



The role of catalyst synthesis on the enhancement of nickel praseodymium (III) oxide for the conversion of greenhouse gases to syngas

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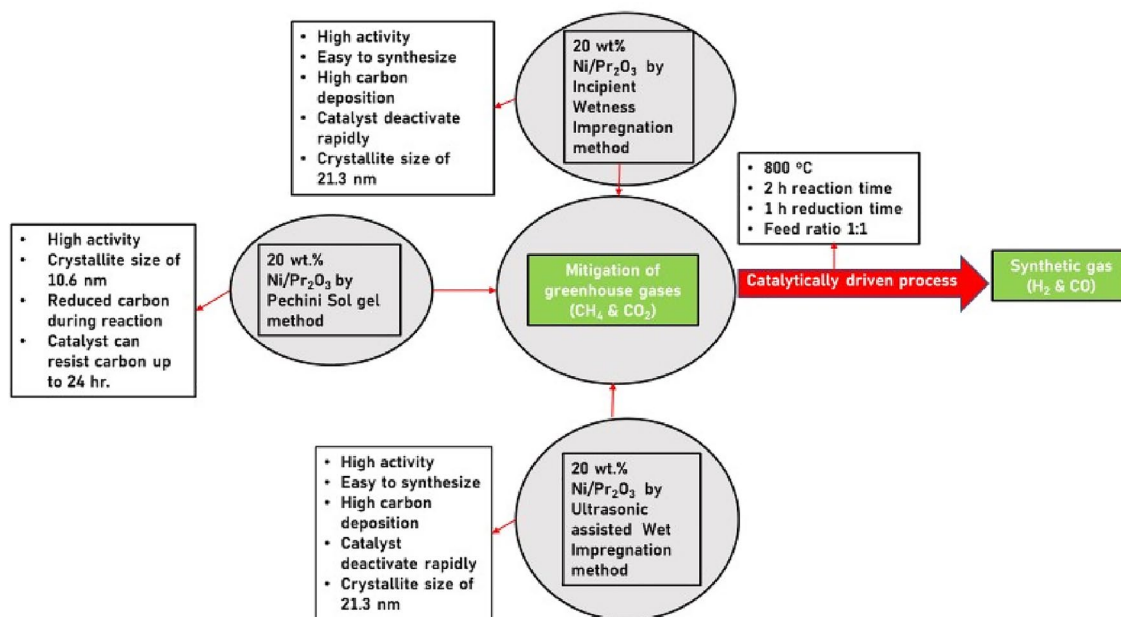
Abstract

Catalytic methane (CH₄) dry reforming (MDR) reaction proceeds with the formation of carbon; hence the effects of the catalyst preparation method on the type of carbon are worth investigating. This study investigated the performance of 20 wt% nickel praseodymium (III) oxide (20 wt% Ni/Pr₂O₃) catalysts prepared by incipient wetness impregnation (IWI), ultrasonic wet impregnation (US-WI), and Pechini sol–gel (PSG) methods. The catalysts crystallite size was approximately 21.3 nm, 21.3 nm, and 10.6 nm, for IWI, US-WI, and PSG catalysts, respectively. Study of the temperature effect on the MDR system showed that higher temperatures favored the MDR reaction with the side reaction playing vital roles. The catalyst synthesized by the PSG method showed higher carbon gasification rate with the stability up to 24 h, whereas catalysts from other synthesis methods were only active for less than 2 h, which could be due to the formation of higher amount of filamentous carbon, balance in oxygen species, and the smaller crystallite size of the PSG-20 wt% Ni/Pr₂O₃. The PSG-20 wt% Ni/Pr₂O₃ catalyst accumulated more filamentous carbon than graphitic carbon. In contrast, the IWI and US-WI catalysts accumulated mainly graphitic carbon which encapsulated the Ni⁰ sites, resulting in excess carbon deposition and reactor clogging within 2 h on stream.

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Graphical abstract



Keywords Methane dry reforming · Greenhouse gases · Nickel catalyst · Synthesis method · Carbon species · Oxygen species

Introduction

The increase in the anthropogenic greenhouse gases, which causes global warming has led to researchers developing different techniques to utilize these environmental pollutant gases (methane (CH₄) and carbon dioxide (CO₂)) by reforming them into more useful feedstock of gaseous fuels or products from gaseous fuels. Therefore, the development of the CH₄ dry reforming (MDR) reaction is an advantageous process technique to mitigate CH₄ and CO₂ and produce synthetic gas which is suitable for Fischer Tropsch Synthesis (Khademi et al. 2021). Other researchers have employed MDR reaction to enhance the quality of Anaerobic Digestion (AD) derived biogas which is mainly composed of CH₄ and CO₂ (Kwon et al. 2018; Moogi et al. 2022). The product of MDR; synthesis gas (syngas) is utilized as feedstock by several manufacturing processes, hence, making the process vital for various prospective applications (Sun et al. 2022). MDR reaction is highly endothermic in nature; therefore, high temperature which corroborates to high heat energy usage is desired (Li et al. 2020). An alternative to the high energy demand of MDR reaction is the use of highly efficient catalysts which increases the syngas yield (Cao et al. 2022). Because higher yield translates to commercial benefits from the

process, it is important to upgrade the catalyst's quality. Some researchers have focused on using noble metal-based catalyst (ruthenium (Ru), rhodium (Rh), iridium (Ir), Platinum (Pt) (Rezaei et al. 2006), Ru (Whang et al. 2017), and Pd, Pd- niobium (Nb) (Ballesteros-Plata et al. 2022)) due to their performance and resistivity toward carbon deposition. Others have used transition metals (Ni-Co (Fan et al. 2011), Ni (Baudouin et al. 2013), and Co (Osazuwa et al. 2017)) because noble metals are quite expensive.

In the current research field, Ni is readily utilized for MDR because it is less expensive and exhibits good performance. Nonetheless, Ni loses its activity easily due to its affinity for carbon deposited during CH₄ cracking (Ekeoma et al. 2022). Moreover, excess Ni affects the Ni-support interaction because it minimizes the catalyst's basic strength (Zanganeh et al. 2013). To solve this problem, researchers have focused on designing new catalysts to enhance the MDR reaction (Liu et al. 2012). In developing a new catalyst, one key parameter that significantly affects the catalyst physicochemical properties and performance toward the MDR reaction is the method of catalyst synthesis (Osazuwa et al. 2021). This parameter could potentially minimize catalyst deactivation resulting from carbon deposits, thereby enhancing the catalyst stability.

According to literature, nature of supports and methods of catalysts' synthesis can promote good performance of Ni-based catalysts (Mustu et al. 2015). For instance, alumina (Al_2O_3) in combination with transition metals (Ni, Co) which are widely utilized catalysts in MDR reactions due to their relatively cheap cost and acceptable performance (Moogi et al. 2022) have been reported to exhibit some deficiencies as support during the synthesis/catalytic process. Common challenges with alumina as supports are alumina dissolution in the aqueous media during supported catalyst synthesis (more evident in Co-based catalyst), rehydration of $\gamma\text{-Al}_2\text{O}_3$ during catalyst implementation and thermal degradation (Kim et al. 2004; Trueba and Trasatti 2005). Silica (SiO_2) in combination with transition metals have been widely utilized and reported (Chong et al. 2021; Owgi et al. 2022) with its major setback being the formation of aggregates/agglomerates during synthesis and its low compatibility with other catalytic materials (Ali et al. 2014). Rare earth metal oxides, such as Sm, Ce and La possess catalytic properties that make them very effective catalyst supports (Osazuwa and Abidin 2020). The step i.e., introducing a rare earth metal as support into the catalyst can limit the carbon formation on the catalyst surface. Moreover, it has been established that rare earth metals oxides (such as cerium (IV) oxide (CeO_2) (Luisetto et al. 2012), Neodymium (III) oxide (Nd_2O_3) and Praseodymium (III) oxide (Pr_2O_3) (Ayodele et al. 2016, 2017)) can supply oxygen to the reaction media. Also, the catalyst reducibility and inhibition of carbon formation are some of other benefits of the addition of alkaline rare earth metals, such as Pr to a metallic catalyst (Li et al. 2011). Therefore, expectations are that Pr_2O_3 can improve the basicity of the catalyst while enhancing CO_2 adsorption.

Furthermore, synthesis methods are vital for the overall properties and behavior of the formulated catalysts (Yosefi et al. 2015). For instance, the sol-gel method has been applied to prepare supported catalytic materials (Sajjadi et al. 2015). Compared to the conventional impregnation technique, the sol-gel technique aids better distribution, thermal resistivity, clogging, and product selectivity (Gonçalves et al. 2006). However, its effect on the formation of specific carbon types and the adsorbed/lattice oxygen of the catalyst have rarely been mentioned in the literature.

In this study, the influence of synthesis methods on the physical/chemical properties and performance of the Ni/ Pr_2O_3 catalyst for MDR reaction was established. The novelty of this present study pertains to the investigation, determination, and comparison of the behavior of the 20 wt% Ni/ Pr_2O_3 catalyst from three different preparation methods (incipient wetness impregnation (IWI), ultrasonic wet impregnation (US-WI), and Pechini sol-gel (PSG) methods) to ascertain the role of the synthesis method. Also, the types of carbon species formed during the reactions were

also identified and the oxygen species associated with each catalyst was related to the carbon gasification and catalyst performance during the MDR reaction. Several characterizations were carried out on all the catalysts to ascertain their physicochemical properties and how these properties affect the MDR reaction at the selected 20 wt% Ni catalyst loading. In addition, the relationship between catalyst preparation and the performance of the 20 wt% Ni/ Pr_2O_3 catalyst at different reaction temperatures was also tested to support the conclusion reached after detailed catalyst characterization. Finally, the best synthesis procedure was selected to ascertain the catalyst stability in the MDR reaction.

Experimental

Catalyst synthesis

In this present study, 20 wt% Ni/ Pr_2O_3 was synthesized using three different synthesis methods: the incipient wet impregnation (IWI), ultrasonic-assisted wet impregnation (US-WI) and the Pechini sol-gel (PSG) methods. Nitrate salt of Nickel (Ni) and Praseodymium (Pr) (99.9%, Sigma Aldrich), citric acid ACS reagent > 99.5% (anhydrous), and ethylene glycol, analytical reagent liquid, 99.8% were employed during the catalysts' preparation. Also, 20 wt% of Ni was adopted as the ideal amount of Ni required since existing literature have reported this amount as the optimum Ni wt% loading that can give the desired catalytic behavior in the MDR reaction (Sepehri et al. 2018). In comparison, others have applied 20 wt% of Ni catalyst for methane reforming (Amin et al. 2012) and butanol reforming, respectively (Varkolu et al. 2021).

Synthesis of the support

The support (Pr_2O_3) was synthesized following established procedure from literature (Ay and Üner 2015). Prior to applying all three synthesis methods, the required Pr (NO_3)₃.6H₂O salt was mixed in distilled water. The solution was stirred for 3 h and dried for 24 h at 110 °C. Post drying, the sample was placed in a furnace and calcined at 600 °C for 4 h to yield the Pr_2O_3 support.

Incipient wetness impregnation (IWI) method

A batch of 20 wt% Ni/ Pr_2O_3 was synthesized using the IWI method previously reported in (Singh et al. 2018; Jawad et al. 2020). The Ni metallic salt used was dissolved in distilled water. The aqueous metallic salt was then used to impregnate the already prepared Pr_2O_3 support. It should be noted that

when using the IWI method, the volume of the impregnating solution must be the same as the support's pore volume. The mixture was dried overnight at about 100–120 °C, before the sample was calcined for 5 h at 850 °C using 5 °C min⁻¹ ramping rate. The resulting material was then grounded and sieved to the desirable size (140–250 µm).

Ultrasonic-assisted impregnation synthesis (US-WI) method.

Ultrasonic-assisted wet impregnation (US-WI) method was utilized using an ultrasonic generator furnished with a probe (Setiabudi et al. 2018; Roslan et al. 2022). The required Ni nitrate salt needed to synthesize 20 wt% Ni/Pr₂O₃ catalyst was mixed in distilled water twice the quantity of Ni nitrate salt. The salt solution was mixed in an ultrasonic bath for about 5 min. The support (Pr₂O₃) was then added to the resulting solution and continuously mixed using the ultrasonic bath at 80 °C until a paste-like form of the mixture was obtained. The obtained paste was dried for about 24 h at around 110 °C to eradicate all traces of water molecules before calcination at 850 °C at 5 °C min⁻¹. This step was followed by grinding and sieving of the calcined material to the desired size (140–250 µm).

Pechini sol–gel (PSG) synthesis method

The PSG method employed to prepare 20 wt% Ni/Pr₂O₃ was adopted from previous studies (Pechini et al. 1967; Kakihana 1996; Mishra et al. 2019). The process entails the in-situ polymerization of the sol–gel process by adding ethylene glycol. The Ni nitrate salt and synthesized support (Pr₂O₃) was dissolved at ambient conditions in 2 M citric acid solution with 2:1 citric acid to metal molar ratio. The role of citric acid as a chelating agent was to assist homogeneous distribution of metal, and to create a segregate from the solution. In addition, ethylene glycol was added as a complexing agent to the solution in a 2:1 ratio of citric acid to ethylene glycol. The sample mixture was subsequently stirred at 25 °C for 2 h and ammonia was added to adjust the pH to become less acidic. Heat was applied to the resulting mixture at 80 °C for 4 h and continuously stirred. The formulated gel was oven-dried at 110 °C. The grounded form of the xerogel material was obtained using an agate crucible before annealing at 850 °C for 5 h at 5 °C min⁻¹. The calcined material was further grounded and sieved to the desirable size (140–250 µm).

Catalyst characterization

The physical properties of all the catalysts were obtained using the N₂ physisorption analyses. The data was analyzed and processed by a Thermo Scientific acquisition analyzer which is furnished with a degasser station and a surfur acquisition (version 1.2.1) software. The crystalline structure was evaluated by powder X-ray diffraction (XRD) measurements with Cu Kα radiation (λ = 0.154 nm). The range of the analysis using a Rigaku Miniflex II instrument was recorded at 2θ = 2°–70° at a rate of 0.02° over 2 s. This procedure was followed by matching the peaks with known structures in the Inorganic Crystal Structure Database (ICSD). Also, the particle crystallite size for all 20 wt% Ni/Pr₂O₃ catalysts synthesized by the IWI, US-WI and PSG methods were computed employing the Williamson-Hall model shown in Eq. 1 (Khorsand Zak et al. 2011; Himabindu et al. 2021).

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D_{hkl}} + (4\epsilon \sin \theta) \quad (1)$$

where θ and λ (Cu Kα) are the Bragg angles of diffraction, and wavelength, respectively, β_{hkl} is the peak width at half-maximum intensity, P is the shape factor (0.9) and D_{hkl} is the crystallite size of the 20 wt% Ni/Pr₂O₃ catalysts.

The binding energy and surface composition for the calcined catalysts (wide and narrow scan) were obtained using X-ray photoelectron spectroscopy (XPS). The peak intensities and atomic percentages were obtained using the estimated Gaussian and Lorentzian lines and the intensity ratios. The equipment employed was the PHI-5000 VersaProbe spectrometer which had a hemispherical electron analyzer.

The catalysts morphologies and composition of each element were evaluated at 15 × magnifications using the field emission scanning electron microscope (FESEM) (Schottky-type field emission cathode beam). Resolution images of the catalysts were captured, and the inner shell electrons were excited to obtain the composition of the elements. Energy Dispersive X-ray (EDX) was also used to confirm the presence and composition of elements used for the catalyst's synthesis. The primary composition of the catalyst was obtained by EDX, when inner shell electrons were excited, hence forming specific X-rays with suitable intensity for the analytical data.

A Thermo Scientific Analyzer -TPDRO 1100, was used to ascertain the reduction capacity of the 20 wt% Ni/Pr₂O₃ catalysts samples synthesized by IWI, US-WI, and PSG methods. Pretreatment of about 100 mg of fresh samples was carried out in a 30 mL min⁻¹ flow of Ar at a 10 °C min⁻¹ heating rate until about 300 °C and held for 0.5 h. Reduction of the pretreated catalysts with 30 mL min⁻¹ of 10% H₂ in Ar carrier gas was carried out at 900 °C (at 10 °C min⁻¹) and held for 60 min before subsequently cooled to ambient temperature.

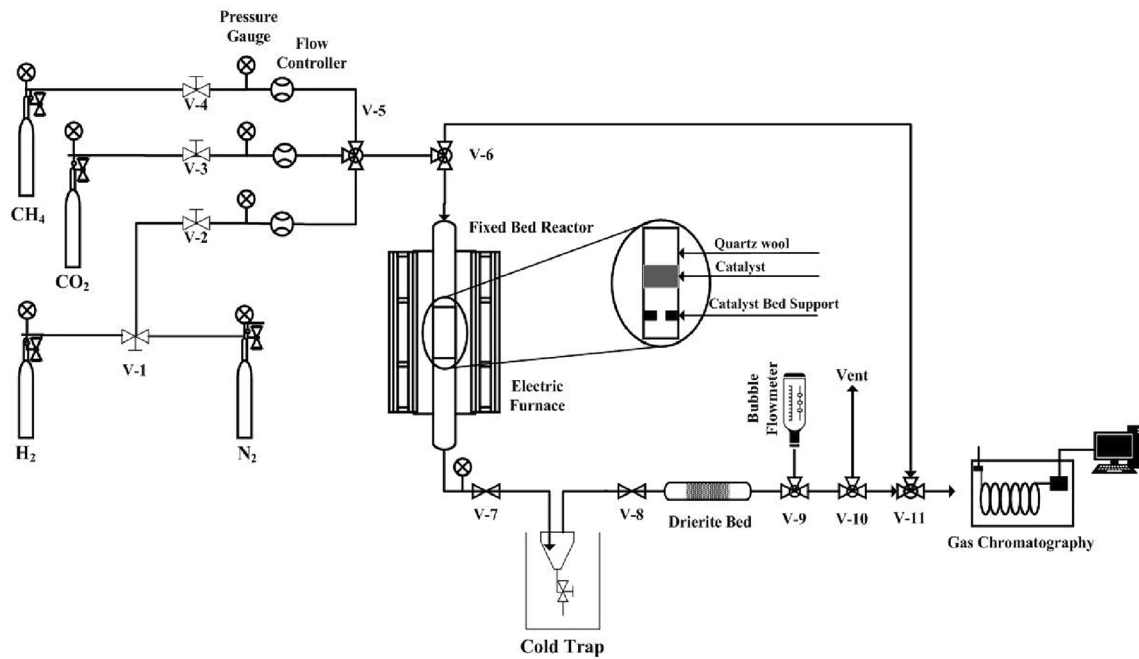


Fig. 1 Schematic representation of the MDR experimental rig

The morphologies of the micro-structures of the calcined and spent Ni/Pr₂O₃ were obtained by transmission electron microscopy (TEM) (JEOL JEM-2100) at 5,000 × magnifications. During the process, various features of the catalyst material were visibly observed.

The solid-state thermal profile of the spent catalysts was obtained by thermogravimetric analysis (TGA) using a TA instrument (Q 500 series). The weight loss (TG) and the derivative weight loss (DTG) of the catalysts were obtained between 25 °C and 900 °C at 10 °Cmin⁻¹ in mixed 80% N₂ and 20% O₂ flow.

Catalytic activity test

A fixed bed reactor in a gas manifold station, and a gas chromatography (GC) instrument was used to conduct the experiment and analyze results from the experimental runs. The GC which was employed to detect unconverted reactants gases (methane (CH₄), carbon dioxide (CO₂)) and products (hydrogen (H₂) and carbon monoxide (CO)) at the outlet stream, was operated using helium (He) (20 mLmin⁻¹) with the temperature of the column at 150 °C. The reactor (inner diameter of 10 mm) was packed with the catalyst (0.1 g) and all experiment were repeated thrice to eliminate errors. Pre-reaction, reduction of the fresh catalysts was carried out in a 50% H₂/N₂ flow (60 mLmin⁻¹) for 1 h at 800 °C (for uniformity) with a ramping of 5 °C min⁻¹. Post-reduction step, the reactor was flushed with N₂ gas while setting the desired reaction temperature. Transport phenomena were minimized by ensuring the

Table 1 Textural properties of calcined the 20wt% Ni/Pr₂O₃

Catalyst (20wt% Ni/Pr ₂ O ₃)	BET Surface Area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	Average pore size (nm)
IWI	6.7	1.28 × 10 ⁻²	7.6
US-WI	8.9	1.29 × 10 ⁻²	5.8
PSG	7.3	9.95 × 10 ⁻³	5.5

catalysts particles are sieved to the desired range 140–250 μm. More also, the gas hourly space velocity (GHSV) was set at about 30,000 h⁻¹ to ensure the transport effects were insignificant. The total pressure of 1 bar with reaction temperature ranged 600–950 °C was employed during the reaction, while N₂ was used throughout the study as a diluent gas. Using feed flow rates and exit gas composition, the reactants conversion and product ratio were obtained using Eqs. (2 - 4) (Moradi et al. 2014). The schematic of the experimental rig for the MDR reaction to produce syngas is represented in Fig. 1.

$$X_{\text{CH}_4} \% = \frac{F_{\text{CH}_4(\text{in})} - F_{\text{CH}_4(\text{out})}}{F_{\text{CH}_4(\text{in})}} \times 100 \quad (2)$$

$$X_{\text{CO}_2} \% = \frac{F_{\text{CO}_2(\text{in})} - F_{\text{CO}_2(\text{out})}}{F_{\text{CO}_2(\text{in})}} \times 100 \quad (3)$$

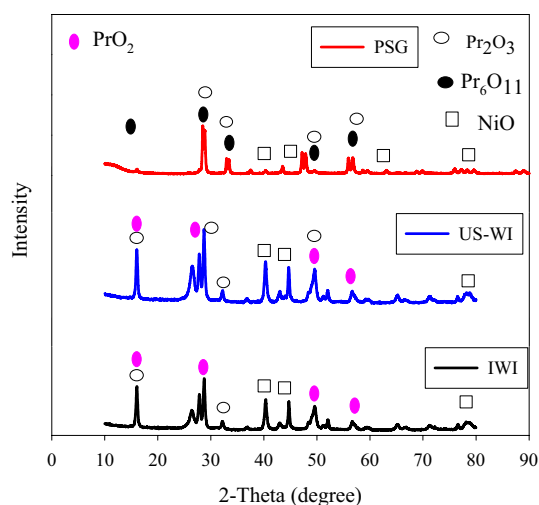


Fig. 2 X-ray diffractogram of the fresh 20 wt% Ni/Pr₂O₃ catalysts

$$\frac{H_2}{CO} \text{ ratio} = \frac{F_{H_2(\text{out})}}{F_{CO(\text{out})}} \quad (4)$$

Results and discussions

Catalyst characterization

Brunauer–Emmett–Teller (BET) analysis

The textural characteristics of the 20 wt% Ni/Pr₂O₃ catalysts synthesized by incipient wetness impregnation (IWI), ultrasonic-assisted wet impregnation (US-WI) and Pechini sol–gel (PSG) method are shown in Table 1. From the table, a reduction in the BET surface area and pore volume was found in the order; US-WI, IWI, and PSG (for the 20wt% Ni/Pr₂O₃ catalysts). The IWI and US-WI synthesized catalyst had very similar pore volume compared to the PSG catalyst. The average pore size of the catalysts reduced in the order IWI, US-WI, and PSG for the synthesized catalyst. This pattern is linked to the formation of the Pr₂O₃ support's pore structure in the presence of NiO at the catalyst's surface. Referring to the International Union of Pure and Applied Chemistry (IUPAC) sorption isotherms, the IWI, US-WI, and PSG synthesized 20wt% Ni/Pr₂O₃ catalysts exhibited type H2 hysteresis loop from a type IV curve thereby revealing the mesoporosity of the synthesized catalyst materials.

XRD analysis

Diffractogram of the 20 wt% Ni/Pr₂O₃ catalysts synthesized by incipient wetness impregnation (IWI), ultrasonic-assisted wet impregnation (US-WI) and Pechini sol–gel (PSG) method are shown in Fig. 2. Peaks matching the XRD data for NiO (PDF 00-001-1239 for PSG synthesized catalyst, PDF 01-089-7131 for IWI and US-WI synthesized catalysts, respectively), Praseodymium (III) oxide (Pr₂O₃) (PDF 00-061-0049 for PSG catalyst, PDF 00-006-0410 for IWI catalyst and US-WI synthesized catalysts, respectively) and Praseodymium (IV) oxide (PrO₂) (PDF 00-024-1006 for IWI and US-WI synthesized catalysts, respectively) are visible on the diffractogram. Interestingly, the PSG synthesized catalysts formed the partially oxidized Praseodymium (III, IV) oxide (Pr₆O₁₁) species phase (PDF 00-041-1219). There were overlap of the Pr₂O₃ (Pr³⁺) and PrO₂ (Pr⁴⁺) phase species for IWI and US-WI synthesized catalysts while Pr₂O₃ (Pr³⁺) and Pr₆O₁₁ (Pr³⁺ and Pr⁴⁺) phases overlapped for the PSG synthesized catalyst. The ease with which Pr³⁺/Pr⁴⁺ redox couples are formed is likely responsible for the co-existence and overlapping behavior of the support (Ahn et al. 2012; Milberg et al. 2017).

Furthermore, the formation of Pr₆O₁₁ phase species for the PSG-Ni/Pr₂O₃ catalyst as against the PrO₂ phase species for the IWI and US-WI catalyst might be responsible for easier release of oxygen molecules which would aid carbon gasification. Different support structure of the same species could potentially present different ability to gasify carbon. This is so because the Pr₆O₁₁ is less stable when compared to the PrO₂ species, hence, the Pr₆O₁₁ species can easily release oxygen ions for the carbon gasification process as compared to the PrO₂ which was present in the IWI and US-WI catalysts. More also, the PSG catalyst presents additional Pr species with additional 11 oxygen atoms (Pr₆O₁₁) while the IWI and US-WI have additional Pr species with 2 oxygen atoms (PrO₂).

The Williamson-Hall model was used to fit XRD data to obtain the nano crystallite size of the samples. As shown in Fig. 3, $\beta_{hkl} \cos \theta$ was plotted against $4 \sin \theta$ using the preferred peaks of the 20 wt% Ni/Pr₂O₃ catalyst. The gradient of the fitted data denoting the strain (ϵ) was -0.0007 , -0.0007 and -0.0015 , respectively, while the y-intercept was 0.0065 , 0.0065 and 0.0131 , for the IWI, US-WI, and PSG catalysts, respectively. From Eq. 1, the values for the particle crystallite size were calculated as 21.3 nm, 21.3 nm, and 10.6 nm, for the IWI, US-WI, and PSG catalysts, respectively. This trend agrees with literature where the crystallite size of Ni catalysts is established to be in the range of 10 – 20 nm (Lui-setto et al. 2015; Goula et al. 2016).

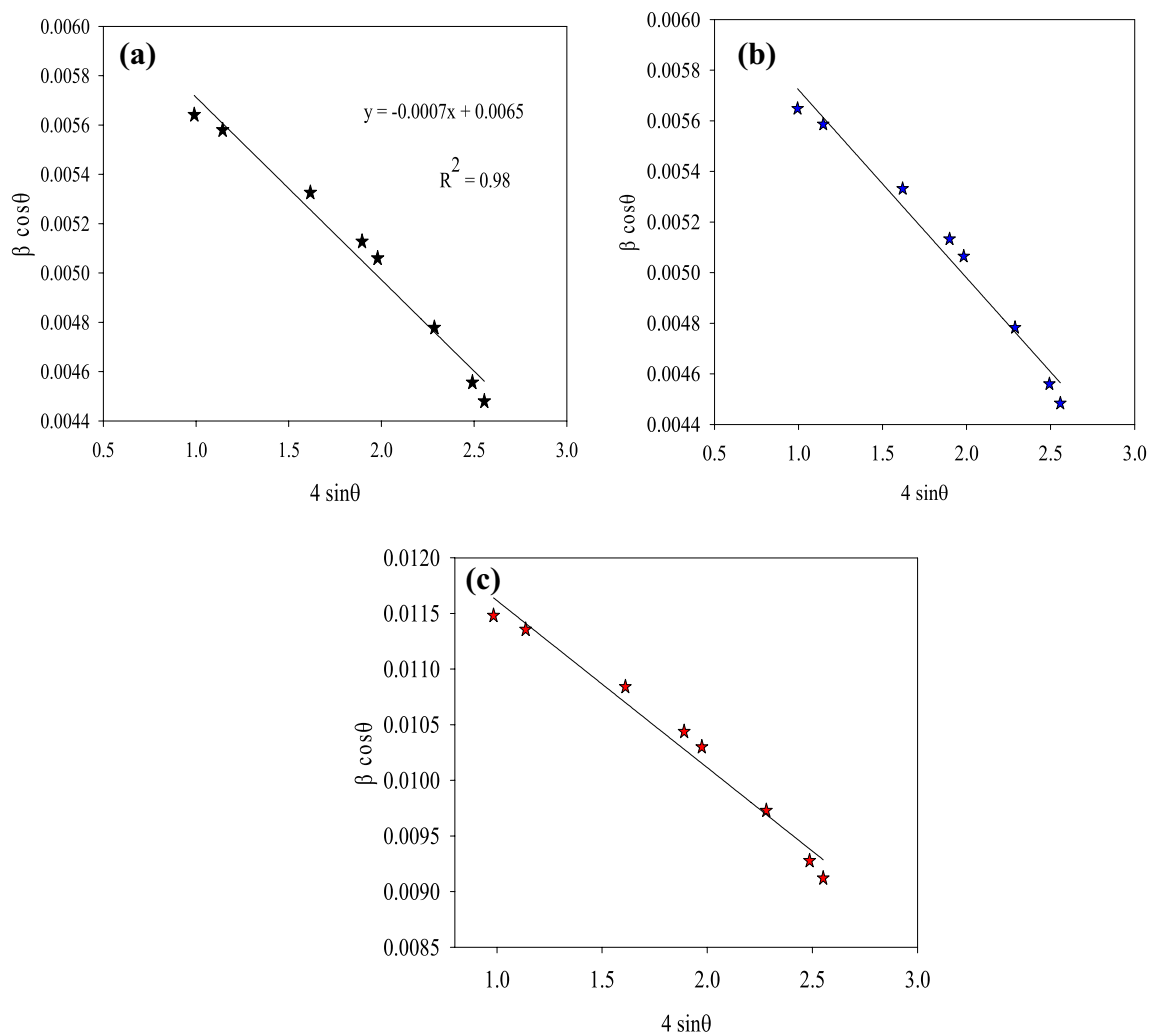


Fig. 3 Williamson-Hall analysis for 20 wt. % Ni/Pr₂O₃ catalyst **a** IWI **b** US-WI **c** PSG synthesis methods

XPS analysis

Wide and narrow scans of the XPS analyses of the calcined 20 wt% Ni/Pr₂O₃ catalyst for the IWI, US-WI, and PSG methods are represented in Fig. 4a–c. Ni (19.26%), Pr (20.26%) and O (60.5%) species can be found in the wide spectra and the data agree with the catalyst's formulations employed for the various synthesis methods. Furthermore, the main binding energy of Ni peaks corresponding to 2p_{3/2} and 2p_{1/2} are seen around 855 and 853 eV, respectively. This indicates the presence of Ni as Ni²⁺ forming nickel oxides (NiO) (Leclercq et al. 1998; Kim et al. 2007). Peaks representing binding energies corresponding to Pr3d_{5/2} and Pr3d_{3/2} species are present in the IWI, US-WI, and the PSG catalysts (Milberg et al. 2017) (Song et al. 2007). The finding agrees with the XRD data (Fig. 2), which confirms the presence of two different Pr phase for IWI and US-WI catalysts (Pr₂O₃ and PrO₂) and PSG catalyst (Pr₂O₃ and Pr₆O₁₁) respectively.

Species of O₂ in the 20 wt% Ni/Pr₂O₃ catalyst

XPS analysis can estimate the quantity and type of surface O₂ species in heterogeneous catalysts. O 1 s XPS spectra for the 20 wt% Ni/Pr₂O₃ catalysts synthesized via IWI, US-WI and PSG methods are shown in Fig. 5. O 1 s species linked to the lattice and adsorbed oxygen can be seen at binding energy of 529 eV and 531 eV, respectively (Kuhn and Ozkan 2008). Upon analysis of the O 1 s XPS spectra, dual peaks representing dual oxygen species were present: adsorbed oxygen species (O_A) and lattice oxygen species (O_L). According to Lee et al., (2018), O_A species are generated via oxygen atoms adsorbed into the oxygen vacancies created by the desorbed mobile lattice oxygen vacated from the bulk of the catalysts. These vacancies are created when O_L species from the catalyst support oxidizes the reactants (cracked CH₄ to form carbon), thereby creating vacant oxygen sites in the catalyst.

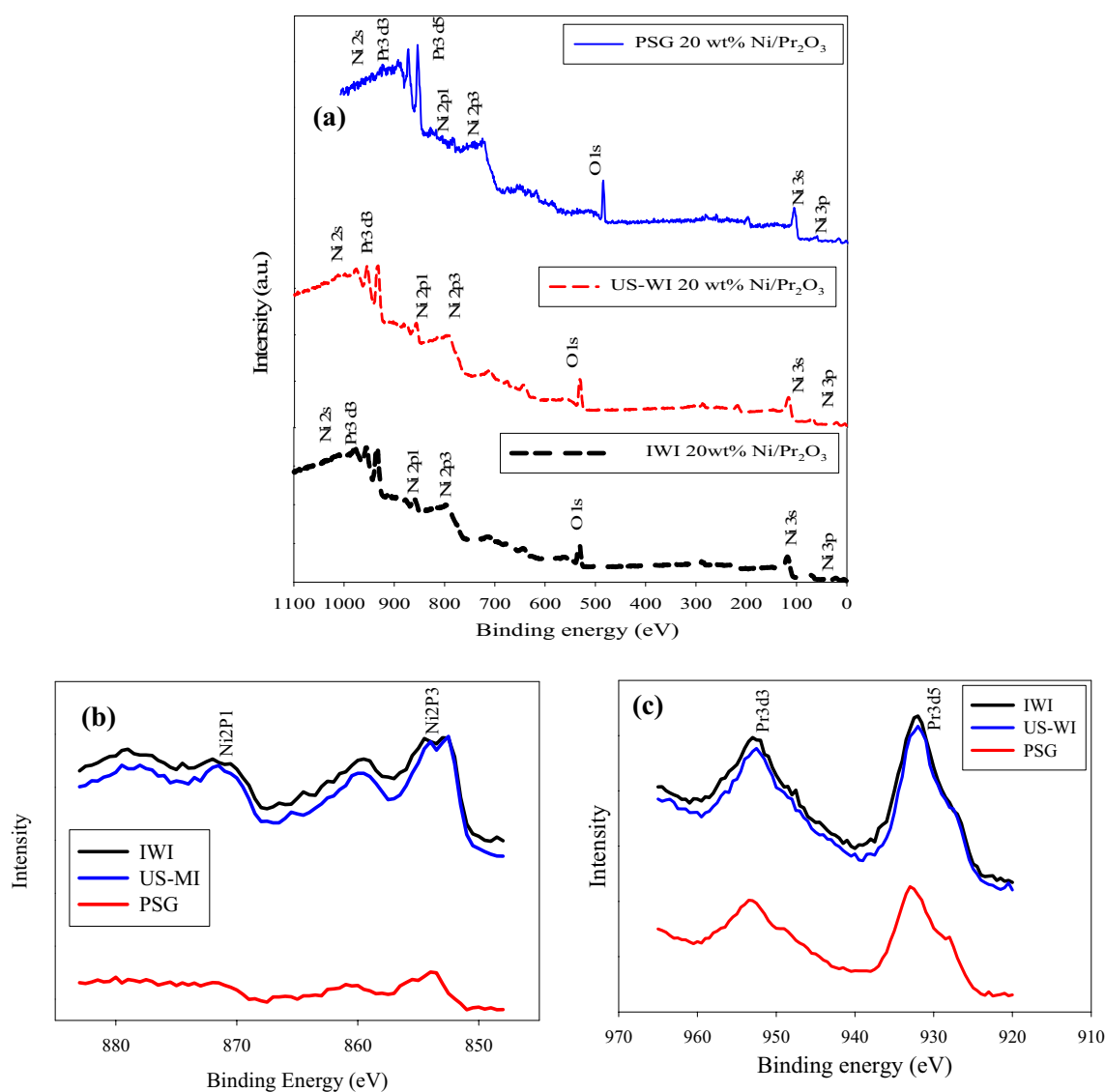


Fig. 4 XPS profile of the **a** calcined 20 wt% Ni/Pr₂O₃ catalysts **b** narrow scan Ni2P1 and Ni2P3 peaks **c** narrow scan Pr3d3 and Pr3d5 peaks for the 20 wt% Ni/Pr₂O₃ catalysts

The relative amount ratio of O_L to O_A was determined using the XPS areas of the peaks for different preparation methods. The result showed that the O_L to O_A ratio increased in the preparation method order: IWI (0.75) ~ US-WI (0.75) > PSG (0.86). More also, the PSG catalyst had near equal amount of O_L and O_A species suggestive of a balance between the oxygen species. This has potentially contributed to the better performance (in terms of stability) of the PSG catalyst when compared to the catalysts from the other synthesis methods (IWI and US-WI).

FESEM analysis

Micrographs (15,000 × magnifications) of the fresh samples from the various synthesis procedures (IWI, US-WI,

and PSG) is represented in Fig. 6a-c. The smoothness and uniformity of the sample catalysts are in increasing order from Fig. 6a, c. This supports higher degree of dispersion and stronger interaction in the sample prepared by PSG method. Also, upon visual inspection, the metal particles in the US-WI synthesized catalyst appears to be more uniform as against the sample synthesized by IWI method. However, FESEM images alone are not sufficient to make conclusive statements on the various catalysts' material.

EDX analysis

EDX analysis of the calcined 20 wt% Ni/Pr₂O₃ synthesized by IWI, US-WI and PSG methods are represented in Fig. 7a-c. Using the EDX analysis, it is difficult to spot the

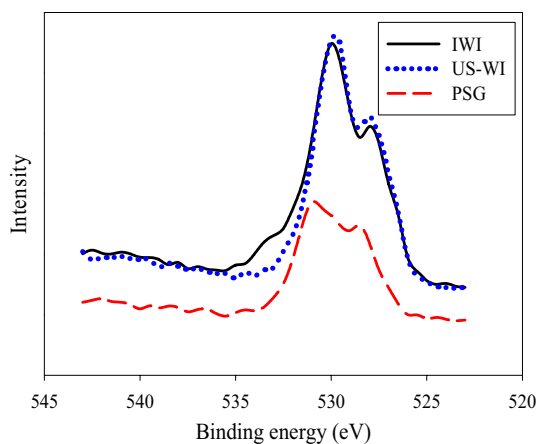


Fig. 5 XPS spectra for the narrow O 1s peaks for the 20 wt% Ni/Pr₂O₃ catalysts

best synthesis method. However, the mapping reveals the presence of Ni, Pr, and O, which are the major components of the catalyst used in this study. The atomic percentage composition of the Ni, Pr, and O are 22%, 17%, and 61%, for the IWI, 17%, 20%, and 63 for the US-WI and 13%, 17% and 70% for the PSG synthesized catalysts, respectively. This composition explains the degree of effectiveness of the synthesis methods in obtaining the specific catalyst material.

Catalyst activity

Effects of synthesis methods on conversion

Tables 2 and 3 depict the dependence of the Average feedstocks' (CH₄ and CO₂) conversion on the catalyst's synthesis methods, i.e., IWI, US-WI, and PSG methods. These experiments were conducted at 800 °C for 2 h for all synthesis

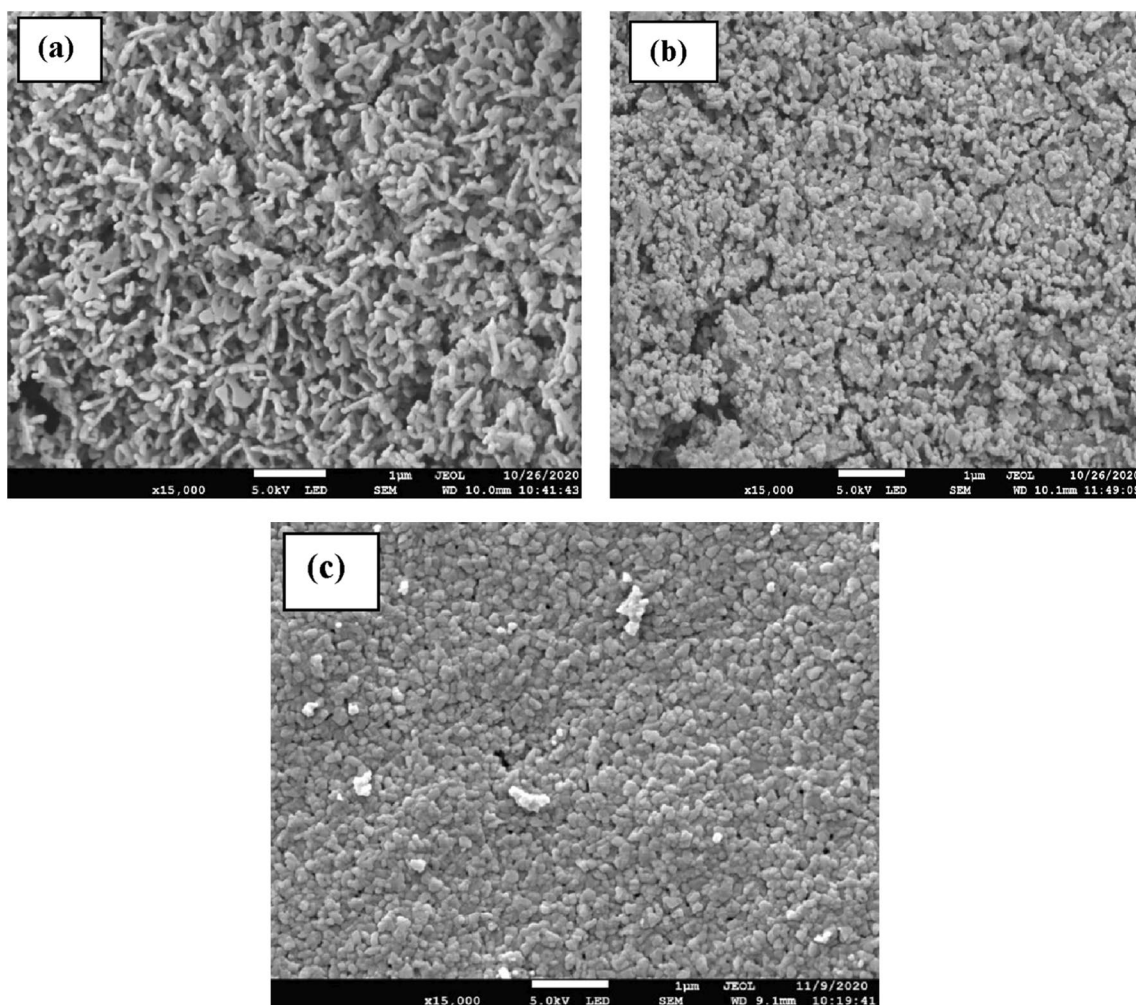


Fig. 6 FESEM images (15,000 magnifications) of the 20wt% Ni/Pr₂O₃ synthesized by a IWI b US-WI c PSG methods

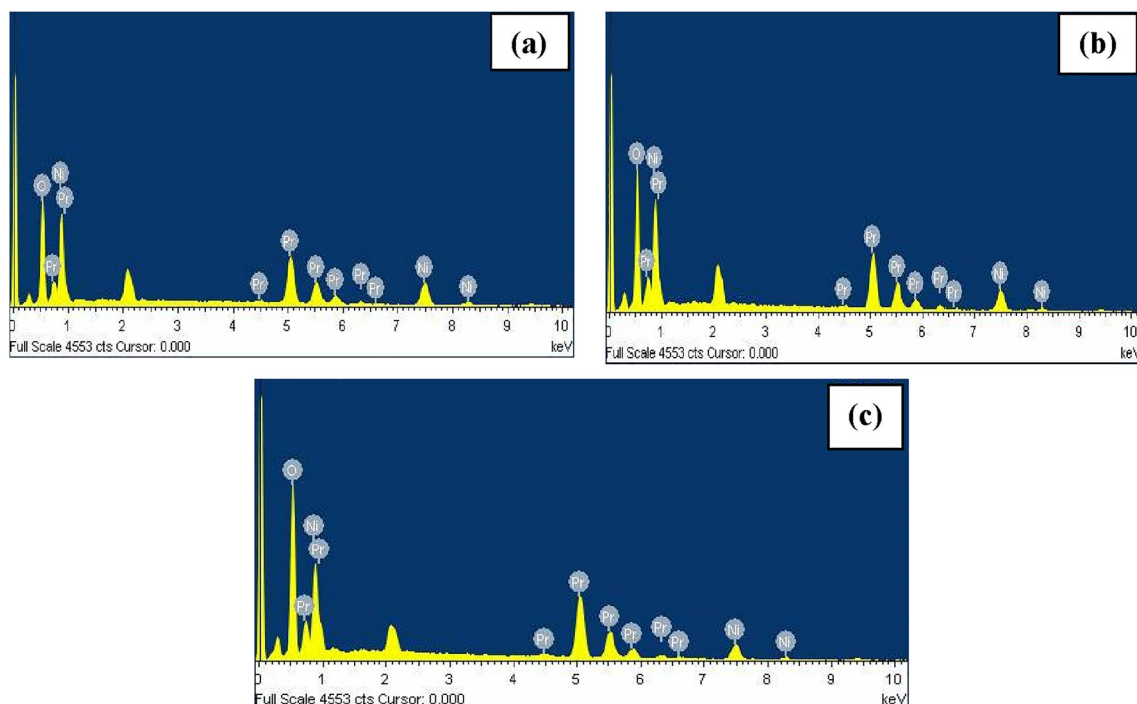


Fig. 7 EDX analysis of the 20 wt% Ni/Pr₂O₃ synthesized by **a** IWI, **b** US-WI **c** PSG methods

Table 2 Average CH₄ Conversion obtained for IWI, US-WI, and PSG catalysts over TOS

Time (h)	CH ₄ conversion		
	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by the IWI method	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by US-WI method	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by PSG method
0.5	88	88	86
1	88	88	88
2	Carbon blockage of the reactor flow line	Carbon blockage of the reactor flow line	89

Table 3 Average CO₂ Conversion obtained for IWI, US-WI, and PSG catalysts over TOS

Time (h)	CO ₂ conversion		
	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by the IWI method	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by US-WI method	20 wt% Ni/Pr ₂ O ₃ catalyst synthesized by PSG method
0.5	88	90	88
1	87	90	97
2	Carbon blockage of the reactor flow line	Carbon blockage of the reactor flow line	90

methods. The catalytic test revealed that the average CH₄ conversions were approximately 88% for the IWI, US-WI, and PSG synthesized catalysts, while average CO₂ conversions were 87.5%, 90% and 92%, respectively, for the IWI, US-WI, and PSG synthesized catalysts. The conversions of CH₄ and CO₂ for IWI and US-WI methods had similar

behavior with respect to the catalyst behavior during the time of reaction. CH₄ and CO₂ conversion for the IWI and US-WI methods were stable until after 1 h, and then slowly eroded until the reactant flow completely stopped at around 2 h due to carbon blockage of the reactor's flow line.

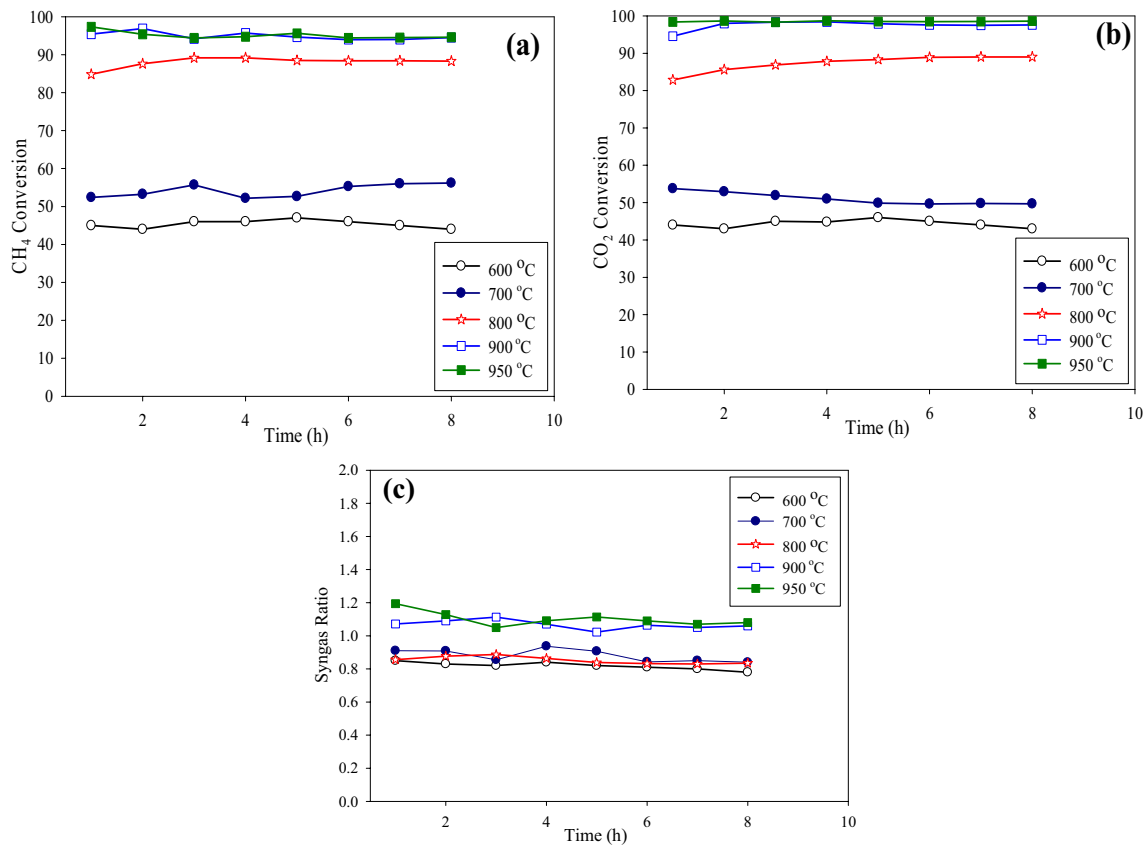


Fig. 8 Temperature effects on MDR reaction over PSG-20 wt% Ni/Pr₂O₃ **a** Average CH₄ **b** Average CO₂ conversion **c** syngas ratio (H₂:CO)

According to Deraz, (2018) in the impregnation method, an appropriate amount of the metal precursor is mixed via diffusional means with the support phase before drying takes place. During the process of diffusion, the overall solution changes thereby releasing heat in a short period (Osazuwa et al. 2021). Also, Jiang, (2006) reported that when the IWI synthesis method is applied, sintering and particles size growth is very likely because the metal and oxide phases possess very high surface energy. Therefore, during this experiment, it is likely that the sudden restriction of flow after 1 h can be attributed to sintering of the metallic particles followed by carbon buildup that block the reactor flow lines since the catalysts were made up of high oxide loading of Pr₂O₃ and its stable species (PrO₂) as described in the XRD data in Fig. 2. More also, with reference to the synthesis method, catalysts synthesized by the IWI method were likely not homogeneously dispersed. Nevertheless, the IWI method can effectively control the capacity of active components. Hence, the method is generally effective when there are no exact particle size requirements but its poor active metal dispersity and uneven distribution of particle size are some of the inherent challenges associated with this technique (Zhang et al. 2014).

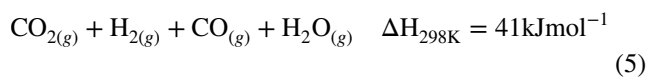
Researchers have tried to enhance this technique by introducing several variations, such as increasing the uniformity of dispersion by employing ultrasonic wave (Setiabudi et al. 2018). This technique uses the cavitation of ultrasound wave to achieve the uniform dispersion of metals in the support (Passos et al. 2005). The cavitation nuclear bubble breakdown generates a local temperature, pressure, impact wave and a micro jet, thereby creating a new and unique physico-chemical environment that cannot be achieved during the simple impregnation procedure (Zhang et al. 2014). However, in the current experiment, the ultrasonic wave assisted wetness impregnation did not improve the 20 wt% Ni/Pr₂O₃ catalyst's performance possibly due to the loading of metal employed.

For the PSG synthesis method, CH₄ conversion increased slightly from about 86% to 89%, and CO₂ conversion increased from 88 to 97% after 1 h before dropping slightly to 90% after 2 h time on stream (TOS). During the catalyst synthesis using PSG method, citric acid and ethylene glycol undergo esterification reaction (Lin et al. 2007). The organic structure breakdown due to heating is inhibited to alter the formation of the resulting catalyst and its physicochemical properties. Furthermore, the non-dependence on the process conditions resulting from positively charged

ions in the formulated catalyst and the low temperature treatment ensures sintering is eliminated. Hence, initial pressure buildup due to carbon deposits was not observed as the catalyst remained active. Extensive studies and reviews have been published on the PSG method (Dimesso 2018; Osazuwa et al. 2021), while other researchers have found the application of this method highly productive (Majid et al. 2005; Jana et al. 2010; Shin et al. 2018; Bai et al. 2019). For instance, Majid et al., (2005) successfully synthesized SrFeOx catalysts using the PSG method. The method produced higher quality material which possessed better catalytic properties. Shin et al., (2018) synthesized Ni/ZrO₂-Al₂O₃ catalyst for MDR reaction and carried out a comparative study using the PSG and other synthesis methods. The synthesized PSG catalyst had the highest stability under the given experimental conditions. According to Danks et al., (2016), the dissolution of the metallic salt, citric acid, and ethyl glycol in water created a homogenous mixture. Hence, the introduction of heat activated the polyesterification reaction to form a polymer matrix before the final calcination of the polymeric structure.

Determination of the effective reaction temperature

Figure 8A–c represents the temperature effects study on the MDR reaction in the temperature range 600 °C – 950 °C. The study was carried out by employing the PSG- 20 wt% Ni/Pr₂O₃ catalysts because this catalyst gave the best result during the preliminary study. The study showed that an increase in reaction temperature has a direct relationship with the MDR reaction. From each experimental run, the conversion of CH₄ (Fig. 8a) and CO₂ (Fig. 8b) were relatively constant with an increase in time for the entire 8 h TOS. The highest CH₄ conversions at 600, 700, 800, 900, and 950 °C were approximately 47%, 56%, 89%, 97%, and 97%, respectively, while the highest CO₂ conversion at 600, 700, 800, 900, and 950 °C, were 46%, 54%, 89%, 98%, 99% respectively. The MDR reaction is accompanied by various side reactions that can alter the reaction performance depending on the overall reaction conditions. At 600 °C (lower temperature), MDR is controlled by the water gas shift (WGS) reaction. At 950 °C (higher temperature range), the net WGS reaction becomes negligible and the backward reaction (the reverse water gas shift (RWGS) reaction shown in Eq. 5) dominates (Lee et al. 2014; Nabgan et al. 2016).



When the temperature is high, the RWGS reaction uses up the reactant (CO₂) and product (H₂) while the WGS reaction at low temperature consumes the product (CO). This justifies the high CO₂ conversion (approximately 100%) observed at

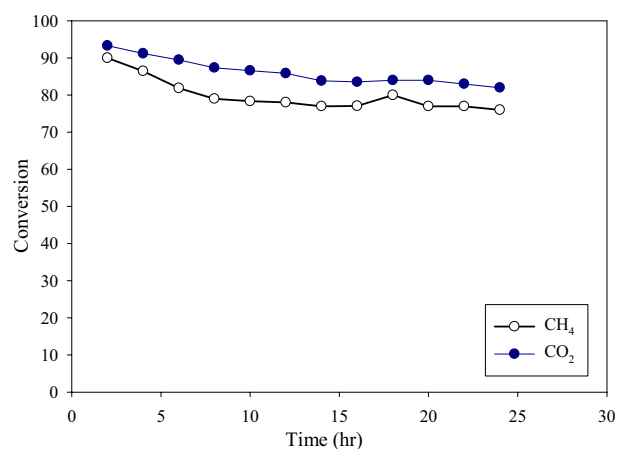
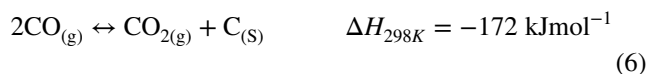


Fig. 9 Stability of MDR reaction over PSG- 20 wt% Ni/Pr₂O₃ catalyst

900 and 950 °C in this study, as shown in Fig. 8b. Hence, to eradicate the effect of the various side reaction on the overall outcome, the MDR reaction is often investigated between 700 – 900 °C. At these conditions, the effects of side reactions are negligible because the catalytically driven CH₄ cracking/reforming is dominant.

Another side reaction that often accompanies MDR reaction is the Boudouard reaction, also known as gasification of char and it is represented in Eq. 6 (Wang et al. 1996; Fan et al. 2009).



During the MDR reaction, the Boudouard reaction proceeds at low temperature (<600 °C) with the decomposition of CO to yield C and CO₂. This is due to the large enthalpy, which shifts the equilibrium toward the decomposition of CO rather than its formation. Nonetheless, when the entropy terms become significant during the reaction, the free energy becomes negative and the reverse Boudouard reaction dominates. Hence, at low temperature conditions, Boudouard reaction is the major carbon source while at higher temperature, the carbon produced is from CH₄ cracking (Baharudin et al. 2022), (Lovell et al. 2017). With reference to Fig. 8b, at higher temperature conditions (>900 °C), CO₂ is almost completely used up (about 99% conversion) to form C and CO in the reverse Boudouard process.

Figure 8c shows the product ratio (syngas ratio) plotted against time for the process over PSG- 20 wt% Ni/Pr₂O₃ catalyst. Overall, the ratio falls between 0.8 and 1.2. The effect of temperature on the syngas ratio is not significant. At lower temperature i.e., 600 °C, the syngas ratio was about 0.8 while at higher temperature, i.e., >900 °C, it shifts slightly to about 1.2. According to De Caprariis et al., (2016), syngas with unity ratio is more desirable as feedstock for fuel production processes. H₂: CO ratio > 1

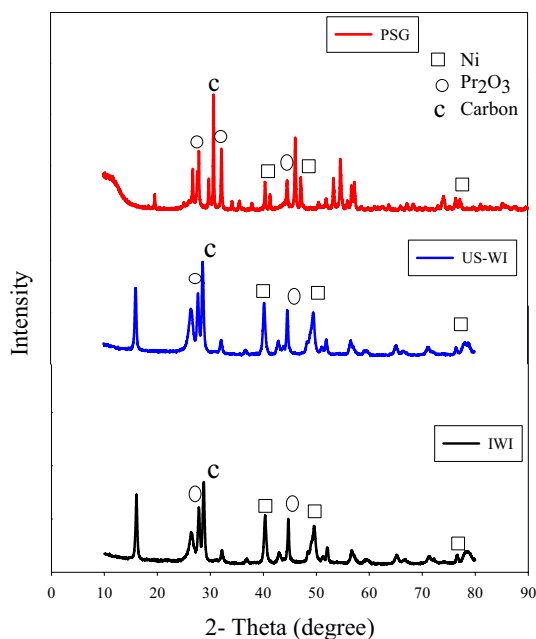


Fig. 10 X-ray diffractogram for the spent PSG-20 wt% Ni/Pr₂O₃ catalysts

indicates the dominance of the Boudouard reaction or hydrocarbon cracking where CO is used up, whereas H₂: CO < 1 indicates that the RWGS reaction has occurred where H₂ and CO₂ are consumed (Lovell et al. 2017).

The MDR reaction using the PSG synthesized 20 wt% Ni/Pr₂O₃ catalyst was endothermic in nature; hence it obeyed the Arrhenius equation with respect to its temperature dependency. During the reaction TOS at a temperature ranging from 600 to 900 °C, there was a steady increase in reactants conversion. However, from > 900 °C, the conversion remained constant due to continuous CH₄ cracking, which dominated as against the Boudouard reaction (Khajenoori et al. 2015).

Carbon study

Stability study

The stability of the MDR reaction over PSG- 20 wt% Ni/Pr₂O₃ catalyst for about 24 h is represented in Fig. 9. This catalyst (PSG- 20 wt% Ni/Pr₂O₃) has been selected for the stability study since it gave the best result in terms of conversion when compared to the IWI and US-WI catalysts. The average reactants' conversion during the stability test was approximately 80% and 86% for CH₄ and CO₂, respectively. Also, the catalyst experienced slight deactivation over 24 h TOS, with the percentage of deactivation in terms of CH₄ conversion about 16%, while CO₂ conversion was 12%. However, the overall volumetric flow of the outlet gas

completely seized after about 24 h due to blockage of the reactor tube due to excess carbon. This means that over the TOS, the catalyst lost its activity, and possessed limited numbers of active sites to continually convert the reactants gases to gaseous H₂ and CO. Hence, the amount of deposited carbon was in excess of the amount of carbon being converted. The carbon deposits encapsulated the metallic site, thereby deactivating the catalyst over 24 h, which eventually resulted in blockage of the reactor. It would be interesting to further study on the effects of promoter on the stability of the PSG- 20wt% Ni/Pr₂O₃ catalyst as a means to enhance its stability.

Used catalyst characterization.

The XRD profile of the spent 20 wt% Ni/Pr₂O₃ catalyst (synthesized via the IWI, US-WI, and PSG method) is represented in Fig. 10. It can be observed that peaks representing metallic Ni, and Pr₂O₃ were found in all spent catalysts. The crystalline structure of metallic Ni (PDF 03–065–2865) was cubic, while the Pr₂O₃, (PDF 01–078–0309) and carbon were hexagonal in nature. Peaks ascribed to the presence of carbon matching the hexagonal crystalline phase (PDF 01–081–9116) were present in all catalysts. The main carbon peak in the PSG- 20 wt% Ni/Pr₂O₃ was less pronounced which could explain its higher stability when compared to the IWI and US-WI 20 wt% Pr₂O₃ catalysts. Also, although the IWI and US-WI 20 wt% Pr₂O₃ catalysts experienced high CH₄ cracking there was lesser carbon gasification occurring as compared to the PSG- 20 wt% Ni/Pr₂O₃ catalyst which had a better ability to resist deactivation and pressure buildup in the reactor (which was caused by excess carbon deposits) after 2 h.

Representative FESEM images of the spent IWI, US-WI, and PSG 20 wt. % Ni/Pr₂O₃ catalysts at 15,000× magnifications are shown in Fig. 11a-c. All catalysts showed visibly pronounced carbon filaments with the IWI and US-WI catalysts showing some form of agglomeration or encapsulation of metallic particles (refer to Fig. 11a, b). The PSG-20 wt% Ni/Pr₂O₃ catalyst represented in Fig. 11c had less agglomeration. Also, upon visible inspection, the particles (indicated in red circles) are smaller in size when compared to the particles of the IWI and US-WI catalysts. The result strongly corroborates with the XRD represented in Fig. 10 for all spent catalysts which showed evidence of carbon formation.

To further prove the existence of carbon and the specific carbon types in the various spent catalysts, TEM images represented in Fig. 12a-c are captured. The images show various degrees of carbon formation for the different synthesis methods. In Fig. 12a, b representing the catalysts synthesized by the IWI and US-WI methods, two carbon types exist. The carbon species are visibly described by the thin elongated tube-like structures (identified as the red arrows)

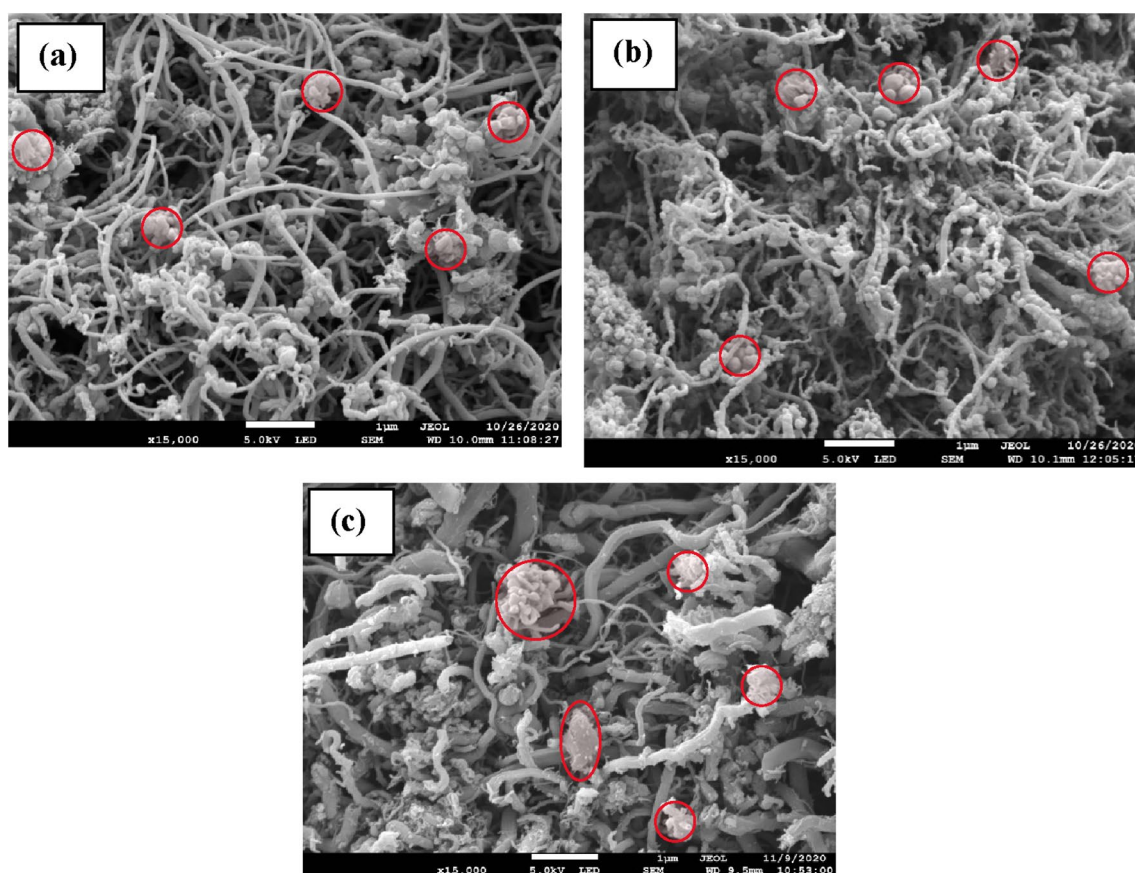


Fig. 11 FESEM images of the 20 wt% Ni/Pr₂O₃ catalyst synthesized by **a** IWI **b** US-WI **c** PSG methods (15,000 × magnifications)

and the darker shade round-like structures (identified as the red circles) which encapsulate the Ni metal, making them clog together. For MDR reaction to proceed, the carbon is produced via CH₄ cracking which deactivates the catalysts and subsequently blocks the reactor tube if not converted in-situ reaction. The encapsulated round-like carbon reported by Son et al., (2014) as graphitic carbon are found on the metal surface phase or accumulates in the reactor tube. When deposited on the metal surface, they deactivate the metal catalyst, while as deposits in the reactor tubes, they block the flow of reactants through the reactor. Spent PSG-20 wt% Ni/Pr₂O₃ represented in Fig. 12c shows obvious thin elongated tube-like carbon nanotubes and very minimal encapsulating round-like (graphitic) carbon after 2 h TOS. Also, the Ni metallic particles (identified as the blue circles) were still visible in the spent PSG-20 wt% Ni/Pr₂O₃ sample as it ensured the catalyst remained active and stable over the reaction time on stream (TOS).

The quantitative study of the loss in weight (TG) and derivative weight loss (DTG) profiles of the 20 wt% Ni/Pr₂O₃ spent catalysts (synthesized by the IWI, US-WI, and PSG methods) are depicted in Fig. 13a, b. The analyses were carried out at 25–900 °C with ramping of 10

°C min⁻¹ in a 20% O₂/ 80% N₂ mixed-flow system. The weight loss shown in Fig. 13a depicts that the TG profile represents carbon removal. The weight loss due to oxidation of carbon for the IWI, US-WI, and PSG catalysts were 47.22%, 44.16% and 18.04%, respectively.

Also, the stability of the catalysts is dependent on the carbon species. The behavior of the samples in terms of their weight loss are linked to two types of carbonaceous species as confirmed by the TEM studies. According to previous studies, oxidation of easily oxidized filamentous or amorphous carbon occurs around 400 – 500 °C, while above 500 °C, the TG is attributed to encapsulated or graphitic carbon oxidation (Trimm 1999; Wang and Lu 2000; Koo et al. 2008).

DTG profile represented in Fig. 13b reveals two peaks for the IWI and US-WI catalysts respectively at point 1 and 2, while the DTG profile of the PSG catalysts also had two overlapping peaks at point 3 and 4. Peaks at point 1, visible in the range of 200–330 °C for the spent IWI and US-WI catalysts represents the loss of adsorbed water.

Peaks at point 2 for the IWI and US-WI catalysts occurred in the range of 450–650 °C and peaked at around 560 °C. During the reaction study, for the IWI and US-WI

Fig. 12 TEM Images of the 20 wt% Ni/Pr₂O₃ **a** IWI **b** US-WI **c** PSG- 20 wt% Ni/Pr₂O₃ at 15,000 × magnifications. (Scale bar for all images 2000 nm)

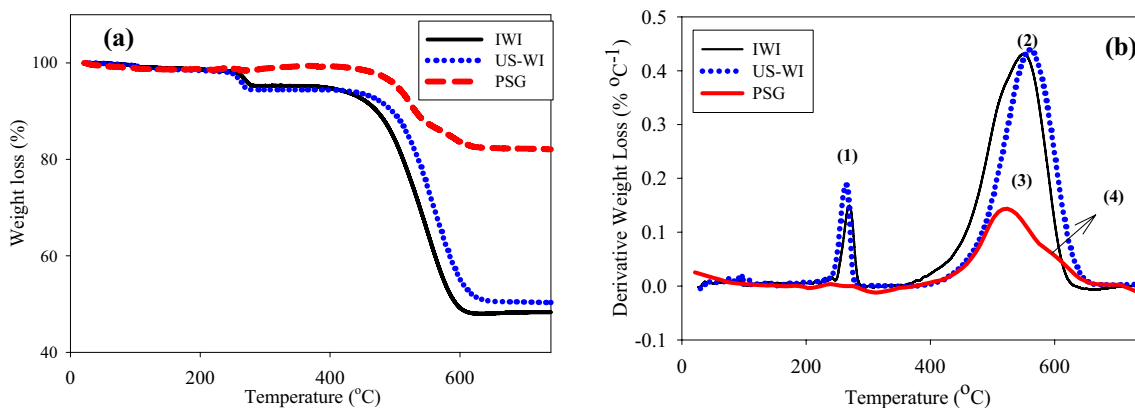
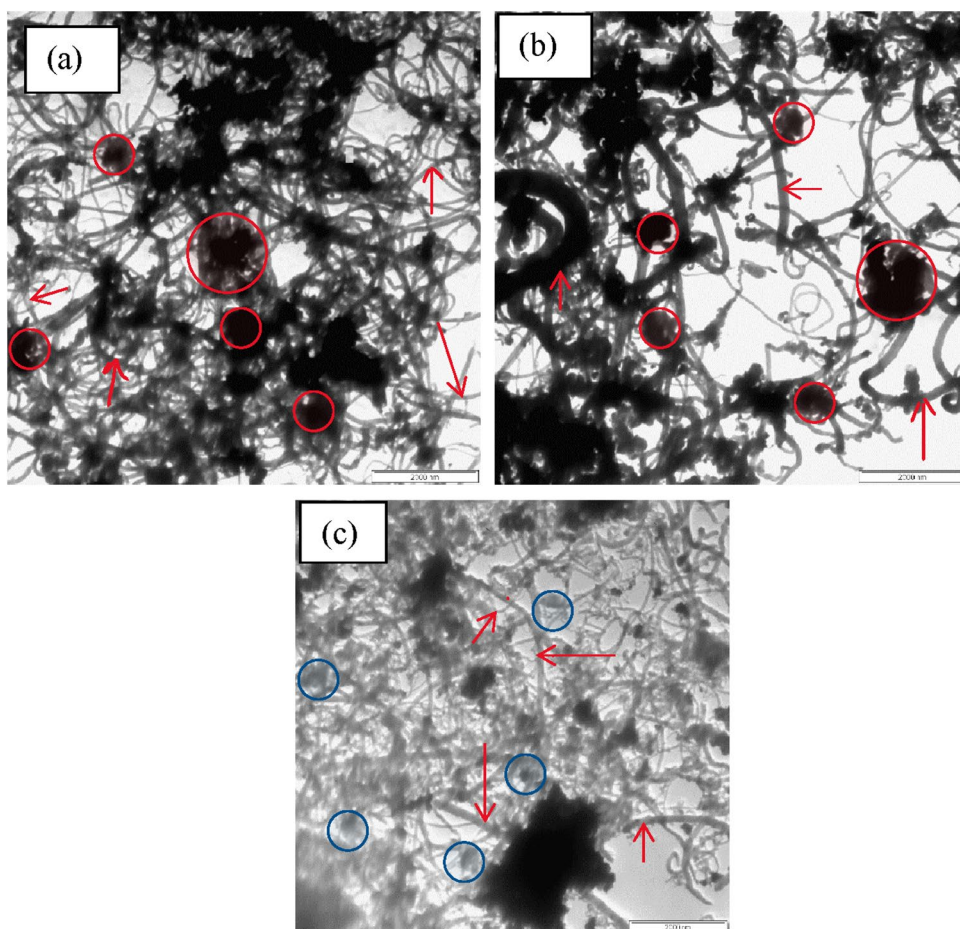


Fig. 13 TPO of the spent the 20 wt% Ni/Pr₂O₃ catalysts **a** weight loss **b** derivative weight loss

catalysts, the reaction had stopped suddenly before 2 h of reaction time suggesting that catalyst deactivation had occurred. According to literature such reaction behavior can be as a result of graphitic or encapsulated carbon formation (Wang and Lu 2000; Koo et al. 2008). Overlapping peaks at point 3 and 4 for the PSG catalyst occurred in the range of 400–650 °C. The initial peak at point 3 is

significantly larger in size than the slightly visible peak at point 4. In relation to the behavior of the PSG catalyst during reaction (catalyst remained active after 2 h of reaction time) and to further explain the dual carbon types resulting from the double peaks, peak at point 3 (peaked at about 500 °C) would likely be associated with the easily oxidized filamentous or amorphous carbon formation

which corroborates with the FESEM analysis, whereas the less intense/visible peak at point 4 (peaked at around 600 °C) is likely from the oxidation of graphitic carbon. The result shows that the PSG- 20wt% Ni/Pr₂O₃ catalyst has better resistance to deactivation amongst all prepared catalysts since dual carbon species are formed (filamentous and graphitic carbon) with a larger amount been filamentous carbon in nature. Moreover, the intensity of the peaks representing oxidation of carbon for the IWI and US-WI catalysts are much larger than the overlapping peaks representing the PSG catalyst. In addition, for the PSG catalyst, the intensity of the peak resulting from oxidation of filamentous carbon (peak at point 3) was larger than the peak representing the oxidation of graphitic carbon (peak at point 4), indicative of a higher amount of easily oxidized carbon than the unreactive carbon species in the spent PSG catalyst. In summary, the catalyst synthesized by the PSG method had greater stability because of the amount and type of carbon species formed.

Conclusions

In the present study, three samples of 20 wt% Ni/Pr₂O₃ were prepared by IWI, US-WI, and PSG methods. The variables investigated in the work were the methods of catalyst preparation, catalysts' activity, reaction temperature and stability. The O 1 s peaks confirmed a much better balance between lattice and adsorbed O₂ peaks for the PSG catalyst compared to the IWI and US-WI catalysts. The XPS results corroborated the results of the catalytic test carried out for the three samples after 2 h TOS at 800 °C post-reduction. The catalytic test revealed that the average CH₄ conversions were approximately 88% for the IWI, US-WI, and PSG catalysts, whilst average CO₂ conversions were 87.5%, 90% and 92%, for the IWI, US-WI, and PSG catalysts, respectively. However, before 2 h of the reaction time, the system over the IWI and US-WI catalysts stopped because of total restriction of reactants' flow due to excessive carbon build-up. There was no significant difference between the catalysts synthesized by IWI and US-WI methods as most of the experimental results and characterization were similar, hence the ultrasonication step for the US-WI catalysts did not significantly affect the 20 wt% Ni/Pr₂O₃ catalyst in the MDR reaction.

The catalyst's crystallite size obtained using the William-Hall equation was about 21.3 nm, 21.3 nm, and 10.6 nm, for IWI, US-WI, and PSG catalysts, respectively. This could further explain the reduction in carbon deposition and the improved catalyst stability in the reaction over the PSG catalysts. Also, in the TGA profile, the amount of unreactive carbonaceous species was lower on the PSG catalysts because of the reduced crystallite size, enhanced dispersion,

and balance ratio in the oxygen species (lattice to adsorbed oxygen ratio).

During the temperature effects study (600–950 °C) at < 700 °C and > 900 °C for the PSG catalyst, side reactions like RWGS and Boudouard reaction significantly influenced the reaction outcomes. At 600 °C, MDR reaction was affected by the WGS reaction, whilst at > 900 °C the net WGS reaction was negligible and the backward reaction i.e., the RWGS reaction, dominated.

Compared to the IWI and US-WI synthesis methods, the PSG synthesis method was better because it allows for the preparation of catalysts with smaller crystallite size (10 nm) that are uniformly dispersed thereby enhancing the carbon gasification rate. Also, the relative ratio of oxygen species is closer to unity and higher (0.85) in the PSG catalyst as compared to the IWI (0.75) and US-WI (0.75) catalyst. Consequently, the PSG catalyst attained stability for up to 24 h TOS because it accumulated more filamentous carbon, whereas the IWI and US-WI catalysts accumulated mainly graphitic carbon which encapsulated the Ni⁰ active sites, causing excess carbon retention that clogged the reactor and restricted flow. However, the PSG catalysts could not withstand the rate of carbon deposition after 24 h which creates a platform for further studies on the possibility of enhancing the stability of the PSG- 20 wt. % Ni/ Pr₂O₃ catalysts by either using double support or promoters.

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References

- Ahn K, Yoo DS, Prasad DH et al (2012) Role of multivalent Pr in the formation and migration of oxygen vacancy in Pr-doped ceria: experimental and first-principles investigations. *Chem Mater* 24:4261–4267. <https://doi.org/10.1021/cm3022424>
- Ali ME, Rahman MM, Sarkar SM, Hamid SBA (2014) Heterogeneous metal catalysts for oxidation reactions. *J Nanomater*. <https://doi.org/10.1155/2014/192038>
- Amin MH, Mantri K, Newnham J et al (2012) Highly stable ytterbium promoted Ni/ γ -Al₂O₃ catalysts for carbon dioxide reforming of methane. *Appl Catal B Environ* 119–120:217–226. <https://doi.org/10.1016/j.apcatb.2012.02.039>
- Ay H, Üner D (2015) Dry reforming of methane over CeO₂ supported Ni, Co and Ni–Co catalysts. *Appl Catal B Environ* 179:128–138. <https://doi.org/10.1016/j.apcatb.2015.05.013>
- Ayodele BV, Khan MR, Lam SS, Cheng CK (2016) Production of CO-rich hydrogen from methane dry reforming over lanthania-supported cobalt catalyst: kinetic and mechanistic studies. *Int J Hydrogen Energy* 41:4603–4615. <https://doi.org/10.1016/j.ijhydene.2016.01.091>
- Ayodele BV, Abdullah SB, Cheng CK (2017) Kinetics and mechanistic studies of CO-rich hydrogen production by CH₄/CO₂ reforming over Praseodymia supported cobalt catalysts. *Int J Hydrogen Energy* 42:28408–28424. <https://doi.org/10.1016/j.ijhydene.2017.09.037>
- Baharudin L, Rahmat N, Othman NH et al (2022) Formation, control, and elimination of carbon on Ni-based catalyst during CO₂ and CH₄ conversion via dry reforming process: a review. *J CO₂ Util* 61:102050. <https://doi.org/10.1016/j.jcou.2022.102050>
- Bai Y, Wang Y, Yuan W et al (2019) Catalytic performance of perovskite-like oxide doped cerium (La_{2-x}Ce_xCoO₄ ± y) as catalysts for dry reforming of methane. *Chinese J Chem Eng* 27:379–385. <https://doi.org/10.1016/j.cjche.2018.05.016>
- Ballesteros-Plata D, Infantes-Molina A, Rodríguez-Castellón E et al (2022) Improving noble metal catalytic activity in the dry reforming of methane by adding niobium. *Fuel* 308:121996. <https://doi.org/10.1016/j.fuel.2021.121996>
- Baudouin D, Rodemerck U, Krumeich F et al (2013) Particle size effect in the low temperature reforming of methane by carbon dioxide on silica-supported Ni nanoparticles. *J Catal* 297:27–34. <https://doi.org/10.1016/j.jcat.2012.09.011>
- Cao ANT, Pham CQ, Nguyen TM et al (2022) Dysprosium promotion on Co/Al₂O₃ catalysts towards enhanced hydrogen generation from methane dry reforming. *Fuel* 324:124818. <https://doi.org/10.1016/j.fuel.2022.124818>
- Chong CC, Cheng YW, Bahari MB et al (2021) Development of nanosilica-based catalyst for syngas production via CO₂ reforming of CH₄: a review. *Int J Hydrogen Energy* 46:24687–24708. <https://doi.org/10.1016/j.ijhydene.2020.01.086>
- Danks AE, Hall SR, Schnepf Z (2016) The evolution of “sol-gel” chemistry as a technique for materials synthesis. *Mater Horizons* 3:91–112. <https://doi.org/10.1039/c5mh00260e>
- de Caprariis B, de Filippis P, Palma V et al (2016) Rh, Ru and Pt ternary perovskites type oxides BaZr(1-x)MexO₃ for methane dry reforming. *Appl Catal A Gen* 517:47–55. <https://doi.org/10.1016/j.apcata.2016.02.029>
- Deraz NM (2018) The comparative jurisprudence of catalysts preparation methods: I. precipitation and impregnation methods. *J Ind Environ Chem* 2:19–21
- Dimesso L (2018) Pechini processes: an alternate approach of the sol-gel method, preparation, properties, and applications. *Handb Sol-Gel Sci Technol Process Charact Appl*. https://doi.org/10.1007/978-3-319-32101-1_123
- Ekeoma BC, Yusuf M, Johari K, Abdullah B (2022) Mesoporous silica supported Ni-based catalysts for methane dry reforming: a review of recent studies. *Int J Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2022.05.297>
- Fan MS, Abdullah AZ, Bhatia S (2009) Catalytic technology for carbon dioxide reforming of methane to synthesis gas. *ChemCatChem* 1:192–208. <https://doi.org/10.1002/cctc.200900025>
- Fan MS, Abdullah AZ, Bhatia S (2011) Hydrogen production from carbon dioxide reforming of methane over Ni-Co/MgO-ZrO₂ catalyst: process optimization. *Int J Hydrogen Energy* 36:4875–4886. <https://doi.org/10.1016/j.ijhydene.2011.01.064>
- Gonçalves G, Lenzi MK, Santos OAA, Jorge LMM (2006) Preparation and characterization of nickel based catalysts on silica, alumina and titania obtained by sol-gel method. *J Non Cryst Solids* 352:3697–3704. <https://doi.org/10.1016/j.jnoncrysol.2006.02.120>
- Goula MA, Charisiou ND, Papageridis KN, Siakavelas G (2016) Influence of the synthesis method parameters used to prepare nickel-based catalysts on the catalytic performance for the glycerol steam reforming reaction. *Cuihua Xuebao/chinese J Catal*. [https://doi.org/10.1016/S1872-2067\(16\)62518-4](https://doi.org/10.1016/S1872-2067(16)62518-4)
- Himabindu B, Latha Devi NSMP, Rajini Kanth B (2021) Microstructural parameters from X-ray peak profile analysis by Williamson-Hall models: a review. *Mater Today Proc* 47:4891–4896. <https://doi.org/10.1016/j.matpr.2021.06.256>
- Jana P, De La Peña O’Shea VA, Coronado JM, Serrano DP (2010) Cobalt based catalysts prepared by Pechini method for CO₂-free hydrogen production by methane decomposition. *Int J Hydrogen Energy* 35:10285–10294. <https://doi.org/10.1016/j.ijhydene.2010.07.125>
- Jawad A, Rezaei F, Rownaghi AA (2020) Highly efficient Pt/Mo-Fe/Ni-based Al₂O₃-CeO₂ catalysts for dry reforming of methane. *Catal Today* 350:80–90. <https://doi.org/10.1016/j.cattod.2019.06.004>
- Jiang SP (2006) A review of wet impregnation - An alternative method for the fabrication of high performance and nano-structured electrodes of solid oxide fuel cells. *Mater Sci Eng A* 418:199–210. <https://doi.org/10.1016/j.msea.2005.11.052>
- Kakihana M (1996) “Sol-Gel” preparation of high temperature superconducting oxides. *J Sol-Gel Sci Technol* 6:7–55. <https://doi.org/10.1007/BF00402588>
- Khademi MH, Alipour-Dehkordi A, Tabesh M (2021) Optimal design of methane tri-reforming reactor to produce proper syngas for Fischer-Tropsch and methanol synthesis processes: a comparative analysis between different side-feeding strategies. *Int J Hydrogen Energy* 46:14441–14454. <https://doi.org/10.1016/j.ijhydene.2021.01.215>
- Khajenoori M, Rezaei M, Meshkani F (2015) Dry reforming over CeO₂-promoted Ni/MgO nano-catalyst: effect of Ni loading and CH₄/CO₂ molar ratio. *J Ind Eng Chem* 21:717–722. <https://doi.org/10.1016/j.jiec.2014.03.043>
- Khorsand Zak A, Majid WH, Abrishami ME, Yousefi R (2011) X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods. *Solid State Sci* 13:251–256. <https://doi.org/10.1016/j.solidstatesciences.2010.11.024>
- Kim P, Kim Y, Kim H et al (2004) Synthesis and characterization of mesoporous alumina for use as a catalyst support in the hydrodechlorination of 1,2-dichloropropane: effect of preparation condition of mesoporous alumina. *J Mol Catal A Chem* 219:87–95. <https://doi.org/10.1016/j.molcata.2004.04.038>

- Kim DK, Stöwe K, Müller F, Maier WF (2007) Mechanistic study of the unusual catalytic properties of a new Ni{single bond}Ce mixed oxide for the CO₂ reforming of methane. *J Catal* 247:101–111. <https://doi.org/10.1016/j.jcat.2007.01.011>
- Koo KY, Roh HS, Seo YT et al (2008) Coke study on MgO-promoted Ni/Al₂O₃ catalyst in combined H₂O and CO₂ reforming of methane for gas to liquid (GTL) process. *Appl Catal A Gen* 340:183–190. <https://doi.org/10.1016/j.apcata.2008.02.009>
- Kuhn JN, Ozkan US (2008) Surface properties of Sr- and Co-doped LaFeO₃. *J Catal* 253:200–211. <https://doi.org/10.1016/j.jcat.2007.10.005>
- Kwon BW, Oh JH, Kim GS et al (2018) The novel perovskite-type Ni-doped Sr_{0.92}Y_{0.08}TiO₃ as a reforming biogas (CH₄ + CO₂) for H₂ production. *Appl Energy* 227:213–219. <https://doi.org/10.1016/j.apenergy.2017.07.105>
- Leclercq E, Rives A, Payen E, Hubaut R (1998) X-ray photoelectron spectroscopy and infrared spectroscopy studies for the mechanism of the enantioselective hydrogenation of methyl acetoacetate over mixed nickel-cerium oxides. *Appl Catal A Gen* 168:279–288. [https://doi.org/10.1016/S0926-860X\(97\)00359-1](https://doi.org/10.1016/S0926-860X(97)00359-1)
- Lee HC, Siew KW, Gimbin J, Cheng CK (2014) Synthesis and characterisation of cement clinker-supported nickel catalyst for glycerol dry reforming. *Chem Eng J* 255:245–256. <https://doi.org/10.1016/j.cej.2014.06.044>
- Lee G, Kim I, Yang I et al (2018) Effects of the preparation method on the crystallinity and catalytic activity of LaAlO₃ perovskites for oxidative coupling of methane. *Appl Surf Sci* 429:55–61. <https://doi.org/10.1016/j.apsusc.2017.08.092>
- Li H, Xu H, Wang J (2011) Methane reforming with CO₂ to syngas over CeO₂-promoted Ni/Al₂O₃-ZrO₂ catalysts prepared via a direct sol-gel process. *J Nat Gas Chem* 20:1–8. [https://doi.org/10.1016/S1003-9953\(10\)60156-9](https://doi.org/10.1016/S1003-9953(10)60156-9)
- Li K, Pei C, Li X et al (2020) Dry reforming of methane over La₂O₂CO₃-modified Ni/Al₂O₃ catalysts with moderate metal support interaction. *Appl Catal B Environ* 264:118448. <https://doi.org/10.1016/j.apcatb.2019.118448>
- Lin J, Yu M, Lin C, Liu X (2007) Multifunctional oxide optical materials via the versatile pechini-type sol-gel process: synthesis and characteristics. *J Phys Chem C* 111:5835–5845. <https://doi.org/10.1021/jp070062c>
- Liu D, Wang Y, Shi D et al (2012) Methane reforming with carbon dioxide over a Ni/ZrO₂-SiO₂ catalyst: influence of pretreatment gas atmospheres. *Int J Hydrogen Energy* 37:10135–10144. <https://doi.org/10.1016/j.ijhydene.2012.03.158>
- Lovell EC, Horlyck J, Scott J, Amal R (2017) Flame spray pyrolysis-designed silica/ceria-zirconia supports for the carbon dioxide reforming of methane. *Appl Catal A Gen* 546:47–57. <https://doi.org/10.1016/j.apcata.2017.08.002>
- Luisetto I, Tuti S, Di Bartolomeo E (2012) Co and Ni supported on CeO₂ as selective bimetallic catalyst for dry reforming of methane. *Int J Hydrogen Energy* 37:15992–15999. <https://doi.org/10.1016/j.ijhydene.2012.08.006>
- Luisetto I, Tuti S, Battocchio C et al (2015) Ni/CeO₂-Al₂O₃ catalysts for the dry reforming of methane: the effect of CeAlO₃ content and nickel crystallite size on catalytic activity and coke resistance. *Appl Catal A Gen* 500:12–22. <https://doi.org/10.1016/j.APCATA.2015.05.004>
- Majid A, Tunney J, Argue S et al (2005) Preparation of SrFeO_{~2.85} perovskite using a citric acid assisted Pechini-type method. *J Alloys Compd* 398:48–54. <https://doi.org/10.1016/j.jallcom.2005.02.023>
- Milberg B, Juan A, Irigoyen B (2017) Redox behavior of a low-doped Pr-CeO₂(111) surface. A DFT+U study. *Appl Surf Sci* 401:206–217. <https://doi.org/10.1016/J.APSUSC.2016.12.245>
- Mishra A, Shafiefarhood A, Dou J, Li F (2019) Rh promoted perovskites for exceptional “low temperature” methane conversion to syngas. *Catal Today*. <https://doi.org/10.1016/j.cattod.2019.05.036>
- Moogi S, Hyun Ko C, Hoon Rhee G et al (2022) Influence of catalyst synthesis methods on anti-coking strength of perovskites derived catalysts in biogas dry reforming for syngas production. *Chem Eng J* 437:135348. <https://doi.org/10.1016/J.CEJ.2022.135348>
- Moradi GR, Rahmanzadeh M, Khosravian F (2014) The effects of partial substitution of Ni by Zn in LaNiO₃ perovskite catalyst for methane dry reforming. *J CO₂ Util* 6:7–11. <https://doi.org/10.1016/j.jcou.2014.02.001>
- Mustu H, Yasyerli S, Yasyerli N et al (2015) Effect of synthesis route of mesoporous zirconia based Ni catalysts on coke minimization in conversion of biogas to synthesis gas. *Int J Hydrogen Energy* 40:3217–3228. <https://doi.org/10.1016/j.ijhydene.2015.01.023>
- Nabgan W, Mat R, Abdullah TAT et al (2016) Development of a kinetic model for hydrogen production from phenol over Ni-Co/ZrO₂ catalyst. *J Environ Chem Eng* 4:4444–4452. <https://doi.org/10.1016/j.jece.2016.10.013>
- Osazuwa OU, Abidin SZ (2020) An overview on the role of lanthanide series (rare earth metals) in H₂ and syngas production from CH₄ reforming processes. *Chem Eng Sci* 227:115863. <https://doi.org/10.1016/j.ces.2020.115863>
- Osazuwa OU, Setiabudi HD, Rasid RA, Cheng CK (2017) Syngas production via methane dry reforming: a novel application of SmCoO₃ perovskite catalyst. *J Nat Gas Sci Eng* 37:435–448. <https://doi.org/10.1016/j.jngse.2016.11.060>
- Osazuwa OU, Abidin SZ, Fan X et al (2021) An insight into the effects of synthesis methods on catalysts properties for methane reforming. *J Environ Chem Eng* 9:105052. <https://doi.org/10.1016/j.jece.2021.105052>
- Owgi AHK, Jalil AA, Hussain I et al (2022) Enhancing resistance of carbon deposition and reaction stability over nickel loaded fibrous silica-alumina (Ni/FSA) for dry reforming of methane. *Int J Hydrogen Energy*. <https://doi.org/10.1016/J.IJHYDENE.2021.12.134>
- Passos FB, de Oliveira ER, Mattos LV, Noronha FB (2005) Partial oxidation of methane to synthesis gas on Pt/CexZr1-xO₂ catalysts: the effect of the support reducibility and of the metal dispersion on the stability of the catalysts. *Catal Today* 101:23–30. <https://doi.org/10.1016/J.CATTOD.2004.12.006>
- Pechini MP, Pechini M, Pechini M, Pechini MP (1967) Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor 1967
- Rezaei M, Alavi SM, Sahebdelfar S, Yan ZF (2006) Syngas production by methane reforming with carbon dioxide on noble metal catalysts. *J Nat Gas Chem* 15:327–334. [https://doi.org/10.1016/S1003-9953\(07\)60014-0](https://doi.org/10.1016/S1003-9953(07)60014-0)
- Roslan NA, Zainal Abidin S, Osazuwa OU et al (2022) Enhanced syngas production from glycerol dry reforming over Ru promoted -Ni catalyst supported on extracted Al₂O₃. *Fuel* 314:123050. <https://doi.org/10.1016/J.FUEL.2021.123050>
- Sajjadi SM, Haghighi M, Rahmani F (2015) Sol-gel synthesis of Ni-Co/Al₂O₃-MgO-ZrO₂ nanocatalyst used in hydrogen production via reforming of CH₄/CO₂ greenhouse gases. *J Nat Gas Sci Eng* 22:9–21. <https://doi.org/10.1016/j.jngse.2014.11.014>

- Sepehri S, Rezaei M, Wang Y et al (2018) The evaluation of autothermal methane reforming for hydrogen production over Ni/CeO₂ catalysts. *Int J Hydrogen Energy* 43:22340–22346. <https://doi.org/10.1016/j.ijhydene.2018.10.016>
- Setiabudi HD, Chong CC, Abed SM et al (2018) Comparative study of Ni-Ce loading method: beneficial effect of ultrasonic-assisted impregnation method in CO₂ reforming of CH₄ over Ni-Ce/SBA-15. *J Environ Chem Eng* 6:745–753. <https://doi.org/10.1016/j.jece.2018.01.001>
- Shin SA, Noh YS, Hong GH et al (2018) Dry reforming of methane over Ni/ZrO₂-Al₂O₃ catalysts: effect of preparation methods. *J Taiwan Inst Chem Eng* 90:25–32. <https://doi.org/10.1016/j.jtice.2017.11.032>
- Singh S, Bahari MB, Abdullah B et al (2018) Bi-reforming of methane on Ni/SBA-15 catalyst for syngas production: influence of feed composition. *Int J Hydrogen Energy* 43:17230–17243. <https://doi.org/10.1016/j.ijhydene.2018.07.136>
- Son IH, Lee SJ, Song IY et al (2014) Study on coke formation over Ni/γ-Al₂O₃, Co-Ni/γ-Al₂O₃, and Mg-Co-Ni/γ-Al₂O₃ catalysts for carbon dioxide reforming of methane. *Fuel* 136:194–200. <https://doi.org/10.1016/j.fuel.2014.07.041>
- Song Z, Liu W, Nishiguchi H et al (2007) The Pr promotion effect on oxygen storage capacity of Ce-Pr oxides studied using a TAP reactor. *Appl Catal A Gen* 329:86–92. <https://doi.org/10.1016/j.apcata.2007.06.023>
- Sun Z, Liu H, Bai H et al (2022) The crucial role of deoxygenation in syngas refinement and carbon dioxide utilization during chemical looping-based biomass gasification. *Chem Eng J* 428:132068. <https://doi.org/10.1016/j.cej.2021.132068>
- Trimm D (1999) Catalysts for the control of coking during steam reforming. *Catal Today* 49:3–10. [https://doi.org/10.1016/S0920-5861\(98\)00401-5](https://doi.org/10.1016/S0920-5861(98)00401-5)
- Trueba M, Trasatti SP (2005) γ-alumina as a support for catalysts: a review of fundamental aspects. *Eur J Inorg Chem*. <https://doi.org/10.1002/ejic.200500348>
- Varkolu M, Kunamalla A, Jinnala SAK et al (2021) Role of CeO₂/ZrO₂ mole ratio and nickel loading for steam reforming of n-butanol using Ni-CeO₂-ZrO₂-SiO₂ composite catalysts: a reaction mechanism. *Int J Hydrogen Energy* 46:7320–7335. <https://doi.org/10.1016/j.ijhydene.2020.11.240>
- Wang S, Lu GQM (2000) Effects of promoters on catalytic activity and carbon deposition of Ni/g-Al₂O₃ catalysts in CO₂ reforming of CH₄. *J Chem Technol Biotechnol* 59:589–595
- Wang S, Lu GQ, Millar GJ (1996) Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: state of the art. *Energy Fuels* 10:896–904. <https://doi.org/10.1021/ef950227t>
- Whang HS, Choi MS, Lim J et al (2017) Enhanced activity and durability of Ru catalyst dispersed on zirconia for dry reforming of methane. *Catal Today* 293–294:122–128. <https://doi.org/10.1016/j.cattod.2016.12.034>
- Yosefi L, Haghighi M, Allahyari S, Ashkriz S (2015) Effect of ultrasound irradiation and Ni-loading on properties and performance of CeO₂-doped Ni/clinoptilolite nanocatalyst used in polluted air treatment. *Process Saf Environ Prot* 95:26–37. <https://doi.org/10.1016/j.psep.2015.02.006>
- Zanganeh R, Rezaei M, Zamaniyan A (2013) Dry reforming of methane to synthesis gas on NiO-MgO nanocrystalline solid solution catalysts. *Int J Hydrogen Energy* 38:3012–3018. <https://doi.org/10.1016/j.ijhydene.2012.12.089>
- Zhang G, Du Y, Xu Y, Zhang Y (2014) Journal of industrial and engineering chemistry effects of preparation methods on the properties of cobalt/carbon catalyst for methane reforming with carbon dioxide to syngas. *J Ind Eng Chem* 20:1677–1683. <https://doi.org/10.1016/j.jiec.2013.08.016>

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