Ni/CeO₂-C catalyst. The higher dispersion of CeO₂ support would maximize the Ni-CeO₂ interface, which may benefit its reaction performance. From the EDX result, it is clear that the Ni species is more uniformly supported on the Ni/CeO₂-M catalyst than that of the Ni/CeO₂-C catalyst. In contrast with the large Ni particles over the commercial CeO₂, the particle size of the CeO₂ is remarkably smaller. Moreover, there are no particles > 15 nm found over the Ni/CeO₂-M catalyst, which agrees with the CO chemisorption result in Table 1. The highly dispersed Ni indicates a stronger metal–support interaction over the CeO₂ prepared via the microreactor synthesis method, and the increase in metal dispersion would provide more active sites for activation of CH₄ and CO₂, beneficial to the enhancement of a dry reforming reaction.

To further reveal the chemical and physical properties of the reduced catalysts, Raman spectroscopy study was performed, as shown in Figure 3. In the Raman spectra, the strength of the Raman peak near 460 cm^{−1} was attributed to that of the first-order F_{2g} peak in CeO₂. The OD peak near 570 cm^{−1} was associated with oxygen vacancies in CeO₂ [35,36]. The concentration of oxygen vacancies can be represented by the ratio of I_{OD}/I_{F2g} [37]. As shown in Figure 3a, the intensity of the D peak in the Ni/CeO₂-M catalyst is stronger and has a higher ratio (0.469) than that of the Ni/CeO₂-C catalyst (0.037), demonstrating that higher concentrations of oxygen vacancies can be obtained by the Ni/CeO₂-M catalyst. Furthermore, the presence of Ce³⁺ in the CeO₂ support can be proved by the peak shift of the F_{2g} peak. As shown in Figure 3b, the first-order F_{2g} peak in the Ni/CeO₂-M catalyst has lower Raman shifts, which is due to the lattice expansion and mode softening when

two Ce^{4+} ions ($0.970 \text{ \AA}$) are replaced by two Ce^{3+} ions (ionic radius $1.143 \text{ \AA}$) for oxygen vacancy generation [36,38]. The high concentration of oxygen vacancies in the Ni/CeO₂-M catalyst enables the interaction between Ni and CeO₂ to drive the metal dispersion via Ni-O_v-CeO_x [39], hindering Ni particle sintering, which is expected to improve the stability.

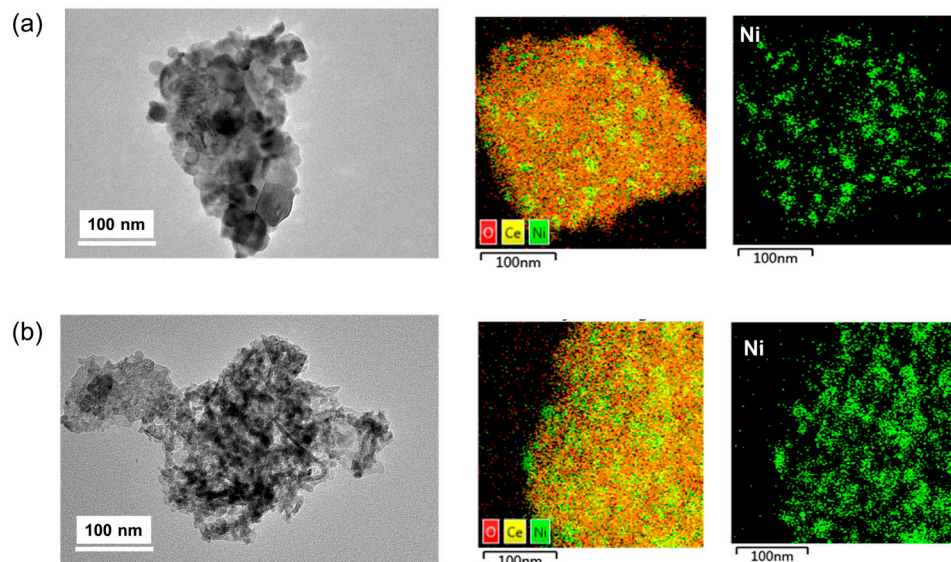


Figure 2. TEM and EDX images of (a) reduced Ni/CeO₂-C catalyst and (b) reduced Ni/CeO₂-M catalyst.

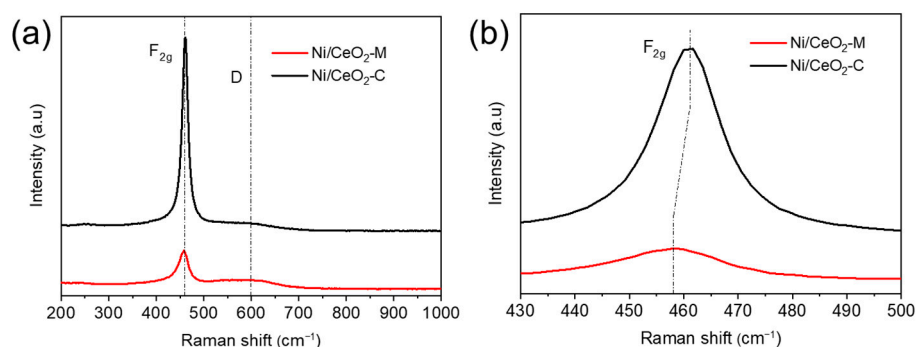


Figure 3. (a) Raman profile and (b) enlarged profile of reduced Ni/CeO₂-C and reduced Ni/CeO₂-M catalysts.

2.2. Reaction Performance

The catalytic performance in DRM of the as-prepared catalysts was evaluated at 800°C under a relatively high space velocity of $90,000 \text{ mL/g/h}$. In this work, the blank tube and pure CeO₂ support with different preparation methods were also tested, as shown in Figure S2. As shown in Figure 4a, the initial CO₂ conversion of the Ni/CeO₂-M catalyst is 14% higher than that of the Ni/CeO₂-C catalyst with higher CH₄ conversion of 23% and both of the catalysts could significantly improve their catalytic performance compared with blank tube and pure CeO₂ support. As is shown in Figure S3, the apparent activation energy (E_a) of Ni/CeO₂-C and Ni/CeO₂-M catalysts was measured at low CO₂ and CH₄ conversions (below 10%) to minimize the limitations of heat and mass transport. The lower apparent activation barriers for both CO₂ and CH₄ are obtained over the Ni/CeO₂-M catalyst, consistent with its higher DRM activity. The Ni species possesses the turnover frequency of CH₄ (TOF), $\sim 3.1 \text{ s}^{-1}$, for the DRM over the Ni/CeO₂-M catalyst. The catalytic performance based on TOF is compared with previously reported ceria catalysts in the literature for DRM (Table S1). The Ni/CeO₂-M catalyst exhibits a good DRM activity compared to the reported Ni-based catalysts. The better catalytic performance may be

attributed to the synergistic effect of the higher density of oxygen vacancies and dispersed Ni species on CeO₂; Ni species assist the lower dissociation temperature and surface oxygen species promote the conversion of CO₂.

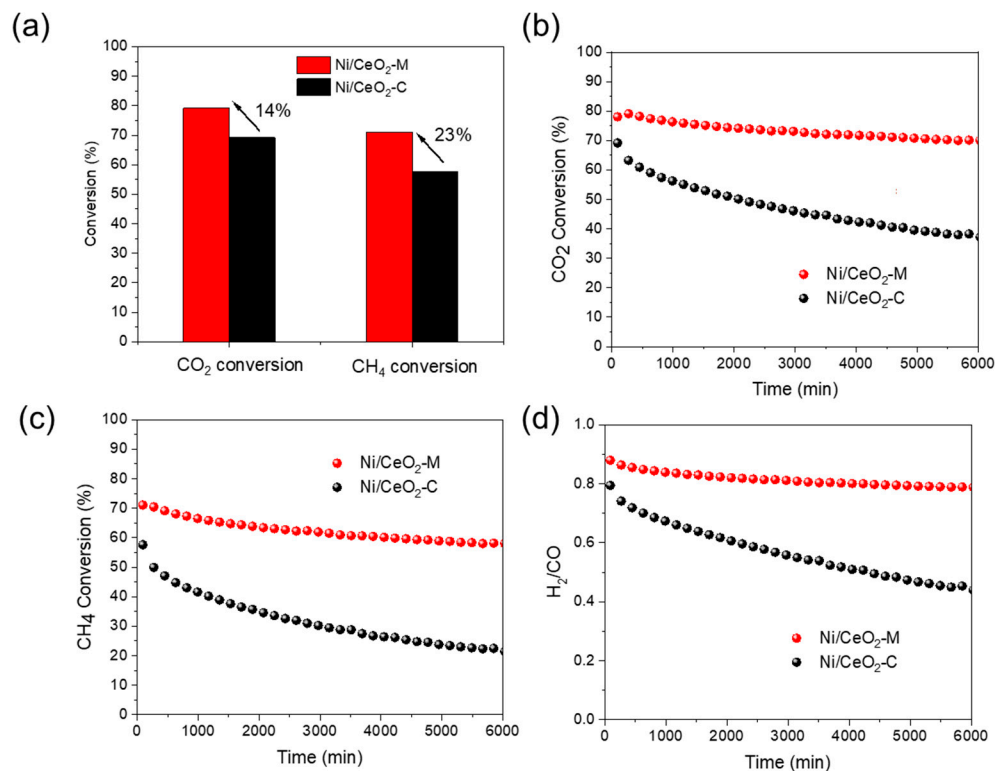


Figure 4. (a) Catalytic performance comparison; (b) CO₂ conversion during 50 h, (c) CH₄ conversion during 50 h, and (d) H₂/CO ratio during 50 h of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

The stability of the Ni/CeO₂-M catalyst is also excellent, as shown in Figure 4b,c. Under conditions of WHSV = 90,000 mL/g/h at 800 °C, it maintains 86% of CO₂ conversion and 90% of CH₄ conversion after 50 h. In comparison, the Ni/CeO₂-C catalyst loses more than 63% of its CO₂ conversion (from 58% to 21%) with the same trends of CH₄ conversion (from 69% to 37%) under the same reaction conditions. The better stability indicates that CeO₂ prepared via the microimpinging stream reactor could effectively hinder Ni sintering and coke deposition. It has been reported that the stronger interaction over Ni and oxygen vacancy could improve the Ni dispersion and the resistance to sintering under high reaction temperature [12,15,40]. Furthermore, the ratio of H₂/CO over the Ni/CeO₂-M catalyst is closer to 1, exceeding that of the Ni/CeO₂-C catalyst (Figure 4d), indicating the superior ability to suppress the reverse water–gas shift reaction (RWGS, CO₂ + H₂ ↔ CO + H₂O). Thus, the microimpinging stream reactor could prepare the Ni/CeO₂-M catalyst with higher conversion and stability with a higher ratio of H₂ to CO.

2.3. Mechanism Investigation

2.3.1. TGA and Raman Spectroscopy Characterizations

The amount of coke deposition in the spent catalysts after the stability test at 800 °C was measured using TGA–DTG (Figure 5a). A weight loss of approximately 3.2% is observed for the used Ni/CeO₂-C catalyst in a temperature range of 400–700 °C, with a DTG peak with the maximum weight loss rate [41], indicating the combustion of carbonaceous deposits on the catalyst. On the other hand, the spent Ni/CeO₂-M catalyst undergoes no obvious weight loss and no obvious DTG peak was observed. The difference in coke formation on the two catalysts is also confirmed via Raman spectra, as shown in Figure 5b. The vibrational peak centered at around 1345 cm^{−1} corresponds to the D band, and the G

band is at around 1580 cm^{-1} , respectively [42]. The D band and G band mainly contribute to the amorphous carbon and the well-graphitized and ordered carbon species, respectively. The greater intensity in both the D band and G band occur in the spent Ni/CeO₂-C catalyst, suggesting a higher amount of coke, which is consistent with the TGA–DTG results. Compared with the well-graphitized and ordered carbon species (G band), the amorphous carbon (D band) tends to be oxidized and removed easily by the oxygen species in the catalyst. A higher peak ratio of I_D/I_G (1.04) over the Ni/CeO₂-M catalyst demonstrates that the amorphous carbon over catalysts is dominant and it would easily be removed with the assistance of oxygen species. Thus, the Ni/CeO₂-M catalyst could significantly suppress the coke formation on the catalyst.

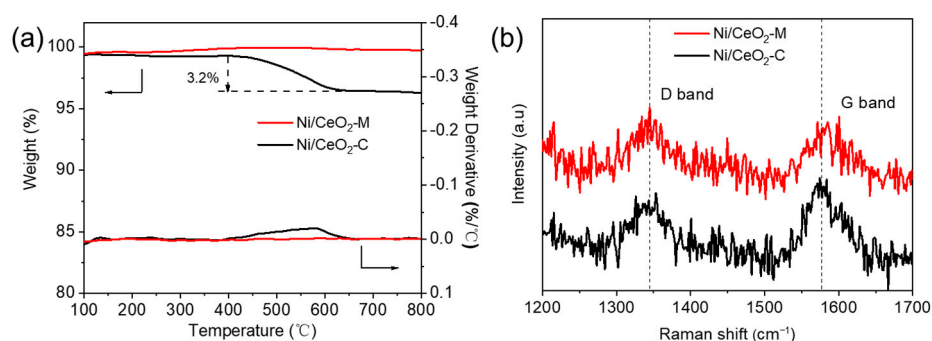


Figure 5. (a) TGA–DTG result and (b) Raman spectra of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

2.3.2. CO₂ and CH₄-TPSR Characterizations

The small amount of carbon deposits are mainly composed of active carbon species formed over the Ni/CeO₂-M catalysts. It has been reported that the active carbon intermediates from methane could be oxidized directly by the oxygen vacancies via a Mars–van Krevelen-type redox mechanism [43]. The CO₂-TPSR was carried out to investigate the density of oxygen vacancies via monitoring the concentration of CO ($\text{CO}_2 + \text{O}_{\text{vac}} \rightarrow \text{CO}$). From the profiles, as shown in Figure 6a, CO production starts at about 193 °C over the Ni/CeO₂-M catalyst. Compared with the higher temperature of CO₂ dissociation over the Ni/CeO₂-C catalyst at 450 °C, the lower temperature indicated that the abundant oxygen vacancy on the Ni/CeO₂-M catalyst accelerates the CO₂ activation ability. The same trend could be found over the CO₂-TPSR of CeO₂ in Figure S4a. Furthermore, the higher intensity of CO over Ni/CeO₂-M catalyst indicates a higher density of oxygen vacancies for CO₂ activation.

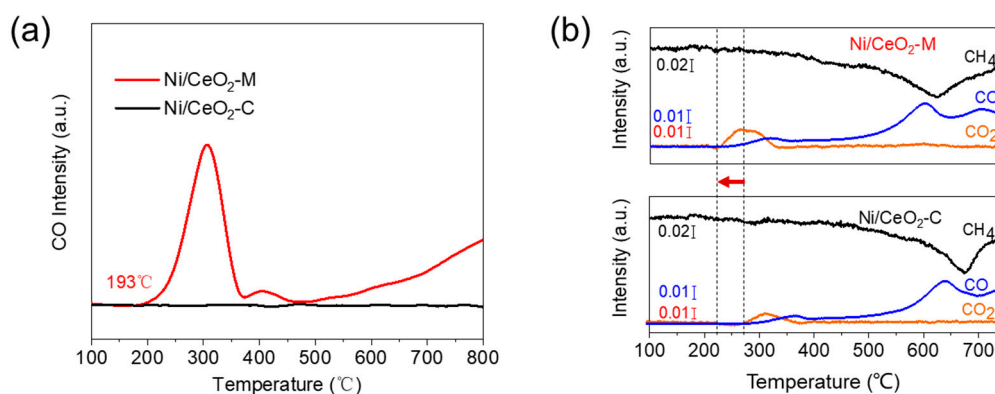


Figure 6. (a) CO₂-TPSR profile and (b) CH₄-TPSR profile of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

Then, the CH₄-TPSR experiments were employed to further investigate the coke deposition behaviors (Figure 6b and Figure S4b). During the process of CH₄-TPSR, several simultaneous processes occur, namely: (i) generation of carbon species on the catalyst

surface as a result of the methane decomposition and (ii) oxidation of these species to CO_2 , and then to CO due to the mobile oxygen in the lattice of CeO_2 [44]. The oxygen vacancies could assist the dissociation of C-H bonds and oxidation of carbon deposits. From Figure 6b, it is clear that the CO peaks of the $\text{Ni/CeO}_2\text{-M}$ catalyst shift to lower temperatures compared with the $\text{Ni/CeO}_2\text{-C}$ catalyst (255°C to 215°C), indicating that the high density of surface oxygen species in the $\text{Ni/CeO}_2\text{-M}$ catalyst is more active to the conversion of CH_4 to CO , which hinders the carbon deposition and increases its stability.

2.3.3. H_2 -TPR and XAFS Characterizations

A higher dispersion of Ni over CeO_2 prepared via the microimpinging stream reactor, confirmed via TEM and CO chemisorption, was observed. A stronger interaction between Ni and CeO_2 is expected to tune the Ni dispersion and electronic state. The H_2 -TPR profiles, indicating the interaction between metal and support, are shown in Figure 7a. Peaks between 150 and 300°C are attributed to a reduction in different Ni species: the peak between 150 and 220°C is assigned to the reduction in free surface NiO and the next peak, around $220\text{--}300^\circ\text{C}$, is assigned to the reduction in bulk NiO [45,46]. The reduction peak occurring at a higher temperature usually means that it is hard to reduce with stronger metal–support interactions [47,48]. For the $\text{Ni/CeO}_2\text{-M}$ catalysts, stronger metal–support interactions are shown, which verified that the reduction in various Ni species occurred at a higher temperature, as shown in Figure 7a. The stronger interaction would benefit maintaining the Ni dispersion and hindering its agglomeration under 800°C .

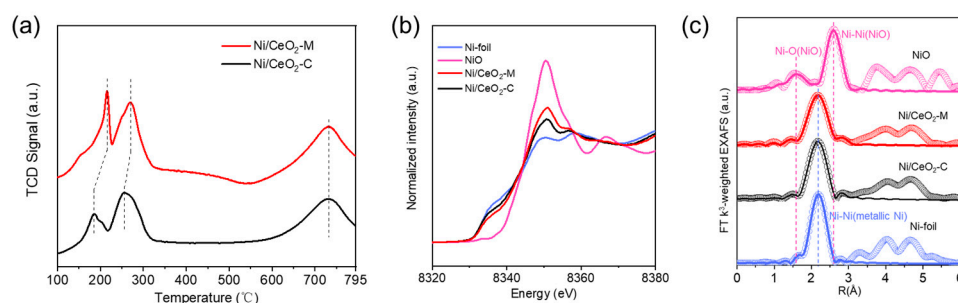


Figure 7. (a) TPR profile; (b) XANES and (c) EXAFS of spent $\text{Ni/CeO}_2\text{-C}$ and spent $\text{Ni/CeO}_2\text{-M}$ catalysts.

In addition to the H_2 -TPR experiment, the electronic state of the catalysts is also detected by X-ray absorption near the edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies of Ni K-edge with a near air-free method, shown in Figure 7b,c. The Ni K-edge XANES spectra over CeO_2 remains in a reduced state. However, a higher Ni^{2+} content is found over the $\text{Ni/CeO}_2\text{-M}$ catalysts at 64.0%, according to the results of linear combination fitting (LCF, Figure S5). The higher oxidation state of Ni ($\text{Ni}^{\delta+}$) originates from the electron transfer between Ni and CeO_2 support. The higher “white line” of the $\text{Ni/CeO}_2\text{-M}$ catalyst further hints a stronger interaction between the Ni and CeO_2 prepared by the microimpinging stream reactor. The Fourier transforms of k^3 -weighted Ni K extended X-ray absorption fine structure (EXAFS) signals of all the samples are shown in Figure 7c. For both fresh samples, the shapes of the Fourier transformed scattering resemble that of the Ni-Ni shell with some differences in the intensity of the backscattering peaks. The main backscattering peak around 2.2 Å corresponds to a Ni–Ni shell in Ni foil, while the peak around 1.7 Å corresponds to a Ni–O shell and the peak around 2.6 Å is assigned to a Ni-Ni shell in NiO [49]. Over the $\text{Ni/CeO}_2\text{-C}$ and $\text{Ni/CeO}_2\text{-M}$ catalysts, the main peak is aligned with the Ni-Ni shell of Ni foil, indicating the reduced state. The EXAFS has been fitted as shown in Figure 7c and the details are listed in Table 2. The coordination number (CN) of Ni-Ni in the $\text{Ni/CeO}_2\text{-M}$ catalysts (9.80 ± 0.30) is significantly smaller than that of the $\text{Ni/CeO}_2\text{-C}$ catalysts (11.40 ± 0.70). The faintish intensity of Ni-Ni over the $\text{Ni/CeO}_2\text{-M}$ catalysts suggests a smaller Ni particle size, respectively, and in the sample

of the Ni/CeO₂-M catalyst, the intensity of Ni-O and Ni-Ni (NiO) is stronger than that of the Ni/CeO₂-C catalyst, respectively. With the fitting results, the Ni/CeO₂-M catalyst has a larger coordination number of Ni-Ni (NiO) of 6.9. Combined with linear combination fitting, the higher oxidation state of Ni (Ni^{δ+}) over the Ni/CeO₂-M catalyst results from a stronger metal–support interaction [50], contributing to the Ni dispersion and hindering its agglomeration. The same trends could also be found over the Ni-ceria catalysts in the literature for DRM with X-ray Photoelectron Spectroscopy (XPS) characterization, where the peak area assigned oxygen vacancies and Ni^{δ+} is in a stronger intensity [51,52].

Table 2. Fitting details of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

Samples	Ni-Ni (Metallic Ni)		Ni-Ni (NiO)		Ni-O (NiO)	
	R (Å)	CN	R (Å)	CN	R (Å)	CN
Ni	2.49 ± 0.004	12.0	-	-	-	-
NiO	-	-	2.95 ± 0.03	12.0	2.09 ± 0.03	6.0
Ni/CeO ₂ -M	2.47 ± 0.01	9.80 ± 0.30	2.98 ± 0.002	6.90 ± 1.10	2.12 ± 0.01	4.90 ± 0.40
Ni/CeO ₂ -C	2.48 ± 0.001	11.40 ± 0.70	3.05 ± 0.07	0.30 ± 0.20	2.14 ± 0.04	2.20 ± 0.40

2.3.4. Two-Step TSR and In-Situ Raman Spectroscopy Characterizations

As is shown in Figure 8a, two-step TSR experiments were performed to evaluate the DRM reaction behaviors of the Ni/CeO₂-C and Ni/CeO₂-M catalysts at a reaction temperature of 800 °C [53,54]. After switching the gas from H₂/Ar to CH₄/Ar, CO is detected immediately for all reduced catalysts when the oxygen vacancies in the catalyst react with the carbon intermediates from CH₄ dissociation. The CO peak area of the Ni/CeO₂-M catalyst (0.76) is higher by 31% than that of the Ni/CeO₂-C catalyst (0.58), as shown in Figure 8b, agreeing with the abundant oxygen vacancies in the Ni/CeO₂-M catalyst. When the gas is switched to CO₂/Ar, more CO is generated as follows:



The amount of CO could be the descriptor for the CO₂ activation ability. It is clear that the Ni/CeO₂-M catalyst could produce more CO in Figure 8b. Therefore, the involvement of more surface oxygen species in the DRM reaction could be helpful to the activation of CO₂ and the elimination of the surface coke deposition.

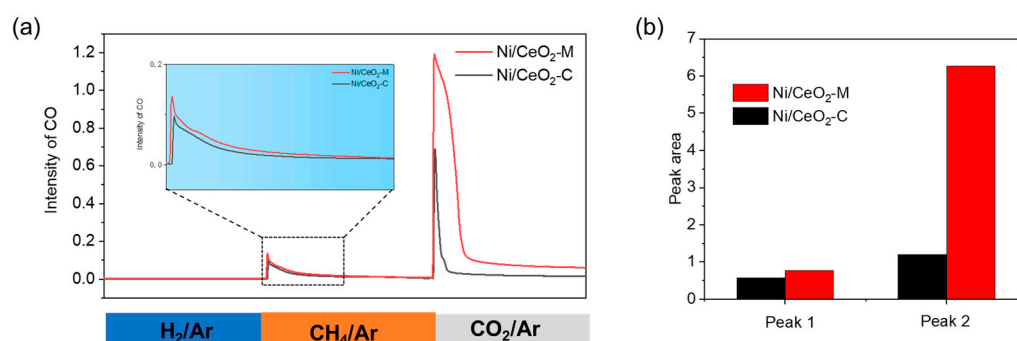
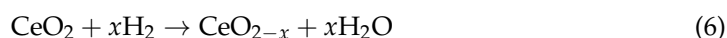


Figure 8. (a) Two-step TSR profile; (b) peak area of CO of Ni/CeO₂-C and Ni/CeO₂-M catalysts.

To further investigate the reaction mechanism in the catalysts and demonstrate the important roles the oxygen vacancies play in activating CO₂ and carbon deposition, in-situ Raman spectroscopy study was performed under different atmospheres, as shown in Figure 9. The peak near 460 cm^{−1} is assigned to CeO₂ F_{2g} mode, and another one near 600 cm^{−1} is attributed to the oxygen defects. As the results of in-situ Raman reveal, the

exposure to H_2/Ar causes a downshift in F_{2g} Raman band frequency over the $\text{Ni}/\text{CeO}_2\text{-M}$ catalyst (Figure 9a) as follows [55]:



However, there is no shift under H_2/Ar over the $\text{Ni}/\text{CeO}_2\text{-C}$ catalyst, which indicated that the $\text{Ni}/\text{CeO}_2\text{-M}$ catalyst generates more oxygen vacancies than the $\text{Ni}/\text{CeO}_2\text{-C}$ catalyst at the same temperature and atmosphere. When the gas is switched to CH_4/Ar , the T_{2g} Raman band tends to shift to high frequency, respectively. Furthermore, the D and G bands are generated simultaneously, indicating that the oxygen vacancies participate in the CH_4 dissociation over all of the catalysts. For the $\text{Ni}/\text{CeO}_2\text{-M}$ catalyst, the D and G bands quickly vanish when the CO_2 is introduced to the reactor and oxidize the carbon deposition. However, there are still obvious D and G bands over the $\text{Ni}/\text{CeO}_2\text{-C}$ catalyst, indicating a weaker carbon oxidation ability. Based on the results of two-step TSR and in-situ Raman spectroscopy study, more oxygen vacancies could be generated over the $\text{Ni}/\text{CeO}_2\text{-M}$ catalyst and more mobile oxygen could be transferred, leading to an enhancement in the activation of CO_2 and oxidation of surface coke.

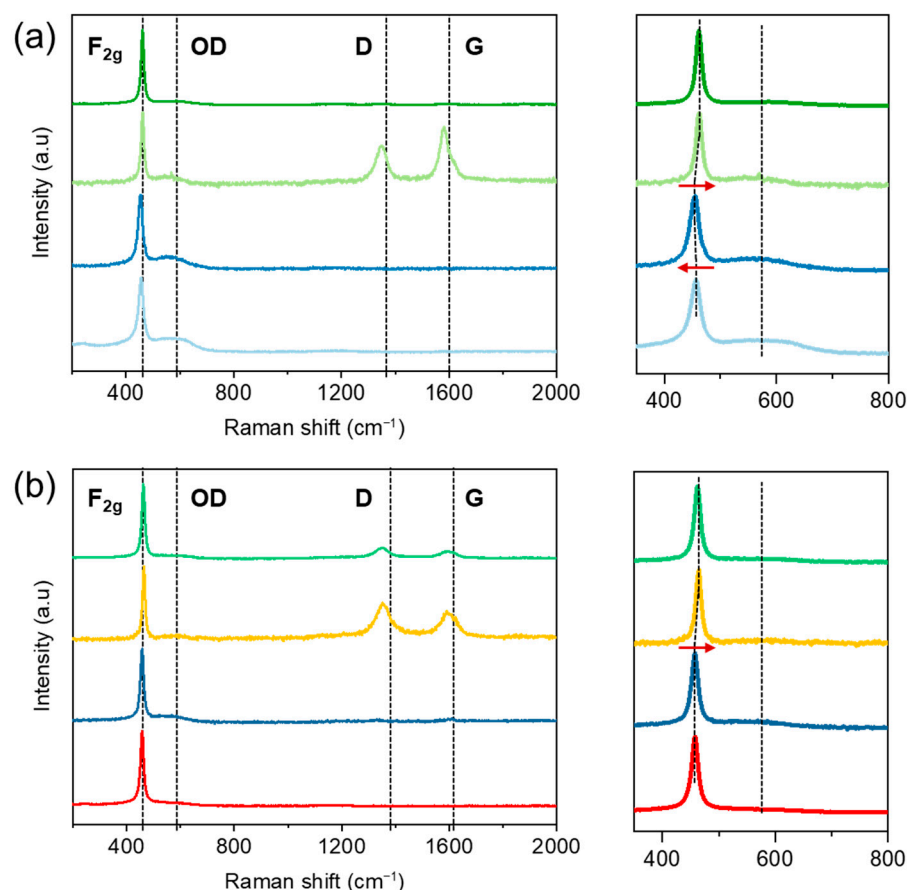


Figure 9. In-situ Raman spectroscopy study result of (a) $\text{Ni}/\text{CeO}_2\text{-M}$ catalysts, and (b) $\text{Ni}/\text{CeO}_2\text{-C}$ catalysts.

3. Experimental Section

3.1. Catalyst Preparation

The commercial CeO_2 support was supplied from Sigma. The improved CeO_2 support was prepared by co-precipitation continuous synthesis via a microimpinging stream reactor, as shown in Figure S6. The microimpinging stream reactor system is composed of two pumps (2PB, SZWEICO, Beijing, China) and a mini T-junction (SS-2MTF, XIONGCHUAN,

China). The materials of the reactor and tube were 316L stainless steel. The details of the system are shown in Figures S6 and S7 and listed in Table S2.

Typically, 0.01 mol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aladdin, Shanghai, China) was dissolved into 250 mL of ethyl alcohol as the precursor solution. Ammonia (28%, Beijing Chemical Plant, Beijing, China) was diluted with deionized water to 0.2 mol/L as the precipitating agent. Two solutions were pumped into the mini T-junction with a flow rate of 100 mL/min in which they could mix homogeneously and produce precipitation. The resultant precipitation was washed with 99.7% ethyl alcohol and centrifugated three times and dried at 100 °C for 12 h. The dried solid was calcined at 500 °C with a heating rate of 10 °C/min for 5 h under air.

The Ni/CeO₂-C and Ni/CeO₂-M were prepared by the impregnation method with 5 wt% of Ni. The CeO₂ support and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98%) were dissolved into ethyl alcohol and vigorously stirred at 80 °C until the ethyl alcohol was evaporated completely. The samples were dried at 100 °C for 12 h and calcined at 400 °C with a heating rate of 10 °C/min for 2 h under air.

3.2. Catalyst Characterization

The catalyst crystal structures were confirmed by an X-ray diffractometer (XRD) with a Cu K α X-ray source (D8 Advance, Bruker, Billerica, MA, USA). The range of scanning 2θ degrees was from 10° to 80° with a 2°/min scanning rate. The surface area measurements were analyzed via a N₂ adsorption instrument (ASAP 3020, Micromeritics, Norcross (Atlanta), GA, USA) with the BET analysis method. The samples were degassed under a vacuum at 300 °C for 6 h and the BET area was calculated with the region of P/P_0 between 0.05 and 0.35. The electron microscope (FEI Tecnai 30, FEI, Houston, TX, USA) equipped with energy-dispersive X-ray spectroscopy (EDX) was used for the morphology investigation of both reduced catalysts. X-ray absorption fine structure (XAFS) of the spent catalyst with a near air-free method as described in Supporting Information was carried out in the fluorescence mode at National Synchrotron Radiation Research Center (NSRRC). The XAFS was analyzed and fitted with the assistance of Artemis software [56]. The absorption edge (K edge) energy was selected at 8333 eV. The R range between 1 and 3 was used for the extended X-ray absorption fine structure (EXAFS) fitting with R-factor below 0.0009.

The H₂ temperature-programmed reduction (H₂-TPR) and CO chemisorption characterization were conducted using a chemisorption analyzer (AutoChem II 2920, Micromeritics, Norcross (Atlanta), GA, USA) with a thermal conductivity detector (TCD). For the H₂-TPR, 50 mg of samples was reduced in the 10% H₂/He at 50 mL/min. The temperature was set from 20 to 800 °C with a 10 °C min^{−1} heating rate. The CO chemisorption characterization was carried out as follows: 100 mg of sample was reduced in 10% H₂/He at 50 mL/min flow rate for 2 h at 800 °C. After Ar flow being purged for 10 min, 50 pulses of CO via a 50 μL gas loop were used to evaluate the metal dispersion. The turnover frequency (TOF), Ni dispersion (D_{Ni}), and Ni particle size (d_{Ni}) are calculated based on the values of CO chemisorption uptakes. The calculation formula is as follows:

$$\text{TOF} = \frac{F_{\text{reactant}}^{\text{in}} \times X_{\text{reactant}}}{C_{\text{CO}} \times m_{\text{catalyst}}} \quad (7)$$

$$D_{\text{Ni}} = \frac{C_{\text{CO}} \times M_{\text{Ni}}}{m_{\text{catalyst}} \times w_{\text{Ni}}} \quad (8)$$

$$d_{\text{Ni}} = \frac{6M_{\text{Ni}}}{\rho D_{\text{Ni}} N_{\text{a}} S_{\text{a}}} \quad (9)$$

where $F_{\text{reactant}}^{\text{in}}$ is the flow rate of reactant, mol/s; X_{reactant} is the conversion of the reactant, %; C_{CO} is the CO uptake value of each catalyst based on CO chemisorption, mol CO/g; m_{catalyst} is the weight of catalyst used, g; w_{Ni} is the Ni loading of catalyst, wt%, which is verified by inductively coupled plasma-atomic emission spectrometry (ICP-OES, PerkinElmer 8300,

PerkinElmer, Norwalk, CT, USA); M_{Ni} is the atomic weight of Ni, 58.69 g/mol; ρ is the Ni density, 8.902 g/cm³; N_a is the Avogadro's number, 6.02×10^{23} ; S_a is the area of each surface Ni atom, 6.5×10^{-20} m²/atom.

A Raman spectrometer (LabRam HR Evolution, Horiba, Paris, France) with a laser wavelength of 532 nm was used to characterize the structure of the coke on the spent catalysts. The thermogravimetric and differential thermal analysis (TGA/DTG, EVO2, Thermo, Waltham, MA, USA) was performed to evaluate the amount of coke deposited on the spent catalysts. The spent catalysts were firstly degassed with Ar at 200 °C for 30 min. Then the catalysts were heated from 30 to 800 °C at a 10 °C/min heating rate with flowing air.

3.3. Reaction Performance and Mechanism Studies

A continuous fixed-bed flow reactor was used to evaluate the activity of dry reforming of methane (DRM). The catalyst (40 mg, 40–60 mesh) was pretreated at a flow of 10 mL/min H₂ at 800 °C for 2 h. After being reduced, the gas flow was adjusted to the required reactants (CH₄:CO₂:N₂ = 15 mL/min:15 mL/min:30 mL/min) and the reaction temperature was raised to 800 °C for 50 h. The reactor outlet gases were analyzed online by the gas chromatograph (2010PLUS, Shimadzu, Kyoto, Japan) equipped with FID and TCD detectors. The conversions of CH₄ (X_{CH_4}) and CO₂ (X_{CO_2}) were calculated with the mole flow rate at the inlet and outlet of the reactor:

$$X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (10)$$

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \quad (11)$$

The ability to activate CH₄ was investigated by CO₂-assisted CH₄-TPSR. The catalyst was firstly reduced in a 10 mL/min H₂ flow at 800 °C for 2 h. After reduction, the catalyst was cooled down to 30 °C, and exposed to 10 mL/min CO₂ for 20 min. Then the sample was heated to 800 °C with a heating rate of 5 °C/min at a 25 mL/min 10% CH₄/Ar flow. The ability to activate CO₂ was evaluated by CO₂-TPSR. The catalyst was reduced consistent with the CH₄-TPSR. After being cooled to 30 °C, the reduced sample was heated to 750 °C with a 5 °C/min heating rate during the flow of 25 mL/min 20% CO₂/Ar. The production of CO₂-TPSR and CH₄-TPSR were detected by mass spectrometry.

The in-situ Raman spectroscopy study was carried out under reaction conditions. The reactor was equipped from Harrick Scientific Products Inc with different gases (H₂, CH₄, or CO₂). The spectra were obtained with an Argon laser (532 nm) excitation at 4 scans and 30 s acquisition time.

The two-step transient surface reaction (two-step TSR) was used to study the reaction mechanism as shown in Figure S8 [53,54]. The catalyst of 100 mg was firstly reduced in a 10 mL/min H₂ flow at 800 °C for 2 h. After purging with Ar flow for 10 min, CH₄/Ar was switched into the reactor. For 30 min, the gas was switched from CH₄/Ar to CO₂/Ar. The production was detected by an FTIR (Nexus 670, Thermo, Waltham, MA, USA) with a transmission cell.

4. Conclusions

A novel microimpinging stream reactor was used to prepare CeO₂-M support and the Ni/CeO₂-M catalyst could achieve higher CO₂ conversion and better stability compared with Ni supported on commercial CeO₂ for DRM. The improved conversion and stability of the Ni/CeO₂-M catalyst are attributed to the higher density of oxygen vacancies over CeO₂-M due to the better micromixing performance. CO₂ and CH₄ could be effectively activated with the assistance of oxygen vacancies and the carbon deposition could be oxidized to CO, avoiding carbon deposition. Furthermore, Ni could be stabilized and drove the dispersion via Ni-O_v-CeO_x, hindering Ni particles sintering. This work provides a

simple method for high-performance catalysts preparation for DRM and its mechanism study guides the design of new Ni with high stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12060606/s1>, Figure S1. (a) XRD patterns and (b) Raman profile of CeO₂-C and CeO₂-M catalysts. Figure S2. (a) CO₂ conversion during 50 h, (b) CH₄ conversion during 50 h, and (c) H₂/CO ratio during 50 h of the blank tube and pure CeO₂ support with different preparation methods. Figure S3. Apparent activation for: (a) CO₂ and (b) CH₄ of CeO₂-C and CeO₂-M catalysts. Table S1. Comparisons of TOF for typical Ni-based catalysts. Figure S4. (a) CO₂-TPSR profile; and (b) CH₄-TPSR profile of CeO₂-C and CeO₂-M. Figure S5. Linear combination fitting (LCF) of XANES spectra for the reduced catalysts. Figure S6. Scheme picture of microimpinging stream reactor system. Figure S7. Photo and structure of the mini T-junction. Table S2. Details of the microimpinging stream reactor system. Figure S8. Schematic diagram of two-step transient surface reaction. Figure S9. Diagrammatic sketch of the tube with values at the ends. Figure S10. (a) CO₂ conversion (b) CH₄ conversion, and (c) H₂/CO ratio of Ni/CeO₂-B and Ni/CeO₂-M catalysts. References [21,57–59] are cited in the Supplementary Material.

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