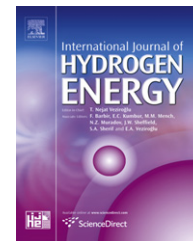


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Steam reforming of glycerol over Ni/Mg/ γ -Al₂O₃ catalysts. Effect of calcination temperatures

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ABSTRACT

The aim of this work is to study the catalytic activity of Ni(10%) based catalysts supported over γ -Al₂O₃ modified with Mg (3%) for the steam reforming of glycerol. Catalysts have been prepared by incipient wetness impregnation method; analysing the effect of the calcination temperature of the modified support and the calcination temperature of the catalysts. Catalysts were characterized by temperature programmed reduction, (TPR), x-ray diffraction (DRX) and BET surface area. All catalysts were tested for this reaction in a fixed bed reactor.

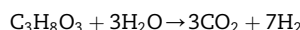
The best performance was achieved with the catalyst calcined at 500 °C being the optimum calcination temperature for the modified support of 900 °C. This behaviour is ascribable to the formation of MgAl₂O₄ spinel which favours the dispersion of Ni^o, responsible of the catalytic activity.

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1. Introduction

Lately, as a consequence of the development of fuel cells hydrogen has gained importance as an energy vector, in addition to its important role in the chemistry and petrochemical industry. Furthermore in order to diminish the effects of global warming, alternatives to produce hydrogen and syngas from renewable sources are being considered [1]. Additionally, the production of biodiesel from the transesterification process of vegetable oils has considerably increased, causing that the international market price of glycerol, main subproduct of this process, markedly decreased [2].

Hence, in this context hydrogen production from the steam reforming of glycerol seems as a promising alternative. The global reaction that describes the production of hydrogen from glycerol is:



The major part of published studies regarding this reaction, is based on noble metal catalysts [2–7] and/or nickel supported over alumina, carbon or modified alumina with cerium, lanthanum, magnesium or zirconium [8,9]. A catalyst for this reaction has to promote the rupture of the C–C bond and the “water gas shift reaction” (WGS). The noble metals (Rh, Pt, Pd) are very active and selective for the reforming reaction; however their employment at large scale is limited by their high costs [2,7,10]. For that reason, nickel based catalysts are widely employed for this kind of process at large scale.

Still, catalysts based on nickel supported over alumina suffer deactivation due to the formation of coke and/or the sintering of the metallic phase, related to the low thermal resistance of γ -Al₂O₃. Thus, the modification of the support by

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basic oxides (MgO, CaO,...) has been proposed by many researchers [11,12].

The aim of this study is to analyse the effect of the calcination temperature of the modified support and the calcination temperature of the catalyst, on the activity and selectivity of Ni/ γ -Al₂O₃ catalysts modified with Mg in the steam reforming of glycerol.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by the incipient wetness impregnation method. For this purpose aqueous solution of Mg(NO₃)₂·6H₂O (99% Merck) and Ni(NO₃)₂·6H₂O (99% Merck) were prepared and γ -Al₂O₃ (Rhône Poulenc) was used. First the γ -Al₂O₃ was impregnated with 3% of Mg; the samples were dried in a muffle at 120 °C for 6 h, followed by the precalcination at different temperatures (350 °C, 600 °C and 900 °C) with a rate of 10 °C/min, maintaining the precalcination temperature for another 6 h in the same muffle. Regarding the impregnation with Ni, a content of 10% was fixed; after impregnation the catalysts were dried also at 120 °C for 6 h and then calcined at different temperatures (500 °C, 700 °C and 800 °C) for 6 h in the mentioned muffle.

2.2. Characterization

The catalysts were characterized by x-ray diffraction (DRX), surface area (BET) and temperature programmed reduction (TPR).

The characterization by DRX was performed in Siemens D 5000 equipment, with Cu K α radiation. BET surface area was obtained in Micromeritics ASAP 2020 equipment.

Temperature programmed reduction (TPR) of the catalysts were carried out in Micromeritics (Autochem II, 2920) equipment, with a thermic conductivity detector (TCD). The catalyst (100 mg) was placed in a quartz U-shaped tube reactor. Previously to the temperature programmed reduction, the samples were pretreated under a flow of Ar (50 mL/min) at 300 °C for 1 h. During the TPR technique, the samples were heated from 50 °C, at a rate of 5 °C/min, to 1000 °C under a flow of 100 ml/min of a mixture 2% H₂/Ar.

2.3. Catalytic tests

The catalytic test were carried out in a stainless-steel continuous flow fixed bed reactor (\square : Reactor diameter = 12 mm) at atmospheric pressure in an electrical furnace equipped with temperature controllers. All the catalysts were compared at a fixed contact time (defined on base of glycerol molar flow) of 3.09 g_{cat} h/mol_{glycerol} at 600 °C; with a water to glycerol molar ratio ($R = n_{H_2O}/n_{C_3H_8O_3}$) of 9:1 and a molar fraction of glycerol in the feed of 2%. For all the catalytic tests, 45.5 mg of catalysts were used, diluted with an inert material in a ratio 10:1. In addition, catalysts were reduced in situ under a flow of 100 ml/min of pure hydrogen with a heating ramp of 10 °C/min to reach 700 °C, keeping this temperature for 1 h.

The liquid mixture of water and glycerol was feed to the reactor by a syringe pump (APEMA PC 11U) and the liquid mixture was vaporized in the first third of the reactor. Regarding the carrier gas (Ar) and the reference gas (N₂) they were both fed to the reactor by mass flow controllers (Aalborg AFC).

Moreover, in order to minimize mass transfer effects and ensure chemical control catalysts particle size was between 44 μ m < dp < 125 μ m and total feed flow was higher than 200 ml/min.

The gaseous products were analysed on-line by TCD and FID detectors. Regarding liquid phase products, this stream was condensed during the reaction time and then analysed after 4 h of reaction. To determined N₂, H₂, CO, CO₂ and CH₄ CarboxenTM 1010 Plot (30 m \times 0.530 mm) column was employed; while a CP-PoraBOND Q (10 m \times 0.32 mm) column was used for the liquid feed mixture and for the condensed mixture during reaction.

In order to analyse the kinetics results, the following parameters were considered:

- Glycerol global conversion: $x_T(\%) = \frac{F_{gli}^e - F_{gli}^s}{F_{gli}^e} 100$
- Glycerol conversion to gaseous products: $x_G(\%) = \frac{F_{CO_2} + F_{CO} + F_{CH_4}}{3 \cdot F_{gli}^e} 100$
- H₂ yield: $Y_{H_2} = \frac{F_{H_2}}{F_{gli}^e}$

3. Results and discussion

3.1. Calcination temperature of the modified support

The results were obtained for the catalysts with 10 wt.% Ni supported over modified γ -Al₂O₃ with 3 wt.% Mg. The modified supported was calcined at different temperatures: 350 °C, 600 °C and 900 °C previously to impregnation with Ni; while the catalysts was calcined at 500 °C as explained above.

Fig. 1, shows the DRX patterns for the modified supports calcined at 350 °C and 900 °C. The reflections observed in the DRX of the support calcined at 900 °C are characteristic of the MgAl₂O₄ spinel formation [12], whereas for the support calcined at 350 °C the DRX pattern is similar to γ -Al₂O₃ pattern.

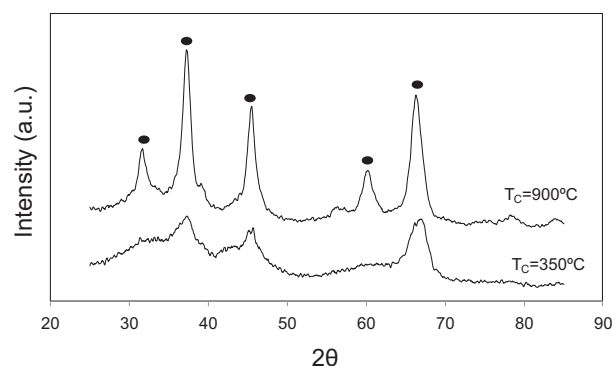


Fig. 1 – DRX pattern for the supports Mg calcined at 350 °C and 900 °C. (●) MgAl₂O₄.

The characteristic reflections observed for the support calcined at 900 °C; might be attributed to a strong interaction between Mg and alumina related to the high calcination temperature; in agreement with the results published by Takehira et al. [13].

The DRX patterns for the catalysts with the supports calcined at different temperatures (350 °C and 900 °C) are presented in Fig. 2, for the catalyst with the support calcined at 900 °C the characteristic reflections of MgAl_2O_4 are observed. Besides, reflections at $2\theta = 43$ and 62° are observed which might be assigned to the presence of NiO [12] and not to MgO since its characteristic reflections were not observed in the DRX pattern of the support. Concerning the catalyst with the support calcined at 350 °C, no significant changes in the DRX were observed comparing it with the support DRX pattern.

The TPR patterns for the fresh catalysts with the support calcined at different temperatures are exposed in Fig. 3. A significant decrease in the reduction temperature of the catalyst was observed as the calcination temperature of the modified support was increased. For the catalyst with the support calcined at 350 °C the average reduction temperature was 733 °C; while for the support calcinated at 900 °C the average reduction temperature was only 536 °C. The corresponding reduction peaks for the catalyst with support calcined at 350 °C and 600 °C were attributed mainly to the reduction of the non-stoichiometric NiAl_xO_y spinel [12,14]. Concerning the catalyst with the support calcined at 900 °C the reduction peak could be deconvoluted into three components at reduction temperature of 380 °C, 536 °C attributed to free ONi and ONi with weak interaction with alumina ($\text{NiO-Al}_2\text{O}_3$) [11,12], and a minor contribution at 753 °C which can be assigned to the reduction of the non-stoichiometric NiAl_xO_y spinel.

Regarding the kinetics results, the obtained yields to H_2 over the catalysts prepared with supports calcinated at different temperatures, were compared (Fig. 4). The results of catalytic activity shown that the higher yield to H_2 was obtained for the catalyst which support had been calcined at higher temperature ($Y_{\text{H}_2} = 4.8$ for the catalyst with the support calcined at 900 °C). In Tables 1 and 2 additional kinetics results are shown as a function of the support calcination temperature. A complete conversion of glycerol was only achieved

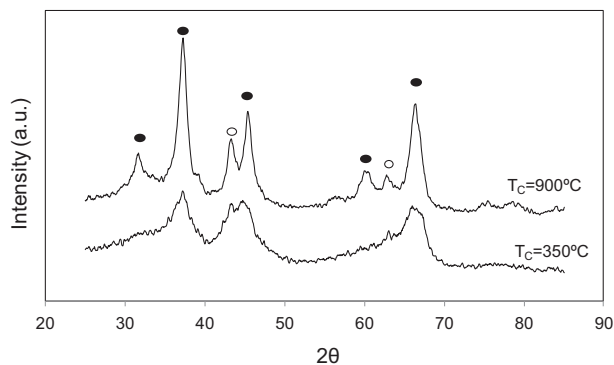


Fig. 2 – DRX pattern for $\text{Ni}(10)\text{Mg}(3)\gamma\text{-Al}_2\text{O}_3$. Different calcination temperatures of the support: 350 °C and 900 °C. (●) MgAl_2O_4 . (○) NiO.

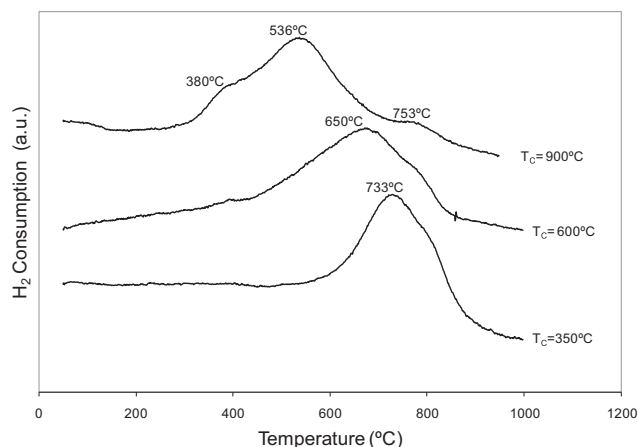


Fig. 3 – TPR profile $\text{Ni}(10)\text{Mg}(3)\gamma\text{-Al}_2\text{O}_3$. Different calcination temperatures of the support: 350 °C, 600 °C y 900 °C.

when support calcination temperature was higher than 600 °C, whereas regarding glycerol, conversion to gaseous products only for the catalyst with the support calcined at 900 °C was possible to achieve conversions near 80%. Therefore, it might be concluded that as high the calcination temperature of the support is, lower is the interaction between the active phase and the support.

In Table 1, the BET surface areas are shown. It could be appreciated that the surface area decreases considerably when the support is calcinated at 900 °C. Nevertheless this diminution does not determine the kinetic behaviour.

3.2. Calcination temperature of the catalysts

In order to analyse the effect of catalysts calcination temperature, different temperatures were considered: 500 °C, 700 °C and 800 °C, keeping constant the calcination temperature of the support at 900 °C (bearing in mind the previous results). The DRX patterns for the catalyst calcinated at different temperatures are presented in Fig. 5. For the three samples the characteristic reflection of the MgAl_2O_4 spinel were observed [12]. Only for the catalyst calcinated at 500 °C, reflections attributable to NiO were detected. In particular, for the catalyst calcinated at 800 °C, the intensity of the reflections corresponding to MgAl_2O_4 spinel was higher compared

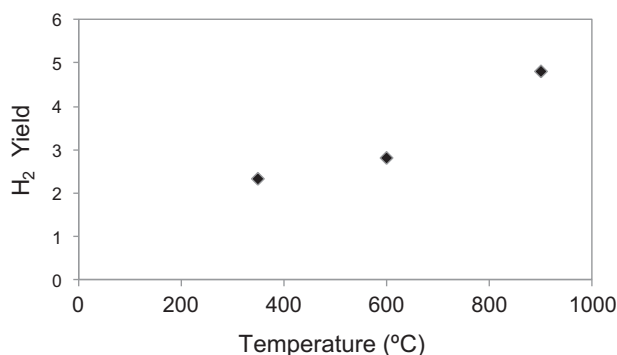


Fig. 4 – Yield to H_2 as a function of the calcination temperature of the support. $\text{Ni}(10)\text{Mg}(3)\gamma\text{-Al}_2\text{O}_3$.

Table 1 – Kinetics results for the steam reforming the glycerol over Ni(10)Mg(3)Al₂O₃ catalysts with the modified support calcined at different temperatures.

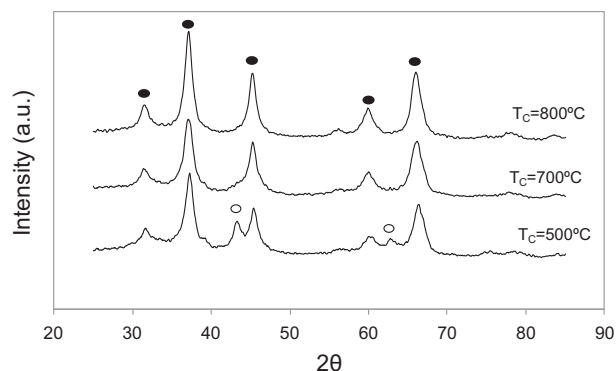
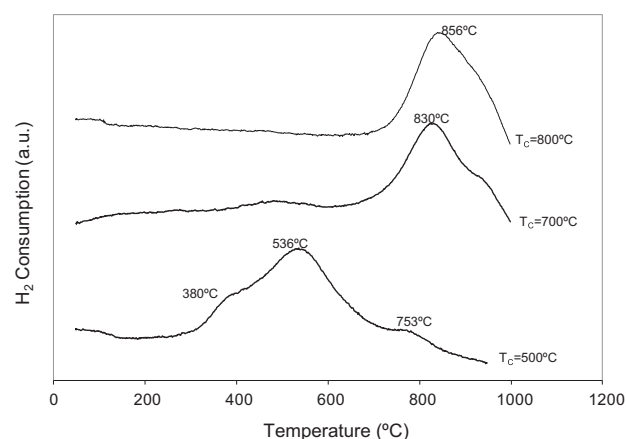
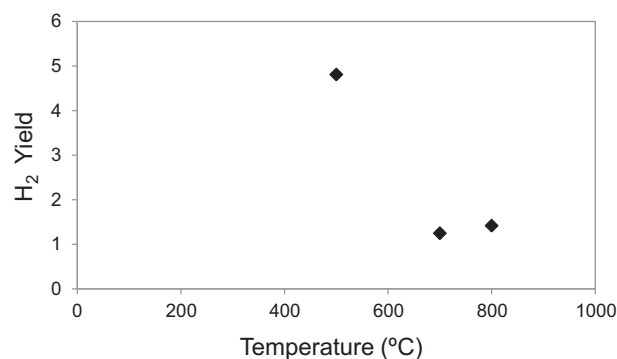
Support calcination temperature (°C)	Glycerol global conversion. x_T (%)	Glycerol conversion to gaseous products. x_G (%)
350 °C	75.32	40.92
600 °C	94.72	49.57
900 °C	91.23	79.28

Table 2 – Area BET for Al₂O₃ calcined at 350 °C and 900 °C, modified support (Mg(3)Al₂O₃) and catalyst (Ni(10)Mg(3)Al₂O₃) calcined at 900 °C.

	Support calcination temperature (°C)	BET area (m ² /g)
Al ₂ O ₃	350	247
Al ₂ O ₃	900	122
Mg(3) Al ₂ O ₃	900	89
Ni(10)Mg(3) Al ₂ O ₃	900	82

with the DRX pattern of the calcined support. As it is known the overlapping between the reflections corresponding to MgAl₂O₄ and NiAl₂O₄; it could be assumed that the intensity increment was due to the formation of NiAl₂O₄. Thus it might be concluded from these results that a higher calcination temperature for the catalyst favours a stronger interaction between the active phase and the support.

The TPR profiles obtained for the catalysts calcined at different temperatures (Fig. 6) are compatible with the DRX pattern obtained. For both catalysts, that calcinated at 800 °C and the one calcinated at 700 °C, the reduction temperatures resulted 856 °C and 830 °C respectively; being the predominant specie the NiAl₂O₄ spinel [11,12]. The catalyst calcined at 500 °C, has a markedly lower reduction temperature, with a temperature for the main peak of 536 °C. As explained above the broad reduction profile of this catalyst might be attributed to the contribution of three species, ONi which reduces at 380 °C, NiO weakly interacting with the alumina and a minor contribution of the non-stoichiometric NiAl_xO_y spinel.

**Fig. 5 – DRX pattern for Ni(10)Mg(3)γ-Al₂O₃. Different calcination temperatures of the catalysts: 500 °C, 700 °C y 800 °C. (●) MgAl₂O₄ or NiAl₂O₄. (○) NiO.****Fig. 6 – TPR profile of Ni(10)Mg(3)γ-Al₂O₃. Different calcination temperatures of the catalyst: 500 °C, 700 °C y 800 °C.****Fig. 7 – Yield to H₂ as a function of the calcination temperature of the catalyst. Ni(10)Mg(3)γ-Al₂O₃.**

On regard to the catalytic results, again the yields to H₂ (Fig. 7) obtained with the catalysts calcinated at different temperatures were compared. The higher catalytic activity observed for the catalyst calcined at the lower temperature (500 °C) might be explained by the presence of NiO with weak interaction with the support; whereas poor performance shown by the others catalysts might be attributed to the formation of the inactive NiAl₂O₄ spinel [12]. Further kinetic results are presented in Table 3. As can be concluded from the results, the catalyst calcined at 500 °C was the more selective

Table 3 – Kinetics results for the steam reforming the glycerol over Ni(10)Mg(3)Al₂O₃ catalysts calcined at different temperatures.

Catalyst calcination temperature (°C)	Glycerol global conversion. x_T (%)	Glycerol conversion to gaseous products. x_G (%)
500 °C	91.23%	79.28%
700 °C	73.06%	23.36%
800 °C	78.41%	27.94%

for the steam reforming of glycerol since the obtained conversion to gaseous products was almost equal to glycerol global conversion. On the other hand, when calcination temperature increased, selectivity for steam reforming of glycerol abruptly decreased, what is reflected in the low conversions to gaseous products even though global conversion was almost complete.

Considering the exposed results, it could be concluded that a high calcination temperature of the catalyst favours a stronger interaction between the active phase and the support by the formation of inactive species such as the NiAl_2O_4 spinel [12].

4. Conclusions

The following variables for the preparation of catalysts, by incipient wetness impregnation method, were considered in this work: calcination temperature of the modified support, and calcination temperature of the catalyst. The comparison between the catalysts was based on the structural and reducing characteristic of the solids. In addition its incidence over the catalytic activity for the steam reforming of glycerol was analysed.

Between the main results, it was concluded that a higher calcination temperature of the modified support generates weaker interaction between it and the metallic phase (Ni°), increasing the metallic dispersion and thus the catalytic activity. This behaviour is attributable to the formation of the MgAl_2O_4 spinel that improves the dispersion of NiO on the support.

On regard to the catalyst calcination temperature, higher calcination temperature favours the formation of the NiAl_2O_4 spinel, which diminished the contribution of exposed metallic Ni and therefore the catalytic activity. The higher hydrogen yield was obtained over the catalyst calcined at 500°C ; this might be explained by the presence of NiO with weak interaction with the support.

Consequently, in order to prepare a catalyst active and selective for the steam reforming of glycerol; it is recommended to employed high calcination temperatures for the modified support, and low calcination temperature of the catalyst.

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