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Insight into Ca doping effects on Ni/Mg/Al hydrotalcite-derived catalysts for methane dry reforming: Performance and carbon deposition

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ABSTRACT

A series of Ca-modified Ni/Mg/Al hydrotalcite catalysts were prepared via a co-precipitation method. The catalytic stability tests of all catalysts were carried out in a fixed-bed reactor for 36h. Multiple characterization techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption-desorption (BET), H₂ temperature-programmed reduction (H₂-TPR) and thermogravimetry-differential thermal analysis (TG-DTA), were adopted to investigate the chemical structure, carbon deposition, and physical characteristics of the as-prepared catalysts. The HTC_a8 catalyst delivered CH₄ and CO₂ conversions of 88% and 91%, respectively, coupled with remarkable stability and anti-sintering performance. BET characterization results demonstrated that HTC_a8 possessed abundant mesoporous structures with favorable specific surface area and pore volume. In addition, TG-DTA analysis indicated that the HTC_a8 catalyst generated the minimum amount of coke deposits, which endowed it with superior anti-coking performance, and the formed carbon species were easily eliminated. In summary, the HTC_a8 catalyst exhibited the optimal

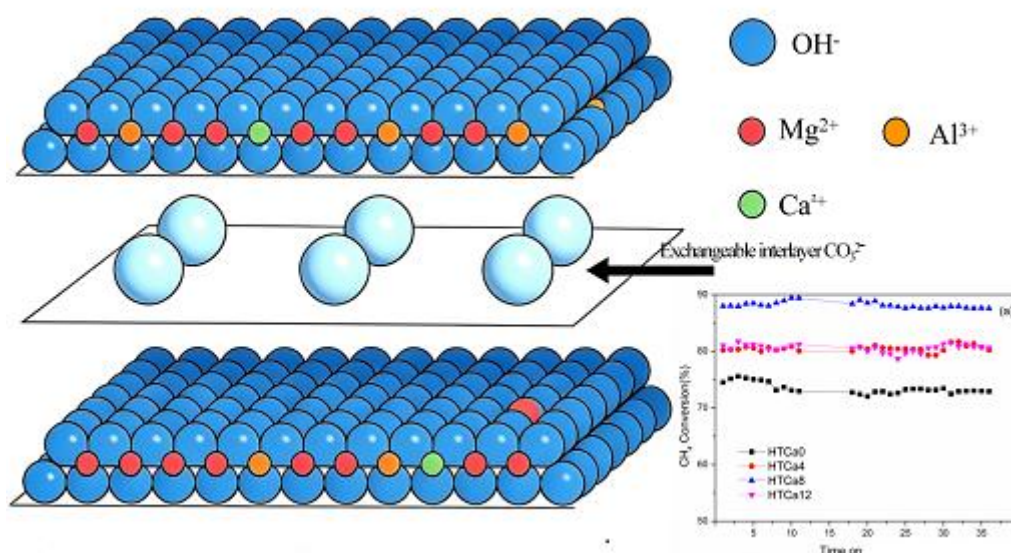
comprehensive catalytic performance among all the prepared samples.

Keywords: Dry reforming of methane; Hydrotalcite; Ni-based catalysts; Syngas; Ca

Highlights

- Ca promoted Ni/Mg/Al hydrotalcite-derived catalysts were obtained.
- The incorporation of Ca promoted the dispersion of Ni.
- The enhanced strong interaction between Ni and support.
- HTC_{Ca}8 exhibited high CH₄ conversion and superior stability.

Graphical Abstract

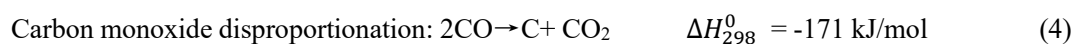
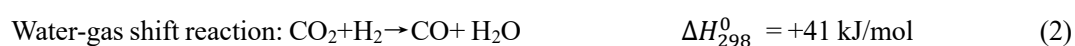


Introduction

The escalating accumulation of atmospheric greenhouse gases, predominantly carbon dioxide (CO₂) and methane (CH₄), constitutes one of the most pressing environmental challenges in recent years [1, 2]. Methane exhibits a global warming potential approximately 27 times greater than that of CO₂ over a 100-year period, with anthropogenic activities contributing nearly 30% of current temperature rise attributed to methane emissions [3]. In response to the Paris Agreement extensive

research has been directed toward technologies that simultaneously reduce emissions and generate valuable chemical feedstocks [4, 5].

Methane dry reforming (DRM) simultaneously converts two major greenhouse gases into high-value syngas consisting of hydrogen and carbon monoxide. The obtained syngas can be applied to multiple clean chemical manufacturing routes, including Fischer-Tropsch synthesis, methanol production and hydrogen generation. Given its dual advantages of greenhouse gas emission reduction and waste carbon resource recycling, DRM technology attracts growing research interest worldwide. The core chemical reactions occurring during DRM processes are displayed as follows [6, 7]:



However, CO_2 reforming consumes greenhouse gas feedstocks but faces two prominent drawbacks: excessive energy input and severe carbon deposition on catalyst surfaces [8, 9]. Current DRM catalyst systems are mainly divided into noble metal catalysts and non-noble metal catalysts. Noble metals including Pt, Ru and Rh possess outstanding catalytic activity and excellent anti-coking performance for DRM, but their exorbitant price and scarce natural reserves severely restrict large-scale industrial application [10]. Nickel-based catalysts have become the most mainstream active system for DRM research at present due to their low cost, strong methane activation capacity and catalytic activity close to noble metals [11-13]. However, Unfortunately, the relatively low Tammann temperature (581 °C) of nickel leads to severe particle migration and sintering catalysts

during long-term DRM tests [14,15]. Graphitic carbon deposition, resulting from Ni-promoted deep dehydrogenation of methane and CO disproportionation, is known to cover active sites and block pores [13,16]. Thus, designing Ni-based catalysts with improved sintering resistance and coke tolerance is essential for DRM commercialization. To overcome these deactivation pathways, researchers have devised a range of strategies, such as introducing basic oxide promoters, constructing bimetallic alloys, designing core-shell confinement architectures, and reinforcing metal-support interactions. [13,17,18].

Layered double hydroxides (LDHs) draw extensive research attention in recent years and serve as distinctive platforms for the fabrication of mixed metal oxide catalysts, owing to their special two-dimensional layered crystal structures. The general chemical formula of LDH materials is written as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ [19]. The hydrotalcite structure contributes to catalysis through several mechanisms [20-23]: (i) atomic-level cation dispersion in brucite-like layers ensures highly dispersed oxide nanoparticles after calcination with strong synergistic effects; (ii) the "memory effect" enables layered structure reconstruction upon rehydration, allowing re-dispersion of deactivated species and incorporation of functional anions; (iii) high surface area and basicity of LDH-derived mixed oxides facilitate CO₂ adsorption and provide abundant anchoring sites to suppress particle migration. Despite these benefits, LDH-derived Ni-based catalysts still suffer from gradual deactivation at high temperatures due to incomplete coke elimination and limited thermal stability of the mixed oxide matrix [24]. Numerous investigations have demonstrated that among these, the addition of alkaline earth metal promoters, has shown notable promise in enhancing catalyst stability [22]. Several promotional effects of Ca have been reported [13,20,25,26]: (i) CaO enhances CO₂ adsorption and activation through its basicity, promoting

carbon gasification via the reverse Boudouard reaction; (ii) Ca addition improves Ni dispersion by strengthening metal – support interactions; (iii) Ca can adsorb CO₂ competitively to inhibit oxidation and segregation of Ni-based active phases. Topaloğlu [20] recently compared Ni-impregnated Mg-Al and Ca-Al type hydrotalcite-derived catalysts, revealing that Ca-containing samples exhibited structural changes and CaCO₃ formation during DRM, though the coke amount was higher than on Mg-Al counterparts. However, the ionic radius of Ca²⁺ (100 pm) is larger than that of Mg²⁺ (72 pm) and Ni²⁺ (69 pm), making its substitution into the brucite-like layer challenging and potentially causing structural distortion [20]. Moreover, the optimal Ca/(Ni+Mg) ratio, the resulting effects on the textural properties, and the relationship between Ca content and coke resistance remain insufficiently understood.

In this work, we propose to synthesize a series of Ca-modified Ni-Mg-Al hydrotalcite-derived catalysts with varying Ca content via a one-step co-precipitation method. The effects of Ca substitution on the layered structure, textural properties, and reducibility were systematically investigated. The catalytic performance and coke resistance of the derived mixed oxides were evaluated in the DRM reaction at 750 °C. The relationships between Ca content, basicity, metal-support interaction, and carbon deposition behavior were established through comprehensive characterization. This study aims to provide a fundamental understanding of how Ca incorporation into the hydrotalcite framework influences the structural evolution and catalytic stability, offering a rational design strategy for high-performance DRM catalysts.

Experimental

Preparation of catalyst

A series of Ni/Mg/Al catalysts with varying Ca loadings (0, 4, 8, and 12 wt%) were synthesized via the co-precipitation method and denoted as HTC_a0, HTC_a4, HTC_a8, and HTC_a12, respectively. Appropriate amounts of Ni(NO₃)₂ • H₂O, Mg(NO₃)₂, Al(NO₃)₃, Ca(NO₃)₂ were weighed according to stoichiometric calculation and dissolved in 500 mL deionized water. A mixed precipitant containing KOH and Na₂CO₃ was prepared in another 500 mL deionized water to maintain the pH value around 10. The metal salt solution and precipitant solution were simultaneously added dropwise into a beaker under continuous stirring at 80 °C with constant pH kept at approximately 10 to complete precipitation reaction. The obtained precipitate was filtered and washed repeatedly three times to eliminate residual impurities. The filter cake was subsequently dried at 100 °C for 10 h until fully dehydrated. After drying, the solid precursor was calcined at 800 °C for 6h. The target catalysts were collected after natural cooling to ambient temperature.

Catalyst performance evaluation

An atmospheric-pressure tubular fixed-bed quartz reactor was utilized to assess the catalytic activity of as-prepared samples. Quartz wool was laid at the bottom of the quartz reaction tube with an inner diameter of 7 mm. A total of 0.10 g ground catalyst particles screened to 20-50 mesh was weighed and fully blended with 0.5 g quartz sand for thermal homogenization. The homogeneous mixture was loaded into the quartz tube, and quartz wool was stuffed at both sides of the catalyst bed to fix the packing position. The assembled quartz tube was subsequently installed inside the

fixed reaction apparatus for subsequent reforming tests.

Prior to the methane dry reforming reaction, the catalyst bed was reduced in a pure hydrogen stream with a volumetric flow rate of 50 mL/min. The furnace temperature was raised from ambient temperature to 750 °C and maintained at this setpoint for 1 h to complete in-situ reduction. A gaseous mixture of CO₂ and CH₄ with a molar ratio of 1:1 was then introduced into the reactor, and the continuous catalytic reaction lasted for 36h to carry out long-term stability measurement.

Gas effluents exiting the reactor were passed through a drying unit to remove vapor impurities before being delivered to an online gas chromatograph equipped with a thermal conductivity detector (TCD). The instantaneous concentrations of CH₄, CO₂, H₂ and CO were quantified in real time. The conversion rates of methane and carbon dioxide as well as the molar ratio of H₂ to CO were calculated based on the chromatographic data.

The formula for calculation is given below [27,28]:

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

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

$$R_{H_2/CO} = F_{H_2,out} / F_{CO,out}$$

X represents the conversion rate of the reactant.

F_{in} and F_{out} denote the inlet gas flow rate and outlet product gas flow rate, respectively.

R is defined as the hydrogen-to-carbon molar ratio.

Catalyst characterization

Nitrogen adsorption-desorption measurements were conducted to explore the specific surface area and pore structural properties of the synthesized catalysts using an ASAP2020 analyzer. Before analysis, all samples were pretreated under vacuum at 200 °C for 2 h to eliminate surface-adsorbed

water and adventitious impurities. When the heating procedure finished, the sample tubes naturally cooled down to ambient temperature and were subsequently purged with nitrogen gas. After the liquid nitrogen preparation and basic experimental parameters were set, the internal gas pipeline of the analyzer was thoroughly cleaned. The system pressure was evacuated to below 0.1 kPa, and the formal adsorption and desorption acquisition procedures started immediately afterward.

Crystalline phase compositions and structural features of the catalyst materials were identified via X-ray diffraction analysis. Diffraction data were acquired using a Rigaku SmartLab diffractometer with Cu K α monochromatic radiation at a wavelength of 0.15418 nm. The instrument operational parameters were fixed at a voltage of 40 kV and a current of 40 mA. The diffraction scanning range covered a 2θ interval from 10° to 80°, while the scanning rate and step size were maintained at 5 °/min and 0.02°, respectively.

Hydrogen temperature-programmed reduction (H₂-TPR) tests were performed on a TP-5079 (Tianjin Xianquan) instrument to evaluate the reducibility of the synthesized catalysts. All samples were first thermally treated at 200 °C for 30 min with a linear heating rate of 10 °C/min, which effectively removed surface adsorbed pollutants. After the pretreatment process completed, the feed gas was switched to 10% H₂/Ar (50 mL/min) mixed gas. The furnace temperature was linearly increased to 750 °C at a rate of 10 °C/min to record the hydrogen consumption profiles during catalyst reduction.

Thermogravimetric tests were performed on Rigaku TG-8120 thermo-weight analyzer to trace the mass variation of catalyst samples under programmed heating environments. This technique was applied to quantify the carbon deposition level of catalysts before and after catalytic reactions. All measurements proceeded under an air atmosphere with a maximum heating temperature of 800 °C.

Real-time mass loss signals were continuously recorded throughout the heating process to intuitively analyze the carbon deposition behavior and thermal stability of the catalysts.

Transmission electron microscopy (TEM) tests were carried out on a JEOL-JEM-2100F transmission electron microscope to characterize the microstructural morphology, metal dispersion and carbon deposition of the samples. All microscopic photographs were obtained at an accelerating voltage of 200 kV for comprehensive microstructural observation of the catalysts.

Results and Discussion

BET analysis of catalysts

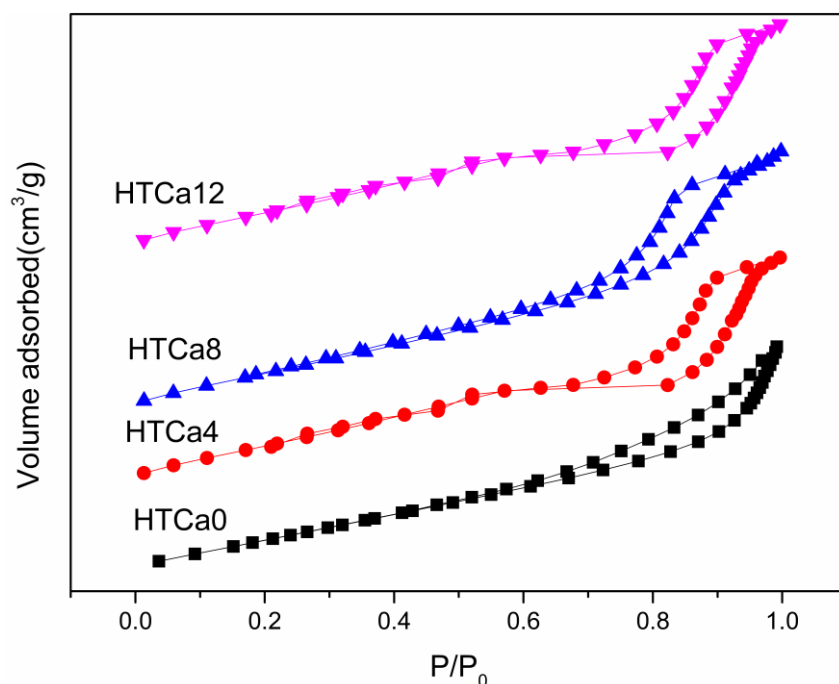


Fig. 1 N₂ physisorption adsorption-desorption isotherms of the calcined catalysts

The structural properties of the calcined catalysts with different Ca contents were obtained using N₂ adsorption-desorption analysis, and the results were summarized in Table 1. The BET specific surface areas of the samples were found to be in the range of 256.2-347.1 m²/g, with total pore volumes of 0.806-1.037 cm³/g and average pore diameters of 6.9-8.5 nm. It was observed that

the BET surface area increased with increasing modification content from HTC_a0 to HTC_a8, reaching a maximum value of 347.1 m²/g for HTC_a8, followed by a decrease to 303.0 m²/g for HTC_a12. This trend indicated that an appropriate amount of modifier was beneficial for enhancing the surface area, whereas excessive loading led to pore blockage or particle agglomeration, and the variation trend observed in this work is consistent with the findings reported by Świrk et al. regarding yttrium-modified Ni-based hydrotalcite-derived catalysts [29]. The N₂ adsorption-desorption isotherms of all samples exhibited a Type II pattern with an H₂-type hysteresis loop, it confirms the presence of mesoporous channels formed by the stacking of catalyst particles. The pore size distributions revealed that HTC_a8 possessed a broader distribution extending to larger mesopores, while HTC_a12 shifted toward smaller pores due to partial pore constriction caused by excess Ca. Based on these textural properties, HTC_a8, with the highest surface area and the most developed porosity, was expected to exhibit superior catalytic performance by providing better active metal dispersion and facilitating reactant diffusion [24].

Table 1 Structural properties of Ca-modified NiMgAl catalysts with varying Ca loadings

Catalysts	Specific surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Average pore diameter (nm)	Ni particle size (nm) ^a		Deposited carbon ^b (mg/g _{cat} ·h)
				reduced	spent	
HTC _a 0	256.2	0.840	7.3	9.2	10.9	1.271
HTC _a 4	338.9	0.893	7.5	9.7	12.3	1.039
HTC _a 8	347.1	1.037	8.5	7.2	7.9	0.813
HTC _a 12	303.0	0.806	6.9	13.6	19.3	1.263

^a Calculated using Scherrer formula.

^b Quantified by thermogravimetry.

XRD characterization of catalysts

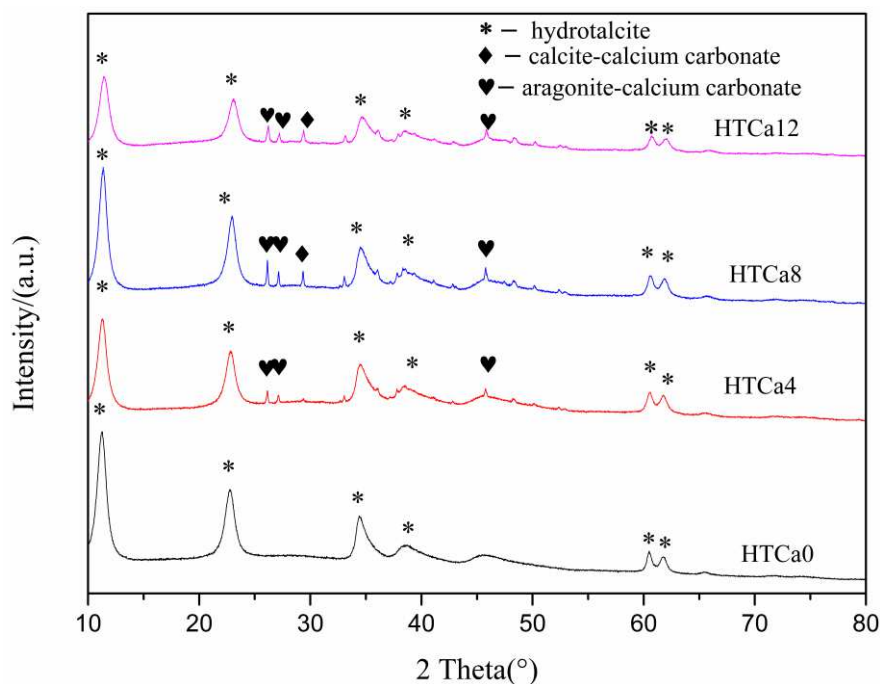


Fig. 2 XRD patterns of dried NiMgAl hydrotalcite-derived catalysts

Fig.2 showed the XRD patterns of the catalysts after drying. It can be observed that all of the catalysts exhibited diffraction lines characteristic of hydrotalcite phase at diffraction angles $2\theta=11.3^\circ, 22.9^\circ, 34.8^\circ, 38.74^\circ, 60.58^\circ, 61.78^\circ$. Simultaneously, with the increase of calcium doping amount, diffraction lines characteristic of hydrotalcite phase decreased in sequence. This probably indicated that increasing Ca loading resulted in a decrease of LDH crystallinity. Furthermore, diffraction peaks attributable to orthorhombic aragonite-type calcium carbonate were observed at 2θ values of $26.1^\circ, 27.3^\circ$, and 45.9° for the Ca-containing catalysts. With the increase of Ca loading, the diffraction peaks corresponding to trigonal calcite appeared at $2\theta=29.36^\circ$, which strongly suggested that calcium salts reacted with carbon-containing functional groups to form calcium carbonate. Finally, no obvious diffraction peaks of Ni were detected; this probably implied that some Ni atoms were embedded in the LDHs lattice.

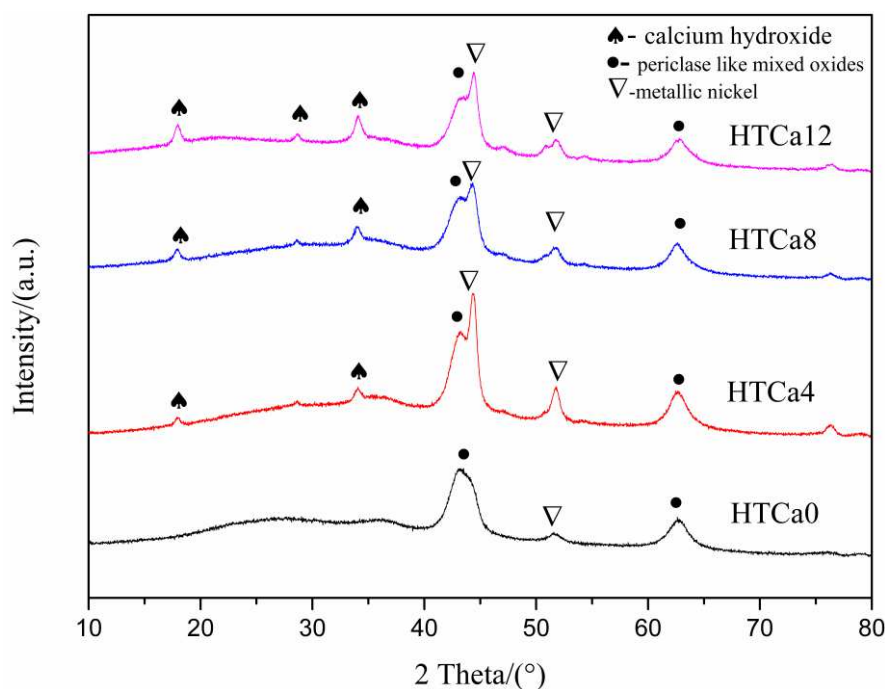


Fig. 3 XRD patterns of reduced catalysts

The XRD patterns of the reduced catalysts were shown in Fig.3. The LDH structure completely collapsed, and the characteristic diffraction peaks of calcium hydroxide appeared at $2\theta=18^\circ, 34.2^\circ$. The characteristic diffraction peaks of $\text{Mg}(\text{Al},\text{Ni})\text{O}$ periclase were observed at $2\theta=43.32^\circ, 62.94^\circ$ for all catalysts after reduction, which indicated that the mixed catalyst supports had been successfully prepared. Two new characteristic peaks at $2\theta=44.5^\circ$ and 51.8° corresponding to metallic Ni emerged, proving that nickel-containing hydrotalcite had been partially reduced into metallic nickel nanoparticles. The average Ni crystallite size was calculated via the Scherrer equation using the peak at 51.8° . Moderate Ca doping (HTCa8) achieved the smallest Ni grain size of 7.2 nm with highly dispersed Ni species. The Ni crystallite size of the unmodified catalyst was 9.2 nm, while the 12 wt% Ca-doped sample possessed the largest Ni crystallite size of 13.6 nm, indicating that excessive Ca doping induced severe agglomeration of Ni crystallites.

H₂-TPR experiments

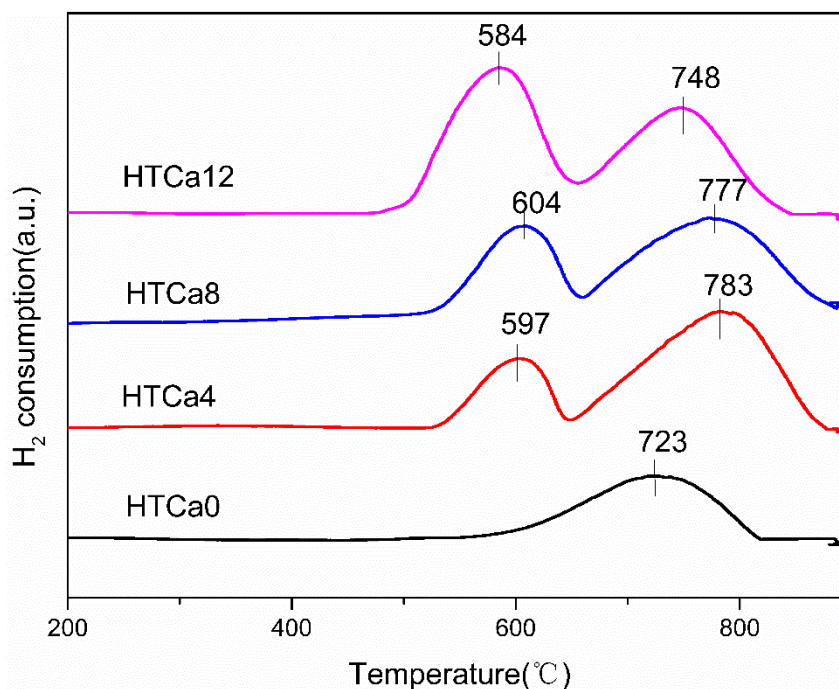


Fig. 4 H₂-TPR profiles of catalysts

Fig. 4 shows the H₂-TPR hydrogen consumption curves of HTCa catalysts. For the undoped HTCa0 catalyst, only a single reduction peak at 723 °C was observed in the H₂-TPR profile, which is attributed to the reduction of NiO species with a relatively strong metal–support interaction [22]. Upon Ca doping, two distinct reduction peaks emerged for the Ca-containing catalysts. The lower-temperature peak is assignable to metal oxide species that interact weakly with the support, whereas the higher-temperature peak corresponds to those with strong metal–support interaction. For HTCa4, the medium-temperature and high-temperature reduction peaks were located at 597 °C and 783 °C, respectively. For HTCa8, these peaks shifted slightly to 604 °C and 777 °C. This shift suggests that an appropriate amount of Ca doping moderately strengthens the metal–support interaction, likely due to the formation of a more homogeneous dispersion of active species. With further increasing Ca loading to 12 wt% (HTCa12), both reduction peaks shifted to lower temperatures (584 °C and 748 °C, respectively), indicating a weakening of the metal–support

interaction at higher Ca content. Notably, the integrated area of the low-temperature peak increased significantly, while that of the high-temperature peak decreased correspondingly. This trend implies that excessive Ca doping promotes the formation of metal species that are more easily reducible, whereas the proportion of strongly interacting species is reduced, possibly due to the segregation of excess CaO that partially covers the support surface and attenuates the interaction with Ni species [29].

TEM Characterization of reduced catalysts

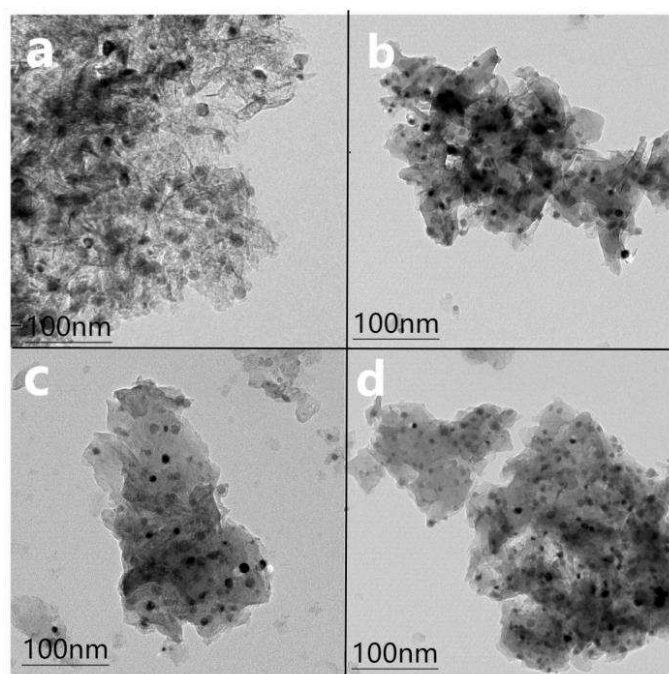


Fig. 5 TEM micrographs of the reduced catalysts: (a) HTCa0, (b) HTCa4, (c) HTCa8, (d) HTCa12

Fig. 7 displayed the TEM images of reduced catalysts with different Ca doping contents. For the undoped HTCa0 catalyst, Ni particles were unevenly distributed with an average size of ~10 nm and a tendency to agglomerate. Upon introduction of Ca (HTCa4 and HTCa8), the particle size decreased and the dispersion improved significantly, which can be ascribed to the enhanced metal–support interaction induced by Ca doping. For HTCa8, tiny Ni nanoparticles were uniformly

anchored on the support surface, and the crystallite size reached the minimum value of 7.2 nm. The introduction of moderate Ca strengthened the metal–support interaction, which restrained the migration and coalescence of Ni species during high-temperature reduction and thereby improved Ni dispersion [30]. However, further increasing the Ca loading to 12 wt% led to the formation of larger Ni crystallites (~13.6 nm), likely due to the destruction of the hydrotalcite structure and the segregation of excess CaO species.

Evaluation of catalyst activity

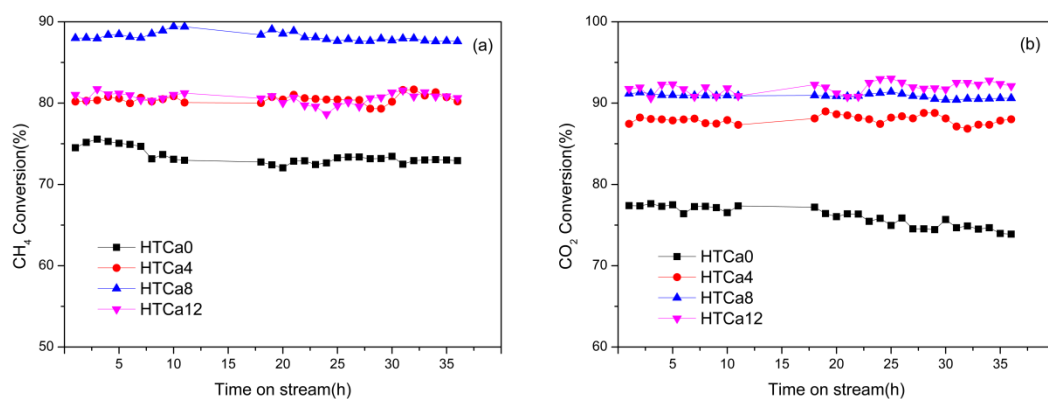


Fig. 6 Catalytic performance of different samples: Conversion rates of (a) CH₄ and (b) CO₂ (T = 750 °C, CH₄/CO₂ = 1, GHSV = 48 000 mL/(g·h).)

Fig.6 shows the methane and CO₂ conversions measured during the DRM reaction at 750 °C.

It can be seen that the methane conversion rates decreased as following: HTCa8 > HTCa12 ≈ HTCa4 > HTCa0. The lower methane conversion measured for HTCa0 (74%). With Ca doping, the initial methane conversion over HTCa4 reached 80%, notably higher than that over HTCa0. In particular, HTCa8 initially exhibited the highest methane conversion (~88%), and conversion rate remained relatively stable during the 36-h long-term stability test. With excessive Ca loading, the CH₄ conversion rates of HTCa12 decreased to 82%. This decline is likely attributable to the larger Ni particle size and the destruction of the hydrotalcite structure in the HTCa12 catalyst as confirmed

by XRD and TEM. As displayed in Fig. 6(b), the CO₂ conversion over each catalyst shows a trend identical to that of CH₄ conversion. For all catalysts, the CO₂ conversion was invariably higher than the CH₄ conversion, and this discrepancy can be plausibly explained by the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) [31,32]. Notably, the HTCa8 catalyst achieved a CO₂ conversion as high as 91%, which remained stable throughout the reaction. The affinity of CaO toward CO₂ not only strengthens CO₂ adsorption and activation on the catalyst but also offers a beneficial activation pathway for the RWGS reaction via the enhanced interaction.

XRD characterization of spent catalysts

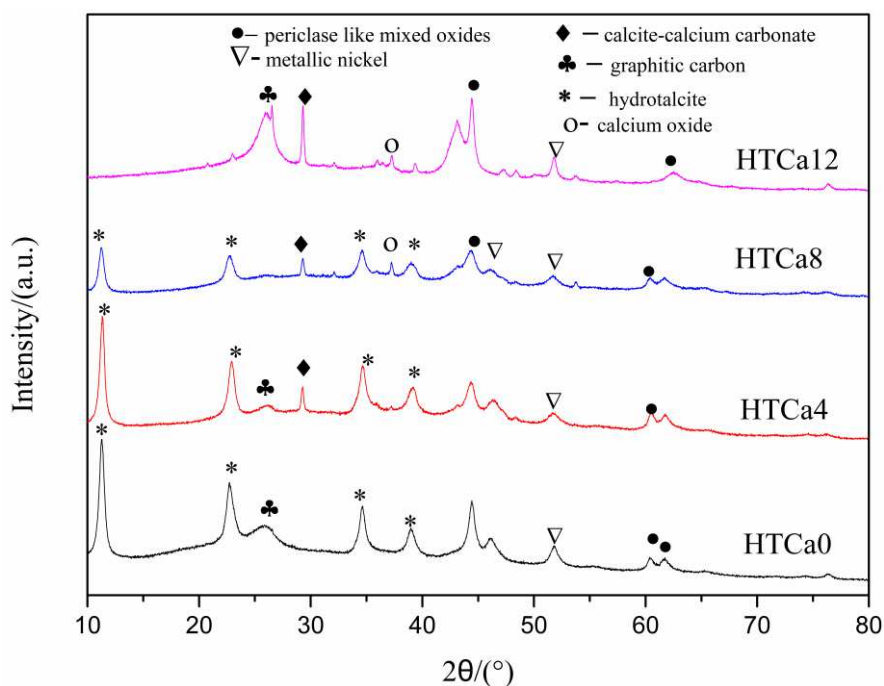


Fig. 7 XRD patterns of spent catalysts

XRD patterns of the spent catalysts after catalytic reaction are displayed in Fig. 7. It is noteworthy that the diffraction peaks of the hydrotalcite phase re-emerged in the post-reaction catalyst. The appearance of diffraction peaks at 11.30°, 22.90°, and 34.80° (2θ) for the reconstructed hydrotalcite phase can be ascribed to both the rehydration of the oxide matrix by H₂O from the RWGS side reaction and the incorporation of carbonate anions into the interlayer galleries, thereby

leading to the re-establishment of the layered architecture.

The reformation of the hydrotalcite phase is also considered a sign of the catalyst's structural resilience and can contribute to the re-dispersion of active metal species, which is beneficial for catalytic stability. A sharp diffraction peak at $2\theta=26^\circ$ assigned to graphitic carbon was clearly observed on all catalysts, demonstrating the presence of coke deposition. In comparison, substantially lower intensity of graphitic carbon diffraction peaks was detected for HTCa8, which is ascribed to the positive effect of Ca doping on inhibiting carbon formation. The nickel grain size of the spent HTCa12 sample increased significantly to 19.3 nm after the reaction, which was mainly attributed to particle sintering and excessive carbon encapsulation. In contrast, the HTCa8 sample exhibited negligible grain growth, with a final nickel particle size of approximately 7.9 nm. The optimal calcium doping amount successfully constructed abundant basic sites and triggered strong metal-support interaction, which effectively inhibited the agglomeration and growth of nickel nanoparticles during the catalytic reaction.

TEM Characterization of carbon deposits on the catalyst after reaction

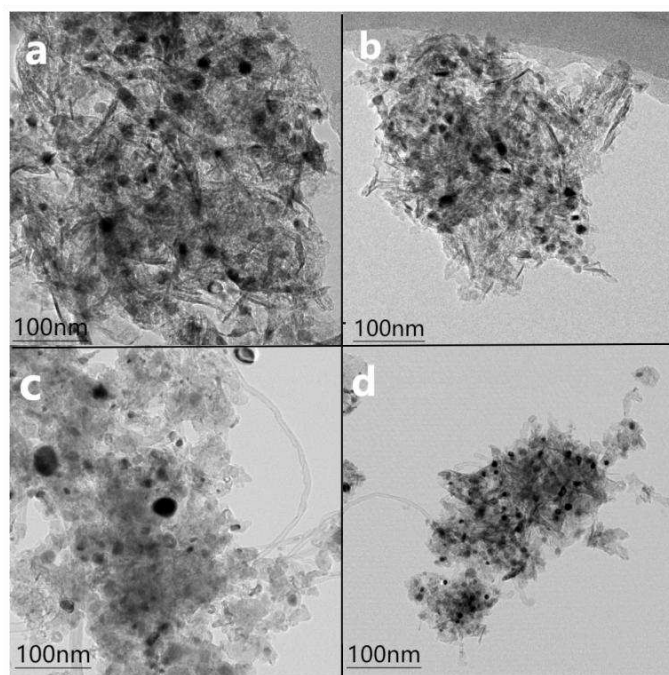


Fig. 8 TEM micrographs of spent catalysts after methane dry reforming: (a) HTC a0, (b) HTC a4, (c) HTC a8, (d) HTC a12

The TEM images of spent catalysts after methane reforming was shown in Fig. 8. All samples displayed varying degrees of Ni sintering after the reaction, which matched the grain growth trend obtained by comparing fresh and spent XRD data. Filamentous carbon nanofibers were formed on spent HTC a0 and HTC a4 catalysts, which wrapped around Ni nanoparticles, blocked active sites, and promoted metal agglomeration [33]. In the case of the spent HTC a8 catalyst, a marked decrease in filamentous carbon was observed, accompanied by the formation of carbon nanotubes (CNTs). Carbon nanotubes (CNTs) are believed to exert little negative influence on the catalytic behavior, which likely accounts for the outstanding activity and stability observed for HTC a8. For HTC a12, however, severe carbon deposition was detected, which also consisted mainly of CNTs, but the overwhelming quantity likely led to pore blockage and active-site coverage, thus undermining the catalytic performance.

TG-DTA Thermogravimetric analysis of spent catalysts

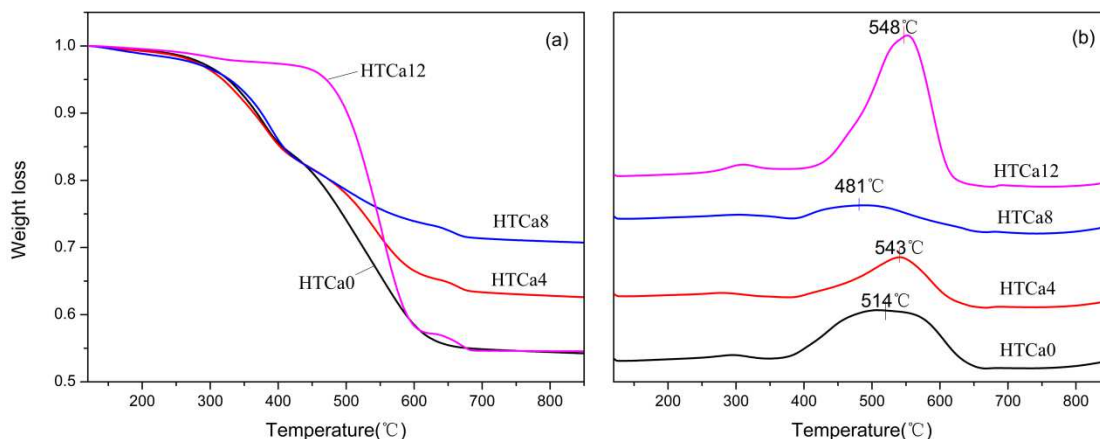


Fig. 9 (a) TG and (b) DTA profiles of spent catalysts

To further investigate the carbon deposition behavior of the spent catalysts, thermogravimetry-differential thermal analysis (TG-DTA) was performed on the four catalysts, and the analytical results were presented in Fig. 9 (a) and (b).

As could be seen from the TG curves, the total weight loss varied markedly with the catalyst composition. As presented in Fig. 9(a), all catalysts exhibited a distinct weight loss profile in the temperature range of 300-700 °C, which was primarily ascribed to the combustion of deposited carbonaceous species. The HTCa8 catalyst presented the least weight loss during thermal oxidation (27.4%), whereas the HTCa0 and HTCa12 catalysts displayed the most pronounced weight loss of 45.8 wt% and 45.6 wt%, which indicated a marked suppression of coke formation upon moderate calcium incorporation.

More importantly, the DTA profiles provided critical insights into the nature of the deposited carbon species. It was demonstrated that two carbon species, amorphous carbon and graphitic carbon, formed over nickel-based catalysts. As illustrated in Fig. 9(b), the HTCa0, HTCa4 and HTCa12 catalysts exhibited a dominant oxidation peak at approximately 550-600 °C, which was characteristic of graphitic carbon that formed via CH₄ decomposition on Ni crystallites [34,35].

Such carbon species were notoriously difficult to gasify and were primarily responsible for the rapid catalyst deactivation. In contrast, the HTC_a8 catalyst displayed a weak and broad oxidation peak at a much lower temperature, centered at approximately 481 °C, which was ascribed to amorphous or poorly ordered carbon species. The decrease in oxidation temperature clearly indicated that Ca modification fundamentally altered the formation pathway of carbon deposits. The HTC_a12 catalyst with excessive Ca loading exhibited a significant TGA weight loss of ~46.61% and an upward shift in the oxidation temperature. These effects stem from both CaCO₃ decomposition and heavy carbon accumulation, which are likely caused by the degradation of the hydrotalcite structure and the sintering of Ni particles. This observation was consistent with the findings reported by Chatla [36]. In their research, the NiMgAl-5Zn and NiMgAl-10Zn catalysts exhibited a notable shift of DTG oxidation peaks toward higher temperatures (approximately 500 °C and 600 °C) compared to the NiMgAl-3Zn catalyst (300°C - 450 °C).

Conclusions

Ca-modified Ni/Mg/Al hydrotalcites were synthesized by co-precipitation. XRD confirmed the presence of orthorhombic aragonite-type calcium carbonate and trigonal calcite with Ca doping. BET analysis revealed that the incorporation of Ca generated abundant mesopores with high surface area, facilitating Ni dispersion. After reduction, the layered structure transformed into periclase-like mixed oxides. Furthermore, the presence of Ca²⁺ shifted the reduction of the Ni²⁺ to higher temperatures and strengthened metal-support interaction, effectively suppressing Ni sintering at high temperatures. Importantly, Ca altered the carbon deposition pathway, converting filamentous carbon into carbon nanotubes, as verified by TEM and TG-DTA. Among the catalysts, HTC_a8 exhibited the highest CH₄ and CO₂ conversions of 88% and 91%, respectively, with excellent

stability during 36 h of DRM at 750 °C. The superior performance of HTC_a8 is attributed to the enhanced Ni dispersion, strong metal-support interaction, and modified coke morphology, which together contribute to outstanding anti-sintering and anti-coking properties.

Acknowledgements

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List of abbreviations

XRD	X-ray diffraction
TEM	Transmission electron microscopy
BET	Brunauer-Emmett-Teller
H ₂ -TPR	H ₂ temperature-programmed reduction
TG-DTA	Thermogravimetry-differential thermal analysis
DRM	Methane dry reforming
LDHs	Layered double hydroxides
TCD	Thermal conductivity detector
HTCa0	Ni/Mg/Al catalyst with 0 wt% Ca loading
HTCa4	Ni/Mg/Al catalyst with 4 wt% Ca loading
HTCa8	Ni/Mg/Al catalyst with 8 wt% Ca loading
HTCa12	Ni/Mg/Al catalyst with 12 wt% Ca loading

Conflict of interest

The authors affirm that there exist no professional or financial interests that may cause any conflict of interest regarding the research presented in this manuscript.

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Fig. 1 N₂ physisorption adsorption-desorption isotherms of the calcined catalysts

Fig. 2 XRD patterns of dried NiMgAl hydrotalcite-derived catalysts

Fig. 3 XRD patterns of reduced catalysts

Fig. 4 H₂-TPR profiles of catalysts

Fig. 5 TEM micrographs of the reduced catalysts: (a) HTC_a0, (b) HTC_a4, (c) HTC_a8, (d) HTC_a12

Fig. 6 Catalytic performance of different samples: Conversion rates of (a) CH₄ and (b) CO₂

(T = 750 °C, CH₄/CO₂ = 1, GHSV = 48 000 mL/(g·h).)

Fig. 7 XRD patterns of spent catalysts

Fig. 8 TEM micrographs of spent catalysts after methane dry reforming: (a) HTC_a0, (b) HTC_a4, (c) HTC_a8, (d) HTC_a12

Fig. 9 (a) TG and (b) DTA profiles of spent catalysts