

The influence of Ni and Co supported in the Brazilian diatomite for H₂ production via methane dry reforming

A influência de Ni e Co suportados em diatomita brasileira para produção de H₂ via reforma a seco do metano

La influencia de Ni y Co apoyado en la diatomita brasileña para la producción de H₂ a través de La reforma em seco de metano

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Abstract

Brazilian diatomite was used as catalytic support for the dry reforming of methane. The active phases used were Ni and Co at different concentrations. The catalysts were calcined at 500 °C for 5 h and characterized by XRD, BET, TPR and SEM. The XRD results of the catalysts showed that there was formation of NiCo₂O₄ spinels for bimetallic catalysts, in addition to the expected NiO and Co₃O₄ phases. Catalytic tests were performed at 700 °C with a space velocity of 18 L·h⁻¹·g⁻¹, demonstrating a synergistic effect between the active phases (Ni and Co). The Ni₈Co₂/D catalyst showed the highest yield for H₂, the best stability and the lowest rate of carbon formation between bimetallic catalysts. SEM results after the reaction indicated the presence of carbon filaments. According to the results, Brazilian diatomite can be applied as a catalytic support in the dry reforming reaction of methane.

Keywords: Diatomite; Nickel; Cobalt; Hydrogen; Dry reforming.

Resumo

A diatomita brasileira foi usada como suporte catalítico para a reforma a seco do metano. As fases ativas utilizadas foram Ni e Co em diferentes concentrações. Os catalisadores foram calcinados a 500 °C por 5 h e caracterizados por DRX, BET, TPR e SEM. Os resultados de DRX dos catalisadores mostraram que houve formação de espinélio de NiCo₂O₄ para os catalisadores bimetalícos, além das fases esperadas de NiO e Co₃O₄. Os testes catalíticos foram realizados a 700 °C com velocidade espacial de 18 L·h⁻¹·g⁻¹, demonstrando um efeito sinérgico entre as fases ativas (Ni e Co). O catalisador Ni₈Co₂/D apresentou maior rendimento para H₂, melhor estabilidade e menor taxa de formação de carbono entre os catalisadores bimetalícos. Os resultados de MEV após a reação indicaram a presença de

filamentos de carbono. De acordo com os resultados, a diatomita brasileira pode ser aplicada como suporte catalítico na reação de reforma a seco do metano.

Palavras-chave: Diatomita; Níquel; Cobalto; Hidrogênio; Reforma a seco.

Resumen

La diatomita brasileña se utilizó como soporte catalítico para el reformado en seco de metano. Las fases activas utilizadas fueron Ni y Co a diferentes concentraciones. Los catalizadores se calcinaron a 500 °C durante 5 h y se caracterizaron por XRD, BET, TPR y SEM. Los resultados de XRD de los catalizadores mostraron que había formación de espinelas de NiCo₂O₄ para catalizadores bimetálicos, además de las fases esperadas de NiO y Co₃O₄. Las pruebas catalíticas se realizaron a 700 °C con una velocidad espacial del 18 L·h⁻¹·g⁻¹, lo que demuestra un efecto sinérgico entre las fases activas (Ni y Co). El catalizador Ni8Co2/D mostró el mayor rendimiento para H₂, la mejor estabilidad y la menor tasa de formación de carbono entre catalizadores bimetálicos. Los resultados de SEM después de la reacción indicaron la presencia de filamentos de carbono. Según los resultados, la diatomita brasileña se puede aplicar como soporte catalítico en la reacción de reformado en seco del metano.

Palabras clave: Diatomita, Níquel, Cobalto, Hidrógeno; Reformado en seco.

1. Introduction

The H₂ is an important raw material in various industry segments and in the production of inputs such as ammonia, dimethyl ether and methanol, or in the production of energy using fuel cells. Ninety-six percent (96%) of all hydrogen produced in the world comes from primary hydrocarbons such as methane, ethanol and biomass derived compounds (García-Labiano *et al.*, 2015). Among its processes of obtaining H₂, the dry reforming of methane (DRM), reaction 1, has attracted attention for using two greenhouse gases (CH₄ and CO₂). The H₂ may be produced via subsequent processes of separation of syngas (H₂ and CO). The dry reforming reaction has a strong endothermic character, requiring temperatures above 700 °C to obtain high yield levels (Luisetto *et al.*, 2017; M. Wang *et al.*, 2017; Zhang *et al.*, 2015).



Metals containing Pt, Rh and Pd have excellent activities and low coke formation, however, they are expensive and scarce (Németh *et al.*, 2015; Yu *et al.*, 2016). Thus, Ni is the most appropriate for presenting similar activity and having a lower relative cost than noble metals. On the other hand, Ni suffers from deactivation by coke formation and sintering (Mette *et al.*, 2015). Thus, the use of supports or of a second phase are studied to minimize deactivation problems. Many studies have used Al₂O₃, SiO₂ or MgO oxides as support or the addition of Co or Fe as a second active phase (He *et al.*, 2014; Huang *et al.*, 2016; Taherian *et al.*, 2017; Yasyerli *et al.*, 2011). Several routes have been tested to improve of the properties catalytic supports. However, these methods are usually time consuming and demand the use of expensive reagents. In this sense, natural materials have been studied as catalytic supports with the aim of reducing the cost of preparing the catalyst and making better use of natural resources, and diatomite stands out among these materials.

Diatomite is a mineral composed of the fossilised remains of microscopic single-celled aquatic plants called diatoms, and has about 60 to 90% of amorphous silica in its chemical composition (Y. Wang *et al.*, 2016). Studies point to this material being used as a filtration aid for the removal of heavy metals and organic pollutants (Tanniratt *et al.*, 2016; Xia *et al.*, 2017) as a source of silica in the synthesis of zeolites (Garcia *et al.*, 2016; Nascimento *et al.*, 2014) in the preparation of photocatalysts (B. Li *et al.*, 2015), besides of support from oxygen carriers in Chemical Looping Combustion (Romário, 2021) and in the production of ceramic bricks (Costa *et al.*, 2021). Recently, diatomite has been highlighted as catalytic support due to some properties such as thermal and mechanical resistance (Liu *et al.*, 2018). The study of (Jabbour *et al.*, 2015) evaluated the performance of catalysts with 5% Ni supported on two types of diatomite (German and American) in the dry reforming of methane, indicating good reactivity and stability. However, the influence of Co in the active phase on dry reforming reactions has not yet been studied. In order to improve the catalytic activity, bimetallic catalysts have been reported in the literature.

Cobalt has easy availability, is a low-cost metal, and it can be combined with Ni to improve reactivity and stability. Thus, the objective of this study is to evaluate the influence of different concentrations of Ni and Co supported by Brazilian diatomite in H₂ production via methane dry reforming.

2. Methodology

2.1 Catalyst Preparation

The diatomite used as catalytic support in this study came from the mining company Dianorte Ltda., located in the state of Rio Grande do Norte, Brazil. The diatomite was subjected to a heat treatment at 700 °C for 4 h at a rate of 10 °C·min⁻¹. The catalysts were prepared by wet impregnation by setting the active phase at 10% (p/p). For this, nickel (Ni(NO₃)₂·6H₂O) and cobalt (Co(NO₃)₂·6H₂O) nitrates from Sigma-Aldrich were used as precursors. Catalysts with different levels of these metals were prepared and which were named according to their starting composition, such as Ni“x”Co“y”/D (in which “x” or “y” = 0, 2, 5, 8 or 10, with “x+y”=10 5 (p/p): Ni10/D; Ni8Co2/D; Ni5Co5/D; Ni2Co8; Co10/D. The quantities of metallic nitrates were dissolved in 5 ml of distilled water under constant stirring. After complete dissolution, the diatomite was added to the solution, keeping the suspension under constant stirring for 2 h at room temperature. The materials were then heated to 100 °C to evaporate part of the solvent, and then kept at 60 °C for 10 h in an oven. Finally, the catalysts were calcined at 500 °C for 5 h at a rate of 10 °C·min⁻¹.

2.2 Characterizations

The presence of crystalline phases was verified by X-ray diffraction in a Shimadzu XRD-7000 diffractometer using CuK α radiation ($\lambda = 1.5409 \text{ \AA}$) with a voltage of 30 kV and 30 mA. The analyses were performed in the range of 2 θ between 10° and 80°, at a rate of 0.02 and speed of 2°·min⁻¹. Textural analyses were carried out by adsorption/desorption of N₂ using ASAP 2020 equipment by Micrometrics, in which the samples were pretreated for 1 h at 90 °C, and subsequently under high vacuum ($\approx 267 \text{ Pa}$) for 8 h at 200 °C. The temperature-programmed reduction (TPR) profiles were obtained using a Quantachrome Chembet 3000, where 50 mg of the catalyst were heated to 100 °C under a N₂ flow to clear the samples' surfaces of possible adsorbed molecules. Next, the sample was heated to 900 °C at a rate of 10 °C·min⁻¹. Particle morphology was obtained by scanning electron microscopy (SEM) using Shimadzu SSX 550 Super Scan equipment with a tungsten filament operating at 15 kV.

2.3 Catalytic activity tests in dry methane reforming

The catalytic tests were performed in a micro quartz type “U” reactor, following the conditions according to (Medeiros *et al.*, 2016). First, 100 mg of the catalyst were activated under a 10 mL·min⁻¹ flow of H₂ (10% mol in N₂) at 600 °C for 1 h. After activation, the reactor temperature was increased to 700 °C and a 1:1 mixture of CH₄ and CO₂ (20% in N₂) was introduced under a space velocity of 18 L·h⁻¹·g⁻¹ for 10 h. The composition reading of the reactor output gases was performed on a Varian CP 3800 gas analyzer equipped with a Thermal Conductivity Detector (TCD). CH₄ and CO₂ conversions, yields to H₂ and CO, H₂/CO ratio were calculated using equations 1 to 5, respectively.

$$CH_4\text{conversion}(\%) = \frac{(CH_4)_{in} - (CH_4)_{out}}{(CH_4)_{in}} \times 100 \quad (1)$$

$$CO_2\text{conversion}(\%) = \frac{(CO_2)_{in} - (CO_2)_{out}}{(CO_2)_{in}} \times 100 \quad (2)$$

$$CO_{yield} = \frac{(CO)_{out}}{(CH_4)_{in} + (CO_2)_{in}} \times 100 \quad (3)$$

$$H_2_{yield} = \frac{(H_2)_{out}}{(CH_4)_{in}} \times \frac{100}{2} \quad (4)$$

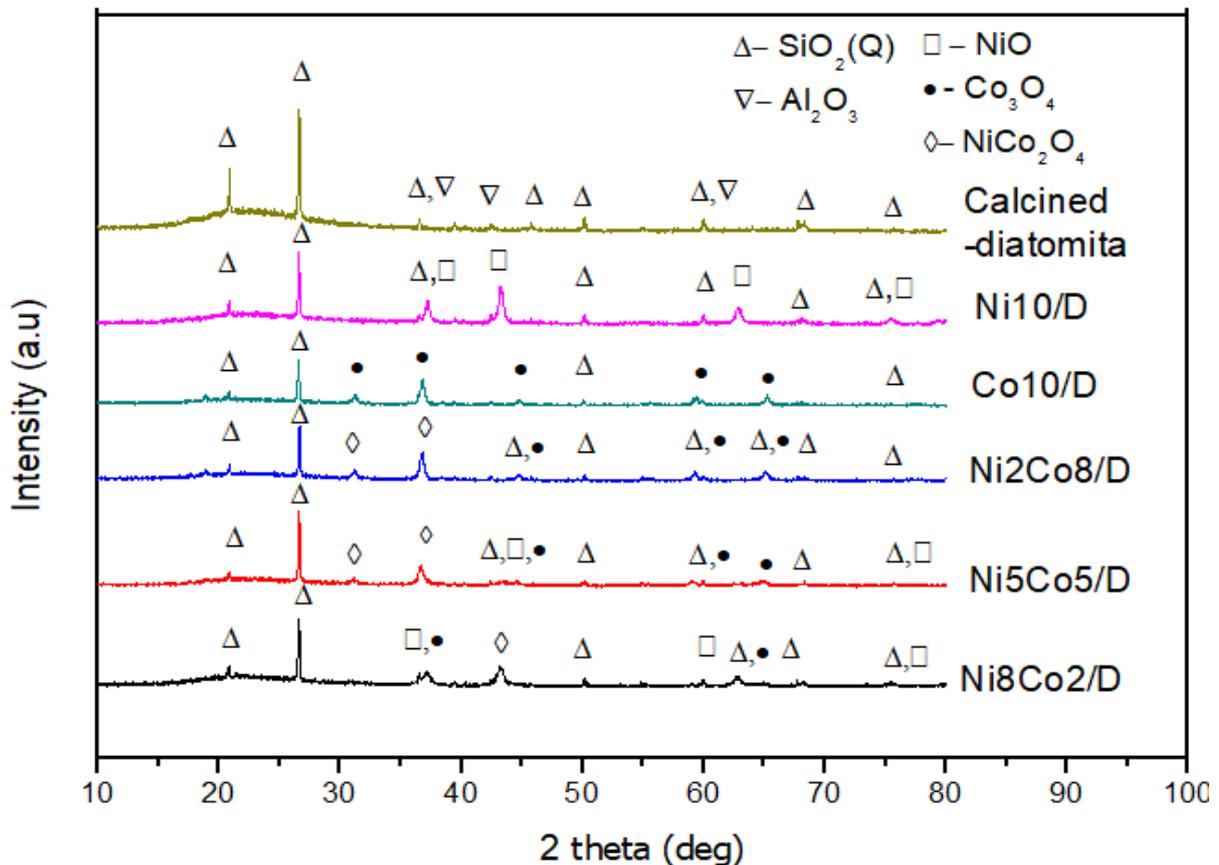
$$(H_2/CO)_{syngas\ ratio} = \frac{(H_2)_{produced}}{(CO)_{produced}} \quad (5)$$

3. Results and Discussion

3.1 Characterization of the support and catalysts

X-ray diffractograms of the diatomite and the calcined catalysts are shown in Figure 1. All samples have a 2θ main peak at the 26.6° position corresponding to quartz (a major component of the diatomite structure), which was confirmed by ICSD N° 01-082-0511 (Pirsaraei *et al.*, 2015). Alumina (another diatomite component) was confirmed by ICSD N° 01-076-0939, in which the main peaks are 2θ = 36.5° and 60.0° (Pirsaraei *et al.*, 2015). The NiO phase at 2θ = 37.1° and 43.2° positions was confirmed by ICSD N° 01-078-0429 (Guo & Shi, 2013), and the diffraction peaks related to the Co₃O₄ phase were confirmed by ICSD N° 01-074-2120 in the positions 2θ = 31.4° and 36.6°. The presence of NiCo₂O₄ spinel was confirmed in bimetallic catalysts by the crystallographic data sheet ICSD N° 01-073-1702 in the positions 2θ = 31.1° and 36.5° (Estephane *et al.*, 2015).

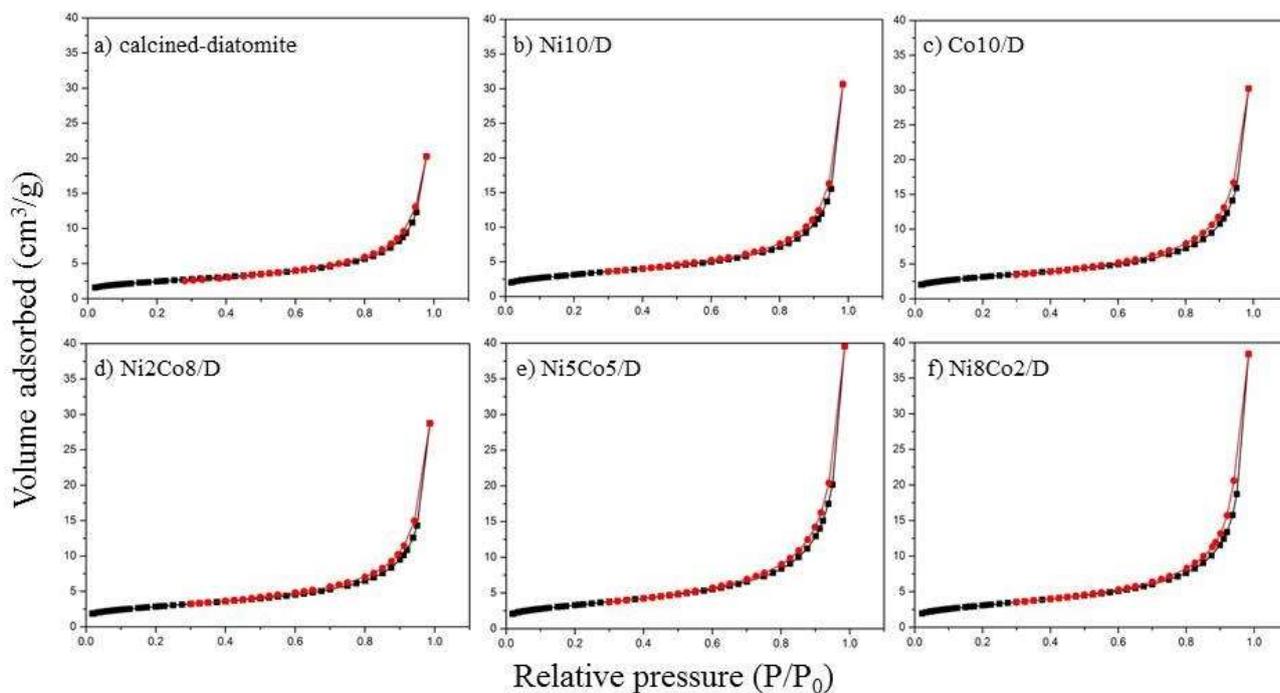
Figure 1 - XRD patterns of catalysts and support.



Source: Research data (2021).

The Figure 2 presents the adsorption and desorption curves of the support and of the monometallic and bimetallic catalysts. An analysis of the graphs shows that all the isotherms presented similar behaviors to that of the support (diatomite), which are type II (D. Li *et al.*, 2014) according to IUPAC classification. Table 1 shows the textural properties of the diatomite and the calcined catalysts, in which we can observe that the calculated values of specific area were very similar, corresponding to 9 m²·g⁻¹ for the support and ranging from 10 m²·g⁻¹ to 16 m²·g⁻¹ for the catalysts. Mean pore diameter values were also calculated, finding 140 Å for the support and between 160 Å and 210 Å for the catalysts. All these values suggest the presence of mesopores (Thommes *et al.*, 2015). The Table 1 further shows that the porous volume values for the catalysts are larger than the porous volume calculated for the calcined support. This set of results allows us to suggest that these particles contain mesopores which are primarily from interparticulate spaces, and which is in agreement with the data of increased porous volume after impregnation of the metals. Furthermore, it was possible to verify an increase in the mean pore diameter value calculated for the bimetallic catalysts as the Ni concentration increased. This is probably related to the fact that there are more NiO particles than Co₃O₄ particles for the same amount of metal.

Figure 2 - N₂ adsorption–desorption isotherms.



Source: Research data (2021).

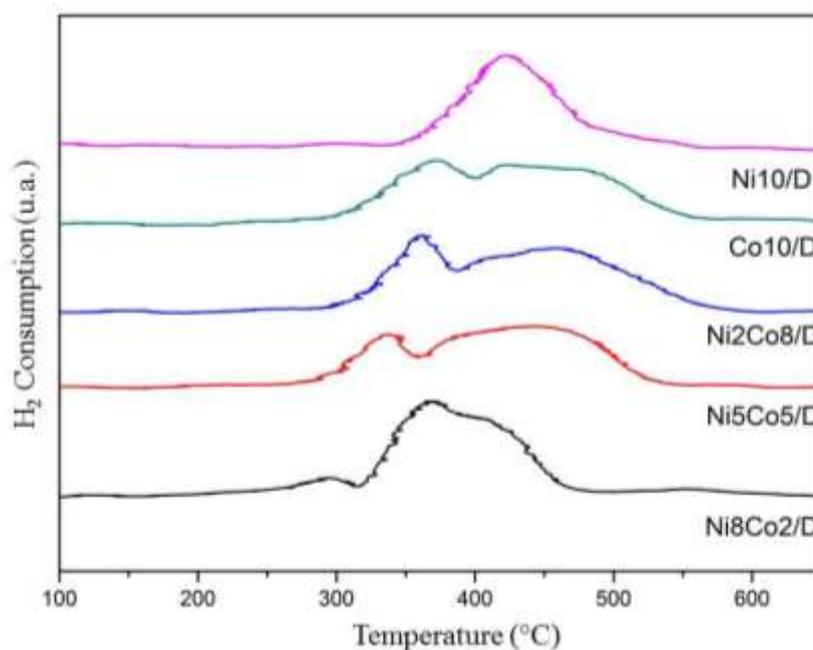
Table 1 - Textural properties of the support and catalysts.

Support/Catalyst	Composition (wt %)		Specific area (m ² ·g ⁻¹)	Pore size (Å)	Pore volume (cm ³ ·g ⁻¹)
	Ni	Co			
Calcined-diatomita	-	-	9	140	0.03
Ni10/D	10	-	11	170	0.05
Co10/D	-	10	11	160	0.05
Ni2Co8/D	2	8	10	170	0.04
Ni5Co5/D	5	5	12	200	0.06
Ni8Co2/D	8	2	11	210	0.06

Source: Research data (2021).

Figure 3 shows the reduction profiles of mono and bimetallic catalysts. The presence of a single H₂ consumption peak at 424 °C was observed in the TPR profile of the Ni₁₀/D catalyst, corresponding to the reduction of Ni²⁺ nickel oxide to Ni⁰. The reduction of nickel oxide supported by diatomite can occur at lower temperatures starting at 360 °C, indicating poor interaction between the metal/support (Guo & Shi, 2013). Therefore, the results obtained in this study suggest a strong interaction between NiO and Brazilian diatomite. On the other hand, the reduction profile of the Co₁₀/D catalyst showed two peaks at 369 °C and 439 °C. The first event is related to the reduction of Co₃O₄ to CoO. The second event is related to the reduction of CoO to Co⁰ (E. J. Fernandes, R.C.M. Silva, H.Á. Oliveira, B.B. Toledo, M.B.T. Moura, 2014). For bimetallic catalysts, the profiles suggest an overlap of the NiO and Co₃O₄ reduction events depending on their respective concentrations (X. Wang *et al.*, 2015). The combination of Ni and Co in the Ni₈Co₂/D catalyst promoted a lower reduction temperature between bimetallic catalysts. This may be associated with the formation of a mixed oxide of Ni and Co, as the amount of Co increases (Fakeeha *et al.*, 2015).

Figure 3 - H₂-TPR profiles catalysts.

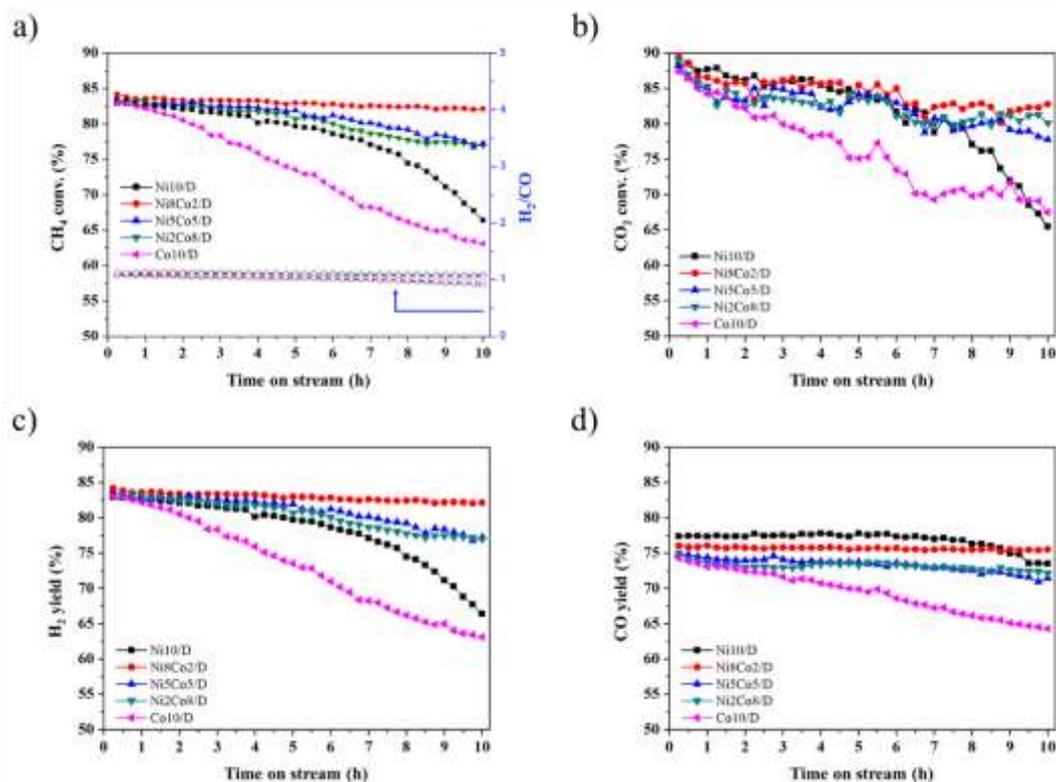


Source: Research data (2021).

3.2 Catalytic Tests

Figure 4 shows the catalytic performance of all catalysts versus the dry reforming methane. Figure 4(a) shows the conversion percentages of CH₄ and the molar H₂/CO ratios for the studied catalysts. From these results, all catalysts were found to have initial CH₄ conversions over 85%. Monometallic catalysts (Ni₁₀/D and Co₁₀/D) presented the lowest levels of stability during the 10 h. On the other hand, the bimetallic catalysts presented good stability, especially the Ni₈Co₂/D catalyst, which demonstrated the greatest stability over time. This shows the synergistic effect between metals in which the addition of 2% Co probably favored the increase of Ni reactivity (Gallego *et al.*, 2008; Gao *et al.*, 2017). For the CO₂ conversions shown in Figure 4(b), all catalysts demonstrate loss of stability. However, similar to that observed for the conversion of CH₄, bimetallic catalysts had greater stabilities, once again highlighting the Ni₈Co₂/D catalyst.

Figure 4 - Catalytic performance for DRM of the catalysts: (a) conversion to CH₄ and molar ratio H₂/CO, (b) conversion to CO₂, (c) yield to H₂ and (d) yield to CO, as a function of time.



Source: Research data (2021).

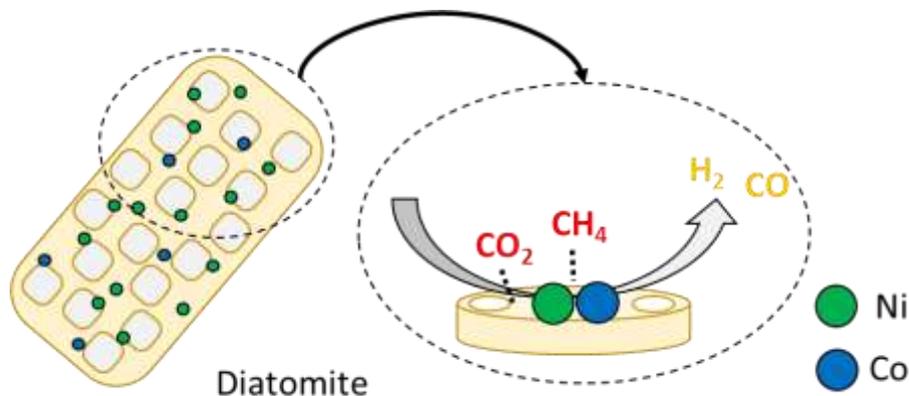
Figures 4(c) and (d) respectively show the yield percentages to H₂ and to CO. The catalyst Ni8Co2/D had the highest yields to H₂ and CO, since the parallel reactions leading to yield loss were more prominent for the other catalysts. With only 2% of Co, the Ni8Co2/D catalyst obtained a 3% increase in yield to H₂ when compared to the Ni10/D and Co10/D catalysts. In relation to CO yield, the Ni8Co2/D catalyst once again obtained the highest yield. Studies report that the addition of cobalt in Ni catalysts improves its catalytic performance (Gao *et al.*, 2017). However, bimetallic catalysts with higher concentrations of Co (Ni5Co5/D and Ni2Co8/D) did not present higher CO yields than the Ni10/D catalyst, indicating that the concentration may influence catalytic performance. As observed in the yield to H₂, the Co10/D catalyst showed the lowest CO yield. The H₂/CO ratios are shown in Figure 4(a), where it is possible to observe that the ratio values were slightly above 1, suggesting the occurrence of CH₄ cracking reactions (reaction 2).



According to the obtained results, all the catalysts were active, had high CH₄ (Fig. 4a) and CO₂ (Fig. 4b) conversion values and high yield to H₂ (Fig. 4c), demonstrating that Brazilian diatomite behaved very promisingly as a catalyst support in DRM. The Figure 5 shows the schematic representation of the Ni and Co bimetallic phase performance supported by diatomite. The synergistic interaction between the metals and the diatomite promoted good levels of H₂ yield during the dry

reforming reaction of methane. This may be associated with the contribution of organized oxides in the form of frustules in the diatomite, such as SiO_2 , Al_2O_3 and Fe_2O_3 , which favored better bimetallic catalyst performance.

Figure 5 - Schematic of the diatomite structure and the metallic phases in DRM.

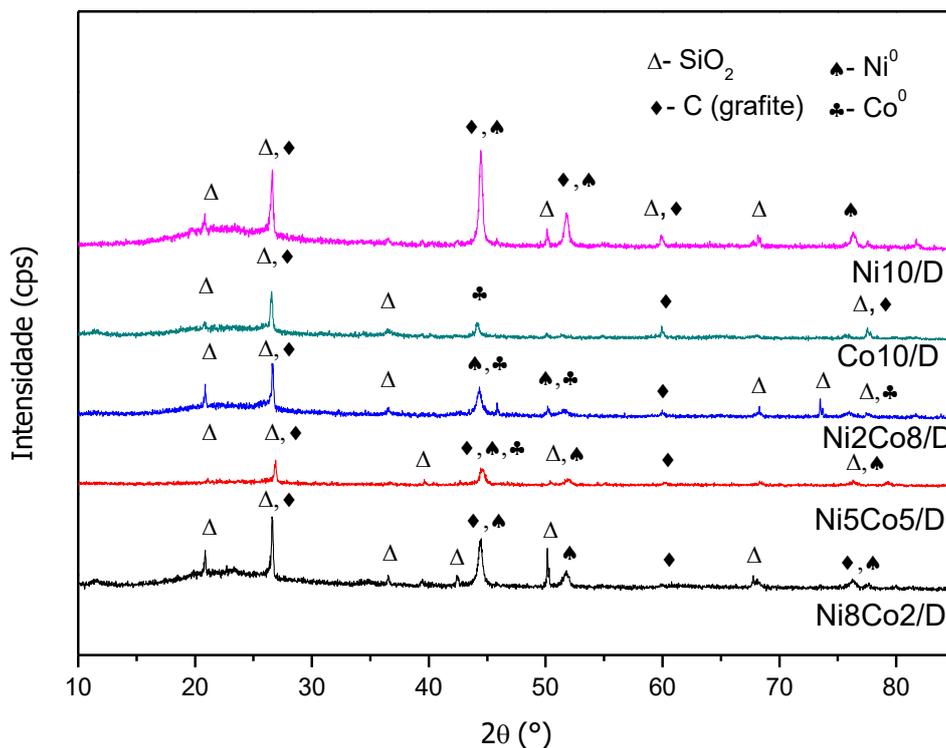


Source: Research data (2021).

3.3 Characterization of the catalyst after the reaction (DRM).

The Figure 6 presents the phases formed after the DRM. In observing the XRD patterns, the presence of quartz in the diatomite can be found for all catalysts. Metal phases corresponding to each catalyst were also found, namely: Ni^0 and Co^0 identified by ICSD (N° 03-065-2865) and (N° 01-089-4307), respectively. There may be metal-metal interaction in bimetallic catalysts containing Ni and Co due to the reduction of the metal phases, in which the formation of a Ni-Co alloy may occur. During the catalytic reform, small displacements of the Ni^0 and Co^0 peaks were observed for bimetallic catalysts; an indication that the Ni-Co alloy formation took place (Gallego *et al.*, 2008). The presence of carbon graphite ($2\theta = 26.5^\circ$; Fig. 6) was found among all the catalysts, indicating coke formation during the reaction. Crystallite sizes of the catalysts were calculated using the Scherrer equation and the results expose that the active metal particles are below 50 nm, even after 10 h of reaction.

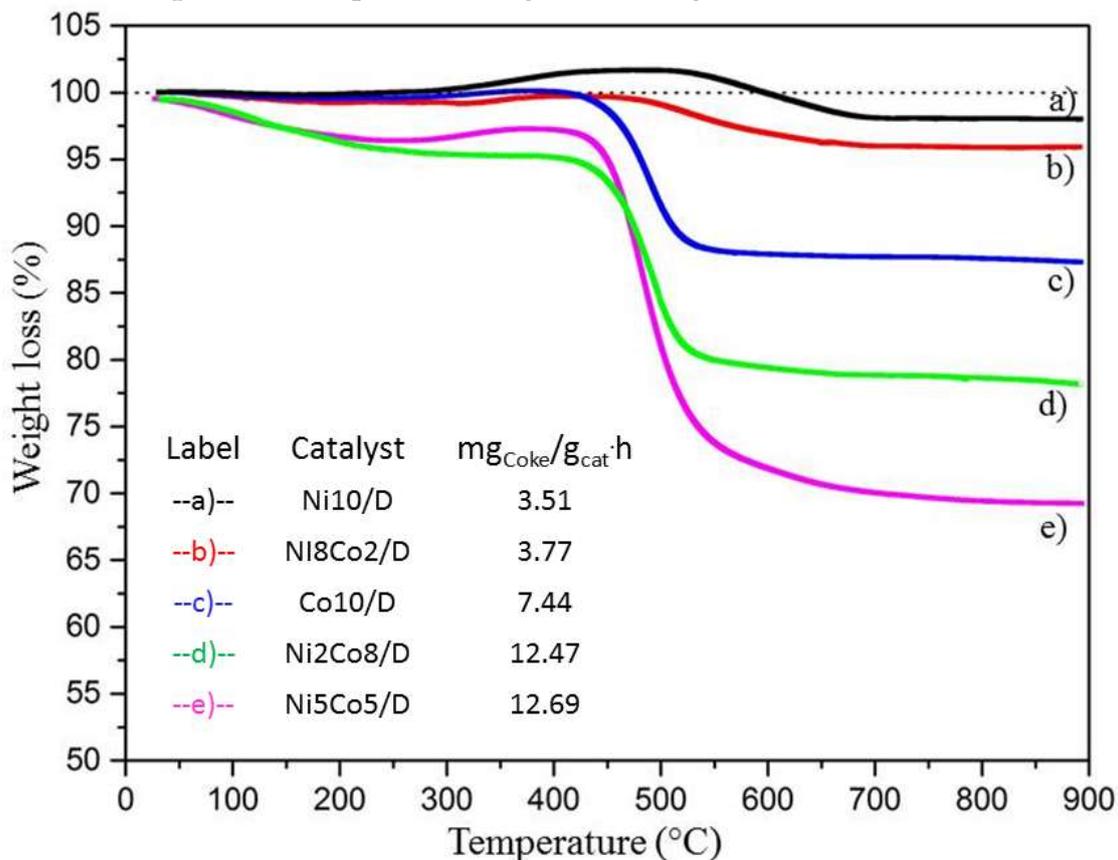
Figure 6 - XRD patterns of the catalysts after the reaction.



Source: Research data (2021).

The Figure 7 shows the mass loss curves obtained from thermogravimetric analysis (TGA). The amount of coke formed for each catalyst was determined by burning carbon from the TGA in an oxidizing atmosphere. According to the results, the Ni monometallic (Ni10/D) catalyst and catalysts with higher concentrations of Ni (Ni8Co2/D) showed lower mass loss, meaning they formed smaller amounts of coke when compared to catalysts with higher Co concentrations (Co10/D, Ni2Co8/D and Ni5Co5/D). These results after the thermogravimetric analysis corroborate with the results obtained from the dry reforming reactions of methane, in which the catalyst with the highest Ni concentrations presented better conversions of CH₄ (Fig. 4a) and a higher yield to H₂ (Fig. 4c).

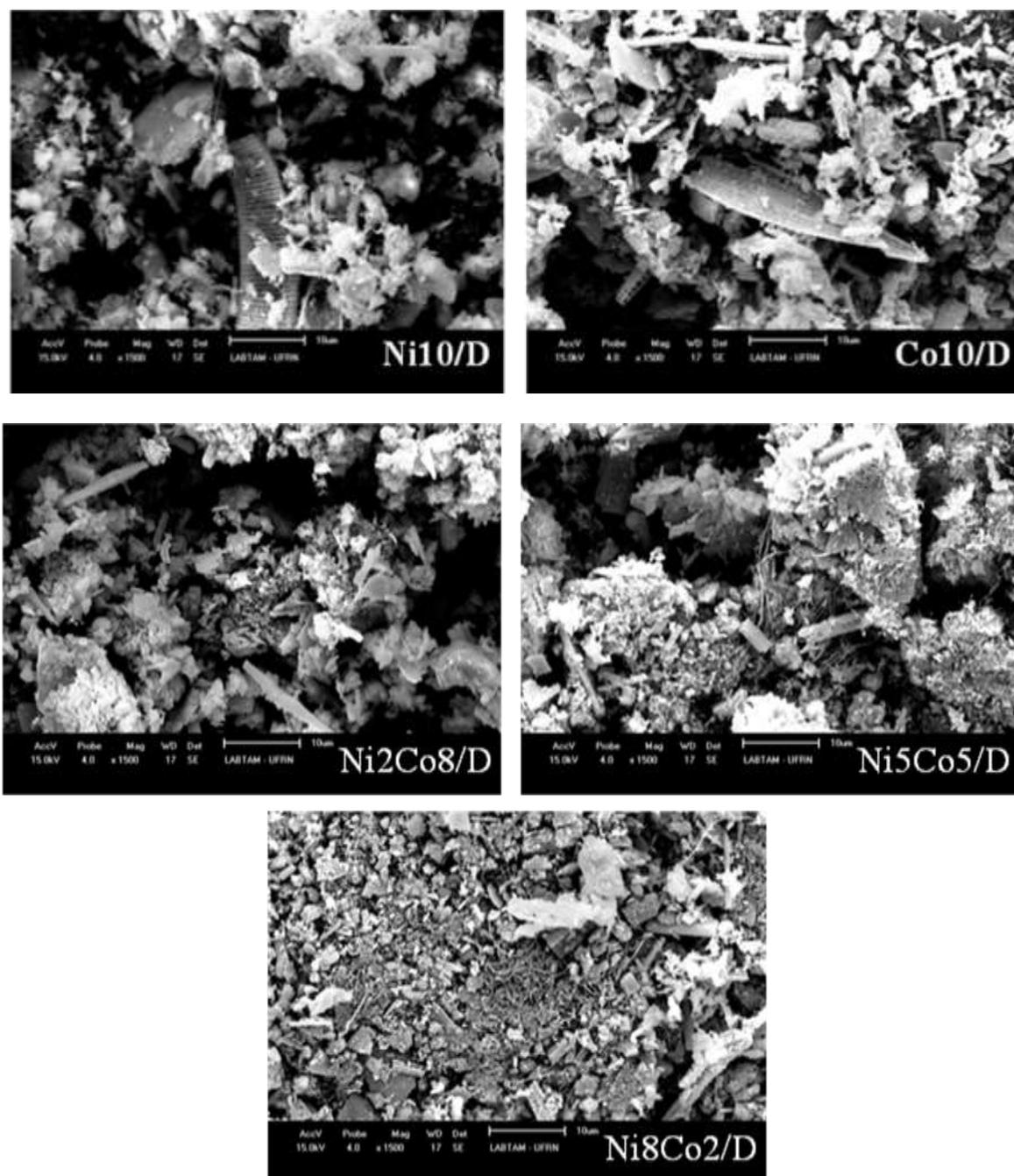
Figure 7 - Thermogravimetric analysis of the catalysts after the reform test.



Source: Research data (2021).

The Figure 8 shows the catalyst micrographs after the reforming test. We found that the diatomite morphology characterized by frustules was maintained. Formed carbon was identified by the presence of filaments on its surface. In turn, carbon was quantified by thermogravimetric analysis. The curves shown in Figure 7 indicate that the monometallic Ni10/D catalyst and the bimetallic Ni8Co2/D catalyst presented the smallest amount of formed carbon. Despite the Ni8Co2/D catalyst having formed slightly higher amounts of carbon than Ni10/D, the latter was the most active and stable. Thus, we can point out that the addition of Co promotes greater formation of carbon, as observed (Figs. 7 and 8) for the catalysts Ni5Co5/D, Ni2Co5/D and Co10/D, which can be associated to an increase in the occurrence of parallel reactions which lead to the formation of carbon; in turn, this increase leads to an increase of deactivation effects.

Figure 8 - Micrograph of the catalysts after the reform test.



Source: Research data (2021).

4. Conclusion

This study showed that Brazilian diatomite is a promising support for Ni-Co catalysts in the dry reforming reaction of methane. Impregnation of Ni, Co and Ni-Co was effective in the diatomite support. The presence of 2% Co allowed a reduction of metallic phases at slightly lower temperatures, better CH₄ conversion and a better yield to H₂ in the 10 h period. This confirms the synergistic effect between Ni and Co in the Ni₈Co₂/D catalyst, which presented the best stability among all catalysts. The support morphology was maintained after the introduction and reduction of the metals, as well as after its use in DRM at 700 °C for 10 h. For future work, it is possible to evaluate the effects of temperature variation and the percentage of promoters based on manganese, phosphorus and cerium supported on white and/or pink diatomite.

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