

Article

Catalytic Performance of Hydroxyapatite-Based Supports: Tailored vs. Commercial Formulations for Dry Reforming of Methane

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Abstract: Catalyst deactivation, mainly due to coke deposition, presents a significant challenge in the process of dry reforming of methane (DRM). This study focused on coke-resistant catalysts for DRM, particularly nickel-based catalysts supported on hydroxyapatite (HAP). A novel HAP formulation (HAP_S) with a Ca/P ratio of 1.54, below the stoichiometric ratio studied in previous studies, was compared with commercial HAP (HAP_C), and both were impregnated with 10 wt% nickel. The synthesis of HAP_S involved low temperature (60 °C), moderate stirring, and a pH of 11, using a custom setup. Dry-reforming reactions were conducted under severe conditions (T = 800 °C) to assess the resistivity of both supports over 120 h. Our findings indicated sustained high conversion rates, reaching 93% for CH₄ and 98% for CO₂ with HAP_S, despite an increase in gas hourly space velocity. Characterisation, including X-ray diffraction, thermogravimetric analysis, and transmission electron microscopy, revealed coke formation using HAP_C, leading to initial deactivation, in contrast with the custom support. This discrepancy may be attributed to the distinct physical and chemical properties of the catalysts, their reaction mechanisms, and the deactivation precursors. Overall, the performance of nickel-based catalysts significantly hinges on support–catalyst interactions, in addition to thermal stability.

Keywords: hydroxyapatite; nickel; dry reforming; syngas; gas hourly space velocity; stability



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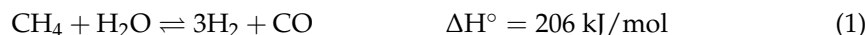


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1. Introduction

Human-induced climate change is currently a major global issue. A high increase in the human population has led to high energy consumption and a major increase in greenhouse gas (GHG) emissions [1,2]. Simultaneously, there is pressing concern about the depletion of fossil resources, including oil, natural gas, and coal, which are expected to decrease in the coming years [2–4]. The need to reduce GHG emissions has led researchers to develop processes that convert these gases into valuable chemicals [5,6]. Although methane (CH₄) and carbon dioxide (CO₂) are considered to be the main contributors to global warming, CH₄ has 25 times the global warming potential of CO₂, and it could remain in the atmosphere for a few years to a thousand years [7]. One of the most promising solutions to minimise GHG emissions is their use as reactants to produce syngas [8], which can be used with a controllable H₂/CO ratio as the raw material of Fischer–Tropsch synthesis to produce different liquid fuels and other chemicals [9]. Syngas production involves various methods, one of which is steam reforming (SMR) (Equation (1)), where methane reacts with water to yield hydrogen (H₂) and carbon monoxide (CO). This process is commonly employed on an industrial scale using nickel–alumina catalysts at temperatures around

800 °C [10]. The water–gas shift (WGS) reaction (Equation (2)) can occur as a secondary reaction, contributing to increased H₂ production. However, challenges arise owing to the energy-intensive nature of WGS, stemming from its high operational temperatures and the necessity for high water-to-hydrocarbon ratios [10,11].



Partial oxidation is a secondary reaction that can take place in the SMR process to produce syngas, using several reactions with oxygen or air (Equation (3)) [12].

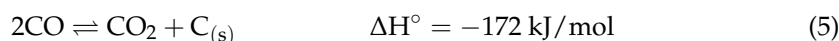


Methane autothermal reforming provides another way to generate H₂ by combining exothermic partial oxidation (Equation (3)) with the WGS (Equation (2)) and SMR reactions (Equation (1)) [13]. DRM is also an attractive solution because it reacts with both major GHG contributors, CO₂ and methane, to produce H₂ and CO (Equation (4)). This process offers a way to utilise CO₂, often deemed a waste product, unlike SRM. By converting carbon dioxide and methane, DRM can be integrated into existing industrial processes, potentially enhancing overall energy efficiency and lowering the carbon footprint of these operations.



However, this reaction is highly endothermic. Generally, temperatures for this process can range from 700 to 1000 °C, or even higher [14,15]. The choice of temperature is influenced by the catalyst activity, reaction kinetics, and desired product composition. In many cases, researchers have found that temperatures in the range of 800 to 900 °C are suitable for DRM [16]. However, this range of temperatures can be accompanied by several side reactions that can lower the selectivity toward syngas, producing water and coke deposits [17]:

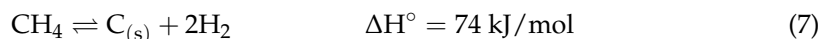
Boudouard reaction:



Reverse WGS (RWGS) reaction:



Methane-cracking reaction:



Carbon-gasification reaction:



Efficient catalysts play a crucial role in improving CO₂ and CH₄ conversion while avoiding coke deposition. Thus, different catalytic formulations have been investigated, including the use of noble metals such as Rh, Pd, and Pt [18,19]. However, noble metals are not favoured for large-scale applications owing to their high cost [20]. Transition metals, such as nickel-based catalysts, have been widely tested for industrial applications because of their availability, low cost, and activity [21]. However, this type of catalyst tends to deactivate faster than noble-metal-based catalysts, due to coke deposition at high temperatures [22–24]. Carbon may form through the various routes of methane cracking (Equation (7)), which typically occurs at temperatures ranging from 800 to 1200 °C, or the Boudouard reaction (Equation (5)), which takes place at temperatures up to 700 °C [25,26].

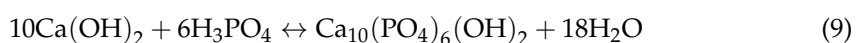
Catalytic supports also play an important role in improving catalytic activity and reducing carbon deposition in DRM [25]. They also help ensure the proper structure of the nickel particles and provide high coke resistance [27]. Many supports are used in the DRM reaction, such as Al_2O_3 , SiO_2 , MgO , TiO , and zeolites. All these catalytic supports were reported to ensure the stabilisation of dispersed nickel particles with a strong metal/support interaction. However, these supports led to major coking on the surface of the catalyst [28]. Hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been used as a new support of DRM in a few studies owing to its thermal stability, low water solubility, capacity to adsorb CO_2 [29,30], tunable specific surface area, mechanical stability, and tunable Ca/P ratio, enabling high conversion and targeted selectivity [31]. For example, bimetallic Co-Ni catalysts supported on HAP exhibited promising performance in the DRM process, achieving significant CH_4 and CO_2 conversion of up to 60–73% and 68–79%, respectively, over extended reaction times of 50–160 h [32]. Moreover, another study of DRM at 700 °C and low pressures showed that the use of nickel over HAP catalyst provides high activity with an initial methane conversion of 75% and stability over 90 h on stream [31], showcasing the potential of HAP as an effective catalyst support for DRM applications.

This study aimed to investigate the catalytic performance of a new formulation of Ni-HAP in the context of DRM under severe reaction conditions. This novel HAP formulation was synthesised under moderate conditions, using low temperatures. A comparative analysis was conducted between this new formulation and a conventional HAP support, highlighting differences in their physical and chemical properties. This study considered unconventional conditions of the DRM reaction, encompassing relatively high temperatures and rigorous stability testing over extended periods exceeding 120 h. X-ray diffraction (XRD), transmission electron microscopy–energy dispersive X-ray spectroscopy (TEM-EDX), scanning TEM (STEM), Brunauer–Emmett–Teller (BET) analysis, temperature-programmed reduction (TPR), inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis coupled with gas chromatography–mass spectrometry (TGA-GCMS) were conducted to assess the properties of fresh and spent catalysts. This comparative analysis highlighted the distinct advantages of a novel HAP formulation in improving the catalytic activity of Ni-HAP, offering valuable insights for commercial viability in DRM applications.

2. Materials and Methods

2.1. Ni-Based Catalyst Preparation

Ni-HAP catalysts were synthesised using the conventional incipient wetness impregnation method [33,34], employing nickel nitrates on two distinct supports: commercial HAP (HAP_C) from Sigma Aldrich (St. Louis, MI, USA) with a purity of $\geq 90\%$, and custom HAP (HAP_S) synthesised using $\text{Ca}(\text{OH})_2$ purchased from Anachemia and 85% phosphoric acid (H_3PO_4) from Fisher Scientific (Waltham, MA, USA). The synthesis protocol involved a low temperature of 60 °C and a pH of 11, as outlined in Figure 1. To initiate the reaction, 20 g of $\text{Ca}(\text{OH})_2$ was dissolved in 125 mL of distilled water with moderate stirring. Subsequently, 27 g of 85% phosphoric acid was added to another 125 mL of distilled water. The resulting phosphoric acid solution was then added to the $\text{Ca}(\text{OH})_2$ solution to form HAP with a theoretical Ca/P ratio of 1.67 (Equation (9)), followed by 24 h of reflux at 60 °C under moderate stirring. Solid sodium hydroxide from Fisher Scientific was diluted in 100 mL of distilled water and added during the experiment to maintain a pH of approximately 11. The synthesised support was filtered and dried overnight at 120 °C. Calcination at 500 °C with a heating rate of 5 °C/min was conducted to remove residual $\text{Na}(\text{OH})$ [35].



Both the custom and commercial supports were impregnated with 10% wt% nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) from Sigma Aldrich. The resulting catalysts were dried overnight at 120 °C and then calcined at 500 °C for 3 h to eliminate residual $\text{Ca}(\text{OH})_2$, along with the removal of any volatile elements and contaminants.

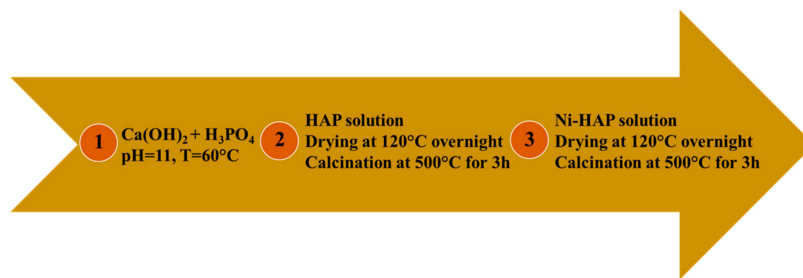


Figure 1. Schematic steps of the controlled formulation for Ni-HAP₅.

2.2. Catalyst Characterisation

In this work, various analytical techniques were employed to comprehensively characterise the supports and catalysts. XRD was performed to determine the crystalline phases, using an X'Pert PRO diffractometer from Panalytical (Malvern, UK), operating with Cu K α radiation over a 2θ range of 20° – 70° . FTIR measurements were performed in transmission mode using KBr pellets containing 1 g of two different HAP supports, analysed in the mid-infrared range (500 – 4000 cm^{-1}) using a PerkinElmer Spectrum 100 instrument from PerkinElmer, Inc., located in Waltham, United States. ICP-OES was performed using a Jobin Yvon Ultima 2 instrument for elemental analysis from HORIBA Scientific based in Longjumeau, France, specifically to verify the concentration of the Ca/P ratio in the synthesised HAP powders. The TEM and STEM analyses, along with EDX spectroscopy and high-angle annular dark-field (HAADF) detection, were conducted using a TFS Spectra Ultra instrument available in the Canadian centre for Electron Microscopy at McMaster University in Hamilton, Ontario. An HAADF detector is a component used in STEM and allows for Z-contrast imaging by directly correlating the signal intensity with the atomic number, providing superior spatial resolution compared with other modes by minimising diffraction effects [36]. These techniques were employed to visualise the surface morphology and characterise coke deposition on the catalyst surface.

The particle size distribution was assessed using Image J software version 1.54. N₂ adsorption–desorption isotherms were obtained to determine specific surface area and porosity, using the BET and Barrett–Joyner–Halenda (BJH) methods, processed using ASAP 2020 software. Before this analysis, the samples were degassed for 24 h at 110°C to remove moisture. TPR experiments were carried out using a Micromeritics Auto Chem II Chemisorb 2750 instrument manufactured by Micromeritics Instrument Corporation, headquartered in Norcross, Georgia, USA, equipped with a thermal conductivity detector (TCD) detector, evaluating the catalyst's thermal stability under reduction conditions. Initially, 77 mg of fresh catalyst was loaded into a u-shaped quartz tube and pretreated in a flow of Ar at 150°C for 1 h at a ramp rate of $20^{\circ}\text{C}/\text{min}$. Subsequently, the sample was cooled to 50°C , followed by heating from 50 to 800°C at a ramp rate of $10^{\circ}\text{C}/\text{min}$ in a flow of $15\%\text{H}_2/\text{Ar}$ at $30\text{ mL}/\text{min}$. Finally, the catalyst was reduced for 1 h using a $15\%\text{H}_2/\text{Ar}$ mixture at 800°C . TGA-MS was conducted to assess the thermal behaviour of the catalysts under air conditions, predicting carbon formation on the spent catalyst surface. The experiments were carried out under a stream of $20\%\text{O}_2$ – $80\%\text{Ar}$ using a temperature range of 20 – 800°C and a heating rate of $10^{\circ}\text{C}/\text{min}$.

2.3. Catalytic Evaluation

DRM was conducted in a fixed-bed quartz reactor with an internal diameter of 6 cm and a length of 120 cm, as illustrated in Figure 2. The reaction was conducted at a controlled temperature of 800°C and monitored using an internal thermocouple. The reaction pressure was maintained at atmospheric pressure. The catalyst (5 g) was loaded into the catalytic bed using quartz wool. The reactor was heated to 800°C , and a gas mixture comprising $50\%\text{CH}_4$ – $50\%\text{CO}_2$ was fed into the reactor at flow rates ranging from 83 to $225\text{ mL}/\text{min}$, without the presence of a carrier gas. Flow rates were adjusted using mass flow controllers (MFCs) from OMEGA (Norwalk, CT, USA). A water trap was

placed at the outlet of the reactor to capture water generated from secondary reactions. Gas chromatography was employed to analyse the compositions of the outlet gases, which were monitored using a mass flow meter (MFM) from OMEGA. Samples of the outlet gases were collected using a syringe every hour during the extended test period and introduced to the GC (Scion 456) equipped with a thermal conductivity detector (TCD). Sample input temperature was 150 °C, while that of the 2 column injectors was 200 °C. H₂, CO, CH₄, and CO₂ were detected in 5 min by the GC.

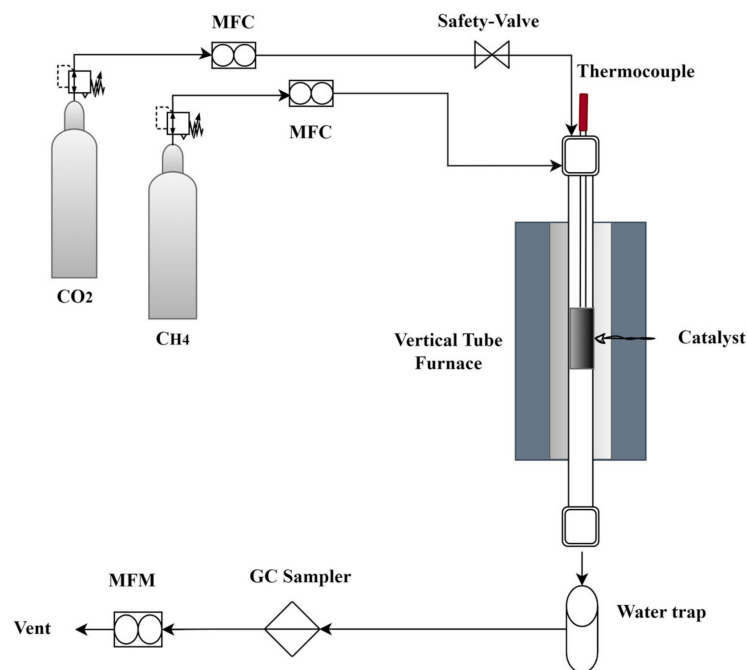


Figure 2. Experimental setup used for DRM.

The experiments were remotely controlled using LabVIEW software (version 5.1). The main products of the reaction were CO and H₂.

The following formulas were used to calculate conversion, yield, and selectivity:

Conversion:

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

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

Yield:

$$Y_{H_2}(\%) = \frac{F_{out,H_2}}{2 \times F_{in,CH_4}} \times 100 \quad (12)$$

$$Y_{CO}(\%) = \frac{F_{out,CO}}{F_{in,CH_4} + F_{in,CO_2}} \times 100 \quad (13)$$

Selectivity:

$$S_{H_2} = \frac{F_{out,H_2}}{2(F_{in,CH_4} - F_{out,CH_4})} \times 100 \quad (14)$$

$$S_{CO} = \frac{F_{out,CO}}{(F_{in,CH_4} + F_{in,CO_2}) - (F_{out,CH_4} + F_{out,CO_2})} \times 100 \quad (15)$$

Carbon (%):

$$B_C = \frac{(F_{out,CO_2} + F_{out,CH_4} + F_{out,CO})}{(F_{in,CO_2} + F_{in,CH_4})} \times 100 \quad (16)$$

H₂/CO ratio:

$$\frac{H_2}{CO} = \frac{\%H_2}{\%CO} \quad (17)$$

where F_{in} and F_{out} are methane flow rate ($\text{mol} \cdot \text{min}^{-1}$) at the inlet and outlet of the reactor, respectively, and B_C is the carbon mass balance.

3. Results and Discussion

3.1. Characterisation of the Supports and Fresh Catalysts

3.1.1. Crystal Structure

XRD was conducted on both the commercial and custom supports, as well as on freshly prepared Ni-HAP catalysts, as depicted in Figure 3. Across all samples, a discernible crystalline phase of HAP was observed. The XRD pattern exhibited well-defined diffraction peaks at 2θ angles of 25.8° , 31.7° , 32.1° , 32.9° , 40° , 47° , and 49° , with variations in peak intensity, indicative of differences in crystallinity. The HAP_C support presented an additional crystalline phase for HCa(PO₄), with major diffraction peaks at 2θ angles of 26° and 31° . This phase has not previously been reported in the literature concerning HAP-supported catalysts. HAP_S exclusively exhibited the presence of Ca₅(PO₄)₃(OH), distinguishing it from HAP_C. Additionally, both impregnated supports contained a crystalline phase of nickel oxide (NiO), resulting from the calcination step. The primary diffraction peaks for NiO were identified at 2θ angles of 37.28° and 43° . The HAP and NiO peaks are consistent with the findings reported by Rego de Vasconcelos et al. [31].

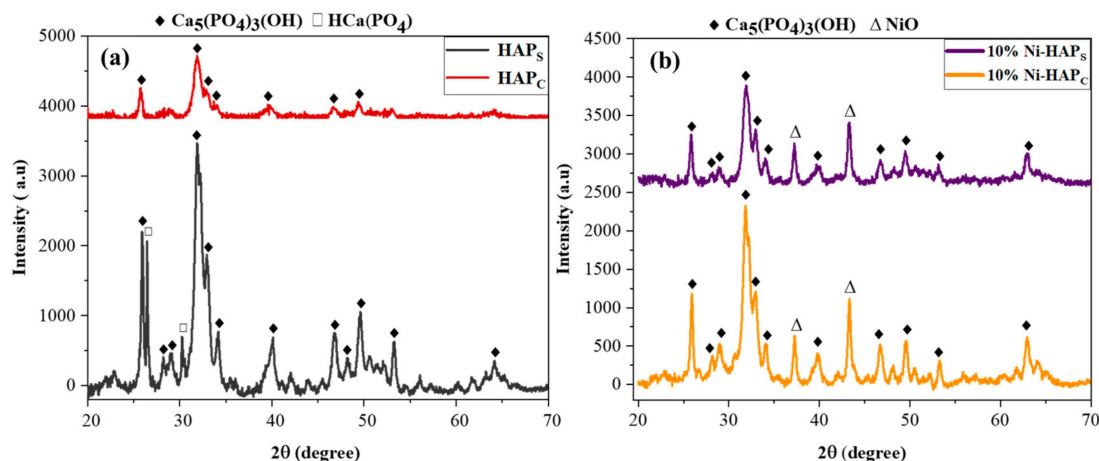


Figure 3. (a) XRD patterns of HAP_S and HAP_C. (b) XRD patterns of 10% Ni over HAP_S and HAP_C.

3.1.2. Molecular Bonding and Composition

The FTIR spectra showcased in Figure 4 delineate distinct absorption peaks corresponding to various vibration modes of P-O bonds within phosphates (PO₄^{3−}) for both HAP supports (HAP_C and HAP_S) and the 10% Ni-HAP catalysts [37,38]. In Figure 4a, the shared absorption peaks in the HAP supports reveal fluctuations in phosphate vibrational frequencies, attributed to disparities in the phase, crystallinity, and chemical composition. Specifically, in HAP_S, peaks were identified at 602, 631, and 962 cm^{-1} , whereas in HAP_C, they manifested at 1056 and 712 cm^{-1} [37]. Additionally, discernible structural hydroxyl bands (OH[−]) were observable around 3570 and 3435 cm^{-1} for HAP_S and at 3435 and 3643 cm^{-1} for HAP_C [38], indicating weaker interactions in the latter case, leading to higher transmittance. Furthermore, peaks associated with B-type carbonate groups (CO₃^{2−}) incorporated into the HAP structure were detected at 1416, 1456, and 2345 cm^{-1} for HAP_S and at 874, 1449, and 2514 cm^{-1} for HAP_C [39,40]. These carbonate-related peaks were attributed to the thermal treatment of HAP, likely due to contamination with CO₃^{2−} ions from atmospheric CO₂ [39]. These findings suggest structural modifications in the HAP supports, aligning with prior research that attributes variations in phase and crystallinity

to multiple influencing factors [40]. For 10% Ni over HAP_S (Figure 4b), the incorporation of this active phase did not significantly alter the vibrational modes of the HAP support. Similarly, the addition of nickel to the HAP structure did not induce notable changes in these vibrational modes. However, when nickel was introduced to HAP_C, it disturbed the vibrations of adsorbed water molecules (Figure 4a), indicating a distinct enrichment of the support's surface by the NiO phase, as investigated in [39].

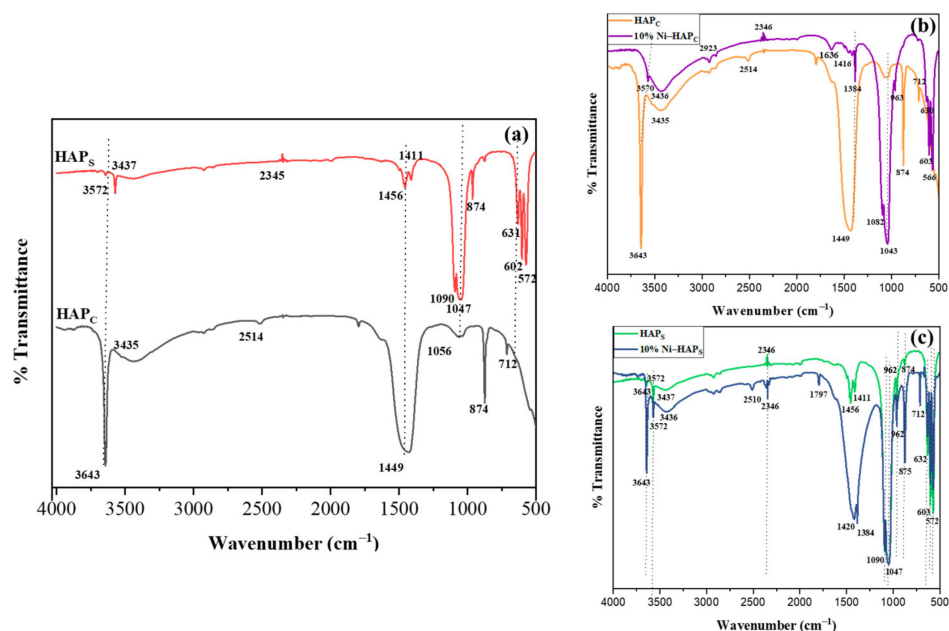


Figure 4. FTIR spectra of the (a) HAP supports, (b) 10% Ni-HAP_C, and (c) 10% Ni-HAP_S.

3.1.3. Elemental Analysis

The ICP-OES results presented in Table 1 elucidate the compositional attributes of the examined supports. HAP_C exhibited a molar Ca/P ratio of 1.38, whereas HAP_S showed a slightly higher ratio of 1.54. This indicates a relatively balanced proportion of calcium to phosphorus in HAP_S, nearing the theoretical Ca/P ratio of 1.67 required for stoichiometric HAP [41]. These findings imply that catalysts incorporating HAP_S exhibit improved CO₂ and CH₄ conversion rates post-nickel-impregnation. In our investigation, nickel-based catalysts deposited over HAP_S displayed an elevated Ca/P ratio, suggesting that HAP_S possesses the capability for efficient substitution between Ni²⁺ and Ca²⁺. These results are consistent with the findings reported by Boukha et al. [42], where X_{CO2} reached 83% and X_{CH4} reached 75% under 750 °C for 24 h. Furthermore, that study indicated that with a Ca/P ratio close to 1.54, the coke deposition was minimal at 0.6%. The outcomes indicate that catalysts with higher Ca/P ratios are more likely to maintain robust stability during the DRM reaction.

Table 1. Ca/P ratio of the HAP supports.

Support/Catalysts	Ca/P Ratio
HAP _C	1.38
HAP _S	1.54
10% Ni-HAP _C	1.38
10% Ni-HAP _S	1.54

3.1.4. Morphology and Elemental Composition

Figure 5 displays the TEM images of freshly calcined Ni-HAP_C and Ni-HAP_S, showing that both samples were predominantly composed of elongated particles characteristic of HAP. The catalysts did not show significant differences in morphology. Close examination

revealed a homogeneous distribution of NiO particles within the catalysts. These NiO particles varied in size from 7 to 60 nm for both fresh catalysts. Notably, HAP_S exhibited larger metallic particles, depicted as dark spots in the images. To analyse the distribution of Ni-based particles on the support surface, TEM-EDX was conducted, as illustrated in Figure 6a,b. In these compositional maps, the consistent presence of Ni, O, Ca, and P was observed for both catalysts. Nickel was found to be uniformly dispersed on the support surface. Ni and O showed similar concentrations, indicating NiO particles, as detected by the HAADF detector. The size of the NiO particles was observed to be less than 50 nm using Image J software.

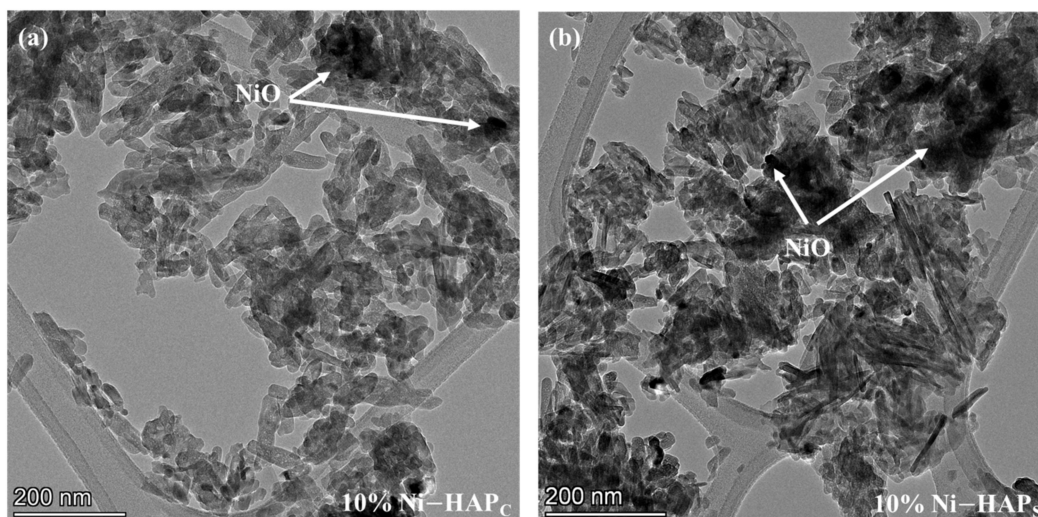


Figure 5. TEM images of freshly calcined nickel-based catalysts on (a) HAP_C and (b) HAP_S.

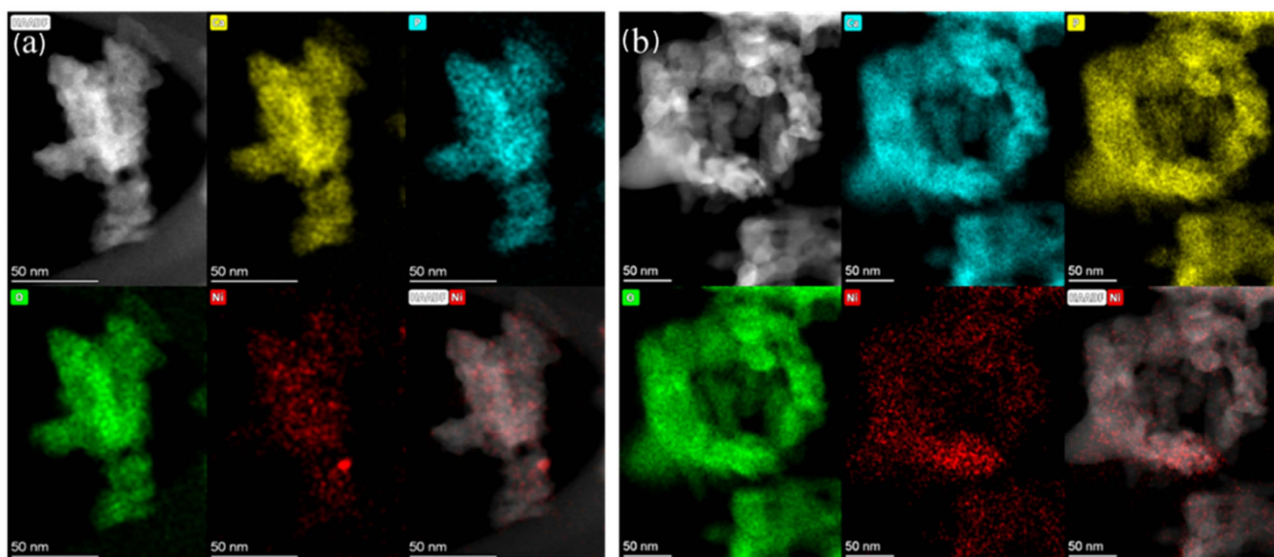


Figure 6. HAADF-STEM-EDX images of fresh (a) 10% Ni-HAP_C and (b) 10% Ni-HAP_S.

3.1.5. Redox Properties

The TPR analysis, as illustrated in Figure 7, was conducted for both freshly calcined catalysts. For the catalyst supported on HAP_C, a minor reduction peak was observed around 350 °C, associated with the reduction in surface oxygen species present on the catalyst [42]. The reduction peaks of NiO are depicted as two overlapping peaks within the temperature range of 400–650 °C. These peaks, occurring at approximately 410 and 480 °C, are attributed to the reduction of NiO particles that have a strong interaction with HAP. The

third peak may be attributed to the reduction of Ni^{2+} species that had been incorporated into the HAP support, replacing Ca^{2+} ions [42]. Regarding the catalyst supported on HAP_S , a single peak was observed at 480°C , which is attributed to the reduction of NiO particles [42].

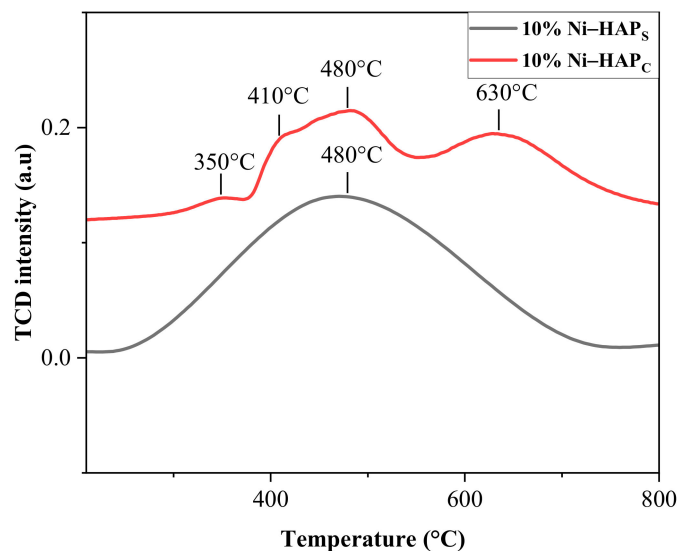


Figure 7. TPR profiles for the 10% Ni-HAP_C and 10% Ni-HAP_S catalysts.

3.1.6. Specific Surface Area and Pore Volume

The nitrogen adsorption–desorption isotherms for the supports and the freshly calcined catalysts are depicted in Figures 8 and 9. All obtained isotherms can be classified as the second type according to the IUPAC classification [42]. The presence of a hysteresis loop in Figure 8a,b indicates the existence of mesopores within the support in all the samples, and the metal impregnation steps did not change the type of isotherm, as presented in Figure 9a,b. However, the quantity of absorbed nitrogen was lower after the impregnation and calcination steps, which was due to a decrease in porosity. The BET method, as summarised in Table 2, yielded a specific surface area of $65\text{ m}^2/\text{g}$ for HAP_C and $72\text{ m}^2/\text{g}$ for HAP_S . After impregnation with nickel nitrates, the specific surface areas were reduced to $45.73\text{ m}^2/\text{g}$ for 10% Ni/HAP_C and $39.35\text{ m}^2/\text{g}$ for 10% Ni-HAP_S . In addition, the pore diameter distribution also decreased for both catalysts, as presented in Table 2. Figure 10a,b also depict the presence of mesopores, indicated by the peaks for pore sizes of $<50\text{ nm}$.

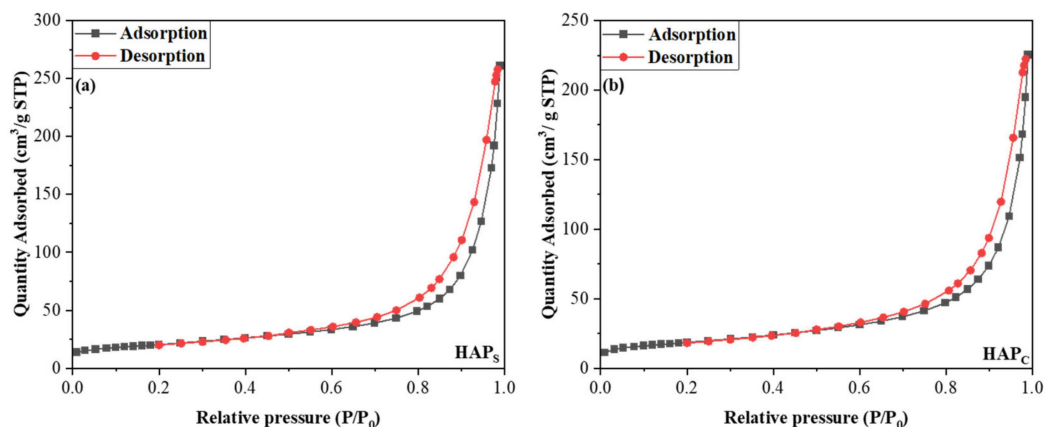


Figure 8. Nitrogen adsorption–desorption isotherms of (a) HAP_S and (b) HAP_C .

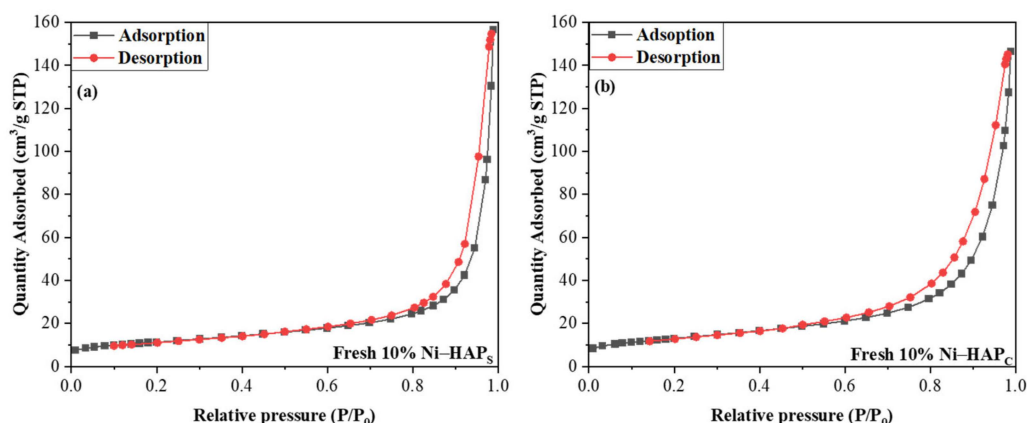


Figure 9. Nitrogen adsorption–desorption isotherms of (a) fresh 10 %Ni-HAP_S and (b) fresh 10% Ni-HAP_C.

Table 2. Specific surface area, pore volume, and pore size of the fresh supports and catalyst.

Catalyst/Support	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
HAP _C	65	0.34	23
HAP _S	72	0.27	15
10% Ni-HAP _C	46	0.0025	14
10% Ni-HAP _S	39	0.003	24

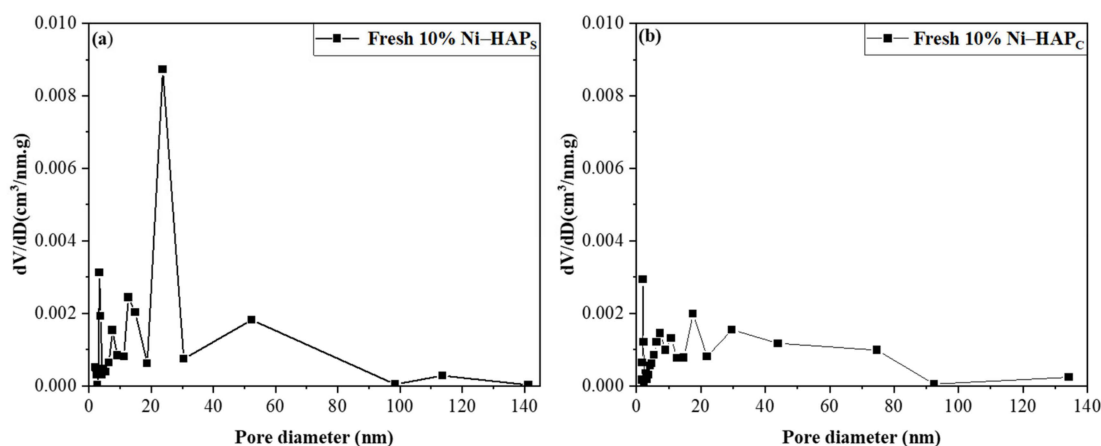


Figure 10. dV/dD profiles for (a) fresh 10% Ni-HAP_S and (b) fresh 10% Ni-HAP_C.

3.2. Catalytic Performance

Evaluation of Catalyst Performance and Stability

In this study, the catalytic performance of the 10% Ni-HAP_C and 10% Ni-HAP_S catalysts were rigorously assessed under severe conditions during the DRM reaction. Operating at 800 °C and atmospheric pressure for 120 h with a CH₄/CO₂ ratio of 1/1, the catalysts demonstrated high resilience. Initial testing was conducted at a fixed gas hourly space velocity (5000 L/h kg of catalyst) for 84 h, followed by an increase to 10,000 L/h kg for the remainder, allowing for a comprehensive evaluation of stability and coke resistance. Despite this shift, both catalysts maintained high activity throughout the test, albeit with differing CH₄ and CO₂ conversion profiles. Notably, the 10% Ni-HAP_S catalyst exhibited a superior CH₄ methane conversion rate of 97%, whereas the 10% Ni-HAP_C catalyst showed higher CO₂ conversion rates, reaching approximately 98–100% (Figure 11). Selectivity analysis indicated distinct reaction pathways, suggesting the occurrence of methane cracking (Equation (7)) or carbon gasification (Equation (8)) for HAP_C, which favours hydrogen

production and solid carbon. Conversely, HAP_S showed higher CO selectivity, suggesting the RWGS reaction (Equation (6)) and carbon gasification (Equation (8)) (Figure 12). The influence of support properties, particularly the Ca/P ratio, on catalyst performance was evident, with HAP_S demonstrating enhanced stability. The results closely aligned with equilibrium calculations determined using FactSage software (version 8.2) (Figure 13) with atmospheric pressure and a CH₄/CO₂ ratio = 1 and were higher in terms of conversions compared with other catalysts, as shown in Table 3, further validating the reliability of the employed methodology.

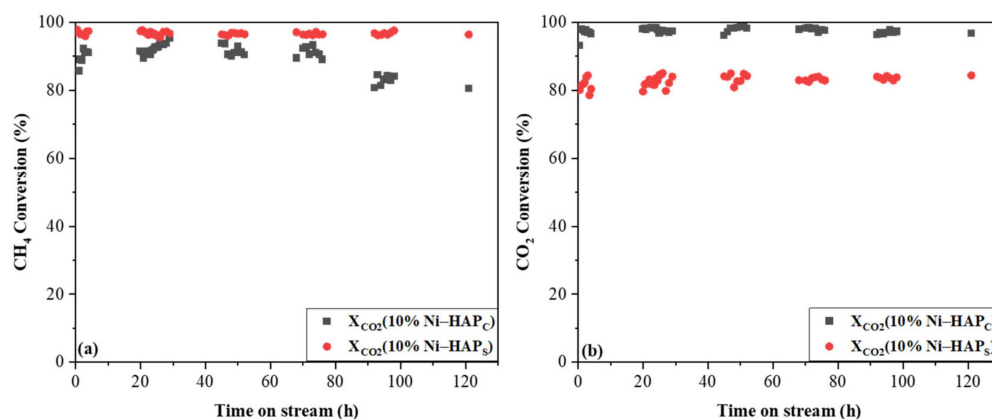


Figure 11. (a) CH₄ conversion and (b) CO₂ conversion using Ni-HAP catalysts.

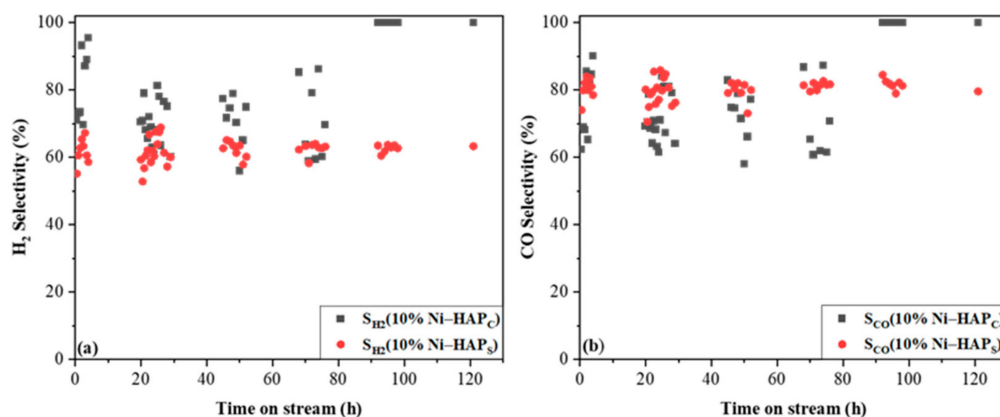


Figure 12. (a) H₂ and (b) CO selectivity using Ni-HAP catalysts.

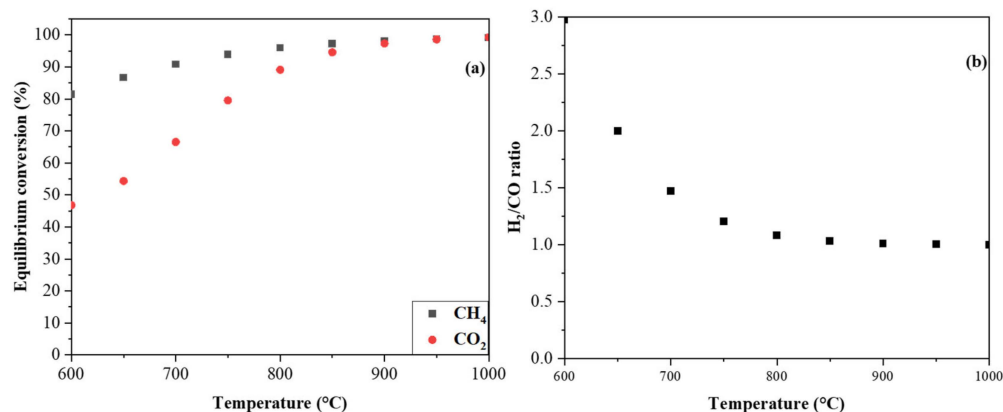


Figure 13. (a) Thermodynamic equilibrium conversion of CH₄ and CO₂ and (b) H₂/CO product ratio inDRM at atmospheric pressure, with a CH₄/CO₂ ratio of 1.

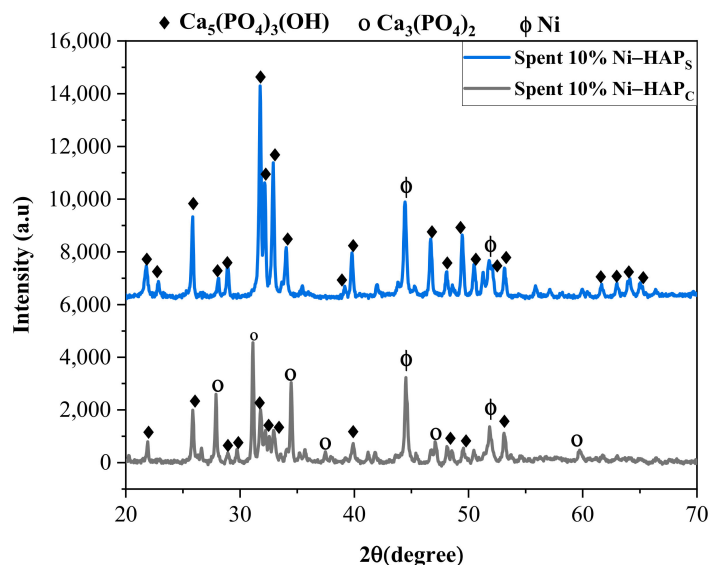
Table 3. Comparison of Ni-HAP_S and Ni-HAP_C catalysts and other catalytic systems.

Metal/Support-Promoters	Conditions	X _{CH4}	X _{CO2}	Reference
10% Ni/HAP _S	T = 800 °C GHSV = 5000–10,000 L/h kg P = 1 atm TOS = 120 h	97–95%	85%	This work
10% Ni/HAP _C	T = 800 °C GHSV = 5000–10,000 L/h kg P = 1 atm TOS = 100 h	82–94%	98–100%	This work
10% Ni-7% CeO ₂ /MgO	T = 700 °C GHSV = 12,000 L/h kg P = 1 atm TOS = 5 h	45%	89%	[43]
5% Rh/ α -Al ₂ O ₃	T = 800 °C GHSV = 60,000 L/h kg P = 1 atm TOS = 4 h	57.2–56.9%	64.4–63.8%	[44]
10% Ni/CeO ₂	T = 760 °C GHSV = 13,400 L/h kg P = 1 atm TOS = 100 h	67.05–82.82%	80–90%	[45]
7.7% Ni/ γ -Al ₂ O ₃	T = 700 °C WHSV = 22,000 h ⁻¹ P = 1 atm TOS = 6 h	60–54%	66%	[46]

4. Characterisation of the Spent Catalyst

4.1. XRD Analysis

The XRD patterns for both the spent 10% Ni-HAP catalysts confirms that HAP and Ni constituted the main phases, as shown in Figure 14. The primary diffraction peaks were observed at 2θ angles of 22°, 26°, 32°, 33°, 40°, 46°, and 49° for HAP and 44.44° and 51.78° for Ni. The presence of Ni is attributed to the reduction of NiO to Ni (Ni°). According to the Scherrer equation, the average crystallite size was approximately 30 nm. Notably, only impregnated HAP_C exhibited the presence of a dehydrated phase of HAP at 2θ angles of 38°, 31°, and 34.5°, which may be associated with the use of high-temperature reactions.

**Figure 14.** XRD patterns of the spent catalysts.

4.2. TEM-STEM-EDX Analysis

TEM images of all the spent catalysts showed the presence of long carbon filaments with different diameters, as depicted in Figure 15a,b and Figure 16a,b. These carbon nanofilaments encapsulated Ni. It is also apparent that the size of the Ni particles increased from thermal sintering. To further elucidate the nature of the carbon, electron energy loss spectroscopy (EELS) was employed for the analysis of the spent catalysts, revealing amorphous and graphitic forms, as shown in Figure 17. The amorphous carbon indicates the presence of disordered and irregular carbon structures, often associated with incomplete combustion products. In contrast, graphitic carbon suggests the formation of more ordered, layered carbon structures, indicative of graphitisation during the catalytic reaction. The coexistence of these carbonaceous species provides insights into the catalyst's deactivation mechanism, highlighting the complex interplay between coke deposition and carbon transformation.

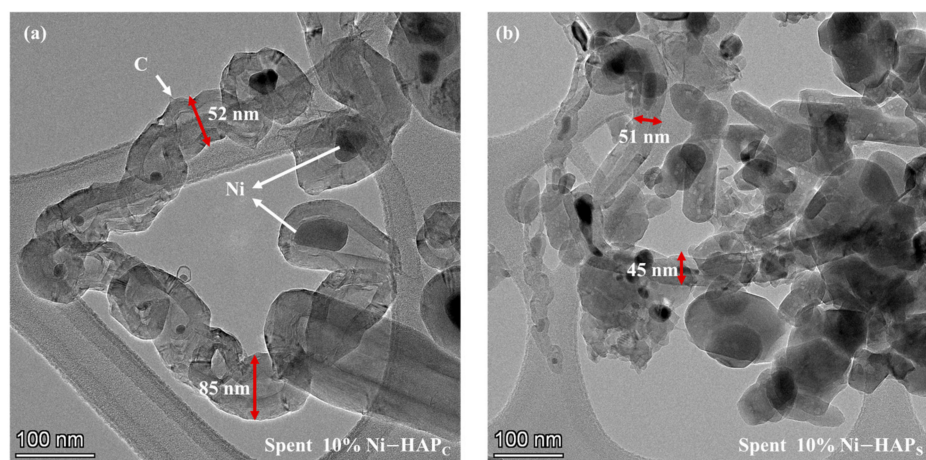


Figure 15. TEM images of (a) spent 10% Ni-HAP_C and (b) spent 10% Ni-HAP_S.

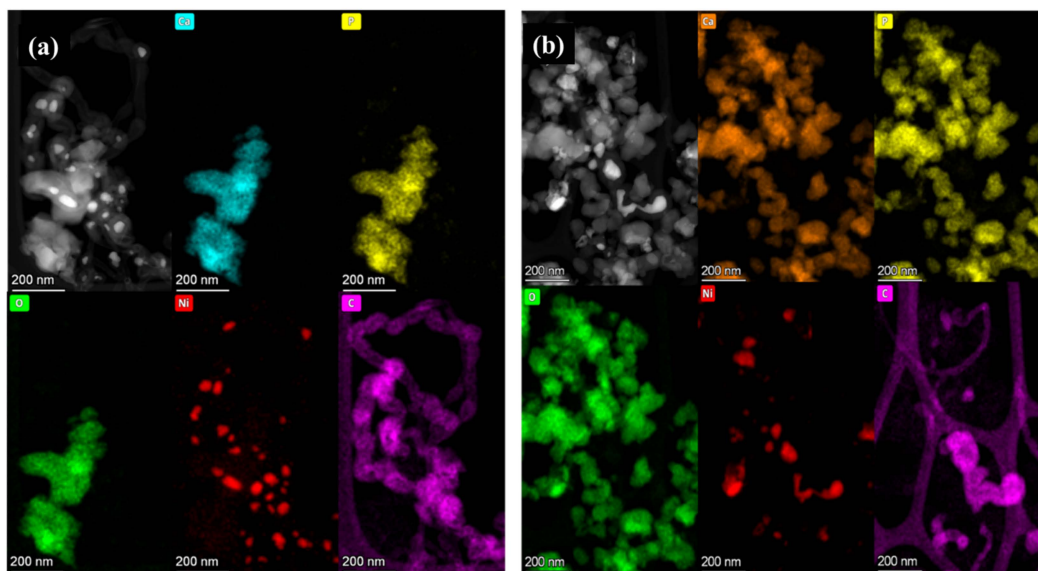


Figure 16. HAADF-STEM-EDX images of (a) the spent 10% Ni-HAP_C and (b) the spent 10% Ni-HAP_S.

The active metal particle size before and after the dry reforming tests on HAP_C and HAP_S was assessed from TEM images using Image J software, and the results are presented in Figures 18 and 19. These figures reveal distinct trends. Active metal agglomeration and more varied particle sizes after DRM tests were more apparent in Ni-HAP_C than in Ni-HAP_S. For the latter, the particles increased from approximately 10–20 to 30–60 nm,

accompanied by a rise in standard deviation from approximately 9.20 to 16.16 nm. In contrast, the Ni-HAP_C particle size grew from approximately 41 to 57 nm, with the standard deviation increasing from approximately 29 to 40 nm. Thus, both catalysts exhibited the agglomeration of Ni particles, resulting from the use of high temperatures, as previously reported [37,47]. This difference in size explains the catalytic activity loss of Ni-HAP_C compared with Ni-HAP_S, usually reported as part of the deactivation mechanism [48].

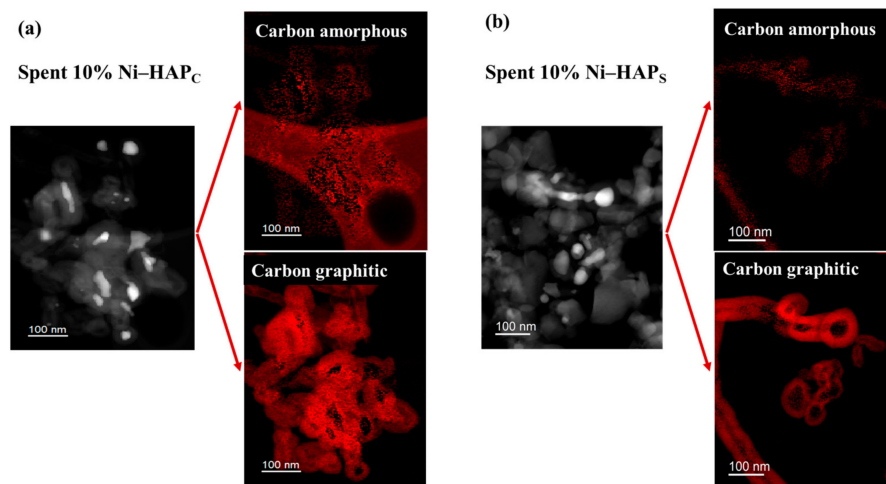


Figure 17. EELS analysis for spent (a) 10% Ni-HAP_C and (b) 10% Ni-HAP_S.

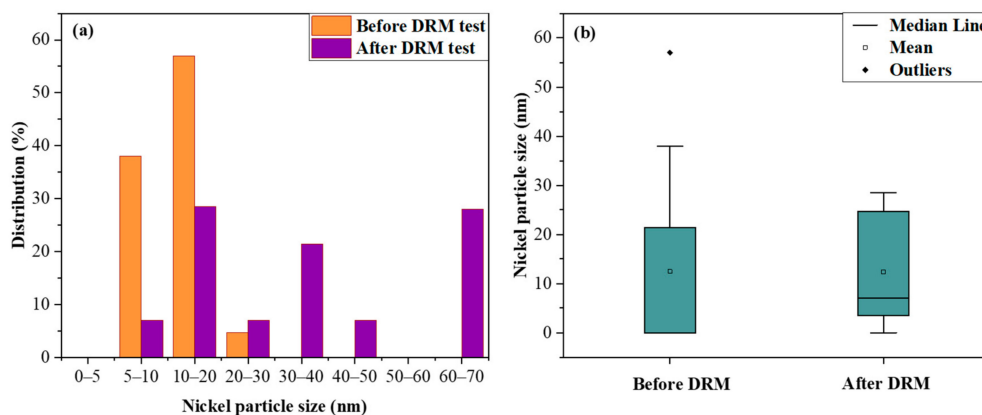


Figure 18. (a) Particle size distribution and (b) standard deviation before and after the DRM test for 10% Ni-HAP_C.

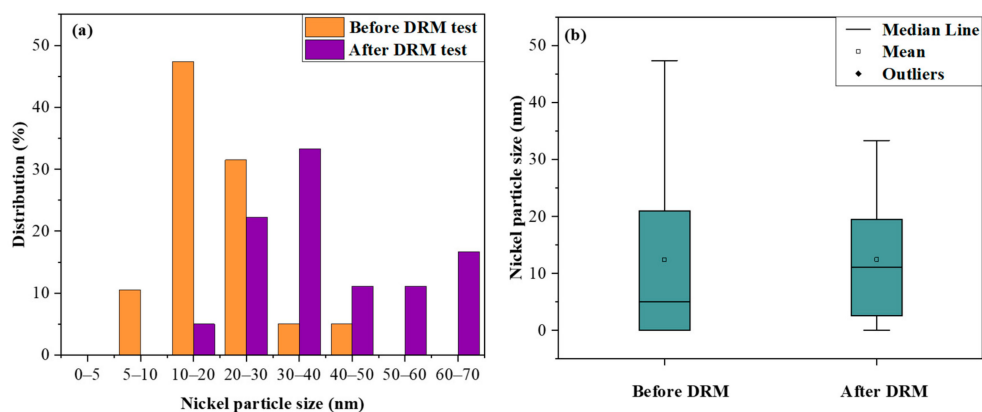


Figure 19. (a) Particle size distribution and (b) standard deviation before and after the DRM test for 10% Ni-HAP_S.

4.3. BET-BJH Analysis

After running the DRM reaction for 120 h, both catalysts exhibited a reduction in their specific surface area, as presented in Table 4. In Figure 20, the hysteresis loop for the spent 10% Ni-HAP_S support is less discernible than that for 10% Ni-HAP_C. This may be attributed to the use of high temperatures, which usually leads to particle coalescence and a gradual sintering process, particularly for this type of bio-ceramic support [49]. The difference between the surface-area loss, which appeared to be more significant for the Ni-HAP_S, was mainly attributed to carbon deposition. As discussed in the next section, Ni-HAP_C presented higher coke deposition according to the TGA-MS analysis. Carbon quantification was two times higher in Ni-HAP_C compared with Ni-HAP_S, with a particle size of lower than 100 nm (Figure 21). Both spent catalysts showed the presence of mesopores with sizes of 3, 10, 15, and 30 nm after 120 h of testing, as depicted in Figure 21a,b. This may be attributed to the increasing temperatures that alter the crystallite size of the catalyst.

Table 4. S_{BET} , pore volume, and pore size of the spent catalysts.

Spent Catalyst	S_{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Spent 10% Ni-HAP _C	15	0.000215	11
Spent 10% Ni-HAP _S	4	0.000130	9

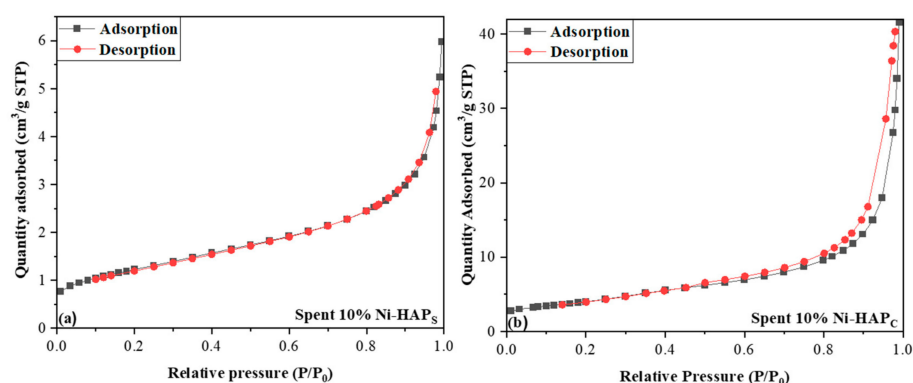


Figure 20. Nitrogen adsorption–desorption isotherms of (a) spent 10% Ni-HAP_S and (b) spent 10% Ni-HAP_C catalysts.

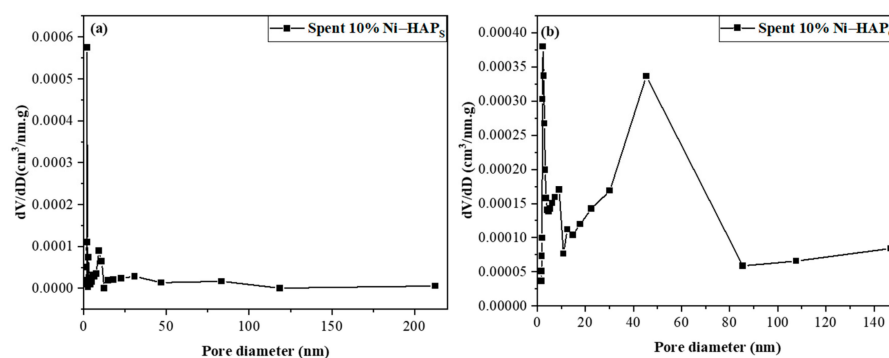


Figure 21. dV/dD profiles for (a) spent 10% Ni-HAP_S and (b) spent 10% Ni-HAP_C.

4.4. TGA-MS Analysis

The extent of carbon deposition on the spent catalysts derived from HAP_C and HAP_S was quantified through TGA analysis, as illustrated in Figure 22a,b. In both cases, minor weight loss was observed below 300 °C, attributed to the oxidation of active amorphous carbon [49,50]. Between 370 and 450 °C, both catalysts exhibited a slight weight gain. This gain was ascribed to the oxidation process, transforming metallic Ni into NiO under the influence of the airflow [51,52]. The most significant weight loss occurred within the range

of 500 to 750 °C, attributed to coke deposition. This weight loss accounted for 27% and 15% of the spent catalysts derived from HAP_C and HAP_S, respectively. Many factors play a role in carbon deposition, such as the Ca/P ratio of the supports. Moreover, the difference between Ca/P ratios is reported to influence the surface properties, and thus the tendency toward coke formation when the Ca/P is less than the stoichiometric value [42].

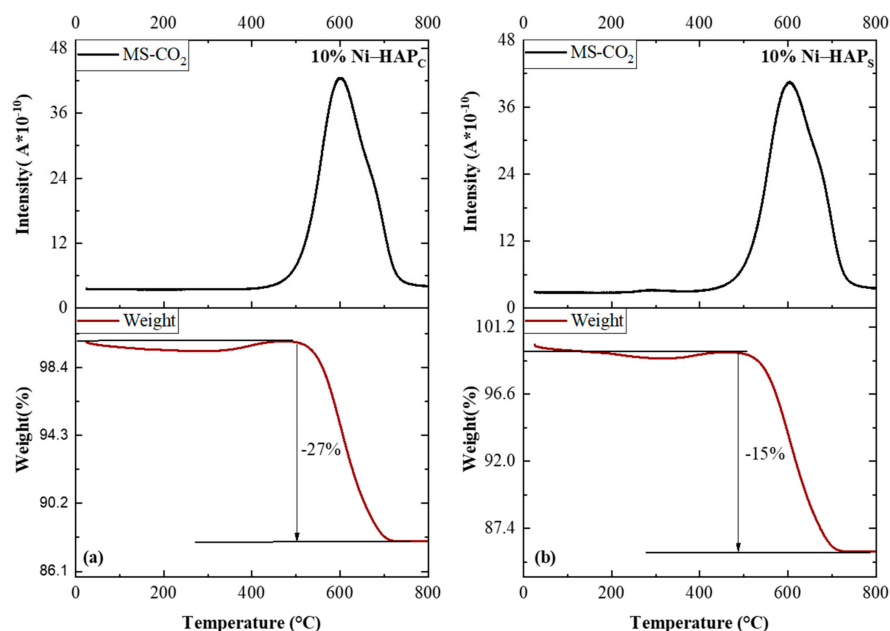


Figure 22. TGA-MS results for the spent (a) 10% Ni-HAP_C and (b) 10% Ni-HAP_S catalysts.

5. Conclusions

This study considered the performance of bio-ceramic supports for Ni-based catalysts in the context of DRM. The impact of the bio-ceramic support was investigated by comparing a new formulation (HAP_S) with a commercial support (HAP_C). The new formulation exhibited a higher specific surface area compared with the commercial support (HAP_S $S_{\text{BET}} = 72 \text{ m}^2/\text{g}$ vs. HAP_C $S_{\text{BET}} = 65 \text{ m}^2/\text{g}$). FTIR spectroscopy and XRD confirmed the efficiency of the employed synthesis method in providing a homogeneous crystalline phase of HAP ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$). In comparison, the commercial support displayed an additional crystalline phase, identified as $\text{HCa}(\text{PO}_4)$. The performance of both catalysts, including their resistivity and selectivity, was based on running the DRM at 800 °C for 120 h. Ni-HAP_S exhibited better CH_4 conversion rates, whereas Ni-HAP_C exhibited better CO_2 conversion rates, highlighting the influence of the Ca/P ratio, pH value, and reaction temperature used in synthesising the HAP support. TGA and STEM analysis of the spent catalysts demonstrated the resistance of HAP_S to coke poisoning compared with the HAP_C. In conclusion, this study demonstrates the efficiency of affordable bio-ceramic support synthesised using unique parameters for catalytic DRM reactions. In the future, the catalyst formulation should be refined to operate at lower temperatures.

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