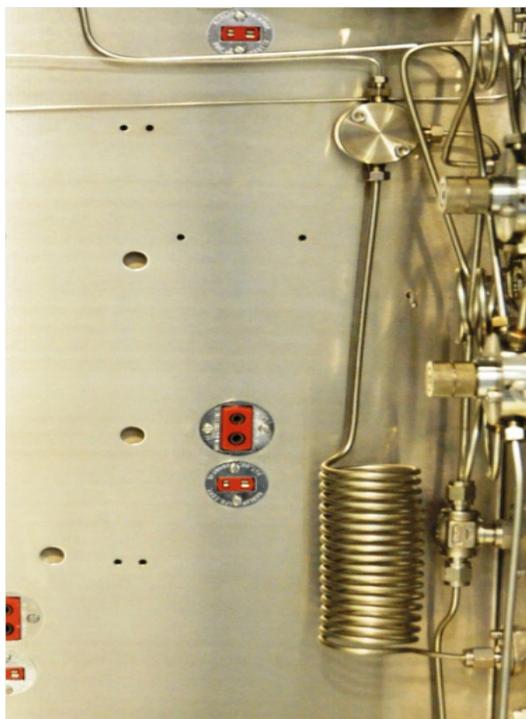
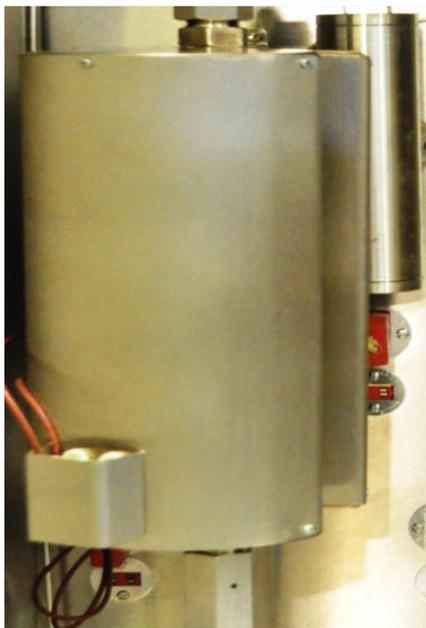


Evaluation of nickel content in Ni-Mg-Al mixed oxides in steam reforming of simulated biogas



**Empresa Brasileira de Pesquisa Agropecuária
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Evaluation of nickel content in Ni-Mg-Al mixed oxides in steam reforming of simulated biogas

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Abstract – Ni-Mg-Al mixed oxides derived from hydrotalcite-like compounds were prepared by a co-precipitation technique, calcined at two temperatures (550 °C and 750 °C) and applied to steam reforming of simulated biogas. Three nickel contents were used in the catalysts (5, 10 and 15%). The catalysts were characterized by X-ray fluorescence, N₂ sorption techniques, X-ray diffraction and temperature-programmed desorption of CO₂. Steam reforming experiments using simulated biogas were carried out at atmospheric pressure and 750 °C, using S/C ratio of 3.2. Catalysts calcined at 750 °C showed nickel and magnesium aluminate phases, resulting in lower density of basic sites. Conversion of CH₄ ranged from 97.4 to 99.6% while CO₂ conversion ranged from 58.5 to 63.5%. The H₂/CO ratio ranged from 2.6 to 3.1. However, the values are not statistically different at a significance level of 0.05.

Index terms: steam reforming, biogas, nickel catalyst, mixed oxides.

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Avaliação do teor de níquel em óxidos mistos Ni-Mg-Al na reforma a vapor do biogás simulado

Resumo – Óxidos mistos de Ni-Mg-Al derivados de compostos tipo hidrotalcita foram preparados, seguindo técnica de coprecipitação, calcinados a duas temperaturas (550 °C e 750 °C) e aplicados a reforma a vapor de biogás simulado. Foram utilizados três teores de níquel (5, 10 e 15%). Os catalisadores foram caracterizados por fluorescência de raios x, adsorção de N₂, difratometria de raios X, dessorção à temperatura programada de CO₂ e análise termogravimétrica. Os experimentos de reforma a vapor foram conduzidos com biogás simulado, à pressão atmosférica e temperatura de 750 °C, utilizando uma razão molar vapor/carbono de 3,2. Os catalisadores calcinados a 750 °C apresentaram fases de aluminato de níquel e magnésio, resultando em menor densidade de sítios básicos. A conversão de CH₄ variou de 97,4 a 99,6%, enquanto a conversão de CO₂ variou de 58,5 a 63,5%. A relação H₂/CO variou de 2,6 a 3,1. No entanto, os valores encontrados não são estatisticamente diferentes no nível de significância de 0,05.

Termos para indexação: reforma a vapor, catalisadores de níquel, biogás, óxidos mistos.

Introduction

Biogas is obtained through a process called anaerobic digestion of organic materials, as animal manure and food wastes, industrial wastewater and energy crops. The digester is the equipment where the anaerobic process takes place, converting the organic material in biogas. The technologies used in the digesters include the wet and dry fermentation systems (Weiland, 2010). In addition, biogas is also produced in landfills. Its main components are methane (CH_4) and carbon dioxide (CO_2), as well as some other gases as hydrogen sulfide (H_2S), hydrogen (H_2) and nitrogen (N_2) (Noyola et al., 2006).

Methane is a fuel gas and the main component of biogas and natural gas. Because of the calorific value of methane, natural gas is used for electricity generation and heating, besides being used for production of hydrogen, methanol and liquid hydrocarbons. Therefore, biogas can be used for the same purposes. However, while natural gas is a fossil fuel, biogas is renewable. Furthermore, methane is greenhouse gas (GHG) if emitted to the atmosphere, accounting for 16% of GHG emissions and with global warming potential 28 times greater than CO_2 over 100 years. Thus, methane emissions currently contribute to about one-third of today's anthropogenic global warming. To prevent methane emissions, biogas from landfills must be collected and flared, if not used for energy production (Rasi, 2009; IPCC, 2014; GMI, 2019; EIA, 2019).

Therefore, the use of biogas for energy generation or production of chemicals has high potential to mitigate the global warming, due to the decrease in methane emissions, as well as reduction in the use of fossil fuels, such as natural gas.

The reforming process has been applied to biogas for production of synthesis gas, which is a mixture of hydrogen (H_2) and carbon monoxide (CO). The main applications of synthesis gas are the production of methanol, hydrogen and liquid hydrocarbons via the Fischer-Tropsch (FT) synthesis (Olah et al., 2013; Yang et al., 2014; Cruz et al., 2018). In this way, the reforming process is a method to obtain higher added value products from biogas.

The main reforming process used in the industry is steam reforming, a technology applied at the large scale to natural gas for hydrogen production. In this process, methane reacts with steam in the presence of a catalyst in temperatures close to 800 °C, pressures around 20 bar and steam:carbon ratios

of 2.5-3.0 (Armor, 1999; Basin et al., 2017; Cancela et al., 2015). Steam reforming of methane results in $H_2:CO$ ratios equal to three (Alves et al., 2013). This process has been used to convert biogas into synthesis gas (Chiodo et al., 2017). Other reforming processes applied to biogas are dry reforming, autothermal reforming and partial oxidation (Charisiou et al., 2016; Galvagno et al., 2013; Izquierdo et al., 2012; Luneau et al., 2015; Calgaro, Perez-Lopez, 2019; Rau et al., 2019).

Steam reforming of biogas is a combined process of steam and dry reforming, coupled with water gas shift reaction. In addition, carbon is formed on the surface of the catalyst as the result of side reactions. The most important and thermodynamically probable reactions in steam reforming of biogas are shown in Table 1 (Annesini et al., 2007; Alves et al., 2013; Brus et al., 2015).

Table 1. Chemical reactions involved in steam reforming of biogas.

| Reaction | ΔH_{298} (kJ·mol ⁻¹) | Name |
|---|--|---------------------------|
| $CH_4 + H_2O \rightleftharpoons 3H_2 + CO$ (1) | 206.2 | Steam reforming |
| $CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$ (2) | 247.4 | Dry reforming |
| $CO + H_2O \rightleftharpoons CO_2 + H_2$ (3) | -41.2 | Water gas shift reaction |
| $CH_4 \rightleftharpoons C + 2H_2$ (4) | 74.9 | Methane decomposition |
| $2CO \rightleftharpoons C + CO_2$ (5) | -172.4 | Boudouard reaction |
| $CO + H_2 \rightleftharpoons C + H_2O$ (6) | -131.3 | Carbon monoxide reduction |

Source: Annesini et al. (2007), Alves et al. (2013) and Brus et al. (2015).

Nickel catalysts are the most used in the steam reforming of methane, but rhodium, ruthenium and other noble metals catalysts can also be used (Simsek et al., 2011; Son et al., 2013; Tuna et al., 2018). Nickel catalysts can be prepared from hydrotalcite-like compounds (HTLCs). These compounds, also known as layered double hydroxides (LDH), can be described by the formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{b+} \cdot (A^{n-})_{b/n} \cdot mH_2O$, where M^{2+} , M^{3+} e A^{n-} are divalent, trivalent cations and anions of charge $n-$, respectively. The divalent cation M^{2+} can be Mg^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} or Mn^{2+} , while the trivalent cations M^{3+} can be Al^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Ni^{3+} , or Co^{3+} . Among the interlayer anion (A), it can be cited some anions as: F^- , Cl^- , Br^- , CO_3^{2-} , NO_3^- , CrO_4^{2-} , $Mo_7O_{24}^{6-}$

(Cavani et al., 1991; Xu et al., 2011; Fan et al., 2014). Nickel incorporated in Mg-Al HTLCs, followed by calcination and reduction, results in nickel catalysts with good performance for steam and dry reforming of methane (Wang et al., 2012; Fonseca et al., 2005; Debek et al., 2016; Lin et al., 2015). The high activity of Ni-Mg-Al catalysts derived from HTLCs is related to small and highly dispersed nickel particles formed, which prevent the sinterization process. They also show high surface areas and the basic property favors the adsorption and activation of CO₂ and consequently the resistance to coke formation in CO₂ reforming of methane (Serrano-Lotina et al., 2011; Lin et al., 2015). However, nickel catalysts obtained from hydrotalcite-like compounds have not been used for biogas steam reforming.

In this work, the influence of the nickel content on mixed oxides Ni-Mg-Al was evaluated in steam reforming of simulated biogas (70 vol. % CH₄ and 30 vol. % CO₂).

Materials and Methods

Mixed oxides Ni-Mg-Al preparation

Mixed oxides (MO) with 5, 10 and 15 wt.% of NiO were obtained from hydrotalcite-like compounds. These compounds were prepared by co-precipitation from aqueous solutions, based on the method described by Villanueva (2005). Solution A, containing mixed metal nitrates (Ni(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O, 2.14 M, with molar ratio M³⁺/(M³⁺ + M²⁺) of 0.25 was added slowly into solution B of Na₂CO₃ and NaOH, 3.37 M, under stirring. The resulting suspension was stirred for more 30 min and aged for 21 h at room temperature. Following, the suspension was filtered and the solid was washed with deionized water at 60 °C. The hydrotalcite-like compounds Ni-Mg-Al obtained were dried at 110 °C for 18 h, crushed and sieved (<0.425 mm). The Ni-Mg-Al mixed oxides were obtained by calcination at 550 °C or 750 °C during 2 h, which were named as XNiMOY (where X is the % of NiO, 5, 10 or 15, and Y is the calcination temperature, 550 and or 750).

Catalysts characterization

The chemical composition of the catalysts was determined by the X-ray fluorescence (XRF) spectrometer model EDX-720, Shimadzu, collected under vacuum conditions (45 Pa) using two channels with the X-ray source set at 50 and 15 kV for Ti–U and Na–Sc, respectively. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method with nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ using a Micromeritics ASAP 2420 instrument. The samples were dried at $100\text{ }^{\circ}\text{C}$ during 1 h and degassed under vacuum at $300\text{ }^{\circ}\text{C}$ for 1 h prior to measurement. X-ray diffraction (XRD) patterns of the catalysts were obtained with a D8 Bruker ASX diffractometer equipped with a LynxEye detector and employing $\text{CuK}\alpha$ ($\lambda = 1.5406\text{ \AA}$; 40 kV, 40 mA) radiation in steps of 0.05° from 5 to 80° . For the measurement of the crystallite mean diameter of metallic Ni crystallites, the Scherrer equation was used utilizing the line characteristic of Ni^0 (200) at $2\theta = 51.8^{\circ}$. The calcined samples were also reduced under pure hydrogen ($30\text{ mL}\cdot\text{min}^{-1}$) at $750\text{ }^{\circ}\text{C}$ for 1 h, after purged under nitrogen at the same temperature for 30 minutes and cooled to room temperature. Finally, the reactor was immersed in a mixture of isopropyl alcohol and liquid nitrogen and the reduced catalyst was passivated under flow of $5\% \text{ O}_2/\text{N}_2$ ($65\text{ mL}\cdot\text{min}^{-1}$) at $-73\text{ }^{\circ}\text{C}$ for 1 h. The quantity of basic sites after calcinations and reduction were determined by temperature-programmed desorption of CO_2 (TPD- CO_2) performed in a fixed bed reactor connected to a mass spectrometer (BALZERS), recording the signal corresponding to the CO_2 mass. Before the analysis, the catalysts were reduced in situ in H_2 flow of $30\text{ mL}\cdot\text{min}^{-1}$, from room temperature to $750\text{ }^{\circ}\text{C}$ ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$), remaining at this temperature for 1 h. The system was purged with helium for 30 min at this temperature and cooled. After reduction, the sample remained in CO_2 flow for 15 min, then purged with helium for more 30 min. After adsorption, the catalyst was heated to $750\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in helium flow.

Steam reforming of simulated biogas

Steam reforming of simulated biogas was carried out in Microactivity Reference PID Eng&Tech equipment with a tubular fixed-bed reactor. The reaction was performed at $750\text{ }^{\circ}\text{C}$ under atmospheric pressure using 100 mg of catalyst diluted with 100 mg of silicon carbide (SiC, Aldrich, product number 378097, 200–450 Mesh particle size) supported on quartz wool. Temperature

was measured by a type-K thermocouple inside the catalytic bed. The reactor was heated up during 20 min in argon flow of $30 \text{ mL}\cdot\text{min}^{-1}$, reaching about $650 \text{ }^\circ\text{C}$ at the end of this period. The catalyst was reduced for 30 min in hydrogen flow of $30 \text{ mL}\cdot\text{min}^{-1}$, while the reactor continued to heat up until the temperature reached $750 \text{ }^\circ\text{C}$. After that, the reactor was purged with argon flow of $30 \text{ mL}\cdot\text{min}^{-1}$ for 10 min. Subsequently, the mixture of CH_4 , CO_2 and H_2O was fed in the reactor, first by-passing the reactor and then flowing through the reactor. CH_4 : CO_2 molar ratio of 2.33:1 (70/30% (v/v)) and steam/carbon ratio (S/C) of 3.2 were used in the tests. The flows were $15.68 \text{ mL}\cdot\text{min}^{-1}$ of CH_4 , $6.72 \text{ mL}\cdot\text{min}^{-1}$ of CO_2 and $0.04 \text{ mL}\cdot\text{min}^{-1}$ of H_2O . The compositions of the effluent gas were analyzed using a gas chromatograph (Shimadzu GC-2014) connected in line with thermal conductivity detector. The conversion of methane (X_{CH_4}) and carbon dioxide (X_{CO_2}) are calculated as follows:

$$X_{\text{CH}_4} = \frac{[\text{CH}_4]_i - [\text{CH}_4]_o}{[\text{CH}_4]_i} \times 100 \quad (1)$$

$$X_{\text{CO}_2} = \frac{[\text{CO}_2]_i - [\text{CO}_2]_o}{[\text{CO}_2]_i} \times 100 \quad (2)$$

where $[\text{CH}_4]$ is the concentration of CH_4 , $[\text{CO}_2]$ is the concentration of CO_2 , and subscripts i and o refer to inlet and outlet of the reactor, respectively.

The selectivities were calculated as follows:

$$S_x = \frac{[X]}{[\text{Products}]} \times 100 \quad (3)$$

where $[X]$ = concentration of product X ($X = \text{H}_2$ or CO) and $[\text{Products}]$ = concentration of H_2 + concentration of CO .

The ratio of H_2/CO is defined in equation (4):

$$R_{\text{H}_2/\text{CO}} = \frac{[\text{H}_2]}{[\text{CO}]} \quad (4)$$

where $[\text{H}_2]$ is the concentration of H_2 and $[\text{CO}]$ is the concentration of CO .

Results e Discussion

Catalyst characterization

The chemical composition of the mixed oxides (MO), as determined by X-ray Fluorescence, obtained from the hydrotalcite-like compounds calcined at 550 °C and 750 °C is shown in Table 2. The results show that the nickel contents are higher than the nominal value. Chmielarz et al. (2002) also found nickel content higher than the intended composition in Ni-Mg-Al hydrotalcite synthesis, attributed to the pH of precipitation (pH = 10), and this value is similar to the pH in the aging step of catalysts preparation. Furthermore, the samples had values of the ratio $M^{3+}/(M^{2+} + M^{3+})$ higher than the nominal value (0.25). This result can be related with the multiple washing with slightly acidic distilled water (pH \approx 6) at the final stage of the preparation procedure, which is sufficient to cause selective dissolution of some magnesium component (Michalik et al., 2008).

Table 2. Chemical composition of the catalysts.

| Catalyst | Chemical composition | | | |
|-----------|----------------------|------------------------------------|--------|---------------|
| | MgO (%) | Al ₂ O ₃ (%) | Ni (%) | Al/(Al+Mg+Ni) |
| 5NiMO550 | 57.9 | 33.3 | 6.6 | 0.30 |
| 10NiMO550 | 54.6 | 30.1 | 11.8 | 0.27 |
| 15NiMO550 | 48.5 | 27.5 | 19.4 | 0.26 |
| 5NiMO750 | 58.8 | 32.7 | 6.3 | 0.29 |
| 10NiMO750 | 54.9 | 29.8 | 11.7 | 0.27 |
| 15NiMO750 | 49.6 | 28.2 | 17.2 | 0.27 |

Textural properties (Table 3) of the catalysts changed with the calcination temperature. The increase in the calcination temperature from 550 °C to 750 °C resulted in an increase in the specific surface area for all samples. The catalysts calcined at 550 °C, the specific surface area is around 260 m²·g⁻¹, and the values are not related with the nickel content. However, the catalysts calcined at 750 °C had a decrease in the specific surface area with the increase of the metal content. Increasing the calcination temperature resulted in an

increased the micropore area for the catalysts with 5% of nickel, while for the catalysts with 10% and 15% of nickel there was an increase in pore volume.

Table 3. Textural properties of the catalysts.

| Catalyst | BET surface area (m ² ·g ⁻¹) | External area (m ² ·g ⁻¹) | Micropore area (m ² ·g ⁻¹) | Pore diameter (Å) | Pore volume (cm ³ ·g ⁻¹) |
|-----------|---|--|---|-------------------|---|
| 5NiMO550 | 260 | 234 | 25,8 | 43,9 | 0,227 |
| 10NiMO550 | 261 | 218 | 42,3 | 64,8 | 0,336 |
| 15NiMO550 | 259 | 212 | 46,5 | 52,3 | 0,270 |
| 5NiMO750 | 332 | 247 | 85,5 | 34,7 | 0,179 |
| 10NiMO750 | 302 | 266 | 35,9 | 66,8 | 0,420 |
| 15NiMO750 | 278 | 239 | 39,5 | 61,9 | 0,404 |

The diffractograms of the hydrotalcite-like compounds Ni-Mg-Al are presented in Figure 1, showing peaks at 2θ close to 11.5°, 22.9°, 34.6°, 38.5°, 46.0°, 60.5° and 61.9°, corresponding to the diffraction planes of (003), (006), (102), (105), (108), (110) e (113), respectively, characteristics of a well-crystallized HTLC in carbonate form. No other phases were present, suggesting that both Ni²⁺ and Al³⁺ have isomorphically replaced Mg²⁺ cations in the brucite-like layers (Rodrigues et al., 2003; Manfro et al., 2013).

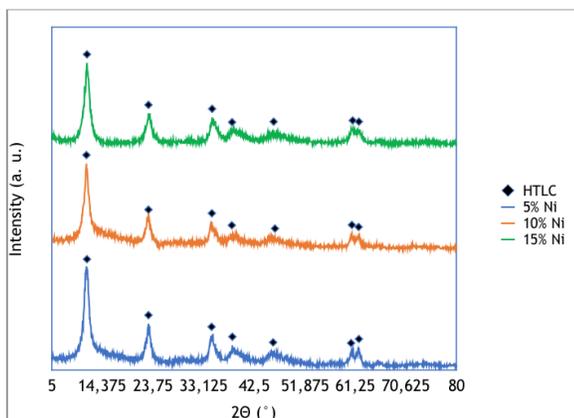


Figure 1. Diffractograms of the hydrotalcite-like compounds Ni-Mg-Al with 5%, 10% and 15% of nickel content.

The diffractograms of the mixed oxides obtained from the HTLC Ni-Mg-Al calcined at 550 °C and 750 °C are shown in the Figures 2 and 3. The catalysts have peaks around 44° e 63° corresponding to the solid solution NiO-MgO. Moreover, crystalline phases of Al₂O₃ were not formed in the mixed oxides, suggesting that Al is part of the crystalline network of the mixed oxides (Daza et al., 2010; Debek et al., 2015). The catalyst 5NiMO750 (Figure 3) also showed the characteristic peak related to nickel aluminate (NiAl₂O₄) and magnesium aluminate (MgAl₂O₄) in 2θ ≈ 37°, but it is not possible to distinguish them because of the similar diffraction pattern.

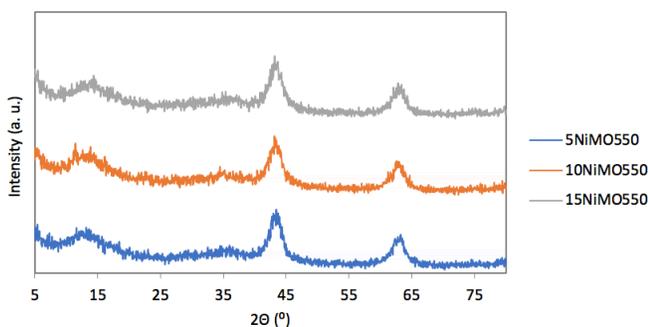


Figure 2. Diffractograms of the mixed oxides obtained from the calcination of the hydrotalcite-like compounds at 550 °C.

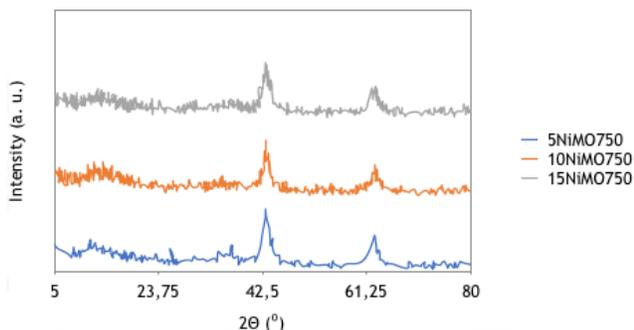


Figure 3. Diffractograms of the mixed oxides obtained from the calcination of the hydrotalcite-like compounds at 750 °C.

The basicity of the mixed oxides obtained from the hydrotalcite-like compounds was evaluated by temperature-programmed desorption of CO₂ (TPD-CO₂) of the samples calcined and reduced at 750 °C. The results of the

TPD- CO_2 of the catalysts are shown in Figure 4 and Figure 5. The TPD- CO_2 profiles were deconvoluted into four peaks, the temperatures of the highest points are around 150 °C, 200 °C, 250 °C, and 315 °C. The peak observed at 100-150 °C is attributed to the desorption of CO_2 from weak -OH groups. Another two peaks at 150-270 °C are assigned to the formation of bidentate carbonates bonded to metal-oxygen pairs, which are related to medium-strength basic sites. Strong basic sites are observed in temperatures above 270 °C, assigned to desorption of unidentate carbonates bonded to O^{2-} of low coordination (Di Cosimo et al., 1998; Debek et al., 2015).

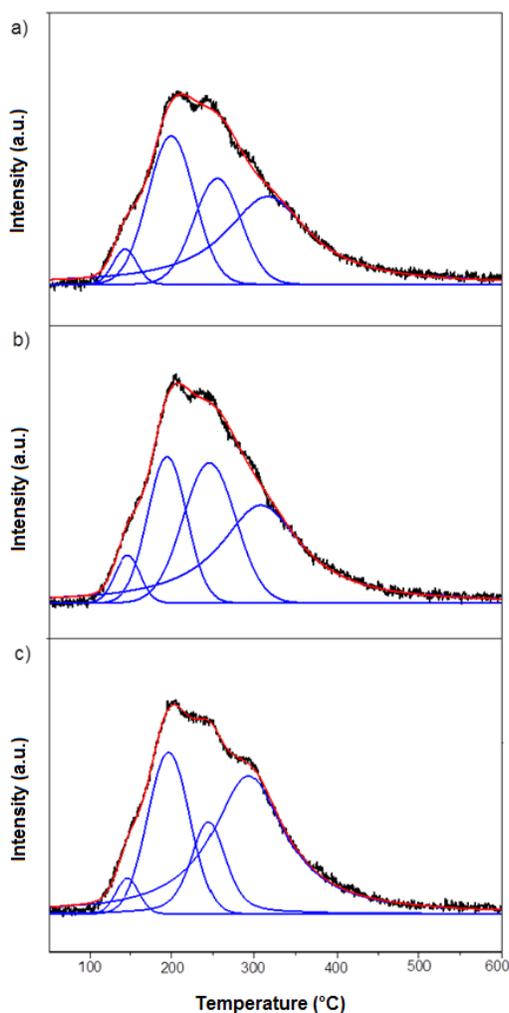


Figure 4. CO_2 -temperature programmed desorption profiles of the catalysts (a) 5NiMO550, (b) 10NiMO550 and (c) 15NiMO550.

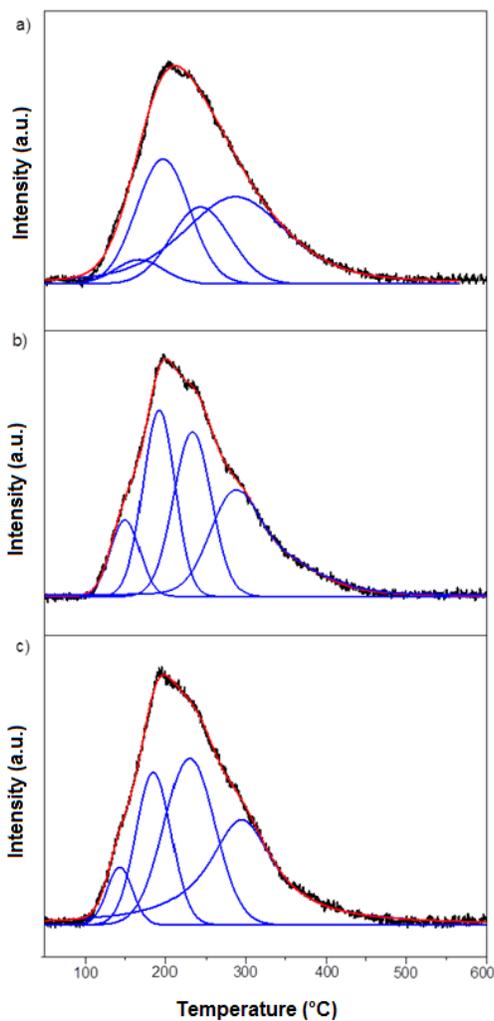


Figure 5. CO₂-temperature programmed desorption profiles of the catalysts (a) 5NiMO750, (b) 10NiMO750 and, (c) 15NiMO750.

Table 4 shows the quantity and the strength of the basic sites in the catalysts. The quantity of the basic sites is in accordance with the values found in the literature (Debek et al., 2015). The density of the basic sites decreases as calcination temperature rises, what can be related with the formation of nickel aluminate (NiAl₂O₄) and magnesium aluminate (MgAl₂O₄), which bloc-

ked the basic sites in the catalyst by removing Ni or Mg from the structure of the mixed oxide. The basicity of the catalysts was not modified significantly when Mg^{2+} was replaced by Ni^{2+} , but it changed the strength of the basic sites. Increasing the nickel content increased the number of strong basic sites in the catalysts calcined at 550 °C, highlighting the interaction between the Ni and Mg cations. However, an opposite trend is observed for the catalysts calcined at 750 °C and the catalyst with the lower nickel content shows a higher percentage of strong basic sites, probably because of the lower formation of nickel aluminate.

Table 4. Basicity of the mixed oxides obtained from hydrotalcite-like compounds Ni-Mg-Al calcined at 550 °C and 750 °C.

| Catalyst | Basicity (% desorption peak area) | | | Basic sites ($\mu\text{mol}\cdot\text{g}^{-1}$) | Density of sites ($\mu\text{mol}\cdot\text{m}^{-2}$) |
|-----------|--------------------------------------|--------|--------|--|--|
| | Weak | Medium | Strong | | |
| 5NiMO550 | 4 | 52 | 44 | 85 | 0.29 |
| 10NiMO550 | 5 | 52 | 43 | 98 | 0.36 |
| 15NiMO550 | 3 | 43 | 54 | 91 | 0.36 |
| 5NiMO750 | 5 | 50 | 45 | 73 | 0.22 |
| 10NiMO750 | 6 | 55 | 39 | 61 | 0.20 |
| 15NiMO750 | 6 | 56 | 38 | 62 | 0.22 |

Steam reforming of simulated biogas

The conversion of methane during the steam reforming of simulated biogas is shown in the Figure 6 for the mixed oxides Ni-Mg-Al obtained from the calcination at 550 °C, while in the Figure 7 are shown the results for the catalysts calcined at 750 °C.

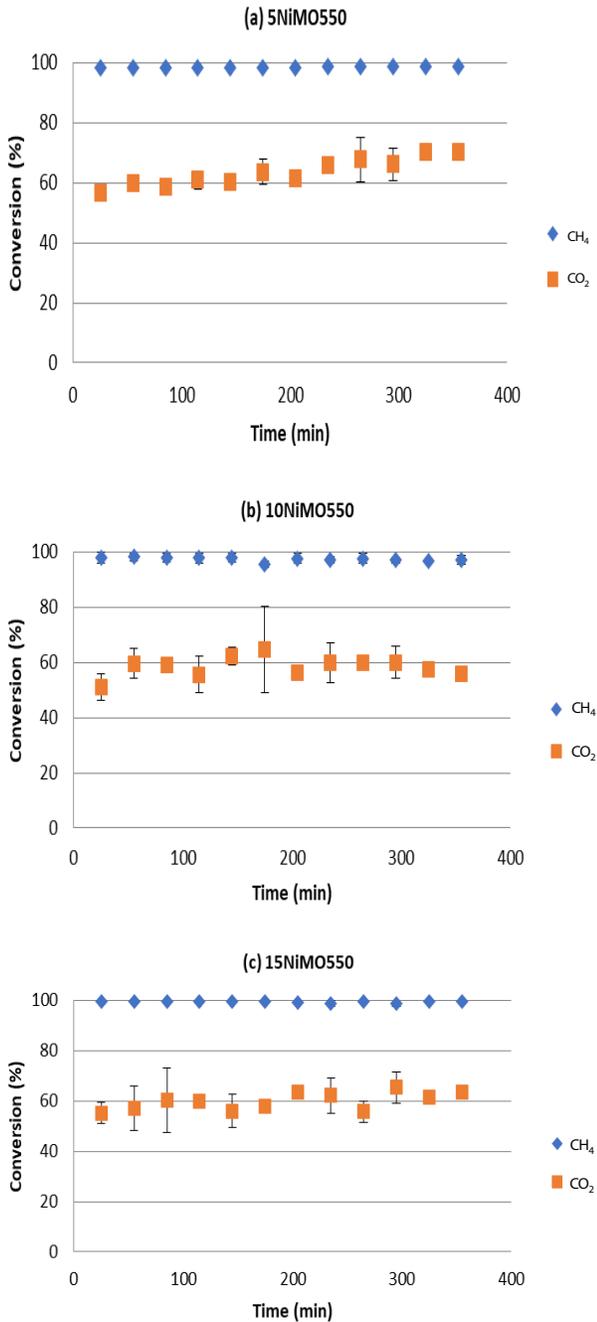


Figure 6. Methane (CH₄) and carbon dioxide (CO₂) conversion in the steam reforming of simulated biogas using Ni-Mg-Al mixed oxides obtained from hydrotalcite-like compounds calcined at 550 °C and steam/carbon ratio of 3.2: (a) 5NiMO550, (b) 10NiMO550, and (c) 15NiMO550.

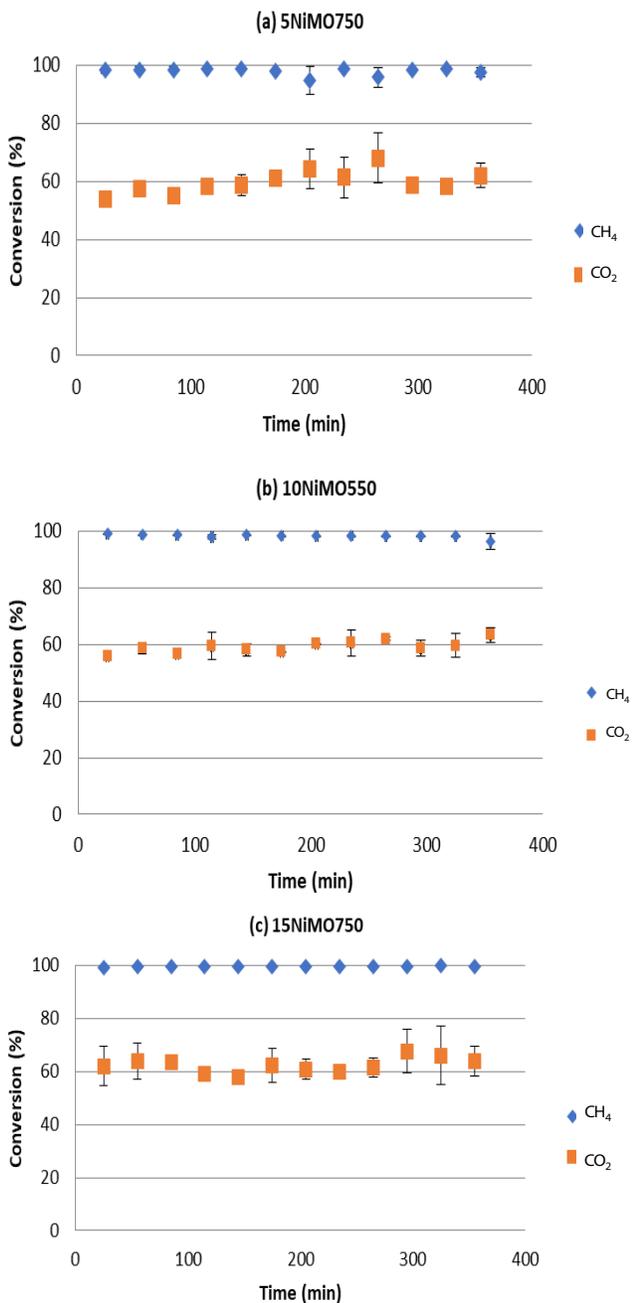


Figure 7. Methane (CH₄) and carbon dioxide (CO₂) conversion in the steam reforming of simulated biogas using Ni-Mg-Al mixed oxides obtained from hydrotalcite-like compounds calcined at 750 °C and steam/carbon ratio of 3.2: (a) 5NiMO750, (b) 10NiMO550, and (c) 15NiMO750.

The results in Figure 6 and Figure 7 showed that the conversion of methane was higher than the conversion of carbon dioxide, what was also found in the literature (Baek et al., 2011; Izquierdo et al., 2012). According to the results from Figure 6, the catalysts are stable during the reaction time. The CO₂ conversion was in the range from 56.5 to 70.3% for 5NiMO550, 55.7 to 63.4% for 10NiMO550 and 55.2 to 65.3% for 15NiMO550. In Figure 7, the CO₂ conversion was in the range from 54.0 to 68.0% for 5NiMO750, 51.2 to 64.6% for 10NiMO750 and 57.7 to 67.8% for 15NiMO750.

The selectivities of H₂ and CO are shown in Figure 8 and Figure 9 for the catalysts calcined at 550 °C and 750 °C, respectively. All catalysts showed higher selectivity to H₂ (67 – 78%) than to CO (22 – 33%) because steam reforming of methane (reaction (1) from Table 1) is the main reaction involved in steam reforming of biogas (Saeba et al., 2014). In the steam reforming of methane without considering other side reactions, for complete conversion of methane, the selectivity of H₂ would be 75% while the selectivity of CO would be 25%, calculated by equation (3). Catalysts 5NiMO550 and 10NiMO550 have higher selectivity to H₂ and lower to CO than catalyst 15NiMO550. The results of the selectivity for catalyst calcined at 750 °C showed more variation during the steam reforming reaction.

In the Table 5 are shown the average values of the conversion of CH₄ and CO₂ and H₂/CO ratio for the reactions using the steam/carbon ratio of 3.2. The average value of CH₄ conversion range from 97.4% to 99.6%, while the average CO₂ conversion is around 60% and the H₂/CO ratio is in the range of 2.6-3.1. Izquierdo et al. (2012) found CH₄ conversion of 100% for biogas steam reforming at 800 °C in fixed bed reactor using Ni/Ce-Zr-Al₂O₃, while the CO₂ conversion decreased with the S/C ratio. Roy et al. (2015) found CH₄ conversion around 95% at 750 °C for S/C ratio of 2.0 using Pd-Rh/(CeZrO₂-Al₂O₃) catalyst. Conversion of CH₄ and CO₂ reached 99.1% and 83.4% for steam reforming of biogas at 725 °C and S/C ratio of 0.4 when using 5%(Co-M1)-0.5%M2/Al₂O₃, where M1 is a noble metal and M2 is a rare earth metal (Itkulova et al., 2014). Using mixed oxides analogous to those used in this work, with 20% Ni, under similar conditions of temperature and CH₄/CO₂ ratio in dry reforming of biogas, Izquierdo-Colorado et al. (2018) obtained conversion of CH₄ close to 45%.w

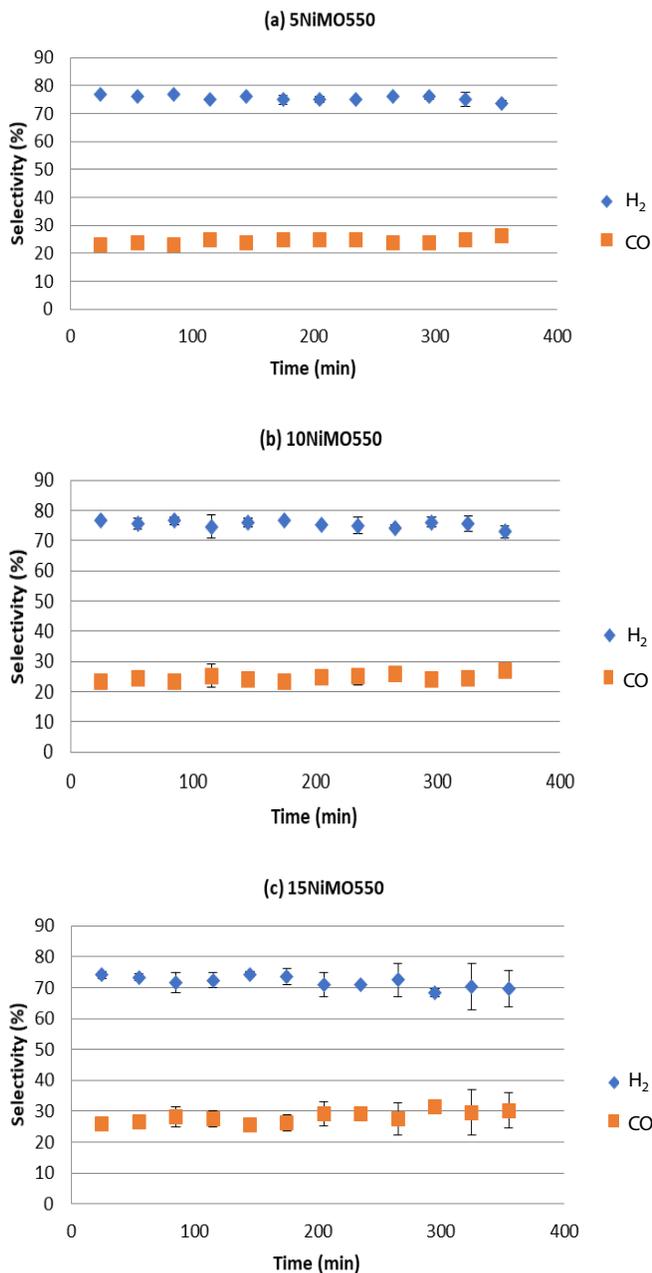


Figure 8. Selectivity of hydrogen (H₂) and carbon monoxide (CO) in the steam reforming of simulated biogas using Ni-Mg-Al mixed oxides obtained from hydrotalcite-like compounds calcined at 550 °C and steam/carbon ratio of 3.2: (a) 5NiMO550, (b) 10NiMO550, and (c) 15NiMO550.

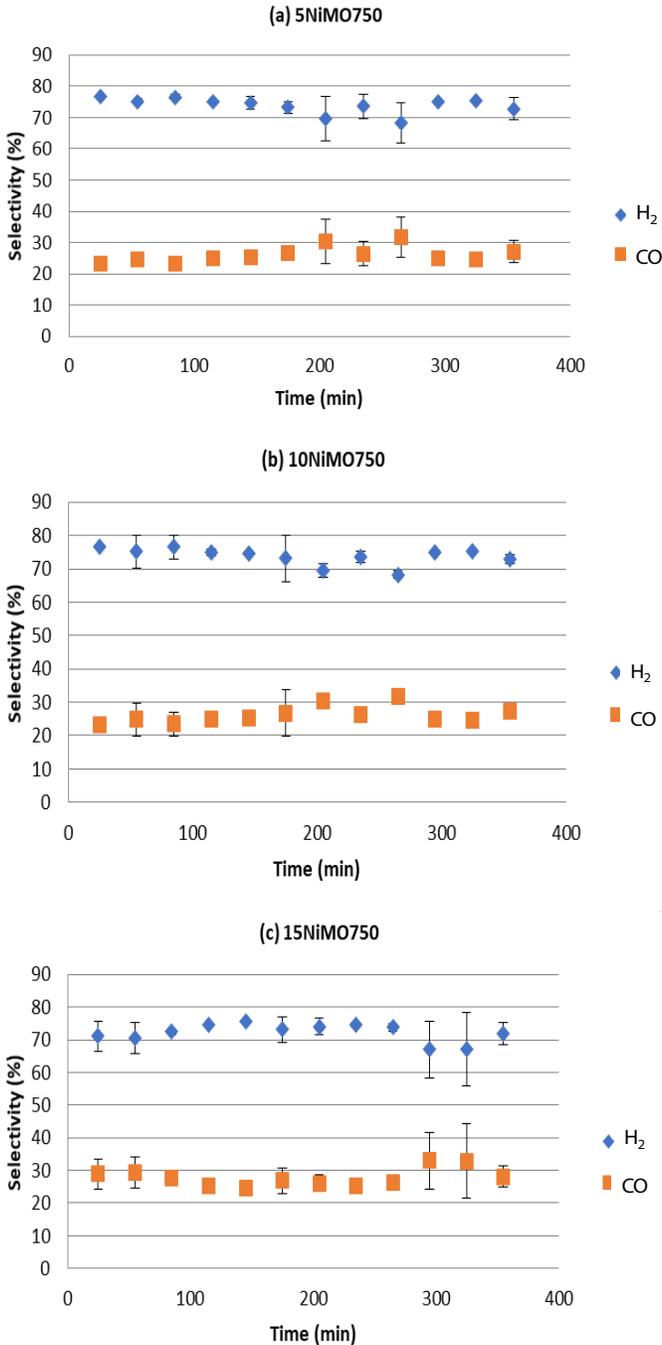


Figure 9. Selectivity of hydrogen (H₂) and carbon monoxide (CO) in the steam reforming of simulated biogas using Ni-Mg-Al mixed oxides obtained from hydrotalcite-like compounds calcined at 750 °C and steam/carbon ratio of 3.2: (a) 5NiMO750; (b) 10NiMO750; (c) 15NiMO750.

Table 5. Average values of methane and carbon dioxide conversion and H₂/CO ratio for the steam reforming of simulated biogas using S/C ratio of 3.2. Values in a column that do not share a superscript capital letter are statistically different ($p < 0.05$) based on ANOVA.

| Catalyst | \bar{X}_{CH_4} (%) | \bar{X}_{CO_2} (%) | $\bar{R}_{H_2/CO}$ |
|-----------|----------------------|----------------------|--------------------|
| 5NiMO550 | 98.5 ^{ABC} | 63.5 ^A | 2.9 ^{AB} |
| 10NiMO550 | 98.3 ^{BC} | 59.2 ^A | 3.1 ^A |
| 15NiMO550 | 99.3 ^{AB} | 59.8 ^A | 2.6 ^B |
| 5NiMO750 | 97.9 ^C | 59.8 ^A | 2.9 ^{AB} |
| 10NiMO750 | 97.4 ^C | 58.5 ^A | 3.0 ^{AB} |
| 15NiMO750 | 99.6 ^A | 62.3 ^A | 2.7 ^{AB} |

In thermodynamic equilibrium analysis of combined steam and carbon dioxide reforming of methane, increasing the (CO₂ + H₂O)/CH₄ ratios increased the CH₄ conversion at temperatures above 650 °C, and an increasing trend in CO₂ conversion is observed above 550 °C, which reflects that carbon dioxide dry reforming is favorable compared to water gas shift reaction at high temperatures, due to its highly endothermic nature. CH₄ conversion of almost 100% is achieved at 750 °C, (CO₂ + H₂O)/CH₄ ratio of 2.9 and CO₂:H₂O of 1.0:2.1 (Jang et al., 2016). The experiments of this paper used (CO₂ + H₂O)/CH₄ ratio of 3.6 and CO₂:H₂O of 1.0:7.4.

Although some variations in the responses of the catalysts were found, neither the nickel content nor the calcination temperature impacted the conversions of CH₄ and CO₂ and the H₂/CO ratio, according to the statistical analysis of the experimental data presented in Table 6. The H₂/CO ratios found in this work are in the same order of the ratios found with commercial catalysts (Izquierdo et al., 2012; Son et al., 2013).

Conclusions

Mixed oxides Ni-Mg-Al obtained from hydrotalcite-like compounds were evaluated in steam reforming of simulated biogas. The catalysts were characterized by XRF, N₂ sorption techniques, XRD and CO₂-TPD. The catalysts had values of the ratio M³⁺/(M²⁺ + M³⁺) in the range of 0.25-0.30, while the values of specific surface area in the range from 260 to 330 m²·g⁻¹. The nickel content

changed the number of strong basic sites, but for the catalysts calcined at 550 °C the strong basic sites increased with the increase of the nickel content, while for the catalysts calcined at 750 °C the strong basic sites decreased with the increase of the nickel content. Despite some changes in some properties of the catalysts, as basic sites and surface area, the nickel content did not change the conversions of the reactants. The methane conversion reached values around 99%. The results show the potential of the mixed oxides Ni-Mg-Al in steam reforming of biogas, obtaining synthesis gas, a gas mixture that can be used to produce methanol, hydrogen and liquid hydrocarbons.

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