

Effect of promoters (Ce, Sr, Cs, and Sm) on the activity and coke formation of FSA support Ni in the dry reforming of methane

A.H.K. Owgi^b, A.A. Jalil^{a,b,*}, M.A.A. Aziz^{a,b}, M. Alhassan^{b,d}, H.U. Hambali^{e,f}, W. Nabgan^c, R. Saravanan^{e,f}, A.H. Hatta^b

^a Centre of Hydrogen Energy, Institute of Future Energy, 81310 UTM Johor Bahru, Johor, Malaysia

^b Faculty of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^c Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av Països Catalans 26, 43007, Tarragona, Spain

^d Department of Chemistry, Sokoto State University, PMB 2134, Airport Road, Sokoto, Nigeria

^e Department of Chemical Engineering, Faculty of Engineering and Technology, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

^f Faculty of Engineering, Department of Mechanical Engineering, University of Tarapacá, Avda. General Velasquez, 1775 Arica, Chile

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ABSTRACT

Methane dry reforming was employed to evaluate the Ni/Fibrous Silica-Alumina catalyst promoted with Cs, Ce, Sr, and Sm. The catalysts were prepared via impregnation followed by the hydrothermal method. X-ray diffraction, Brunauer-Emmett-Teller, Fourier-transform infrared spectroscopy, temperature programmed reduction, Raman, and thermogravimetry Analysis with derivative techniques were employed to characterize them. The results exhibited that adding Cs, Ce, Sr, and Sm promotion reduced the surface area of the catalyst. The consequence of introducing the promoters positively affected the performance of the catalyst. Therefore, the incorporation of Cs with Ni/FSA enhanced the long-term activity throughout the 50 h. The temperature programmed reduction assessment revealed that the addition of Cs improved the reducibility of the Ni catalyst and dropped the reduction temperature of NiO species. Moreover, the Cs-Ni/FSA showed the lowest amount of carbon located among all specimens via thermogravimetry analysis. Cs seems to be the most effective at preventing the formation of carbon, owing to its oxidation property which assists to rid the carbon and renders the durability of the catalyst.

1. Introduction

Currently, the unsustainable exploitation of nonrenewable energy sources (coal, natural gas, and petroleum) to fulfill global desires has led to two significant issues: global warming and oil reserve depletion. Significant endeavors have been conducted to ameliorate these challenges, particularly in the research sector. As a result, there is a critical imperative for significant efforts to reduce Emissions of carbon dioxide, particularly in the industrial areas, which contribute to the emissions. such as the pollutive gases that are generated by the steel industry. The challenge for the steel industry is to eliminate the production of CO₂ and realize clean fuel [1,2]. It indicates that an aggressive strategy must be implemented to create unique technologies and ensure sustainable development. Hydrogen is regarded as the highest potentially clean fuel owing to its diverse resources, significant calorific quality, superior thermally conduct, and high reaction rate, which allows for the

manufacture of hydrogen metallurgy by swapping hydrogen for carbon as the reducing factor. This could successfully reduce CO₂ emissions while also lowering the steel industry's reliance on fossil fuels [3,4].

one of the favorite ways to generate hydrogen are being performed through the dry reforming of methane [5,6]. Particularly intriguing is the substitution of this energy through an admixture of gases of H₂ and CO, known as syngas. Since the dry reforming of methane can convert hazardous ozone-depleting gases, CH₄, and CO₂ into the desirable equimolecular syngas for the Fischer-Tropsch reaction. Owing to the H₂/CO ratio being among the considerable crucial variables in Fischer-Tropsch synthesis to avoid the carbon risk during the process as well as causing the water gas shift activities that produced more H₂, the presence of hydrogen leads to the products producing small-chain hydrocarbons, the (DRM) has obtained considerable attention recently (CH₄ + CO₂ ↔ 2CO + 2H₂, ΔH° 298 K = 260.5 kJ mol⁻¹) [7–9]. Because of its endothermicity, overheating is essential to achieve appropriate

* Corresponding author at: Centre of Hydrogen Energy, Institute of Future Energy, 81310 UTM Johor Bahru, Johor, Malaysia.

E-mail address: aishahaj@utm.my (A.A. Jalil).

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conversion of CH₄ and CO₂. The inability to prevent their appropriateness to loss of activity and extensive carbon deposition caused by agglomeration at the hurtful reaction environment leads to swift and extensive inactivation of catalysts [10–12]. Coke is essentially formed via two mechanisms. The methane cracking reaction: (CH₄ ↔ C + 2H₂ ΔH₂₉₈⁰ = 75 kJ/mol), and the CO decomposition (2CO ↔ 2C + CO₂ ΔH₂₉₈⁰ = 75 kJ/mol) [13–15]. These challenges propelled researchers to investigate suitable catalysts with the potential to enhance catalytic efficiency while limiting carbon deposition. Thus far, materials based on nickel are proven to possess superb DRM effectiveness when evaluated from an industrial perspective owing to their remarkable efficiency, accessibility, and inexpensiveness [16–18].

The most widely discussed metal in the DRM is nickel. Nevertheless, carbon deposition and metal sintering increased the susceptibility of Ni-based catalysts to deactivation. Consequently, considerable investment has progressed into enhancing the function and durability of Ni in the following fields: determining the support and modifying its characteristics, developing a method of preparing the catalyst, and introducing promoters [19–21]. Aspects of support, as previously discussed, have substantial effects on the performance, selectivity, and stabilization of supported Ni catalysts in DRM reactions.

SiO₂ [22], KCC-1 [23], Al₂O₃ [17], ZSM-5 [24], and SBA-15 [10] are variations of support materials. The silica and alumina-silicate-supported Ni catalyst was extensively researched for DRM [25,26]. The initial conversions of Ni/ZSM-5, Ni/Si, and Ni/Al synthesized by impregnation were high, but they were deactivated throughout the period because of sintering and carbon accumulation [27–29].

Numerous adjustment techniques have been investigated to enhance the performance of alumina-silicate supported Ni catalysts, including adjustment of preparation methods, precursors, and pre-treatments; as well as the addition of metal or oxide promoters to control basicity and acidity, and metal-support interaction with Ni distribution.

According to our prior research, Ni-impregnated FSA resulted in a catalyst with great efficiency and long-term stability. The unique morphology of FSA was exhibited for the first time to support Ni in DRM reaction [30]. The extraordinary surface area derived from its fibrous morphology was responsible for the elevated effectiveness, whereas the synthetic route accounted for its long activity by confining Ni crystallites into the framework of support.

This research involves the production of spherical FSA-supported Ni catalysts with several promoters (Ce, Cs, Sm, and Sr). Comparative work was conducted on the catalysts' chemical, physical, and structural characteristics. The aims are to investigate the potential for coking resistance in DRM and to determine the function of promoters in optimizing catalytic efficiency. The combination of several promoters (Ce, Cs, Sm, and Sr) and Ni/FSA catalysts for syngas production. Furthermore, the novel catalysts were evaluated for DRM.

2. Experiment strategy

2.1. Catalysts preparation

The hydrothermal process was employed with the seeds of Al₂O₃ to fabricate FSA. Al₂O₃ was mixed with a solution of toluene (Sigma-Aldrich, > 98 %) and *n*-butanol (Merck, > 98 %). After a half hour of stirring, TEOS was added dropwise. Hexadecyltrimethylammonium bromide (Sigma-Aldrich, CTAB, > 98 %) with urea (Merck, > 98 %) were introduced concurrently to the solution and blended with 720 mL of deionized water. Si/Al = 1.22, toluene/*n*-butanol = 13.7, and urea/CTAB = 3.7 are the most essential ratios. After exposure to 400 W of microwave radiation for six hours, the substance of the sample was vaporized at 120 °C for 24 h. Then the white powder obtained was placed in a furnace to heat for six hours at 550 °C to achieve FSA support.

The impregnation technique was utilized to prepare a variety of metal-based catalysts. Ni and the various metal precursors were

introduced into FSA via an aqueous solution. A substantial quantity of Ni and promoters were loaded at 12.5 wt% and 2 wt%, respectively. The catalysts were synthesized from the different metal nitrates: nickel (II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] (99 %, Sigma-Aldrich), samarium (III) nitrate hexahydrate (99 %, Sigma-Aldrich), cerium (IV) oxide (99 %, Sigma-Aldrich), strontium chloride hexahydrate (99 %, Sigma-Aldrich), cesium nitrate (99 %, Sigma-Aldrich). The impregnated specimens were left to dry at 110 °C for 24 hrs in an atmospheric oven, followed by the oxidation at 550 °C with a thermal rate of 10 °C min^{−1} for three hours. The obtained catalysts were denominated (Ni/FSA, Cs-Ni/FSA, Sr-Ni/FSA, Ce-Ni/FSA, Sm-Ni/FSA).

2.2. Characterization

On a Bruker-D8 diffractometer with monochromatized Cu-K radiation (=1.54056) and a Vantec-1 detector running at 40 kV and 40 mA, the X-ray diffraction (XRD) profiles were documented. Using Micromeritics ASAP-2020 equipment, the Brunauer-Emmett-Teller (BET) pore volume, surface area, and pore diameter of the specimens used in this investigation were determined via N₂-adsorption at 77 K. While the non-local density functional theory (NLDFT) method is for the best calculation of the pore size distribution, which enables precise location predictions for capillary condensation. Fluids are contained in pores with basic geometries in NLDFT models (slit, cylinder, sphere). Since the fluid density and solid–fluid possibility only vary in the orientation corresponding to the pore wall, the models are functionally-one-dimensional [31]. Measurements of H₂-TPR were employed to evaluate the reducibility of the catalysts by the Micromeritics Chemisorb-2720 chemisorption instrument. Subsequently, to get rid of humidity and undesirable impurities, 25 mg of catalyst was treated with helium (20 mL min^{−1}, 60 min, and 300 °C). The patterns of H₂-TPR were identified between the 80 to 800 °C range with a rated temperature of 10 °C/min and a flow of H₂/Ar 10 % (vol.) for 20 mL/min. Additionally, the samples were assessed using Fourier-transform infrared (FTIR) on an Agilent Cary 640 analyser operating at 25 °C with a resolution of 5 cm^{−1} and a wavelength band spanning 400 to 3800 cm^{−1}. To verify the carbon excess on the surface of the catalysts, a Mettler Toledo TGA/SDTA 851e Thermo-gravimetric equipment with a temperature range of 10–900 °C at 10 °C/min with ventilation was employed. The carbonaceous deposits in the spent catalysts were examined using lasers (510 nm) and a 50x magnification microscope lens connected to a Renishaw in Via Raman spectrophotometer and recorded across 1000 and 2000 cm^{−1} wavelengths.

2.3. Catalyst evaluation

The catalytic assessments for dry reforming of methane were performed in stainless steel fixed bed reactor through a prolonged stream with temperatures at 750 °C under ambient pressure. A quartz wool supporter was employed to conserve the position of the 0.2 g of catalyst in the fixed bed reactor. Prior to the evaluation of the catalyst, the sample was subjected to 50 mL min^{−1} of air at 750 °C for 60 min, followed by 50 mL min^{−1} of H₂ at 800 °C for reduction throughout 180 min. The reactor was subsequently cooled to activation temperature under the injection of N₂. The reaction mixture gases were 1:1:2 CH₄:CO₂:N₂ and the total stream was 100 mL/min. With a gas chromatograph analyzer (7820 N Agilent GC), product gases (H₂ and CO) were constantly recorded online. The reaction was conducted to function in the steady-state status for 60 min before being sampled for the temperatures that were taken into account. The estimates for CH₄ and CO₂ conversion and the ratio of H₂/CO have been calculated through equations (1–3) [32–34].

$$\text{Conversion of CH}_4 = \frac{F_{(\text{CH}_4)\text{in}} - F_{(\text{CH}_4)\text{out}}}{F_{(\text{CH}_4)\text{in}}} \times 100 \quad (1)$$

$$\text{Conversion of } CO_2 = \frac{F_{(CO_2)in} - F_{(CO_2)out}}{F_{(CO_2)in}} \times 100 \quad (2)$$

$$H_2/CO = \frac{F_{(H_2)out}}{F_{(CO)out}} \quad (3)$$

3. Results and discussion

3.1. Physicochemical characterizations

The diffraction spectra of each fresh catalyst and the support are shown in Fig. 1. All calcined catalysts diffraction spectra seemed to have a broad and intense band of 2θ in the range of $21\text{--}30^\circ$, where it is prevalently attributed to the amorphous phase of SiO_2 framework (JCPDS card No. 29-0085) [30,35]. In comparison, the catalysts (promoted and unpromoted) revealed that peaks matched to the cubic NiO phase had a slight shift towards lower angles, indicating the release of $NiAl_2O_4$ spinel phase at 25.6° , 35.2° , 43.3° , 52.5° , and 57.5° (98-015-7690 ICSD) [25,36]. Which corresponds to the δ - Al_2O_3 phase. The spinel made it possible for the metal and support to interact extra strongly, preventing carbon accumulation and sintering. Furthermore, the diffraction line for other promoted specimens Sm_2O_3 ($2\theta = 28.3^\circ$, 32.7° and 46.8° , JCPDS card No. 42-1461) [37], SrO ($2\theta = 27.1^\circ$, 35.1° , 50.9° , and 63.9° , JCPDS 75-0263) [38], Cs_2O ($2\theta = 26.5^\circ$, 30.8° , 44.1° , and 54.8° JCPDS card no. 09-0104) [39], did not emerge on the corresponding Sm , Sr , and Cs promoted catalysts, inferring that the promoter nanoparticles were scattered finely beside the XRD observation range. These observations affirm that the FSA framework is still prevalent although the promoters and Ni particles are loaded. The typical

phase spinel-parallel $NiAl_2O_4$ species developed on $Ni-Al_2O_3$ instead of NiO [26,40], meanwhile, spinel frameworks could be envisioned forming with the promoters [41], Ni -P-AL (P = Sm , Cs , Sr , and Ce) phase generated inter that the NiO particles introduced to the FSA were dispersed homogeneously [42].

The FSA demonstrated an abundance of active sites, and oxygen mobility for flexible NiO scattering, which inhibits the potential for the NiO crystal to aggregate and enhances metal-support interaction [7]. A wider combined oxide distribution, as a result of a stronger metal-support interaction, boosted the catalysts' reducibility and diminished crystallinity [43]. However, the peak due to CeO_2 at 56.3° (JCPDS card No. 34-0394) has surfaced, which probably affected the inhibiting of the migration of Nickel ions into the alumina framework, which restricts the interaction between Ni and Al_2O_3 compared with other [44].

Nitrogen physisorption was employed to evaluate the textural properties of the catalysts. Fig. 2 depicted the correlating adsorption/desorption isotherms and distribution of pore size plots. All of the specimens (promoted and unpromoted) presented type IV isotherms with hysteresis loops of the H_3 type, characteristic of mesoporous materials (Fig. 2A). The properties gathered in Table 1 are based on the isotherms depicted in Fig. 2. The fibrous framework catalysts possessed a substantially greater surface area; this was due to their mesoporous character. Furthermore, the capillary condensation, which occurred at $P/P_0 = 0.3$ and 0.9 through FSA, reflects the availability of intraparticle and interparticle voids [7,30]. The surface area of Ni /FSA grew to $645.01 \text{ m}^2/\text{g}$ after loading Ni , indicating that the occurrence was caused by fine scattering with non-blockage in the pores of FSA support [45], while the introduction of promoters exhibited opposing impacts on the catalysts. The decline in the surface area has been identified in the order; $Sm-Ni/FSA > Ce-Ni/FSA > Sr-Ni/FSA > Cs-Ni/FSA$. The Cs -promoted catalyst displayed the lowest surface area, which could be attributed to the nature of Caesium.

The findings of the non-local density functional theory (NLDFT) method for all the pore diameters of the specimens are shown in Fig. 2B. FSA found mesopore organization with a dominant peak in the $30\text{--}70 \text{ \AA}$ band and thin peaks in the $100\text{--}200 \text{ \AA}$ region. The slight peaks created by the spacing amongst dendrimeric molecules are owing to mesopores generated via surfactant self-assembly. Overall, there seemed to be no discernible difference in both Ni /FSA and FSA regarding pore dispersion because the particles of Ni scattered tiny [30,42,46]. It became clear that the mesopore volume had slightly diminished as a consequence of the metal nanoparticles being uniformly distributed within the mesopore. Nevertheless, variances in the distribution of pore sizes of the promoted catalysts imply potential textural qualities that may be essential in optimizing catalytic efficiency.

The potential of NiO to be reducible to its metallic phase (Ni^0) possesses an appreciable impact on catalytic effectiveness [47]. The H_2 -TPR

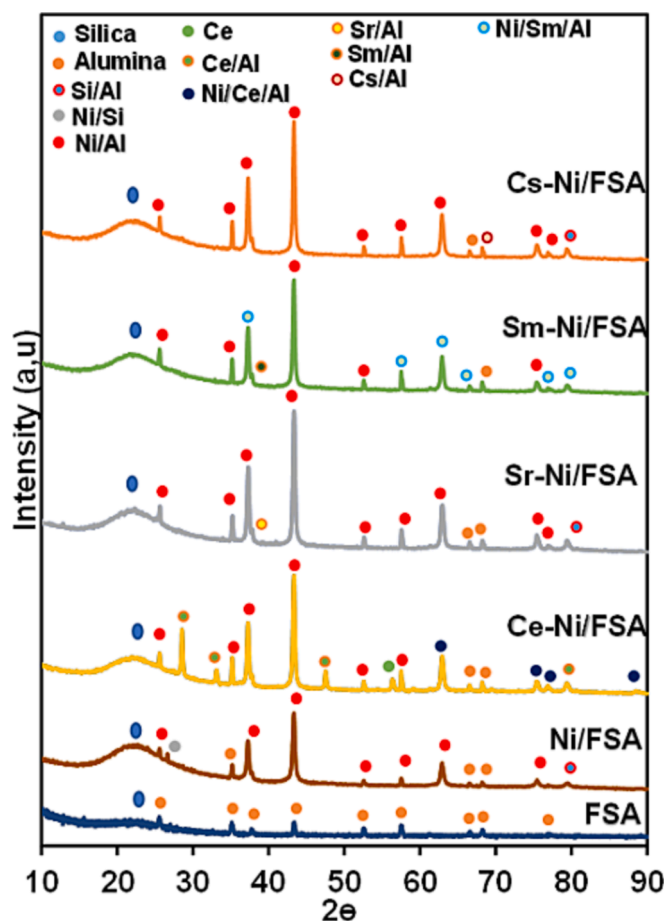


Fig. 1. XRD patterns of FSA support, Ni supported FSA and promoted ($Ce-Ni/FSA$, $Sr-Ni/FSA$, $Cs-Ni/FSA$, $Sm-Ni/FSA$).

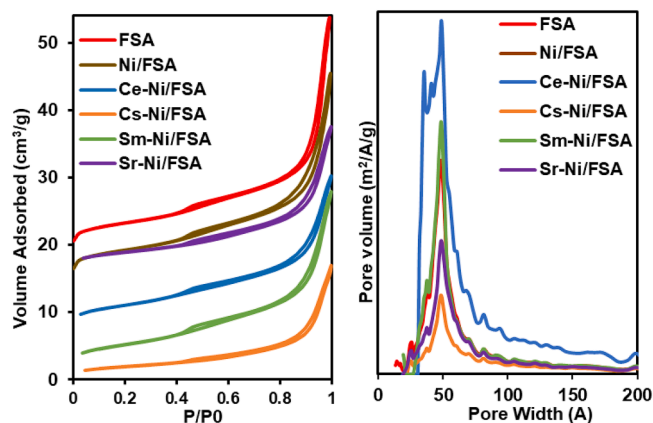


Fig. 2. A) Nitrogen adsorption-desorption isotherms, B) the pore size distribution for the catalysts.

Table 1

Textural properties of various Ni amount beside on catalyst.

Catalyst	Surface Area (m ² /g)	Microporevolume (cm ³ /g)	Total Pore Volume (cm ³ /g)	Pore Size (nm)
FSA	334.92	0.0038	1.21	14.45
Ni/FSA	645.01	0.0056	1.91	11.84
Sm-Ni/FSA	336.51	0.0027	0.93	11.11
Ce-Ni/FSA	327.02	0.0024	0.80	9.85
Sr-Ni/FSA	234.91	0.0027	0.74	12.71
Cs-Ni/FSA	152.74	0.0032	0.58	15.41

patterns of promoted catalysts are shown in Fig. 3. Almost all the specimens exhibited high reduction peaks compared to their unpromoted counterparts, reflecting an increase in the reducibility of NiO species in promoted catalysts. The Ni/FSA catalyst showed a broad peak from 360 to 550 °C ascribed to NiO species, however, the slight decrease after the addition of Sm explained the samarium influence on nickel interaction with FSA.

Ni oxidation to form the SmNiO₃ phases in the presence of Sm probably diminished the interaction via FSA and accelerates the reduction of Ni into Ni⁰ [48,49]. However, the Ce promoted has shifted peaks centered at 500 °C this peak could be in close proximity to Ce⁴⁺, which is deposited at the surface of CeO₂ nanoparticles [50,51]. Therefore, the shoulder via peak at 700 °C could have emerged to the complicated reduction NiAlxOy species that vigorously interacted. The

existence of a NiO-CeO₂ homogeneous combination was verified at the shoulder peak at 800 °C with a relative intensity of the peak at 400 °C. Additionally, the correlation between the reduction of Ce⁴⁺ → Ce³⁺ in CeO₂ bulk correlated to CeAlO₃ generation was confirmed through the shoulder peak at 800 °C [52,53], which was validated by the XRD profile. Furthermore, the amount of hydrogen consumed grows through the Cs promoter at 450 °C, indicating an increase in Ni oxidation [54,55]. This property aids in prolonged activity and also improves the capability for carbon deposition resistance.

The peak shifts to a slightly broad shoulder with raise in temperature (around 555 °C) due to the introduction of Sr clusters. As well, the presence of Sr shifted the peak of NiO reduction to higher temperatures owing to the nickel has interacted with SrO, while SrO is more complicated to reduction than NiO [56].

The interaction between various promoters (Ce, Sm, Cs, and Sr) and FSA-supported Ni was detected through FTIR analysis displayed in Fig. 4 in the 400 to 4000 cm⁻¹. A wavelength of 460, 800, 960, 1080, 1220, cm⁻¹ manifested in all specimens, denoting the siliceous construction, as Si engages with neighbouring atoms (e.g., Si-O, Si-OH, Si-O-Al, Si-O-Si, and Al-O-Al). The vibrations of the OH group in water are reflected via the 3400 and 1640 cm⁻¹ bands. The shoulder bands were approximately between 1090 and 1240 cm⁻¹ and exhibited an asymmetric stretching of the Si-O-Si structure internally and externally. The bands that appeared at 800 cm⁻¹ and 960 cm⁻¹ were related to the symmetric stretching of Si-O-Si and exterior silanol compounds (Si-OH), respectively [30,57,58].

The T-O-T bending vibration (T = Si or Al) created a distinctive peak at 460 cm⁻¹ attributed to the Al-O octahedral bond in the Al-O stretching phases or Si-O-Al. The restricted band at 970 cm⁻¹ in Ni/FSA might be inferred as showing the interaction of transitional metal atoms with SiO stretching vibrations proximate to the surrounding siliceous

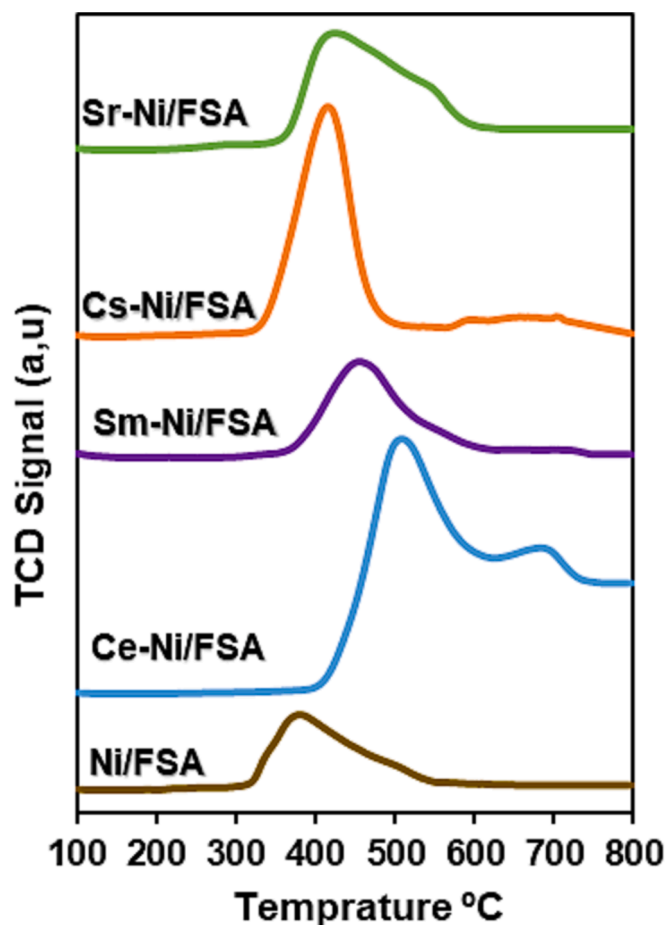


Fig. 3. H₂ temperature-programmed reduction of unpromoted and promoted catalysts.

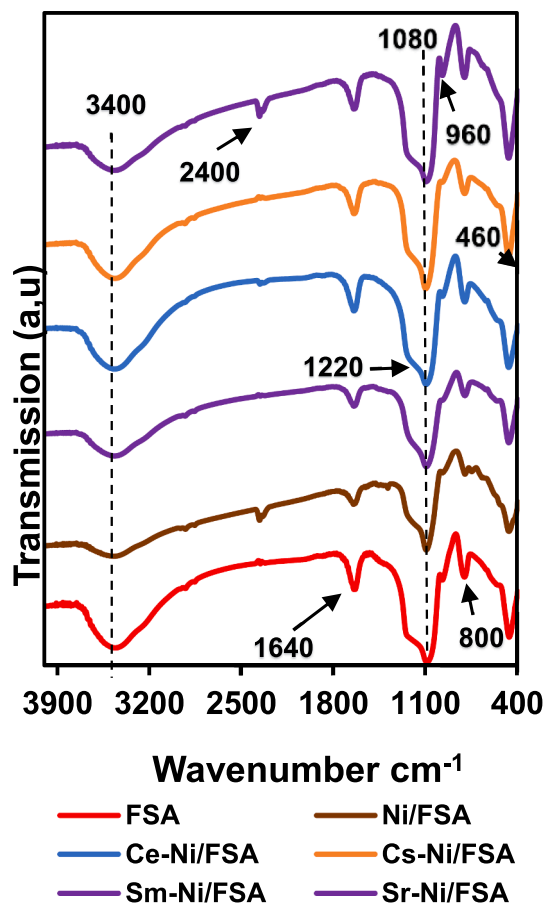


Fig. 4. IR study, KBr-FTIR patterns of FSA, Ni/FSA, Ce/FSA, Sm-Ni/FSA, Cs-Ni/FSA, Sr-Ni/FSA.

substance frame [27,59]. Variational generation of Si-OH group surfaces driven through Ni nanoparticles on FSA to form Si-O-Ni-bonds could thus, be indicated by shifts in the transmittance band. After promoters were doped on the catalyst, the slightly increased intensities differed when compared to their pristine support owing to a reduction in the core components' siliceous framework, which permitted NiO to scatter within their surface for dealumination, and the silica catalyst's composition, which reflected O-Si and O-Al alteration via the metallic ions of the promoters (Ce, Cs, Sm, Sr) with the originally formed Si-O-Si and Al-O-Al bonds. Furthermore, the $\text{C}\equiv\text{N}$ stretching group is responsible for the peak at approximately 2400 cm^{-1} that was clearly visible via Ni/FSA and Sm-Ni/FSA. The electron density attributable to the $\text{C}\equiv\text{N}$ group affects the frequency of the $\text{C}\equiv\text{N}$ stretching peak(s), with larger electron intensities typically causing shorter frequencies. Thus, the orientation informs something about the sort of molecule the group is associated with [60].

3.2. Activity test

The catalytic runs for the promoted and unpromoted catalysts were carried out at 750°C throughout a 50 h stream with a stoichiometric feed ratio ($\text{CH}_4:\text{CO}_2 = 1$). The observed results of catalytic performance are summarized in Fig. 5. The DRM approach documented by [61] implies that the metallic activity sites conduct CH_4 activation, while the oxygen vacancies on the support perform CO_2 oxidation [62]. Consequentially, the DRM reaction was produced through CH_4 decomposition releasing H_2 and a surface carbonaceous molecule on the metal's active surface (Ni), and was followed via a CO_2 reaction depicting surface carbon, which formed CO at the FSA surface.

As exhibited in Fig. 5(a) and (b), the evaluation of CH_4 and CO_2 conversion was developed following the introduction of the Cs promoter compared with other promoters, perhaps owing to the Cs has significant oxygen vacancies and redox abilities. However, the addition of Sm was destructive to the efficiency of the catalyst after 50 h of TOS, which dropped through the first hour from CH_4 conversion (91 % to 75 %) and CO_2 conversion (90 % to 53 %). Realized from the H_2 -TPR result is that the presence of Sm reduced the metal support interaction as well as support active sites. The blockage of the active site and weak interactions between FSA and Ni have been suggested to hasten Ni sintering, leading to catalyst deactivation throughout the DRM reaction [63,64]. Therefore, prominent sintering could be associated with the

behavior that was observed.

Indeed, the sequence of deactivation in all specimens throughout the reaction was $\text{Sm-Ni/FSA} > \text{Ce-Ni/FSA} > \text{Sr-Ni/FSA} > \text{Ni/FSA} > \text{Cs-Ni/FSA}$ as shown in Fig. 5 which is related to the redox capabilities of the promoters [65,66]. Actually, the redox potentials of the metals not only enhance the long activity of the catalyst but also efficiently boosted carbon gasification, preventing the catalyst from deactivation.

According to the previous study, the adsorption of Cs atoms in a monolayer dramatically enhances the oxidation of the Ni surface. Moreover, the layer of Cs changed the orientation crystallographic of the oxide film. The hexagonal arrangement of Cs has shifted the surface potential contours through NiO development to follow the symmetry of the Cs layer instead of the symmetry of the Ni metallic. Furthermore, the introduction of the Cs increases the sticking coefficient of O about 15 times. As the sticking coefficient of O goes up, oxidation should be enhanced through the site exchange mechanism [54,67,68].

Fig. 5C shows that the steam ratio of H_2/CO had a linear relationship with the percentage of conversions Fig. 5(A, B). The variation in the effectiveness of the catalyst performance indicates that the redox properties affect catalyst activity for DRM.

Besides, the H_2/CO ratio of most of the specimens exhibited a stoichiometric value of 1. However, attending the metals promoter (Cs, Sm, Ce, Sr) caused the various ratio of H_2/CO due to the differences in their physicochemical properties. As shown in Fig. 5C, the Cs-promoted catalyst showed inferior performance compared to other samples owing to the oxidation property that increases the generation of CO. Moreover, the Sr, as well as Sm promoted samples exhibited the highest H_2/CO ratios which could lessen the possibility for reverse water gas shift reaction RWGS ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) and inclination to boost the reaction temperature. Due to a portion of the H_2 -produced consumption being utilized to convert CO_2 to CO, RWGS is associated with a decrease in the ratio of syngas and the potential to expand by increasing the reaction temperature, as suggested by thermodynamics [2,21,69,70]. Furthermore, the surface area plays the role of syngas ratio (H_2/CO), the (Sm and Sr) promoted Ni/FSA showed high surface area than Cs-promoted Ni/FSA, which provides extra oxygen storage on the catalyst, whereas oxidizes the C to CO with intermediate carbonate atom production on reducible basic supports, so preventing coke generation [7].

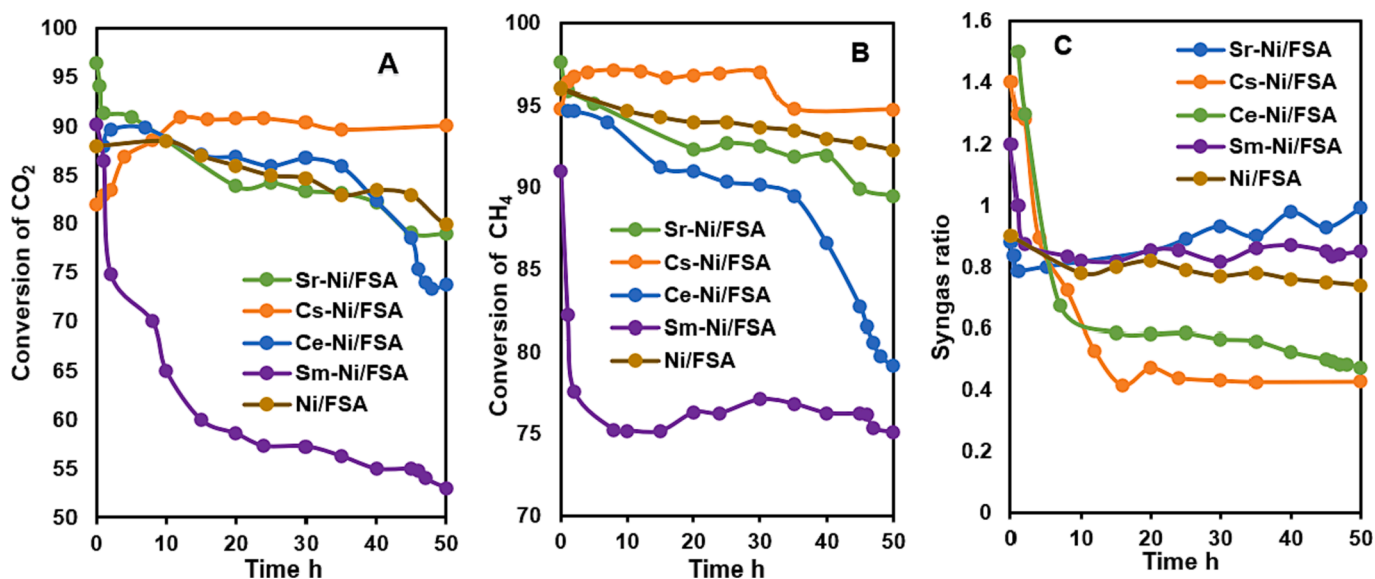


Fig. 5. Catalytic performance over the catalysts with various promoted (Cs, Ce, Sm, and Sr) Ni/FSA (Condition: $\text{CO}_2/\text{CH}_4 = 1:1$, GHSV = $50,000\text{ mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, $P = 1\text{ atm}$, $T = 500\text{ to }850^\circ\text{C}$). (A) CO_2 conversion; (B) CH_4 conversion; and (C) H_2/CO ratio.

3.3. Coke characterization after long activity

Available literature [11,71,72] claims that carbonaceous species are always created during CO₂ reforming with CH₄. Traces of coke deposit on the spent catalysts were analyzed using Raman, XPS, XRD, TGA, and DTG techniques. The TGA and DTG spectra of the used (promoted and unpromoted) catalysts are displayed in Fig. 6. The quantity of coke deposited through the surfaces of each spent catalyst was determined and contrasted by employing the thermogravimetric analysis. The observed weight percent decline in the TGA curves was driven by the oxidation of carbon accumulated to CO₂.

As illustrated by the Figure, during O₂ oxidation, the mass percentage declined relatively; indicating that additional carbon had been introduced onto the surface. According to Fig. 6A, the majority of the spent catalysts exhibited two distinct behavioral types with identical characteristics. The initial peak at the minimal oxidation degree of 100 °C, is ascribed to the formation of amorphous carbon on the catalyst's surface, which seems to oxidize at less temperatures than most of the crystalline carbon. At temperatures exceeding 650 °C, the graphite carbon oxidizes [35,73]. previous studies have demonstrated that the crystallite size of Ni catalysts has a significant impact on carbon deposits and elimination restrictions because narrower Ni crystalline phase catalysts tend to produce less coke [74].

The carbon of the spent specimens can be categorized, according to Fig. 6A The Sm-Ni/FSA has the highest mass amount of carbon, which is supported by the peak at 700 °C via weight loss of 63.5 %. This is the principal mechanism of catalyst deactivation. In contrast, the Sr-Ni/FSA and Ce-Ni/FSA possess notable peaks described in the different categories of carbon with percentage weight loss of 30 and 42.5 % respectively, which were higher than Ni/FSA. However, based on Cs-Ni/FSA, there is no likelihood for the formation of amorphous carbon at 100 °C, owing to amorphous carbon being uncomplicated to oxidize than graphitic carbon, which signifies the oxidation of the amorphous carbon through the Cs property.

Fig. 6B displays the differential thermogravimetry profiles of the spent catalysts in relation to temperature shifts. Decomposition peaks were easily distinguished as belonging to distinct forms of carbon denoted as C α , C β , and C γ . Syngas is usually generated from amorphous C α oxidized carbon at low temperatures. However, higher temperatures result in the oxidation of C β and C γ , which are clearly correlated to the catalytic inefficiencies [75]. The weight losses in all specimens are attributed to C, whereas the weight loss of peaks at approximately 100 °C is responsible by C α , while the modest peak around 550 and 750 °C is ascribed to C β with C γ also probably the effect of the polymerization and rearrangement of functional carbon atoms.

As a practical phenomenon, the Ni/FSA-promoted Cs was observed

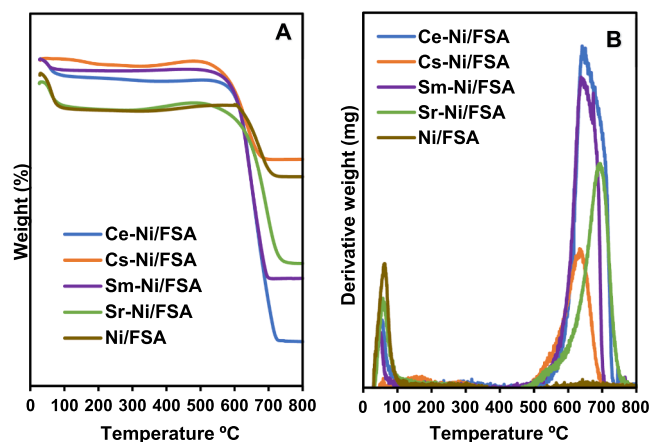


Fig. 6. Analysis of carbon deposition on spent catalysts by (A) TGA, and (B) DTG profiles.

to be the best Ni promoter to inhibit carbon accumulation on catalysts while also enhancing catalytic effectiveness and stability. Furthermore, the occurrence of coke disarmament by Reverse Boudouard reaction ($C + CO_2 \rightarrow 2CO$) and carbonaceous gasification ($C + H_2O \rightarrow CO + H_2$) has led to the notion that Cs-Ni/FSA had the least quantity of coke [22,76].

The Raman spectra (Fig. 7) revealed the various carbon species generated throughout the period of 50 h of long performance. The disorder-generated (D-band) at 1350 cm⁻¹ and the graphite carbon (G-band) at 1590 cm⁻¹ are two distinct peaks attributed to sp²-bonded carbon [23]. Band intensity is a measure of the estimated amount of carbon, whereas the IG/ID band ratio was employed to determine whether rapidly graphite carbon is formed. Because of consequence, a higher IG/ID ratio is indicative of increased rates of graphitic carbon formation. The catalysts possess extremely amorphous carbon with inconsistent properties, implying a highly vulnerable to deactivation and a rejuvenation mechanism more complex to perform [75].

The I_G/I_D ratios of Ni/FSA, Cs-Ni/FSA, Sm-Ni/FSA, Ce-Ni/FSA, and Sr-Ni/FSA were 0.9, 0.8, 1.5, 1.1, and 1.03, respectively. The Cs-Ni/FSA sample observed the lowest ID/IG ratio and the thinnest band regions through the Raman wavelengths hypothesizing that only a minute quantity of carbon should be deposited on Cs-Ni/FSA, with the majority of the amorphous carbon getting disordered due to oxidation.

According to Fig. 8, the XRD profile of the spent catalysts are noticeably different from those of fresh. Reflections at $2\theta = 26.5^\circ$ (JCDPS 26–1080) revealed the existence of crystalline carbonaceous species, frequently characterized as graphitic carbon (002), for promoted and unpromoted specimens [11,77]. Which was the highest with Sm-Ni/FSA compared to other samples. Superior carbon resistance observed for Cs-Ni/FSA and Sr-Ni/FSA was strongly attributed to the oxygen storage capacity. Additionally, the peak at approximately 44.6° is due to the

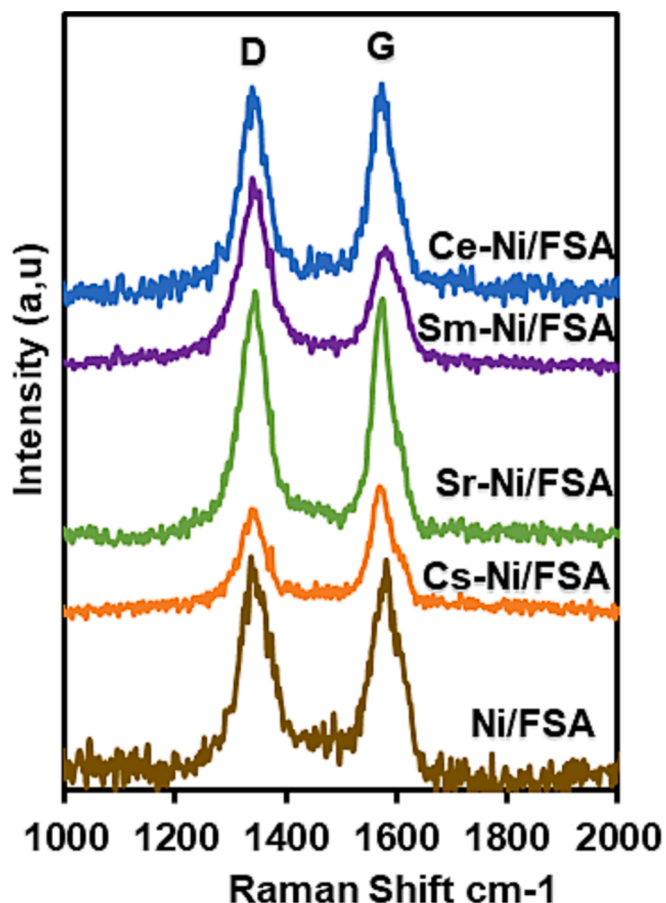


Fig. 7. Raman spectroscopy of spent catalyst.

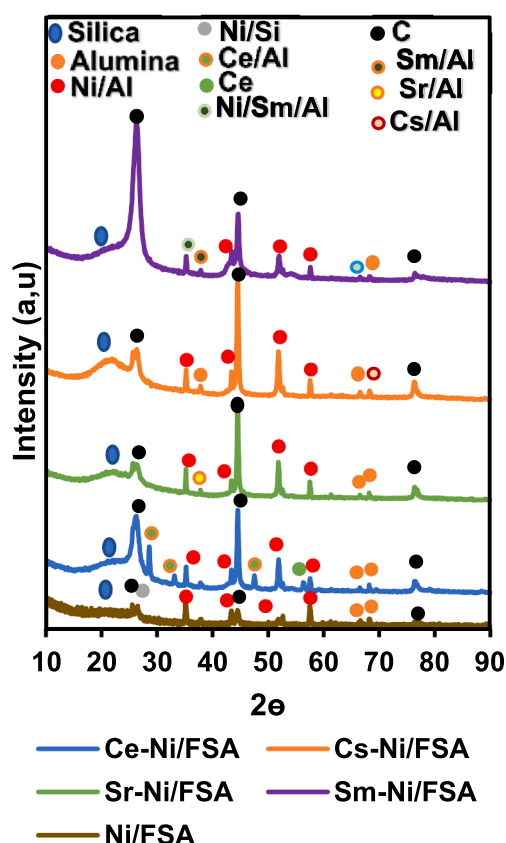


Fig. 8. Wide-angle XRD pattern for the spent catalyst of Ni/FSA, Cs-Ni/FSA, Sm-Ni/FSA, Ce-Ni/FSA, and Sr-Ni/FSA.

reflections of carbon nanostructures (100) and (101). The peak at 77° corresponds to (110) graphite carbon [78,79]. As noticed via the Sm-Ni/FSA was the maximum level found. This illustrates that the crystallinity of Sm-Ni/FSA has expanded more than its fresh, suggesting that the metal sintering that happened was definitely enough to be shown by XRD. The quantity of oxygen and the size of the Ni⁰ provided evidence that the Cs-Ni/FSA catalyst seemed to cause less Ni-sintering, which improved significantly the stability of the catalyst in DRM functions.

3.4. Conclusion

In this research, the effects of (Cs, Sm, Ce, and Sr) promotion on the physiochemical properties and catalytic abilities of Ni/FSA catalysts synthesized employing the impregnation technique have been investigated. The BET surface area and the pore width were reduced with the incorporation of the promoters into Ni/FSA. The TPR profile reveals that the introduction of Cs to the Ni/FSA catalyst altered the reduction temperature of NiO species and the specimen reduced effectively under reaction environments, compared to other catalysts investigated. Cs promotion onto the Ni/FSA catalyst had boosted methane conversion and prevented carbon accumulation, as proven by the long activity test (93 % of CH₄ conversion and 91 % of CO₂ conversion). However, the agglomeration of active metals with an excess of Ce, Sm, and Sr promoter blocks the pores of FSA which leads to losing the activity around 45 % of Sm-Ni/FSA.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

The data that has been used is confidential.

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