

Syngas production from biogas reforming over La-promoted Ni/Al₂O₃ catalyst

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ABSTRACT

Greenhouse gases (GHG's) trap heat and make the planet warmer with human activities being responsible for almost all of the increase in GHG's in the atmosphere over the last 150 years. As is well documented, the largest source of anthropogenic greenhouse gas emissions comes from burning fossil fuels for electricity, heat, and transportation.

In this respect, the energetic utilization of biogas, a gas mixture consisting mainly of CH₄ and CO₂, via the dry reforming of biogas is of enormous interest, as it converts these two greenhouse gases into synthesis gas (H₂/CO mixtures). Biogas is produced in landfills, in agricultural operations, and during the treatment of wastewater; with landfill gas being a particularly large source of biogas, producing 13.5 billion m³ of methane per year.

In this contribution, a comparative study of catalytic performance for nickel supported on un-promoted and promoted with La₂O₃ alumina catalysts is reported for the biogas dry reforming reaction. Catalysts were synthesized applying the wet impregnation method at a constant metal loading (8 wt. %) in order to investigate the effect of the reaction temperature on (i) methane and carbon dioxide conversion, (ii) hydrogen and carbon monoxide yield, (iii) H₂/CO molar ratio of the produced gas mixtures at the outlet of the reactor.

The as synthesized samples were characterized by various techniques such as X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and N₂ absorption/desorption isotherms (BET). Their chemical composition was determined using the Inductively Coupled Plasma Emission Spectrometry (ICP). Catalytic testing experiments were performed in a fixed-bed reactor at atmospheric pressure and temperatures ranging from 500 to 850 °C and a feed gas mixture with a molar CH₄/CO₂ ratio of 1.5, simulating an ideal model biogas.

It was concluded that the Ni/LaAl catalyst exhibit higher values for methane conversion (X_{CH₄}), carbon dioxide conversion (X_{CO₂}) and hydrogen yield (Y_{H₂}) compared to the ones of the Ni/Al catalyst, for the entire temperature range under investigation, i.e., 550 to 850 °C. It was also evidenced that the presence of lanthanum oxide in the support ensures a quite stable H₂/CO molar ratio approaching unity (ideal for the produced syngas) even for low reaction temperatures.

1. INTRODUCTION

The first to theorize upon the impact of carbon dioxide (CO_2) on the earth's climate was the Swedish Nobel prize laureate Svante August Arrhenius in 1896. In its original form, Arrhenius' greenhouse law reads as follows: *if the quantity of carbonic acid [CO_2] increases in geometric progression, the augmentation of the temperature will increase nearly in arithmetic progression*. However, his ideas were initially met with criticism and fell into obscurity until around the 1950s when growing concern about mankind's increasing impact on the environment and refined analytical methods revitalized the issue of greenhouse gases (GHG's). Separate threads of research were pursued by isolated groups of scientists, although an increasing number of studies pointed towards a connection between global warming and anthropogenic emissions of greenhouse gases [1, 2]. Nevertheless, mainstream media and politicians largely ignored these results and only expressed concern over these findings much later. Indeed, it took until the late 1980's when the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) began to investigate the role of carbon dioxide and other emissions, with their interest leading to the establishment of the Intergovernmental Panel on Climate Change (IPCC). IPCC's findings are now becoming the very familiar horsemen of a planetary apocalypse, and have led to international agreements such as the Kyoto Protocol (1997) and its Doha Amendment (2012). In these agreements, industrialized nations have pledged to cut down their GHG emissions as it is "unequivocal" that Earth's climate is warming, leading to severe weather (storms, precipitation, and drought), melting and thawing of the ice caps and rising sea levels [3-6]. The vast majority of GHG's are related with the way we use energy, namely fossil fuels such as coal, natural gas and oil. Figure 1 shows the world's total primary energy supply by resource for the years 1993 and 2011; it also shows the prediction for the year 2020 [7]. The global strategy to reduce dependence on fossil resources is based on reducing energy consumption, by applying energy savings programs focused on energy demand reduction and energy efficiency in the transportation, industrial and domestic sectors, and by developing and promoting renewable energy systems (RESs), which include wind power, photovoltaic (PV) cells, concentrating solar power (CSP), hydroelectric plants and biomass/ bioenergy [8, 9].

One of the most interesting options for RES development is the use of biogas, as it presents a number of advantages in comparison to other systems, namely that: (a) its chemical energy can be converted into mechanical energy by controlled combustion processes in stationary engines, which then put in motion the generators to promote a direct conversion into electrical energy, (b) it can be used to co-generate thermal energy, generating hot water and steam with the engine's high temperatures, (c) it can be burned to generate heat energy in boilers, and (d) it can be applied as fuel to automotive and stationary engines [10-13]. Essentially, biogas is a mixture of different gases produced by the breakdown of organic matter (i.e., biomass) in the absence of oxygen. The main components of biogas are methane (55-75%) and carbon dioxide (24-44%), which are the principal greenhouse gases. It is worth noting that methane has approximately 21 times the greenhouse gas effect of carbon dioxide [14, 15]. Biogas is produced in landfills, in agricultural operations, and during the treatment of wastewater. Landfill gas is a particularly large source of biogas, producing 13.5 billion m^3 of methane per year; with researchers suggesting that biogas from landfills alone is the second largest source of anthropogenic methane emissions in the United States [16-18]. Figure 2 shows the number of biogas plants that were operational in Europe in 2013 [19].

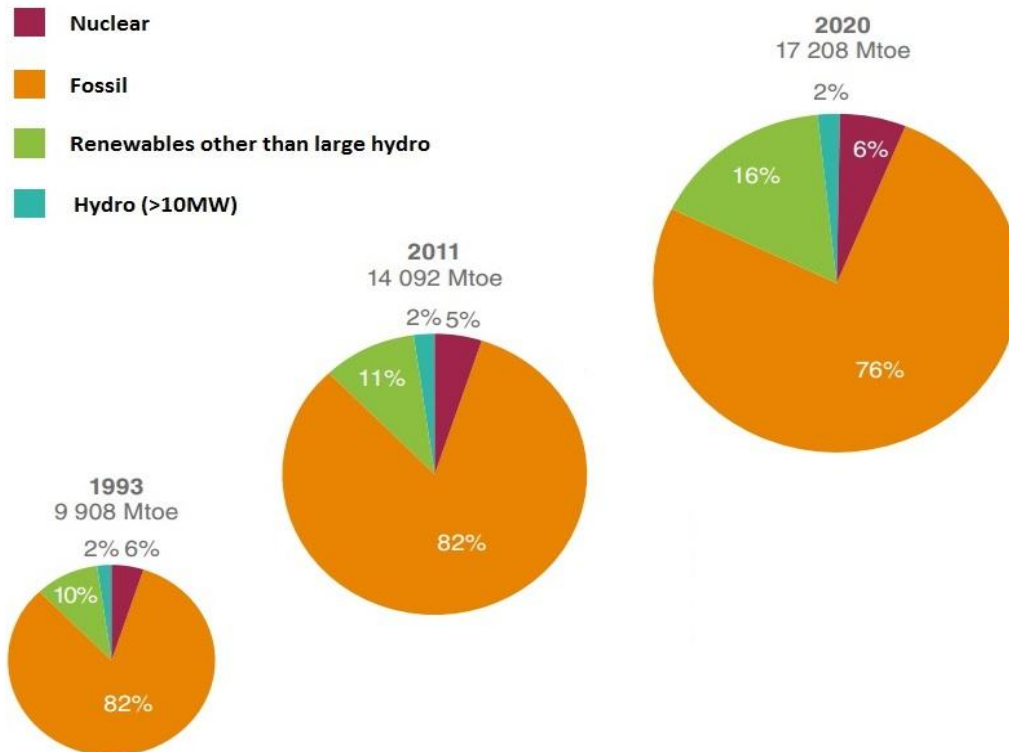


Figure 1. Total primary energy supply by resource [7]

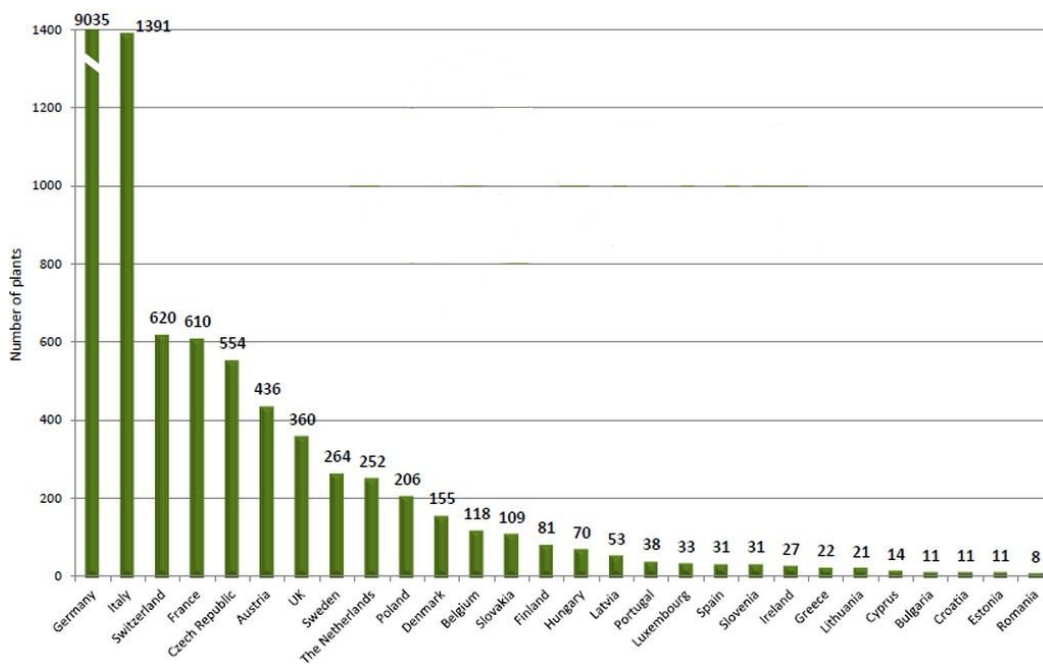


Figure 2. Operational biogas plants in Europe in 2013 [19]

One of the reasons why biogas mixtures are not more widely used for energy is because the high CO_2 content decreases the heating value and flame stability of the gas mixture. This leads to increased CO , NO_x , and unburned hydrocarbon emissions when the biogas is combusted in an engine, turbine, or boiler compared to pure CH_4 or natural gas. For these reasons biogas is often burned, or flared, and emitted to the atmosphere as CO_2 and H_2O , without extracting any of the latent chemical energy [20]. The CO_2 may be separated from the CH_4 to produce a pure CH_4 stream to use as a natural gas replacement or to produce compressed natural gas (CNG) or liquefied natural gas (LNG) that can be used as a transportation fuel. The separation of CO_2 from CH_4 is accomplished by membrane separation, pressure swing adsorption (PSA), or amine scrubbing. The methane is then compressed to above 3000 psi to produce CNG or further cooled until the CH_4 liquefies to produce LNG. Due to the high pressures and cryogenic temperatures needed to produce CNG and LNG, the processes are expensive and usually most suitable for large CH_4/CO_2 flows where economies of scale can be obtained [20, 21]. These options for biogas use are summarized in Figure 3. Flaring is the most common method to dispose of CH_4/CO_2 mixtures, but wastes the heating value of the CH_4 . Combustion of biogas in engines or turbines for electricity production, or in boilers for direct heating, are popular applications, but suffer from increased emissions due to the abundance of CO_2 in the biogas. Catalytic reforming is another option that has the potential to fully utilize the energy contained in the biogas, with nickel (Ni) based catalysts being extensively studied for the biogas dry reforming reaction. However, such catalysts suffer from fast deactivation by coking that can even lead to reactor blocking. It is thus desirable to learn more about their coking behavior, and their structural and catalytic stability.

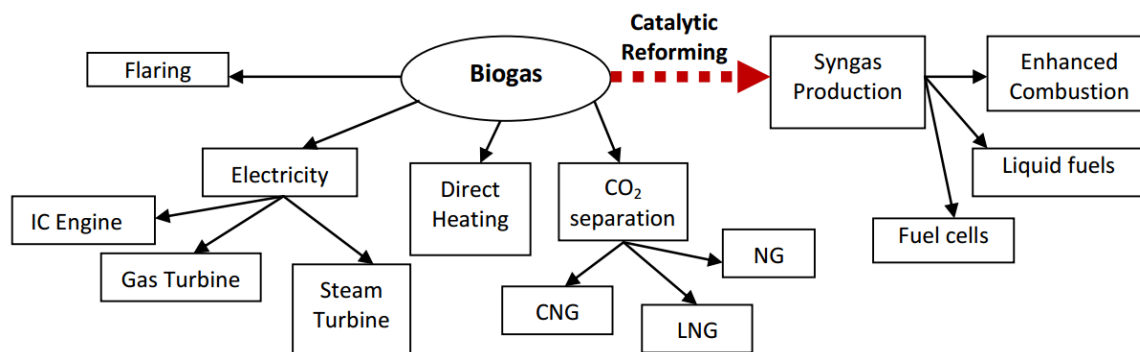


Figure 3. Summary of current technologies for CH_4/CO_2 utilization [21]

In this contribution, a comparative study of catalytic performance for nickel supported on un-promoted and promoted with La_2O_3 alumina catalysts is reported for the biogas dry reforming reaction. Catalysts were synthesized applying the wet impregnation method at a constant metal loading (8 wt. %) in order to investigate the effect of the reaction temperature on (i) methane and carbon dioxide conversion, (ii) hydrogen yield, (iii) H_2/CO molar ratio of the produced gas mixtures at the outlet of the reactor.

The as synthesized samples were characterized by various techniques such as X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and N_2 absorption/desorption isotherms (BET). Their chemical composition was determined using the Inductively Coupled Plasma Emission Spectrometry (ICP). Catalytic testing experiments were performed in a fixed-bed reactor at temperatures ranging from 500 to 850 °C and a feed gas mixture with a molar CH_4/CO_2 ratio of 1.5, simulating an ideal model biogas.

2.0 MATERIALS AND METHODS

2.1 Catalysts Preparation

The alumina support was purchased in pellet form from Akzo, while the lanthanum-alumina (containing 4 wt. % La_2O_3) was obtained from W. R. Grace (MI-386) in powder form. The physicochemical properties of the γ -alumina and lanthanum-alumina used in this study are presented in Table 1. The γ - Al_2O_3 support was crashed and sieved to 350-500 μm , while the LaAl support was first pelletized and then crashed and sieved to the same size. The as prepared supports were calcined at 800 $^\circ\text{C}$ for 4 h. The catalysts were prepared via the wet impregnation technique using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solutions with the proper concentration (0.17 M), in order to obtain final catalysts with Ni content of about 8 wt. %. The nickel nitrate for the catalyst preparation was obtained from Sigma Aldrich. All solutions for catalyst preparation throughout this study utilized distilled and de-ionized pure water generated by NANOpure Diamond UV unit (Barnstead International). The resulting slurries were evaporated using a rotary evaporator at 75 $^\circ\text{C}$ for 5 h and dried at 120 $^\circ\text{C}$ for 12 h followed by calcination at 800 $^\circ\text{C}$ for 4 h. The samples were labeled as Ni/Al and Ni/LaAl.

Table 1. Physicochemical properties of the γ -alumina and lanthanum-alumina used in the study

Property	Al	LaAl
Radius (R)	$1.58 \times 10^{-3} \text{ m}$	n/a
Mean pore diameter (α)	$7.8 \times 10^{-9} \text{ m}$	n/a
Surface area (S_{BET})	$281 \text{ m}^2 \text{ g}^{-1}$	$176 \text{ m}^2 \text{ g}^{-1}$
Bed density (ρ_{B})	$5.7 \times 10^5 \text{ g m}^{-3}$	n/a
Pore volume (V_{p})	0.65 ml g^{-1}	0.77 ml g^{-1}
Average length (L)	5.2 mm	n/a

Note: n/a = not available

2.2 Catalysts Characterization

The Specific Surface Area (SSA) of the catalytic samples were determined by the N_2 adsorption-desorption isotherms at -196 $^\circ\text{C}$ using the Nova 2200e (Quantachrome) flow apparatus, according to Brunauer-Emmett-Teller (BET) method at the relative pressure in the range of 0.05–0.30.

The total pore volume calculation was based on nitrogen volume at the highest relative pressure, whereas the average pore size diameter was determined by the Barrett-Joyner-Halenda (BJH) method. Prior to the measurements the samples were degassed at 350 $^\circ\text{C}$ for 5 h under vacuum.

The total metal loading (wt. %) of the final catalysts was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a Perkin-Elmer Optima 4300DV apparatus. The wavelengths selected were at 341.476, 227.022, and 231.604 nm. The selected conditions of the measurement were: Plasma flow: 15 L/min, Auxiliary flow: 0.2 L/min, Nebulize flow: 0.6 L/min, RF Power: 1300 watts, Plasma View: radial view, and Sample Flow Rate: 2 mL/min. The acid digestion procedure involved the weighting of each sample to the nearest 0.00001 g in a Teflon beaker and its transportation to a fume hood, where 1 ml of concentrated sulphuric acid was added. The mixture was then heated to dryness at low heat on a hot plate overnight. Afterwards, 2 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid were added to the beaker with the heating being terminated after 5-10 min, when the reaction of dissolution was completed. At this point, about 2 ml of de-ionized water

were added and the beaker was left to cool. The resulting solution was loaded in a 50 ml volumetric flask in order to make up an accurate fixed volume adding de-ionized water. Each sample was measured thrice, in order to check repeatability.

The catalysts' crystalline structure was determined by applying the X-ray diffraction (XRD) technique, using a ThermoAl diffractometer with Cu-K α radiation at 40 kV and 30 mA ($\lambda=1.54178$ nm). Diffractograms were recorded in the $2\theta=2-70^\circ$ range at a scanning rate of 0.04° over 1.2 min^{-1} . The diffraction pattern was identified by comparison with those of known structure in the JCPDS (Joint Committee of Powder Diffraction Standards) database. It should be noted that the XRD technique was used for both fresh and reduced samples.

Morphological examination of both fresh and used catalysts was done using Scanning Electron Microscopy (SEM) in a JEOL 6610LV. The elemental analysis, by means of Energy Dispersive Spectroscopy (EDS), was carried out using a large area (80 mm^2) silicon drift detector (X-Max 80 Oxford Instruments). Images, elements maps and spectra were acquired and analyzed with the AZtech Nanoanalysis software (Oxford Instruments).

2.3 Catalytic performance

The biogas reforming reaction was carried out at atmospheric pressure, in a fixed-bed reactor (Figure 4) at temperatures ranging from 500 to 850 °C. The total flow rate used was 100 ml min^{-1} , consisting of a gas mixture of CH₄/CO₂/He (30% v/v, 20% v/v and 50% v/v respectively), corresponding to a Weight Hourly Space Velocity (WHSV) of $120,000\text{ mL g}^{-1}\text{ h}^{-1}$. Thus, the feed gas mixture had a constant molar CH₄/CO₂ ratio of 1.5 simulating an ideal model biogas [22].

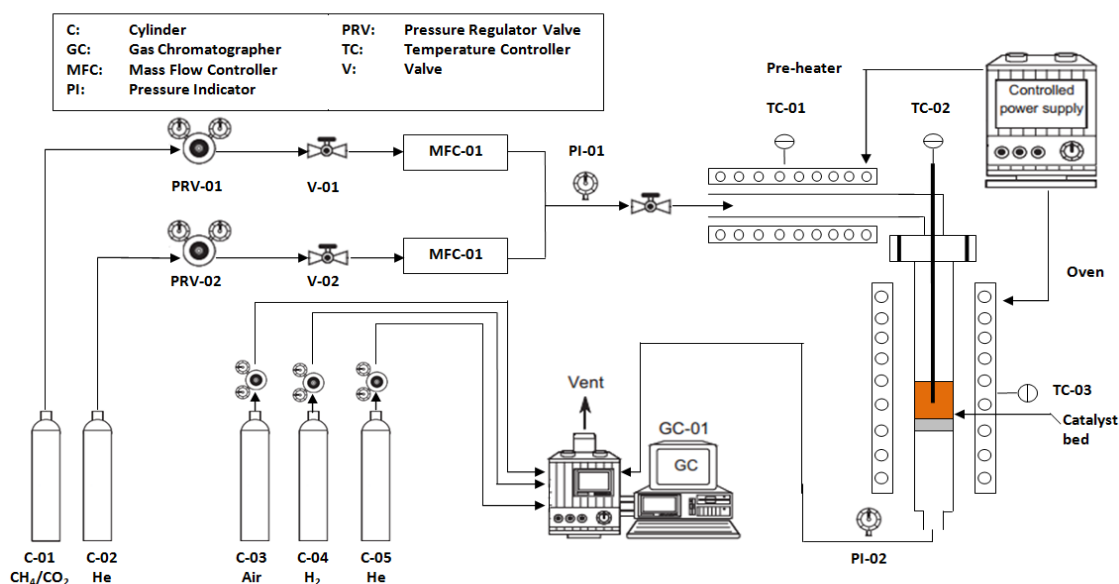


Figure 4. Schematic flow chart of experimental setup for activity test of catalysts towards biogas dry reforming

The amount of catalyst used in the catalytic bed was 50 mg. The reaction temperature was controlled by a thermocouple placed in the middle of the catalytic bed. The gaseous reaction products were analyzed on-line by gas chromatography in a CG-Agilent 7890A gas chromatograph with two columns in parallel;

HP-Plot-Q (19095-Q04, 30 m length, 0.530 mm I.D.) and HP-Molesieve (19095P-MSO, 30 m length, 0.530 mm I.D.), equipped with a TCD and FID detectors. Prior to performing any catalytic reaction measurement, catalysts were in situ activated by flowing pure hydrogen for 2 hours at 800 °C.

According to the analysis and metering system mentioned above, the conversion of CO₂ and CH₄ can be calculated as defined in Eqs. (1) and (2). Moreover, the selectivity of H₂, the yield of H₂ and the yield of CO can be calculated as defined in Eqs. (3)–(5), respectively:

$$X_{CH_4} (\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100 \quad (1)$$

$$X_{CO_2} (\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100 \quad (2)$$

$$S_{H_2} (\%) = \frac{F_{H_2}}{2(F_{CH_4,in} - F_{CH_4,out})} \times 100 \quad (3)$$

$$Y_{H_2} (\%) = \frac{F_{H_2}}{2F_{CH_4,in}} \times 100 \quad (4)$$

$$Y_{CO} (\%) = \frac{F_{CO}}{F_{CH_4,in} + F_{CO_2,in}} \times 100 \quad (5)$$

where $F_{i,in}$ or $F_{i,out}$ is the flow rate of each component in feed or effluent.

3.0 RESULTS AND DISCUSSION

3.1 Characterisation results

In Table 2 the physicochemical properties of all samples are presented. As can be observed, the specific surface area (SSA) for the supported nickel on Al₂O₃ catalyst was significantly lower than the one of the supporting material (γ-Al₂O₃, 195 m² g⁻¹, after calcination at 800 °C), whereas the pore volume (V_p) was not significantly altered. The lower surface area can be attributed to the fact that the internal surface area of the support pore system is probably progressively covered by nickel species adsorbed on alumina active sites forming a layer [23, 24]. It should also be noted that both catalyst samples (Ni/Al and Ni/LaAl) have comparable SSA's. The ICP results (metal loading) indicate that the desired metal level was achieved for both catalysts.

Figure 5 and 6 depict the XRD patterns of the Ni/Al and Ni/LaAl catalyst after calcination and after reduction. Characteristic peaks at 2θ= 35.2°, 47.2° and 67.6° (for the Ni/Al), and 2θ= 35.1°, 47.1°, 60.02° and 67.4° (for the Ni/LaAl) assigned to poorly crystalline γ-Al₂O₃ and peaks of the spinel nickel aluminate phase (NiAl₂O₄), indicated by the intensity of diffraction lines at 2θ=19°, 32°, 37°, 60.2° and 65.9° can be observed for both samples. It should be noted that an additional peak at 2θ=45° is observed

for the Ni/Al catalyst which can be attributed to either NiAl_2O_4 or NiO [25]. The formation of NiAl_2O_4 is caused by the reaction of NiO and Al_2O_3 due to the high calcination temperature, i.e., $T=800^\circ\text{C}$ [26]. The appearance of two small peaks at $2\theta=44^\circ$ and 51.2° on the reduced samples indicate the presence of metallic Ni^0 [27]. On the other hand, no diffraction peaks of the La_2O_3 phase were detected in either the calcinated or reduced Ni/LaAl samples (Figure 5), indicating either an amorphous structure or that La_2O_3 is highly dispersed in the $\gamma\text{-Al}_2\text{O}_3$ [28, 29].

Table 2. Characterization results of the calcined catalysts

Catalyst/ Support	SSA (m^2g^{-1})	V_p (ml g^{-1})	Metal loading (Ni, wt%)
Al	195	0.65	-
LaAl	n/a	0.70	-
8Ni/Al	158	0.58	7.14
8Ni/LaAl	159	n/a	7.79

Note: c = calcinated, r = reduced, u = used, n/a = not available

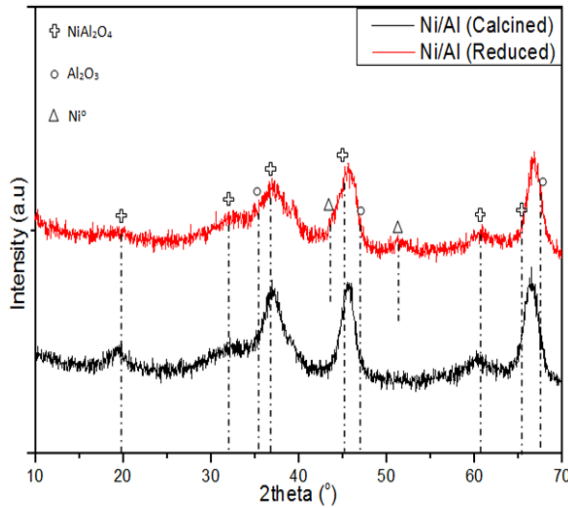


Figure 5. XRD patterns of calcined and reduced Ni/Al catalysts

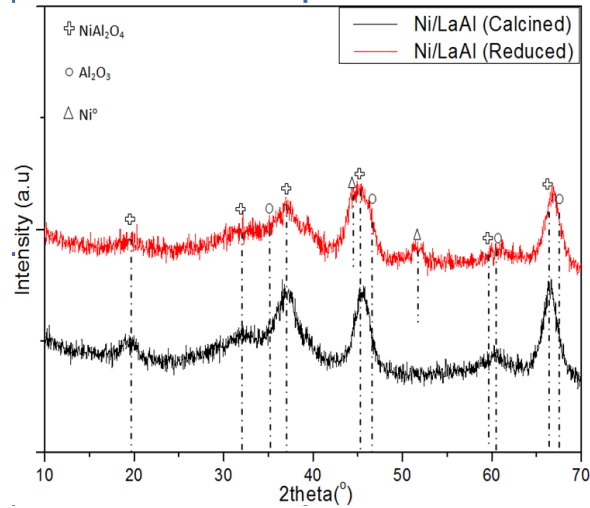


Figure 6. XRD patterns of calcined and reduced Ni/LaAl catalysts

Figure 7(a) shows the SEM images of the Ni/Al catalyst before use. As can be clearly observed the catalyst is of non uniform morphology and includes particles of different sizes. EDS Ni measurements are in broad agreement with the ICP results presented on Table 2, showing a metal loading of 8.2% (Fig. 7(b)). Figure 7(c) shows the SEM images of the same catalyst after use. It is obvious that the catalyst has undergone significant transformation in its morphology, while it is interesting to note the appearance of carbon in the form of filaments, confirmed also by the carbon mapping presented in Figure 7(d). Figure 8(a) shows the SEM images of the Ni/LaAl catalyst before use and Figure 8(b) the elemental analysis of the same sample.

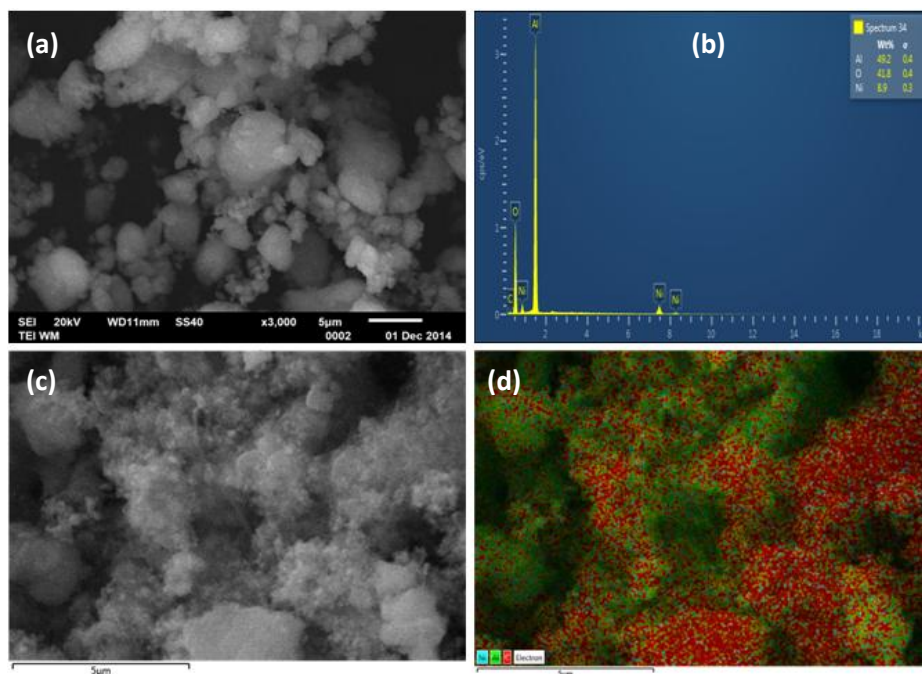


Figure 7. SEM images of the fresh Ni/Al catalyst: (a) fresh sample, (b) EDS of fresh sample, (c) used sample, (d) mapping of used sample

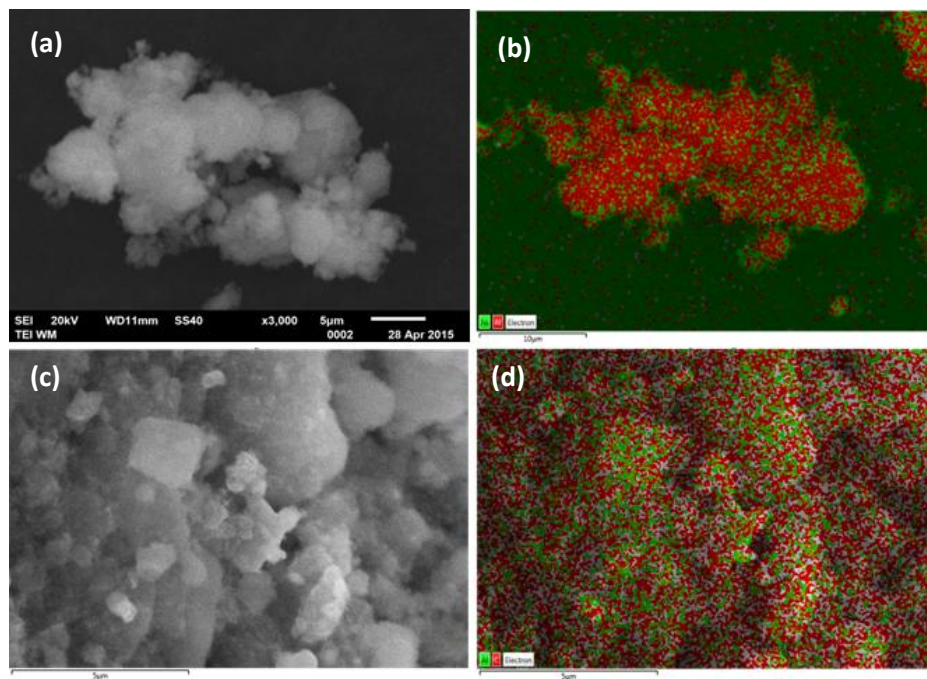


Figure 8. (a) SEM images of the used Ni/LaAl catalyst: (a) fresh sample, (b) mapping of fresh sample, (c) used sample, (d) mapping of used sample

The morphology of this catalyst is different to the morphology of the Ni/Al catalyst, with particles appearing more agglomerated; however, micro and nano particles are also present. The elemental analysis

suggests that Ni (green color) appears more likely to be found on the edges of the sample (Fig. 8(b)). Again, the SEM image of the used sample (Fig. 8(c)) reveals a transformation in the catalyst's morphology. A comparison of the carbon mapping of the two catalysts (Fig. 7(d) and Fig. 8(d)) shows that carbon is more dispersed on the Ni/LaAl sample, as opposed to appearing concentrated on specific areas for the Ni/Al sample.

3.2. Catalytic activity and selectivity

In Figure 8 the influence of the reaction temperature to the methane (X_{CH_4}) and carbon dioxide (X_{CO_2}) conversion (Fig. 8(a) and 8(b) respectively), to the hydrogen (Y_{H_2}) yield (Fig. 8(c)) and to the molar ratio H_2/CO (Fig. 8(d)) is shown.

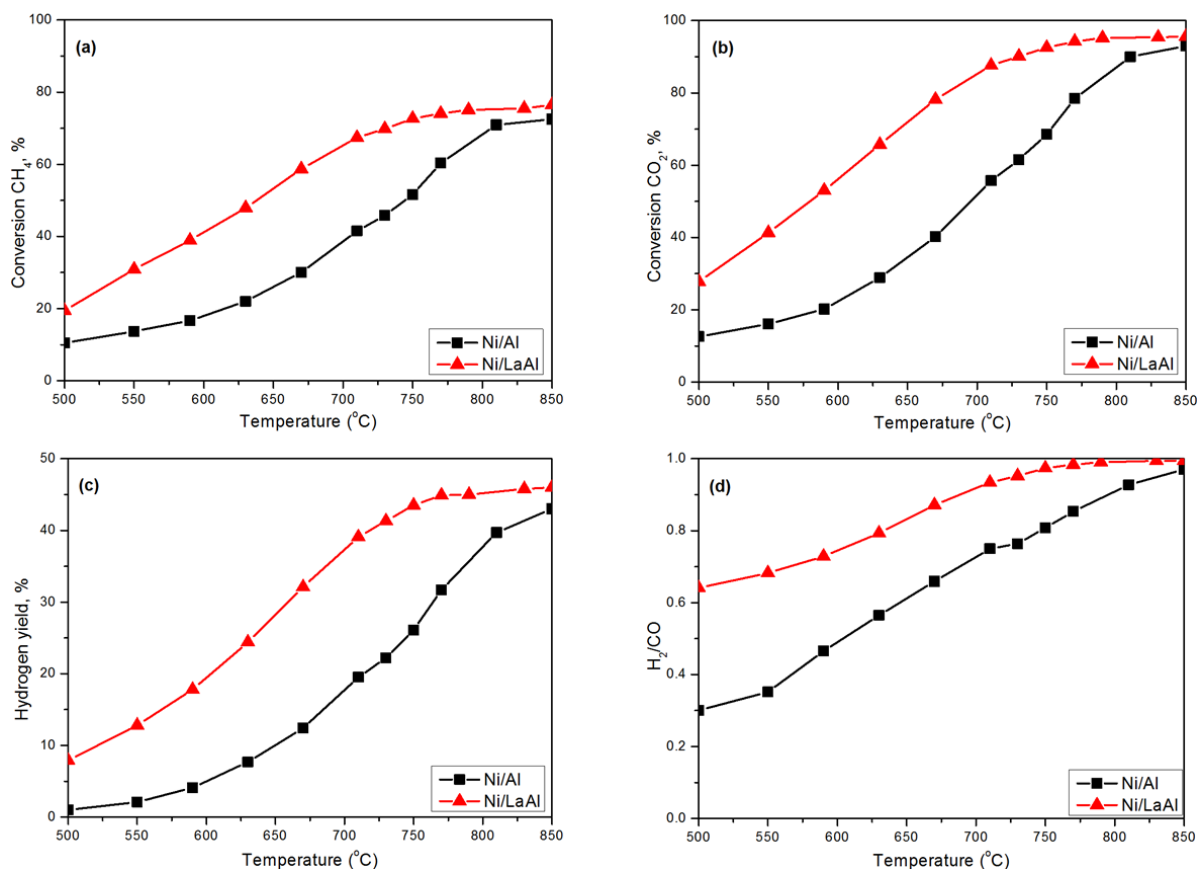


Figure 8. (a) Conversion of CH_4 , (b) Conversion of CO_2 , (c) Hydrogen yield, (d) Molar ratio H_2/CO

As is obvious from the figures, catalysts' activity, as well as hydrogen production, increased with increasing temperature, which is in accordance with the strong endothermic character ($\Delta H = 247.3$ kJ/mol) of the dry reforming reaction [30]. It can be also observed that the Ni/LaAl catalyst exhibits significantly higher values for the X_{CH_4} , X_{CO_2} and Y_{H_2} compared to the ones of the Ni/Al catalyst for the entire temperature range. At CH_4/CO_2 ratio being equal to 1.5, CO_2 gas acts as a limiting reactant and is not able to convert CH_4 completely. Therefore, the high conversion of CH_4 at higher temperatures can be

ascribed to the methane decomposition reaction ($\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$), as the predominant reaction to form hydrogen and carbon [15,24].

In addition, thermodynamics predict that for CH_4/CO_2 ratios > 1 , the amount of H_2 produced enhances within the temperature under investigation. This is because CO_2 is the limiting reactant and the Reverse Water Gas Shift (RWGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) cannot simultaneously improve along with the dry reforming reaction, as much as when the CH_4/CO_2 is lower than unit. As the RWGS is not being much involved whenever the CH_4/CO_2 ratio is lower, the DMR reaction ($\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$) proceeds better and faster, suppressing the methane decomposition reaction, which causes the lower amount of H_2 production. On the other hand, higher temperatures favour CO production since all the reactions involved in CO production are endothermic. Higher experimental CO and H_2 yields than their equilibrium ones, along with high methane conversions, could provide evidence for significant ability of the catalyst in dissociation of CO_2 followed by CO and O production, as well as improving CO_2 reforming of methane.

As it can be observed in Figure 8(d), the H_2/CO molar ratio increases with increasing temperature approaching the value of 1, for $T = 850^\circ\text{C}$ for both catalysts. However, it is obvious that this value is considerably higher for the Ni/LaAl sample for the whole temperature range (with values ranging from 0.65 to 1.0 as opposed to 0.3 to 1 for the Ni/Al sample), revealing an improved catalytic performance. Thus, it seems safe to assume that the presence of lanthana in the support ensures a high and quite stable H_2/CO molar ratio (almost ideal for the produced syngas) even for low reaction temperatures.

The promotional effect of lanthana to the catalytic activity and stability of the Ni/LaAl catalyst can be attributed to the basic nature of La_2O_3 , the intimate interaction between Ni and the support, and rapid decomposition/ dissociation of CH_4 and CO_2 , which results in preventing coke formation. Moreover, it has been reported that the addition of La_2O_3 to Ni/D- Al_2O_3 catalysts can increase the dispersion of Ni particles on the supports and reduce the agglomeration of Ni particles during the reforming reaction [31]. Furthermore, it has also been reported that La_2O_3 can adsorb and react with CO_2 to form $\text{La}_2\text{O}_2\text{CO}_3$ species on the surface of catalyst which can speed up the conversion of surface CH_x species ($x = 0-3$) [32]. Verykios and co-workers [33, 34] proposed that the collaboration between nickel and lanthanum species produces a unique type of collegial active sites at the Ni- La_2O_3 interface that boosts the activity and stability of the catalyst. Martinez et al. [35] reported that addition of La within a certain bound can increase the Ni dispersion in catalyst which in turn improves the conversion level and enhances the catalyst stability.

4. CONCLUSIONS

It was concluded that the Ni/LaAl catalyst exhibit higher values for methane conversion (X_{CH_4}), carbon dioxide conversion (X_{CO_2}) and hydrogen yield (Y_{H_2}) compared to the ones of the Ni/Al catalyst for the entire temperature range under investigation, i.e., 550 to 850°C . It was also evidenced that the presence of lanthanum oxide in the support ensures a quite stable H_2/CO molar ratio approaching unity (ideal for the produced syngas) even for low reaction temperatures. The promotional effect of lanthana to the catalytic activity and stability of the Ni/LaAl catalyst can be attributed to the basic nature of La_2O_3 , the intimate interaction between Ni and the support and the rapid decomposition/ dissociation of CH_4 and CO_2 .

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