

Article

Comparative Study on Ni/MgO-Al₂O₃ Catalysts for Dry and Combined Steam–CO₂ Reforming of Methane

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Abstract

The dry reforming of methane (DRM) and the combined steam–CO₂ reforming of methane (CSCRM) are promising routes for syngas production while simultaneously utilizing two major greenhouse gases—CO₂ and CH₄. In this study, a series of Ni/MgO-Al₂O₃ catalysts with varying Mg/Al molar ratios (Ni/MgAl(*x*), *x* = 0.5–0.9), along with Ni/MgO and Ni/Al₂O₃, were synthesized, characterized, and evaluated in both the DRM and CSCRM. Ni/MgO and Ni/Al₂O₃ exhibited a lower activity due to fewer active sites and a poor CH₄/CO₂ activation balance. In contrast, Ni/MgAl(0.6), Ni/MgAl(0.7), and Ni/MgAl(0.8) showed an enhanced activity, attributed to more abundant active sites and a more balanced activation of CH₄ and CO₂. Ni/MgAl(0.7) delivered the best DRM performance, whereas Ni/MgAl(0.8) was optimal for the CSCRM, likely due to its greater number of strong basic sites promoting CO₂ and H₂O adsorption. At 750 °C and 0.1 MPa over 100 h, Ni/MgAl(0.7) maintained a stable DRM performance (77% CH₄ and 86% CO₂ conversion; H₂/CO = 0.9) at 120 L/(g_{cat}·h), while Ni/MgAl(0.8) achieved a stable CSCRM performance (80% CH₄ and 62% CO₂ conversion; H₂/CO = 2.1) at 132 L/(g_{cat}·h). This study provides valuable insights into designing efficient Ni/MgO-Al₂O₃ catalysts for targeted syngas production.

Keywords: dry reforming of methane; combined steam–CO₂ reforming of methane; syngas; Ni/MgO-Al₂O₃; structure–performance relationship



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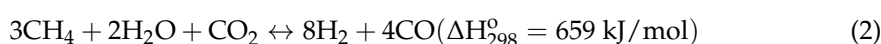
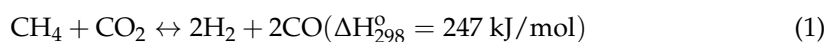
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1. Introduction

CO₂ and CH₄ are major greenhouse gases that significantly contribute to global climate change [1]. The dry reforming of methane (DRM, Equation (1)) and the combined steam–CO₂ reforming of methane (CSCRM, Equation (2)) convert CO₂ and CH₄ into valuable syngas while simultaneously mitigating both gases, attracting considerable interest from academic and industrial communities. A key distinction between the DRM and CSCRM lies in the H₂/CO molar ratio of the produced syngas: the DRM yields a ratio of approximately one, suitable for dimethyl ether synthesis and higher alcohol production [2,3], whereas the CSCRM generates syngas with a H₂/CO ratio of around two, which is preferred for methanol synthesis and the Fischer–Tropsch conversion to liquid fuels [4,5].



Nickel-based catalysts are widely used in reforming reactions due to their low cost and high catalytic activity. However, they are prone to sintering and coke deposition under high-temperature conditions, leading to catalyst deactivation [6–8]. Therefore, developing nickel-based catalysts with an enhanced sintering resistance and coke inhibition capabilities is critical for advancing reforming technologies. The choice of support materials plays a crucial role in promoting Ni particle dispersion and improving the catalytic performance of Ni-based catalysts in CH₄ reforming reactions. Among various supports, the magnesium aluminate (MgAl₂O₄) spinel is a promising candidate due to its excellent thermal stability (melting point of 2135 °C [9]), high mechanical strength, and chemical inertness. Guo et al. [10] reported that Ni/MgAl₂O₄ exhibited a high DRM activity and stability owing to the high sintering resistance and low acidity of MgAl₂O₄ as well as its ability to promote Ni dispersion. Similarly, Hadian et al. [11,12] demonstrated that nanocrystalline MgAl₂O₄-supported Ni catalysts showed a high catalytic activity in both the DRM and the combined dry reforming and partial oxidation of methane. Additionally, Kim et al. [13] found that Ni/MgAl₂O₄ subjected to an inert-annealing treatment exhibited improved structural properties, leading to a high CH₄ conversion and the enhanced durability in the steam reforming of methane (SRM). Yu et al. [14] further demonstrated that Ni supported on sol-gel-derived MgAl₂O₄ showed a high activity and stability for the CSCR. M.

Unfortunately, MgAl₂O₄ alone lacks sufficient basic sites for effective CO₂ adsorption [15,16]. In contrast, MgO exhibits a strong Lewis basicity and is often incorporated to enhance the basicity, resistance to coking, and overall catalytic performance of catalysts [17,18]. As a result, catalyst supports containing MgAl₂O₄ and MgO have garnered increasing attention. Fang et al. [19] reported that Ni/MgO-Al₂O₃ with excess MgO possessed a higher number of surface basic sites than Ni/MgAl₂O₄ without MgO, leading to the improved adsorption and activation of CO₂ and CH₄ and thereby enhancing the DRM activity. Similarly, Park et al. [20] demonstrated that the Mg/Al ratio influenced not only the basicity of Ni/MgO-Al₂O₃ catalysts but also their Ni dispersion and reducibility. The optimal catalyst with a Mg/Al ratio of 0.55 exhibited the highest number of Ni active sites, the greatest basicity, and the best DRM performance. More recently, Tao et al. [21] found that the coordination configuration of Ni in MgAl₂O₄, which depended on the Mg content, affected the metal-support interaction, the crystallinity of deposited carbon species, and the thermal stability of Ni/MgO-Al₂O₃ catalysts. The effect of the Mg/Al ratio has also been explored in the CSCR. Schiaroli et al. [22] observed that increasing the Mg/Al ratio improved the activity of Ni-Rh/MgO-Al₂O₃ by enhancing the CO₂ adsorption on the catalyst surface. Koo et al. [23] noted that both low and high MgO contents promoted coke formation—the former due to inactive NiAl₂O₄ and surface acid sites and the latter owing to the agglomeration of free Ni species. They further reported that a Ni/MgO-Al₂O₃ catalyst with a Mg/Al ratio of 0.5 exhibited an optimal catalytic activity in the CSCR [24].

The literature survey indicates that Ni/MgO-Al₂O₃ catalysts are promising for both the DRM and CSCR, with the Mg/Al ratio being a key factor influencing the catalytic performance. However, its effect may differ between these two distinct processes, suggesting that the optimal Mg/Al ratio could vary accordingly. Although many studies have investigated the DRM and CSCR individually, making direct comparisons between their findings is challenging due to differences in catalyst preparation methods and reaction conditions. For example, Ni/MgO-Al₂O₃ catalysts prepared using home-made MgO-Al₂O₃ were evaluated for the DRM at 800 °C under a high gas hourly space velocity (GHSV) of 1,500,000 h^{−1} [20], whereas those derived from commercial MgO-Al₂O₃ were tested for the CSCR at 650–750 °C with a GHSV of 530 L/(g_{cat}·h) [24]. To develop high-performance Ni/MgO-Al₂O₃ catalysts tailored to specific reforming routes—the DRM for higher alcohols and the CSCR for liquid fuels—a direct comparison of the two processes under

similar conditions is crucial. This approach would enable an accurate assessment of the effect of the Mg/Al ratio on the DRM and CSCR. However, to the best of our knowledge, no such comparative study has been reported to date.

To bridge this gap, a series of Ni/MgO-Al₂O₃ catalysts with Mg/Al molar ratios ranging from 0.5 to 0.9 were prepared, characterized, and evaluated in this study. Ni/MgO and Ni/Al₂O₃ were also included as reference catalysts. To ensure a meaningful comparison, both DRM and CSCR were conducted under identical temperature and pressure conditions with comparable GHSV values, differing only in the feed composition. The structure–performance relationships of the catalysts were investigated to elucidate the influence of the Mg/Al ratio on each process. Finally, the most effective catalysts for the DRM and CSCR were subjected to long-term stability tests over 100 h.

2. Results and Discussion

2.1. Catalytic Performance

Figure 1 presents the catalytic performances of the Ni/Al₂O₃, Ni/MgO, and Ni/MgAl(x) catalysts in the DRM and CSCR as a function of the time on stream (TOS). The equilibrium conversions of CH₄ and CO₂, calculated using the ASPEN Plus[®] simulator, are 83.8% and 90.6% for the DRM and 89.9% and 68.5% for the CSCR, respectively. For Ni/Al₂O₃ in the DRM, the initial CH₄ and CO₂ conversions at TOS = 1 h are 62.6% and 72.5%, respectively. However, these values gradually decrease to 50.3% and 60.6% after 30 h of reaction, suggesting a catalyst deactivation. In contrast, under CSCR conditions, the CH₄ and CO₂ conversions of Ni/Al₂O₃ show an opposite trend, increasing from 45.6% and 18.7% at TOS = 1 h to 54.2% and 29.2% after 30 h, respectively, which implies a catalyst reactivation. Compared to Ni/Al₂O₃, Ni/MgO demonstrates a lower catalytic activity, particularly in the CSCR. Due to the significantly low activity of Ni/MgO in the CSCR, only 10 h of TOS testing was conducted.

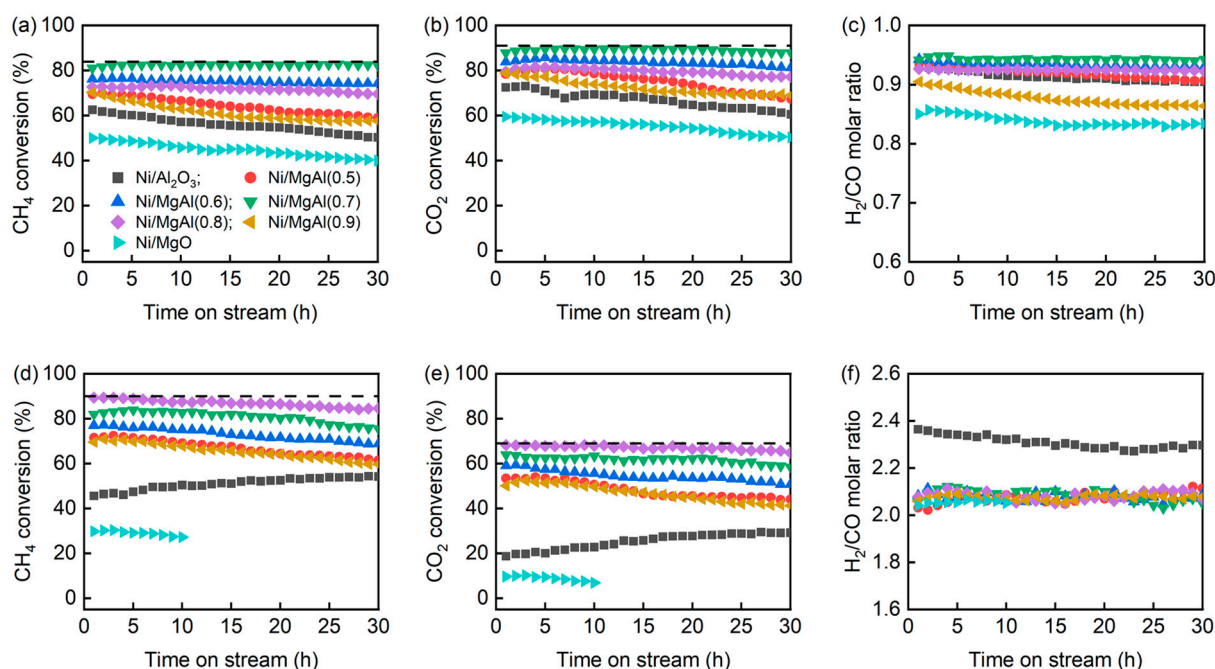


Figure 1. (a–c) DRM and (d–f) CSCR performances of various catalysts (Reaction conditions: (a–c) CH₄/CO₂ = 1/1, GHSV = 120 L/(g·h), temperature = 750 °C; (d–f) CH₄/H₂O/CO₂ = 2.5/2/1, GHSV = 132 L/(g·h), and temperature = 750 °C. The dashed lines correspond to the equilibrium conversion data of CH₄ and CO₂).

The catalytic activities of Ni/MgAl(*x*) in both the DRM and CSCRm are superior to those of Ni/Al₂O₃ and Ni/MgO, highlighting the promoting effect of MgO and Al₂O₃ mixed oxides. In general, the activity of Ni/MgAl(*x*) initially increases with the increasing *x*, reaches a maximum, and then declines. However, the optimal catalysts for the DRM and CSCRm differ. For the DRM, Ni/MgAl(0.7) shows the best performance, maintaining a high and stable CH₄ conversion (81.0–82.3%) and CO₂ conversion (87.9–89.6%) over 30 h. In contrast, for the CSCRm, Ni/MgAl(0.8) is the most effective catalyst, with the CH₄ conversion slightly decreasing from 89.4% to 84.5% and the CO₂ conversion decreasing from 68.2% to 64.8% over the same period.

For the DRM process, the CO₂ conversions over all catalysts are consistently higher than the corresponding CH₄ conversions, which can be attributed to the reverse water–gas shift (RWGS) reaction [25–27]. This leads to the H₂/CO molar ratios below one. Notably, Ni/MgO exhibits the lowest H₂/CO ratio (0.83–0.85), followed by Ni/MgAl(0.9) (0.86–0.9) and the other catalysts (0.9–0.95). In contrast, for the CSCRm, the CH₄ conversions exceed the CO₂ conversions, likely due to the CH₄ decomposition [14,28] and the WGS reaction [29]. As a result, the H₂/CO ratios are larger than two. Interestingly, the H₂/CO ratio over Ni/Al₂O₃ (2.27–2.36) is much higher than those of the other catalysts (2.02–2.12). It is anticipated that the different behaviors of the catalysts for the DRM and CSCRm are linked to their physicochemical properties. Therefore, in the following section, the properties of both fresh and spent catalysts will be explored in detail.

2.2. Physicochemical Properties of Catalysts

2.2.1. Fresh Catalysts

The N₂ adsorption–desorption isotherms and pore size distribution curves of the supports and catalysts are presented in Figures S1 and S2, with the textural data (specific surface area, pore volume, and average pore diameter) summarized in Table 1. All supports and catalysts exhibit IV hysteresis loops and unimodal mesoporous structures [30]. The specific surface area and pore volume of Al₂O₃ are significantly higher than those of MgO. For the mixed oxide supports, as the Mg/Al ratio increases from 0.5 to 0.9, the surface area and pore volume initially increase and then decrease, with MgAl(0.8) showing the highest values. This suggests that the textural properties of the supports can be tuned by adjusting the Mg/Al ratio. After the Ni loading on the support, the specific surface area of each catalyst, except for Ni/MgO, decreases as expected compared to the support. However, the surface area of Ni/MgO is nearly twice that of MgO, likely due to the formation of smaller particles.

Table 1. Physicochemical properties of different catalysts.

Sample ^a	S _{BET} (m ² /g)	V _p ^b (cm ³ /g)	d _p ^b (nm)	Ni Content ^c (wt.%)	H ₂ Uptake (μmol/g)	d _{Ni-XRD} ^d (nm)	d _{Ni-HRTEM} ^e (nm)
MgO	21.9	0.12	32.7				
Al ₂ O ₃	197.0	0.53	10.6				
MgAl(0.5)	92.1	0.40	17.3				
MgAl(0.6)	133.1	0.54	19.4				
MgAl(0.7)	141.7	0.71	20.5				
MgAl(0.8)	155.0	0.92	24.6				
MgAl(0.9)	110.8	0.49	17.9				

Table 1. Cont.

Sample ^a	S _{BET} (m ² /g)	V _p ^b (cm ³ /g)	d _p ^b (nm)	Ni Content ^c (wt.%)	H ₂ Uptake (μmol/g)	d _{Ni-XRD} ^d (nm)	d _{Ni-HRTEM} ^e (nm)
Ni/MgO	41.8	0.15	28.0	10.3	3.4	-	4.9
Ni/Al ₂ O ₃	135.1	0.50	14.0	10.2	14.4	6.9	6.4
Ni/MgAl(0.5)	50.3	0.40	31.0	9.6	17.8	10.3	8.8
Ni/MgAl(0.6)	100.4	0.56	22.0	9.5	19.5	8.9	8.3
Ni/MgAl(0.7)	107.8	0.53	18.1	9.5	22.1	8.5	7.6
Ni/MgAl(0.8)	108.5	0.41	13.2	9.8	24.8	7.9	7.1
Ni/MgAl(0.9)	81.0	0.37	16.9	9.7	16.9	11.4	10.5

^a The first seven entries refer to the supports, while the last seven correspond to the catalysts after the Ni loading.

^b The pore volume and average pore diameter were acquired from the adsorption branch by the BJH method.

^c The Ni content was measured by ICP-OES. ^d The average Ni particle size was determined by XRD. ^e The average Ni particle size was obtained by HRTEM.

Figure 2 shows the H₂-TPR profiles of Ni/Al₂O₃, Ni/MgO, and Ni/MgAl(x), with the maximum temperature limited to 800 °C due to instrument constraints. All catalysts except Ni/MgO exhibit a prominent high-temperature reduction peak centered between 700 and 800 °C, which is indicative of strong metal–support interactions [31]. In contrast, Ni/MgO shows no distinct peak but instead displays a gradually increasing H₂ consumption curve up to 800 °C, suggesting that the Ni species in this catalyst are extremely difficult to reduce. This behavior is attributed to the formation of a MgO–NiO solid solution, facilitated by the shared face-centered cubic structure of NiO and MgO, which significantly impedes the reduction [32]. Compared to Ni/MgO and Ni/Al₂O₃, the Ni/MgAl(x) catalysts show a relatively easier reduction. As the value of x increases from 0.5 to 0.9, the reduction peak temperature gradually rises from 740 to 780 °C, implying that the reducibility of Ni/MgAl(x) is dependent on the Mg/Al ratio. Similar findings have been reported by other researchers [21,33,34]. Tao et al. [21] demonstrated that excessive Mg occupies the octahedral sites in the nonstoichiometric Ni-doped MgAl₂O₄ spinel, thereby impeding the reduction of Ni species. It should be noted that the supports (Al₂O₃, MgO, and MgAl(x)) themselves display no reduction peaks, confirming the absence of reducible species in the support materials.

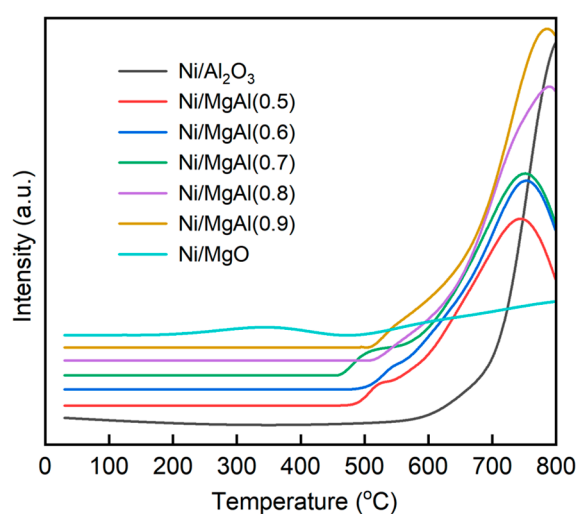


Figure 2. H₂-TPR profiles of various catalysts (signal intensity shown as raw output).

Figure 3 presents the XRD patterns of supports and reduced catalysts. Both Al₂O₃ and Ni/Al₂O₃ exhibit characteristic diffraction peaks indexed to γ-Al₂O₃ (JCPDS #10-0425). In the case of Ni/Al₂O₃, the Ni(200) diffraction peak (JCPDS #04-0850) is clearly

detected, indicating the presence of face-centered cubic Ni. In contrast, no Ni-related peaks are identified in Ni/MgO, where only MgO diffraction peaks (JCPDS #45-0946) appear. The absence of Ni peaks is probably attributed to the low abundance of Ni particles, as supported by the H₂-TPR analysis. Further evidence is provided by the much lower H₂ uptake of Ni/MgO (3.4 µmol/g, Table 1), which is an order of magnitude lower than that of other catalysts (14.4–24.8 µmol/g). The low H₂ uptake suggests a limited number of metal active sites, which likely explains the poor catalytic activity of Ni/MgO in both the DRM and CSCRM processes (Figure 1). For MgAl(x) and Ni/MgAl(x), the peaks corresponding to the MgAl₂O₄ spinel (JCPDS #21-1152) are observed. In samples with x = 0.8 and 0.9, MgO is faintly detected. Given the high calcination temperature (830 °C), the formation of NiAl₂O₄ in Ni/Al₂O₃ is feasible [35,36]. However, identifying NiAl₂O₄ in the XRD pattern is challenging due to the peak overlap with γ-Al₂O₃. Based on the reactivation behavior of Ni/Al₂O₃ observed during the CSCRM process, it can be inferred that a portion of the Ni species remains in the form of NiAl₂O₄ even after the reduction treatment. The in situ reduction of Ni from NiAl₂O₄ during the reaction is probably responsible for the observed reactivation phenomenon of Ni/Al₂O₃.

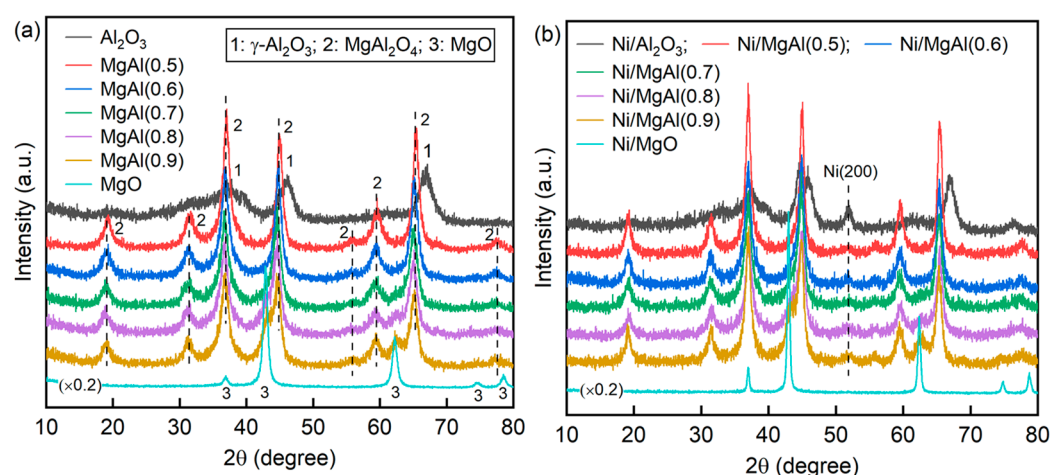


Figure 3. XRD patterns of (a) supports and (b) fresh reduced catalysts (the intensities for MgO and Ni/MgO are scaled by a factor of 0.2 for a clear comparison).

Based on the Ni(200) peak of the reduced catalysts (except Ni/MgO), the Ni crystallite size can be estimated using the Scherrer equation. As presented in Table 1, Ni/Al₂O₃ shows an average Ni particle size of 6.9 nm, which is smaller than that of Ni/MgAl(x). This is probably owing to its high reduction temperature, which originates from the reduction of Ni²⁺ in the NiAl₂O₄ spinel. For Ni/MgAl(x), as x increases from 0.5 to 0.8, the Ni particle size decreases from 10.3 to 7.9 nm; however, for Ni/MgAl(0.9), it increases to 11.4 nm. This trend generally correlates with the specific surface area of the MgAl(x) support, where a larger surface area promotes metal dispersion, leading to smaller Ni particles. Table 2 shows the lattice parameters of MgAl₂O₄ for both MgAl(x) and Ni/MgAl(x). These parameters are calculated through cell refinement using Jade 6.5 software. The lattice parameters of the fresh catalysts are consistently smaller than those of their corresponding supports. This reduction implies that Ni is incorporated into the MgAl₂O₄ lattice, as the ionic radius of Ni²⁺ (0.55 Å) is smaller than that of Mg²⁺ (0.57 Å) [37].

Table 2. Lattice parameters of MgAl_2O_4 in $\text{MgAl}(x)$ and $\text{Ni/MgAl}(x)$.

Mg/Al Molar Ratio (x)	Lattice Parameter of MgAl_2O_4 in $\text{MgAl}(x)$ and $\text{Ni/MgAl}(x)$ (Å)			
	$\text{MgAl}(x)$	Fresh $\text{Ni/MgAl}(x)$	Spent $\text{Ni/MgAl}(x)$ in DRM	Spent $\text{Ni/MgAl}(x)$ in CSCR
0.5	8.0636	8.0515	8.0622	8.0593
0.6	8.0728	8.0588	8.0678	8.0687
0.7	8.1025	8.0611	8.0652	8.0746
0.8	8.0975	8.0791	8.0921	8.0817
0.9	8.0801	8.0615	8.0816	8.0765

Figure 4 illustrates the morphologies of the supports and catalysts, the microstructures of the catalysts, as well as the elemental distribution across the catalysts. As shown in the FESEM images, $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{MgAl}(x)$ exhibit bulk granular morphologies similar to their respective supports. In contrast, Ni/MgO displays smaller particles compared to MgO , which is consistent with the larger specific surface area of Ni/MgO relative to MgO . The HRTEM analysis reveals distinct microstructural differences in $\text{Ni}/\text{MgAl}(x)$. For $\text{Ni}/\text{MgAl}(0.5)$, Ni nanoparticles (dark spots) are dispersed on plate-like particles. However, for $\text{Ni}/\text{MgAl}(x)$ ($x = 0.6\text{--}0.9$), needle-like particles appear, and their quantity increases with x . The lattice fringe analysis (Figure S3) confirms that the plate-like particles correspond to MgAl_2O_4 , while the needle-like particles are attributed to MgO . This is consistent with the composition of $\text{MgAl}(0.5)$, which matches the stoichiometric MgAl_2O_4 , whereas $\text{MgAl}(x)$ ($x = 0.6\text{--}0.9$) contains excess MgO beyond the stoichiometric ratio.

For all catalysts, Ni particles are well dispersed on the supports, as indicated by the EDS mapping analysis. From the HRTEM images, the average Ni particle sizes of the catalysts can be determined. Ni/MgO exhibits the smallest Ni particle size (4.9 nm), followed by $\text{Ni}/\text{Al}_2\text{O}_3$ (6.4 nm) and $\text{Ni}/\text{MgAl}(x)$ (7.1–10.5 nm). This trend is likely associated with the reducibility of the catalysts, as the Ni species in the NiO-MgO solid solutions and NiAl_2O_4 spinel are more difficult to reduce, resulting in smaller Ni particles [38–40]. Notably, Ni/MgO contains a limited amount of Ni particles, further supporting the challenges in its reduction. This observation aligns with its low H_2 uptake. The Ni particle sizes determined by HRTEM closely match those obtained from XRD and exhibit the same variation trend (Table 1).

The interactions of CO_2 with the catalysts can be analyzed using CO_2 -TPD. Figures S4 and 5a show the CO_2 -TPD profiles of the supports and catalysts, respectively. The desorption peaks below 200 °C, between 200 and 400 °C, and above 400 °C are generally assigned to the release of carbon oxides from weak, medium, and strong basic sites, respectively [41–43]. The total basicity of each sample, which reflects the overall number of basic sites, can be estimated by integrating the areas of all desorption peaks. Compared to the supports, the catalysts exhibit a reduced total basicity due to the coverage of basic sites by Ni particles. Among the catalysts, $\text{Ni}/\text{Al}_2\text{O}_3$ shows the lowest total basicity, consisting exclusively of weak basic sites. In contrast, Ni/MgO exhibits the highest total basicity, encompassing weak, medium, and strong basic sites. $\text{Ni}/\text{MgAl}(x)$ contains both weak and medium basic sites, and as x increases, both the total basicity and the proportion of medium basic sites increase. Accordingly, the strength of CO_2 -catalyst interactions follow the order of $\text{Ni}/\text{Al}_2\text{O}_3 < \text{Ni}/\text{MgAl}(0.5) < \text{Ni}/\text{MgAl}(0.6) < \text{Ni}/\text{MgAl}(0.7) < \text{Ni}/\text{MgAl}(0.8) < \text{Ni}/\text{MgAl}(0.9) < \text{Ni}/\text{MgO}$.

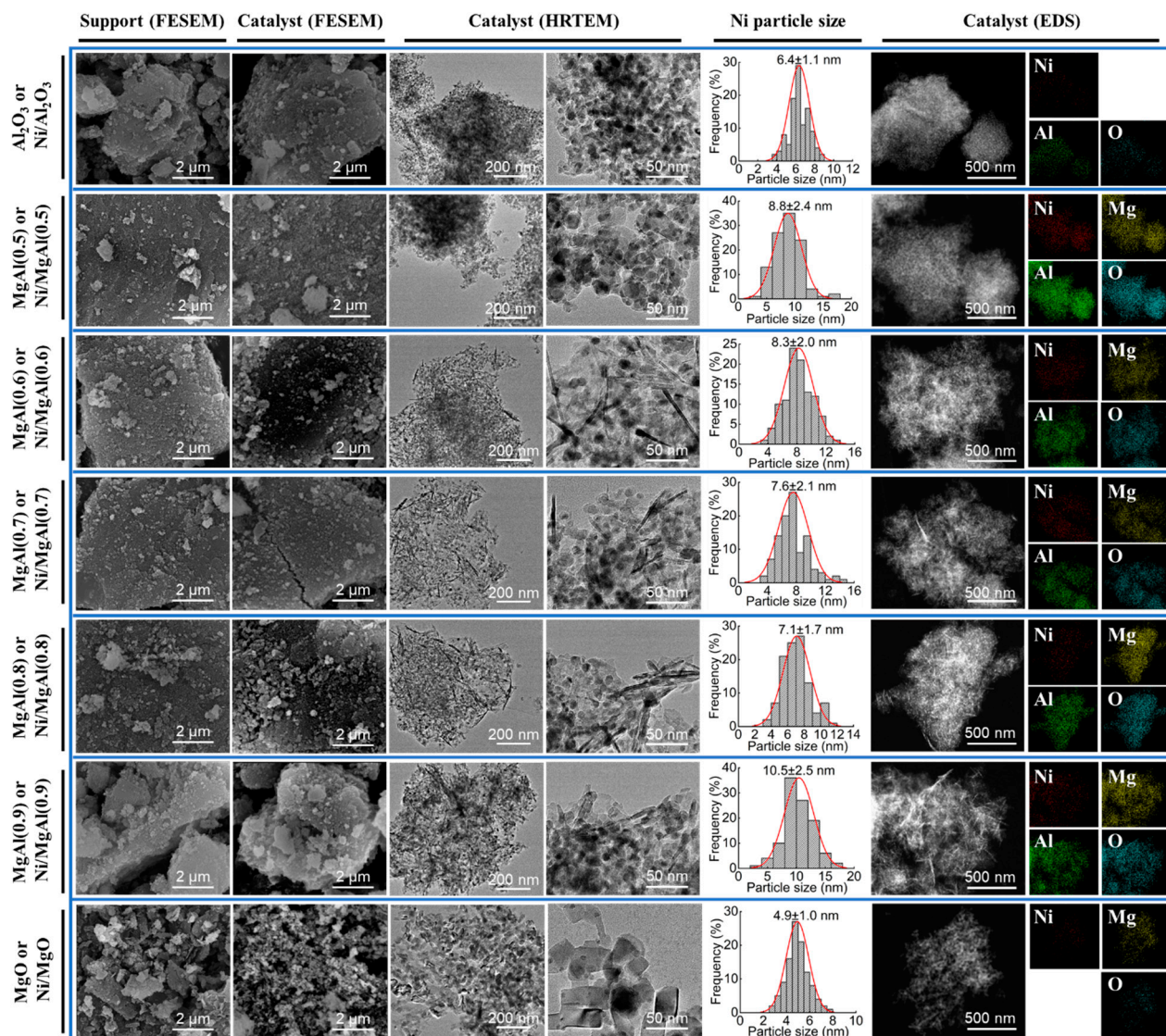


Figure 4. FESEM images of supports and fresh catalysts, along with HRTEM images, Ni particle size distributions, and EDS mapping of fresh catalysts.

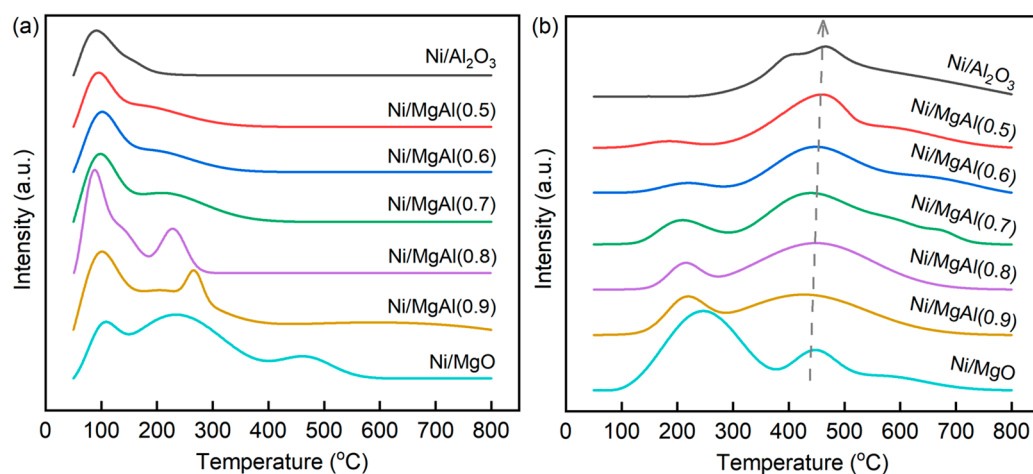


Figure 5. (a) CO_2 -TPD and (b) CH_4 -TPD curves of various catalysts.

CH_4 -TPD measurements are used to investigate the ability of metal sites to adsorb and activate CH_4 . Figure 5b presents the CH_4 -TPD profiles of the catalysts. The desorp-

tion peaks below 300 °C and above 400 °C correspond to weak (σ sites) and strong (τ site) adsorption sites for CH₄, respectively [44]. From Ni/MgO to Ni/MgAl(*x*) with the decreasing *x*, and further to Ni/Al₂O₃, the proportion of σ sites decreases, while that of τ sites increases. Additionally, the τ -site peak shifts toward higher temperatures, indicating stronger interactions between CH₄ and Ni. Consequently, the strength of CH₄–Ni interactions follows the order of Ni/MgO < Ni/MgAl(0.9) < Ni/MgAl(0.8) < Ni/MgAl(0.7) < Ni/MgAl(0.6) < Ni/MgAl(0.5) < Ni/Al₂O₃. This trend is opposite to that observed for CO₂–catalyst interactions.

The number of metal active sites (indicated by H₂ uptake), CH₄–Ni interactions, and CO₂–catalyst interactions are key factors influencing the DRM and CSCRM performance of the catalysts. Ni/MgAl(0.6), Ni/MgAl(0.7), and Ni/MgAl(0.8) possess the highest number of active sites while exhibiting moderate CH₄–Ni interactions and CO₂–catalyst interactions. This balance likely promotes a suitable match between the CH₄ activation and CO₂ activation, leading to the high initial activity in both the DRM and CSCRM, as shown in Figure 1. In contrast, Ni/MgO and Ni/Al₂O₃ exhibit the lowest number of active sites; moreover Ni/MgO shows the strongest CO₂–catalyst interactions but the weakest CH₄–Ni interactions, whereas Ni/Al₂O₃ demonstrates the weakest CO₂–catalyst interactions but the strongest CH₄–Ni interactions. This imbalance leads to a mismatch between the CH₄ activation and CO₂ activation, ultimately resulting in the low activity in both the DRM and CSCRM.

Regarding Ni/MgAl(0.6), Ni/MgAl(0.7), and Ni/MgAl(0.8), the initial activity in the DRM follows the sequence of Ni/MgAl(0.7) > Ni/MgAl(0.6) > Ni/MgAl(0.8), whereas in the CSCRM, the order is Ni/MgAl(0.8) > Ni/MgAl(0.7) > Ni/MgAl(0.6). It has been established that the competitive dissociative adsorption of CO₂ and H₂O occurs on the basic sites of the catalyst [29,45,46]. Thus, a higher number of stronger basic sites are preferred in the CSCRM to enhance the CO₂ adsorption and activation, explaining the highest CSCRM activity of Ni/MgAl(0.8). In the DRM, where no steam is introduced, the strong CO₂ adsorption could hinder the transfer of activated CO₂, making relatively weaker basic sites more favorable [47,48]. Consequently, Ni/MgAl(0.7) exhibits the highest DRM activity. This indicates that the CSCRM requires more and stronger basic sites for effective CO₂ adsorption and activation compared to DRM.

The H₂/CO molar ratio in the DRM is influenced by the CO₂–catalyst interactions or the basicity of the catalysts (Figure 6a). Previous studies have shown that an increased catalyst basicity enhances CO₂ adsorption and activation, as well as the CO selectivity in the RWGS [49,50]. Considering that Ni/MgO has the highest total basicity and the strongest CO₂–catalyst interactions, more RWGSs are expected to occur on this catalyst, resulting in the lowest H₂/CO ratio (Figure 1c). Likewise, Ni/MgAl(0.9), with the second-highest basic strength, exhibits the second-lowest H₂/CO ratio. In contrast, the H₂/CO ratio in the CSCRM is likely affected by the CH₄–Ni interactions (Figure 6b). Ni/Al₂O₃ displays the strongest CH₄–Ni interactions and CH₄ adsorption, which are likely to promote the CH₄ decomposition [51]. Additionally, the acid sites of γ -Al₂O₃ can further facilitate the CH₄ decomposition [23,36,52]. As a result, Ni/Al₂O₃ yields a notably higher H₂/CO in the CSCRM compared to the other catalysts (Figure 1f).

2.2.2. Spent Catalysts

After 30 h of TOS testing in either the DRM or CSCRM, most catalysts experience partial deactivation, as evidenced by the decline in CH₄ and CO₂ conversions shown in Figure 1. It is widely recognized that the deactivation mechanisms in methane reforming reactions are primarily associated with the coke formation and metal particle sintering. The presence and quantity of coke can be analyzed by the XRD, Raman, and TGA. As presented

in Figure 7a, all spent catalysts in the DRM exhibit distinct Ni diffraction peaks, suggesting the growth of the Ni crystallite size. Indeed, the Ni crystallite size of each spent catalyst (Table 3) is larger than that of its fresh counterpart (Table 1). In addition to Ni, γ - Al_2O_3 , MgAl_2O_4 , and MgO , crystalline silica is detected, which is attributed to the quartz sand used to dilute the catalyst. Although efforts were made to separate the spent catalyst from quartz sand particles using a magnet, some quartz sand remained in the catalyst. Since the (006) plane of coke at $2\theta = 26.6^\circ$ (JCPDS #26-1076) overlaps completely with the (101) plane of the quartz sand (JCPDS #46-1045), it is impossible to determine the presence of the coke formation from the XRD patterns alone.

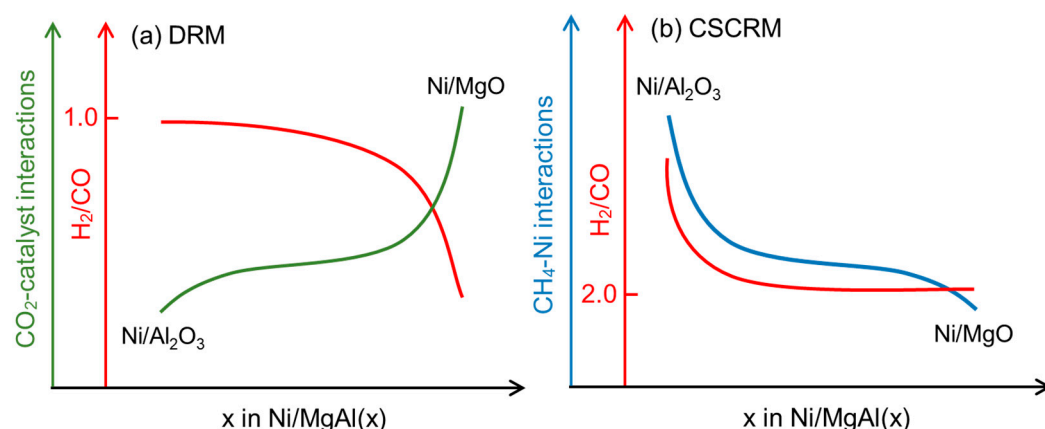


Figure 6. A schematic diagram of the correlation between the reactant–site interactions, H_2/CO ratio, and Mg/Al ratio in the (a) DRM and (b) CSCRM.

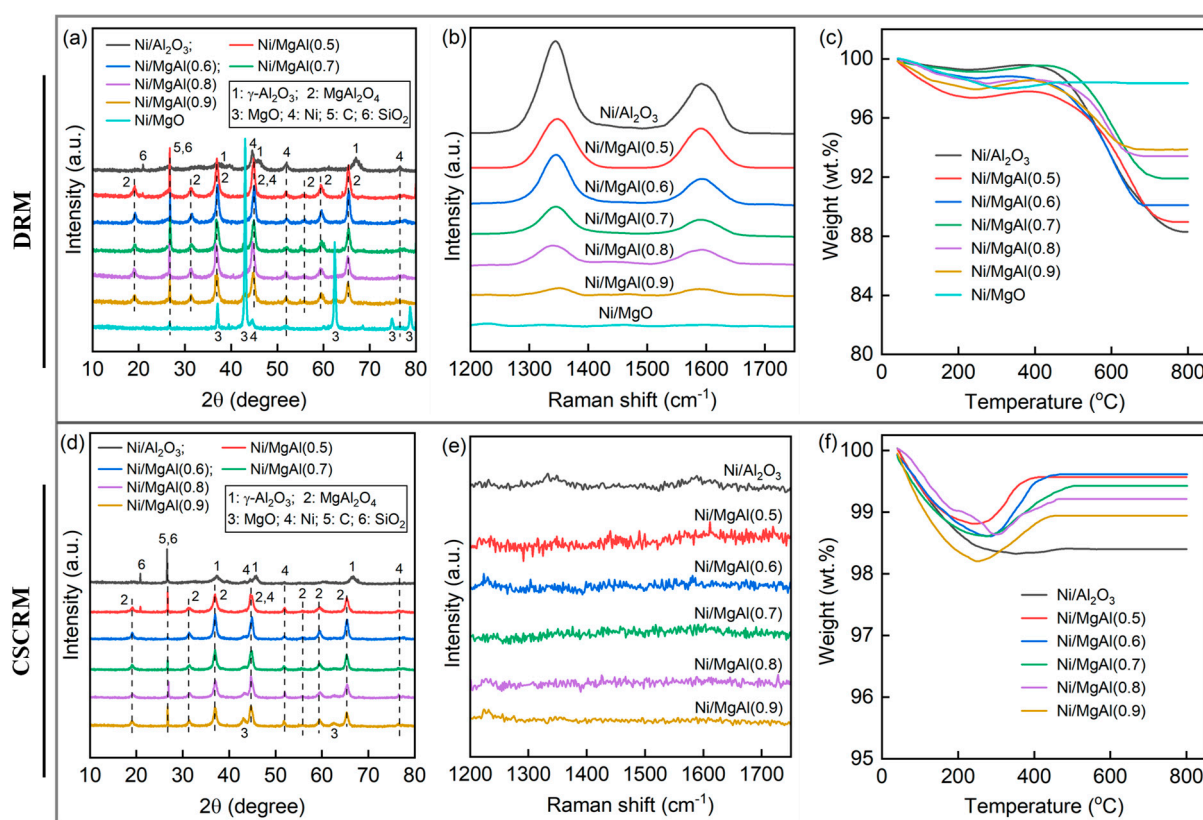


Figure 7. (a,d) XRD patterns, (b,e) Raman spectra, and (c,f) TGA profiles of spent catalysts ((a–c) DRM; (d–f) CSCRM).

Table 3. Ni particle sizes and coke deposition of spent catalysts in DRM and CSCR. M.

Catalyst	DRM				CSCR. M		
	$d_{\text{Ni-XRD}}^a$ (nm)	$d_{\text{Ni-TEM}}^b$ (nm)	Coke ^c (wt.%)	Coking Rate (wt.%/h)	$d_{\text{Ni-XRD}}^a$ (nm)	$d_{\text{Ni-TEM}}^b$ (nm)	Coke ^c (wt.%)
Ni/ γ -Al ₂ O ₃	8.7	8.4	11.3	0.38	8.8	9.0	n.d.
Ni/MgAl(0.5)	15.5	13.7	9.0	0.30	16.3	15.9	n.d.
Ni/MgAl(0.6)	11.7	12.8	8.6	0.29	13.6	14.3	n.d.
Ni/MgAl(0.7)	10.8	11.5	7.7	0.26	14.0	12.7	n.d.
Ni/MgAl(0.8)	11.7	10.9	5.2	0.17	13.4	11.8	n.d.
Ni/MgAl(0.9)	13.1	13.0	4.7	0.16	14.8	15.4	n.d.
Ni/MgO	8.2	8.6	n.d.	-	-	-	n.d.

^a Average Ni particle size was determined by XRD. ^b Average Ni particle size was obtained by HRTEM. ^c Coke deposition (graphitic carbon) was measured by TGA.

Figure 7b shows the Raman spectra of spent catalysts in DRM. Except for Ni/MgO, all catalysts display two peaks at around 1340 and 1590 cm⁻¹, corresponding to the structural defects of graphite (D bond) and in-plane carbon–carbon stretching vibrations of graphite layers (G bond), respectively [53,54]. This confirms the coke formation. From Ni/Al₂O₃ to Ni/MgAl(0.5), Ni/MgAl(0.6), . . . , and Ni/MgAl(0.9), the peak intensities of both the D bond and G bond gradually decrease, implying a reduction in the coke deposition. No peaks are observed for Ni/MgO, indicating the absence of the coke formation. This trend aligns with the basic intensity and total basicity of the catalysts, as more and stronger basic sites enhance the CO₂ adsorption, thereby supplying more surface oxygen to inhibit the coke deposition [55,56].

Figure 7c further presents the TGA profiles of the spent catalysts. These curves can be divided into three regions: (1) the desorption of H₂O and CO₂ below 200 °C, (2) the removal of the amorphous carbon and oxidation of metallic Ni between 200 and 400 °C, and (3) the gasification of graphitic carbon above 400 °C [55,57]. The amorphous carbon is readily oxidized, whereas the graphitic carbon is less reactive, leading to a catalyst deactivation [14,58,59]. Based on the TGA curves, the amount of graphitic carbon in each catalyst is determined, as listed in Table 3. Consistent with the Raman analysis, catalysts with a stronger basicity exhibit a lower graphitic carbon deposition. Notably, no detectable carbon formation was observed on Ni/MgO, whereas Ni/ γ -Al₂O₃ shows the highest coke content (11.3 wt.%) and coking rate (0.38 wt.%/h).

Like the spent catalysts in the DRM, those in the CSCR. M exhibit an increase in the Ni crystallite size (Figure 7d and Table 3). However, both the D bond and G bond are indiscernible in the spent catalysts of the CSCR. M, except for very weak signals observed for Ni/Al₂O₃ (Figure 7e). Although the CH₄ decomposition occurs in the CSCR. M, as evidenced by the H₂/CO ratio exceeding two, the formed coke can react with steam at high temperatures, releasing carbon oxides and hydrogen. Consequently, no coke is detected in the spent catalysts. This is further supported by the TGA analysis (Figure 7f), where no weight loss is observed above 400 °C, confirming the absence of the graphitic carbon. Since Ni/MgO is only tested for 10 h in the CSCR. M due to its low activity, its spent sample is not analyzed.

Figures S5 and S6 present the HRTEM and EDS mapping images as well as the Ni particle size distributions of the spent catalysts in the DRM and CSCR. M, respectively. Similarly to the XRD results, the HRTEM analysis confirms an increase in the Ni particle size after 30 h of operation (Table 3). However, Ni particles maintain a uniform distribution on the supports. Both XRD and HRTEM analyses indicate that the Ni particle growth is more pronounced in the CSCR. M than in the DRM. This difference can be explained by the role of steam in

accelerating Ni particle sintering. As demonstrated by Sehested et al. [60], steam enhances sintering kinetics through the generation of $\text{Ni}_2\text{-OH}$ complexes on the nickel surface. These complexes have a significantly lower energy barrier for formation compared to nickel adatoms, while their diffusion energy barrier is much higher. This dual effect—easy formation but hindered mobility—promotes a localized structural reorganization, ultimately driving the particle coalescence and growth under steam-containing environments.

The lattice parameters of MgAl_2O_4 in the spent Ni/MgAl(x) catalysts are determined from the XRD patterns and summarized in Table 2. In both the DRM and CSCRM, the lattice parameters of the spent catalysts are consistently larger than those of their fresh counterparts, indicating the reduction of Ni from the Ni- MgAl_2O_4 matrix during the reforming process. Interestingly, Ni/MgAl(0.7) undergoes the least change in the lattice parameter of MgAl_2O_4 before and after the DRM reaction, while Ni/MgAl(0.8) exhibits the smallest variation in the CSCRM. The structural stability of MgAl_2O_4 throughout the reaction process is beneficial, contributing to the superior stability of Ni/MgAl(0.7) in the DRM and Ni/MgAl(0.8) in the CSCRM. In addition, the relatively small Ni particle size and low coke deposition (in DRM) further enhance the catalytic performance of Ni/MgAl(0.7) in the DRM and Ni/MgAl(0.8) in the CSCRM. Based on these findings, these two catalysts are selected for a 100 h TOS evaluation in the following section.

2.3. Long-Term Test of Screened Catalysts

Over 100 h of the DRM reaction, Ni/MgAl(0.7) exhibits excellent stability (Figure 8a), with CH_4 and CO_2 conversions of 77.2% and 86.4% at 100 h, declining by only 5.4% and 2.9%, respectively, compared to their values at 1 h. The H_2/CO ratio remains stable between 0.92 and 0.94. In comparison, Ni/MgAl(0.8) shows a relatively lower stability in the CSCRM (Figure 8b), with CH_4 and CO_2 conversions of 80.0% and 62.1% at 100 h, decreasing by 10.5% and 8.9%, respectively, from their initial values. Nevertheless, most of the activity loss occurs within the first 50 h of the CSCRM, after which the catalyst remains stable. Additionally, the H_2/CO ratio stays steady at 2.06–2.09 throughout the process. For Ni/MgAl(0.8) in the CSCRM, the average Ni particle size increases from 7.1 nm in the fresh state to 11.8 nm after 30 h of the TOS and further to 18.4 nm after 100 h of the TOS (Figure 8d). This substantial growth indicates a pronounced sintering of Ni particles, which accounts for the observed decline in catalytic activity. In comparison, Ni/MgAl(0.7) in the DRM shows a more moderate increase in the Ni particle size, from 7.6 nm to 11.5 nm and then to 13.2 nm (Figure 8c) over the same period. It is noteworthy that Ni particles remain well-dispersed on both Ni/MgAl(0.7) and Ni/MgAl(0.8) despite varying degrees of particle size growth.

Regarding the coke deposition, no graphitic carbon is detected on Ni/MgAl(0.8) during the initial 30 h of the CSCRM (Figure 7e,f), and only a minimal amount (0.5 wt.%) forms after 100 h of evaluation (Figures S7 and S8). In contrast, Ni/MgAl(0.7) in the DRM exhibits a higher coke deposition, reaching 7.7 wt.% after 30 h and 9.5 wt.% after 100 h. As shown in Figure 8c,d, carbon nanotubes are observed on the spent Ni/MgAl(0.7) but are absent on the spent Ni/MgAl(0.8). Despite the relatively high initial coking rate of Ni/MgAl(0.7) (0.26 wt.%/h during the first 30 h), the markedly lower rate observed thereafter (0.026 wt.%/h from 30 to 100 h, only one-tenth of the initial rate) highlights good anti-coking properties. In addition, the lattice parameters of MgAl_2O_4 in Ni/MgAl(0.7) and Ni/MgAl(0.8) after 100 h of operation are determined to be 8.0673 and 8.0904 Å, respectively, based on their XRD patterns (Figure S9). Compared to the values after 30 h (8.0652 Å for Ni/MgAl(0.7) and 8.0817 Å for Ni/MgAl(0.8)), Ni/MgAl(0.7) demonstrates a greater structural stability of MgAl_2O_4 . Therefore, Ni/MgAl(0.7) is a promising candidate for the DRM process. As for Ni/MgAl(0.8), although it experiences an initial activity

decay, its performance remains stable thereafter, making it a good catalyst for the CSCRM. Nevertheless, extended stability testing beyond 100 h would be required to fully assess both catalysts' durability.

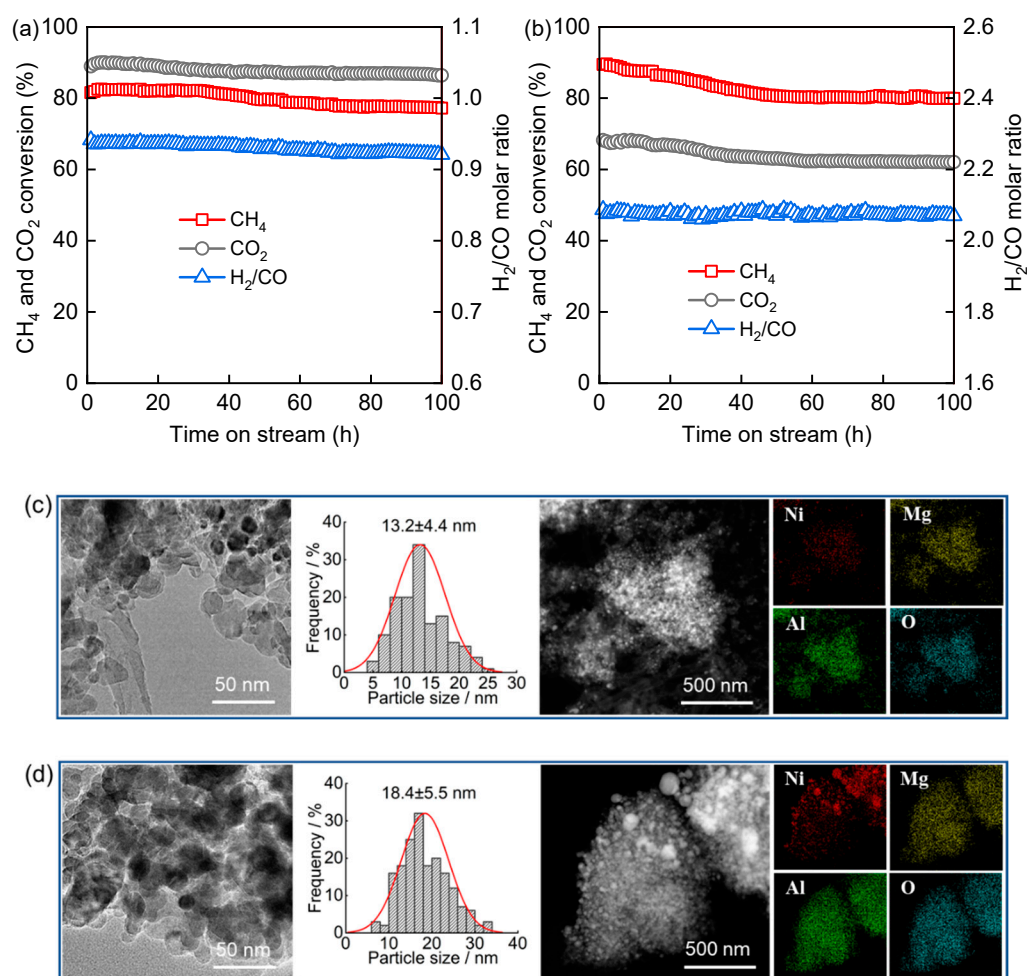


Figure 8. Catalytic performance of (a) Ni/MgAl(0.7) in DRM and (b) Ni/MgAl(0.8) in CSCRM, as well as HRTEM, Ni particle size distribution, and EDS mapping of (c) spent Ni/MgAl(0.7) and (d) spent Ni/MgAl(0.8).

3. Experimental Section

3.1. Materials

Mg(NO₃)₂·6H₂O (≥99.0%), Al(NO₃)₃·9H₂O (≥99.0%), and Ni(NO₃)₂·6H₂O (≥98.0%) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NH₃·H₂O (25–28%) and absolute ethanol (≥99.7%) were obtained from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Urea (≥99.0%) and MgO (≥99.9%) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). γ-Al₂O₃ (≥99.0%) was purchased from Alfa Aesar China (Tian Jin) Co., Ltd. (Tianjin, China). All chemicals were used without further purification.

3.2. Support Preparation

The MgO-Al₂O₃ mixed oxide supports were synthesized using the co-precipitation method. First, predetermined amounts of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in 150 mL deionized water. NH₃·H₂O was then added at a rate of 30 mL/h using a metering pump under vigorous stirring until the solution reached a pH of 10.5. The mixture was stirred at room temperature for 4 h, after which the resulting precipitate was

filtered, repeatedly washed with absolute ethanol, and dried at 120 °C for 12 h. Finally, the precipitate was calcined in a muffle furnace by heating from room temperature to 830 °C at 5 °C/min and holding at 830 °C for 2 h. The Mg/Al molar ratio in MgO-Al₂O₃ was adjusted by varying the amounts of Mg and Al nitrates. In this study, five MgO-Al₂O₃ supports were prepared with Mg/Al ratios of 0.5, 0.6, 0.7, 0.8, and 0.9. For simplicity, these supports are denoted as MgAl(x), where x (= 0.5, 0.6, 0.7, 0.8, and 0.9) represents the Mg/Al molar ratio.

3.3. Catalyst Preparation

A series of Ni/MgAl(x) catalysts with a Ni loading of 10 wt.% were synthesized by urea hydrolysis using pre-synthesized MgAl(x) supports. First, 0.55 g of Ni(NO₃)₂·6H₂O and 1 g of urea were dissolved in 60 mL of deionized water in a round-bottomed flask under stirring, followed by the addition of 1 g of MgAl(x) and continued stirring for 2 h. The mixture was then gradually heated to 90 °C in a water bath under vigorously stirring. When the pH value of the solution reached 8.0, the mixture was cooled to room temperature and allowed to age statically for 6 h. The resulting solid was filtered, repeatedly washed with deionized water, dried at 120 °C for 12 h, and calcined at 830 °C for 2 h. Finally, the obtained catalyst powder (Ni/MgAl(x)) was pressed, crushed, and sieved to obtain particles in the 80–100 mesh range for subsequent catalytic performance evaluation. For comparison, Ni/MgO and Ni/Al₂O₃ catalysts were prepared using the same method with commercial MgO and Al₂O₃ supports, maintaining a Ni loading of 10 wt.%.

3.4. Catalyst Characterization

The specific surface area, pore volume, and average pore diameter of the samples were acquired by a N₂ physical adsorption instrument (Micromeritics ASAP 2460). The Brunauer–Emmett–Teller (BET) method was employed to calculate the specific surface area, while the Barrett–Joyner–Halenda (BJH) equation was used to determine the pore volume and average pore diameter. H₂ temperature-programmed reduction (H₂-TPR), CO₂ temperature-programmed desorption (CO₂-TPD), and CH₄ temperature-programmed desorption (CH₄-TPD) were conducted on a Micromeritics AutoChem 2920 instrument. For H₂-TPR, about 100 mg of catalysts was loaded into a quartz tube, purged with N₂ until the baseline stabilized, and then heated from room temperature to 800 °C at 10 °C/min in a flow of 10% H₂/N₂ (v/v, 30 mL/min). A thermal conductivity detector (TCD) was used to record the variation in the outlet signal with temperature. For CO₂-TPD, the reduced catalyst was loaded into a quartz tube, purged with He at 150 °C for 30 min, and then cooled to 50 °C. CO₂ was introduced for pulse adsorption until saturation, followed by He purging for 2 h to remove weakly adsorbed CO₂. The temperature was then increased from 50 to 800 °C at 10 °C/min under He flow, with the desorbed species monitored using a TCD to quantify CO₂ uptake. The procedure for CH₄-TPD was similar to that of CO₂-TPD. H₂ chemisorption experiments were performed on a Micromeritics AutoChem 2930 instrument. The crystal structure of the samples was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance equipped with a Cu K α radiation source (λ = 1.5406 Å) over a 2 θ range of 10–80°. The actual Ni loading of the catalyst was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 725ES). The micromorphology of the samples was observed by a field emission scanning electron microscope (FESEM, Nova NanoSEM 450). High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100) with energy-dispersive X-ray spectroscopy (EDS) mapping was employed to analyze the dispersion and particle size of metallic Ni. The amount of carbon deposition on the spent catalysts was quantified using a thermogravimetric analyzer (TGA, PerkinElmer TGA-4000). Raman spectroscopy was performed on a laser micro-Raman spectrometer

(LabRAM HR Evolution) with a laser wavelength of 532 nm. The measurement range was set from 1000 to 1800 cm^{-1} to identify the types of carbon deposits on the catalyst surface.

3.5. Catalytic Performance Test

The catalytic performance in DRM and CSCRM reactions was evaluated using a fixed-bed reactor (a 10 mm diameter U-shaped quartz tube). Then, 0.05 g of 80–100 mesh catalyst was uniformly mixed with 0.45 g of quartz sand of the same size and loaded into the isothermal section of the reactor, which was supported by high-temperature quartz wool. Prior to the reaction, the catalyst was reduced in 30% H_2/N_2 (v/v , 100 mL/min) by heating from room temperature to 800 °C at 10 °C/min, followed by maintaining at 800 °C for 2 h. After reduction, the hydrogen flow was stopped, and the system was purged with N_2 for 30 min to remove residual H_2 . The temperature was then adjusted to 750 °C for the DRM or CSCRM reaction. For DRM, the reaction conditions were as follows: $T = 750$ °C, $P = 0.1$ MPa, $\text{CH}_4:\text{CO}_2 = 1:1$ (v/v), total gas flow rate = 100 mL/min, and GHSV = 120 $\text{L}/(\text{g}_{\text{cat}} \cdot \text{h})$. For CSCRM, the conditions were as follows: $T = 750$ °C, $P = 0.1$ MPa, $\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2 = 2.5:2:1$ ($v/v/v$), total gas flow rate = 110 mL/min, and GHSV = 132 $\text{L}/(\text{g}_{\text{cat}} \cdot \text{h})$.

The product gas was first passed through an ice trap to remove steam and then mixed with 10 mL/min of N_2 as an internal standard. The resulting gas mixture was analyzed online by a dual-channel microgas chromatograph (Inficon 3000). The conversions of CH_4 (α_{CH_4}) and CO_2 (α_{CO_2}), as well as the H_2/CO molar ratio ($R_{\text{H}_2/\text{CO}}$), were calculated using Equations (3)–(5), respectively.

$$\alpha_{\text{CH}_4} = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100\% \quad (3)$$

$$\alpha_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100\% \quad (4)$$

$$R_{\text{H}_2/\text{CO}} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CO},\text{out}}} \quad (5)$$

where $F_{i,\text{in}}$ and $F_{i,\text{out}}$ are the molar flow rates of species i at the reactor inlet and outlet, respectively.

4. Conclusions

Five Ni/MgO- Al_2O_3 catalysts (Ni/MgAl(x), $x = 0.5, 0.6, 0.7, 0.8$, and 0.9) were successfully synthesized via co-precipitation and urea hydrolysis, with Ni/MgO and Ni/ Al_2O_3 prepared for comparison. The characterization reveals that all catalysts possess mesoporous structures. The reducibility of Ni/MgAl(x) surpasses that of Ni/MgO and Ni/ Al_2O_3 , which is attributed to the formation of less reducible phases in the latter systems: a NiO-MgO solid solution in Ni/MgO and a NiAl_2O_4 spinel in Ni/ Al_2O_3 . In contrast, Ni/MgAl(x) forms a MgAl_2O_4 spinel structure with a partial Ni incorporation into the lattice, resulting in more metal active sites. Ni/MgO shows the strongest CO_2 -catalyst interactions (facilitating CO_2 adsorption and activation) but the weakest CH_4 -Ni interactions (for CH_4 adsorption and activation), whereas Ni/ Al_2O_3 displays the opposite behavior. This activation imbalance results in their poor performance in both the DRM and CSCRM. In comparison, Ni/MgAl(x) ($x = 0.6$ – 0.8) exhibits a high catalytic performance, which is mainly attributed to their abundant active sites and balanced activation capability. Notably, Ni/MgAl(0.7) achieves the highest DRM activity, while Ni/MgAl(0.8) excels in the CSCRM, highlighting the importance of fine-tuning the catalyst composition for specific reforming conditions. Both catalysts also exhibit a good stability during 100 h of operation, demonstrating their potential for long-term applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15070659/s1>, Figure S1: (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of supports. Figure S2: (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of catalysts. Figure S3: Lattice fringes of reduced (a) Ni/MgAl(0.7) and (b) Ni/MgAl(0.8) catalysts. Figure S4: CO₂-TPD curves for supports and catalysts (solid lines: supports; dashed lines: catalysts). Figure S5: HRTEM, Ni particle size distributions, and EDS mapping images of the spent catalysts in DRM. Figure S6: HRTEM, Ni particle size distributions, and EDS mapping images of the spent catalysts in CSCRM. Figure S7: Raman spectra of spent Ni/MgAl(0.7) in DRM and spent Ni/MgAl(0.8) in CSCRM after 100 h. Figure S8: TGA profiles of spent Ni/MgAl(0.7) in DRM and spent Ni/MgAl(0.8) in CSCRM after 100 h. Figure S9: XRD patterns of spent Ni/MgAl(0.7) in DRM and spent Ni/MgAl(0.8) in CSCRM after 100 h.

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Conflicts of Interest: The authors declare no conflicts of interest.

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