Effect of La_2O_3 addition on Ni/Al_2O_3 catalysts to produce H_2 from glycerol

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Aim

- Production of hydrogen from glycerol via the steam reforming reaction

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Introduction

Introduction

- Fossil based energy = socio-economic development **BUT** anxiety over limited nature of the resources, issues of accessibility and affordability, effects of climate change, etc.

- Amongst RES, biomass attracts attention, especially in the field of biofuels, as the only realistic alternative to petro-oil

- Biodiesel – high production cost, production of glycerol (approximately 10% of biodiesel yields)

- Glycerol – over 2000 industrial uses (as additive in food, tobacco and pharmaceuticals)

- Glycerol – hydrogen production

Glycerol steam reforming

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (1)$$

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (4)$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad (5)$$

$$2CO \rightarrow CO_2 + C \qquad (6)$$

$$CH_4 \rightarrow 2H_2 + C \qquad (7)$$

$$CO + H_2 \rightarrow H_2O + C \qquad (8)$$

$$C_3H_8O_3 \rightarrow H_2 + 3H_2O + 3C \qquad (9)$$

Catalysts - Supports

Catalyst – Key role in reaction pathway & product distribution

- Co, Cu, Ir, Pd, Pt, Rh, Ru, Ni, Ni-Sn, Ni-Co, Ni-Cu, Ni-Pt, Ni-Ru
  - Ni – most investigated (due to current widespread use in petroleum and natural gas industries + considerable intrinsic activity)
  - Suffer from deactivation due to carbon formation and particle sinterization

Support – affects the selectivity of catalysts

- ZrO_2, TiO_2, MgO, CeO_2, SiO_2, Al_2O_3 (and additions of ZrO_2, MgO, CeO_2 on Alumina)

Contribution

- Comparative study of catalytic performance for nickel (Ni) supported on un-promoted and promoted with La_2O_3 alumina catalysts
- Catalysts were synthesized applying the wet impregnation method at a constant metal loading (8 wt. %)
- The synthesized samples, at their calcined or/and reduced form, were characterized by XRD, BET, ICP, SEM, EDS, carbon analysis
- The performance of the catalysts was studied in order to investigate the effect of the reaction temperature on:
  - Glycerol total conversion
  - Glycerol conversion to gaseous products
  - Hydrogen selectivity and yield
  - Selectivity of gaseous products
  - Selectivity of liquid products

Experimental

Preparation

Supports

- Alumina support - Akzo
- Lanthanum-alumina (4 wt. % La_2O_3) - W.R. Grace (MI-386)
- Support – 350-500 μm, calcinated at 800 °C for 4 h

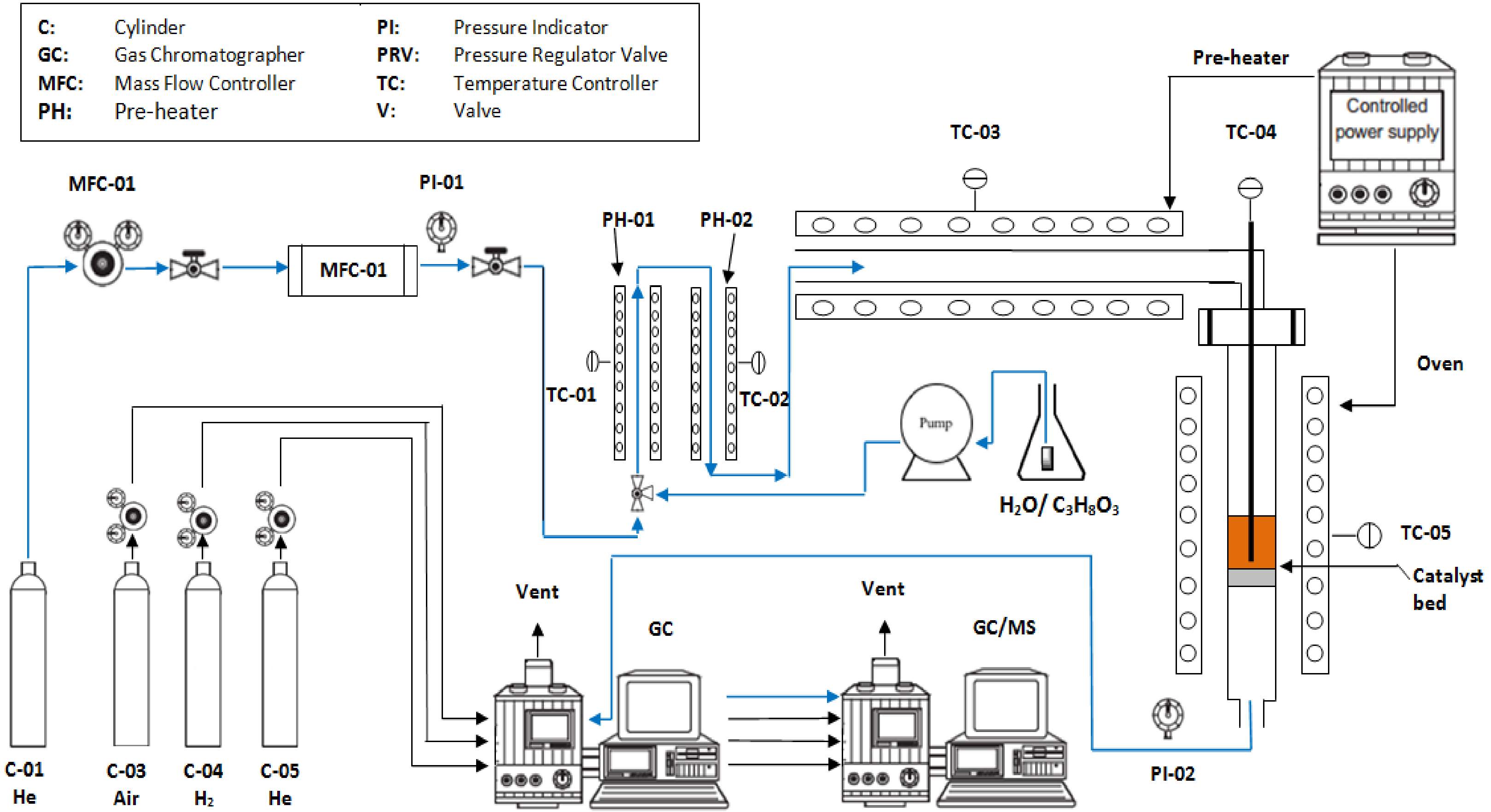
Catalysts

- Catalysts prepared by wet impregnation technique
- $Ni(NO_3)_2$ $6H_2O$ aqueous solutions (0.17M) - Sigma Aldrich
- Ni content 8 wt. %
- Slurries evaporated using a rotary evaporator at 75 °C for 5 h
- Dried at 120 °C for 12 h
- Calcined at 800 °C for 4 h
- Labeled as Ni/Al and Ni/LaAl

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)
- The **percentile concentration of carbon** in the used catalysts was measured by quantitative infrared spectroscopy performed with a Leco CHN-200 analyser, using 0.1 g of each sample

Experimental setup



C:	Cylinder	**PI:**	Pressure Indicator
GC:	Gas Chromatographer	**PRV:**	Pressure Regulator Valve
MFC:	Mass Flow Controller	**TC:**	Temperature Controller
PH:	Pre-heater	**V:**	Valve

Figure 1. Schematic flow chart of experimental setup for activity test of catalysts towards glycerol steam reforming

Reaction metrics

- Performance of the catalysts in the gas phase is reported in terms of H_2 yield, H_2, CO, CH_4 and CO_2 selectivity, glycerol conversion into gaseous products, and total glycerol conversion (global conversion)
- Performance of the catalysts in the liquid phase is reported in terms of acetol ($C_3H_6O_2$), acetone [$(CH_3)_2CO$], allyl alcohol (CH_2=$CHCH_2OH$), acetaldehyde (C_2H_4O) and acetic acid (C_2H_4O) selectivity

$$\%glycerol\ conversion_{(global\ conversion)} = \left(\frac{Glycerol_{in} - Glycerol_{out}}{Glycerol_{in}}\right)\times 100$$

$$\%glycerol\ conversion_{(gaseous\ \ products)} = \left(\frac{C\ atoms\ \ in\ the\ gas\ \ products}{total\ C\ atoms\ \ in\ the\ \ feedstock}\right)\times 100$$

$$H_2\ \ yield = \frac{H_2\ moles\ \ produced}{moles\ of\ \ glycerol\ in\ the\ \ feedstock}$$

$$\%H_2\ \ selectivity = \left(\frac{H_2\ moles\ \ produced}{C\ atoms\ \ produced\ in\ the\ gas\ \ phase}\right)\times\left(\frac{1}{RR}\right)\times 100$$

where, RR is the reforming ratio (7/3), defined as the ratio of moles of H_2 to CO_2 formed

$$\%\ \ selectivity\ of\ i = \left(\frac{C\ atoms\ in\ species\ i}{C\ atoms\ \ produced\ in\ the\ gas\ \ phase}\right)\times 100$$

where, species *i* refers to CO, CO_2 and CH_4

$$\%\ \ selectivity\ of\ i' = \left(\frac{C\ atoms\ in\ species\ i'}{C\ atoms\ \ produced\ in\ the\ liquid\ \ phase}\right)\times 100$$

where, species *i* refers to acetol, acetone, allyl alcohol, acetaldehyde and acetic acid

Results & Discussion

Characterization results (1/4)

Table 1. Physicochemical properties of all samples

Sample	SSA m²/g	Vp	ICP (Ni, wt. %)
Al (untreated)	281	-	n/a
Al (calcined)	195	0.65	n/a
Ni/Al (calcined)	158	0.58	7.14
LaAl (untreated)	176	-	n/a
La/Al (calcined)	-	0.70	n/a
Ni/LaAl (calcined)	159	n/a	7.79

Al & Ni/Al

- 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

LaAl & Ni/LaAl

- Less marked reduction in the SSA
- Pore volume (Vp) was not significantly altered

Ni/Al & Ni/ LaAl

- Both catalyst samples have almost identical SSA's
- The ICP results show that the desired metal level was achieved for both catalysts

Characterization results (2/4)

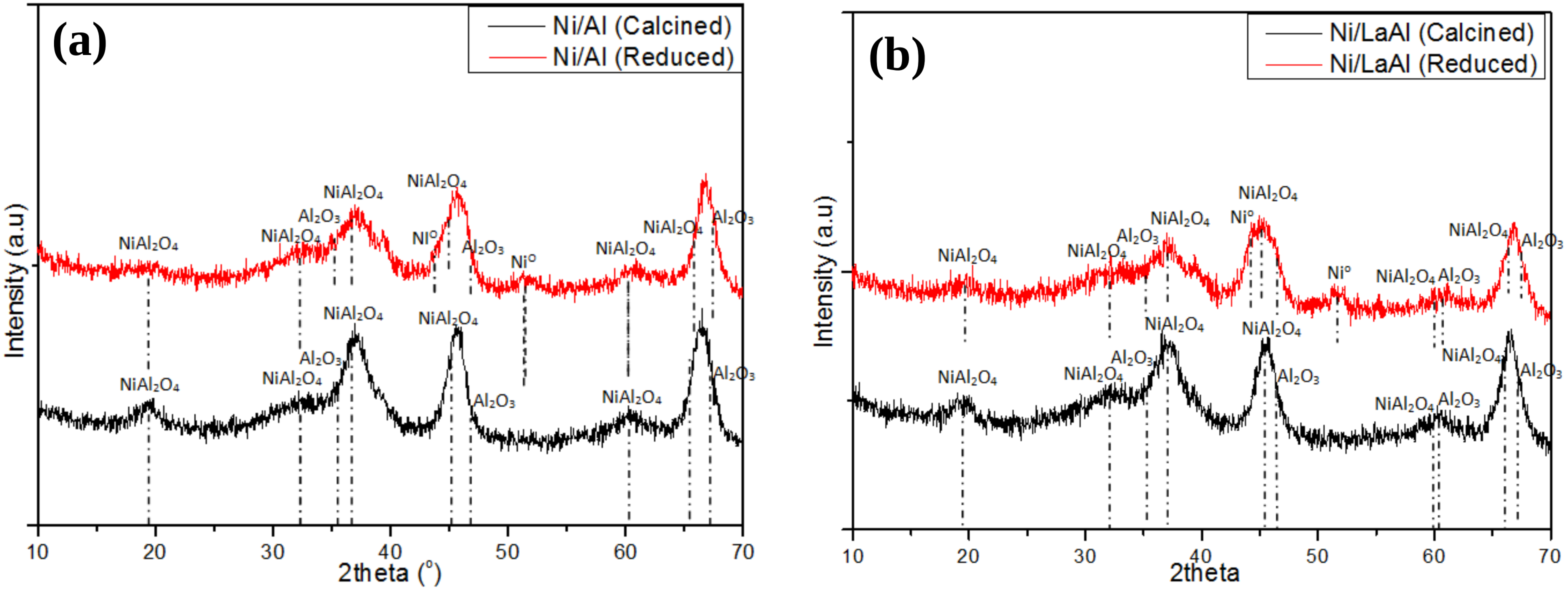


Figure 2.
XRD patterns of calcined and reduced
(a) Ni/Al catalyst,
(b) Ni/LaAl catalyst

Diffractograms

- $2\theta = 35.2^o$, 47.2^o and 67.6^o (γ-Al_2O_3)
- $2\theta=19^o$, 32^o, 37^o, 45^o, 60.2^o and 65.9^o (nickel aluminate)
- NiO not detected (expected at $2\theta=43.5°$ and $63.1°$)
- no diffraction peaks of the La_2O_3 phase

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^o) at $2\theta=44^o$ and 51.2^o

Characterization results (3/4)

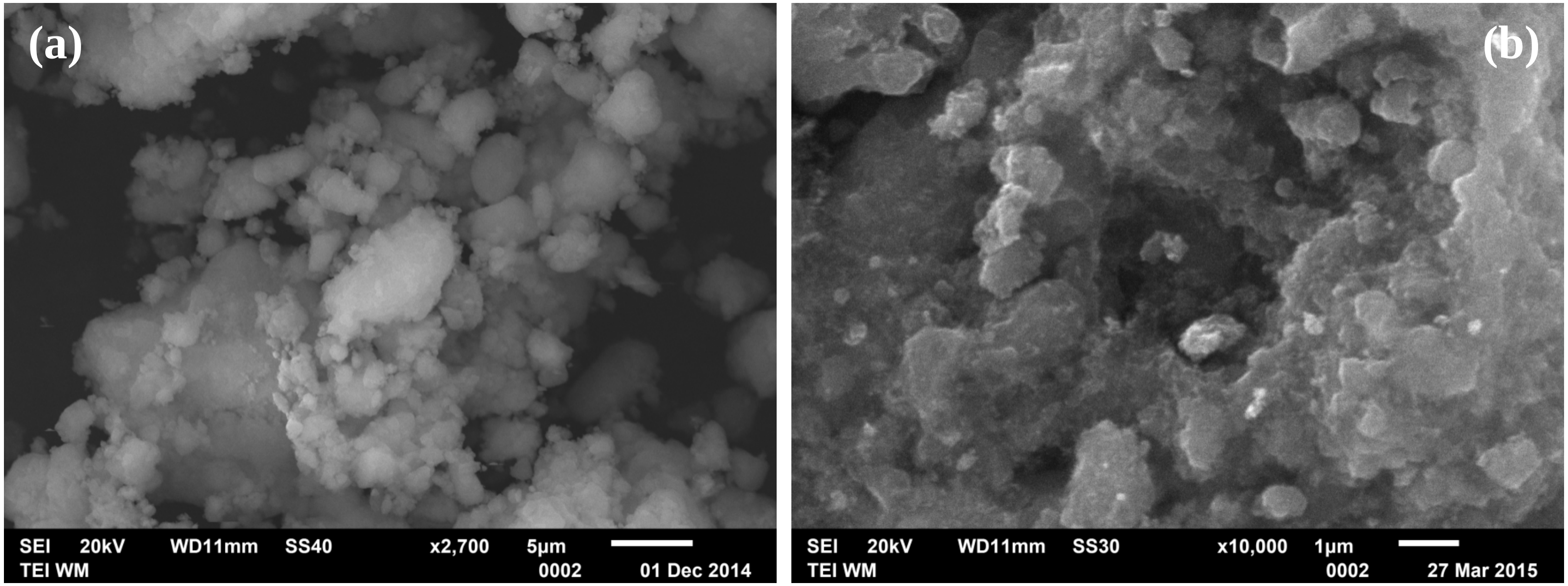
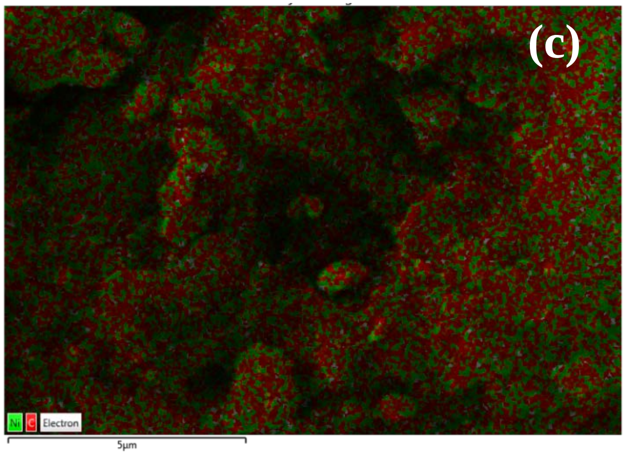


Figure 3. SEM images of the Ni/Al catalyst (a) fresh catalyst, (b) used catalyst, (c) carbon mapping of the used catalyst



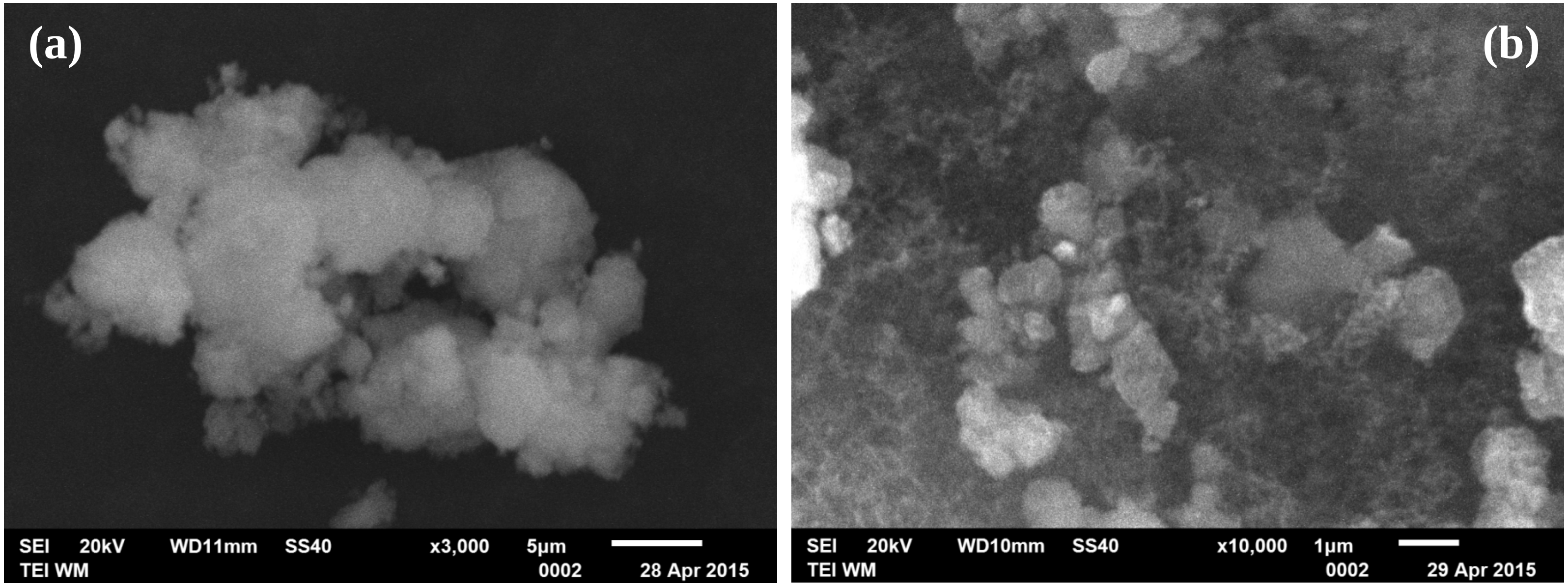
Fresh

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

Used

Significant transformation in morphology with plane particles and others with rugged appearance

Characterization results (4/4)



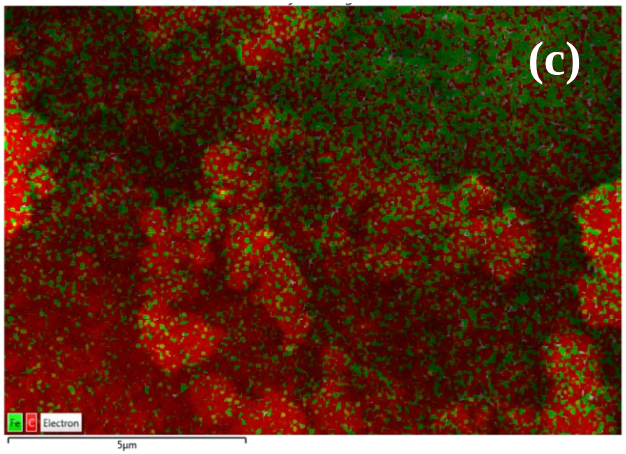


Figure 4. SEM images of the Ni/LaAl catalyst (a) fresh catalyst, (b) used catalyst, (c) carbon mapping of the used catalyst

Fresh
Ni/LaAl catalyst comprises of larger aggregates than the Ni/Al catalyst, it also includes particles at sizes that can be measured in nm.

Used
- Corrosion, cracking, fragmentation into smaller particles
- Carbon filaments surround the catalyst surfaces and partially cover the cracked surface

Catalytic activity and selectivity (1/5)

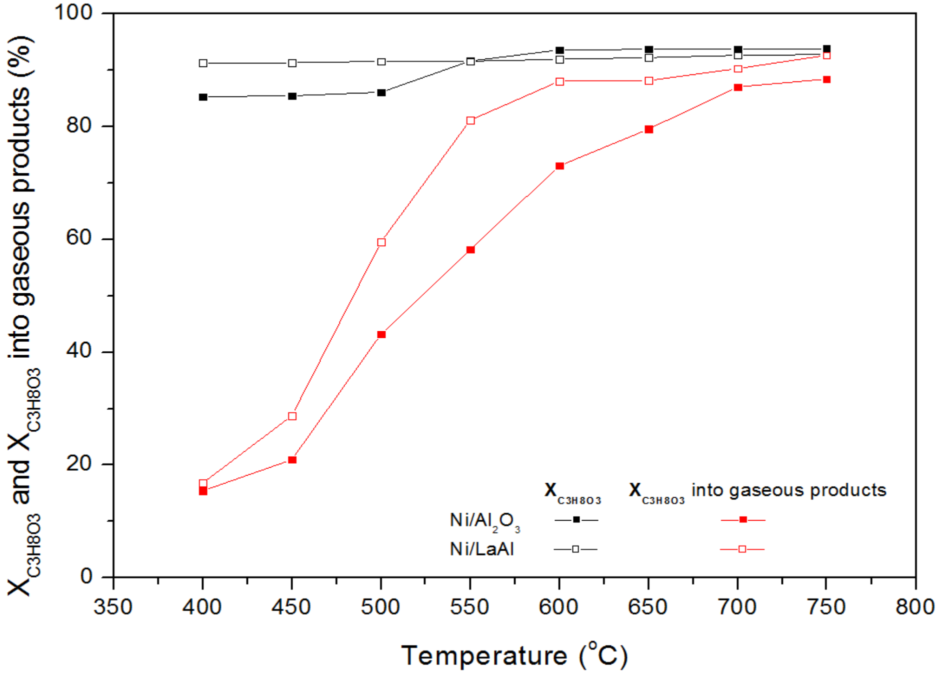


Figure 5.
Total glycerol conversion and glycerol conversion into gaseous products

- Both catalysts show improvements with increased temperatures
- The Ni/LaAl catalyst exhibits significantly higher conversions into gaseous products
- Difference is particularly marked between 500-600°C, where the Ni/LaAl catalysts conversion is ~60-80%, as opposed to ~40-60% for the Ni/Al catalyst
- Total glycerol conversion is essentially flat

Catalytic activity and selectivity (2/5)

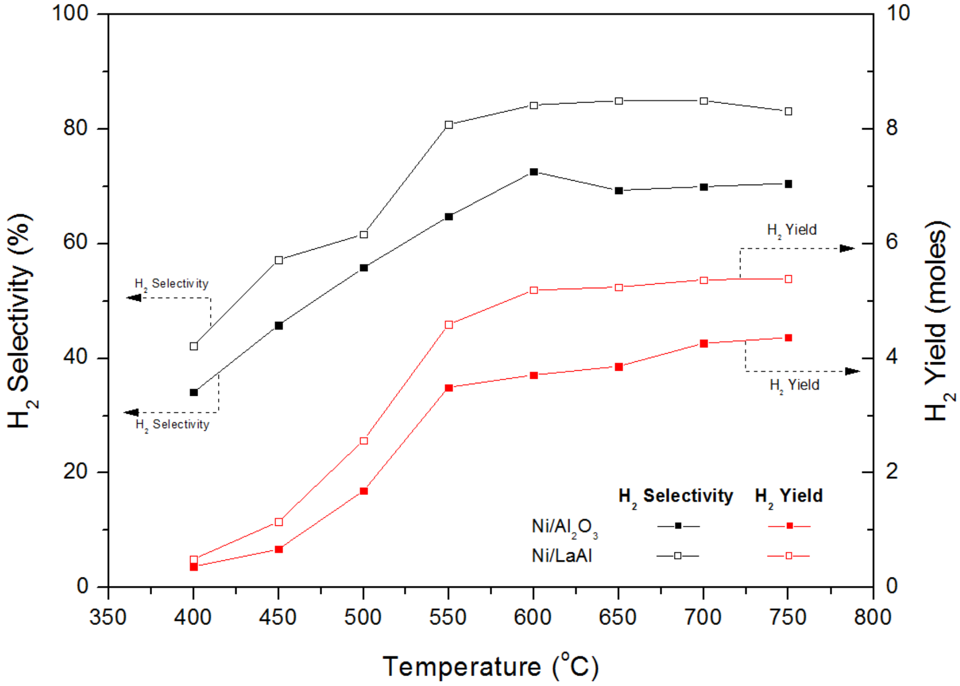


Figure 6.
Hydrogen yield and selectivity

- The concentration of H_2 increases with increasing temperatures for both catalysts
- For Ni/LaAl, hydrogen yield and hydrogen selectivity is significantly enhanced for the entire temperature range

Catalytic activity and selectivity (3/5)

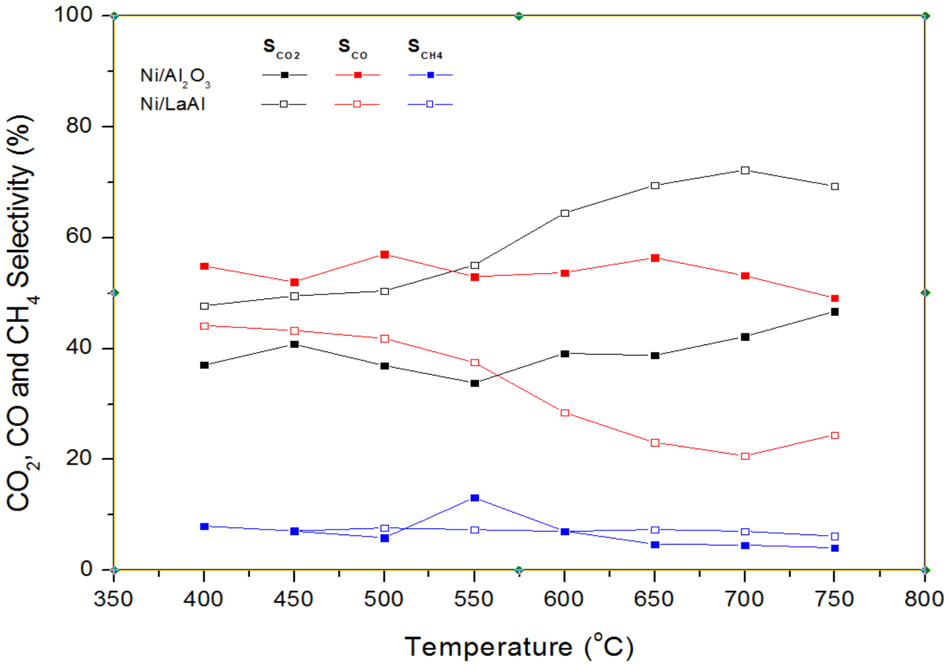


Figure 7.
CO_2, CO and CH_4 selectivity (%)

- For both catalysts, the formation of CH_4 is considerably low during the whole test
- For Ni/LaAl the production of CO_2 (selectivity) increases with temperature, while that of CO decreases
- The opposite is true for the Ni/Al catalyst, i.e., the production of CO_2 (selectivity) decreases with temperature, while that of CO increases (significant as the presence of CO in the gas mixture can adversely affect the performance of both anode and cathode in proton-exchange fuel cells (PEMFCs) acting as poison)

Catalytic activity and selectivity (4/5)

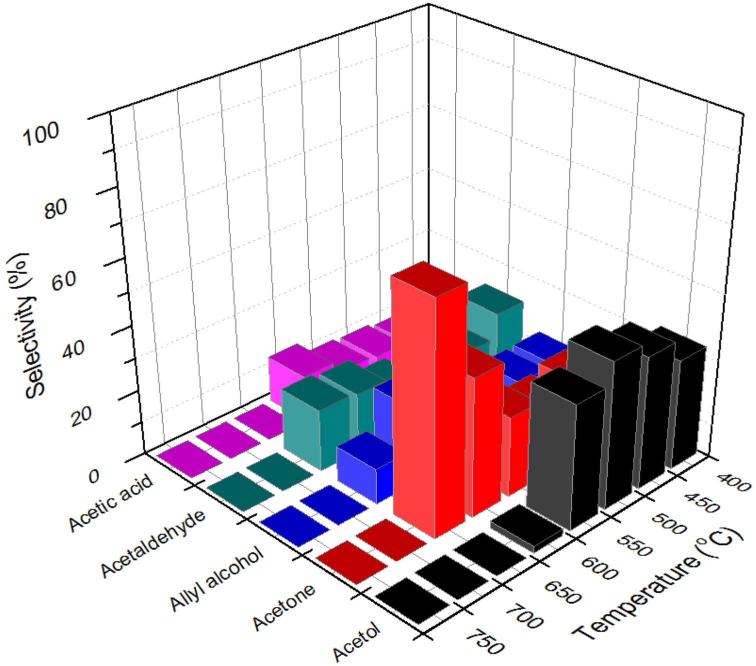


Figure 8.
Liquid products' selectivity for the Ni/Al catalyst

- Liquid effluents where present mainly at relatively low temperature ranges, which can be attributed to the different reaction routes that convert glycerol to liquid products
- For the Ni/Al catalyst the reaction compounds were produced from 400-650°C
- Thus, the Ni/Al catalyst exhibits high glycerol conversion into liquid products (and hence, low glycerol conversion into gaseous products)

Catalytic activity and selectivity (5/5)

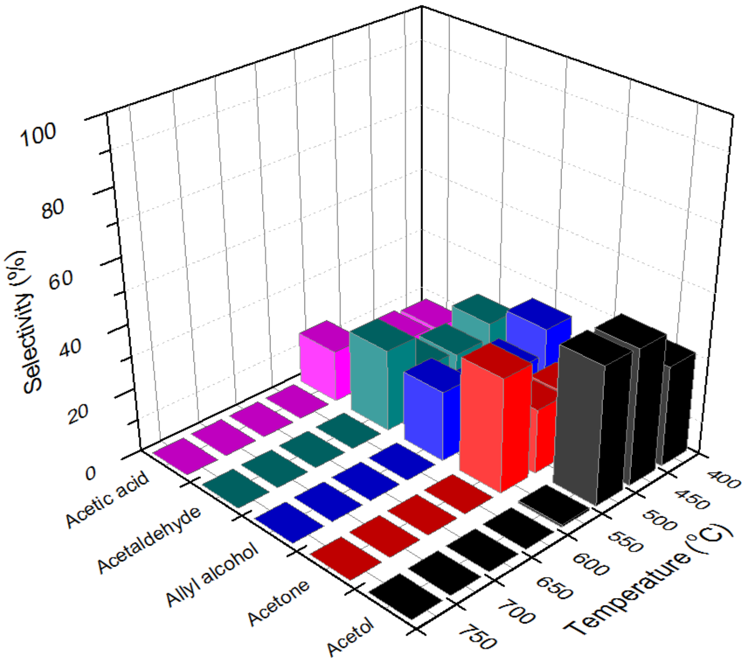


Figure 9.
Liquid products' selectivity for the Ni/LaAl catalyst

Ni/LaAl catalyst produces liquid products only up to 550°C, with acetol (~40% at 500°C) and acetone (~30% at 550°C) as the main byproducts

Conclusions

- **Ni/Al catalyst**
  - the major gaseous products formed were H_2 and CO
  - liquid reaction compounds were produced from 400-650°C
- **Ni/LaAl catalyst**
  - the major gaseous products formed were H_2 and CO_2
  - liquid reaction compounds were produced from 400-550°C
- **Methanation did not play any major role**

- Measurements on the used samples revealed that the percentage of carbon formed was almost double on the Ni/Al catalyst than that formed on the Ni/LaAl catalyst

- In concluding, the addition of lanthanum to Ni catalysts supported on alumina favors the formation of gaseous H_2 and CO_2, minimizes liquid effluents and inhibits the formation of carbon during the reaction
- The fall in carbon formation may be attributed to the lanthanum's redox properties, which offer alternative routes to the removal of carbon

Thank you

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