Production of hydrogen from steam reforming of glycerol using nickel catalysts supported on $\text{Al}_2\text{O}_3$, $\text{CeO}_2$ and $\text{ZrO}_2$

Abstract
Nickel catalysts supported on $\text{Al}_2\text{O}_3$, $\text{CeO}_2$ and $\text{ZrO}_2$ were prepared by wet impregnation method and evaluated in steam reforming of glycerol. The catalysts were characterized by chemical composition, textural analysis, crystalline structure and reducibility. The structural characterization of the catalysts revealed a good dispersion of Ni particles using the $\text{Al}_2\text{O}_3$ support, needing higher reduction temperature. The reactions were performed at 500°C with 10 vol.% glycerol solution in a continuous flow reactor. All catalysts showed conversions close to 100%. The selectivity to gas products and formation of liquid by-products were found to be dependent on the type of support. The $\text{H}_2$ selectivity showed the following trend: $\text{ZrO}_2 > \text{Al}_2\text{O}_3 \approx \text{CeO}_2$. The catalyst supported on $\text{CeO}_2$ showed low activity for water-gas shift reaction, with the highest $\text{CO}$ selectivity. All catalysts presented a low formation of CH$_4$. In the liquid phase some by-products were identified (hydroxyacetone, acetic acid, lactic acid, acetaldehyde, acrolein and ethanol) and secondary reaction routes were proposed. Coke formation was higher on Ni/Al$_2$O$_3$ catalyst, but no deactivation was observed during 8 h of reaction.

Keywords
Hydrogen • Glycerol • Steam reforming • Nickel • Catalysts

1. Introduction
The search for alternative energy sources is increasing in the world motivated by predictions that point to a progressive decrease in the production of fossil fuels. Besides the shortage, another problem associated with the use of fossil fuels is the continuing increase in emissions of pollutants, especially those related to global warming. These greenhouse gases affect human health and also cause imbalances in fauna and flora, such as acid rain. Therefore, there is a great necessity for alternative fuels that do not affect the environment [1].

Motivated by concerns about air pollution, energy security and climate change, the notion of “hydrogen economy” is moved beyond the area of the scientists and engineers, it is a matter of policy issues and treated by business leaders. The interest in hydrogen, the simplest element and most abundant in the universe, is increasing due to technological advances in fuel cells, a potential successor to batteries in portable electronics, power stations and the internal combustion engine [2]. For hydrogen to become a truly sustainable energy source, it should be promoted its production from renewable resources; more than 95 % of hydrogen produced today comes from nonrenewable resources, based on fossil fuels [3,4].

Glycerol is a chemical used for more than two centuries in a variety of applications, such as production of nitroglycerin and esters. Glycerol is also widely used in food, pharmaceutical, cosmetics, toiletries and cleaning industries. The demand and supply of glycerol in the world market was in equilibrium by the end of the 1990s. With the production of biofuels, especially biodiesel, this equilibrium has been completely changed. Biodiesel is produced by the transesterification of vegetable oils and animal fats, and glycerol is a byproduct of this reaction. One ton of biodiesel yields about 110 kg of crude glycerol (glycerin) or 100 kg of pure glycerol [3]. In Brazil, according to National Agency of Petroleum, Natural Gas and Biofuels (ANP), the production of biodiesel (B100) in 2010 was approximately 2.4 million m$^3$, generating 240,000 m$^3$ of glycerin, creating a surplus of glycerin in the Brazilian market. Thus, glycerol is a product that has a large potential market, however, with increasing biodiesel production, their supply has risen substantially and the price of glycerin has fallen to about US 0.11 kg$^{-1}$ [5].

Dumesic et al. [6,7] have produced hydrogen from oxygenated biomass-derived compounds, including glycerol, through the aqueous phase reforming (APR). Although the catalyst has provided stability for a long period, the high pressure and low...
reaction rates have prevented its use as a commercially viable process. On the other hand, the steam reforming process can be performed at atmospheric pressure. The steam reforming is the most efficient energy technology available, and with greater profitability [8]. It is highly endothermic and should ideally be performed at high temperatures, low pressures, and high steam/glycerol ratios to obtain high conversions [9].

The steam reforming of glycerol generates H₂ and CO₂ as the main gas products and CH₄ and CO at low concentrations, but also other alkanes and liquid by-products can be formed [6]. The series of reactions most widely accepted to represent the steam reforming of glycerol is Eq. (1)-(5) [8,10]:

Decomposition of glycerol:

\[ C₃H₆O₃ \rightarrow 4H₂ + 3CO \quad (1) \]

Shift reaction:

\[ CO + H₂O \leftrightarrow H₂ + CO₂ \quad (2) \]

Methanation reactions:

\[ CO + 3H₂ \leftrightarrow CH₄ + H₂O \quad (3) \]

\[ CO₂ + 4H₂ \leftrightarrow CH₄ + 2H₂O \quad (4) \]

The overall reaction of steam reforming of glycerol can be written as:

\[ C₃H₆O₃ + 3H₂O \rightarrow 3CO₂ + 7H₂ \quad \Delta H_{298K} = 346.4 \text{ kJ/mol} \quad (5) \]

Supported Pt, Ru, Pd and Ni are the most used catalysts in the reforming of oxygenated organics, in both APR and steam reforming, showing good catalytic activity and selectivity for hydrogen production. Unwanted products can be formed due to the occurrence of parallel reactions by breaking of the C-O bonds of the oxygenated organic, forming alcohols or organic acids. Thus, a good catalyst to produce hydrogen by reforming reactions has to be more active for cleavage of the C-C, O-H and C-H bonds rather than the C-O bonds and promote the removal of adsorbed carbon monoxide by the water gas shift reaction [11].

Catalysts based on noble metals have a lower sensitivity to carbon deposition and higher activity. Nevertheless, considering the high cost and limited availability of the noble metals, it is more economical to develop catalysts based on non-noble metals such as nickel, with good performance and high resistance to carbon deposition [12].

Alumina is one of the most widely used supports in catalysis due to its high surface area, which allows a great dispersion of the active phase. In addition, the alumina has relevant characteristics such as high porosity, good mechanical strength and high thermal stability, forming a diffusion barrier that prevents the active phase migration to form clusters of larger particles with lower activity [13].

There is evidence that the support has a significant effect on the overall catalytic behavior and the use of reducible oxides, like ZrO₂ and CeO₂, can result in additional benefits when compared to irreducible oxides, such as Al₂O₃. The reducibility and oxygen transfer capacity of ZrO₂ and CeO₂ have shown to be fundamental in keeping the active phase surface free of carbon deposits [14,15]. Zhuang et al. [15] have reported that CeO₂ increases the dissociation of water and accelerates the reaction of steam with adsorbed species on the nickel surface near the boundary area between the metal and support, thereby decreasing the carbon deposition and promoting the stability of the catalyst during the reforming of hydrocarbons.

In this contribution, we have investigated the effect of different supports (Al₂O₃, ZrO₂ and CeO₂) on the activity and hydrogen selectivity of Ni catalysts in steam reforming of glycerol. For this purpose, structural and morphological properties of the catalysts were studied and secondary reaction routes were proposed based on identification of the by-products formed in liquid phase.

2. Experimental

2.1. Catalyst preparation

The Ni/Al₂O₃ (NiAl), Ni/ZrO₂ (NiZr) and Ni/CeO₂ (NiCe) catalysts were prepared by the wet impregnation method, with 20 wt.% of NiO. For preparation of NiAl and NiZr, γ-Al₂O₃ and ZrO₂ were calcined at 500°C for 16 h under air flow (60 mL min⁻¹) to remove water and possible undesirable organic materials, because the bare supports were supplied in the form of pellets (Saint Gobain). For NiCe, CeO₂ was prepared from cerium nitrate (Vetec) by calcination at 500°C for 3 h under air flow (60 mL min⁻¹).

Appropriate amount of nickel nitrate (Vetec) was dissolved in deionized water and mixed to the support in a rotary evaporator. The mixture was heated to 80°C under slight vacuum for evaporation of water, followed by drying at 110°C overnight. Then the catalysts were calcined at 500°C for 3 h using a heating rate of 10°C min⁻¹ under air flow (60 mL min⁻¹).

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) using a Rigaku (Rix 3100) spectrometer.

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Miniflex II X-ray diffractometer equipped with a graphite monochromator using CuKα radiation (30 kV and 15 mA). The measurements were carried out with steps of 0.05° using a counting time of 1 second per step and over the 2θ range of 10° and 90°.

The textural properties of the catalysts were determined by N₂ adsorption-desorption at -196°C in a Micromeritics ASAP 2000. The specific area was obtained using the BET method and pore volume and diameter were obtained by BJH method. Prior to the analysis the samples were outgassed for 24 h at 200°C.
The catalyst performance is presented in terms of glycerol conversion and H₂, CO₂, CO, and CH₄ selectivity. Performance parameters were calculated based on the following equations:

\[
X_{\text{Glycerol in}} \times \%	ext{Glycerol out} \times 100
\]

\[
H_2 \text{ Selectivity,} \% = \frac{\text{H}_2 \text{ moles produced}}{\text{C atoms produced in gas phase}} \times \frac{1}{RR} \times 100
\]

\[
\text{Selectivity of } i \text{,} \% = \frac{\text{C atoms in species } i}{\text{C atoms produced in gas phase}} \times 100
\]

where RR is the H₂/CO₂ reforming ratio; it is 7/3 in the case of the glycerol steam reforming.

3. Results and discussion

3.1. Catalyst characterization

The chemical composition of the synthesized catalysts is presented on Table 1. As expected, the NiO loading of the catalysts was very close to the nominal value (20 wt.%) and the small differences could be related to experimental errors during synthesis procedure. Table 1 also summarizes the textural characteristics of the catalysts. The BET areas of the supports are 260, 85 and 70 m²g⁻¹ for Al₂O₃, CeO₂ and ZrO₂, respectively. After impregnation with NiO all catalysts showed a reduction in the BET area in relation to the bare support. This area reduction can be due to partial obstruction of the pores of the support by NiO particles. Analyzing the average pore diameter of the catalysts, it was observed that all solids are mesoporous (20 – 500 Å).

The XRD patterns of catalysts after calcination are shown in Figure 1(a). The catalysts presented two phases, one related to the support and another to nickel species. NiAl sample presented low crystallinity, with broad peaks at 2θ = 37.5°, 45.7° and 66.8°, which are characteristic of γ-alumina. NiCe presented fluorite CeO₂ crystalline phase (JCPDS 34-0394) with peaks at 2θ = 28.6°, 33.1°, 47.5° and 56.3°, which represent the (111),

| Catalyst | NiO (wt.%) | S_{BET} (m²g⁻¹) | V_{por} (cm³g⁻¹) | D (Å) | d_{NiO} (nm) | d_{Ni} (nm) |
|----------|------------|----------------|-----------------|-------|-------------|-------------|
| NiAl     | 22.1       | 123            | 0.44            | 112.7 | -           | 6.3±1.5     |
| NiCe     | 23.7       | 62             | 0.15            | 84.2  | 25.0±2.3    | 44.8±2.5    |
| NiZr     | 20.2       | 37             | 0.18            | 190.5 | 22.7±4.6    | 25.7±1.5    |

*Calculated by the Scherrer equation using (200) plane of NiO.
*Calculated by the Scherrer equation using (111) plane of Ni.
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Figure 2 shows the TPR profiles of the catalysts. The NiAl catalyst presented a reduction peak at higher temperatures compared to the other catalysts, suggesting the existence of a strong interaction between nickel and alumina support. The single reduction peak at 730°C of NiAl catalyst is characteristic of incorporation of NiO into Al$_2$O$_3$ with formation of a spinel phase (NiAl$_2$O$_4$), which adversely affects the reduction of nickel (in general at temperatures above 600°C) [19,20].

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Figure 1 shows the XRD patterns of the NiAl, NiCe and NiZr catalysts after reduction at 900°C, 700°C and 650°C, respectively. The final reduction temperature corresponds to the end of H$_2$ consumption in TPR profiles, considering the peaks associated with nickel reduction. The XRD patterns showed that NiO was completely reduced to metallic Ni (JCPDS 4-850), with diffraction peaks at 2$\theta$ = 44.5°, 51.8° and 76.3°, correspondent to (111), (200) and (220) planes, respectively. The phases relative to the supports did not present any significant modification.

Table 1 shows the average crystallite size of NiO and Ni, obtained by the Scherrer equation, using the (200) plane of NiO and (111) plane of Ni. Due to the absence of well-defined diffraction peaks corresponding to NiO phase for NiAl catalyst, it was not possible to calculate the NiO crystallite size for this sample. The average crystallite sizes of NiO for NiCe and NiZr samples are very similar. After the reduction process NiZr sample showed a slight increase in the crystallite size of Ni phase. On the other hand, NiCe sample exhibited a large increase in the size of the Ni crystallite phase. This increase can be related to a weak interaction between NiO and CeO$_2$ phases [18]. The Ni crystallites in NiAl sample presented the smallest average size, approximately 6 nm, which can be associated with the large dispersion of the NiO combined in the spinel phase and stronger interaction between nickel and alumina, reducing the mobility of the nickel particles during the reduction.

Figure 1. XRD patterns of the nickel catalysts after calcination (a) and reduction (b).

![Figure 1. XRD patterns of the nickel catalysts after calcination (a) and reduction (b).](image)

Figure 2. TPR profiles of the nickel catalysts.

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TPR profile of NiCe catalyst presents four reduction peaks, at 300°C, 420°C, 550°C and 925°C. Since Ni²⁺ is reduced to Ni⁰ without going through intermediate oxides, the hydrogen consumption peaks appearing in different temperature regions are assigned to the reduction of different species [21]. The peaks at temperatures below 300°C can be attributed to reduction of free NiO species segregated on the surface of the support [22]. Peaks observed at 420°C and 550°C may be related to the reduction of NiO strongly bounded to the CeO₂ support [23] and partial reduction of the surface ceria forming nonstoichiometric cerium oxides (CeOₓ). [22]. The peak observed at higher temperature (925°C) can be attributed to the partial reduction of bulk CeO₂ to Ce₂O₃. According to Shyu et al. [24], the reduction of bulk CeO₂ to Ce₂O₃ occurs at temperatures above 800°C.

NiZr catalyst presented two reduction peaks: 445°C and 580°C. Generally, low temperature peaks are attributed to the reduction of large NiO particles, while the higher temperature peaks are attributed to the reduction of NiO in intimate contact with the oxide support [25]. Based on this analysis, the reduction peak at low temperature (445°C) corresponds to the reduction of relatively free NiO particles. This temperature is higher than that of NiCe due to the stronger interaction between NiO and ZrO₂. The reduction peak at high temperature (580°C) can be attributed to NiO with strong interaction with the support, also observed by Xu and Wang [26], together with a partial reduction of zirconia.

Table 2 shows the experimental consumption of H₂ calculated by integrating TPR profiles, theoretical consumption considering the reduction of Ni²⁺ to Ni⁰ and the reduction degree (ratio of experimental to theoretical consumption). The catalysts supported on ceria and zirconia presented reduction degrees above 100 %, which is associated with a partial reduction of support, forming suboxide species. NiAl catalyst presented a reduction degree of 88 %, due to the difficulty to reduce nickel aluminate. According to Youn et al. [27] the interaction between the metal and support increases with decreasing size of metallic species, resulting in a poor reducibility of the supported metal. This is consistent with our XRD results, which showed a good dispersion of Ni on the alumina support.

3.2. Catalytic tests
Catalytic activity of nickel supported on Al₂O₃, CeO₂ and ZrO₂ in steam reforming of glycerol in terms of H₂ selectivity is displayed in Figure 3. H₂ selectivity of NiAl catalyst showed a constant increase in the first 4 h of reaction reaching 94%. From the fourth hour of reaction there was a reduction in H₂ selectivity, which remained relatively constant until the end of the catalytic test, with an average of 68%. The same behavior was observed with the NiCe catalyst, which presented an initial H₂ selectivity of 55% that increased to 74% in the third hour of reaction and then remained almost constant until the end of the catalytic test, with an average of 67%. Zhang et al. [22] obtained an H₂ selectivity of 87% in steam reforming of glycerol at 500°C using Ni/CeO₂ prepared by deposition-precipitation method. H₂ selectivity of NiZr catalyst presented an opposite behavior to the other catalysts in the first hours of reaction: an initial high H₂ selectivity (87%), which was reduced to 76% in the third hour of reaction and then was kept constant up to the end of reaction, with an average of 78%.

Although the NiAl catalyst has reached the highest H₂ selectivity (94%), NiZr catalyst had the best performance for most of the reaction time, with an average H₂ selectivity 10% higher at the final part of the test. Comparing the H₂ selectivities (Figure 3) and Ni crystallite sizes (Table 1) it seems that Ni dispersion is not clearly related to the catalytic activity for H₂ formation, as observed by Iriondo et al. [28] for La₂O₃ modified Ni/Al₂O₃ catalysts.

Figure 4 displays CO, CH₄ and CO₂ selectivities of the catalytic tests performed with the NiAl, NiCe and NiZr catalysts. Among these three compounds it can be clearly observed that CO₂ is the
main reaction product. Table 3 shows the average conversion and selectivities after 3 h of reaction, which is approximately the time needed to reach the steady-state operation. NiAl catalyst showed CO₂ selectivity always above 90% and the average CO and CH₄ selectivity from 3 to 8 h of reaction was 1.4% and 1.7%, respectively. The reaction with NiCe catalyst showed CO₂ selectivity between 75 and 80%, average CH₄ selectivity of 3.1% and the highest CO selectivity compared to other catalysts, of about 20.9%. Finally, the reaction with NiZr catalyst showed a high CO₂ selectivity, with an average of 91.9%. In this test the average selectivity to CO and CH₄ was similar, 4.2% and 3.8%, respectively.

It is well known that Ni has moderate activity in the water-gas shift reaction (Eq. 2) [29], resulting in low formation of CO, as observed in the tests with NiAl and NiZr catalysts. It can be noticed that the support has definitely a great influence on the catalytic performance. These tests showed that nickel supported on CeO₂ has lower activity for water-gas shift reaction, as a consequence it presented the highest selectivity to CO and the lowest selectivity to H₂ (Table 3). Supported Ni catalysts have high activity in the methanation reactions of CO and CO₂ (Eq. 3 - 4) [7], and the formation of methane was significant, mainly for NiCe and NiZr catalysts.

The liquid phase of the reactions was analyzed using HPLC. Figure 5(a) shows the composition of the liquid phase and the conversion of glycerol obtained in test with NiAl catalyst. The test performed with NiCe catalyst (Figure 5(b)) also showed high glycerol conversion, close to 100% after 3 h of main reaction product. Table 3 shows the average conversion and selectivities after 3 h of reaction, which is approximately the time needed to reach the steady-state operation. NiAl catalyst showed CO₂ selectivity always above 90% and the average CO and CH₄ selectivity from 3 to 8 h of reaction was 1.4% and 1.7%, respectively. The reaction with NiCe catalyst showed CO₂ selectivity between 75 and 80%, average CH₄ selectivity of 3.1% and the highest CO selectivity compared to other catalysts, of about 20.9%. Finally, the reaction with NiZr catalyst showed a high CO₂ selectivity, with an average of 91.9%. In this test the average selectivity to CO and CH₄ was similar, 4.2% and 3.8%, respectively.

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The liquid phase of the reactions was analyzed using HPLC. Figure 5(a) shows the composition of the liquid phase and the conversion of glycerol obtained in test with NiAl catalyst. The conversion of glycerol has an initial increase, reaching almost 100% on the fourth hour of reaction and maintaining constant until the end of the reaction. In the liquid phase it was identified acetic acid, lactic acid, acetaldehyde, acrolein and hydroxyacetone (acetol). The presence of acetic acid was found only in the first 2 h of reaction, with very low amounts (less than 0.05 g L⁻¹). The concentration of most of by-products decreased during the reaction until the fifth hour, reaching concentrations as low as 0.1 g L⁻¹. The only by-products formed during the whole reaction period were hydroxyacetone and acrolein.

The test performed with NiCe catalyst (Figure 5(b)) also showed high glycerol conversion, close to 100% after 3 h of reaction.

![Figure 4. CO, CH₄ and CO₂ selectivity of NiAl, NiCe and NiZr catalysts. Same reaction conditions of Figure 3.](image)

Table 3. Average glycerol conversion and selectivities after 3 h of reaction.

| Catalyst | Conversion (%) | H₂ Selectivity (%) | CO Selectivity (%) | CO₂ Selectivity (%) | CH₄ Selectivity (%) |
|----------|---------------|--------------------|--------------------|--------------------|--------------------|
| NiAl     | 99.0          | 74.9               | 1.4                | 96.9               | 1.7                |
| NiCe     | 99.7          | 68.7               | 20.9               | 76.0               | 3.1                |
| NiZr     | 99.9          | 77.5               | 4.2                | 91.9               | 3.8                |
reaction. Besides the by-products already identified in the test with NiAl, it was also observed the presence of ethanol at low concentrations, around 0.1 g L\(^{-1}\), and traces of pyruvaldehyde. In this test the main by-product formed was acetaldehyde, followed by hydroxyacetone, lactic acid and acrolein. The concentration of these by-products is initially high and then presents successive reductions, reaching a minimum around the fourth hour of reaction. After this period there is an opposite behavior, with successive increases up to the end of the reaction. The by-product concentrations in this test were the highest between all tests.

Figure 5(c) presents the results obtained in the test with the NiZr catalyst. The conversion of glycerol was almost constant and close to 100%. The compounds found in the liquid phase were acetic acid, lactic acid, acetaldehyde, acrolein and hydroxyacetone, all of them with very low concentration, below 0.2 g L\(^{-1}\). As in the test of the NiAl catalyst, acetic acid was observed only in the first two hours of reaction.

The formation of lactic acid occurs by the reaction of isomerization of glyceraldehyde (Eq. 7), which is formed from the dehydrogenation of glycerol (Eq. 6)\(^{[30-32]}\).

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{OH} \quad \text{H}_2 \\
\text{glycerol} & \quad \text{glyceraldehyde}
\end{align*}
\]  

(H6)

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{OH} \\
\text{glyceraldehyde} & \quad \text{OH} \quad \text{H} \quad \text{OH} \quad \text{H}_2 \quad \text{OH} \\
& \quad \text{H} \quad \text{OH} \\
& \quad \text{H} \quad \text{OH} \\
& \quad \text{H}_2 \quad \text{O} \quad \text{OH} \\
& \quad \text{lactic acid}
\end{align*}
\]  

(H7)

Hydroxyacetone and acrolein are formed from glycerol by dehydration reactions. According to Chai et al.\(^{[33]}\) and Corma et al.\(^{[34]}\) the dehydration reaction of glycerol can be initiated by either the central –OH (Eq. 8) or terminal –OH (Eq. 9), which results in parallel formation of two enol intermediates. These enols undergo a rapid rearrangement to 3-hydroxypropionaldehyde (3-HPA) and hydroxyacetone, respectively. The 3-HPA can be easily dehydrated to form acrolein (Eq. 8).

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{OH} \\
\text{glycerol} & \quad \text{3-HPA} \quad \text{acrolein}
\end{align*}
\]  

(H8)

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{glycerol} & \quad \text{hydroxyacetone}
\end{align*}
\]  

(H9)

Pompeo et al.\(^{[35]}\) proposed some reaction pathways involved in steam reforming of glycerol. In a possible scheme of reactions, the acetaldehyde is formed from pyruvaldehyde coming from the dehydrogenation of hydroxyacetone; the break of a C-C bond of the pyruvaldehyde leads to CO and acetaldehyde (Eq. 10). In this same work, it was also proposed that hydration of acetaldehyde leads to 1,1-ethanediol, which then suffers a dehydrogenation reaction resulting in acetic acid (Eq. 11).

\[
\begin{align*}
\text{HO} & \quad \text{OH} \quad \text{C} \quad \text{O} \\
\text{hydroxyacetone} & \quad \text{pyruvaldehyde} \quad \text{acetaldehyde}
\end{align*}
\]  

(H10)

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{acetaldehyde} & \quad \text{1,1-ethanediol} \quad \text{acetic acid}
\end{align*}
\]  

(H11)

King et al.\(^{[36]}\) suggested some reaction routes for ethanol production from aqueous phase reforming of glycerol. In their
reaction scheme, dehydrogenation, decarbonylation, and dehydration occur sequentially forming acetaldehyde, which can be hydrogenated to ethanol, according to Eq. 12.

\[
\begin{align*}
\text{glycerol} & \quad \overset{\text{dehydrogenation}}{\rightarrow} \quad \text{glyceraldehyde} \\
\text{glyceraldehyde} & \quad \overset{\text{dehydration}}{\rightarrow} \quad \text{ethanol} \\
\text{ethanol} & \quad \overset{\text{hydrogenation}}{\rightarrow} \quad \text{acetaldehyde}
\end{align*}
\]  \tag{12}

In our experiments, the ethanol is probable formed from the hydrogenation of acetaldehyde, which is formed from the break of the C-C bond of the pyruvaldehyde, according to Eq 10. This is reinforced by the presence of pyruvaldehyde in the reaction with NiCe catalyst, which was the only catalyst that showed formation of ethanol.

The catalysts after reaction were subjected to thermogravimetric analysis (TGA) to investigate the formation of carbonaceous residues. The quantification of carbonaceous products was carried out from the weight loss shown in Figure 6(a). From the derivative of the TG curves (DTG) (Figure 6(b)) it can be clearly seen that the main weight loss for all catalysts is in the range of 490-630°C, which is associated with the oxidation of coke deposited on the catalyst. The weight loss in this temperature range for NiAl, NiCe and NiZr catalysts was 23%, 16.8% and 13%, respectively. Only NiAl sample presented a small weight loss below 300°C.

According to Sánchez-Sánchez et al. [37] the thermograms of the Ni catalysts used in ethanol steam reforming can be divided in three different temperature regions: region I at temperatures below 300°C represents the loss of water and volatile species; region II between 300-530°C is attributed to filamentous coke associated with Ni particles; and region III at temperatures above 530°C is related to oxidation of coke deposits with different graphitization degrees. In our case, the coke was mainly oxidized in the third region of temperature, showing that filamentous coke was not predominant, in agreement with SEM images that will be shown later.

The rate of carbon formation was calculated considering the amount of coke formed in 8 h of reaction (Figure 7). The coke formation was the highest on the NiAl catalyst. According to Srisiriwat et al. [38] the coke formation is associated with the mobility of oxygen in the catalyst supports. Supports as Al₂O₃ have lower oxygen mobility than CeO₂ and ZrO₂ and therefore present a higher coke formation. It is well known that CeO₂ and ZrO₂ have good capacity to store and transfer oxygen and as result promote the gasification of coke deposited [39,40]. Adhikari et al. [41] associated the formation of coke with acidity of the support; increasing the acidity of the support the coke formation increases. The presence of acid sites on Al₂O₃ is much more significant compared to CeO₂ and ZrO₂ [42]. This is in agreement with our results, the high rate of coke formation on the NiAl catalyst can be related to the lower oxygen mobility and higher acidity of Al₂O₃ than CeO₂ and ZrO₂.

Although all catalysts have shown coke formation, no deactivation was observed during the reaction period. Thus, this carbon formed is not of encapsulating type, which causes the blockage of active Ni sites [10]. SEM analysis was performed to investigate the type of coke formed on the used samples. Figure 8 shows the SEM images of the fresh and used NiZr catalyst. It is possible to observe the presence of agglomerated particles of graphitic carbon on the used sample, but neither filamentous nor encapsulating coke was formed during reaction. The coke morphology was similar for all three catalysts.

![Figure 6. Thermogravimetric analysis (TGA) of the NiAl, NiCe and NiZr catalysts after reaction. (a) weight loss in percentage (%) and (b) derivative weight loss (%/°C).](image-url)
CO₂ selectivity (above 95%) while the CO selectivity was higher for NiCe catalyst (about 20%). The conversion of glycerol was almost total in all reactions, with no apparent deactivation during 8 h of reaction. Several liquid by-products were identified: hydroxyacetone, lactic acid, acetic acid, acetaldehyde, acrolein for all catalysts and ethanol for NiCe catalyst. The concentration of these by-products is relatively low in tests with NiAl and NiZr catalysts; however with NiCe catalyst the concentrations are significant. Based on these liquid by-products, secondary reaction routes were proposed.

The rate of coke formation showed the following order NiZr < NiCe < NiAl. By SEM analysis it was identified the presence of large graphitic coke particles distributed over the catalyst. This coke formation is not associated with catalyst deactivation. Based on its high H₂ selectivity and low coke formation, Ni/ZrO₂ catalyst was found to be the best catalyst compared to Ni/Al₂O₃ and Ni/CeO₂ at the reaction conditions investigated.

4. Conclusions

Nickel catalysts supported on Al₂O₃, ZrO₂ and CeO₂ were prepared and their morphological and structural properties were evaluated. NiAl catalyst showed larger BET surface area and smaller Ni crystallites sizes, due to a stronger interaction between nickel and alumina, forming a spinel type phase that reduces at high temperatures (about 730 °C). NiCe catalyst presented the biggest Ni crystallite size, which may be related to a weak interaction between the support and NiO phase, with a partial sintering during the catalyst reduction. The catalysts supported on ceria and zirconia presented reduction degrees above 100 %, which is associated with a partial reduction of the support, forming suboxide species.

The catalysts were evaluated in steam reforming of glycerol at 500°C. The average H₂ selectivity showed the following tendency: NiZr > NiAl = NiCe. NiAl catalyst showed the highest CO₂ selectivity (above 95%) while the CO selectivity was higher for NiCe catalyst (about 20%). The conversion of glycerol was almost total in all reactions, with no apparent deactivation during 8 h of reaction. Several liquid by-products were identified: hydroxyacetone, lactic acid, acetic acid, acetaldehyde, acrolein for all catalysts and ethanol for NiCe catalyst. The concentration of these by-products is relatively low in tests with NiAl and NiZr catalysts; however with NiCe catalyst the concentrations are significant. Based on these liquid by-products, secondary reaction routes were proposed.

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