

Article

Synergistic Role of ZrO₂ Promoter and Ni–NiO–ZrO₂ Networks in Improving Ni Catalysts for Dry Methane Reforming at Low Temperature

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Abstract

In this work, a rational catalyst design based on interfacial architecture engineering is proposed for low-temperature dry methane reforming (DMR) at 550 °C. Ni-based catalysts containing 10 wt% Ni were developed on a γ -Al₂O₃ support modified with 9 wt% MgO–1 wt% ZrO₂. Zirconia promoters were introduced either by dry impregnation or via an ammonia vapor-assisted route to construct a Ni–NiO–ZrO₂ interfacial network. The effects of ZrO₂ content (0, 1, and 3 wt%) and synthesis route on metal–support interactions, oxygen mobility, and coke resistance were systematically investigated. ZrO₂ promotion increased the fraction of reducible Ni species and preferentially enhanced CO₂ activation, thereby promoting the reverse water–gas shift (RWGS) reaction and lowering the H₂/CO ratio. In contrast, ammonia vapor-assisted preparation induced the formation of an LDH-derived Ni–NiO–ZrO₂ surface network, which increased the concentration of surface-accessible Ni species, suppressed excessive zirconia coverage, and significantly improved apparent oxygen mobility. These synergistic structural features are consistent with enhanced oxygen-assisted carbon removal and improved coke management through regulation of the nature of carbon species, leading to more balanced activation of CH₄ and CO₂. Overall, this study provides insights into interfacial structure–performance relationships for designing efficient Ni-based catalysts for CO₂ utilization.

Keywords: Ni–ZrO₂ catalysts; dry methane reforming; oxygen mobility; metal–support interaction; ammonia vapor-assisted impregnation

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1. Introduction

Net zero emissions in energy production are defined as a process wherein the cumulative greenhouse gas (GHG) emissions arising from both the production and utilization stages of energy or derived products are effectively neutralized [1]. Within this conceptual framework, the dry methane reforming (DMR) process represents an attractive process that aligns with the net zero paradigm [2–4]. The overall DMR reaction consumes two of the most prevalent atmospheric greenhouse gases (methane (CH₄) and carbon dioxide (CO₂)) to yield synthesis gas (syngas), which is primarily composed of hydrogen (H₂) and

carbon monoxide (CO) (Equation (1)). Hydrogen can be directly utilized as a clean energy carrier, while syngas serves as a valuable intermediate for the synthesis of sulfur-free and nitrogen-free hydrocarbons or other chemical products [5,6]. Consequently, when assessed on a system-wide basis, DMR does not result in a net increase in atmospheric GHG concentrations.

Typically, the DMR process relies on efficient catalysts to alleviate severe reaction conditions; however, it still operates at high temperatures of 650–800 °C under atmospheric or elevated pressures [7,8]. Among various catalytic systems, nickel-supported catalysts are the most widely employed owing to their favorable balance of activity, stability, and cost-effectiveness. In such systems, metallic Ni particles dispersed on suitable supports serve as the primary active sites for reforming reactions [2,5]. Nonetheless, high operating temperatures required for DMR accelerate Ni particle sintering and intensify parasitic reactions, including the Boudouard reaction (Equation (2)) and methane decomposition (Equation (3)). These processes collectively lead to carbon deposition that remains unoxidized on the catalyst surface [7,9–11]. Additionally, the reverse water–gas shift (RWGS) side reaction may occur because CO₂ acts as a reactant and water can be formed through reduction by hydrogen (Equation (4)), thereby decreasing the H₂/CO ratio in the syngas product [12,13]. Therefore, operating DMR at lower temperatures is highly desirable, as it can effectively mitigate Ni sintering and suppress carbon deposition. However, owing to the highly endothermic nature of the DMR reaction, achieving sufficient activity at reduced temperatures remains challenging. This limitation necessitates the rational design of Ni-based catalysts, including optimization of metal–support interactions, active site dispersion, and support composition, to enable efficient low-temperature DMR operation.



The mitigation of these challenges relies on the rational design of Ni-based catalysts with synergistic physicochemical properties, including well-defined interfacial interactions that can be reinforced through the formation of structural networks. Such architectures facilitate the efficient adsorption and dissociation of CH₄ and CO₂, as well as the transfer of reaction intermediates, thereby favoring the desired DMR pathway [14–17]. Furthermore, catalytic performance can be further improved when the support promotes water dissociation and supplies active oxygen species, which contributes to suppressing carbon accumulation and Ni sintering [10,18].

On this basis, numerous studies have focused on the development of highly dispersed Ni catalysts with strong metal–support interactions using high-surface area supports such as γ -Al₂O₃. Although these systems exhibit improved resistance to sintering, the role of the support extends beyond metal dispersion alone. In particular, the acidic nature of Al₂O₃ facilitates CH₄ activation but is less effective in promoting CO₂ adsorption, which can result in carbon deposition. To overcome this limitation, mixed metal oxide supports, including MgAl₂O₄, Mg₂Zr_xAl_{1-x}, and CeO₂–Al₂O₃, have been investigated to enhance surface basicity and oxidation capacity [19–23]. However, their synthesis is often complex and typically yields limited quantities. More recently, a surface modification strategy for commercially available γ -Al₂O₃ has been proposed, in which 9 wt% MgO and 1 wt% ZrO₂ are incorporated via a simple impregnation method. The presence of MgO increases surface basicity and thus enhances CO₂ adsorption, while the introduction of a

small amount of ZrO_2 improves oxygen mobility and stabilizes reactive oxygen species. At this optimized composition, the synergistic MgO – ZrO_2 interaction favored the formation of labile oxygen species that are capable of oxidizing carbon precursors at Ni active sites, thereby effectively suppressing coke formation during DRM. Moreover, this approach enables large-scale and cost-effective modification of $\gamma\text{-Al}_2\text{O}_3$, offering a practical pathway for catalyst development [24]. In addition to support modification, the incorporation of suitable promoters represents another effective strategy to further improving the activity and stability of Ni-based catalysts in DMR.

Promoters are often incorporated into Ni-based catalysts to improve their activity and stability in DMR. Oxides of alkali and alkaline earth metals such as K, Mg or Ca increase catalyst basicity, thereby enhancing CO_2 adsorption and facilitating the conversion of carbon species formed from CH_4 decomposition into CO [25–27]. Meanwhile, CeO_2 and ZrO_2 act as redox promoters, providing high oxygen storage and transfer capacities that suppress carbon deposition by promoting oxygen mobility across the catalyst surface [28–30]. In addition, hierarchical surface modification can be achieved by forming layered hydroxides (LH) or layered double hydroxides (LDH) via the ammonia vapor diffusion impregnation method. These sheet-like structures generate interconnected architectures that can facilitate oxygen transfer between active metal species and their oxides. Furthermore, the LH/LDH-derived structures exhibit a so-called “memory effect,” enabling partial reconstruction of hydroxide phases under suitable conditions and promoting the formation of hydroxide-related intermediates, thereby preventing the condensation of surface intermediates into water [31–33].

While extensive efforts have been devoted to improving Ni-based catalysts for DMR, the simultaneous regulation of support basicity, oxygen mobility, and interfacial metal–support interactions remains challenging, particularly for low-temperature operation. In this study, a synergistic catalyst design strategy is proposed by integrating surface-modified $\gamma\text{-Al}_2\text{O}_3$ with tailored ZrO_2 promotion and controlled synthesis pathways to regulate the interfacial structure of Ni-based catalysts. By tuning both the mode of ZrO_2 incorporation and the synthesis route, this work elucidates how interfacial architecture governs oxygen mobility, surface basicity, and coke resistance under the investigated low-temperature DMR operation. The findings provide fundamental insights into structure–performance relationships and offer a practical framework for the rational design of efficient Ni-based catalysts for CO_2 utilization in the context of net zero emission strategies.

2. Results and Discussion

2.1. Catalyst Properties

The surface morphology of the catalysts was examined by FESEM, as presented in Figure 1. Calcined catalysts prepared via conventional impregnation (Figure 1a–c) exhibited dispersed particles with a relatively isolated distribution, whereas ZrO_2 -promoted samples displayed finer particles compared to the unpromoted catalyst, suggesting improved dispersion of the active species. In contrast, the catalyst synthesized through the ammonia-assisted impregnation method (Figure 1d) exhibited a rough and interconnected surface morphology within the active phase layer, which was indicative of the formation of a NiO – ZrO_2 network during preparation [31,34,35].

Crystalline phases of modified Al_2O_3 support and catalysts were investigated by XRD (Figure 2). The diffraction patterns of all samples displayed characteristic reflections of the $\gamma\text{-Al}_2\text{O}_3$ phase at $2\theta = 31.9^\circ$, 37.6° , 39.5° , 45.8° , 60.9° , and 66.8° (JCPDS No. 00-010-0425) [35,36]. In addition, diffraction peaks corresponding to MgO were observed at $2\theta = 43^\circ$ and 62.3° (JCPDS No. 01-075-0447) [37]. For the catalyst samples, reflections attributed to the NiO phase appeared at $2\theta = 37^\circ$, 43° , and 62.5° (JCPDS No. 01-078-4374) [38]. The diffraction peaks observed at $2\theta = 31^\circ$, 37° , 45.7° , 59° , and 66° were attributed to the presence

of spinel-type phases, specifically NiAl_2O_4 (JCPDS No. 01-078-695) and MgAl_2O_4 (JCPDS No. 01-084-0377) [39,40]. These phases were likely formed through the incorporation of Ni^{2+} or Mg^{2+} ions into the $\gamma\text{-Al}_2\text{O}_3$ crystal lattice, indicating the formation of a thermodynamically stable structure via isomorphous substitution within the Al_2O_3 framework [41,42]. Such structural transformation was expected to enhance the dispersion of metal species on the catalyst surface. However, no diffraction peaks corresponding to ZrO_2 were detected in the support diffractogram, which was ascribed to the low ZrO_2 content and its high dispersion below the XRD detection limit. The NiO crystallite sizes calculated from the XRD data, as summarized in Table 1, revealed that ammonia vapor-assisted impregnation led to larger NiO crystallites compared to conventional impregnation. The formation of these larger crystallites was plausibly associated with the development of an interconnected, network-like surface morphology, as observed in the FESEM images. This observation suggested the growth of coherent NiO domains through interfacial interactions during catalyst preparation.

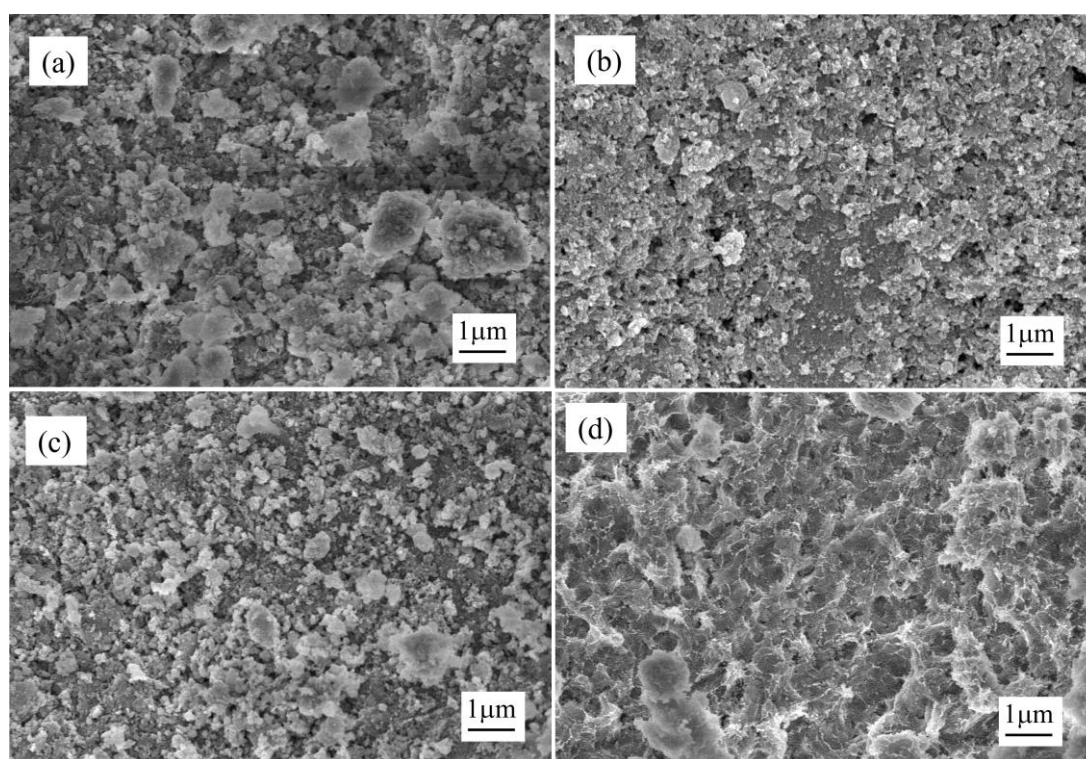


Figure 1. FESEM micrographs of calcined (a) 10N/9M1ZA, (b) 10N1Z/9M1ZA, (c) 10N3Z/9M1ZA, and (d) 10N3Z(T)/9M1ZA catalysts.

The nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves are shown in Figure 3. The specific surface area was determined using the BET method, the pore size distribution was derived from the BJH method based on the desorption branch and the total pore volume was calculated from the adsorption amount at $P/P_0 \approx 0.99$ in accordance with the IUPAC recommendation. All textural parameters are summarized in Table 1. The support and catalysts exhibited type IV isotherms, characteristic of mesoporous materials, with H1-type hysteresis loops associated with relatively uniform and interconnected cylindrical pores [35,43]. The pore size distribution analysis was used to evaluate the BJH method and indicated the predominant pore size of 4.5–5 nm, with the support possessing slightly smaller pores than the catalyst samples. Consistent with this, the BET results showed that the support exhibited the highest specific surface area ($145 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.439 \text{ cm}^3 \text{ g}^{-1}$). Upon incorporation of the active species via the impregnation method, both the surface area and pore volume

decreased, whereas the pore radius increased relative to the support. This behavior was attributed to a pore blocking effect, in which the impregnated species partially occluded smaller pores, thereby limiting access to the internal surface area [24,34,44]. The micropore volume was estimated using the Dubinin–Radushkevich method based on the adsorption data at $P/P_0 < 0.1$. All samples exhibited similar micropore volumes in the range of 0.044–0.050 $\text{cm}^3 \text{g}^{-1}$ (Table 1), indicating that mesoporosity remained dominant after metal loading. A slight decrease in micropore volume after impregnation suggested partial pore blocking of micropores by Ni-based species.

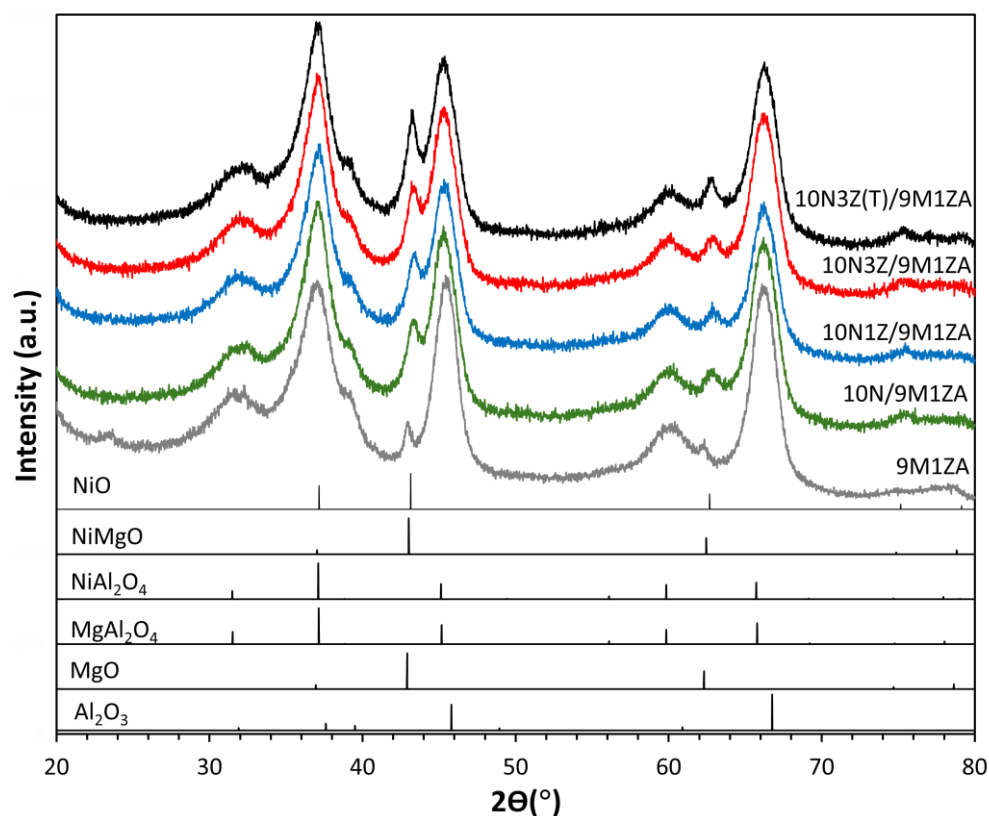


Figure 2. XRD patterns of all catalysts and the modified alumina support.

Table 1. The textural properties of all samples.

Samples	Surface Area ^a ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ^b ($\text{cm}^3 \text{g}^{-1}$)	Micropore Volume ^c ($\text{cm}^3 \text{g}^{-1}$)	NiO Crystallite Size ^d (nm)
9M1ZA support	145	0.439	0.050	-
10N/9M1ZA	125	0.391	0.044	8.59
10N1Z/9M1ZA	132	0.420	0.046	8.63
10N3Z/9M1ZA	124	0.397	0.044	8.67
10N3Z(T)/9M1ZA	137	0.413	0.049	9.71

^a Calculated from BET method. ^b Calculated from single-point adsorption method. ^c Determined from the Dubinin–Radushkevich (DR) method. ^d Determined from XRD results.

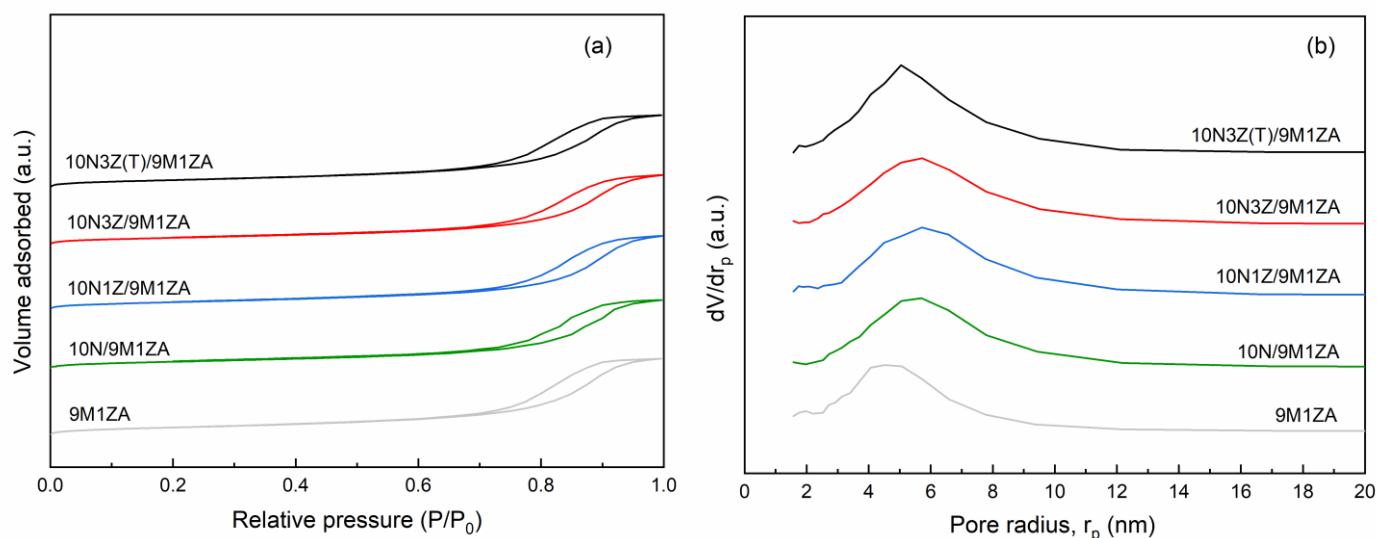


Figure 3. (a) N₂ adsorption–desorption isotherms and (b) pore size distributions of the modified alumina support and all catalysts.

A comparison among the catalysts prepared via incipient wetness impregnation revealed that the catalyst containing 1 wt% ZrO₂ exhibited a higher specific surface area and pore volume than both the undoped sample and that containing 3 wt% ZrO₂. This observation suggested that the incorporation of 1 wt% ZrO₂ enhanced the dispersion of NiO species [45]. However, further increasing the ZrO₂ content to 3 wt% likely induced pore blocking effects, thereby reducing the accessible surface area and pore volume [28]. In contrast, for the catalyst incorporating 3 wt% ZrO₂ within the active phase and prepared via the ammonia-assisted impregnation method, the formation of a network-like surface morphology resulted in an overall increase in surface area. This behavior was consistent with the FESEM observations, which indicated enhanced connectivity and surface coverage in the ammonia-assisted sample.

The reducibility of the prepared catalysts, influenced by metal–support interactions, was evaluated through H₂-TPR. As shown in Figure 4, all catalysts exhibited reduction onset above 500 °C, with major reduction peaks centered above 600 °C, which was characteristic of strong metal–support interactions (SMSI) [46–49]. Nevertheless, the reducibility varied with ZrO₂ content and surface morphology. The undoped catalyst (10N/9M1ZA) showed the lowest reduction temperature, indicating relatively weaker metal–support interactions compared to the ZrO₂-promoted catalysts. In contrast, incorporation of ZrO₂ into the active phase matrix (10N1Z/9M1ZA and 10N3Z/9M1ZA) significantly increased hydrogen consumption, reflecting a higher fraction of reducible Ni species. Although the reduction onset shifted to higher temperatures, suggesting stronger metal–support interactions, the overall reduction was more extensive. This behavior suggested that the presence of ZrO₂ facilitated the reduction of nickel oxide species, possibly via enhanced hydrogen spillover. This enhancement was likely associated with the formation of oxygen vacancies in the ZrO₂ lattice, which promoted hydrogen activation and increased lattice oxygen mobility, thereby generating a higher population of reducible active sites [50,51]. When comparing the two ZrO₂-doped samples prepared by incipient wetness impregnation, the sample containing 1 wt% ZrO₂ exhibited a lower reduction temperature, implying weaker metal–support interactions [28,52]. By contrast, the catalyst containing the 3 wt% ZrO₂ sample showed higher hydrogen uptake and a more uniform reduction profile, indicative of stronger and more homogeneous metal–support interactions. This behavior was attributed to the increased generation of oxygen vacancies and the incorporation of ZrO₂ into the active phase, coupled with its intimate interfacial

integration with the MgO-ZrO₂-modified γ -Al₂O₃ support surface [53,54]. Such structural evolution was expected to strengthen metal–support interactions and influence catalytic performance.

A comparative H₂-TPR analysis between 10N3Z(T)/9M1ZA and 10N3Z/9M1ZA revealed that the ammonia vapor-assisted impregnation induced the formation of an LDH intermediate prior to calcination, resulting in enhanced active site integration [55,56]. The TPR profile of 10N3Z(T)/9M1ZA showed two resolved reduction peaks at 620 °C and 777 °C, whereas 10N3Z/9M1ZA displayed a single peak centered at 782 °C. Furthermore, the O₂-TPD profile of 10N3Z(T)/9M1ZA (Figure 5) indicated enhanced oxygen mobility in the surface region, likely arising from improved connectivity within the active phase layer [24,57,58]. These features were evidenced by the shift in the reduction temperatures and the increased oxygen desorption relative to 10N3Z/9M1ZA, underscoring the crucial role of precursor chemistry and synthesis atmosphere in governing catalyst reducibility and oxygen mobility.

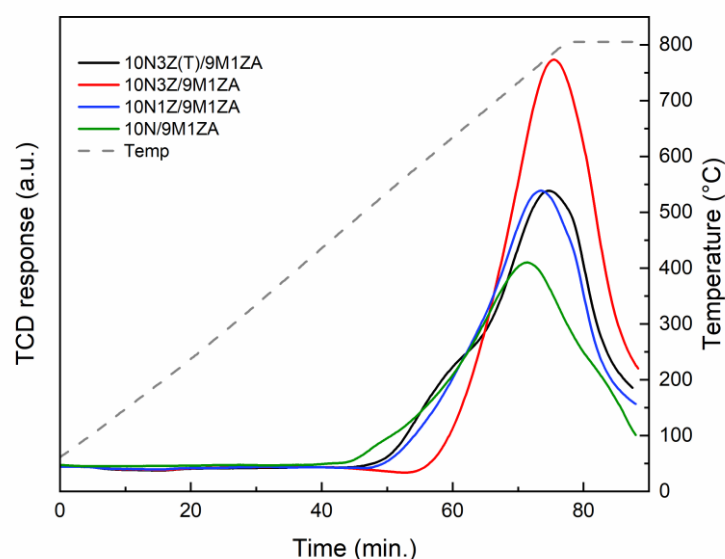


Figure 4. H₂-TPR profiles of all catalysts.

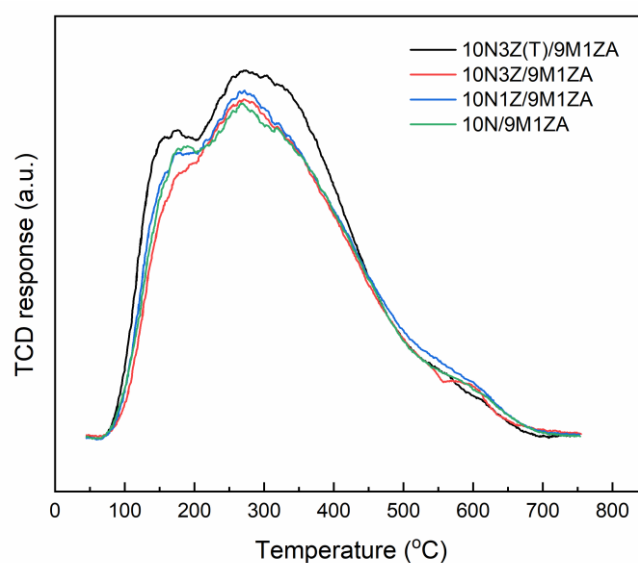


Figure 5. O₂-TPD profiles of all catalysts.

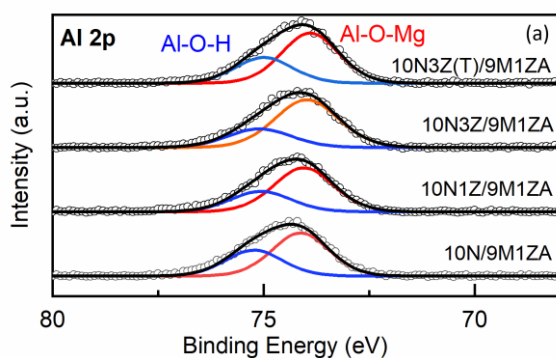
X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical states and elemental distributions of the reduced catalysts with varying ZrO₂ loadings and interfacial structures arising from different synthesis routes. The surface mass concentrations of the constituent elements (Mg, Ni, O and Al) are summarized in Table 2, while the deconvoluted core-level spectra of Al 2p, Zr 3d, O 1s and Ni 2p are presented in Figure 6.

The unpromoted catalyst (10N/9M1ZA) exhibited a surface nickel concentration of 7.89%. Upon the introduction of ZrO₂ as a promoter, a progressive decrease in surface Ni concentration was observed, declining to 6.54% for 10N1Z/9M1ZA and further to 5.25% for 10N3Z/9M1ZA. This inverse correlation between ZrO₂ loading and exposed surface nickel suggested that zirconia species were preferentially deposited in close proximity to, or partially covering, nickel oxide particles. This behavior, commonly described as decoration or shielding, has been frequently reported in promoted Ni-based catalyst systems and can reduce the accessibility of surface Ni active sites [59,60].

Simultaneously, the surface oxygen concentration increased from 49.52% to 52.05% with increasing ZrO₂ loading, consistent with the incorporation of an additional oxide component into the catalyst matrix. In contrast, the aluminum concentration remained relatively constant, indicating that the MgO-ZrO₂-modified γ -Al₂O₃ support surface was not significantly masked by promoter deposition [61]. Notably, the catalyst prepared using ammonia vapor-assisted impregnation, 10N3Z(T)/9M1ZA, exhibited a substantially higher surface nickel concentration of 6.85%, together with a lower oxygen concentration of 49.86%. This corresponded to an increase of more than 30% in exposed surface Ni compared with the conventionally prepared 10N3Z/9M1ZA catalyst. This enhancement was attributed to the formation of LDH-type intermediates during the impregnation step, which modified the metal deposition and redistribution pathway. Upon calcination, these intermediates promoted the development of a more integrated Ni-NiO-ZrO₂ surface network, leading to improved metal dispersion and reduced susceptibility to surface coverage by zirconia species. Consequently, the resulting catalyst exhibited enhanced oxygen mobility and a lower reduction temperature, in agreement with the H₂-TPR and O₂-TPD analyses.

Table 2. XPS quantitative analysis of the prepared catalysts.

Catalysts	Mass Concentration (%)			
	Mg 1s	Ni 2p	O 1s	Al 2p
10N/9M1ZA	1.34	7.89	49.52	41.25
10N1Z/9M1ZA	1.67	6.54	50.87	40.92
10N3Z/9M1ZA	1.90	5.25	52.05	40.79
10N3Z(T)/9M1ZA	1.01	6.85	49.86	42.27



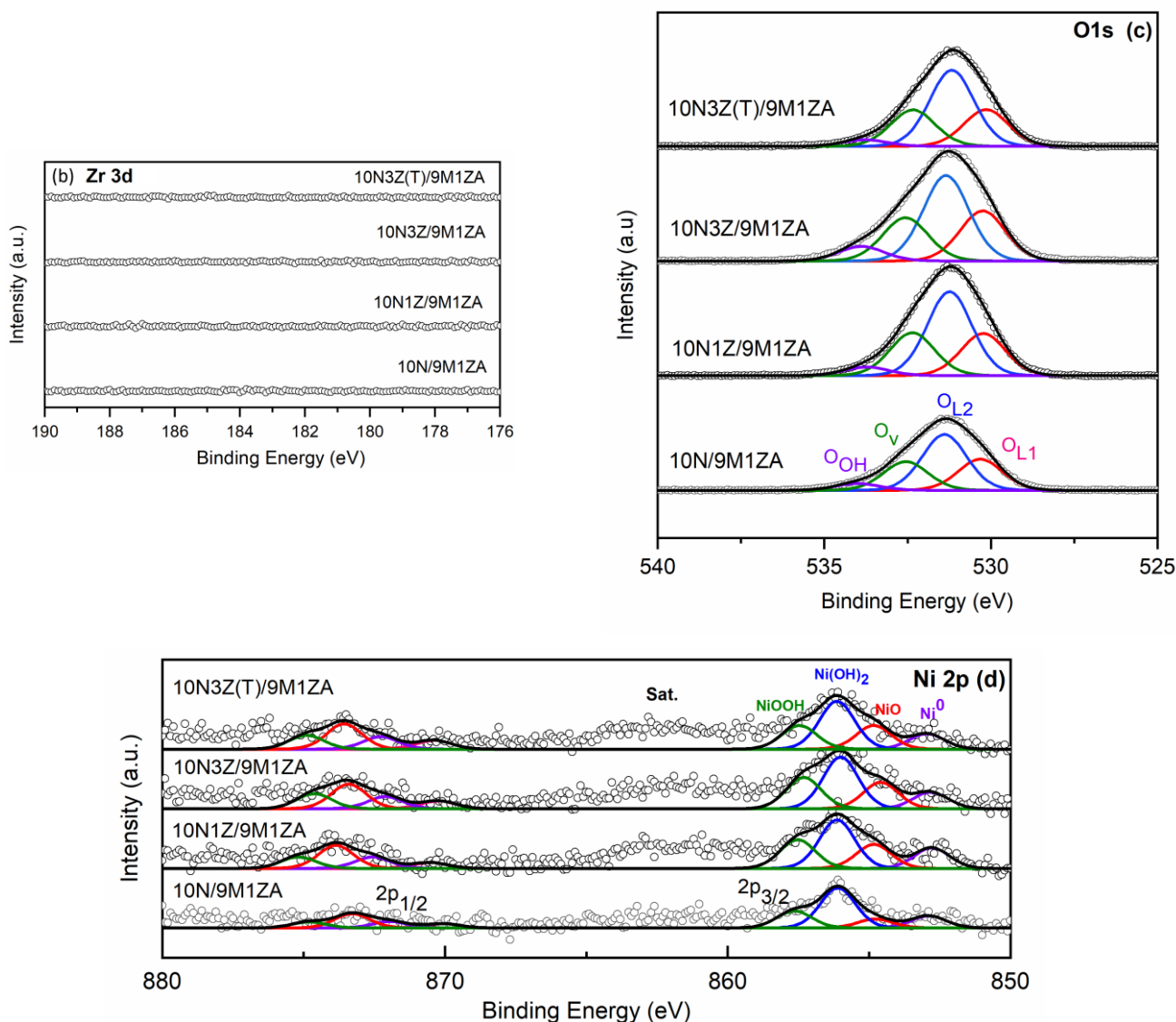


Figure 6. (a) Al 2p, (b) Zr 3d, (c) O 1s, and (d) Ni 2p XPS spectra of all catalysts (open circles: experimental data; black lines: fitted curves; colored lines: deconvoluted peaks).

2.2. Catalytic Performance in the DMR Reaction

The catalytic performance of the prepared catalysts in DMR reaction ($\text{CH}_4:\text{CO}_2:\text{N}_2 = 1:1:1$, 550°C , 6 h) was evaluated in terms of CH_4 and CO_2 consumption rates (Figure 7a,b) and syngas composition expressed as the H_2/CO ratio (Figure 7c). The Ni catalyst supported on modified alumina (10N/9M1ZA) exhibited average CH_4 and CO_2 consumption rates of $0.0405 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ and $0.0387 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively, corresponding to a CH_4/CO_2 consumption rate ratio of 1.05 and an average H_2/CO ratio of 0.56. Upon incorporation of 1 wt% ZrO_2 into the active phase, the CH_4 consumption rate decreased to $0.0341 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, whereas the CO_2 consumption rate increased to $0.0434 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, yielding a CH_4/CO_2 consumption rate ratio of 0.79 and an average H_2/CO ratio of 0.49. Further increasing the ZrO_2 loading to 3 wt % resulted in CH_4 and CO_2 consumption rates of 0.0438 and $0.0553 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively, with a corresponding rate ratio of approximately 0.79 and H_2/CO ratio = 0.49. In contrast, the 3 wt% ZrO_2 -promoted catalyst prepared via ammonia vapor-assisted impregnation delivered closely matched CH_4 and CO_2 consumption rates of 0.0596 and $0.0586 \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively, resulting in a near-unity CH_4/CO_2 consumption rate ratio of 1.02, with an H_2/CO ratio of 0.60. For the two

representative catalysts (10N3Z/9M1ZA and 10N3Z(T)/9M1ZA), duplicate catalytic tests were performed to evaluate reproducibility. The averaged values are presented in Figure 7 with standard deviation as error bars. The repeated experiments showed consistent activity trends, supporting the reliability of the observed catalytic performance.

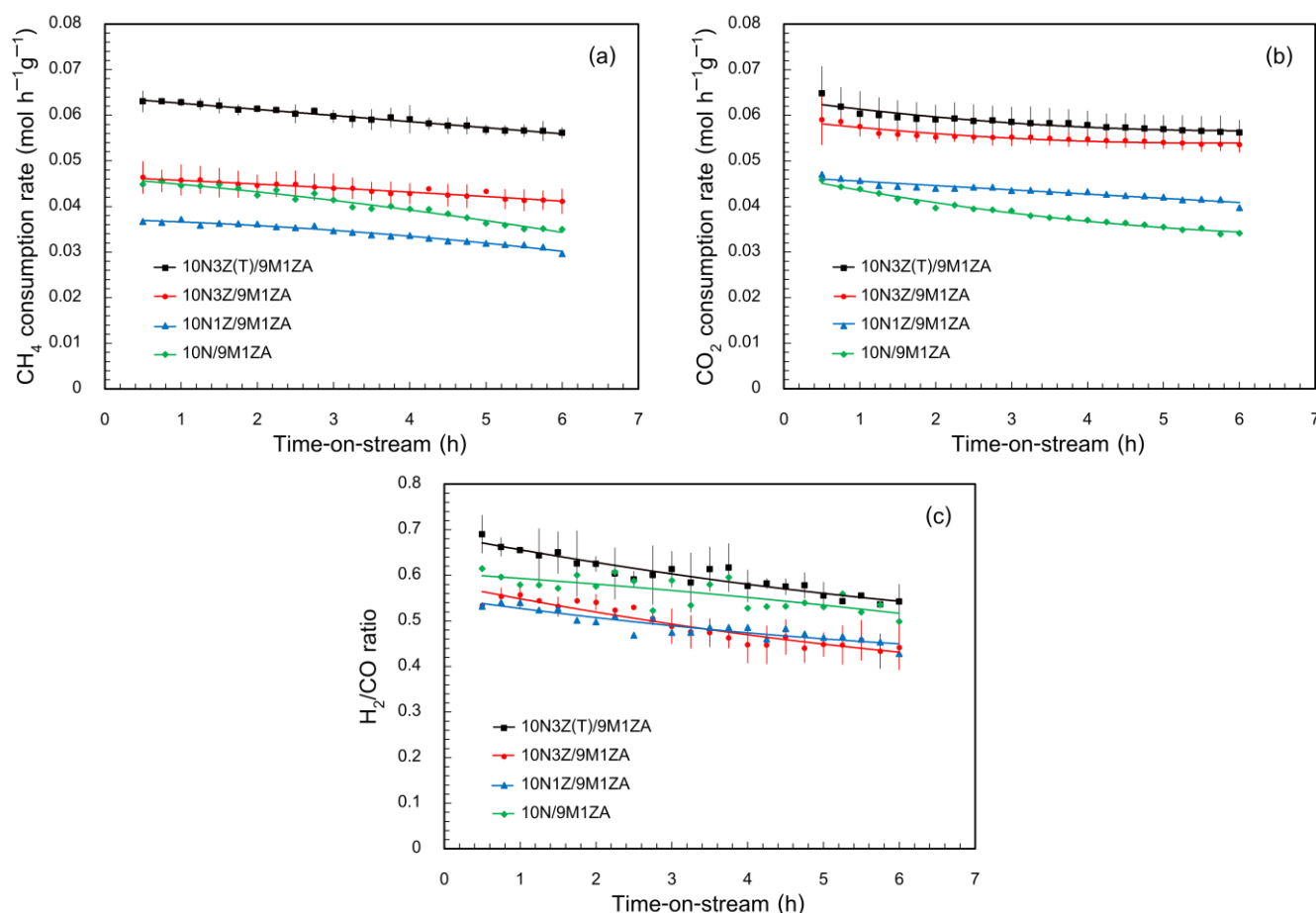


Figure 7. (a) CH₄ consumption rates, (b) CO₂ consumption rates, and (c) H₂/CO ratio for dry methane reforming (DMR) of all catalysts. Reaction conditions: 550 °C, 1 atm and WHSV = 9.823 kg_{feed} h⁻¹ kg_{cat}⁻¹ for 6 h. Error bars represent standard deviation from duplicate experiments for 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA.

Accordingly, variations in CH₄/CO₂ consumption rate ratios and H₂/CO ratios among the catalysts primarily reflected differences in the relative contributions of DRM and RWGS rather than changes in a single dominant reaction. The Ni catalyst supported on modified alumina exhibited CH₄/CO₂ consumption rate ratios and H₂/CO ratios closer to the theoretical values of stoichiometric DMR than the ZrO₂-promoted catalysts. This behavior was attributed to the balanced surface basicity and distribution of active sites provided by the modified alumina support, which enabled comparable activation of both CH₄ and CO₂ [24]. Upon ZrO₂ promotion, the introduction of oxygen vacancies enhanced CO₂ activation; however, partial coverage of Ni active sites by zirconia species favored CO₂-rich pathways and the RWGS reaction, resulting in a lower H₂/CO ratio. At higher ZrO₂ loading (3 wt%), the increased population of reducible Ni species and oxygen vacancies enhanced the overall reaction rate, although surface coverage effects remained influential. In contrast, the 3 wt% ZrO₂-promoted catalyst prepared via ammonia vapor-assisted impregnation formed an integrated Ni–NiO–ZrO₂ surface network that mitigated zirconia-induced site coverage. This hierarchical interfacial structure was associated with enhanced oxygen mobility and suggested to facilitate the transfer of oxygen intermediates

from NiO or ZrO₂ sites to CH_x species activated on metallic Ni, thereby favoring the DMR pathway and resulting in simultaneous improvements in activity and syngas selectivity. These reaction selectivity trends were consistent with the carbon oxidation behavior discussed in the carbon deposition section. It should be noted that the mechanistic interpretation presented here was based on ex situ characterization and catalytic performance trends; direct identification of surface intermediates will require future in situ or operando spectroscopic studies.

2.3. Carbon Deposits on Spent Catalysts

The spent catalysts 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA, recovered after 6 h of DMR reaction at 550 °C, were analyzed to determine the types and quantities of carbon deposits using temperature-programmed oxidation (TPO). The TPO profiles (Figure 8), together with the oxygen consumption during oxidation expressed as the percentage of carbon deposits relative to the catalyst weight (Table 3) revealed that although both catalysts possessed identical bulk compositions, their distinct surface structures resulting from different synthesis routes strongly influenced both the nature and amount of carbon formed. The carbon deposits observed on 10N3Z/9M1ZA were dominated by medium-to-hard-to-oxidize species, giving rise to a broad and continuous oxidation signal spanning 400–800 °C. This oxidation behavior was indicative of a relatively homogeneous population of carbon species, consistent with the uniform surface environment generated by conventional incipient wetness impregnation method.

In contrast, 10N3Z(T)/9M1ZA, synthesized via the ammonia vapor-assisted impregnation method to form a Ni–NiO–ZrO₂ interfacial network, displayed a diverse range of carbon deposits. This was evidenced by well-resolved oxidation peaks corresponding to easy-to-oxidize (120–300 °C, amorphous carbon), medium-to-oxidize (300–700 °C, graphitic carbon) and hard-to-oxidize (700–850 °C, filamentous carbon) species [24,31]. The presence of multiple oxidation features suggested that the networked surface structure created a more heterogeneous distribution of active sites. Such a heterogeneous environment was associated with enhanced surface oxygen availability, favoring the formation of more readily oxidizable carbon species. Moreover, the oxidation temperature of both the easy- and medium-oxidized carbon species on 10N3Z(T)/9M1ZA was shifted to lower values compared to those on 10N3Z/9M1ZA, indicating facilitated carbon removal. Despite this improvement in coke manageability, a fraction of hard-to-oxidize carbon remains, which can be attributed to the higher overall reaction rate of this catalyst, as observed in the catalytic performance tests.

Figure 9 shows the XRD patterns of the reduced and spent 10Ni3Z(T)/9M1ZA and 10Ni3Z/9M1ZA catalysts before and after DMR reaction. After the reaction, an additional diffraction peak was observed at approximately $2\theta \approx 26^\circ$, which was assigned to the (002) crystallographic plane of graphitic carbon. The appearance of this peak provided direct evidence of carbon deposition on the catalyst surface during the DMR process. The intensity of the graphite diffraction peak qualitatively correlated with the extent of coke formation. The formation of graphitic carbon was mainly associated with methane decomposition and the Boudouard reaction occurring on metallic Ni sites under DMR conditions. Nevertheless, despite the occurrence of carbon deposition, both catalysts demonstrate good structural stability after reaction. The characteristic diffraction peaks corresponding to NiO and the MgO–ZrO₂–Al₂O₃ support remained largely unchanged in the spent samples, indicating that the catalyst framework was stable and resistant to phase transformation or severe sintering under high-temperature DMR conditions.

Overall, the formation of a Ni–NiO–ZrO₂ interfacial network on the MgO–ZrO₂-modified alumina support was associated with enhanced oxygen mobility and was consistent with more effective removal of surface carbon species, thereby improving coke tolerance

while sustaining high catalytic activity under low-temperature DMR conditions. Therefore, the key innovation of the ammonia vapor-assisted route lies in tuning the interfacial architecture to control the nature of carbon species rather than merely suppressing carbon formation.

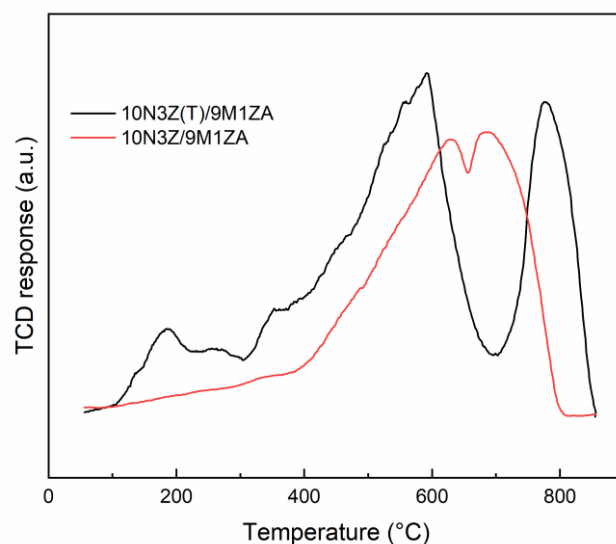


Figure 8. TPO profiles of the spent 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA catalysts.

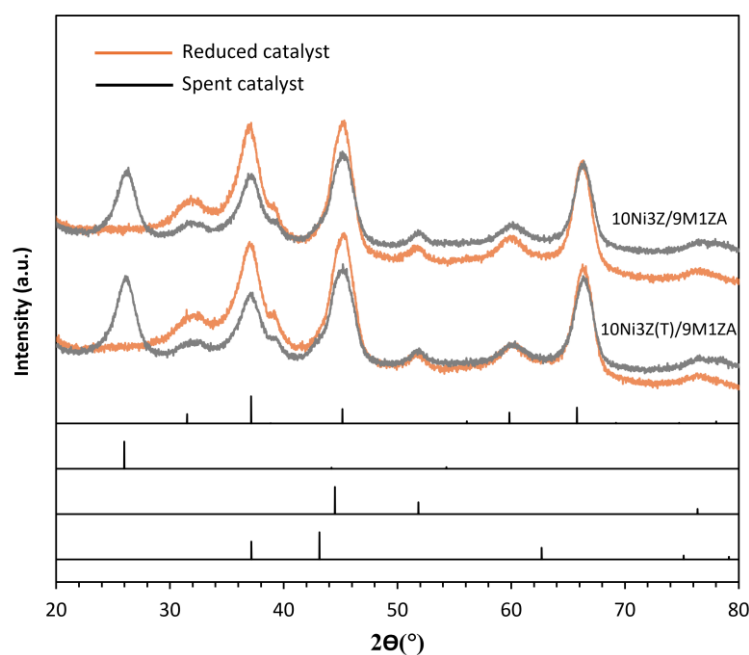


Figure 9. The X-ray diffraction patterns of the reduced and spent 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA catalysts.

Table 3. Oxygen uptake and coke deposition determined from TPO profiles for spent 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA catalysts.

Spent Catalyst	Oxygen Uptake in TPO (mmol g _{cat} ^{−1})	Carbon Deposition (%Dc)
10N3Z/9M1ZA	3.825	4.59
10N3Z(T)/9M1ZA	6.747	8.09

3. Materials and Methods

This study reports the development of Ni-based catalysts supported on γ -Al₂O₃ modified with 9 wt% MgO–1 wt% ZrO₂ (9M1ZA) for low-temperature DMR at 550 °C. Building on the enhanced basicity and oxygen mobility provided by modified support [24], ZrO₂ promoters were introduced to further tailor the interfacial structure between the active phase and the support. ZrO₂ was incorporated either as dispersed species within the Ni phase via incipient wetness impregnation or as a Ni–NiO–ZrO₂ surface morphology formed through an ammonia vapor-assisted impregnation route. Catalysts containing 10 wt% Ni with varying ZrO₂ loadings (0, 1, and 3 wt%) were prepared by incipient wetness impregnation and denoted as 10N/9M1ZA, 10N1Z/9M1ZA, and 10N3Z/9M1ZA, respectively. An additional catalyst containing 10 wt% Ni and 3 wt% ZrO₂ was synthesized using ammonia vapor diffusion and denoted as 10N3Z(T)/9M1ZA. The catalysts were comprehensively characterized by FESEM, H₂-TPR, O₂-TPD, and XPS. Catalytic performance was evaluated in DMR reaction at 550 °C, and carbon deposition on selected spent catalysts was characterized by TPO. In addition, XRD analysis of reduced and spent catalysts was conducted to evaluate structural stability after the DMR reaction.

3.1. Catalyst Preparation

All chemicals were used as received without further purification. Deionized water, γ -Al₂O₃ (98% Sigma-Aldrich, St. Louis, MO, USA), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 98%, Sigma-Aldrich), zirconyl nitrate hydrate (ZrO(NO₃)₂·xH₂O, 98%, Acros Organics, Waltham, MA, USA), and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98%, Acros Organics) were employed for catalyst preparation.

The MgO–ZrO₂-modified alumina support containing 9 wt% MgO and 1 wt% ZrO₂ (denoted as 9M1ZA) was prepared by incipient wetness impregnation following the procedure reported in our previous study [24]. Ni-based catalysts containing 10 wt% Ni with varying ZrO₂ loadings (0, 1, and 3 wt%) were synthesized by impregnating aqueous solutions of Ni(NO₃)₂·6H₂O and Zr(NO₃)₂·xH₂O onto the prepared support. The impregnated samples were dried at 60 °C overnight and subsequently calcined at 650 °C for 5 h in air. The resulting materials were pelletized and sieved to obtain particles in the size range of 355–710 μ m and denoted as 10N/9M1ZA, 10N1Z/9M1ZA, and 10N3Z/9M1ZA, respectively. The catalyst containing 3 wt% ZrO₂ incorporated within the active phase was additionally prepared via an ammonia vapor-assisted impregnation method. The impregnated powder was placed in a sealed vessel containing an aqueous NH₄OH solution and maintained under these conditions for 20 h to induce the formation of layered double hydroxide (LDH) intermediates [31,32]. The resulting material was then dried and calcined under the same conditions as described above to obtain the corresponding oxide catalyst.

3.2. Catalyst Characterization

Field emission scanning electron microscopy (FESEM) was employed to examine the surface morphologies of the catalyst samples using a JEOL JSM-7600F microscope (JEOL Ltd., Welwyn Garden City, UK) operated at an accelerating voltage of 5.0 kV. Prior to imaging, all samples were sputter-coated with a thin layer of platinum (Pt) using a JEOL JFC-1600 coater (JEOL Ltd., Welwyn Garden City, UK).

X-ray diffraction (XRD) analysis was performed to determine the crystalline phases of the fresh catalysts as well as the corresponding reduced and spent samples of the selected catalysts. The measurements were carried out using a Bruker AXS D8 Discover diffractometer equipped with Cu K α radiation (λ = 0.15406 nm), operated at 40 kV and 40 mA. Diffraction patterns were recorded over a 2 θ range of 20–80° at a scanning rate of 0.02° min^{−1}. The average crystallite size of NiO (*d*) was estimated from the full width at

half maximum (FWHM) of the most intense NiO diffraction peak at $2\theta \approx 43^\circ$ using the Debye–Scherrer equation (Equation (5)). In this calculation, K is the shape factor (0.94), λ is the X-ray wavelength (0.15406 nm), β is the line broadening in radians, and θ is the Bragg angle [34,62].

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (5)$$

N₂ physisorption measurements were performed at -196°C using a BET surface area analyzer (Autosorb iQ Station 2, Quantachrome Instruments, Boynton Beach, FL, USA) to investigate the textural properties of the fresh catalysts. Each sample was degassed under vacuum at 350°C for 4 h prior to analysis. Nitrogen adsorption–desorption isotherms were collected over a relative pressure (P/P_0) range of 0.01 to 1.0. The specific surface area was calculated using the multipoint Brunauer–Emmett–Teller (BET) method. The total pore volume was estimated from the nitrogen adsorption amount at $P/P_0 \approx 0.99$ (single-point method), assuming complete pore filling. The average pore diameter and the pore size distribution were evaluated using the Barrett–Joyner–Halenda (BJH) method.

Temperature-programmed reduction with hydrogen (H₂-TPR) was performed using a BELCAT-basic system (BEL JAPAN, Inc., Osaka, Japan) equipped with thermal conductivity detector (TCD) to evaluate the reducibility of the fresh catalysts and the strength of metal–support interactions. Prior to TPR analysis, each catalyst sample was pretreated under an argon (Ar) flow at 200°C for 1 h and subsequently cooled to 50°C . The reduction profiles were recorded under a 5 vol% H₂/Ar gas mixture while heating from 50 to 800°C at a rate of $10^\circ\text{C min}^{-1}$, followed by an isothermal hold at 800°C for 30 min.

Temperature-programmed desorption of oxygen (O₂-TPD) was conducted using the same apparatus as that employed for the H₂-TPR measurements to investigate the oxygen mobility of the fresh catalysts, which is related to the presence of oxygen vacancies. Prior to the measurement, each sample was pre-reduced at 600°C for 1.5 h and then cooled to 200°C under an Ar flow. Isothermal chemisorption of O₂ was subsequently carried out at 200°C for 1.0 h under an O₂ flow. Thereafter, non-chemisorbed oxygen species were removed by purging with Ar at room temperature for 30 min. Oxygen desorption was monitored over the temperature range from room temperature to 750°C at a heating rate of $10^\circ\text{C min}^{-1}$ under an Ar flow.

X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al K α X-ray source (1486 eV). The system was operated under ultra-high vacuum conditions (pressure $< 10^{-8}$ Torr). This technique was employed to investigate the surface elemental composition and oxidation states of the catalysts. High-resolution spectra were collected for Ni 2p, Al 2p, O 1s, and Zr 3d using a pass energy of 20 eV with an energy resolution of 0.1 eV. The binding energy scale was calibrated using the C 1s signal at 284.8 eV. Data analysis was performed using CasaXPS software (version 2.3.26, Casa Software Ltd., Teignmouth, UK), with background subtraction using the Shirley method and peak fitting using Gaussian–Lorentzian functions. The mass compositions were calculated from the integrated peak areas using the corresponding sensitivity factors.

To investigate the type and quantity of carbon deposited on the spent 10N3Z/9M1ZA and 10N3Z(T)/9M1ZA catalysts after DMR reaction, temperature-programmed oxidation (TPO) was conducted using the same apparatus as that employed for H₂-TPR measurements. Prior to analysis, the spent catalysts were degassed at 200°C for 1 h and then cooled to 50°C under an Ar flow. Subsequently, the sample was oxidized from 50 to 850°C at a heating rate of $10^\circ\text{C min}^{-1}$ in a 5 vol% O₂/Ar stream. The oxygen consumption was quantified based on Equation (6) and the carbon deposition (D_c , %) relative to the catalyst weight was calculated according to Equation (7).

$$N_{O_2}(\text{TPO}) = \frac{V_{O_2}}{24,400} \quad (6)$$

$$\%D_c = N_{O_2}(\text{TPO}) \times SF_1 \times MW_C \times 100 \quad (7)$$

where $N_{O_2}(\text{TPO})$ is oxygen uptake obtained from TPO measurements ($\text{mmol g}_{\text{cat}}^{-1}$), V_{O_2} is the amount of oxygen consumed during TPO ($\text{cm}^3 \text{g}_{\text{cat}}^{-1}$), SF_1 is a stoichiometry factor for O_2 in the oxidation reaction ($C:O_2 = 1:1$), and MW_C is the atomic weight of carbon (12 g mol^{-1}).

3.3. Catalytic Test

The catalytic performance in the DMR reaction was evaluated in a tubular fixed-bed reactor containing approximately 0.30 g of catalyst. Prior to reaction, the catalyst was subjected to in situ reduction at 600°C for 3 h under a H_2 flow to activate the metallic Ni phase [24]. The DMR reaction was subsequently carried out at 550°C for 6 h using a feed gas mixture of CH_4 , CO_2 , and N_2 in an equimolar ratio, with a total flow rate of 60 mL min^{-1} . The outlet gas composition was analyzed online using a gas chromatograph (Agilent GC7890A, Agilent Technologies, Santa Clara, CA, USA) equipped with a TCD. The catalytic performance was evaluated in terms of the CH_4 consumption rate (Equation (8)), CO_2 consumption rate (Equation (9)), and the H_2/CO product ratio (Equation (10)). Details of GC calibration, response factors, inlet flow rates, and carbon balance calculations are provided in the Supplementary Information.

$$CH_4 \text{ consumption rate} = \frac{\text{Molar flow rate of } CH_{4,\text{in}} - \text{Molar flow rate of } CH_{4,\text{out}}}{\text{Catalyst weight}} \quad (8)$$

$$CO_2 \text{ consumption rate} = \frac{\text{Molar flow rate of } CO_{2,\text{in}} - \text{Molar flow rate of } CO_{2,\text{out}}}{\text{Catalyst weight}} \quad (9)$$

$$\frac{H_2}{CO} \text{ ratio} = \frac{\text{Molar flow rate of } H_{2,\text{out}}}{\text{Molar flow rate of } CO_{\text{out}}} \quad (10)$$

4. Conclusions

This work demonstrates that combining ZrO_2 promotion with an ammonia vapor-assisted impregnation strategy is an effective approach for developing Ni-based catalysts on a MgO – ZrO_2 -modified support with enhanced activity and improved coke manageability for low-temperature dry methane reforming (550°C). While ZrO_2 promotion strengthens metal–support interactions and improves CO_2 activation, excessive surface coverage of Ni sites can promote reverse water–gas shift (RWGS) side reactions when conventional impregnation is employed.

In contrast, ammonia vapor-assisted impregnation induces LDH-derived intermediates that evolve into a well-integrated Ni–NiO– ZrO_2 surface network upon calcination. This unique interfacial structure increases the availability of surface-accessible Ni species, enhances oxygen mobility, and mitigates excessive masking by zirconia species. As a result, the catalyst exhibits a balance activation of CH_4 and CO_2 , suppressed RWGS contribution, and regulated carbon species formation, leading to superior catalytic performance under low-temperature DMR conditions. These findings highlight the importance of interfacial architecture engineering in designing efficient Ni-based catalysts for CO_2 utilization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16020190/s1>, Sections S1–S5: Gas Analysis and Reaction Performance Calculations for Dry Methane Reforming.

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