Synthesis gas production via the biogas reforming reaction over Ni/MgO-Al_2O_3 and Ni/CaO-Al_2O_3 catalysts

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Aim

- Production of syngas from biogas via the dry reforming reaction

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  - Catalytic performance
  - Reaction metrics

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Introduction

Introduction

- Biogas refers to a gas produced by anaerobic digestion or fermentation of any biodegradable organic matter, including municipal solid waste, sewage sludge, agricultural wastes, animal dung, and energy crops
- Main components of biogas are methane (55-75%) and carbon dioxide (24-44%)

- Biogas advantages:
  - 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
  - it can be used to co-generate thermal energy, generating hot water and steam with the engine's high temperatures
  - it can be burned to generate heat energy in boilers
  - it can be applied as fuel to automotive and stationary engines

Biogas dry reforming

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (\Delta H = 247.3\ kJ/mol)$$

(1) Dry reforming, DR

$$n(CO + H_2O \rightleftharpoons CO_2 + H_2) \qquad (\Delta H = -41.0\ kJ/mol)$$

(2) Water gas shift (WGS)

$$n(CO + 3H_2 \rightleftharpoons CH_4 + H_2O) \qquad (\Delta H = -208.2\ kJ/mol)$$

(3) Methanation (MTH)

$$C_nH_mO_k \rightarrow (n-k)C + \left(\frac{m}{2}\right)H_2 + kCO$$

(4) Decomposition (D)

$$2CO \rightleftharpoons CO_2 + C \qquad (\Delta H = -171.5\ kJ/mol)$$

(5) Boudouard (Boud)

$$C + H_2O \rightleftharpoons CO + H_2 \qquad (\Delta H = 139.0\ kJ/mol)$$

(6) Coke gasification (GS)

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad (\Delta H = -110.5\ kJ/mol)$$

(7) Coke oxidation (CO)

$$C + O_2 \rightarrow CO_2 \qquad (\Delta H = -395.6\ kJ/mol)$$

(8) Coke oxidation (CO)

Catalysts – Supports (1/2)

- Noble (Rh, Ru, Pd and Pt) and non-noble metal (Ni, Co and Fe) based catalysts
- Noble metal catalysts have superior coking resistance, higher stability and activity especially for higher temperature applications, but cannot be applied on an industrial scale due to their high cost
- Ni appears to be the most suitable choice for both technical and economic reasons

- Supports play an important role in catalytic activity due to their chemical effect and their interaction with the active phase
- Supports with large surface area and usually small or medium pores, such as alumina, normally exhibit additional mass transfer limitation issues of the reactant

Catalysts – Supports (2/2)

- Nickel-based on alumina catalysts are reported to be deactivated due to their coking and sintering problems

- To improve the catalytic performance of the nickel/alumina catalysts several parameters are modified, such as the improving characteristics of the support by introducing structural or surface promoters, or differentiating the active metal loading and the catalyst's preparation technique

Contribution

- Comparative study of catalytic performance for nickel (Ni) supported on un-promoted and promoted with 6.0 wt% MgO or CaO alumina catalysts

- Ni loading 8.0 wt. %

- Effect of temperature on
    - methane and carbon dioxide conversion
    - hydrogen yield
    - H_2/CO molar ratio of the produced gas mixtures at the outlet of the reactor

Experimental

Preparation

- The calcium-alumina and magnesium-alumina supports were obtained by impregnating the γ-alumina (Akzo, 350 – 500 μm, S_{BET} = 195 m^2g^{-1}) with an aqueous solution of $Ca(NO_3)_2$ $6H_2O$ and $Mg(NO_3)_2$ $4H_2O$ with appropriate concentration at room temperature

- Supported nickel catalysts were prepared following the wet impregnation method and by using $Ni(NO_3)_2$ $6H_2O$ aqueous solutions with the proper concentration, in order to obtain a final catalyst with Ni content of about 8 wt. %

- All the catalyst samples were evaporated by using a rotary evaporator at 75 °C for 5 hr and dried at 120 °C for 12 hr followed by calcination at 800 °C for 4 hr

- The samples were labeled as Ni/Al, Ni/CaAl and Ni/MgAl

Characterization

- **Specific Surface Areas (SSA)** was measured by N_2 adsorption–desorption isotherms at -196°C, according to Brunauer-Emmett-Teller (BET) method

- The total metal loading (wt%) was determined by **Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES**)

- The crystalline structure of fresh and reduced catalysts was determined by applying the **X-ray diffraction (XRD)** technique (40 kV, 30 mA with Cu K_α radiation, λ=1.54178 nm, diffractograms were recorded in the 2θ=2-70° range at a scanning rate of 0.04° over 1.2 min-^{1})

- Morphological examination of both fresh and used catalysts was done using **Scanning Electron Microscopy (SEM)**

- The elemental analysis was done by **Energy Dispersive Spectroscopy (EDS)**

- **Images, elements maps and spectra** were acquired and analyzed with the AZtech Nanoanalysis software (Oxford Instruments)

Experimental setup

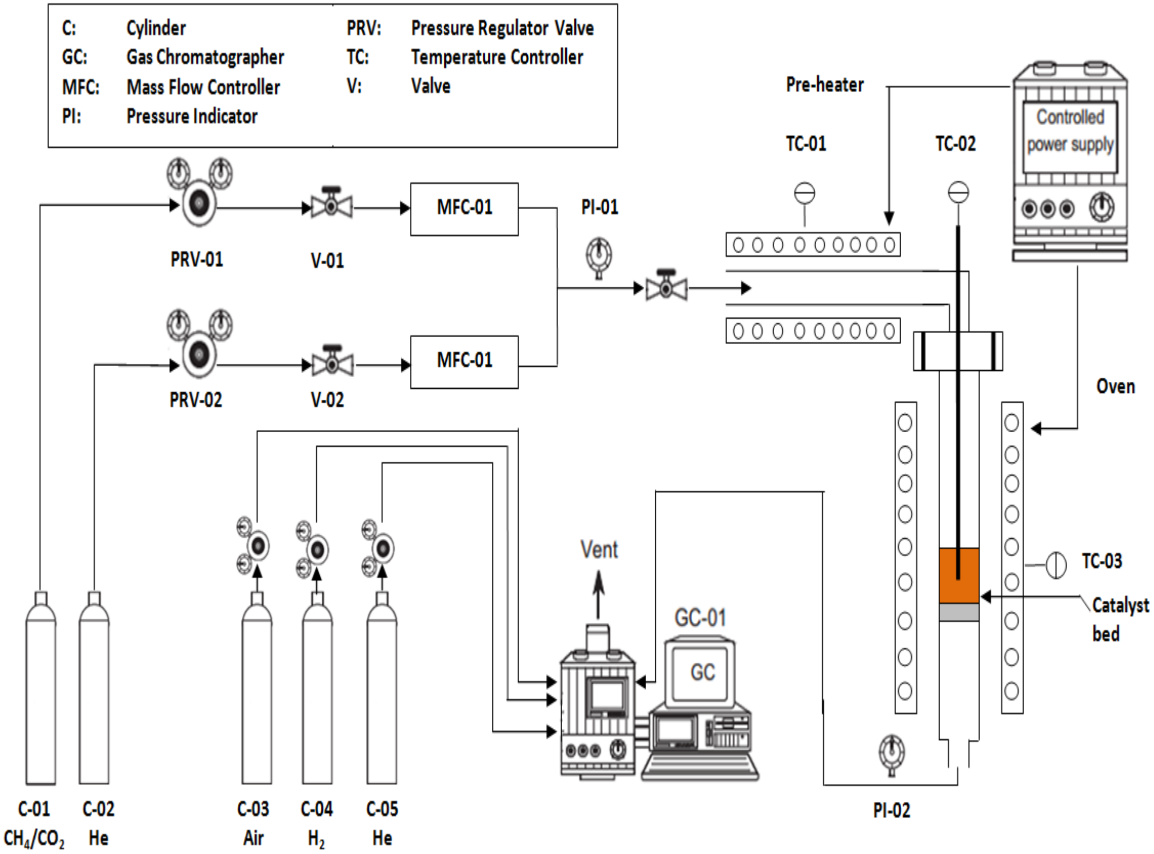


Figure 1. Schematic flow chart of experimental setup for activity test of catalysts

- Fixed-bed reactor

- Temperatures from 500 to 850°C

- Total flow rate = 100 ml min^{-1}

- Gas mixture of $CH_4/CO_2/He$ (30% v/v, 20% v/v and 50% v/v respectively)

- Weight Hourly Space Velocity (WHSV) = 120,000 mL g^{-1} h^{-1}

- Molar CH_4/CO_2 ratio = 1.5

- Amountof catalyst = 50 mg

Reaction metrics

- Conversion of CO_2 and CH_4 can be calculated as defined in Eqs. (1) and (2)
- Selectivity of H_2, the yield of H_2 and the yield of CO can be calculated as defined in Eqs. (3)–(5), respectively

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

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

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

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

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

Results & Discussion

Characterization results (1/5)

Table 1. Physicochemical properties of all samples

Sample	SSA m²/g	Vp ml/g	ICP (wt. %)
Al (untreated)	281	-	n/a
Al (calcined)	195	0.65	n/a
MgO-Al (calcined)	186	0.59	5.68 Mg
CaO-Al (calcined)	181	0.57	6.37 Ca
Ni/Al (calcined)	158	0.57	7.14 Ni
Ni/MgO-Al (calcined)	141	0.52	7.22 Ni
Ni/ CaO-Al (Calcined)	137	0.51	7.37 Ni

- Calcination to 800 °C has significantly decreased the SSA of the Al_2O_3 support from 281 m^2g^{-1} to 195 m^2g^{-1}

-Further reduction of the SSA occurred with the introduction of Ni on the supporting material, whereas the pore volume (Vp) was not significantly altered

- Lower surface area due to the fact that the internal surface area of the support pore system is progressively covered by nickel species adsorbed on alumina active sites forming a layer

- The same reduction is observed with the introduction of MgO and CaO on the alumina support and again with the introduction of Ni

-Pore volume (Vp) was not significantly altered

-The ICP results show that the desired metal level was achieved for both catalysts

Characterization results (2/5)

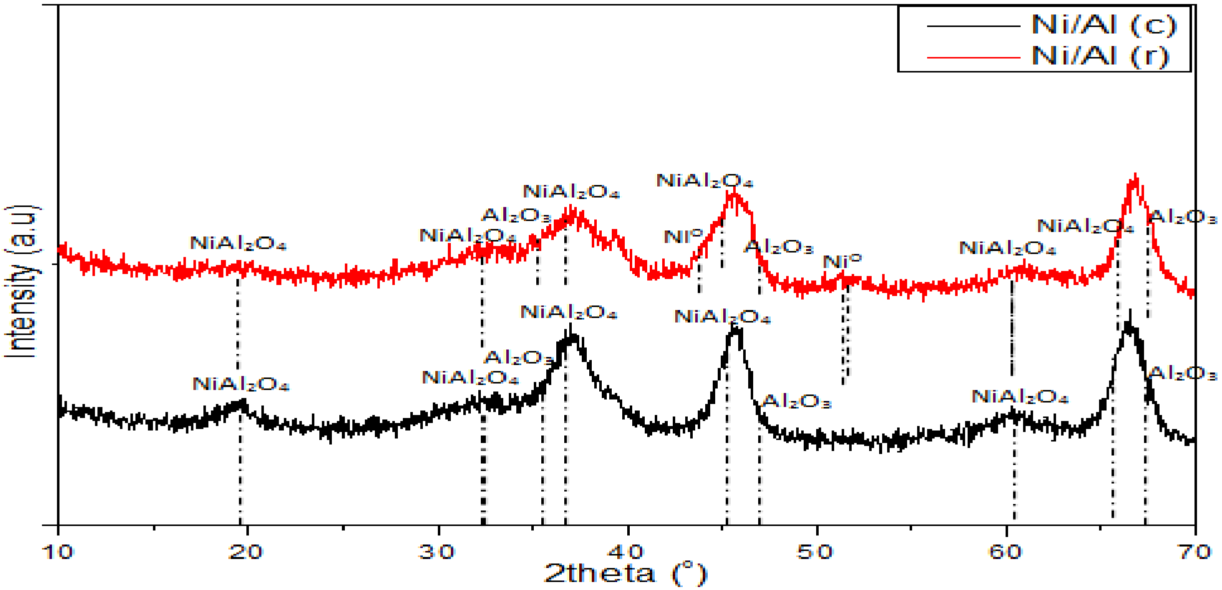


Figure 2. XRD patterns of calcined and reduced Ni/Al catalyst

Diffractograms

- 2θ = 35.2°, 47.2° and 67.6° (γ-Al_2O_3)
- 2θ=19°, 32°, 37°, 45°, 60.2° and 65.9° (nickel aluminate)
- NiO not detected (expected at 2θ=43.5° and 63.1°)

Differences between calcined & reduced

- Decreasing intensities of Al_2O_3 and $NiAl_2O_4$ peaks
- Appearance of small peaks due to the presence of metallic nickel (Ni°) at 2θ=44° and 51.2°

Characterization results (3/5)

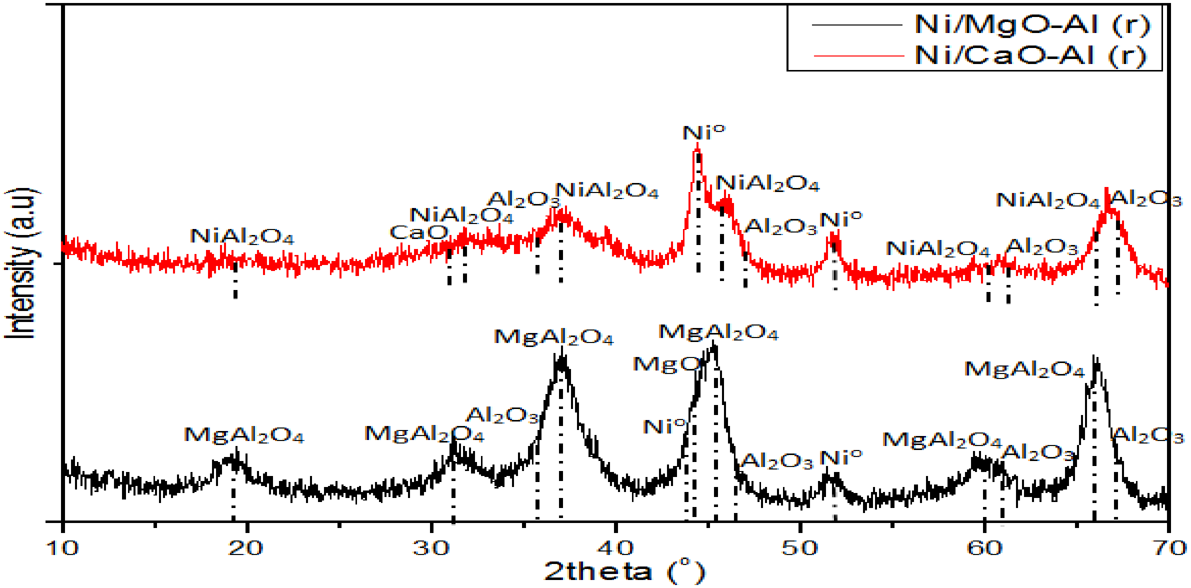


Figure 3. XRD patterns of the reduced Ni/MgO-Al and Ni/CaO-Al catalysts

- For the Ni/MgO-Al sample, characteristic peaks at 2θ= 35.7°, 38.6°, 46.9°, 62.1°, and 67.3° corresponding to γ-Al_2O_3
MgO appears at the diffraction line 2θ= 44.7°, while peaks of the spinel magnesium aluminate phase ($MgAl_2O_4$) at 2θ= 19.2°, 31.5°, 37.1°, 45.3°, 60.0°, and 66.1°.
- For the Ni/CaO-Al sample, peaks assigned to the γ-alumina appear at 2θ= 37.9°, 46.6°, 61.6°, 66.8°, and 68.5°, CaO at 2θ= 31.0° and $NiAl_2O_4$ at 2θ= 19.1°, 31.4°, 37.0°, 45.0°, 60.0°, and 65.9°
- The presence of metallic Ni^o was observed for both catalysts at 2θ=44.4° and 51.5°.
- Size of the peaks of metallic Ni^o are Ni/Al<Ni/MgO-Al<Ni/CaO-Al.

Characterization results (4/5)

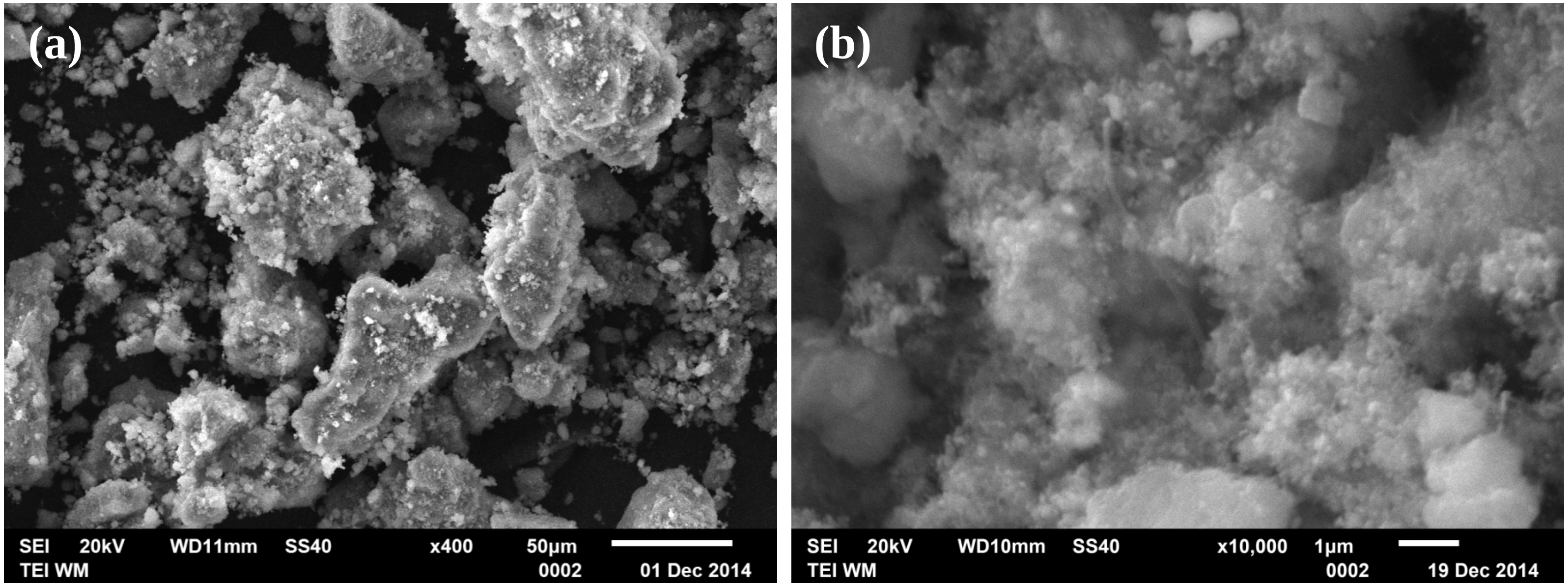
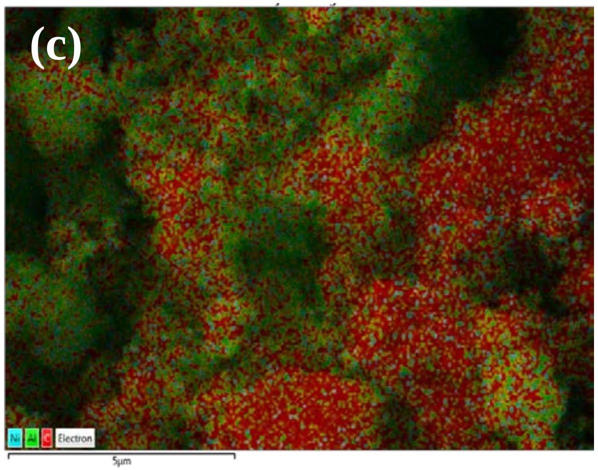


Figure 4. SEM images of the Ni/Al catalyst (a) fresh catalyst, (b) used catalyst, (c) carbon mapping of the used catalyst



Fresh

Non uniform morphology, includes large ensembles, as well as, micro and nano particles (nano particles = NiO or Ni^o, larger particles = alumina)

Used

- Some of the catalyst particles have cracked and fragmented into smaller particles
- Carbon filaments are observed surrounding the catalyst surfaces and partially covering the surface of the reacted catalyst

Characterization results (5/5)

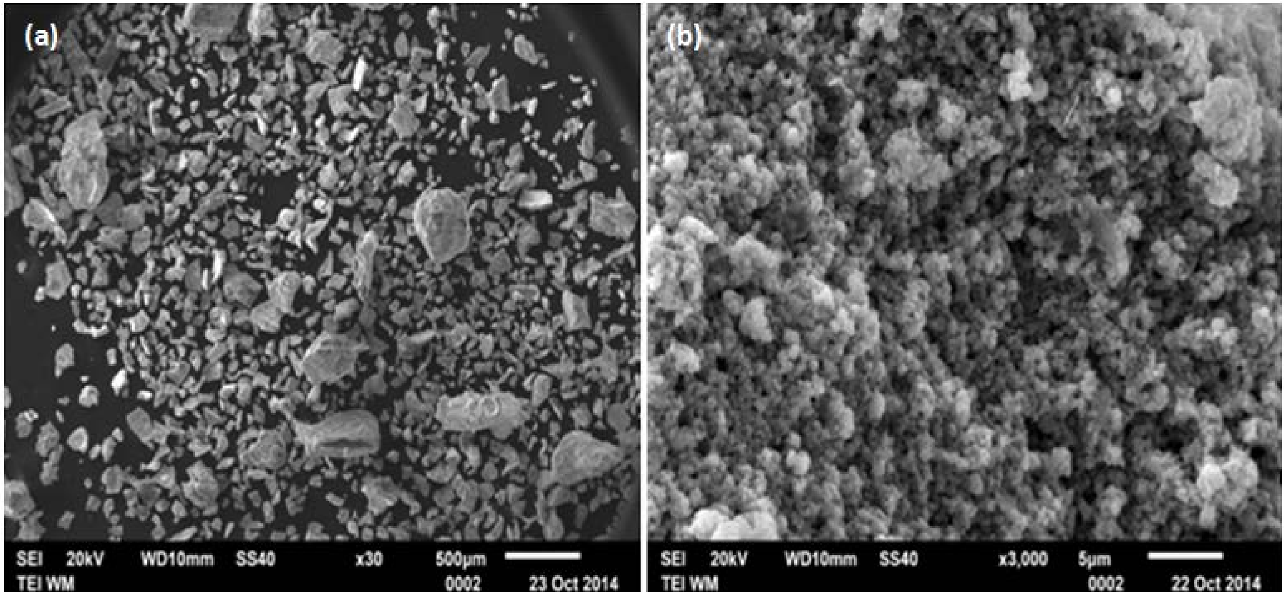


Figure 5. SEM images of fresh Ni/CaO-Al catalyst: (a) x30 magnification, (b) x3000 magnification

The catalyst comprises of much smaller particles than the Ni/Al catalyst, at sizes that can be measured in nm, indicating a better dispersion of the NiO and Ni° particles

Catalytic activity and selectivity (1/3)

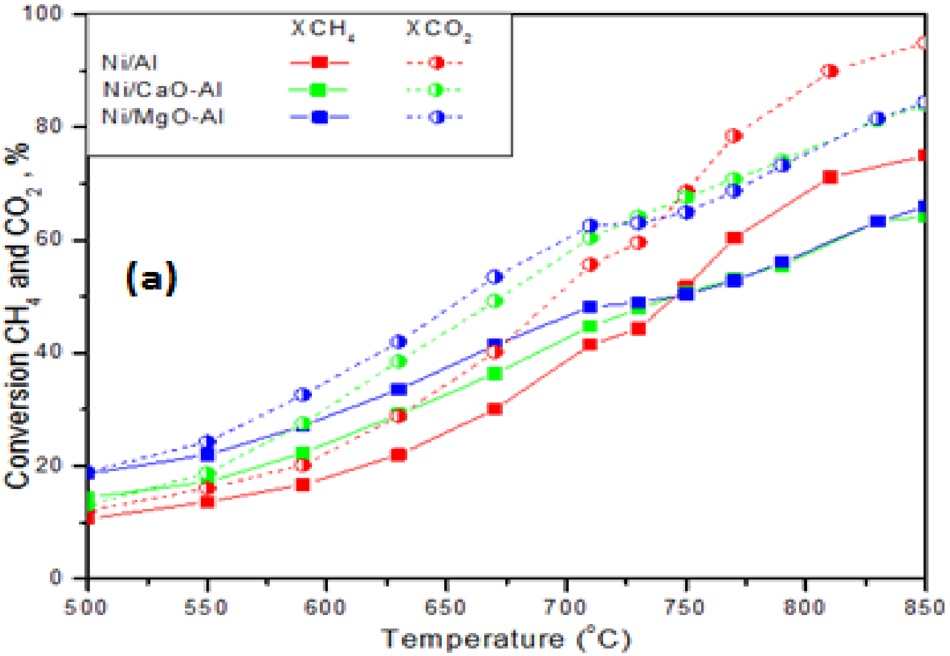


Figure 6.
Conversion of CH_4 and CO_2

- Catalysts' activity increased with increasing temperature, which is in accordance with the strong endothermic character of the dry reforming reaction
- Ni/CaO-Al and Ni/MgO-Al catalysts exhibit higher values for the X_{CH4}, X_{CO2} compared to the ones of the Ni/Al catalyst for temperature ranging between 550 to 750°C, while the opposite is evidenced for T>750°C
- 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
- The high conversion of CH_4 at higher temperatures can be ascribed to the methane decomposition reaction ($CH_4 \leftrightarrow C + 2H_2$), as the predominant reaction to form hydrogen and carbon

Catalytic activity and selectivity (2/3)

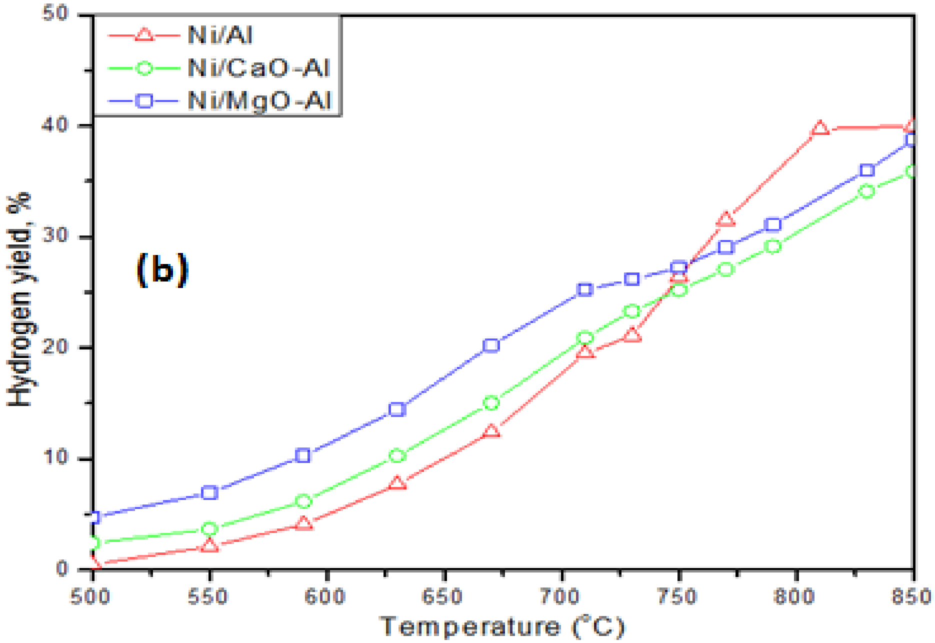


Figure 7.
Hydrogen yield

- For CH_4/CO_2 ratios > 1, the amount of H_2 produced enhances within the investigated temperature, as CO_2 is the limiting reactant and the Reverse Water Gas Shift (RWGS) reaction 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 CH_4/CO_2 ratio is lower, the DMR reaction proceeds better and faster suppressing the methane decomposition reaction

Catalytic activity and selectivity (3/3)

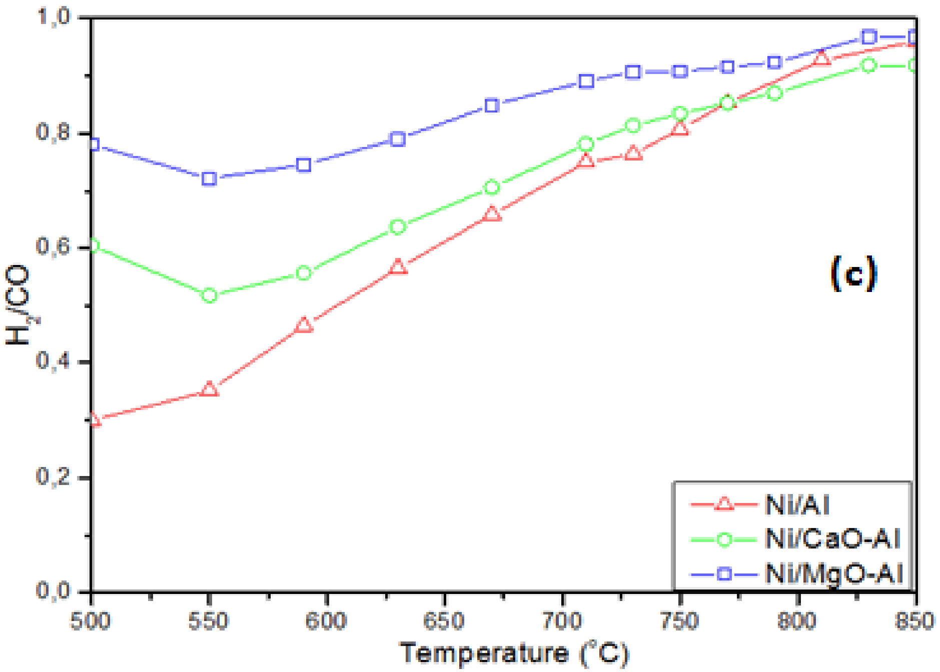


Figure 8.
Conversion of CH_4 and CO_2

- The H_2/CO molar ratio increases with increasing temperature approaching the value of 1, for T = 850 °C for all the catalysts
- Its value remains higher for the catalysts supported on modified with MgO or CaO alumina for the whole temperature range, revealing an improved catalytic performance

Conclusions

- The promotional effect of magnesium and calcium oxide to the catalytic activity and stability of the Ni/MgO-Al and Ni/CaO-Al catalyst can be attributed to the basic nature of MgO and CaO, the intimate interaction between Ni and the support, and rapid decomposition/ dissociation of CH_4 and CO_2, which results in preventing coke formation
- MgO and CaO can release oxygen to oxidize the carbon formed on the catalyst surface
- The Ni/MgO-Al_2O_3 and Ni/CaO-Al_2O_3 catalysts exhibit higher values for methane conversion (X_{CH4}), carbon dioxide conversion (X_{CO2}), hydrogen yield (Y_{H2}) compared to the ones of the Ni/Al catalyst for temperature ranging between 550 to 750°C, while the opposite is evidenced for T>750°C
- The presence of magnesium or calcium oxide in the support ensures a quite stable H_2/CO molar ratio approaching to unity (ideal for the produced syngas) even for low reaction temperatures

Thank you

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