

# Syngas production from methane dry reforming over 15wt%Ni/85wt%CaFe<sub>2</sub>O<sub>4</sub> catalyst

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*Abstract*-In the present study, syngas production from methane dry reforming over 15wt%Ni/85%CaFe<sub>2</sub>O<sub>4</sub> catalyst was investigated. The CaFe<sub>2</sub>O<sub>4</sub> was synthesized by sol gel method using stoichiometric ratio of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O mixed in 30% aqueous NH<sub>3</sub> solution. The 15wt%Ni/85%CaFe<sub>2</sub>O<sub>4</sub> catalysts was synthesized by impregnating required amount of aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 1g of CaFe<sub>2</sub>O<sub>4</sub>. The as-synthesized catalyst was characterized by XRD, SEM, EDX and FTIR for phase identification and crystallinity, morphology, elemental composition, and nature of chemical bonds. The catalytic activity of the catalyst was tested in methane dry reforming using a fixed bed continuous flow reactor. The catalyst activities were measured in terms of the reactant (CH<sub>4</sub> and CO<sub>2</sub>) conversions and the products (H<sub>2</sub> and CO) yield. The activity of catalyst in the methane dry reforming reaction resulted to highest CH<sub>4</sub> and CO<sub>2</sub> conversions of 90.4% and 87.6% respectively with a corresponding H<sub>2</sub> and CO yield of 73.42% and 74.43% respectively. Syngas with H<sub>2</sub>:CO ratio of 0.986 was obtained from the methane dry reforming reaction over the 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst making it suitable for use as chemical intermediate for the synthesis of oxygenated fuels.

*Keywords:* Calcium ferrite; characterization; methane dry reforming; nickel; syngas.

## 1.0 INTRODUCTION

The production of syngas via methane dry reforming has attracted a lot of attentions by researchers in the last two decades [1–3]. This is due to the energy and environmental benefits of the process [4,5]. The methane dry reforming process

simultaneously produces syngas with H<sub>2</sub>: CO ratio of unity suitable as chemical building blocks for the production of oxygenated fuels via Fischer-Tropsch synthesis [6]. Moreover, the process utilized CH<sub>4</sub> and CO<sub>2</sub>, the main contributors to greenhouse effects as feed stock. However, one of the main constraints of the methane dry reforming process is catalyst deactivation through cooking and sintering [7]. In order to overcome these challenges, several researchers have focused on the synthesis of supported metal catalysts with high activity as well as stability [8]. Metals such as, Co, Ni, Ru, Rh, Pd and Pt synthesized on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, CaO, SBA and ZrO<sub>2</sub> have been investigated in methane dry reforming for the production of syngas [9–14]. The findings from this studies showed that the catalysts indicated different degrees of activities based on their physicochemical properties. However, supported noble metals such as Ru, Rh, Pd and Pt displayed excellent activities and stability [15,16]. Nevertheless, due to the expensive nature of these noble metals, their utilization as catalysts in methane dry reforming might not be suitable for scale up process. On the contrary supported nickel catalysts have been reported to have high activity for syngas production in methane dry reforming [17]. Up till now, nickel based catalysts have been synthesized using supports such as Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, MgO, CaO, SBA and ZrO<sub>2</sub> [18–20]. To the best of the author's knowledge, intensive search of literature showed that CaFe<sub>2</sub>O<sub>4</sub> has not been utilized for the synthesis of Ni-catalyst. This study focuses on the syngas production from methane dry reforming over Ni/ CaFe<sub>2</sub>O<sub>4</sub> catalyst.

## 2.0 MATERIAL AND METHODS

### 2.1 Synthesis of Catalysts

Prior to the synthesis of the Ni/CaFe<sub>2</sub>O<sub>4</sub> catalysts, the CaFe<sub>2</sub>O<sub>4</sub> support was prepared by sol-gel technique reported elsewhere [21]. In a typical synthesis, a stoichiometric ratio of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were mixed in 30% aqueous NH<sub>3</sub> solution, and the mixture was stirred at room temperature for 24 h. The solution was then slowly heated to 80 °C and maintained at that temperature level until the water evaporated. The resulting brown dry gel-like slurry was calcined at 450 °C for 2 h followed by heat treatment at 900 °C for 10 h using muffle furnace to obtain CaFe<sub>2</sub>O<sub>4</sub> powder. Finally, CaFe<sub>2</sub>O<sub>4</sub> powders were crushed in the mortar to obtain fine particle size. Thereafter, Ni/CaFe<sub>2</sub>O<sub>4</sub> was synthesized with metal loading of 15 wt% using wet-impregnation method. Required amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O precursor was dissolved in aqueous solution and 1g of CaFe<sub>2</sub>O<sub>4</sub> was added to the solution under stirring for 3h. Subsequently, the slurry was oven dried for 24 h at 120 °C, crushed and finally calcined at 800 °C for 5 h.

### 2.2 Catalyst Characterization

The 15wtNi/CaFe<sub>2</sub>O<sub>4</sub> catalyst was characterized for its physicochemical properties using different techniques. The bond formations of the as-prepared 15wtNi/CaFe<sub>2</sub>O<sub>4</sub> catalyst was confirmed by FTIR spectrum using Perkin Elmer Spectrum BX(II) spectrophotometer. The phase identification and crystallinity of the as-prepared 15wtNi/CaFe<sub>2</sub>O<sub>4</sub> catalyst was characterized by X-ray powder diffraction analysis using RIGAKU miniflex II X-ray diffractometer capable of measuring powdered diffraction pattern from 3 to 145° in 2θ scanning range. The X-ray source is Cu Kα with wavelength (λ) of 0.154 nm radiation. The XRD is equipped with the latest version of PDXL, RIGAKU full function powder-diffraction analysis software. The morphology and the elemental composition of the as-prepared catalyst were determined using JEOL field emission scanning electron microscopy (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDX).

### 2.3 Catalytic activity test

The schematic diagram of the experimental set-up for the hydrogen-rich syngas production from methane dry reforming is represented in Figure 1. The set-up comprised CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> gases. The main reactants for the methane dry reforming are CO<sub>2</sub> and CH<sub>4</sub>, while N<sub>2</sub> and H<sub>2</sub> serve as carrier gas and for reduction, respectively. The stainless steel fixed bed continuous reactor was packed with 200 mg of catalysts supported with quartz wool and heated inside a split-tube furnace that was equipped with K-type thermocouple for measurement of the catalytic bed temperature. The catalyst was reduced in 60 ml/min of 20% H<sub>2</sub> and 80% N<sub>2</sub> prior to the commencement of the catalytic activity test. The flow rate of the inlet gas was maintained at 100 ml/min and individually regulated with the aid of Alicat digital mass flow controller (MFC) (Alicat Scientific Inc., USA). The outlet gas composition (CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>) was measured with gas chromatography (GC) instrument (Agilent Technologies, USA) equipped with thermal conductivity detector (TCD). Two packed columns were used viz. Supelco Molecular Sieve 13x (10 ft. 1/8 in. OD 2 mm ID, 60/80 mesh, Stainless Steel) and Agilent Hayesep DB (30 ft. 1/8 in. OD 2 mm ID, 100/120 mesh, Stainless Steel). Helium (He) gas was used as a carrier with flow rate of 20 ml/min with operating column temperature of 120 °C and detector temperature of 150 °C (column pressure <90 psi). Separation and quantification of gas analytes viz. H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> were performed using Hayesep DB column, whilst CO were analysed using the Molecular Sieve 13 x columns. The conversion of CH<sub>4</sub> and CO<sub>2</sub> as well as the yields of H<sub>2</sub> and CO were calculated using Equations (1)-(4).

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

$$\text{CO}_2 \text{ Conversion (\%)} = \frac{F_{\text{CO}_2\text{in}} - F_{\text{CO}_2\text{out}}}{F_{\text{CO}_2\text{in}}} \times 100 \quad (2)$$

$$\text{H}_2 \text{ yield} = \frac{F_{\text{H}_2\text{out}}}{2 \times F_{\text{CH}_4\text{in}}} \times 100 \quad (3)$$

$$\text{CO yield} = \frac{F_{\text{COout}}}{F_{\text{CH}_4\text{in}} + F_{\text{CO}_2\text{in}}} \times 100 \quad (4)$$

where  $F_{\text{CO}_2\text{in}}$ ,  $F_{\text{CH}_4\text{in}}$ ,  $F_{\text{CO}_2\text{out}}$ , and  $F_{\text{CH}_4\text{out}}$  are the inlet and outlet molar flow rates of  $\text{CO}_2$  and  $\text{CH}_4$ , respectively.  $F_{\text{H}_2}$  and  $F_{\text{CO}}$  are the outlet molar flow rates of  $\text{H}_2$  and  $\text{CO}$ .

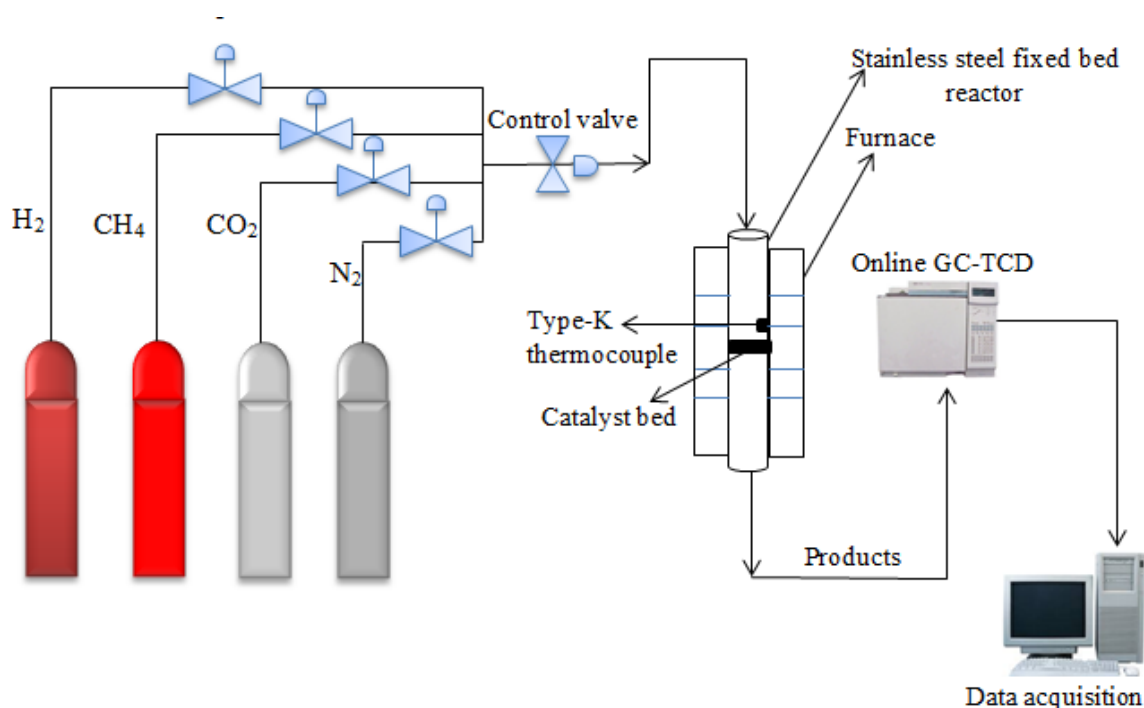


Figure 1: Schematic representation of the experimental set up for the hydrogen-rich syngas production.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Catalyst characterization

The FTIR spectrums of the as-prepared 15wt%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst before and after calcination are depicted in Figure 4. It can be seen that the characteristic structure of CaFe<sub>2</sub>O<sub>4</sub> is displayed by the spectrum. The band at 3223 cm<sup>-1</sup> can be attributed to stretching vibration of OH<sup>-</sup> which could be as result of adsorbed water as well as water molecules present in the freshly prepared catalyst before calcination. The broader shape of the peaks at 3223 cm<sup>-1</sup> for the uncalcined catalyst is due to the presence of higher amount of moisture compare to the calcined catalyst. The bands at 829 and 819 cm<sup>-1</sup> signify Fe-O-H bending vibrations [28]. The stretching vibration metal oxide bonds representing Ca-O, Fe-O and Ni-O can be identifies at 697 and 697 cm<sup>-1</sup>[23].

The XRD patterns of the CaFe<sub>2</sub>O<sub>4</sub> supports as well as the reduced and used 15wt%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalysts are depicted in Figure 5. Interestingly, all the peaks were matched to Ni, NiO and CaFe<sub>2</sub>O<sub>4</sub>. The peaks at  $2\theta = 32.12$  (111), 33.17 (004), 34.30(302), 42.86 (311), 43.82(213), 44.82(304), 49.40(214), 50.97(006), 52.57(404), 60.69(116), 61.06(600), 63.46(216), 65.16(513), 69.41(610), 70.28(108), 75.08(613) and 78.18(118) correspond to the orthorhombic structure of CaFe<sub>2</sub>O<sub>4</sub> [21]. The peaks at  $2\theta = 12.15$ (110), 23.00(220), 35.99 (101), 41.43(100) 47.12(130), 47.92(131), 51.12(103), 58.06(201), 59.33(104), 66.35(014) and 78.15(105) corresponds to cubic structure of Ni. The particle size diameter of the sharpest peak ( $2\theta=42.86$ ) was estimated from Scherrer's equation as 22.47 nm.

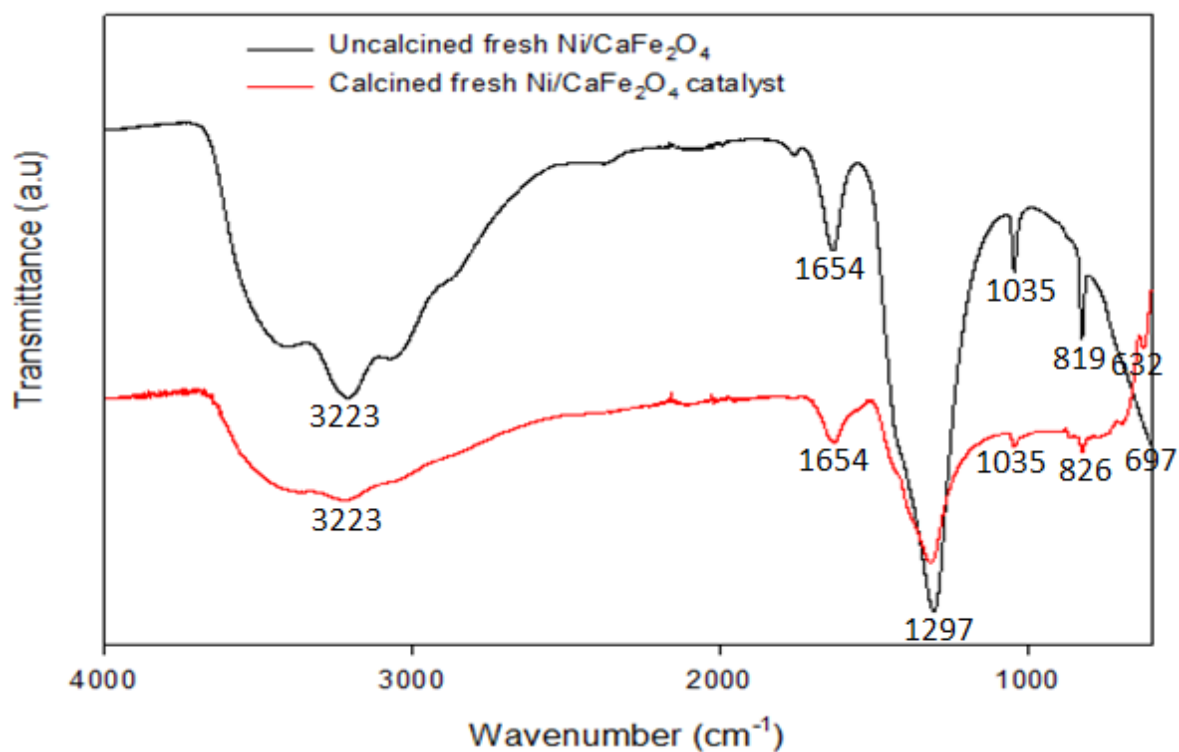


Figure 2: FTIR spectrum of the fresh 15%wtNi/CaFe<sub>2</sub>O<sub>4</sub> catalyst before and after calcination.

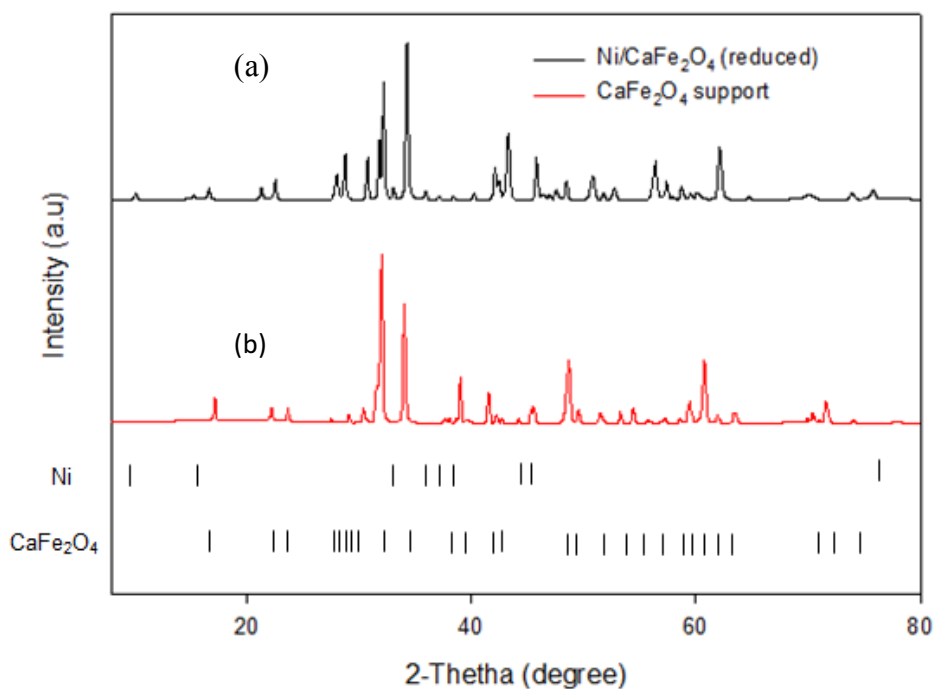
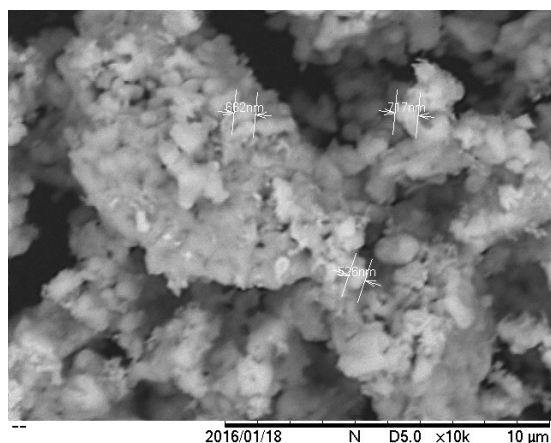
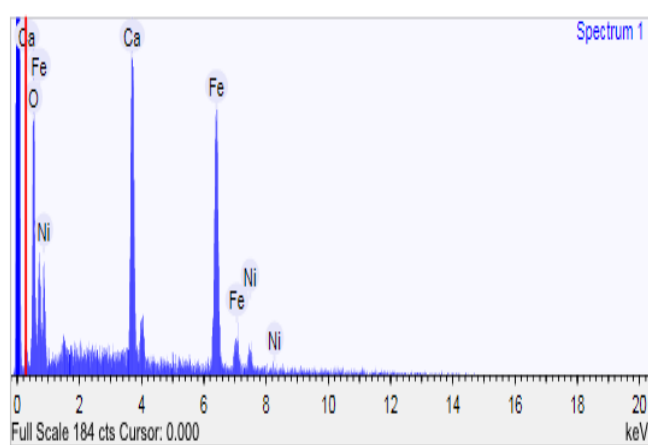


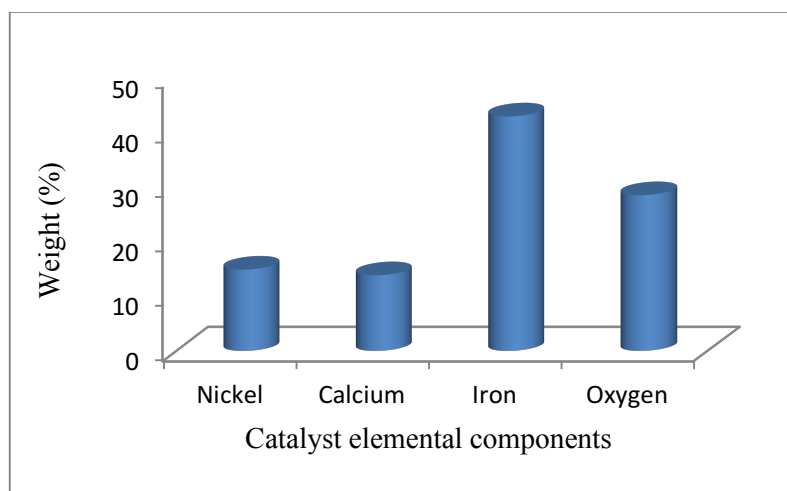
Figure 3: XRD pattern of CaFe<sub>2</sub>O<sub>4</sub>, reduced 15%wtNi/CaFe<sub>2</sub>O<sub>4</sub>.



(a)

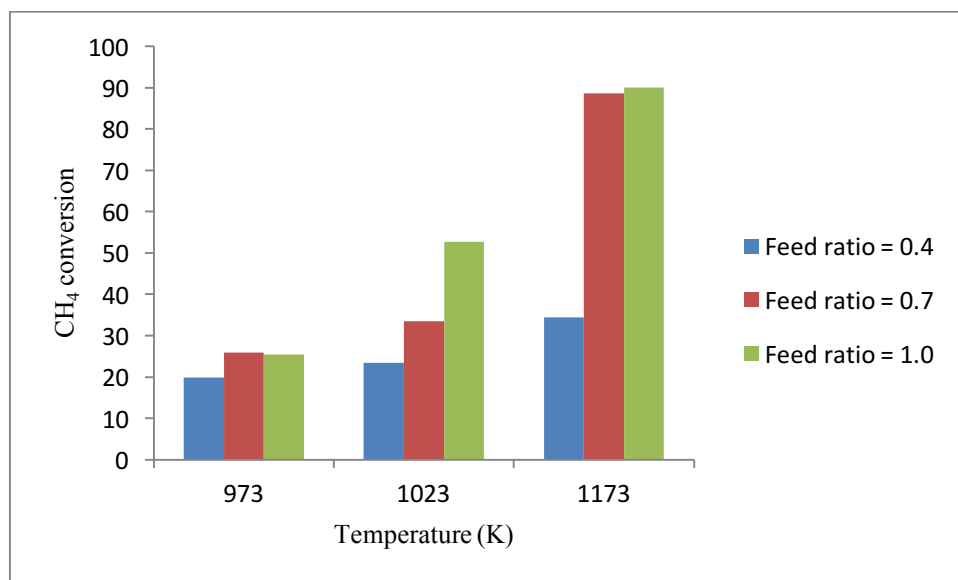


(b)

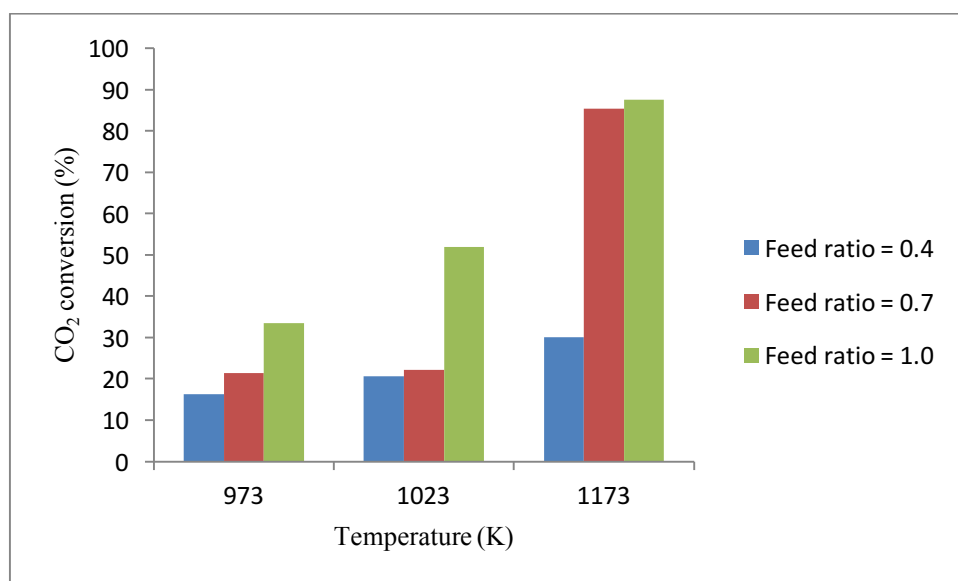


(c)

Figure 4: (a) SEM image (b) EDX micrograph (c) elemental composition of the catalyst from EDX.



(a)



(b)

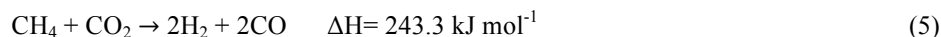
Figure 5: Catalytic activities of 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst in terms of (a) CH<sub>4</sub> conversion (b) CO<sub>2</sub> conversion.

The SEM image, EDX micrograph, elemental composition and the EDX dot mapping are depicted in Figure 6. It can be seen from the SEM image (Figure 6 (a)) the formation of spherical particles of the catalyst with an average diameter of 63.87 nm. Moreover, the identification of Ni, Ca, Fe and O elemental components of the Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst from the EDX micrograph (Figure 6 (b)) show the efficacy of the preparation methods. The elemental compositions obtained from the EDX (Figure 6 (c)) are consistent with the stipulated amount in the as-prepared catalyst. It can be seen from the EDX mapping (Figure 6(d)) that the Ni-species is well distributed on the CaFe<sub>2</sub>O<sub>4</sub> support.

### 3.2 Catalyst activity

#### 3.2.1 Effect of temperature and feed ratio on methane dry reforming

The activity of the 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst in methane dry reforming for syngas production in terms of conversions are depicted in Figure 5. The CH<sub>4</sub> and CO<sub>2</sub> conversions in the methane dry reforming reaction corresponding to Equation 5 increases with increase in temperature and feed (CH<sub>4</sub>: CO<sub>2</sub>) ratio which proved the endothermic nature of the methane dry reforming reaction. At feed ratio of 0.4, the CH<sub>4</sub> conversion increases from 19.78% at 973 K to 34.48% at 1173 K. Similarly, at feed ratios of 0.7 and 1.0, the CH<sub>4</sub> conversion increases from 25.82% and 25.38% at 973 K respectively to maximum values of 88.63% and 90.04%. This trends in consistent with Arrhenius behavior for temperature dependent reactions such as methane dry reforming [24].



Similarly, as the feed ratio and reaction temperature increases from 0.4 to 1.0 and 973-1173 K, there was a corresponding increase in the CO<sub>2</sub> conversion. However, the activity of the catalyst in terms of CO<sub>2</sub> conversion climaxed with the highest CO<sub>2</sub> conversion of 87.6% obtained at feed ratio of 1.0 and 1173 K.

#### 3.2.2 Effect of temperature and feed ratio on syngas yield

The effect of reaction temperature and feed ratio on syngas yields produced from the methane dry reforming reaction over 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst is depicted in Figure 6. Significantly, both the yield of the H<sub>2</sub> and CO produced from the methane dry reforming reaction increases with temperature and feed ratio. Nevertheless, the activity of the catalyst in the methane dry reforming climaxed at feed ratio of 1.0 and reaction temperature of 1173 with corresponding H<sub>2</sub> and CO yields of 73.42% and 74.43% respectively. It is however noted that the CO yield was higher than that of H<sub>2</sub> signifying the interference of side reactions such as reverse water gas shift reaction depicted in Equation 6 with the main methane dry reforming reaction.



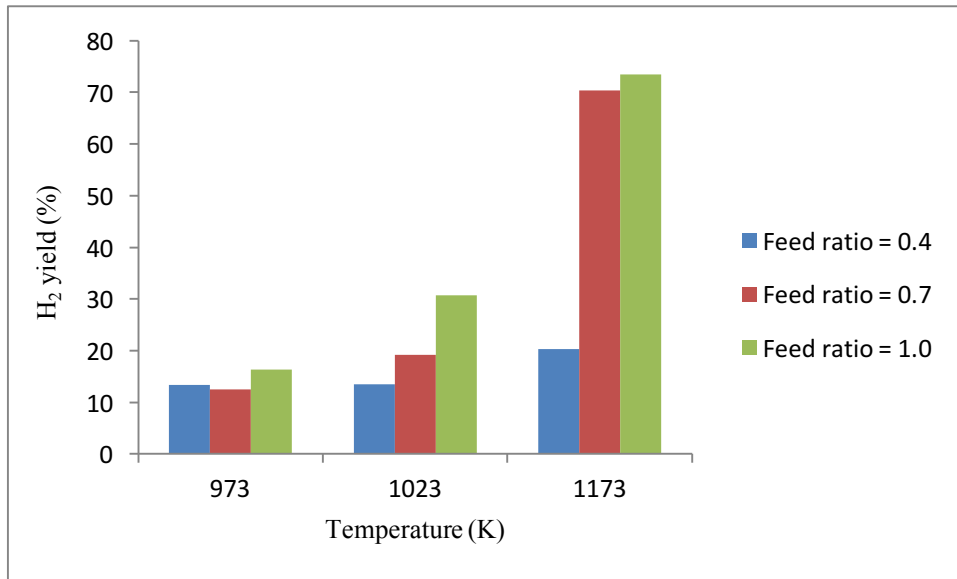
The methane dry reforming reaction over the 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst led to the production of syngas ratio of 0.986 which is close to the theoretical value of 1. Hence, the 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst have the potential to be used in methane dry reforming for producing syngas that can be used as chemical intermediates for subsequent production of oxygenated fuels, olefins and other valuable chemicals [25].

## 4. CONCLUSION

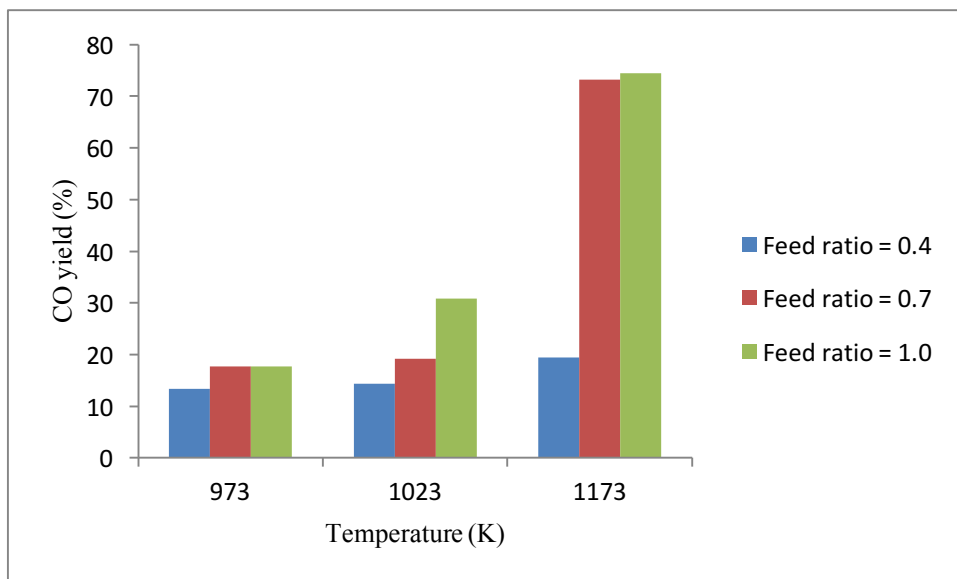
15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst was synthesized via wet impregnation method and subsequently characterized for its physicochemical properties by FTIR, XRD, SEM and EDX. The activity of the as-synthesized catalyst was evaluated in methane dry reforming reaction. The XRD analysis shows that the active Ni phase as well as the CaFe<sub>2</sub>O<sub>4</sub> support with no evidence of impurities. The composition of the as-synthesized catalyst was consistent with that obtained from the EDX analysis. The catalyst showed an impressive performance in the methane dry reforming reaction resulting to highest CH<sub>4</sub> and CO<sub>2</sub> conversions of 90.4% and 87.6% respectively. The activity of the catalyst leads to the production of H<sub>2</sub> and CO yield of 73.42% and 74.43% respectively. Syngas with H<sub>2</sub>: CO ratio of 0.986 obtained from the methane dry reforming reaction over the 15%Ni/CaFe<sub>2</sub>O<sub>4</sub> catalyst is suitable for use as chemical intermediate in Fischer-Tropsch Synthesis.

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(a)



(b)

Figure 6: Effect of temperature and feed ratio on syngas yield (a) H<sub>2</sub> yield (b) CO yield.



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