



Overview of Ni-Based Catalysts for Hydrogen Production from Biogas Reforming

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Abstract: The environmental impact and the forecasted scarcity of fossil fuels have intensified research on renewable energy sources. Hydrogen is a versatile energy carrier that can be produced from renewable sources and plays a key role in achieving global decarbonization targets. Biogas, produced by anaerobic digestion of organic compounds, is rich in methane and carbon dioxide and can be used to produce renewable hydrogen by dry reforming. This review focuses on the recent advances in Ni-based catalysts for biogas reforming. The effect of supports and promoters on catalyst activity, stability, and resistance to carbon deposition will be systematically discussed. This review provides a better understanding of the influence of the synthesis method, metal-support interaction, acid/base sites, and oxygen mobility on catalytic activity. Special emphasis will be given to the development of core-shell structure catalysts and bimetallic catalysts of Ni with other transition metals and noble metals.

Keywords: hydrogen; biogas; reforming; nickel; catalysts

1. Introduction

Interest in renewable energies has increased nowadays due to concerns related to global warming and the depletion of fossil fuel resources. Biogas is considered a sustainable and renewable gaseous fuel because it is produced by the anaerobic digestion of organic compounds. The biomass-derived feedstocks used for biogas production can be seeds, grains, woody crops, agricultural residues, animal manure, sewage sludge, and algae, among others [1].

The worldwide biogas industry has increased by more than 90% between 2010 and 2018, and further growth is still expected [2]. In 2018, 60×10^3 m³ of biogas (35 Mtoe) were produced; Europe (54%) and Asia (30%) were the main producers [3]. The report of the IEA estimates that in 2040, over 260 Mtoe of biogas could be produced worldwide [3].

Biogas is mainly composed of methane (CH₄) (45–75%) and carbon dioxide (CO₂) (25–55%). Other minor components include nitrogen, oxygen, carbon monoxide, hydrogen sulfide, ammonia, aromatics, and siloxanes [1,4–6]. The chemical composition of biogas depends mainly on the origin and quality of the biomass used, the substrate-microorganism relationship, the type of biodigester, and reaction conditions. Typical compositions of raw biogas from different sources are presented in several reviews [1,5–7]. In general, the main impurities are H₂S, which can reach levels of up to 4000 ppm [4,6,7], and siloxanes [8]. It is noteworthy that much less H₂S is contained in raw biogas than in natural gas [7].

Upgrading and purifying technologies are usually necessary to control the level of contaminants, depending on the requirements of biogas utilization. Currently available technologies for removing biogas contaminants include physical and chemical absorption, pressure swing adsorption (PSA), membrane technology, and biological methods [1,5–7].

Almost two-thirds of world biogas production was used to generate electricity and heat; around 30% was consumed in buildings, mainly in the residential sector, for cooking



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and heating, with the remainder upgraded to biomethane and blended into the gas networks or used as a transport fuel [3]. However, biogas has attracted increasing interest as a feedstock to produce high-value-added products, including hydrogen/syngas, methanol, hydrocarbons, and others [1].

Hydrogen is an essential component of a net zero-energy system and has a key role to play in decarbonizing hard-to-abate sectors. The global demand for hydrogen reached 94 Mt in 2021; its market has grown by 6% a year due to the demand from industry (petrochemical, ammonia, and steel) and the transportation sector [9,10]. Almost 96% of H₂ produced worldwide comes from non-renewable sources like natural gas, petroleum, and coal. The technological maturity of H₂ produced from fossil fuels and the available infrastructure, the possibility of carbon capture and storage, and the development of new catalytic materials evidence the renewed interest in reforming technologies [11]. The reforming process is a mature technology for converting natural gas to hydrogen; when biogas is used as feedstock for reforming, the hydrogen produced can be considered renewable and "green".

Biogas is suitable for direct conversion into hydrogen via the dry reforming (DR) reaction because it is rich in CH₄ and CO₂. The great benefit of using DR is the absence of the need to separate CO₂ and add other reactants, such as water and oxygen, as in steam reforming, partial oxidation, or autothermal reforming. Sometimes, a small amount of water and/or oxygen is added to favor the total CH₄ conversion (because the CO_2/CH_4 ratio in biogas is usually lower than 1). Although high concentrations of H₂S and siloxanes may be found in biogas, which can lead to catalyst degradation, current technologies used in biogas processing have shown that these impurities can be significantly reduced or even eliminated [7,8,12,13]. For example, the removal efficiency of H₂S by biological desulphurization reached 100% under optimal conditions [14]. Thus, impurities in biogas are not considered significant concerns during biogas DR [8].

The main goal of this manuscript is to highlight the developments and progress in the dry reforming of biogas, focusing on the Ni-based catalysts used in this reaction. The focus of this review is on model biogas containing only CH_4 and CO_2 ; the influence of contaminants will not be evaluated. The effect of supports and promoters on catalyst activity and stability is extensively discussed, as are catalysts with a core-shell structure and bimetallic catalysts. Since catalyst deactivation is the major problem in the dry reforming process, the catalyst's resistance to coking is also investigated. In the end, we draw conclusions and prospects for further research on hydrogen production from biogas.

2. Reactions Involved in Biogas Reforming

The main reaction in biogas reforming is the dry reforming of methane (DRM), where CH₄ and CO₂ are converted to syngas (a mixture of H₂ and CO), as shown in Equation (1). This is a highly endothermic reaction that requires temperatures ranging between 700 and 900 °C and a CO₂/CH₄ molar ratio between 1 and 1.5 [1,4].

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO, \ \Delta H^0_{298K} = 248 \text{kJmol}^{-1} \tag{1}$$

A typical side reaction is the reverse water-gas shift (RWGS) (Equation (2)), which leads to a higher conversion of CO_2 than CH_4 and reduces the H_2/CO ratio in the syngas [1,15].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \ \Delta H_{298K}^0 = 41 \text{kJmol}^{-1}$$
(2)

In biogas, the CH₄ content is usually higher than that of CO₂. The CO₂/CH₄ ratio close to the unit, necessary for DR, can be adjusted by combusting an adequate quantity of biogas and introducing flue gas into the feed [16]. Another option to achieve total CH₄ conversion when using biogas is the addition of water or oxygen, promoting steam reforming (Equation (3)) or partial oxidation (Equation (4)).

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO, \ \Delta H^0_{298K} = 206 \text{kJmol}^{-1}$$
 (3)

$$CH_4 + 1/2O_2 \rightleftharpoons 2H_2 + CO, \ \Delta H^0_{298K} = -38 \text{kJmol}^{-1}$$
 (4)

The main problem of DRM is the great tendency towards coke formation, which can be formed by methane decomposition (Equation (5)), CO disproportionation (Boudouard reaction) (Equation (6)), and hydrogenation of carbon oxides (Equations (7) and (8)). Among these reactions, only methane decomposition is favored at high temperatures, while the others are favored when operating at lower reaction temperatures (<527 °C) [17,18].

$$CH_4 \approx 2H_2 + C, \ \Delta H^0_{298K} = 75 \text{kJmol}^{-1}$$
(5)

$$2CO \rightleftharpoons CO_2 + C, \ \Delta H^0_{298K} = -172 \text{kJmol}^{-1} \tag{6}$$

$$\mathrm{CO} + \mathrm{H}_2 \rightleftharpoons \mathrm{C} + \mathrm{H}_2\mathrm{O}, \ \Delta\mathrm{H}_{298K}^0 = -131 \mathrm{kJmol}^{-1}$$
(7)

$$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O, \Delta H^0_{298K} = -90 k Jmol^{-1}$$
 (8)

Thermodynamic equilibrium analysis of the DRM and side reactions was performed by Jang et al. [19] using total Gibbs free energy minimization. The CH₄ decomposition (Equation (5)) is favored at high temperatures, but a significant amount of coke formation was observed at low temperatures (Figure 1a). The Boudouard reaction (Equation (6)) is favored at low temperatures and does not occur above 900 °C (Figure 1b). For DRM (Equation (1)), the coke is formed preferentially at low temperatures (Figure 1c), where there is a contribution from both CH₄ decomposition and the Boudouard reaction.



Figure 1. Carbon-containing products for the various reactions: (a) CH_4 decomposition ($CH_4 = 100\%$), (b) Boudouard reaction (CO = 100%), (c) reforming of CH_4 with CO_2 ($CH_4 = 50\%$ and $CO_2 = 50\%$). Reprinted with permission from Ref. [19].

Carbon formation decreases with an increasing CO_2/CH_4 ratio at a constant temperature because CH_4 becomes a limiting reactant and the amount of H_2 available for reactions 7 and 8 is smaller [17]. The tendency for coke deposition is also related to carbon, hydrogen, and oxygen ratios in the feed gas. Lower O/C and H/C ratios lead to higher coke formation. Thus, coke deposition is more likely to occur in DR than steam reforming and partial oxidation [20]. In biogas reforming, adding water and/or oxygen helps decrease coke formation.

Different kinds of carbon that vary in morphology and reactivity are formed during DRM, depending on the reaction temperature. CO and CH₄ dissociate on metals to produce adsorbed atomic carbon (C_{α}), which can form a polymeric carbon film (C_{β}) at low temperatures (<375 °C). At high temperatures (>650 °C), these amorphous forms of carbon are converted to less active graphitic carbon (C_{γ} , C_c), which can encapsulate the metal surface, causing a severe deactivation of the catalyst [21,22]. In the intermediate temperature range (375–650 °C), the precipitation of dissolved carbon at the rear side of metal crystallites leads to the formation of carbon filaments (C_v) [21]. The graphitic forms of carbon (C_{γ} , C_c , C_v) are more difficult to remove from the catalyst surface by oxidation than the amorphous carbon, requiring higher temperatures (in general, >500 °C) [23,24].

3. Ni-Based Catalysts for Biogas Dry Reforming

Transition metals (including Ni, Fe, and Co) and noble metals (including Pt, Pd, Rh, Ru, and Ir) have been investigated as catalysts for biogas reforming. Catalysts based on noble metals usually have higher activity and greater resistance to coke formation; however, their low availability and high cost limit their applicability. In one of the first studies comparing different metal catalysts for DRM, Rostrup–Nielsen and Hansen [25] found the following activity order (the metals were supported on MgO-stabilized Al₂O₃): Ru > Rh, Ni > Ir > Pt > Pd, at 500 and 650 °C, while the order for carbon formation was Ni > Pd >> Ir >Pt > Ru, Rh. Ferreira–Aparicio et al. [26] reported a similar order of activity (on a TOF basis) for catalysts supported on γ -alumina at 450 °C; Rh > Ni > Ir > Pt, Ru > Co. Hou et al. [27] compared noble metals supported on γ -alumina at 800 °C, and the catalytic activity exhibited the order Rh > Ru > Pd > Ir, Pt (after 30 min on stream). From these studies, supported Rh catalysts appear to exhibit the best performance in DRM, followed by Ni; considering the much lower cost of Ni, this seems to be a good option. In fact, most catalysts used in the reforming industry are supported by nickel [18].

3.1. Effect of the Catalyst Support and Promoters

Ni-based catalysts have attracted great interest in dry reforming reactions due to their good catalytic activity and low cost. The main problem with these catalysts is that they are also active in carbon formation reactions, which leads to their deactivation. Several approaches have been investigated to overcome deactivation issues, like support choice and the addition of different promoters. Tables with a summary of the effect of support and promoters on biogas DR are shown in the Supplementary Materials.

The choice of support has a crucial role in the properties of the catalytic system, as it affects the dispersion of the active phase and the stability of the catalytic system through the metal-support interaction. Moreover, the support can influence the reaction mechanism and the carbon deposition, mainly due to its acidic/basic properties. Many oxides have been studied to support nickel in the DR reaction, like Al₂O₃, SiO₂, MgO, La₂O₃, and CeO₂, among others.

Some authors describe that DRM can follow a bifunctional mechanism in which CH_4 is activated on the metal and CO_2 on the acidic/basic support [16,28–30]. On acidic supports, CO_2 activates by forming formate intermediates with the surface hydroxyl groups, and on basic supports, by the formation of oxy-carbonate species [28]. The bifunctional mechanism requires the migration of oxygen and hydrogen species between the metal and the support. Oxygen species that come from the CO_2 activation diffuse from the support to the metal surface to oxidize carbonaceous deposits formed by methane decomposition, while hydrogen species diffuse from the metal surface, where CH_4 is activated, to the

support to react with adsorbed CO_2 [29]. For catalysts supported on inert materials like SiO_2 , the mechanism follows a monofunctional pathway, where both reactants are activated by the metal alone [28–30]. Thus, on inert supports, once carbon formation occurs by methane decomposition, subsequent CO_2 activation is limited, leading to deactivation. The catalysts supported on inert oxides have relatively weak metal-support interaction and are less active and stable than the mildly acidic (Al₂O₃) or basic (MgO, La₂O₃, CeO₂) supports. Monofunctional and bifunctional pathways are represented in Figure 2.



Figure 2. Monofunctional (**a**) and bifunctional (**b**) mechanisms of DRM. M is a Ni site, and S is a support site. Adapted from Ref. [29].

The correlation between surface acidity–basicity, and catalyst activity, and deactivation in DRM was studied by Das et al. [31] for Ni catalysts supported on SiO₂ and Al₂O₃ (both doped with 1 wt.% CeO₂ and 3 wt.% MgO). The supports were prepared by two different methods: the one-step solvothermal method and the sequential impregnation method. A one-step process favors a homogeneous distribution of acidic and basic sites at a moderate concentration, which improves the activity of DRM with fewer side reactions. On the other hand, in the stepwise process, a random distribution of acid/basic sites was observed with fast catalyst deactivation. Catalysts with higher acidity were found to promote methane cracking reactions, while the Boudouard reaction and deactivation owing to metal oxidation were dominant at high basicity.

Alumina is one of the most common supports used in DR reactions as it is inexpensive, has great mechanical and thermal stability, and can achieve high dispersion of the nickel phase. The thermal treatment is an important procedure, determining the reduction degree of the nickel species, the formation of the spinel phase (NiAl₂O₄), and thus the catalytic behavior and stability of these catalysts. Sahli et al. [32] observed that catalysts formed by a solid solution of Al₂O₃ and NiAl₂O₄ without any detectable NiO were more resistant to carbon deposition than the catalyst initially containing NiO in 24 h of DRM at 800 °C. Ribeiro et al. [33] synthesized NiAl₂O₄ catalysts with a high surface area by the combustion method, and they presented excellent stability on DRM. This was attributed to the rearrangement of nickel in the aluminate matrix and the migration of nickel particles through carbon filaments formed during the activation process with a mixture of O₂/CH₄. Zhou et al. [34] studied the effect of NiAl₂O₄ formation on Ni/Al₂O₃ stability during DRM. A catalyst with strong metal-support interaction was obtained with an increase in the final calcination temperature to 900 °C to form NiAl₂O₄ exclusively. This catalyst showed

high resistance to sintering and coking during a long-term DRM reaction (of about 100 h). Similar results were obtained by Bao et al. [35] for NiCeMgAl catalysts synthesized via the refluxed co-precipitation method: the Ni active sites derived from the NiAl₂O₄ spinel structure had longer stability in DRM than those derived from the free NiO.

The preparation methodology of Ni/Al₂O₃ catalysts has a great influence on the activity of DRM. Goula et al. [36] used a new methodology to synthesize Ni/Al_2O_3 catalysts for DRM. In the equilibrium deposition filtration (EDF) technique, the deposition of the desired species takes place through adsorption and/or surface reaction with the receptor sites developed on the support surface (surface oxygens and surface hydroxyls). The authors used NH_4OH solution for pH control and NH_4NO_3 for adjusting the ionic strength during the nickel deposition on alumina. The catalyst prepared by EDF converted more methane and carbon dioxide at temperatures higher than 700 °C compared with that prepared by the impregnation method. The EDF method provided relatively higher Ni dispersion, indicating that the strong metal-support interactions can suppress the diffusion of Ni²⁺ into the Al_2O_3 lattice under mild conditions. Liu et al. [37] showed that the Ni/Al_2O_3 catalyst synthesized by electrospinning exhibited improved metal dispersion, leading to higher activity and superior coke resistance in DRM compared with the catalyst conventionally prepared by the incipient impregnation method. A bimodal porous alumina support was prepared by Shah et al. [38] via the evaporation-induced self-assembly (EISA) method. The nickel supported on bimodal alumina was synthesized by different methods: freeze drying, wet impregnation, urea deposition-precipitation, and chemical vapor deposition. The stable performance of the bimodally structured catalyst in DRM was related to the combined effect of the metal-support interface and the smaller nickel particle size. The catalyst prepared by urea deposition-precipitation was the most active and stable at 700 °C during 100 h on stream. In the urea deposition-precipitation method, slowly changing the pH of the solution causes progressive precipitation of nickel species, and the formation of large ensembles of nickel species is avoided.

Zhang et al. [39] investigated the effect of different supports (Al_2O_3 , MgO- Al_2O_3 , SiO₂, TiO₂, ZrO₂, and MgO) on the catalytic activity of Ni-based catalysts in DRM. The performance of the tested catalysts decreased in the following order: NiO/MgO-Al₂O₃ $> NiO/SiO_2 \approx NiO/MgO > NiO/Al_2O_3 > NiO/ZrO_2 > NiO/TiO_2$. For mixed support MgO-Al₂O₃, Mg²⁺ ions tend to react with the unsaturated Al³⁺ centers on the Al₂O₃ surface, which may reduce the interaction strength between the metal and the support, increasing the metal dispersion. This catalyst was quite stable for 100 h at 750 °C, suggesting a high anti-coking capability. On the other hand, although the initial activity of the Ni/SiO_2 catalyst was very high, it decreased gradually with time on stream. The poor catalytic stability of Ni/SiO₂ was attributed to the weak interaction between NiO and SiO₂, which cannot effectively inhibit the sintering of the active metal Ni during the reaction. Different supports (Al₂O₃, SiO₂, MgO, CeO₂, and ZnO) for Ni catalysts were also studied by Gao et al. [40] in biogas DR (CH₄/CO₂ ratio of 1). Ni/Al₂O₃ showed the highest activity due to its smaller particle size, but seriously plugged the reactor during the stability test (12 h at 750 °C) (Figure 3a). Ni/MgO was less active than Ni/Al₂O₃; however, it showed good stability due to the strong metal-support interaction resulting from the formation of a NiO-MgO solid solution. On the other hand, Ni/ZnO, Ni/CeO₂, and Ni/SiO₂ presented poor activity. TGA profiles of the spent catalysts (Figure 3b) showed a large amount of coke formation for Ni/Al_2O_3 . For Ni/MgO, there was no significant weight loss, indicating its resistance to carbon deposition.



Figure 3. (a) CH₄ conversion during stability testing of Ni catalysts supported on Al₂O₃, SiO₂, MgO, CeO₂, and ZnO for biogas DR and (b) TG profiles of the spent catalysts. Reaction conditions: 750 °C, GHSV = 15,000 mL g_{c1}^{-1} h⁻¹; CH₄:CO₂ = 1; P = 1 atm. Reprinted with permission from Ref. [40].

Several authors studied the effect of adding MgO to Ni/Al₂O₃ catalysts in DRM. Ni/MgO-Al₂O₃ catalysts with different Mg/Al ratios were studied by Min et al. [41]. Higher catalytic activity was observed for the catalysts with a medium MgO/(MgO + Al₂O₃) ratio (0.44–0.86), which was attributed to a high specific surface area and high dispersion of Ni particles. The coke resistance increased with increasing MgO loading. The basicity of MgO helps to inhibit carbon deposition by enhancing CO₂ adsorption; the adsorbed CO₂ reacts with C to regenerate the catalyst. Zhu et al. [42] prepared NiMgAl mixed oxide catalysts derived from hydrotalcite and observed that the mixed oxides with a Mg/Al ratio of 1 exhibited the best catalytic activity and coke resistance. The same result was obtained by Zhan et al. [43] for Ni-Mg-Al catalysts with different Mg contents prepared via a coprecipitation method. The catalyst with 10 mol% Mg and 11 mol% Ni showed the best catalytic activity because of its higher number of basic sites, which caused a minimum amount of carbon deposition on the catalyst.

Ha et al. [44] used Mg-Al mixed oxides derived from hydrotalcites (Mg/Al ratio = 1.3) as supports for Ni catalysts in DRM. The best activity was obtained with the catalyst supported on Mg-Al oxide calcined at 550 °C because it possesses a high surface concentration of Ni. This catalyst presented the highest carbon deposition after 8 h on stream at 600 °C. Modifying the catalyst preparation with citric acid reduced the coke formation and the size of large octahedrally coordinated NiO-like domains, which may easily agglomerate on the surface during DRM. The DRM activity of the NiMgAl mixed oxide catalysts prepared by Nguyen-Phu et al. [45] exhibited a volcano curve as a function of the Mg/Al ratio. The highest activity of the catalyst with a Mg/Al ratio of 1.5 (Ni-Mg_{1.5}AlO_x) was attributed to the dispersion of metallic Ni sites and to the high number of basic sites, which are the active sites for CO₂ activation. The activity of Ni-Mg_{1.5}AlO_x remained stable for 120 h at 727 °C; the high stability was ascribed to its good basicity, suppressing deactivation by coking. Akbari et al. [46] studied the effect of Ni content on the Ni-MgO-Al₂O₃ catalysts (MgO/Al₂O₃ = 1) for DRM. The increase in nickel content (from 2.5 to 15 wt.%) increased both the reactant conversions and the amount of deposited carbon (whisker-type carbon).

In addition to MgO, other promoters have been added to Ni/Al₂O₃ catalysts. A promoter (metal oxide or element) can provide the catalysts with one of the following effects: (1) improve the metal dispersion; (2) enhance the adsorption and activation of CO_2 , decreasing the coking rate; (3) supply surface oxygen species, being reoxidized by CO_2 dissociative adsorption; and (4) "block" carbon growth centers in the metal particles, preventing carbon diffusion and deposition [16].

The Ni/Al₂O₃ catalysts promoted with alkaline earth metal oxides (MgO, CaO, and BaO) were studied in DRM by Alipour et al. [47]. The highest activity was observed for the MgO-promoted catalyst because the addition of MgO increased the nickel reducibility. Carbon

formation was decreased by all three promoters, and this effect was more pronounced for MgO. Different results were obtained by Sengupta and Deo [48], who investigated the addition of MgO and CaO to Ni and Ni-Co/Al₂O₃ catalysts for DRM. The presence of CaO increased the catalytic activity due to additional sites that could strongly adsorb H₂ and CO₂. In contrast, MgO presented the opposite effect due to the strong interaction of MgO and CaO as promoters for Ni/Al₂O₃ catalysts in biogas DR (CH₄/CO₂ ratio of 1.5). They concluded that the catalysts promoted with MgO and CaO exhibit higher activity than Ni/Al₂O₃ catalysts for reaction temperatures between 550 and 750 °C, while the opposite is evidenced for temperatures higher than 750 °C.

Rare earth metal oxides, particularly ceria and lanthanum, have also been studied as supports and promoters for Ni-based catalysts, with promising results. These oxides can improve the dispersion and stabilization of the metal particles and have high activity for the adsorption of CO_2 . Reduction of bulk CeO_2 takes place at temperatures higher than 400 °C, independently of the metal presence, and surface Ce^{3+} sites can activate CO_2 with the formation of CO and simultaneous oxidation of Ce^{3+} to Ce^{4+} [16]. The redox property of ceria and its exceptional oxygen storage capacity help prevent carbon deposition [30,50]. In general, bulk CeO_2 and La_2O_3 are not suitable supports for nickel because the metal decorating effect associated with the strong metal-support interaction (SMSI) reduces the catalytic activity. Therefore, these oxides have been used more as promoters for the DR reaction.

The effect of CeO₂ loading on Ni/Al₂O₃ catalysts for DRM was studied by Damyanova et al. [51]. CeO₂-containing Ni catalysts exhibited higher activity and stability with time on stream than Ni/Al₂O₃, which was mainly related to the degree of nickel dispersion on the catalyst surface. The highest activity and stability of the catalyst with 6 wt.% CeO₂ were associated with the increase in local electron density and accessibility of the active sites caused by the close contact between nickel and cerium species. The catalyst with the highest amount of CeO₂ (12 wt.%) showed a decrease in catalytic activity due to the partial coverage of the active sites by ceria. Li and Veen [52] also showed a partial coverage of the Ni surface on Ni/CeO₂ catalysts after high-temperature reduction (≥ 600 °C), which induces decoration/encapsulation of the Ni particles by a thin layer of reduced ceria. The decoration/encapsulation effect decreased the catalyst activity for the adsorption of CH₄ and CO₂, leading to lower conversions and decreased carbon deposition in DRM.

Lino et al. [53] studied the effect of adding 5 wt.% of CeO₂ to Ni-Mg-Al catalysts derived from hydrotalcites in biogas DR (CH₄/CO₂ = 1.5) at 650 °C. They only observed a significant increase in activity for the catalyst with 25 wt.% of Ni but not for the catalyst with 10 wt.% of Ni, which was related to the basicity enhancement occasioned by the Ce promotion. Despite its highest basicity, the Ni25%/MgAlCe catalyst was not stable, probably due to Ni sintering. Rosha et al. [54] added 10, 20, and 30 wt.% of CeO₂ to the Ni/Al₂O₃-TiO₂ catalyst and observed improved CH₄ and CO₂ conversions in biogas DR (CH₄/CO₂ = 1.5) just for the catalyst with 20 wt.% CeO₂, in comparison with the catalyst without ceria.

Luisetto et al. [55] prepared Ni/CeO₂-Al₂O₃ catalysts by different methods: coprecipitation (CP), wet impregnation (WI), sol–gel (SG), and citric acid (CA), containing 20 wt.% CeO₂. The intrinsic catalytic activity (site time yield) for DRM at 800 °C increased with increasing Ni crystallite size in the following order: CP > WI > SG > CA. The catalyst prepared by the CA method presented a smaller Ni crystallite size (5.8 nm) and a higher content of CeAlO₃ species, which both have a role in inhibiting carbon deposition. Ni/CeO₂-Al₂O₃ catalysts (with 10 wt.% CeO₂) prepared by impregnation and sol–gel methods were compared by Aghamohammadi et al. [56]. A smaller Ni particle size was obtained for the sol–gel synthesized catalyst, which showed higher activity in DRM. Nibased mixed CeO₂-Al₂O₃ oxide catalysts prepared by one-pot EISA, containing 20 wt.% CeO₂, were investigated by Marinho et al. [57]. The catalysts presented mesoporous structures with highly dispersed Ni as NiAl₂O₄ spinel clusters. After reduction, Ni particles with small sizes (<5 nm) were observed. The presence of Ce in strong interaction with Al_2O_3 enhances oxygen mobility and CO_2 adsorption, increasing the catalyst activity for DRM and promoting the carbon removal mechanism.

Yang et al. [58] showed that, although the activity of Ni/Al₂O₃ promoted with both La₂O₃ and CeO₂ (3 wt.% each) was not increased, the carbon deposition in DRM was significantly reduced due to alkaline function and enhancement of metal dispersion. According to Charisiou et al. [59], the modification of Ni/Al₂O₃ catalysts with CeO₂ (10 wt.%) and/or La₂O₃ (4 wt.%) significantly enhances catalytic performance for biogas DR (CH₄/CO₂ ratio of 1.5). The catalysts containing lanthanum (Ni/LaAl and Ni/CeLaAl) performed better than the catalysts with only ceria (Ni/CeAl) (Figure 4). The high catalytic activity was related to the redox reactions of Ce and La species with the deposited carbon.



Figure 4. Activity tests (**a**) and stability tests at 750 °C (**b**) of Ni/Al, Ni/LaAl, Ni/CeAl, and Ni/CeLaAl for biogas DR. Reaction conditions: WHSV = 120,000 mL $g_{cat}^{-1} h^{-1}$; CH₄:CO₂ = 1.5; P = 1 atm. Reprinted with permission from Ref. [59].

The effect of adding CeO₂ and La₂O₃ (10 wt.%) as promoters on the catalytic performance of Ni/Al₂O₃ was also assessed by Farooqi et al. [60]. The Ni/CeO₂-Al₂O₃ catalyst exhibited higher catalytic activity in DRM at 800 °C due to the increase in reducibility and dispersion of Ni. Meanwhile, Ni/La₂O₃-Al₂O₃ presented higher stability during 8 h on stream because La₂O₃ favors CO₂ dissociation. Taherian et al. [61] studied Ni/CaO-Al₂O₃ catalysts promoted with ceria, lanthana, and yttria (10 wt.%). The ceria-promoted catalyst showed the highest catalyst activity in DRM, which was associated with the smallest Ni crystallite size (8.9 nm). The stability of this catalyst during 30 h on stream was due to the reaction of the carbon species with the lattice oxygen, leading to the self-decoking feature in the presence of ceria.

The addition of CeO₂, La₂O₃, and ZrO₂ (5 wt.%) to Ni-Al₂O₃ catalysts was investigated by Shamskar et al. [62]. The catalysts were prepared by simultaneous co-precipitation of metal nitrate solutions with the assistance of ultrasound irradiation. The incorporation of promoters decreased the catalytic activity of DRM due to the coverage of active sites by the promoters. Among all the promoted catalysts, the Ce-promoted sample exhibited lower carbon formation. Rezaei and Alavi [63] studied the addition of these same oxides (also with 5 wt.%) to Ni/MgAl₂O₄ catalysts. In this case, the M-MgAl₂O₄ (M: CeO₂, ZrO₂, and La₂O₃) supports were prepared by sol–gel, and Ni was added later by impregnation. The catalysts supported on promoted supports exhibited higher methane conversion in DRM at all temperatures (550–750 °C). The catalyst promoted with CeO₂ exhibited the highest activity and the lowest coke formation, which was related to the redox properties of the ceria.

Calgaro et al. [64] evaluated the La/Mg ratio in Ni-Mg-La-Al catalysts derived from hydrotalcites for the biogas DR (CH₄/CO₂ ratio of 2.33). The increase in the La/Mg ratio decreased the average crystallite size of Ni and increased the strength of acid sites, improving the catalytic activity at 700 °C. The catalyst with La/Mg = 4 presented the best

activity and stability due to its greater resistance to sintering and a proper combination of acidic and basic sites. Al-Mubaddel et al. [65] studied the effect of different La₂O₃ loadings (0 to 20 wt.%) on Ni/Al₂O₃ catalysts for DRM. The addition of up to 15 wt.% La₂O₃ in support reduces the content of acid sites and increases the basic sites, including super basic sites (related to unidentate carbonates) that lead to optimum catalytic performance.

Charisiou et al. [66] showed that the Ni/(4 wt.%)La₂O₃-Al₂O₃ catalyst is more active and deactivates at a more gradual rate than the Ni/Al₂O₃ in biogas DR (CH₄/CO₂ ratio of 1.56). They concluded that doping Al_2O_3 with La_2O_3 helps to maintain the Ni⁰ phase during the reaction due to higher dispersion and stronger metal-support interactions. Moreover, La_2O_3 addition stabilizes the catalyst by forming a less graphitic type of deposited carbon and enhances its gasification due to the CO_2 adsorption on the basic sites. CO_2 is activated by La₂O₃ through the formation of La₂O₂CO₃, which can react with neighboring carbon species to produce CO and regenerate La_2O_3 , eliminating the deposited carbon. Raman spectroscopy was used to investigate the nature and graphitization order of the carbon formed in the spent catalysts (Figure 5). All catalysts presented two broad bands: the G-band between 1500 and 1600 cm⁻¹, and the D-band between 1300 and 1400 cm⁻¹. The G-band is related to intra-layer displacement in the graphene structure, while the D-band is associated with the disorder-induced vibration of the C-C bond. The ratio between the D and G bands (I_D/I_G) intensities was calculated to show the nature of carbon formed over the catalysts: smaller I_D/I_G values indicate higher crystallinity due to the higher contribution of the graphitized carbon. The crystallinity degree increases with an increase in the reaction temperature, and this increase was more pronounced for the Ni/Al₂O₃ catalyst. The catalyst promoted with La_2O_3 presented higher I_D/I_C ratio values, showing less graphitic carbon, which is associated with its higher stability during biogas DR.



Figure 5. Raman spectra of the (a) Ni/Al₂O₃ and (b) Ni/ La₂O₃-Al₂O₃ catalysts used in biogas DR at different temperatures. Reaction conditions: WHSV = 40,000 mL g⁻¹ h⁻¹; CH₄:CO₂ = 1.56; P = 1 atm. Reprinted with permission from Ref. [66].

Several other studies have shown that lanthanum oxycarbonate ($La_2O_2CO_3$), formed by the reaction of La_2O_3 with CO_2 , is of primordial importance in the mechanism of DRM [67–70]. Li et al. [69] showed that an ordered mesoporous Ni/La₂O₃ catalyst promoted an increase in the metal-support interface by enhancing Ni dispersion. The CO₂-derived species adsorbed at the interface can react quickly with the carbon species generated from CH₄ activation on nickel, and therefore, there is no accumulation of $La_2O_2CO_3$. Thus, this catalyst exhibited superior activity and stability in DRM compared to the catalyst supported on La_2O_3 prepared by calcination of lanthanum nitrate. In another study of this same research group [70], the Ni/La₂O₂CO₃-Al₂O₃ catalyst, produced by the calcination of the Ni/La₂O₃-Al₂O₃ in the CO₂ atmosphere, showed higher activity for DRM than Ni/La₂O₃-Al₂O₃ (Figure 6). La₂O₂CO₃ prevents Ni from entering the alumina and forming NiAl₂O₄, increasing Ni reducibility.



Figure 6. Stability tests of Ni/La₂O₂CO₃-Al₂O₃, Ni/La₂O₃-Al₂O₃, and Ni/Al₂O₃ catalysts for DRM. Reaction conditions: 650 °C, GHSV = 240,000 mL g_{cat}^{-1} h⁻¹; CH₄:CO₂ = 1; P = 1 atm. Reprinted with permission from Ref. [70].

The introduction of ZrO_2 on Ni/Al₂O₃ also helps to improve the dissociation of the CO₂ reaction, reducing coke formation. Moreover, ZrO_2 , which is highly dispersed in Al₂O₃, prevents the formation of the NiAl₂O₄ phase [71–73]. Based on the catalytic activity and coke yield results for DRM, Therdthianwong et al. [71] suggested that the 5–10 wt.% ZrO_2 loading range seems to be suitable for reducing coke formation. Similar results were obtained by Anzures et al. [72]: the catalyst with 5 wt.% of ZrO_2 presented the best performance in DRM due to the high concentration of the medium-strength basic sites and the high specific surface area, with low carbon formation during 36 h of reaction. Shin et al. [73] prepared Ni/ZrO₂-Al₂O₃ catalysts by the modified Pechini sol-gel method, urea hydrolysis, and physical mixing. The catalyst prepared by Pechini sol-gel showed higher stability for DRM because of the enhanced interaction between nickel and support, promoting CO₂ dissociation.

Ceria–zirconia binary oxides have been largely applied as catalyst supports for DRM. Zr^{4+} stabilizes CeO₂, forming solid solutions over all Ce/Zr atomic ratios, and Ce_{1-x}Zr_xO₂ phases exhibit improved textural features, thermal resistance, and oxygen storage/transport properties [16]. According to Iglesias et al. [74], zirconium can be incorporated into ceria cubic lattices up to 15 at.%, while tetragonal features were observed for 25 and 35 at.%. Zr addition enhances support reducibility and metallic dispersion. However, the presence of the zirconium tetragonal phase was detrimental to oxygen mobility. Kumar et al. [75] showed that Ni supported on a ceria–zirconia solid solution was more stable for DRM compared to Ni/ZrO₂ and Ni/CeO₂ catalysts. The stability of the Ce_xZr_{1-x}O₂ solid solution was associated with its enhanced reducibility at lower temperatures. Kambolis et al. [76] observed a significant distortion of the ceria lattice in the ceria-zirconia solid solutions, increasing the number of anion vacancies. These oxygen vacancies are active sites for the dissociative adsorption of CO₂, conferring a much higher activity for Ni catalysts in DRM. The zirconium-rich solid solutions exhibited stronger resistance to the formation of carbonaceous deposits.

Wolfbeisser et al. [77] used $Ce_{1-x}Zr_xO_2$ mixed oxides prepared by co-precipitation and surfactant-assisted co-precipitation as supports for Ni nanoparticles in DRM. The catalyst synthesized by surfactant-assisted co-precipitation was not active for DRM because of the encapsulation of Ni particles by ceria–zirconia particles. The Ni catalyst supported on ceria-zirconia prepared by co-precipitation presented much higher activity than Ni/CeO₂. On the other hand, no improvement in catalytic activity was observed when compared to Ni/ZrO₂, but the stability against the formation of filamentous coke on the ceria–zirconia catalyst was significantly increased.

The role of ceria dopants on the activity of Ni catalysts for DRM was investigated by Luisetto et al. [78]. Ni/Me_{0.15}Ce_{0.85}O_{2- δ} with Me = Zr⁴⁺, La³⁺, or Sm³⁺ were prepared by the citric acid synthetic route. All catalysts showed high stability over 50 h of time on stream at 800 °C, with lower formation of filamentous coke on the catalysts doped with La and Sm. The presence of La and Sm increased the number of oxygen vacancies compared to the Zr-doped sample, but they were not capable of enhancing CO₂ splitting activity.

Zirconia has also been investigated as a catalytic support in DRM because of its moderate acidity and basicity, high thermal stability, and surface oxygen mobility. Zhang et al. [79] showed that the crystalline structure of ZrO_2 support plays an important role in the performance of the Ni catalyst for the DRM. They evaluated amorphous, monoclinic, and tetragonal ZrO_2 as supports and concluded that amorphous ZrO_2 exhibited higher activity and better stability, which was associated with higher Ni dispersion. In contrast, Ni/m-ZrO₂ suffered a continuous decline of activity during 50 h of time on stream, related to the Ni sintering and formation of the encapsulating carbon, which covered the active Ni sites. In another work, this same research group prepared Ni nanoparticles well-dispersed on a mesoporous amorphous zirconia matrix [80]. The anchoring effect promoted by the high surface area of the amorphous structure and the strong interaction between Ni and ZrO₂ leads to high catalyst stability in DRM, with high resistance against Ni sintering and carbon deposition. Zhang et al. [81] reported that different distributions of oxygen species over the monoclinic ZrO2 surface can be obtained by treatment under H2, N2, and O_2 atmospheres. The treatment in H_2 flow promoted the formation of adsorbed oxygen species over the ZrO₂ surface, and the Ni supported on this oxide enhanced CO₂ activation during DRM, promoting the removal of the deposited carbon.

Lou et al. [82] reported a new approach to synthesize Ni nanoparticles supported on ZrO_2 and SiO_2 by using air-stable Ni colloids. The Ni/ ZrO_2 catalyst with a 1.1 nm particle diameter showed high stability for DRM during 60 h on stream, which was attributed to almost all Ni atoms at the perimeter of ZrO_2 . This led to higher accessibility to the oxygen from CO₂ activated at the Ni- ZrO_2 interface, promoting the conversion of surface carbon to CO. According to this study, only Ni atoms at the perimeter are stable catalytic sites in DRM for Ni/ ZrO_2 catalysts.

The effect of adding CeO₂ and La2O₃ to ZrO₂-supported Ni catalysts was studied by Goula et al. [83] in biogas DR (CH₄/CO₂ ratio of 1.5). The promoted catalysts exhibited enhanced basicity, Ni dispersion, and oxygen ion lability values with superior activity (Figure 7). The Ni/CeO₂-ZrO₂ catalyst presented higher stability in 28 h of reaction at 750 °C, with lower formation of carbon deposits. In another study, this same group [84] reported a decrease of ~30–35% in the catalytic activity of Ni/ZrO₂ during 50 h on stream, and it was limited to less than ~15–20% on the catalysts promoted by La₂O₃ and CeO₂. Higher formation of the more reactive amorphous carbon was observed on the promoted catalysts compared to Ni/ZrO₂.



Figure 7. CH₄ conversion (**a**) and CO₂ conversion (**b**) of Ni/ZrO₂, Ni/La₂O₃-ZrO₂ and Ni/CeO₂-ZrO₂ catalysts for biogas DR. Reaction conditions: WHSV = 120,000 mL $g_{cat}^{-1} h^{-1}$; CH₄:CO₂ = 1.5; P = 1 atm. Reprinted with permission from Ref. [83].

Other materials have been studied as supports for Ni catalysts, such as zeolites and mesoporous materials (SBA-15, MCM-41, etc.). Fakeeha et al. [85] compared the activity of Ni catalysts supported on Al_2O_3 , HY, and H-ZSM-5 for DRM. Ni/H-ZSM-5 presented higher stability with time on stream at 700 °C, with lower carbon deposition. The effect of Si/Al ratios in Na-ZSM-5 for Ni catalysts on DRM was studied by Moradi et al. [86]. Increasing the Si/Al molar ratio (from 30 to 90) resulted in the deviation of zeolite structures to the amorphous phase, decreasing the catalytic activity. The catalyst with a Si/Al ratio equal to 30 showed high stability and resistance to coking during 30 h of reaction at 800 °C.

The sintering of metal particles can be effectively controlled by confining them into pore channels of mesoporous SBA-15 support; moreover, it can also resist the formation of carbon [87]. The influence of the Ni introduction methodology on SBA-15 was evaluated by Gálvez et al. [88]. The catalyst prepared by the chemical reduction-precipitation method using ascorbic acid showed enhanced activity and stability in DRM compared to those prepared by conventional impregnation and precipitation methods. This was associated with the confinement of Ni species (NiO and Ni-phyllosilicates) inside the pores of SBA-15 and preferential carbon growth on the external surface of the catalyst. Karam et al. [89] tuned the properties of nickel nanoparticles inside the mesopores of SBA-15 by controlling the calcination rate. The best stability in DRM was obtained for the catalyst calcined at $0.5 \,^{\circ}$ C min⁻¹ because the strong interaction between the active phase and the SBA-15 support strengthened the Ni nanoparticle confinement and free accessibility without pore plugging. Omoregbe et al. [90] reported that Ni/SBA-15 catalyst activity was stable for DRM during 4 h on stream at 700–800 °C, while a slight drop in activity was observed at 650 °C due to carbon deposition.

Kiani et al. [91] investigated the modification of Ni/SBA-16 with a lanthanum promoter for biogas DR (CH₄/CO₂ ratio of 1). The presence of La₂O₃ particles on the catalyst surface decreased the Ni particle size and increased the activity. The maximum activity was obtained for the catalyst with 5.78 wt.%La.

MCM-41-supported nickel catalysts prepared using a facile one-pot method at room temperature were studied by Lovell et al. [92]. The Ni/MCM-41 catalyst showed high activity for DRM, with small nickel particles mostly located inside the MCM-41 pores. Either promoting support acidity by incorporating Al into the MCM-41 framework or reducing support acidity by entrapping Na ions in the MCM-41 pores lowered CH₄ conversion and carbon accumulation during DRM. Aguiar et al. [93] compared Si-MCM-41 obtained from rice husk ash and tetraethylorthosilicate (TEOS) as supports for Ni catalysts in DRM. The use of an alternative source of silica did not change the morphology of the material, but there was a significant decrease in the specific surface area, which resulted in lower catalytic activity. Zhang et al. [94] investigated the role of support structure on the catalytic activity

of DRM, comparing nickel supported on SiO₂, MCM-41, and inverted conical mesoporous silica spheres (MSS). Ni/MSS catalysts exhibited higher activity and stability during 9 h at 800 °C (Figure 8). The inverted-tapered pore structure of MSS improved nickel dispersion and prevented Ni nanoparticle sintering and carbon deposition.



Figure 8. CH₄ conversion during DRM and TEM images of the fresh (**a**) and used (**b**) Ni/MSS catalysts. Reaction conditions: 800 $^{\circ}$ C, CH₄:CO₂ = 1.5. Adapted with permission from Ref. [94].

Table 1 summarizes the properties of each supporter and promoter described in this section, highlighting their main advantages and drawbacks.

		Promoter	
Support		Basic oxides	Reducible oxides
	Al_2O_3	Ex: MgO, CaO Reduce support acidity Increase Ni dispersion, promote CO ₂ adsorption, and inhibit carbon formation	Ex: CeO ₂ , La ₂ O ₃ Redox properties with active surface oxygen species Improve Ni dispersion and prevent carbon deposition
	Inert oxides	Ex: SiO_2 Weak interaction between Ni and support favors sintering	
	Basic oxides	Ex: MgO Strong basicity decreases Ni reducibility and favors deactivation by metal oxidation	
	Reducible oxides	Ex: CeO ₂ , La ₂ O ₃ , Ce _{1-x} Zr _x O ₂ High oxygen storage capacity inhibits carbon deposition Metal decorating effect due to strong metal-support interaction decreases catalytic activity	
	Mesoporous	Ex: SBA-15, MCM-41 High surface area increases Ni dispersion and confinement of Ni particles into pore channels prevents sintering	

Table 1. Summary of supports and promoters for Ni catalysts.

3.2. Core-Shell Catalysts

Ni-based catalysts with a core-shell structure have been successfully used in DRM recently. In a core-shell-structured catalyst, the active nanoparticles are encapsulated by a thermally stable coating, inhibiting particle migration and sintering. Moreover, confining Ni particles within a support shell protects the active phase from coke deposition [30].

Zhang and Li [95] prepared core-shell Ni@SiO₂ catalysts from NiO nanoparticles (NPs) by a facile method. Multiple NiO cores were formed within a single enclosed shell due to the relatively poor dispersion of the NiO NPs in the CTAB solution. The amorphous silica shell inhibited the formation of filamentous carbon on the nickel surface during DRM. Core-shell-structured Ni@SiO₂ catalysts with small-sized Ni NPs (about 5 nm) were synthesized by Wang et al. [96] using a microemulsion method. The silica shell confined the moving space of Ni nanoparticles, providing sintering-free behavior during DRM. At the

same time, the small size of Ni NPs provided low carbon diffusion in Ni crystals, reducing coke formation.

Han et al. [97] also showed that small-sized Ni nanoparticles (5.2 nm) catalyzed the DRM without sintering or coke formation when the Ni NPs were protected by a silica overlayer. Ni NPs were immobilized onto functionalized silica nanospheres (Ni/SiO₂) and then coated with a silica overlayer. The silica-coated Ni catalyst presented high stability over 170 h of the DRM reaction at 800 °C without any degradation in activity, while the Ni/SiO₂ catalyst showed severe deactivation due to sintering and the formation of filamentous carbon (Figure 9). This same research group evaluated Ni/SiO₂ catalysts (with Ni NPs of the same size) coated with overlayers of other metal oxides, including Al₂O₃, MgO, ZrO₂, and TiO₂ [98]. The following order of initial methane turnover frequency was obtained for DRM at 800 °C: Al₂O₃ > MgO >> SiO₂~ZrO₂> TiO₂ (Figure 10). The enhanced activity of Al₂O₃ and MgO catalysts was associated with their greater CO₂ adsorption. In the case of TiO₂, the Ni NPs severely aggregated, resulting in poor activity.



Figure 9. CH₄ (•, •), and CO₂ (\Box , \Box) conversion over the Ni/SiO₂ (red) and the silica-coated Ni/SiO₂ (black) catalysts. Reaction conditions: 800 °C, CH₄:CO₂ = 1, flow rate = 19,000 mL min⁻¹ g_{Ni}⁻¹. Reprinted with permission from Ref. [97].



Figure 10. Dependence of CH₄ turnover frequency on the metal oxide overlayer on Ni/SiO₂. HAADF-STEM images of the catalysts with Al_2O_3 and TiO₂ overlayers (Al or Ti in green and Ni in red). Reaction conditions: 800 °C, CH₄:CO₂ = 1. Adapted with permission from Ref. [98].

Core-shell structured Ni-SiO₂@CeO₂ catalyst, with nickel NPs encapsulated between the silica support and ceria shell, was evaluated by Das et al. [99] in biogas DR (CH₄/CO₂ ratio of 1.5). Ni-phyllosilicate was used as the Ni precursor to produce highly dispersed Ni NPs on SiO₂. The Ni-SiO₂@CeO₂ catalyst presented excellent stability at 600 °C, with no coke detected after 72 h on stream. The higher activity of the core-shell catalyst was related to the high Ni dispersion and reducibility. The CeO₂ shell effectively inhibited the growth of filamentous carbon around the active Ni center. On the other hand, the Ni-SiO₂ catalyst deactivated during 22 h on stream due to the large deposition of coke and reactor blockage, while the Ni/CeO₂ catalyst showed very low activity. Han et al. [100] prepared a (Ni/CeO₂)@SiO₂ catalyst by confining Ni NPs and CeO₂ nanocrystals in SiO₂ nanospheres. (Ni/CeO₂)@SiO₂ catalyst showed higher activity for DRM than Ni@SiO₂, which was associated with the smaller size of Ni nanoparticles and the promoting effect of CeO₂ on CO₂ activation. The silica shell confined the migration of the core components during the reaction, providing resistance to sintering. The Ni-CeO₂@SiO₂ catalyst was also evaluated by Lin et al. [101] in DRM, and no carbon deposition was observed during 100 h of stability testing at 800 °C. The superior coking and sintering resistance of this catalyst was related to the confinement effect of the porous silica shell and the synergistic interaction between Ni and CeO₂ NPs.

Liu et al. [102] developed core-shell Ni-ZrO₂@SiO₂ catalysts with zirconia-modified nickel NPs (Ni-ZrO₂) as the core and microporous silica as the shell. The Ni-ZrO₂@SiO₂ catalyst showed high stability during 240 h of DRM reaction at 800 °C with no coke formation, while Ni@SiO₂ deactivated in 20 h of reaction. The addition of ZrO₂ enhanced NiO reducibility and confined Ni species inside the silica shell, inhibiting Ni sintering. Moreover, ZrO₂ provided an abundance of activated oxygen to Ni NPs, improving their resistance to coking.

 $Ce_{1-x}Zr_xO_2$ mixed oxides have also been used in Ni core-shell catalysts. Das et al. [103] studied the effect of Zr doping on core-shell Ni-phyllosilicate@Ce1-xZrxO2 catalysts (x = 0 to 0.2). In these core-shell catalysts, the particle size of Ni and its growth during reduction/reaction were independent of the Zr doping. The catalysts with x = 0.05-0.1 in the Ce_{1-x}Zr_xO₂ shell presented a significant increase in the intrinsic activity for DRM at 600 °C. The enhancement in DRM activity by a small amount of Zr doping was attributed to the increase in lattice oxygen mobility of the ceria–zirconia shell and stronger metal-support interaction with Ni. They proposed that the lattice oxygen of the ceria-zirconia at the interface with Ni promotes the oxidation of coke precursors and the dissociation of methane. Marinho et al. [104] synthesized Ni@CeZrO₂ (with a Ce/Zr molar ratio of 4.0) and Ni@CeO₂ core-shell catalysts by the sol–gel method and compared them with Ni/CeO_2 prepared by impregnation. The control of Ni particle size and the high oxygen mobility of the Ni@CeZrO₂ catalyst inhibited carbon deposition over 24 h of the DRM reaction at 800 °C. This same research group studied the effect of metal dopants on the performance of Ni@CeMeO₂ (Me = Gd, Sm, and Zr) catalysts for DRM [105]. The doping with Zr improved the thermal stability of the catalyst, leading to the formation of small Ni NPs, while Ni metal sintering was observed for Ni@CeO₂, Ni@CeGdO₂, and Ni@CeSmO₂. The Ni@CeZrO₂ catalyst showed higher resistance to coke formation during the DRM reaction because of its smaller Ni crystallite size and higher ceria reducibility. On the other hand, the larger Ni particles and poor redox behavior of Ni@CeGdO₂ and Ni@CeSmO₂ were responsible for the high carbon formation on these catalysts.

3.3. Bimetallic Catalysts

Industrially, Ni-based catalysts are the most widely used for DRM. However, they have some drawbacks, such as catalytic deactivation due to coke deposition and sintering and low catalytic activity when compared to catalysts based on noble metals. An effective strategy to improve the performance of nickel-based catalysts is to use bimetallic Ni catalysts [106,107]. By forming alloys of Ni with other metals, such as transition metals (Co, Cu, Fe) and noble metals (Pt, Rh, Ru), it is possible to enhance reducibility, increase the specific surface area, reduce the size of metallic particles, and inhibit carbon deposition, resulting in a better performance than that of a single Ni catalysts [108]. Tables with a summary of the effect of transition metals and noble metals on Ni catalysts for biogas DR are shown in the Supplementary Materials.

3.3.1. Ni and Transition Metals

Among Ni-based bimetallic catalysts, Ni-Co bimetallic catalysts have received significant interest. Part of this stems from findings that adding Co to Ni catalysts improves coke formation resistance and increases chemical stability. In addition, bimetallic catalysts demonstrate superior metallic dispersion compared to monometallic catalysts of Ni or Co [109–111]. Studies show that Co-based catalysts can reduce the rate of coke formation by oxidizing the carbon deposited on the surface [112,113]. However, monometallic Co catalysts show poor catalytic performance in DRM, which is the main reason for their lower application compared to Ni-based catalysts [114].

Kim et al. [110] prepared a series of catalysts with a fixed Ni content (7.5 wt.%) and Co contents in the range from 0 to 9 wt.% using the evaporation-induced self-assembly (EISA) method. The catalysts were evaluated in the steam methane reforming process. The optimal Co content was 5 wt.%, related to the higher relative concentration of Ni°/Ni_{total} (37.6%) on the catalyst surface determined by X-ray photoelectron spectroscopy (XPS). Depending on the reaction conditions, a total CH₄ conversion was obtained (GHSV = 10,000 mL g_{cat}^{-1} h⁻¹ and 800 °C). Adding Co to the catalysts drastically reduced the coke production rate and improved the catalytic efficiency during steam methane reforming.

You et al. [115] prepared and evaluated a series of Ni–Co/ γ -Al₂O₃ bimetallic catalysts with a fixed loading of 12 wt.% Ni but with different Co contents for CH₄ steam reforming. The results showed that adding Co can effectively improve the resistance to coke formation and the reaction stability of the Ni/Al₂O₃ catalyst, with a reasonable loss of catalytic activity at lower temperatures (650–750 °C). However, at 800 °C and with GHSV = 18,000 mL g_{cat}⁻¹ h⁻¹, the Ni-Co bimetallic catalysts exhibited the same activity as the Ni/Al₂O₃ catalyst (CH₄ conversion around 90–95%) but with improvements promoted by Co, i.e., reduction in coke production rate and maintenance of catalytic activity during the evaluated period (160 h). XRD and transmission electron microscopy analyses of the reduced catalysts showed that adding Co leads to the formation of Ni-Co alloys on the surface, which play a fundamental role in suppressing coke formation in bimetallic Ni-Co catalysts. However, Ni-Co alloy formation can also block part of the low-coordination Ni active sites and decrease metallic dispersion.

Sheng et al. [113] suggested that Ni and Co act as catalysts for CH_4 decomposition and CO_2 reduction, respectively, during the DRM reaction, and the carbon deposits combine with active oxygen to release CO, thus regenerating the metal surface. The same result was evidenced by Horlyck et al. [116]. In their work, the investigation of the side reactions (Boudouard, methane cracking, and reverse water-gas shift) demonstrated that Co has a high affinity for removing carbon species deposited via oxidation. At the same time, Ni is more active in the decomposition of CH_4 . Furthermore, even a low Co load (2.5 wt.%) in the catalysts promotes increased resistance to carbon deposition.

The proportion between Ni and Co in the bimetallic catalyst is a factor that affects methane conversion and synthesis gas quality in reforming processes. Lyu et al. [117] synthesized different Ni-Co/Al₂O₃ bimetallic catalysts. Keeping the Ni loading fixed at 5 wt.%, the Co content was varied to obtain Co/Ni molar ratios of 0.3, 0.5, 0.7, and 0.9. Employing these catalysts in the DRM at 700 °C, the results showed that the catalyst with a molar ratio of 0.5 presented the best catalytic performance during the 100 h of reaction, presenting CO₂ and CH₄ conversions of 81.6% and 73.1%, respectively. A similar result was observed by Zolghadri et al. [118] in the steam reforming of methane at 700 °C. Among different Ni-Co/Al₂O₃-based catalysts, the 10Ni-10Co catalyst presented the best results, with the highest CH₄ conversion and H₂ yield and the lowest carbon deposition due to improved dispersion of Ni and Co particles.

Several studies show that the Ni-Cu alloy presents better results when compared to Ni monometallic catalysts [119–123], and like Ni, Cu has low costs compared to noble metals. Ni and Cu have a face-centered cubic (fcc) crystalline structure and a similar atomic radius with lattice parameters a = 3.524 Å and 3.615 Å, respectively. Such characteristics favor the formation of a homogeneous solid solution of Ni-Cu. However, Cu tends to

segregate on the surface of the Ni/Cu alloy, depending on the temperature and reaction conditions [124,125].

Kitla et al. [126] demonstrated, using the techniques of hydrogen chemisorption and FTIR spectroscopy of CO adsorption, that regardless of the nominal bulk composition of the catalysts, the surface of the bimetallic particles was substantially enriched by Cu with almost the same composition. Naghash et al. [127] observed that at high reduction temperatures (700 °C) and Cu loadings, Cu tended to segregate to reduce interfacial surface energies. Song et al. [128] observed through X-ray photoelectron spectroscopy (XPS) that the surface of the catalysts presents a Cu/Ni molar ratio much higher than the bulk, indicating that the alloy surface is enriched in Cu. In this study, employing hydrotalcite-like compounds (HTlcs) as catalytic precursors, the authors evaluated the effect of monometallic catalysts (Ni and Cu) and four other catalysts with molar ratios of Cu/Ni = 0.1, 0.25, 0.5, and 1.0 in DRM (reaction conditions: 600 °C, CH₄/CO₂/N₂ = 1/1/2, SV = 60,000 mL g_{cat}^{-1} h⁻¹). The Ni monometallic catalyst initially showed a slight increase in the CH₄ and CO₂ conversions and H_2/CO ratio with time on stream, with a maximum of 51%, 63%, and 0.8, respectively. However, the conversions and the H_2/CO ratio decreased after approximately 10 h on the stream, which was attributed to catalytic deactivation by coke formation. On the other hand, the Cu monometallic catalyst showed much lower conversions (<5%), indicating that metallic Cu has low activity for the reaction. The performance of bimetallic catalysts was dependent on the alloy composition. Catalysts with Cu/Ni ratios = 0.25 and 0.5 showed a drastic improvement in catalytic performance, and both catalysts exhibited stable activity during the investigated period (25 h), with high resistance to coke formation. This resistance was associated with a decrease in CH₄ decomposition and an increase in CO₂ dissociation as a result of Ni-Cu alloying. The activity of the Cu/Ni = 0.25 catalyst is close to that of thermodynamic equilibrium and slightly higher than that of the Cu/Ni = 0.5catalyst, which can be attributed to the higher number of Ni active sites on the surface. At higher Cu loading (Cu/Ni = 1.0), there is a decrease in activity and catalytic stability, indicating that there exists an optimal Ni-Cu composition.

Nataj et al. [129] observed similar results using different contents of Ni (5, 7.5, and 10 wt.%) and Cu (0, 1, 2, 3, and 4 wt.%) supported on alumina in the DRM. Under optimized conditions, it was observed that low Cu contents (1 wt.%) promoted high activity and catalytic stability with higher resistance to coke deposition as well as high resistance to sintering of the active phase. However, catalysts with high Cu loadings (2, 3, and 4 wt.%) were less active and deactivated, mainly due to active site sintering and Ni coverage by the Cu-enriched phase. Under optimized conditions, using a catalyst with 10 wt.% of Ni and 0.83 wt.% of Cu at 750 °C, CH₄ and CO₂ conversions above 95% were obtained with a H₂/CO ratio = 1. A similar result was observed by Lee et al. [130] in DRM. Catalysts with 10 wt.% Ni supported on γ -Al₂O₃ were prepared with 1, 5, 7.5, and 10 wt.% Cu by the wet impregnation method. The 1 wt.% Cu addition to the Ni/Al₂O₃ catalyst improved the stability and activity during 16 h on stream, showing a stable CH₄ conversion of about 90%. This increase in performance was associated with the suppression of carbon deposition. However, catalysts with content greater than 5 wt.% Cu deactivated faster (8–10 h) than the Ni/Al₂O₃ catalyst due to the increased coke deposition.

Han et al. [131] evaluated DRM on catalysts with low loadings of Ni (4 wt.%) and Cu (0.2, 0.5, and 1.5 wt.%) supported on SiO₂, which were prepared by electrostatic adsorption of the Ni-ammonia and Cu-ammonia complexes. Over the entire temperature range evaluated (600–750 °C), the catalyst with a Cu content of 0.5 wt.% was the one that presented the highest performance, displaying conversions of CH₄, CO₂, and H₂/CO ratios around 80%, 85%, and 0.9, respectively. Except for the catalyst with 0.5 wt.% Cu, all catalysts showed activity loss with time on stream (50 h) at 750 °C (Figure 11). The superior performance of this catalyst was associated with the smaller alloy size and an appropriate addition of Cu, which promoted CO₂ activation. The authors also observed that a higher Cu loading (1.5 wt.%) favors the formation of Cu clusters, which could cover more Ni atoms on the surface and make CH₄ activation more difficult.



Figure 11. CH₄ conversion with temperature (**A**) and time on stream at 750 °C (**B**) for DRM with Ni-Cu catalysts containing 4 wt.% of Ni and different Cu loadings. Reaction conditions: GHSV = 60,000 mL g_{c1}^{-1} h⁻¹ and CH₄/CO₂ = 1. Reprinted with permission from Ref. [131].

The synergistic effect between Ni and Fe has been investigated by several researchers in methane reforming. Although Fe has low activity in methane steam reforming, it has high activity in the WGSR reaction and easily forms alloys with Ni [132]. The study carried out by Kim et al. [133], combining the techniques *operarando* XRD and X-ray absorption spectroscopy (XAS), observed that under DRM conditions, the Fe is partially oxidized to FeO, leading to partial segregation and the formation of a Ni-rich NiFe alloy. FeO is preferably formed on the catalyst surface, which reacts through a redox mechanism with carbon deposits to form CO, and then the Ni-Fe alloy is regenerated. The authors proposed that due to the absence of detection of any phase of FeO in the XRD, FeO is likely to be located on the surface as small domains covering a fraction of the surface of the Ni-rich particles, thus providing that carbon removal sites (FeO) are close enough to active sites (Ni) for methane reforming. These findings may explain the increased catalytic stability of bimetallic Ni-Fe catalysts.

The control of the composition of the Ni-Fe alloy is fundamental for good catalytic performance, and this is directly related to the preparation method of the catalysts [134]. As highlighted by Tomishige et al. [134], traditional methods such as co-impregnation are not efficient for producing uniform Ni-Fe alloy particles, as is the case with the impregnation of Ni in mixed oxide supports containing Fe. The Ni-Fe alloy is generated during the reduction; however, controlling the Ni/Fe ratio is very difficult. Otherwise, synthesizing catalysts using precursor oxides containing Ni and Fe, such as hydrotalcite-type compounds and perovskites, is more effective for obtaining Ni-Fe alloy particles with a controlled composition. The effect of Fe in the Ni-Fe alloy has positive and negative aspects for the catalytic activity. The breaking of C-H bonds occurs mainly on the surface of Ni atoms, and the formation of the Ni-Fe alloy decreases the number of surface Ni atoms. On the other hand, Fe can be oxidized more easily than Ni, and the presence of oxidized Fe species is related to positive aspects since this is where the carbonaceous species are oxidized [134]. Therefore, synthesizing catalysts with an adequate Fe composition in the Ni-Fe alloy is fundamental for obtaining high activity and stability.

Braga et al. [132] synthesized Ni and Fe catalysts supported on CeO₂ by two different methodologies, incipient wetness impregnation (IWI) and mechanochemical ball milling (BM), and evaluated the performance of these catalysts in the steam reforming of methane. The characterization of the catalysts showed that adding Fe increased the dispersion of Ni-Fe particles compared to the monometallic catalyst (Ni/CeO₂). Catalysts synthesized by the mechanochemical methodology showed the highest reducibility and H₂ production rate, and these results were correlated to smaller particle sizes (Ni or NiFe) and stronger metal-support interactions. The performance of the Fe_{0.1}Ni_{0.9}/CeO₂-BM catalyst was similar to that of the monometallic catalyst at high temperatures (950 °C). However, coke

formation was practically null on the bimetallic catalyst, while the monometallic catalyst showed high coke deposition, even in the catalytic evaluation carried out for a few hours.

Li et al. [135] prepared Ni and Fe catalysts with the content of metal Ni and Fe of 7.25% and 2.49% for Ni₃Fe₁/Al₂O₃ and 4.98% and 5.03% for Ni₁Fe₁/Al₂O₃, respectively, by an evaporation-induced self-assembly method. Both catalysts showed relative stability in DRM during the evaluated period (50 h). However, the catalyst with equimolar content (Ni_1Fe_1/Al_2O_3) showed higher CH₄ and CO₂ conversion values and higher H₂/CO molar ratios. This result was associated with the greater availability of FeO_x in the dealloying process offered by the catalyst in the equimolar composition. The authors observed a structural evolution of the Ni-Fe alloy during DRM. Due to the segregation of Fe from Ni-Fe alloys during DRM, the spent Ni₁Fe₁/Al₂O₃ and Ni₃Fe₁/Al₂O₃ catalysts formed particles of Ni₃Fe₁ alloy and Ni, respectively.

Song et al. [136] evaluated the effect of adding Fe on the Ni/Al_2O_3 catalyst in lowtemperature DRM. The catalysts were synthesized by a modified evaporation-induced self-assembly (mEISA) method, including a microwave treatment and an EISA process. The performance of the bimetallic catalyst (9.6 wt.% Ni and 4.2 wt.% Fe) was superior to that of the monometallic catalyst (15.7 wt.% Ni) in the entire temperature range evaluated (400–550 °C), with a maximum conversion of 26.6% to CH₄ and 37.8% for CO₂ and with an H_2/CO molar ratio close to 0.7. During the stability tests, the bimetallic catalyst showed stable catalytic activity throughout the evaluated period (20 h). On the other hand, the monometallic catalyst showed a gradual reduction in the conversion of CH_4 and CO_2 . The characterizations of the spent catalysts showed that on the NiFe/Al₂O₃ catalyst, there was the formation of FeO_x due to the segregation of Fe, and this promoted the stabilization of the metallic state of Ni. Three species of carbon deposition were identified in the spent catalysts: active carbon (C_{α}), less active carbonaceous species (C_{β}), and inactive graphitic carbon (C_{γ}) . The authors observed that in the absence of Fe in the catalyst, the active species of C_{α} could not be converted quickly and effectively into CO. These species accumulated and crystallized, generating even more carbonaceous species of the C_{β} and C_{γ} types, leading to the deactivation of the Ni/Al_2O_3 catalyst. Furthermore, there was a large formation of carbon filaments and encapsulated coke with high graphitization on the Ni/Al₂O₃ catalyst and only partially encapsulated coke with low graphitization on the NiFe/Al₂O₃ catalyst. Thus, forming the metallic alloy (Ni-Fe) increased the resistance to coke deposition.

Thalinger et al. [137] synthesized two perovskites, $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (lanthanum strontium ferrite, LSF) and $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (strontium titanium ferrite, STF), and then the perovskites were impregnated with Ni (10 mol%). The Ni/Al₂O₃ catalyst was synthesized by coprecipitation as a reference. After treatment with H₂, Ni-Fe alloy formation was observed due to Fe exsolution in LSF and STF catalysts. However, the LSF catalyst showed higher Ni-Fe alloying due to its greater reducibility than STF, which suppressed catalytic performance in methane steam reforming. The more reducible the perovskite support, the stronger the deviation from the catalytic behavior of Ni/Al₂O₃. The authors concluded that the activity of supported Ni–Fe catalysts could be controlled by carefully selecting the complex oxide support and reduction conditions.

3.3.2. Ni and Noble Metals

The literature unanimously points out that the main factors affecting the stability of Ni catalysts in DRM are related to coke formation and sintering processes. Both processes are related to the high temperatures typically employed in DRM. The sintering process is thermodynamically favored by the high temperatures used in DRM, resulting in losses of metal surface area and, consequently, a decrease in the number of active sites of the catalyst. Activity loss can also occur due to carbon deposition on the catalyst's active sites. Furthermore, the DRM operation can be interrupted by reactor obstruction caused by excessive coke formation [138,139].

Several measures can be taken to prevent the processes that lead to the deactivation of Ni-based catalysts. One of these measures is controlling the size of the metallic sites on the surface because the sites that produce carbon are larger than those required for CH_4 reforming. By forming alloys of Ni with noble metals, it is possible to control the size of the metallic sites and thus regulate the deposition and gasification of carbon on the catalysts [108,139,140]. This effect can be observed in the work of Pawelec et al. [141], where different Pt (0.3–0.5 wt.%) and Ni (1–12 wt.%) catalysts supported on ZSM-5 zeolite were prepared and evaluated in DRM at 500 °C. The catalytic test conducted using the Pt6Ni catalyst (0.5 wt.% Pt and 6 wt.% Ni) showed no significant deactivation during the evaluated period, and the stability of this catalyst was attributed to the presence of small Ni metal particles on the catalyst surface, which were generated by a "dilution" effect promoted by Pt, resulting in higher Ni dispersion. Although carbon formation was not completely suppressed, it was significantly reduced during the catalytic test conducted with the Pt6Ni catalyst. Furthermore, the deposition of carbon on the surface of the Ni crystals did not significantly affect the catalytic activity of this catalyst.

The activity of Pt and Ni bimetallic catalysts can also be enhanced by the synthesis methodology employed. García-Diéguez et al. [139] synthesized monometallic and bimetallic Pt and Ni catalysts supported on nanofibrous γ -Al₂O₃ using two distinct methodologies, reverse microemulsion (ME) and incipient wetness impregnation (IM), and these catalysts were evaluated in DRM. Characterization of the catalysts revealed that the addition of Pt and the ME synthesis favored the formation of NiO instead of the nickel aluminate phase, resulting in a facilitated reduction of NiO to Ni° during the pretreatment. The ME synthesis positively influenced the overall carbon formation, reducing its formation by 90% and 70% compared to the 4Ni/Al₂O₃ and 0.04Pt4Ni/Al₂O₃ catalysts, respectively. Stability tests at 700 °C showed that all catalysts synthesized by ME exhibited more stable results. Additionally, the addition of Pt to Ni catalysts had a beneficial effect, particularly for the catalyst prepared by ME. Thus, the activity and stability of the catalysts can be improved by adding Pt and choosing the catalyst preparation method.

Dai et al. [142] encapsulated Ni-Pt catalysts supported on silicalite-1 in a hollow zeolite. Catalytic tests of DRM (800 °C, atmospheric pressure, GHSV = 72,000 mL g_{c1}^{-1} h⁻¹, and $CH_4/CO_2 = 1$) revealed that the encapsulated catalysts exhibited high stability and resistance to carbon deposition. The initial conversions of CO_2 and CH_4 were 78–83% and 75–80%, respectively. However, after only 1 h of time on stream, the monometallic Ni catalyst (1.5 wt.%) without encapsulation (1.5Ni/S-1) was deactivated completely, while the bimetallic catalyst (1.5 wt.% Ni and 0.5 wt.% Pt) without encapsulation (1.5Ni-0.5Pt/S-1) showed a continuous activity loss and was deactivated after 6 h of time on stream (Figure 12a). With the encapsulation of these catalysts, it was possible to maintain high activity without any signs of deactivation throughout the evaluated period (6 h). Among the encapsulated catalysts (1.5Ni@Hol S-1 and 1.5Ni-0.5Pt@Hol S-1), the bimetallic catalyst exhibited higher conversions of CO₂ (83%), and CH_4 (77%). The authors performed thermogravimetric analysis (TGA) to determine the amount of carbon deposited on the catalysts after 6 h on the stream. The 1.5Ni-0.5Pt@Hol S-1 catalyst showed only a 1% mass loss, while the 1.5Ni-0.5Pt/S-1 catalyst exhibited a mass loss of 11.4%, a similar value to that exhibited by the 1.5Ni@Hol S-1 catalyst (10.3%). The significant catalytic deactivation observed for the 1.5Ni/S-1 catalyst can be attributed to the rapid carbon deposition on this catalyst since it exhibited a mass loss of 31%. Carbon deposition was also investigated by transmission electron microscopy (TEM) analysis (Figure 12b), which revealed that although the 1.5Ni@Hol S-1 catalyst exhibited a similar amount of carbon deposition as the 1.5Ni-0.5Pt/S-1 catalyst, coke was not produced on the encapsulated particles. Thus, this could be why the 1.5Ni@Hol S-1 catalyst displayed coke formation but did not lose its catalytic activity. Additionally, it can be observed in Figure 12b that carbon filaments are formed on the non-encapsulated Ni particles within the hollow crystal.



Figure 12. CO₂ and CH₄ conversion and TEM images of the spent catalysts for (**a**) 1.5Ni/S-1, (**b**) 1.5Ni@Hol S-1, (**c**) 1.5Ni-0.5Pt/S-1, and (**d**) 1.5Ni-0.5Pt@Hol S-1 catalysts. Reaction conditions: 800 °C, atmospheric pressure, GHSV = 72,000 mL g_{cat}^{-1} h⁻¹, and CH₄/CO₂ = 1. Adapted with permission from Ref. [142].

The beneficial effect of adding Pt to Ni-based catalysts supported on Al₂O₃ for DRM could be observed in the works of the García–Diéguez group [143,144]. These studies have shown that adding Pt to Ni catalysts reduces the size of the metallic crystals compared to monometallic Pt and Ni catalysts. An increase in catalytic activity can be achieved not only by introducing a small amount of Pt (0.4 wt.%) into Ni catalysts (10 wt.%) but also by adding a higher amount of Ni (10 wt.%) to Pt (4 wt.%) catalysts. These findings indicate the existence of a synergistic effect between Pt and Ni. Furthermore, adding small amounts of Pt significantly increases the stability of Ni-based catalysts, as Pt inhibits coke deposition and reduces the operating temperature. The loss of CO₂ conversion was reduced from 1.4% h^{-1} to 0.4% h^{-1} with the addition of 0.4 wt.% of Pt to the Ni catalyst (10 wt.%) supported on Al₂O₃ in stability tests (14 h) of DRM at 700 °C.

In addition to the sintering of metallic particles, operating DRM at high temperatures leads to the segregation of the Pt-Ni alloy. In the study conducted by Egelske et al. [145], Pt and Ni catalysts supported on γ -Al₂O₃ were prepared and evaluated in DRM at different temperatures. The results revealed that DRM at 700 °C promotes the segregation of Pt-Ni alloy particles; consequently, the Pt-rich ensembles induce methane activation in coke, leading to catalyst deactivation. The authors presented evidence that the observed loss of catalytic activity was associated with increased coke formation. Although sintering processes occurred, they did not play a significant role in the activity loss.

In addition to Pt-Ni alloys, Ni alloys with other noble metals, such as Rh, Pd, and Ru, have been evaluated in DRM. Hou et al. [27] evaluated different metals (Ru, Rh, Pt, Pd, Ir, Ni, and Co) in DRM, and among the noble metals, Rh showed the best results in terms of resistance to carbon deposition and higher catalytic activity. Thus, Rh was selected to be added to Ni at different molar ratios. The reactions, carried out at 800 °C with $CH_4/CO_2 = 1, 60,000 \text{ mL } g_{cat}^{-1} \text{ h}^{-1}$ and atmospheric pressure, revealed that the reforming activity of the bimetallic catalysts (Rh-Ni) increased with an increase in the Rh loading, while the coke formation rate decreased. Although the catalytic tests lasted only 4 h, the reactions performed with catalysts having Rh/Ni molar ratios greater than 0.1 did not display coke formation. Even increasing the space velocity to 150,000 mL $g^{-1} \text{ h}^{-1}$, no coke deposition was detected in the catalytic test with the catalyst composed of the molar ratio Rh/Ni = 0.1.

Due to DRM being an endothermic reaction and the carbon being easily formed at low temperatures, it is more appropriate to carry out DRM at temperatures above 800 °C. However, the operation at low temperatures could save resources and costs and limit the sintering processes at active sites [146]. Thus, searching for a catalyst that exhibits resistance to coke deposition during DRM operation at lower temperatures is necessary. With this intention, Mao et al. [147] synthesized monometallic catalysts of Rh (2.2 wt.%) and Ni (2.2 wt.%) and bimetallic catalysts of Rh (0.6 wt.%)-Ni (1.6 wt.%) supported on MgAl₂O₄, and evaluated them in biogas DR. The reaction conditions were 400–800 $^{\circ}$ C, CH₄/CO₂ = 1, WHSV = 18,000 mL g_{cat}^{-1} h⁻¹, and atmospheric pressure. The catalytic evaluations conducted at 600 °C showed initial conversions of CH₄ and CO₂ of around 42% and 53%, respectively, for all catalysts. During the stability test, the Ni-MgAl₂O₄ catalyst showed a continuous loss of catalytic activity. On the other hand, the Rh-MgAl₂O₄ and RhNi-MgAl₂O₄ catalysts showed no apparent deactivation during the 20 h of evaluation. By evaluating the carbon deposition on the spent catalysts, a mass loss of 21% was obtained for the Ni-MgAl₂O₄ catalyst and only 1.5% for Rh-MgAl₂O₄, while the bimetallic catalyst showed no mass loss. Thus, the authors suggest that the presence of Rh significantly increases the performance of the catalysts in terms of resistance to carbon deposition during DRM.

Jóźwiak et al. [148] reported similar results, where a series of monometallic (Rh and Ni) and bimetallic (Rh-Ni) catalysts with a metallic content of 5 wt.% supported on SiO₂ were synthesized and evaluated in DRM. After 24 h on stream at 700 °C, the catalysts were evaluated concerning activity loss and carbon deposition. The Ni monometallic catalyst exhibited the highest activity loss (7.31%) among all catalysts, while the Rh monometallic catalyst presented an activity loss of 2.86%. The TGA of the spent Ni monometallic catalyst showed a mass loss of 21.6%, while there was no mass loss for the spent Rh monometallic catalyst. The bimetallic catalysts showed distinct performances depending on the Rh and Ni content. The activity loss was reduced with an increase in the Rh content in the catalysts, so that the 3.75Ni-1.25Rh, 2.5Ni-2.5Rh, and 1.25Ni-3.75Rh catalysts presented activity losses of 5.96%, 1.58%, and 1.12%, respectively. In contrast, carbon deposition did not follow the same trend, obtaining mass losses of 34.2%, 42.1%, and 1%, respectively. This considerable amount of carbon deposition on the catalyst surface was associated with the Ni-rich metallic phase. Furthermore, the authors suggested that although high carbon deposition occurred on the 2.5Ni-2.5Rh catalyst, the low activity loss (1.58%) observed is due to the type of carbon deposited, which has graphite-like structures.

Romano et al. [149] synthesized several mono and bimetallic catalysts based on Ni, Rh, and Pd supported on γ -Al₂O₃ and CeO₂-Al₂O₃. DRM catalytic tests performed at 700 °C, CH₄/CO₂ = 1, and WHSV = 30,000 mL g_{cat}⁻¹ h⁻¹ revealed that the Ni monometallic catalysts suffered deactivation by coke deposition. In contrast, the Rh monometallic catalysts showed remarkable activity and stability, with no evidence of deactivation during the evaluated period (96 h). Adding Rh to Ni monometallic catalysts enhanced the reducibility of nickel oxide species and increased the catalytic activity. The CH₄ and CO₂ conversions obtained by the 15%Ni/CeO₂-Al₂O₃ catalyst in 48 h of reaction were 57.7% and 72.4%, respectively. With the addition of 1% Rh (14%Ni1%Rh/CeO₂-Al₂O₃), the conversions obtained were increased to 68.3% (CH₄) and 81.4% (CO₂). On the other hand, Pd-based catalysts showed low catalytic performance. The Pd/CeO₂-Al₂O₃ monometallic catalysts lost their catalytic activity due to coke deposition, and the bimetallic catalyst (14.5%Ni0.5%Pd/CeO₂-Al₂O₃) presented conversions similar to the catalytic test performed with 15%Ni/Al₂O₃ catalyst, where conversions of 51.6% and 63.8% were obtained for CH₄ and CO₂, respectively, after 48 h.

Other researchers have investigated the addition of Pd to Ni-based catalysts with promising results. The metals Pd and Ni do not form alloys, mainly because Pd has a lower surface tension and a larger atomic radius than Ni [150]. Ma et al. [151] evaluated the addition of Pd to Ni catalysts supported on ordered mesoporous alumina (MA). The catalytic stability of mono and bimetallic catalysts in DRM at 750 °C can be seen in Figure 13.

The Pd/MA catalyst showed the lowest initial conversion of CH_4 and CO_2 , around 75% and 82%, respectively. After 8 h of catalytic evaluation, the Pd/MA catalyst presented a significant loss of catalytic activity. The other catalysts maintained high CH_4 and CO_2 conversion values during the 100 h evaluation. While the Ni/MA catalyst showed a slight activity loss, the PdNi/MA bimetallic catalyst remained completely stable during the evaluation period. The carbon deposition on the spent catalysts was analyzed using TGA, TEM, and Raman techniques. It was observed that the bimetallic catalyst had the lowest coke deposition, and the addition of Pd prevented the formation of filamentous carbon, which was associated with a loss of catalyst activity.



Figure 13. Catalytic stability tests of Ni/MA, Pd/MA, and PdNi/MA catalysts. (a) CH₄ conversion; (b) CO₂ conversion. Reaction conditions: 750 °C, CH₄/CO₂ = 1 and W/F = 1 g h mol⁻¹. Reprinted with permission from Ref. [151].

Steinhauer et al. [150] extensively studied Pd- and Ni-based catalysts. Several catalytic supports were evaluated, and it was found that the catalytic activity of the bimetallic catalysts strongly depends on the support. The supports were ranked in terms of catalytic activity in the following order: $ZrO_2-La_2O_3$, $La_2O_3 > ZrO_2 > SiO_2 > Al_2O_3 > TiO_2$. In addition, the activity of bimetallic catalysts was superior to that of Pd and Ni monometallic catalysts. In this study, the effect of the Ni/Pd ratio was also evaluated, and the best conversion of CH₄ (73%) and CO₂ (78%) obtained in DRM at 700 °C was obtained by using the ratio (by weight) Ni/Pd = 4 (7.5 wt.% NiPd supported on 93% $ZrO_2-7\%$ La₂O₃). Finally, the authors evaluated the metal loading content on the catalysts and observed a clear trend toward an increase in conversions and yield (CO and H₂) with increased metal content (1 wt.% to 20 wt.%). However, metal loadings above 10 wt.% led to reactor blockage at higher reaction temperatures (600–700 °C) due to the massive coke formation.

Singha et al. [152] synthesized Ni monometallic and Pd-Ni bimetallic catalysts supported on MgO by a polymer-assisted hydrothermal method. The catalysts were prepared by deposition of Pd and Ni by sublimation of the respective precursor salts. Stability tests revealed that the synthesized catalysts were highly stable in the DRM at 750 $^\circ$ C, WHSV = 70,000 mL g_{cat}^{-1} h⁻¹, CH₄/CO₂ = 1. After 100 h of catalytic evaluation, the 5 wt.% Ni-MgO catalyst showed a reduction in conversion of only 0.4% and 0.9% for CH_4 (from 94.8% to 94.4%) and CO₂ (from 97.0% to 96.1%), respectively. With the addition of 0.2 wt.% Pd to the 5 wt% Ni-MgO catalyst, the conversion reduction was even smaller after 100 h of time on stream: 0.1% (from 96.8 to 96.7) and 0.4% (from 96.2% to 95.8%), respectively, for CH₄ and CO₂. In addition to the high stability promoted by Pd, the RWGS was almost annulled since the H_2/CO ratio remained at about 1 (0.99). The authors observed very low values of carbon deposition on the catalysts. The mono and bimetallic catalysts presented a mass loss of 1.5 wt.% and 0.3 wt.% after 100 h of time on stream, respectively. The low values of coke deposition were associated with the basic properties of MgO. In addition, the authors highlighted that the proximity of Pd and Ni particles decreased carbon deposition and improved the coke removal properties of the bimetallic catalyst.

The literature presents several DRM studies demonstrating the increase in the catalytic performance of Ni-based catalysts when associated with small amounts (<1 wt.%) of noble metals [153]. In order to develop a catalyst that has high activity and catalytic stability and presents a low cost, the performance of ruthenium (Ru) catalysts has been investigated since, among the noble metals, Ru is the cheapest. In addition, Ru was one of the first metals to show activity and stability for DRM [154].

Luisetto et al. [155] evaluated Ru and Ni catalysts supported on γ -Al₂O₃ (powder and monolithic structure) in DRM. The bimetallic catalysts present higher conversions and H_2/CO molar ratios than the monometallic Ni catalysts in the temperature range of 600-800 °C. The catalytic test performed at 700 °C with $CH_4/CO_2 = 1$ and 180,000 mL $g_{cat}^{-1} h^{-1}$ presented CO₂ conversion of approximately 12% and 30%, and CH₄ conversion of 8% and 23%, and an H₂/CO molar ratio of 0.45 and 0.7, respectively, for mono and bimetallic catalysts supported on γ -Al₂O₃ (powder). It was demonstrated that the beneficial effect of ruthenium is not on promoting Ni dispersion but on keeping the surface reduced. Regarding stability tests, the catalysts with monolithic structures showed different behaviors at 800 °C. The activation with time on stream demonstrated by the monometallic Ni catalyst was associated with the presence of the NiAlO_x phase, which requires a long time to be completely reduced, and in this way, the number of Ni^o active sites increases, improving the performance of the catalyst. After reaching the steady-state condition, the Ni catalyst rapidly deactivated due to carbon deposition, whereas Ni-Ru remained stable. The bimetallic catalyst showed not only a lower carbon content on the spent catalyst but also a different morphology of the carbon filaments, with a base growth mechanism instead of a tip growth, justifying its higher stability.

Zhou et al. [156] synthesized Ru-Ni-MgO catalysts from a single precursor, Ru_xN_yMg_{1-x-y}(OH)(OCH₃) derived from solvothermal synthesis. This study evaluated two catalyst pretreatments: calcination with subsequent reduction (CR) and direct reduction (DR). The CR pretreatment of the precursors led to the segregation of Ru and the formation of large and small metallic particles because RuO_2 has low solubility in the NiO-MgO solid solution. Nevertheless, small and uniform metallic particles of the Ru-Ni alloy were obtained through the DR pretreatment, provided that the Ru content in the Ru-Ni alloy does not exceed 3 mol% because higher levels of Ru lead to the formation of a separate Ru-rich phase. The catalytic activity in DRM was evaluated at 760 $^{\circ}$ C, CH₄/CO₂ = 1, and GHSV = 86,000 mL g_{cat}^{-1} h⁻¹ during 100 h, and the pretreatment influenced the initial performance of the catalysts. The catalyst Ni_{0.07}Mg_{0.93}O-CR showed the highest initial conversion among the CR catalysts, and it slowly decreased over time. On the other hand, o Ru_{0.07}Mg_{0.93}O-CR catalyst showed the opposite behavior, with an initial low conversion that increased with time. Regarding the bimetallic catalysts, the Ru_{0.035}Ni_{0.035}Mg_{0.93}O-CR catalyst did not show catalytic activity during the first 15 h; after that, the conversion slowly increased to almost the same value as the other CR catalyst at the end. The Ru_{0.003}Ni_{0.067}Mg_{0.93}O-CR catalyst showed only a slightly lower initial conversion than the monometallic Ni catalyst. Thus, these results showed that introducing Ru to catalysts promotes an initial reduction of catalytic activity in CR samples due to oxidation of the Ru surface by CO_2 . However, when reaching the steady state, the H_2 produced maintains a highly reducing atmosphere, preserving the samples in their metallic state. The catalysts prepared by direct reduction ($Ru_xN_yMg_{1-x-y}O$ -DR) exhibited the highest initial activity and gradually deactivated during the stability test. Even small loads of Ru (Ru:Ni ratio of 3:67) in the catalyst are sufficient to increase the activity since the Ru_{0.003}Ni_{0.067}Mg_{0.93}O-DR catalyst showed better results than the monometallic Ni catalyst (Ni_{0.07}Mg_{0.93}O-DR). Thus, the authors observed that although the initial catalytic activity is strongly dependent on the pretreatment, with the reaction time, the differences presented by the catalysts pretreated with CR and DR were suppressed. The catalysts showed similar activity when the operation reached the steady state, which was related to the formation of thermodynamically stable catalyst structures.

Wysocka and Rogala [157] evaluated the effect of Ru (1 wt.%) on Ni-based catalysts (7 wt.%), as well as the effect of different catalytic supports (SiO₂, ZrO₂, Al₂O₃, and

MgAl₂O₄) on DRM, at 800 °C with CH₄/CO₂ = 1. Although the catalytic tests were carried out for only 2 h, the effect of the support on the catalytic performance could be observed. The Ni/Al₂O₃ catalyst showed the highest CH₄ (95%) and CO₂ (85%) conversions. On the other hand, the Ni/SiO₂ catalyst showed the worst results, with conversions in the range of 37% and 45% for CH₄ and CO₂, respectively. Thus, the catalytic activity of Ni-based catalysts followed the following order: Ni/Al₂O₃ > Ni/MgAl₂O₄ > Ni/ZrO₂ > Ni/SiO₂. Adding Ru to the catalysts increased CH₄ conversion for all catalysts, while the effect on CO₂ conversion had the opposite behavior, except for the Ru-Ni/SiO₂ catalyst. There was a reduction in the H₂/CO molar ratio compared to catalysts containing only Ni, which was related to the enhancement of CH₄ dissociation. The high activity presented by catalysts supported on Al₂O₃ and MgAl₂O₄ (mono and bimetallic) was associated with the strong interaction of the active phase with the supports, in addition to the fact that these catalysts present lower carbon depositions.

Alvarez et al. [158] carried out a study using spectroscopy techniques under reaction conditions, such as in situ and operando characterization methods, in order to elucidate the nature of the active sites of the Ru-Ni/MgO/Al₂O₃ catalyst in the DRM reaction and to clarify how the Ru-Ni combination increases the resistance to carbon deposition under reaction conditions. The catalysts supported on MgO/Al₂O₃ were synthesized with a nominal content of 0.5 wt.% Ru and 15 wt.% Ni. The catalytic tests were performed at different temperatures (550–650 °C), CH₄/CO₂ = 1, and a space velocity of 150,000 mL g_{cat}^{-1} h⁻¹. The results shown in Figure 14 revealed that, regardless of the evaluated temperature, the Ni/MgAl catalyst presented the highest catalytic performance, while the Ru/MgAl catalyst was the least active. Regarding the H_2/CO molar ratio, all catalysts presented a ratio smaller than one, and the molar ratio decreased from Ni/MgAl to Ru/MgAl catalysts. Thus, the addition of Ru reduced the catalytic activity of Ni in DRM. The authors suggested that the reduction of the Ni catalyst activity by adding Ru could be caused by a local change in the electronic structure. The surface of Ni typically presents terraces and step-edge sites, and the reactivity of the catalytic surface is often dominated by low-coordinated atoms, with step-edge sites being more reactive. The addition of Ru decreases the activity of Ni catalysts because the Ru atoms are located on the more reactive step-edge sites of Ni particles due to the limited solubility between Ru and Ni. However, analysis of the operando DRIFTS showed that the presence of Ru favors the gasification of adsorbed carbon and prevents CO dissociation.



Figure 14. Catalytic performance for CH_4 and CO_2 conversion and H_2/CO molar ratio as a function of time-on-stream and temperature for the mono and bimetallic catalysts. Reaction conditions: GHSV = 150,000 mL g_{cat}⁻¹ h⁻¹, atmospheric pressure, and $CH_4/CO_2 = 1$. Reprinted with permission from Ref. [158].

4. Conclusions and Prospects

Biogas is a promising renewable feedstock for hydrogen production because it is rich in methane and carbon dioxide, which can be used together in a dry reforming reaction. In this review, we discussed in detail the role of supports and promoters in the activity of Ni-based catalysts for biogas reforming. In particular, tuning the surface acidity/basicity of alumina by adding alkaline metal oxides such as MgO and CaO can promote CO_2 activation and reduce carbon formation. The addition of rare earth metal oxides, especially CeO_2 and La_2O_3 , to alumina, can also have a beneficial effect by generating active surface oxygen species that enhance the metal-support interaction and help with coke removal. Mixed oxides such as $Ce_{1-x}Zr_xO_2$ are good candidates as supports for Ni catalysts with improved oxygen storage capacity.

The synthesis methodology greatly impacts the dispersion of metal active sites and metal-support interaction, which affects the catalyst activity and resistance to coke formation. Alternative preparation methods, like evaporation-induced self-assembly (EISA), have been used successfully for Ni-based catalysts. Catalysts with a core-shell structure have attractive properties for dry reforming because the encapsulation of Ni particles within a support shell protects the active phase from sintering and coke deposition. The performance of bimetallic catalysts of Ni with other transition metals (Co, Cu, and Fe) and noble metals (Pt, Pd, Rh, and Ru) was highlighted due to the positive effect of Ni alloying on metal dispersion and coke suppression. The synergism between noble metals and nickel enhances nickel reducibility, increasing the catalytic activity even with very low loadings of noble metals. Among the transition metals, Co has shown better properties in combination with Ni and, among the noble metals, Pt and Rh.

Further research should focus on developing promoters with proper basicity and redox ability and on catalysts supported on mesoporous materials (like SBA-15 and MCM-41) because their high surface area enables a good dispersion of active metals. Special attention should be given to new catalysts with core-shell structures and the formulation of bimetallic catalysts. Moreover, it is essential to evaluate the effect of biogas impurities, such as H₂S and siloxanes, on the catalyst activity for dry reforming since almost all research carried out until now has focused on simulated biogas feed containing only methane and carbon dioxide.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal13091296/s1, Table S1: Influence of promoter on the activity of Ni/Al₂O₃ catalysts for biogas DR; Table S2: Influence of support on the activity of Ni catalysts for biogas DR; Table S3. Influence of transition metals on the activity of Ni bimetallic catalysts for biogas DR; Table S4. Influence of noble metals on the activity of Ni bimetallic catalysts for biogas DR.

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