Methane dry reforming using Ni/Al$_2$O$_3$ catalysts: Evaluation of the effects of temperature, space velocity and reaction time

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1. Introduction

Concern for the environment and the search for alternative energy sources have led to the development of technologies aimed at economic development coupled with minimization of environmental impacts. An ideal energy source is one that is inexpensive, clean, renewable and sustainable. One such source energy that is promising is biogas produced by the anaerobic decomposition of plant and animal wastes, typically composed of 55–75% methane (CH$_4$) and 25–44% carbon dioxide (CO$_2$), associated with traces of other gases such as hydrogen sulfide (H$_2$S), ammonia (NH$_3$), hydrogen (H$_2$), nitrogen (N$_2$), oxygen (O$_2$) and water vapor (H$_2$O) [1–4].

Methane reforming with CO$_2$ is a relevant process from the environmental standpoint because CO$_2$, one of the gases responsible for the greenhouse effect, can be converted, together with CH$_4$, into H$_2$ and CO (Eq. (1)) [5,6]. This process is endothermic, thus requiring high temperatures and with low pressures. In general, dry reforming (DR) takes place at temperatures varying from 600 to 900 °C, using a CH$_4$/CO$_2$ molar ratio of 1–1.5 to obtain H$_2$ yields of about 50% [6–9].

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^\circ = +247.0 \text{kJ/mol}$$ (1)

The main reaction may be accompanied by parallel reactions such as reverse water-gas shift (Eq. (2)), methanation (Eq. (3)), carbon monoxide decomposition by the Boudouard reaction (Eq. (4)), the undesired methane decomposition reaction (Eq. (5)), and also CO reduction (Eq. (6)) [1,10].

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298}^\circ = -41.0 \text{kJ/mol}$$ (1)
\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298} = +165.0 \text{ kJ/mol} \]  
(2)

\[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad \Delta H_{298} = -172.0 \text{ kJ/mol} \]  
(3)

\[ \text{CH}_4 \rightarrow 2\text{H}_2 \quad \Delta H_{298} = +75.0 \text{ kJ/mol} \]  
(4)

\[ \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \quad \Delta H_{298} = -131.0 \text{ kJ/mol} \]  
(5)

One of the main problems of the DR process is the coke formation. To minimize coke formation, it requires adjustments the process parameters such as temperature, flow rate, support and active phase \([6,8,11]\).

Nickel based alumina catalysts (Ni/Al\(_2\)O\(_3\)) have been recognized as the most effective materials for methane reforming reactions, due to their low cost and high activity \([5,6,9]\). Although several studies have focused on this type of catalyst, few of them have correlated the reaction variables with H\(_2\) production efficiency.

Therefore, the purpose of this study was to perform methane reforming in the presence of carbon dioxide, using Ni/Al\(_2\)O\(_3\) catalysts with different mass contents of Ni, and to evaluate the influence of reaction variables (temperature, space velocity and reaction time) on hydrogen production.

2. Materials and methods

2.1. Preparation of the catalysts

The Ni/Al\(_2\)O\(_3\) catalysts with metal loading of 15% and 30% weight were obtained by wet impregnation with an aqueous solution of nickel nitrate hexahydrate [Ni(NO\(_3\))\(_2\)6H\(_2\)O] (Sigma-Aldrich) on a commercial Al\(_2\)O\(_3\) support. After impregnation in a rotary evaporator, the catalyst was oven-dried at 110 °C for 24 h. The material was ground into particles of approximately 0.05 mm, and then calcined under the following conditions: at 3.0 °C min\(^{-1}\) from room temperature to 200 °C/60 min; followed by 500 °C/60 min, and at 5.0 °C min\(^{-1}\) up to 800 °C/4 h.

2.2. Characterization of the catalysts

The metal content was quantified by flame atomic absorption spectrometry (FAAS) (Varian SpectraAA 50). The textural analysis was performed on N\(_2\) isotherms, using a Quantachrome Instruments NOVA 2000e surface area analyzer.

The crystalline phases were analyzed qualitatively by X-ray diffraction (XRD) using a Shimadzu Lab XRD-6000 X-ray diffractometer, at a 2θ angle between 5° and 70°, with CuK\(_\alpha\) radiation (\(\lambda = 1.5406\) Å), operating at 40 kV, 30 mA, and a continuous scanning rate of 1.5°/min.

Temperature programmed desorption of ammonia (TPD-NH\(_3\)) was performed in a Quantachrome Instruments ChemBET 3000 multipurpose unit equipped with a thermal conductivity detector to verify the acid strength of active sites in the samples. About 100 mg of sample was placed in the unit and pretreated for 60 min at a temperature of 300 °C under nitrogen at a flow rate of 30 mL min\(^{-1}\). Then, samples were reduced under with 30 mL/min of 5% H\(_2\)/N\(_2\) mixture flow, followed by ammonia adsorption at 100 °C. After adsorption, the physisorbed portion was purged with N\(_2\) gas, followed by desorption of chemisorbed NH\(_3\) at a rate of 10 °C min\(^{-1}\) up to 700 °C.

For the temperature program reduction, samples were submitted to a 1.75% H\(_2\)/Ar mixture flow of 30 mL/min, with a 10 °C/min heating rate from room temperature until 1000 °C. The outlet gas was analyzed by a TCD, so the H\(_2\) consumed by the catalyst could be accomplished.

2.3. Catalytic tests

A methane dry reforming system was built (see Fig. 1) and it consists in four gas cylinder with manometers for pressure regulation. All tubes used in the system are 314 stainless still \(\frac{1}{4}\) in. All gases pass through the regulator system (1), where inlet pressure and flow can be controlled. The tube-reactor connections are quick-coupler. Gases are mixture in a gas camera of 250 mL internal volume, where the inlet flow cross a single-pass valve (2), so gases still flow in only one direction. After that, the mixture flow comes in an electric pre-furnace (5) for previous heating; here, 6 m of tube is used to guarantee the temperature condition. Then, the reaction mixture goes to the reforming furnace (6) and so the tubular U-shaped reactor (7), where the reaction begins. Digital controllers are used in the pre-furnace and reactor to reach the

![Fig. 1. Schematic diagram of the reactor used for methane dry reforming.](image-url)
necessary power, and each one has K thermocouple for temperature control. The outlet gas flow is monitored using a glass flow system control.

The catalyst was activated in situ in all the tests, using a H₂ flow of 40 mL min⁻¹ for 10 h at the reaction temperature. After that, N₂ flow was used for previous inert conditions.

First, the catalytic tests were conducted with constant space velocity (WHSV - reactants flow per mass of catalyst) at 30 L h⁻¹ g⁻¹cat with a fixed amount of 300 mg of catalyst and a CO₂:CH₄ molar ratio of 1, at temperatures of 600, 650 and 700 °C, for the 15% Ni/Al₂O₃ and 30% NiAl₂O₃ catalysts. Then, tests were performed with different WHSV (15 and 45 L h⁻¹ g⁻¹cat) and mass of catalyst (600 and 200 mg), a temperature of 650 °C and reaction time of 4 h. For the long during tests, reaction time was extended up to 10 h.

The gas product was analyzed in an Agilent 7890A gas chromatograph equipped with a TCD detector.

3. Results and discussion

3.1. Characterization of the catalysts

Table 1 lists the N₂ physisorption results obtained for the catalysts after calcination and for non-calcined alumina. Fig. 2 shows the N₂ adsorption and desorption isotherms.

It was found that the specific surface area of the impregnated materials decreased in relation to the support, as a result of the impregnation of Ni in the pores and on the surface of alumina. According to IUPAC (1976) [12], the isotherms of the materials can be classified as type IV, which is characteristic of mesoporous solids (pores with average diameter of 20 Å < Φ < 500 Å).

Table 1 shows that the average pore diameters ranged from 70 to 115 Å, indicating that the catalysts are mesoporous. The graph in Fig. 3 shows the pore size distribution according to the BJH model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m² g⁻¹)</th>
<th>Pore size/volume (cm³ g⁻¹) (BJH)</th>
<th>Mean pore diameter (Å) (BJH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>200</td>
<td>0.63</td>
<td>72.9</td>
</tr>
<tr>
<td>15% Ni/Al₂O₃</td>
<td>143</td>
<td>0.68</td>
<td>114.9</td>
</tr>
<tr>
<td>30% Ni/Al₂O₃</td>
<td>118</td>
<td>0.48</td>
<td>114.0</td>
</tr>
</tbody>
</table>

It was noted monomodal pore volume distribution of the materials, with well-defined maximum distribution.

The reduction on surface area was attributed to the active phase in the internal porous, which causes pore blocking; so, no NiO diffraction peaks could be observed in the diffractogram of the catalysts, as it can be seen in Fig. 4. There was an increase on the crystallinity of the catalysts compared to pure support. It was not identified changes on support phase crystallinity; the NiAl₂O₄ formation in the same theta position of some Al₂O₃ diffraction peaks revealed a great active phase dispersion and strong metal support interaction (SMSI) [13]. This oxide, although the low reducibility to metallic Ni, is favourable on high thermal reaction since no sinterization can took place.

Although no NiO diffraction peak was found on the XRD diffractograms, the TPR profiles showed different oxides in each catalyst (Fig. 5), both with high interaction with the support.

Two H₂ consumption peaks were detected in the catalysts with different Ni contents (Fig. 5). The first peak of the 15% Ni/Al₂O₃

Fig. 2. N₂ adsorption/desorption isotherms of non-calcined Al₂O₃, and of 15% Ni/Al₂O₃ and 30% NiAl₂O₃ catalysts calcined at 800 °C.

Fig. 3. Pore size distribution after desorption (dV(logD) cm³/g) of non-calcined Al₂O₃, and 15% NiAl₂O₃ and 30% NiAl₂O₃ catalysts calcined at 800 °C.

Fig. 4. XRD patterns of (a) non-calcined Al₂O₃, (b) 15% NiAl₂O₃ calcined at 800 °C, and (c) 30% NiAl₂O₃ calcined at 800 °C.
catalyst appeared at 631 °C and the second at 831 °C. The first peak of the 30% Ni/Al₂O₃ catalyst appeared at 759 °C and the last at 940 °C, indicating that an increase in the nickel composition did not alter the formation of oxides. The first peak in both catalysts may be attributed to NiO species of small sizes unidentified by XRD, dispersed in the alumina matrix, while the last peak may indicate the reduction of nickel oxide with more interaction with the support, probably the NiAl₂O₄ phase identified by XRD [14]. The 15% Ni/Al₂O₃ catalyst showed a slight reduction, indicating that the reduction of the oxide with the highest interaction occurred in two steps. The interaction between metal and support was more intense in the last peak, where the nickel reduction temperature was higher.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Acidity (TPD-NH₃).</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Desorbed ammonia (mmol NH₃/g)</td>
<td>0.074</td>
</tr>
<tr>
<td>Decreased acidity⁴</td>
<td>–</td>
</tr>
<tr>
<td>⁴ In relation to the Al₂O₃ support.</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. TPR profiles of the 15% NiAl₂O₃ and 30% NiAl₂O₃ catalysts calcined at 800 °C.

Fig. 6. Molar fraction of products obtained at WHSV = 30 L h⁻¹ g⁻¹ cat⁻¹ at different temperatures: (a) CH₄; (b) CO₂; (c) CO, and (d) H₂.
The analysis of TPD-NH₃ indicated two desorption peaks of the alumina support, with the maximum desorption temperature of the first peak at 206 °C attributed to weak acid sites and the maximum temperature of the second peak at 459 °C attributed to stronger acid sites. The incorporation of Ni on alumina led to the formation of an ammonia desorption peak in both catalysts: one at 269 °C for the 15% Ni/Al₂O₃ catalyst and the other at 335 °C for the 30% Ni/Al₂O₃ catalyst. Table 2 shows the quantification of the acid sites.

The addition of Ni reduced the acidity and led to the formation of only one NH₃ desorption peak. The reduction to a single ammonia desorption peak suggests that the incorporation of the metal occurred preferentially at one type of acid site, causing this group to become coated. The decrease in acidity favors the stability of the catalyst, reducing the deposition of carbon and preventing its deactivation [6].

3.2. Catalytic tests in methane dry reforming

Fig. 6 illustrates the results of the molar fraction of the gas product obtained in the tests in the range of temperatures. In Fig. 6, note that at the temperature of 650 °C the 30% Ni/Al₂O₃ catalyst presented a higher percentage of CH₄ (average of 59%), followed by the reaction performed at 600 °C. In the other experiments, the percentage of CH₄ was found to fall within the range of 30–40%. These results showed that not only complete dry reforming occurred, but also other undesired reactions, so the non-stoichiometric conversion was reached.

The highest percentage of H₂ (d) was obtained at 700 °C, where the first hour of reaction yielded values of 50 and 38% for the 15% Ni/Al₂O₃ and 30% Ni/Al₂O₃ catalysts, respectively. However, in the fourth hour of reaction, the molar fraction of H₂ dropped down to 41 and 32% for the same order catalysts, which may be attributed to the higher rate of coke formation at this temperature. In addition, the percentage of CO₂ (b) at 700 °C was found to increase over time-on-stream, indicating that the deactivation rate of the catalyst at 700 °C was higher than the other catalysts. The formation of CO (c) was observed at lower temperatures, and at 600 °C the 15% Ni/Al₂O₃ catalyst showed a CO molar fraction of 7–18% in the time range evaluated, while the 30% Ni/Al₂O₃ catalyst varied from 10 to 13%. At 650 °C, the catalysts presented an average of 3.82% of CO.

The results suggested the occurrence of parallel reactions, such as the water-gas shift reaction (Eq. (2)), in which CO reacts with H₂O to form CO₂ and H₂, and the Boudouard reaction (Eq. (4)). Another parallel reaction was the reduction of CO (Eq. (6)) by H₂, forming C and H₂O. In general, increasing the load of Ni metal resulted in a lower conversion of the reactants (Fig. 7) at the same temperature, indicating that the parallel reactions occurred more effectively, so the molar fractions of the products was farther from the stoichiometric proportions. The increase in nickel loading led to the formation of larger crystallite sizes, and hence less dispersion, which is unfavorable for the conversion of reagents.

Fig. 7. Conversion of (a) CH₄ and (b) CO₂ at different temperatures, using WHSV = 30 h⁻¹, 8.8 at⁻¹.
The temperature of 650°C was chosen for the tests with different WHSV values, since the reactions at 700°C showed an increase in coke formation that partially obstructed the reactor. Fig. 8 illustrates the molar fractions of the products of the reactions at 650°C with different space velocities (WHSV of 15 and 45 L h⁻¹ g₉cat⁻¹).

The highest molar fractions of H₂ (d) (27–30%) were obtained in the test with the 15% Ni/Al₂O₃ catalyst at a WHSV of 15 L h⁻¹ g₉cat⁻¹. The larger H₂ selectivity was reached for this catalyst with lower metal loading, which is in accordance with the catalyst properties and the dry reforming mechanism. The nickel dispersion favored CH₄ decomposition and C gasification. Then, no completely deactivation occurred for that catalyst. This reaction mechanism also explains the absence of CO since no adsorbed C underwent its gasification [18].

The formation of CO (d) (2–3%) occurred only in the test with 15% Ni/Al₂O₃ using a WHSV of 15 L h⁻¹ g₉cat⁻¹ and in the test with 30% Ni/Al₂O₃ (26–28%) using a WHSV of 45 L h⁻¹ g₉cat⁻¹. Fig. 9 shows the CH₄ and CO₂ conversion rates (%) at different space velocities.

The conversion profile for CH₄ pointed out for decreasing conversion with increasing the WHSV, for the same catalyst. This was expected cause the lower flow residence time. On the other side, for the same WHSV, the increase on nickel loading led to lower reaction rate, which was attributed to the quick catalyst deactivation. For the 15% Ni/Al₂O₃ with WHSV = 15 L h⁻¹ g₉cat⁻¹, the increase on CH₄ conversion respect to time-on-stream indicated a constant product desorption and no deactivation.

The results indicated that a larger amount of catalyst (lowest space velocity) in the reaction bed favored CH₄ conversion. In general, larger WHSV was desfavorable for CH₄ conversion since small bed length was used, and that was also observed by Rahemi et al. [18].

For CO₂, an opposite behavior was presented in Fig. 9. The increase on WHSV favored its conversion using the 15% Ni/Al₂O₃ catalyst. This revealed that CO₂ is not consumed in the final elementary steps of the reaction, since the adsorption and
conversion of this reactant was further for higher WHSVs. For the 30% Ni/Al₂O₃, the same behavior was not observed. The higher nickel loading increased the CH₄ decomposition in the metal surface, and hence less active sites was free for CO₂ adsorption. So, the mechanism passed for the no-stoichiometric way and a fast deactivation from CH₄ decomposition decreased the CO₂ conversion.

Besides the mechanism and catalyst properties, it is important to consider that all involved reactions in the dry reforming process (i.e. water gas shift reaction, for example) could reach – or not – the thermodynamic equilibrium. Fig. 10 indicates the reactants conversion in the temperature range for both 15 and 30% Ni/Al₂O₃ catalyst.

Since a maximum on CH₄ conversion was observed for 15% Ni/Al₂O₃ catalyst, there is evidence of thermodynamic due to kinetic controlling process. For the another one, 30% Ni/Al₂O₃ did not reach the equilibrium conversion, so the progressive increase on conversion with temperature; in this case, the surface properties of the catalyst, as probably higher crystallite sizes, could reduce the reaction rate far from the equilibrium conditions. On the other side, a minimum on CO₂ conversion was observed at 650 °C, which indicates that the water gas shift reaction equilibrium could be reached, so all the CO content formed during the reaction was converted to CO₂ and led the small conversion. In fact, here, CO₂ was formed again in the process. At 750 °C, the CO₂ conversion raised up and no CO in the outlet gas composition was attributed principally to the Boudouard pathway. This occasioned a blocking on the flow through the reactor.

To evaluate the stability of the catalysts, two randomly chosen reactions were performed for 10 h, and the results are shown in Fig. 11.

Fig. 11 presents the molar fractions and conversion of the components of the gas products from the reactor during the 10 h reaction-on-stream for the 15% and 30% Ni/Al₂O₃ catalysts. Both reactions remained stable during the 10 h of reaction, which indicated no significant loss of catalytic activity during the process. This stability can be attributed to the lower strength of the active sites, and to the presence of the NiAl₂O₃ phase, which indicates the high metal/support interaction, hindering metal sintering.
4. Conclusions

In the dry reforming reactions, the increase on reaction temperature led to higher H$_2$ yields and higher CH$_4$ and CO$_2$ conversion rates. Increasing the space velocity (WHSV of 45 Lh$^{-1}$ g$_{\text{cat}}^{-1}$) decreased the CH$_4$ conversion rates, indicating that a larger amount of catalyst in the catalytic bed favored the reforming reaction. In general, the highest conversion rates were observed in the reactions conducted with the catalyst with the lower metal content (15% Ni/Al$_2$O$_3$). The results of the tests in which reaction time was extended to 10 h indicated that no significant loss of catalytic activity occurred during the reaction.

Biogas can therefore be considered an important raw material for the production of H$_2$, since it has a low cost and renewable source composed of two gases that are harmful to the environment. Under optimized conditions, the use of low cost catalysts that are simple to obtain, such as Ni/Al$_2$O$_3$, can contribute to render the dry reforming process as one of the most promising routes for the production of hydrogen.

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References