

Article

Influence of Catalytic Support on Hydrogen Production from Glycerol Steam Reforming

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Abstract

The use of hydrogen as an energy carrier represents a promising alternative for mitigating climate change. However, its practical application requires achieving a high degree of purity throughout the production process. In this study, the influence of the type of catalytic support on H₂ production via steam glycerol reforming was evaluated, with the objective of obtaining syngas with the highest possible H₂ concentration. Three types of support were analyzed: two natural materials (zeolite and dolomite) and one metal oxide, alumina. Alumina and dolomite were coated with Ni at different loadings, while zeolite was only evaluated without Ni. Reforming experiments were carried out at a constant temperature of 850 °C, with continuous monitoring of H₂, CO₂, CO, and CH₄ concentrations. The results showed that zeolite yielded the lowest H₂ concentration (51%), mainly due to amorphization at high temperatures and the limited effectiveness of physical adsorption processes. In contrast, alumina and dolomite achieved H₂ purities of around 70%, which increased with Ni loading. The improvement was particularly significant in dolomite, owing to its higher porosity and the recarbonation processes of CaO, enabling H₂ purities of up to 90%.

Keywords: catalytic reforming; alumina; dolomite; zeolite; Ni; H₂ purity



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1. Introduction

Historically, fossil fuels have dominated the global energy matrix. Although significant advances have been made in the development of renewable energies, hydrocarbons continue to be the main source of primary energy. Currently, according to data provided by the Energy Institute [1], more than 60% of global electricity is generated from fossil fuels, with coal being the main contributor, with a share of 35%. Obtaining energy from these fuels generates significant pollution due to emissions of nitrogen oxides, sulfur dioxide, greenhouse gases, and particulate matter. These pollutants contribute to climate change, ocean acidification, and air quality degradation, with serious economic and environmental consequences.

In this context, the United Nations Framework Convention on Climate Change (UNFCCC), held in Glasgow (COP26), marked a milestone in the global effort to decarbonize and limit global warming. To this end, renewable energies such as hydroelectric, wind, and solar power are presented as crucial alternatives for a sustainable energy future, as their inexhaustible nature and absence of polluting emissions make them key elements of

the energy transition. However, the variability in its production requires coexistence with conventional energy sources to guarantee supply. That is why H_2 is emerging as an energy carrier with great potential to contribute to reducing the carbon footprint by providing secure, competitive, and CO_2 -free energy.

The versatility of hydrogen allows it to be used in both internal combustion engines and fuel cells, generating only water vapor. Despite the promising potential, large-scale implementation of H_2 faces challenges such as high production costs, the need for specific infrastructure, and the requirement for high purity. Currently, H_2 can be produced from various renewable and non-renewable sources—such as water, natural gas, methane, ethanol, and glycerol—using different processes, including electrolysis, gasification, partial oxidation, autothermal reforming, dark fermentation, and steam reforming [2,3]. Other routes have also been explored, including photocatalysis, which harnesses solar energy to produce H_2 with excellent purity [4,5].

With the growing global emphasis on sustainability and the circular economy, the use of inexhaustible resources such as seawater in electrolysis processes [6,7] or by-products from other industries, such as glycerin for use in steam reforming processes [8,9], are becoming promising options for hydrogen production. However, it is necessary to ensure the quality of the H_2 produced, particularly its purity. The presence of contaminants such as carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and sulfur-containing compounds, often generated in many of the current hydrogen production processes, such as steam reforming, the most widely used among the production techniques [3,10], can seriously affect the subsequent use of this energy carrier. This underscores the critical role of purification in the hydrogen production chain to meet the high purity standards required for various hydrogen applications. In this context, hydrogen carriers have recently gained attention as an alternative route, since they allow the selective release of hydrogen streams with negligible CO content [11–13].

There are different ways to improve the purity of hydrogen before its final application. One of them is based on increasing the purity of the gas during the production process using different types of catalysts [14,15]. The choice of catalyst plays a decisive role in determining the effectiveness of the steam reforming process, since it should have the capacity to promote the cleavage of C–C, O–H, and C–H bonds and inhibit the formation of the C–O bonds. Furthermore, it should promote the shift of CO to CO_2 , as well as promote dehydrogenation and hydrogenation processes.

A wide range of studies have explored the application of various catalysts, spanning from noble metals such as Pt [16], Pd [17], Ir [18], Rh [19], and Ru [20] to non-noble metals like Ni [21] and Co [22]. Pt-based catalysts have been reported to reach H_2 selectivities above 90% in glycerol reforming at moderate temperatures [23], while Ru/ Al_2O_3 can achieve H_2 yields of 95% with high stability for the steam reforming of ethanol, with methane being the only byproduct [24]. Noble metals, such as Au and Ag, have occasionally been tested, but their application has been mostly limited to photocatalytic systems and remains scarce in thermal catalytic reforming [25,26]. While noble metal catalysts (e.g., Pt, Ru, Rh) typically exhibit higher activity and stronger resistance to coke formation compared to their non-noble counterparts [27] (an important parameter that causes the deactivation of the catalyst), their high cost limits their practicality for large-scale industrial use. Among the non-noble metals, Ni-based systems typically produce H_2 yields in the range of 60–75% with lower purity due to the formation of CO and CH_4 [28], and Cu-based catalysts show moderate activity with faster deactivation than Ni due to sintering and coke deposition [29–31]. Recent studies have also investigated other non-noble metal catalysts as cost-effective alternatives, reporting promising activity and selectivity in reforming reactions like zinc and indium [32,33].

Unlike the noble metal catalysts, the use of Ni as a catalyst improves the reforming process at an affordable production cost [34], allowing it to be subsequently extrapolated to industrial applications. For this reason, Ni is the most widely used commercial catalyst, especially on Al₂O₃ catalytic supports [9,35]. However, as previously reported in [21,35], Ni-based catalysts are prone to carbon deposition and metal particle sintering, phenomena that inevitably result in their gradual deactivation [36]. To improve the stability of Ni catalysts, their performance has been investigated on different types of supports, particularly various metal oxides (e.g., Al₂O₃, SiO₂, La₂O₃, CeO₂, ZrO₂) [23,37,38], which may even be doped with transition metals (e.g., Fe, Co, Sn) [39,40], noble metals (e.g., Ag, Pt, Pd, Ir) [41,42], lanthanide metals (e.g., La, Ce, Pr) [39,43], and alkaline earth metals (e.g., Mg, Ca, Ba) [39,43].

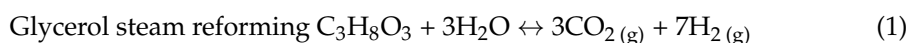
The support material plays an important role in the overall performance of a catalytic system since some physicochemical properties of the support—such as thermal stability at elevated temperatures, surface area (which influences catalyst dispersion), pore size distribution, and the basicity of active sites—strongly affect process efficiency [21]. Soares et al. [44] assessed the gas-phase conversion of glycerol into synthesis gas over supported Pt catalysts at 623 K. Five different supports were evaluated, and they found that Pt supported on Al₂O₃, ZrO₂, CeO₂/ZrO₂, and MgO/ZrO₂ exhibited deactivation during the operating time, while Pt supported on carbon showed stable conversion of glycerol to synthesis gas for at least 30 h. Pompeo et al. [16] evaluated the effect of different supports (specifically SiO₂, ZrO₂, γ -Al₂O₃, and α -Al₂O₃ modified with Ce and Zr) in steam reforming of glycerol using Pt catalysts at temperatures lower than 450 °C. This study found that neutral supports (SiO₂) are better than acidic ones (ZrO₂ and γ -Al₂O₃) for promoting selective hydrogen production and catalyst stability. This is because, as pointed out in [37], greater basicity of the support also leads to CO₂ activation, which helps to oxidize deposited coke to CO and also reduces coke formation from methane decomposition.

Although Ni-based catalysts are widely used in steam reforming, the influence of the support remains a key challenge. Alumina, while common, is prone to deactivation through coke deposition and Ni sintering; dolomite has been less explored despite its favorable porosity and CO₂ capture capacity; zeolites often suffer structural instability at high temperatures. These knowledge gaps highlight the importance of evaluating different supports under identical conditions. Accordingly, the aim of this study is to assess the optimization of the hydrogen production process through a reforming process, comparing the yields obtained by three different supports and a Ni catalyst to increase the purity of the outlet gas mixture before it is introduced into a subsequent purification process. This study will contribute to deeper knowledge of the influence of different catalytic supports, both with and without active catalysts, which were selected considering the cost of the process for a possible scalability of the study to industry.

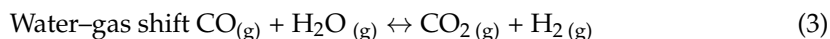
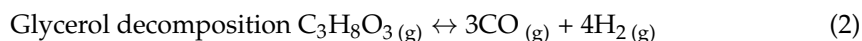
2. Glycerol Reforming Process

Glycerol steam reforming (GSR) is considered a promising alternative for H₂ production [45], as it closely resembles current industrial processes, and as a by-product of other industries, glycerol is readily available and economically viable.

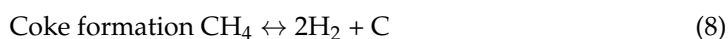
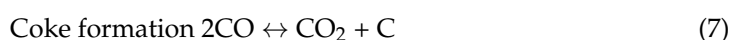
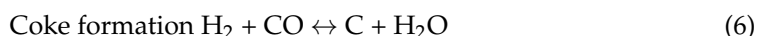
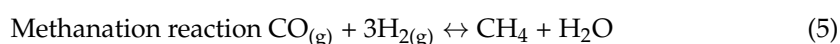
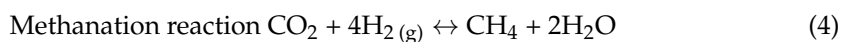
The feasibility of this process has been extensively examined, as glycerol's molecular structure provides a favorable hydrogen-to-carbon ratio, enabling high H₂ yields. According to the overall reaction (Equation (1)), one mole of C₃H₈O₃ can theoretically generate up to seven moles of H₂ (g).



Thus, it is the combination of the following two reactions:



The reaction pathway is highly complex, with several competing processes potentially occurring. In particular, CO_2 and CO hydrogenation can result in methane formation, while secondary reactions such as dehydration, dehydrogenation, cyclization, and polymerization may take place, ultimately contributing to coke deposition [46].



The quantities of H_2 , CO_2 , CO , and CH_4 produced, as well as the C formation, depend on reaction conditions such as concentration of glycerol, supply flow rate, temperature, and the pressure of the reaction.

3. Materials and Methods

Glycerol steam reforming tests were carried out in a stainless-steel fixed bed reactor with a total length of 700 mm and an inner diameter of 48 mm, located in a vertical electrical tubular furnace (TR4, Hobersal) capable of heating to 1200°C and connected with a gas analyzer (Mamos, Madur), which allows a continuous measurement of the concentrations of H_2 , CO_2 , CO , and CH_4 (Figure 1, similar setup to that used in [8]).

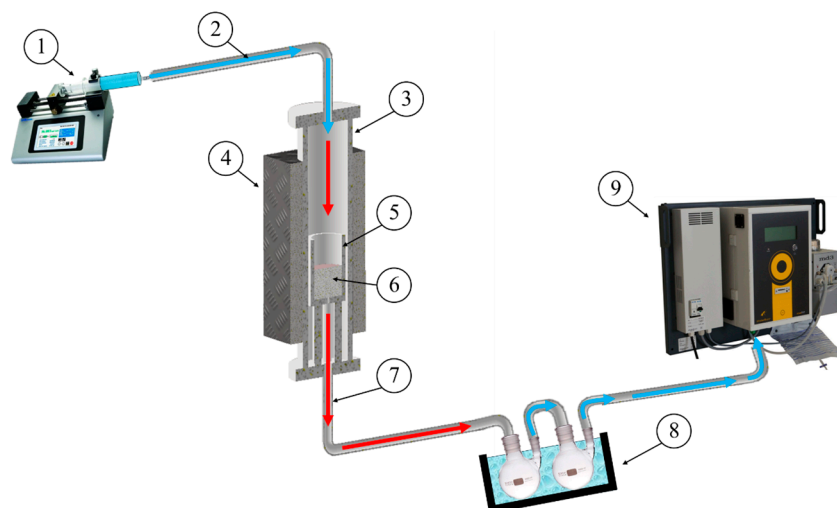


Figure 1. Scheme of the glycerol steam reforming system: syringe pump (1), glycerol flow (2), cylindrical reactor (3), electrical tubular furnace (4), perforated cylinder bucket (5), catalyst support as fixed bed (6), syngas (7), condensate tank (8), and gas analyzer (9).

Glycerol was supplied to the top of the reactor using a syringe pump with a feed rate set at 0.855 mL/min , which is the optimal value using this setup, according to [8], to maximize the production and purity of the hydrogen generated. This parameter was kept constant in order to compare the influence of different supports under identical conditions, rather than to re-optimize the operating point for each catalyst.

The tubular reactor houses a perforated bucket where the support is placed up to a fixed bed height (in this case, 4 cm), so that the glycerol must flow through the bed until it reaches the lower outlet of the reactor. After leaving the reactor, the gaseous products were condensed in a thermostatic bath, and the resulting dry gas was sent to the gas analyzer, where both its composition and flow rate were measured.

Prior to initiating the glycerol reforming process, a catalyst support conditioning step was performed. This procedure involved the activation of the Ni catalyst by heating the reactor to 700 °C at a rate of 10 °C/min. Once the target temperature of 700 °C was reached, it was maintained for 30 min while a gas mixture of H₂ and N₂ (50:50 vol.%) was introduced. After this period, only N₂ was supplied, which was maintained until all residual gases were purged from the reactor and the test temperature of 850 °C was achieved. This process was carried out both in the tests where the supports were impregnated with Ni and in those where only the support was used without impregnation.

In this study, three types of supports were assessed: one an oxide metallic (porous γ -Al₂O₃) usually used in steam reforming processes, and two natural porous materials (dolomite and zeolite).

The alumina used was γ -alumina, which is suitable for high-temperature applications. This alumina had a diameter of approximately 0.5 cm, an apparent porosity of around 7%, and a water absorption capacity of around 3%. As reported in several studies, this support is characterized by a high specific surface area, which promotes effective metal dispersion [47]. However, at elevated temperatures, it undergoes phase transformations, sintering, and a consequent loss of surface area [34]. In all catalytic tests with alumina as support, a total of 43 g of material was used.

The zeolite employed was clinoptilolite (Ca,Na,K)₆(Si₃₀Al₆)O₇₂·20H₂O, supplied by Zeopol, with an average grain size of 0.6 cm. Zeolites are crystalline aluminosilicates characterized by a three-dimensional framework of SiO₄ and AlO₄ tetrahedra. Owing to their high specific surface area and the selective capture of impurities such as CO₂, they are commonly used in subsequent hydrogen purification processes by physisorption [48–50], thereby yielding purified hydrogen. However, several studies also report their application as catalytic supports during high-temperature hydrogen production. Yao et al. [51] evaluated different reforming temperatures (650, 750, and 850 °C) using Ni with zeolite as the catalyst for hydrogen production. They found that the optimal operation temperature was 850 °C. In the zeolite tests, 47 g of support was used in each experiment.

Dolomite is a double carbonate of Ca and Mg (CaMg(CO₃)₂) that decomposes into its respective oxides as temperature increases (in this case, after calcination, 57% CaO and 37% MgO). MgO is formed at around 500 °C, while CaO is generated at higher temperatures (800–900 °C), so a partial decomposition of CaO and complete decomposition of MgO was expected under the operation conditions of the test (i.e., 850 °C) [52,53]. This material has been widely applied for H₂ purification through the chemisorption of impurities, primarily carbon dioxide (CO₂). However, several studies have also explored its use as a catalytic support during H₂ production. Zhang et al. [54] reported that NiO-impregnated dolomite, when employed as a reactor bed in high-temperature steam gasification of biomass, enhanced H₂ yield. Similarly, Gallucci et al. [55] demonstrated the effectiveness of dolomite as a CO₂ sorbent in steam gasification processes, attributing its performance to CaO recarbonation at approximately 800 °C, a temperature comparable to that used in the present study. In the experiments with dolomite as support, 42 g of material were employed.

Each of the three supports exhibited a different degree of basicity. Alumina is amphoteric, containing both acidic and basic sites, which is why it is generally considered a neutral or slightly acidic support. The acidity of γ -alumina is lower than that of natural zeolites, which, like alumina, possess both Brønsted and Lewis acid sites [56]. Finally, dolomite

is the most basic of the three supports, since upon thermal decomposition it generates alkaline earth oxides (CaO and MgO), both of which are strongly basic.

The impregnation of the support with the Ni catalyst was carried out by the wet impregnation method, because it is a simple, reproducible, and scalable technique that allows for adequate dispersion of Ni species on porous supports. The process involves the following steps: the support was first calcined at 650 °C (heating rate of 10 °C/min) in an air atmosphere for 3 h to remove residual impurities, and in the case of the dolomite, to create active MgO and part of CaO. Once cooled to room temperature, the support was immersed, with continuous stirring, in a nickel-nitrate solution of predetermined concentration for 20 min (two solutions with different concentrations were used, one at 10 wt% and the other at 12 wt%, to obtain two different amounts of Ni deposition). After impregnation, the material was dried in an oven at 110 °C for 2 h, followed by cooling to room temperature. This procedure was repeated by immersing the sample in the nickel-nitrate solution once more to promote the formation of active phases such as nickel oxide (NiO) and to enhance the stability and dispersion of nickel species.

The amount of nickel dry matter that remained on the corresponding support was measured by the gravimetric method according to Equation (9), which is often applied when a consolidant or water repellent is applied to a stone substrate [57–59].

$$\text{Ni dry matter (\%)} = 100 \times (W_f - W_d)/W_d \quad (9)$$

where W_d corresponds with the initial dry weight of the support before the impregnation process, and W_f is the weight of the support after 7 days of drying.

Each support was evaluated in duplicate, both in the absence and presence of the catalyst, with two different Ni loadings. This approach enabled the comparison of the performance of the bare support with that of the Ni-loaded supports, as well as the assessment of the influence of Ni content on the H_2 production process. In all cases, the production temperature was maintained at 850 °C for 40 min, the bed height at 4 cm, and the particle diameter of all supports between 5 and 6 mm.

Mineral phase characterization was performed by X-ray diffraction using a Philips X'Pert Bragg Brentano X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV (generator voltage), 30 mA (tube current) with 0.02° scan step size, 200 s/step of counting time, and a data angle range (2θ) of 5–80°.

The hydrogen production efficiency of the reforming process was determined using the following equation, which compares the average H_2 concentration obtained in the reforming tests with the catalytic support (CS) with those obtained with the nickel-impregnated support (CNi/S).

$$\text{Efficiency (\%)} = 100 \times (\text{CNi/S} - \text{CS})/\text{CS} \quad (10)$$

4. Results and Discussion

4.1. Supports Without Ni

Figure 2 and Table 1 present the concentrations of the main components of the synthesis gas at the reactor outlet for the different supports evaluated—alumina, dolomite, and zeolite—in the absence of Ni impregnation.

The data obtained during the reforming process indicate that dolomite is the support that provides the highest H_2 concentrations, both in terms of maximum and average values throughout the steam reforming process. In addition, this support leads to a significant reduction in CO_2 and CO concentrations compared to the other two supports evaluated. This behavior can be attributed, as reported by Gallucci et al. [55], to the ability of CaO, released at temperatures above 800 °C, to undergo recarbonation to $CaCO_3$ in the presence of CO_2 , which would reduce the concentration of this gas in the environment. This direct

removal of CO₂ by carbonation with CaO promotes the thermodynamic equilibrium of the water–gas shift reaction to the hydrogen production side [10,54]. Moreover, the enhanced CO₂ capture also leads to a reduction in CO content, as this process can shift the CO equilibrium toward higher CO₂ conversions (Equation (7)). This effect may promote greater coke formation, which would explain the increased CH₄ production observed when using this support (Equation (8)).

Table 1. Maximum and average content (in %) of the main compounds contained in the syngas composition using different supports.

Alumina	H ₂	CO ₂	CO	CH ₄
Maximum (%)	70.8	20.8	7.3	7.4
Average (%)	62.0	16.8	5.8	5.7
Dolomite	H ₂	CO ₂	CO	CH ₄
Maximum (%)	71.6	16.6	5.9	9.2
Average (%)	65.1	13.8	4.8	7.7
Zeolite	H ₂	CO ₂	CO	CH ₄
Maximum (%)	54.2	20.9	9.6	8.7
Average (%)	51.0	18.2	7.5	7.4

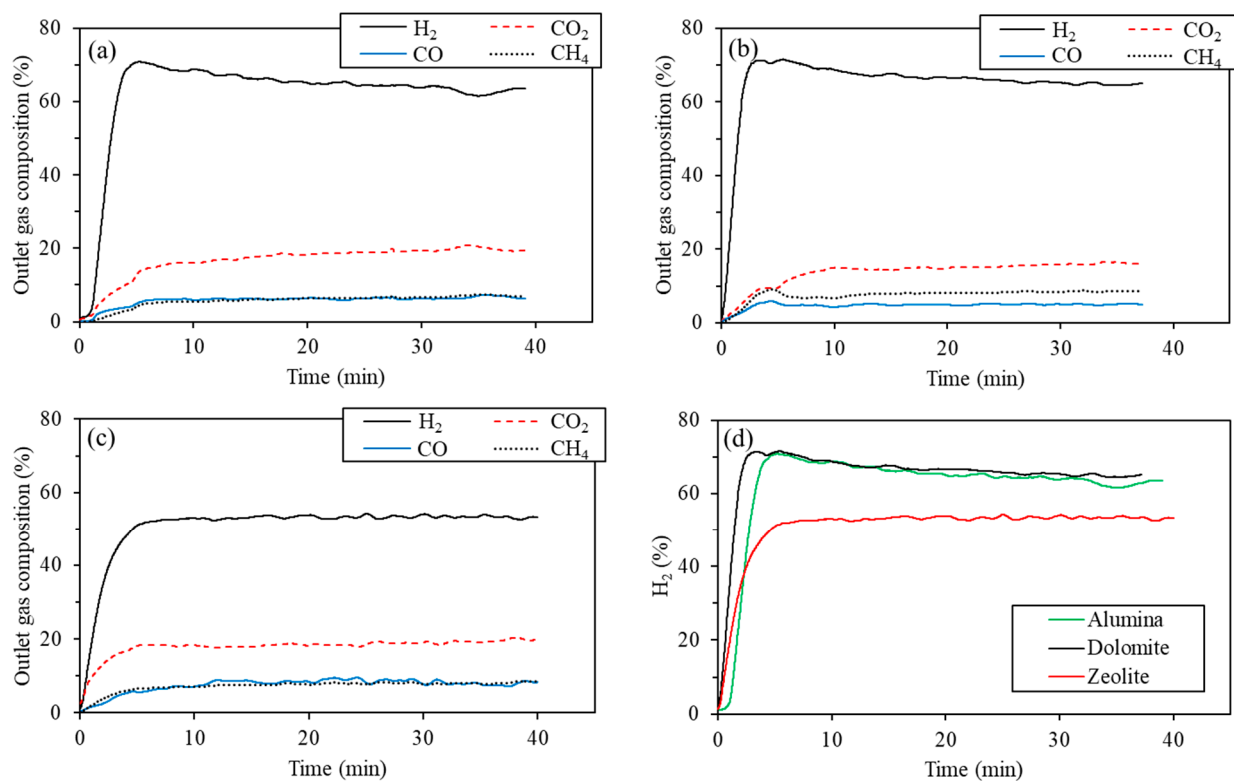


Figure 2. Average concentration of H₂, CO₂, CO, and CH₄ in syngas using different supports (n = 2): alumina (a), dolomite (b), zeolite (c). A comparison between the supports with respect to H₂ concentration (in %) is also shown (d).

The catalytic support that showed the worst performance was zeolite, both in terms of H₂ (with a final concentration of around 50%), CO₂, and CO concentration. This behavior could be attributed to the following: (1) The fact that the primary adsorption mechanism of zeolite is based on physical adsorption processes, whose effectiveness decreases at temperatures above 100 °C as thermal energy disrupts weak physical bonds [60]. The higher acidity of

this support means that CO₂ adsorption occurs through these weak interactions, such as electrostatic forces or hydrogen bonds. At elevated temperatures, chemisorption mechanisms become more dominant, involving the formation of stronger chemical bonds and thus offering better capture performance [60]. (2) The possible collapse of the structure due to the calcination process such as occurred in previous studies [50]. XRD pattern performed on a zeolite sample previously calcined at 800 °C, a temperature 50 °C lower than the operating temperature of the oven, shows a large reduction in peak intensity and an increase in peak broadening compared to the natural zeolite pattern, suggesting a significant loss of crystallinity and amorphization of the samples due to thermal decomposition (Figure 3). This loss of crystallinity and the possible generation of sintering processes, which usually occurs at temperatures higher than 630 °C [61,62], influence the adsorption capacity of the zeolite since they reduce the specific surface area of the material.

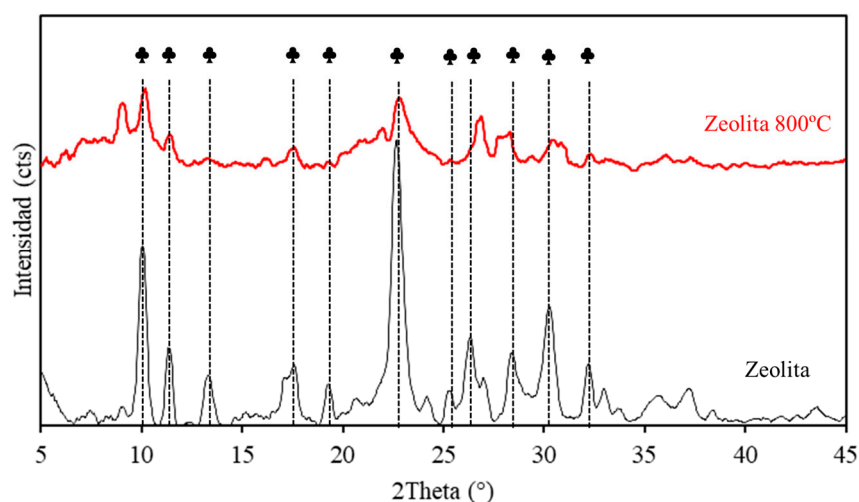


Figure 3. XRD pattern of the natural zeolite (black line) and that calcined at 800 °C (red line). ♣: clinoptilolite (JCPDS card 83-1260).

Due to its low adsorption capacity at elevated temperatures, this adsorbent was excluded from the subsequent stages of the study.

4.2. Supports with Different Concentrations of Ni

Table 2 shows the dry matter percentages for both alumina and dolomite achieved after the wet impregnation process with the two nickel-nitrate solutions at 10 and 12 wt%. It can be observed that, after the impregnation process, dolomite is able to retain a greater amount of nickel. This behavior is attributed to the fact that, as an ornamental rock, dolomite exhibits higher accessible porosity than porous alumina, along with a broader distribution within the mesopore and macropore ranges; both aspects facilitate greater metal deposition and good dispersion throughout the particle. This behavior is consistent with prior reports showing that dolomite supports, due to their basicity and porous structure, facilitate more uniform dispersion and stronger anchoring of Ni species [63]. It is also evident that increasing the concentration of the nitrate solution leads to a greater amount of nickel deposited on the support surface.

Table 2. Dry matter of NiO in each support (in %) obtained with different nickel-nitrate concentrations (10 and 12 wt%).

Ni(NO ₃) ₂ Concentration	10 wt%	12 wt%
Alumina	9%	12%
Dolomite	31%	37%

The results obtained from the reforming test (Figure 4 and Table 3) indicate that the addition of Ni as a catalyst enhances the efficiency of the reforming process, leading to a higher H_2 purity. This effect becomes more pronounced with increasing Ni loading on the alumina support. Furthermore, a higher NiO content results in a lower amount of CH_4 produced. This behavior is associated with the reduced concentrations of CO_2 and CO generated, which otherwise may promote methanation reactions, as described in Section 2 (Equations (4) and (5)).

A notable observation in Figure 4d is that, with lower NiO loads on the Al_2O_3 support, specifically 9 wt%, gradual catalyst deactivation occurs. This deactivation causes a decrease in H_2 purity, which approaches values similar to those obtained with the uncoated support. This observation agrees with previous reports showing that Ni/ Al_2O_3 catalysts are prone to deactivation under reforming conditions. The main causes are coke deposition, sintering of Ni particles, and blockage of active sites, which progressively reduce catalyst activity and H_2 purity during time-on-stream [64]. Similar behavior has been reported in both glycerol and methane reforming systems, where carbon accumulation and structural changes significantly compromise the long-term stability of Ni/ Al_2O_3 catalysts [36].

Regarding the dolomite support (Figure 5), it is again observed that the addition of Ni enhances the reforming efficiency and hydrogen concentration compared with the non-impregnated support. However, beyond a certain Ni loading point (approximately 31 wt%), no significant improvement is observed, indicating a saturation effect in the distribution of active sites. Specifically, at 31 wt% Ni, higher loadings do not justify the additional cost, as the gain in efficiency is negligible.

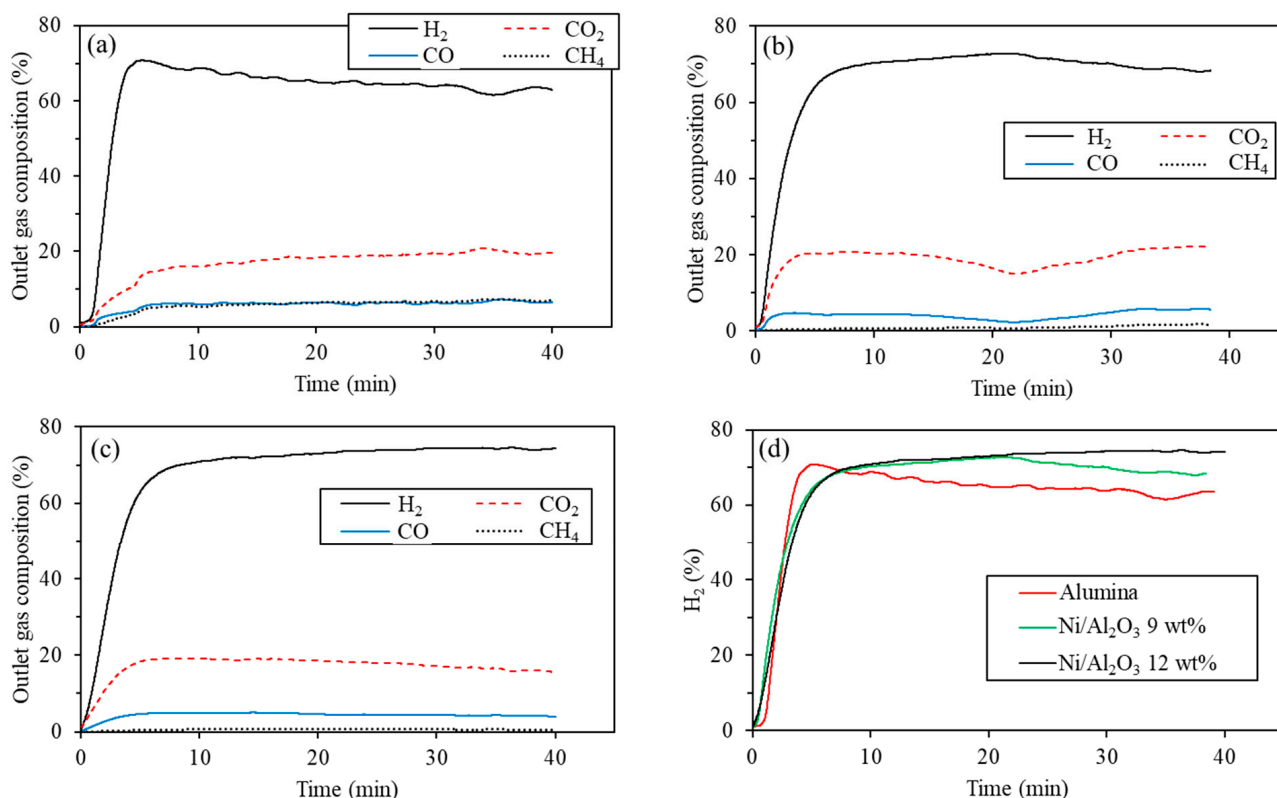
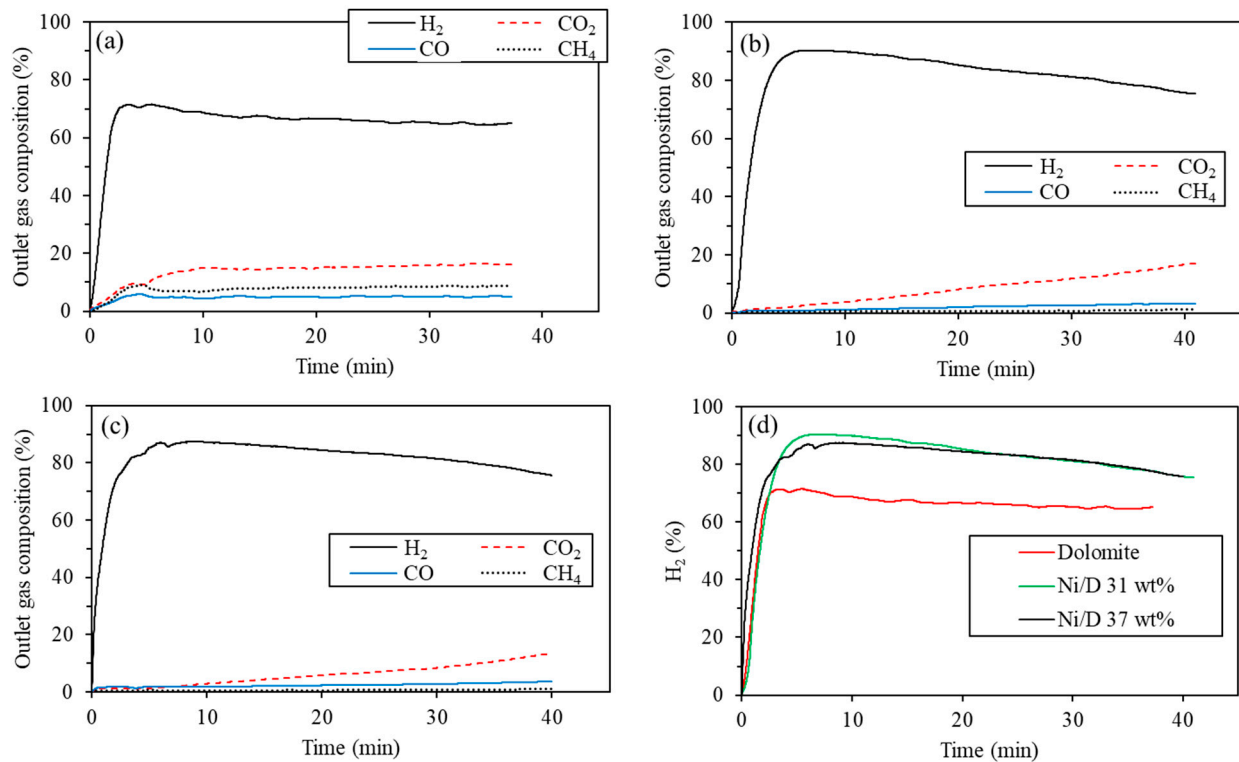


Figure 4. Average concentration of H_2 , CO_2 , CO , and CH_4 in syngas using different alumina supports ($n = 2$): alumina without Ni (a), Ni/ Al_2O_3 9 wt% (b), and Ni/ Al_2O_3 12 wt% (c). A comparison between the three supports with respect to H_2 concentration (in %) is also shown (d).

Table 3. Maximum and average content (in %) of the main compounds contained in the syngas composition using different supports, with and without a catalyst.

Alumina	H ₂	CO ₂	CO	CH ₄
Maximum (%)	70.8	20.8	7.3	7.4
Average (%)	62.0	16.8	5.8	5.7
Ni/Al ₂ O ₃ 9 wt%	H ₂	CO ₂	CO	CH ₄
Maximum (%)	72.8	22.3	5.9	1.8
Average (%)	66.2	18.7	4.1	0.9
Ni/Al ₂ O ₃ 12 wt%	H ₂	CO ₂	CO	CH ₄
Maximum (%)	76.0	19.2	5.0	0.8
Average (%)	70.1	16.4	4.2	0.6
Dolomite	H ₂	CO ₂	CO	CH ₄
Maximum (%)	71.6	16.6	5.9	9.2
Average (%)	65.1	13.8	4.8	7.7
Ni/D 31 wt%	H ₂	CO ₂	CO	CH ₄
Maximum (%)	90.3	16.7	3.3	1.2
Average (%)	81.0	8.0	2.0	0.7
Ni/D 37 wt%	H ₂	CO ₂	CO	CH ₄
Maximum (%)	87.5	13.6	3.6	1.1
Average (%)	81.3	5.9	2.4	0.7

The same thing happens when comparing the other gas concentrations, i.e., CO₂, CO, and CH₄. In all cases, insignificant differences are also obtained.

**Figure 5.** Average concentration of H₂, CO₂, CO, and CH₄ in syngas using different alumina supports (n = 2): dolomite without Ni (a), Ni/D 31 wt% (b), Ni/D 37 wt% (c). A comparison between the three supports with respect to H₂ concentration (in %) is also shown (d).

Comparatively, among the supports evaluated, the highest performance is achieved using dolomite as the support with Ni as the catalyst, reaching efficiencies of approximately 25%, corresponding to an average hydrogen concentration exceeding 80% and a maximum higher than 90% (Table 4). This could be related to (1) the better dispersion of Ni in this support than in Al_2O_3 support due to the presence of both MgO [65] and CaO [66]; (2) the higher content of Ni adsorbed by the support increasing the number of active sites on the catalyst surface, as occurs in [67]; (3) the presence of basic oxides, such as MgO and CaO, able to promote the water–gas shift reaction (Equation (3)), increasing H_2 production [68]; and (4) the different porous structure, since alumina is a support characterized by a larger specific surface area than dolomite due to its smaller pores. The presence of these smaller pores inhibits intra-particle diffusion of reactants and products [23]. Moreover, like what was observed with the nickel-free supports, the concentrations of CO_2 , CO, and CH_4 are lower than those obtained with the alumina support, partly due to the carbonation processes occurring in dolomite and to the higher basicity of this support compared to alumina.

Table 4. Maximum and average hydrogen concentrations, in %, obtained from the reforming processes using alumina and dolomite, both with and without Ni. The efficiency achieved with each support when is coated with Ni is also shown.

Support	Maximum (%)	Average (%)	Efficiency (%)
Alumina	70.8	62.0	-
Ni/ Al_2O_3 9 wt%	72.8	66.2	6.8
Ni/ Al_2O_3 12 wt%	76.0	70.1	13.1
Dolomite	71.6	65.1	-
Ni/D 31 wt%	90.3	81.0	24.4
Ni/D 37 wt%	87.5	81.3	24.9

5. Conclusions

This study demonstrates that the incorporation of Ni significantly improves the reforming efficiency and hydrogen concentration compared with non-impregnated supports. Among the tested materials, zeolite showed the lowest performance and poor thermal stability at high temperature, while alumina exhibited moderate activity with partial deactivation at lower Ni contents. Dolomite, on the other hand, showed the most promising performance due to its higher porosity, greater nickel dispersion, the presence of basic oxides (CaO and MgO) that promote the water–gas shift reaction, and its capacity to capture CO_2 via recarbonation, which shifts the equilibrium toward hydrogen production. However, beyond a certain Ni loading of approximately 31 wt%, no further improvement in efficiency was observed, indicating a saturation effect in the distribution of active sites.

Future work should focus on correlating catalyst structure and performance, optimizing key operating parameters, and exploring Ni-based catalyst modifications to improve stability and coking resistance. Additionally, scale-up tests and preliminary techno-economic assessments under industrially relevant conditions would allow a broader evaluation of dolomite- and alumina-supported catalysts.

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