COMPARATIVE EVALUATION BETWEEN STEAM AND AUTOTHERMAL REFORMING OF METHANE PROCESSES TO PRODUCE SYNGAS

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Abstract. Steam (SRM) and autothermal (ATR) reforming of methane processes were evaluated through thermodynamical and stoichiometric analyses that benefit hydrogen production, using a Ni/γ-Al2O3 catalyst. Comparisons between these processes allowed for methane conversions as high as 80% on the SRM process, with 72% in hydrogen yield; on the other hand, for the ATR process, 30% of methane conversion was obtained. On both processes, it was possible to reach about 80% of hydrogen selectivity. The ATR process is suggested for hydrogen production, at the experimental conditions tested, due to the high H2/CO ratio obtained and the very low CO yield.

Keywords: steam reforming; autothermal reforming; methane; hydrogen; nickel catalyst

1. INTRODUCTION

There has been growing interest in producing cleaner fuels via catalytical reforming processes of natural gas (NG) as raw material. Natural gas reforming leads to the formation of synthesis gas (syngas, H2+CO) and hydrogen, which has application on petroleum refining (e.g., hydrocracking, Minderhoud et al., 1986) and hydrotreatment, methanol to gasoline (MTG) production, ammonia production (Price et al., 2001) and hydrocarbons synthesis through Fischer-Tropsch reaction (Hensman, 2002).

Limitations due to the thermal conditions employed in reforming processes have conducted to deactivations of nickel catalysts upon operation, mainly in physical and chemical coke formations. Steps of involved reactions, including methane decomposition and carbon monoxide disproportionilization, occur and are thought to be responsible for carbon deposition on solid catalysts. The presence of steam can compensate coke formation through water gas-shift reaction (WGSR).

Reforming processes carried out in the industry have used supported nickel catalysts, which are susceptible to deactivation through coke deposition, sintering and/or formation of phases resulted by metal-support interaction. Novel nickel catalysts, based on modified preparative methodologies, indicate perspectives of higher stability and resistance to deactivation. Assessment of the salt precursor effect (Wang and Lu, 1998), considering the particle sizes of nickel oxide in a Ni/γ-Al2O3 catalyst, prepared from nickel nitrate, showed slightly lower sizes when the salt precursor was nickel nitrate. In addition, an elevated Ni/Al ratio (Turlier and Martin, 1982), under XPS measurements, suggests that this system contains a higher amount of nickel sites. Elevated metal loads (up to 16% in weight) caused stronger effects of carbon deposition in the process (Parizotto et al., 2006). On the other hand, a catalyst prepared with a smaller content of nickel reduced itself at higher temperatures, promoting more interactions with the support, which is an indication of the presence of the NiAl2O4 phase. Growths of the nickel crystals
observed were responsible to the whiskers formation (Kim et al., 2000).

Steam reforming of methane (SRM) usually involves steps of methane decomposition and of carbon monoxide disproportion alization, which are usually responsible for coke deposition over the solid catalyst. Phenomena such as WGSR are therefore useful in enhancing the overall reforming process.

Autothermal reforming of methane (ATR) is a combination of the SRM and the non-catalytic partial oxidation of methane (POX or NC-POM), under thermally neutral conditions, considering the heat lost to surroundings. The process associates the cited effects through the operation of a catalyst bed. By doing this, the process can be operated at much lower temperatures than those in the SRM or in the NC-POM. The reforming temperature is directly affected by the feeding molar ratios O_2/CH_4 and H_2O/CH_4 when natural gas is used as fuel. The composition of products is affected by reforming temperature, feeding molar ratios, catalyst activity and selectivity and by contact time with the catalyst bed.

In this research, the methane steam reforming processes (SRM) and autothermal reforming (ATR) processes were examined by evaluating the possibilities of maximization of hydrogen productions, carrying out stoichiometric and thermodynamical studies on these processes.

2. MATERIALS AND METHODS

The methodology involved the catalyst preparation and its characterization, as well as the catalyst evaluation through the operation of the processes to compare the steam and the autothermal reformings of methane.

2.1. Catalyst Preparation and Characterization

The catalyst preparation with nominal composition Ni(5 wt.%)/γ-Al_2O_3 involved a thermal pre-treatment of alumina, impregnation with excess solution and calcination of the catalyst precursor. The activation of the pre-catalyst material occurred through in situ reduction reactions within a fixed-bed reactor.

A total of 30 g of catalyst were prepared, using a Ni(NO_3)_2·6H_2O solution and a γ-alumina support, promoting the quantification of 5% in metal weight. By controlling the pH (7.0), the mixture was maintained in rotaevaporation (40 rpm, 95°C), under 150 mmHg of vacuum, during 5 hours, until complete vaporization of the solution water. The complete drying of the material occurred in a furnace, at 120°C, for 12 hours. The calcination of the nitrate was made at a heating rate of 5°C/min, reaching 600°C, for 5 hours, under an argon atmosphere, in a 120 cm^3/min flow rate. The final activation, made in situ, allowed for NiO reduction. With this purpose, the reactor was heated at 10°C/min, reaching 800°C, under an inert atmosphere. After reaching 400°C, a hydrogen flow rate (50 cm^3/min) was added, with the NiO reduction occurring at 600°C and at 770°C.

The prepared catalyst was characterized in terms of surface area, pore volume and pore average diameter via the following techniques: Atomic Absorption Spectroscopy (AAS); B.E.T. method; X-Ray Diffraction (XRD); Fourier Transform Infrared Spectroscopy (FTIR); Scanning Electron Microscope (SEM); Energy Dispersive Spectroscopy (EDS). The following thermogravimetric analyses were also performed: Thermogravimetry (TG), Derivate Thermogravimetry (DTG) and Differential Thermal Analysis (DTA).

2.2. Catalyst evaluation and operation of the processes

The methane steam reforming processes were carried out by loading a fixed-bed reactor with 200 mg of catalyst. The conditions established were ambient pressure, temperatures between 750°C and 850°C, feeding molar ratio of CH_4:H_2O = 1:2, according to the upper limit of maximization of hydrogen production presented in Figure 1, using argon (50% volume) as diluent. The total volumetric flow rate was 0.8 L/min. With regard to the autothermal reforming, the conditions were the same, except for the total volumetric flow rate, which was 0.4 L/min, and the feeding molar ratio of CH_4:O_2:H_2O = 5:1:9, under argon (56% volume), using 60 mg of
catalyst. The operational range of the process was close to the steam reforming of methane (SRM).

Aiming the maximization of hydrogen production, the catalyst systems were evaluated through autothermal reforming of methane \( \text{(CH}_4 + \text{aO}_2 + \text{bH}_2\text{O} \rightarrow \text{cCO} + \text{dCO}_2 + \text{eH}_2) \), establishing conditions under a stoichiometric analysis, typically \( c = 0, d = 1 \) and \( a \geq 0 \) with \( b \leq 2 \) (see Figure 1).

Some experimental restrictions must be pointed out when suggesting the best methodology to be followed. At the flow rate range used, external mass transfer limitations are not observed. As far as the temperature working range is concerned, a thermodynamical study taking into account the mechanism ruling the steam reforming and the autothermal reforming was performed. This leads to some conclusions. For instance, methane cracking can occur from 921 K (648°C), however, until 886 K (613°C), all methane oxidation reactions are possible, at any operation temperature. Steam reforming reactions are effected from 959 K (686°C), but in order to enable dry reforming (CO\textsubscript{2} reforming), which is a necessary condition to decrease CO\textsubscript{2} as final product in the autothermal reforming reaction, an operation temperature between 967 K (694°C) and 1,459 K (1,186°C) is required. Below 1,004 K (731°C), reactions between methane and carbon monoxide are favoured, producing coke. In view of this, it is suggested here that upper temperatures be used to operate this system. Partial regeneration of the catalyst through coke elimination is overachieved if operating above 984 K (711°C). At this point, CO\textsubscript{2} disproportionation easily occurs. Unfortunately, the WGSR occurs below 980 K (707°C), consuming syngas. Finally, the steam must not be decomposed, except above 5,499 K (5,226°C). In view of this, working in the temperature range of 1,004 K (731°C) and 1,459 K (1,186°C) is thoroughly recommended. Under these conditions, methane cracking and combustion reactions, dry reformings and coke eliminations will be favoured. Therefore, the selected temperature working range was 1,023 K (750°C) and 1,123 K (850°C) to the catalyst evaluation.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

The nickel content in the catalyst, after measurements on Atomic Absorption Spectroscopy (AAS, Varian spectrometer, Model AA 220 FS, Fast Sequential Operation), was 5.755% ± 0.0289% in weight.

![Figure 1](http://www.portalabpg.org.br/bjpg)
Results on textural characteristics expressed as surface area, pore volume and pore average diameter (B.E.T. method, ASAP 2010, Micromeritics) are presented in Table 1.

In the sequence, a decrease in the surface area is observed for in natura alumina. The reduction promoted a decrease of about 50% in the surface area of the catalyst, corroborated by the metal deposition on the support. An increasing relation occurs with the pore average diameter, indicating a predominance of meso and macropores on the prepared catalyst, compatible with the decrease in its surface area.

Figure 2 presents the XRD analyses (X-Ray Diffractometer, Siemens D5000) performed during all steps of the catalyst preparation. The presence of the delta-alumina and gamma-alumina phases was identified. After catalyst reduction, the presence of metallic nickel could be identified with accuracy in Figure 3, where alterations in the structure between the calcination and the reduction steps were observed too.

Infrared analyses (FTIR, Bruker IFS 66) indicated the presence of crystallization water and hydrogen bonds (3,451 and 1,637 cm\(^{-1}\)), verifying that the quantity of the crystallization water (sharp point intensity) decreases as the final step of catalyst preparation is reached. The presence of NO\(_2\) groups (1,631 cm\(^{-1}\)) and nitrate anions (1,383 and 827 cm\(^{-1}\)) was highlighted, mainly on the impregnated support, a small amount of which remains on the calcined material (Figure 4).

Complementation of the identification of the nickel presence in final catalyst was detected through Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) (Scanning Electron Microscope Jeol JSM-6360). In Figure 5, microscopy patterns of the pre-treated support and reduced catalyst are presented, possibly detecting the subtle presence of nickel metallic on catalyst.

Energy Dispersive Spectroscopy (EDS) measurements allowed to estimate that the aluminium-oxygen ratio, in average, was Al:O = 2:2.919 (Al\(_2\)O\(_{2.919}\) or almost Al\(_2\)O\(_3\)), meaning the presence of alumina with oxygen

<table>
<thead>
<tr>
<th>Material</th>
<th>Area B.E.T. / (m(^2)/g)</th>
<th>Pore average diameter / Å</th>
<th>Pore volume / (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In natura alumina</td>
<td>226</td>
<td>68</td>
<td>0.385</td>
</tr>
<tr>
<td>Pre-treated alumina</td>
<td>145</td>
<td>102</td>
<td>0.370</td>
</tr>
<tr>
<td>Calcined catalyst</td>
<td>105</td>
<td>125</td>
<td>0.330</td>
</tr>
<tr>
<td>Reduced catalyst</td>
<td>107</td>
<td>129</td>
<td>0.345</td>
</tr>
</tbody>
</table>

Figure 2. X-Ray diffractograms of the in natura and thermally pre-treated $\gamma$-Al\(_2\)O\(_3\) support

Figure 3. X-Ray diffractogram of the catalyst Ni(5.75 wt.%)/$\gamma$-Al\(_2\)O\(_3\) after calcination and after reduction steps.
vacancies of 2.60%, which, at first, must be compared with the Atomic Absorption Spectroscopy (AAS) result, around 5.75%. This is an indication that about 45.2% of the deposited nickel is superficially available.

In order to thermally control the calcination operation of the catalyst precursor salt and quantitatively analyze the deposited carbon as coke, after the reforming operations, thermogravimetric analyses (Thermogravimetric Analyser Shimadzu TGA-50) were performed. The results are shown in Figure 6. Loss of water (12.99% in weight) was observed until the limit of 154.9°C. NO₂ emissions (around 10.04%) occur at the maximal temperature of 541.4°C. Until 1,000°C additional mass loss was not identified, assuring the physical stability to this catalyst until this temperature.

Thermogravimetry was performed to determine the quantity of deposited coke, after two hours of operation at a stationary state, quantifying the presence of 11.09% of coke mass, in average, in the sample mass of the catalyst.

3.2. Catalyst processes evaluation

Methane steam and autothermal reformings with the Ni(5.75 wt.%)/γ-Al₂O₃ catalyst, were performed in a fixed-bed reactor, at 1,023 K and 1,123 K, under 1 atm, and H₂, CO and CO₂ were generated as main products, allowing comparative evaluations of these processes.

Operations of these reforming processes
were carried out under the contact time conditions \( \tau = \frac{m_{\text{cat}}}{Q_{\text{total,react}}} \) and spatial velocities \( GHSV = \frac{\rho_{\text{cat}} Q_{\text{total,react}}}{m_{\text{cat}}} \) listed on Table 2, where \( m_{\text{cat}} \) is the catalyst mass (kg), \( Q_{\text{total,react}} \) is the total volumetric flow rate of the gases in the reactor inlet (m\(^3\)/h), and \( \rho_{\text{cat}} \) is the catalyst density (kg/m\(^3\)), at the standard temperature and pressure (STP), 25°C and 1 atm.

Within the GHSV range operated, it was possible to consider that there were no limitations to external mass transfer at the reforming processes assayed (Ma et al., 1996).

In Figures 7 and 8, higher methane conversions at both operating temperatures in

<table>
<thead>
<tr>
<th>Operation</th>
<th>( Q_{\text{total,react}} ) (cm(^3)/min)</th>
<th>( \tau ) (kg_{\text{cat}}·s·m(^{-3}))</th>
<th>GHSV / h(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM</td>
<td>800</td>
<td>15.00</td>
<td>530,400</td>
</tr>
<tr>
<td>ATR</td>
<td>400</td>
<td>9.00</td>
<td>884,000</td>
</tr>
</tbody>
</table>

Figure 6. Thermal analyses of the catalyst support impregnated with the salt precursor

Figure 7. Methane conversion in the steam reforming, pressure = 1 atm. Catalyst Ni(5.75 wt.%)/(\(\gamma\)-Al\(_2\)O\(_3\)).

Figure 8. Methane conversion in the autothermal reforming, pressure = 1 atm. Catalyst Ni(5.75 wt.%)/(\(\gamma\)-Al\(_2\)O\(_3\)).
the steam reforming processes are highlighted. Conversions around 80% in the SRM were clearly higher than those obtained in the ATR process, of approximately 30%. These conversion rates correspond to yields around 72% in H₂, 28% in CO and 50% in CO₂.

In both cases, hydrogen selectivity reached, at 1,023 K, a level close to 80% (Figures 9 and 10), considering CO and CO₂ produced at low amounts. When operating at 1,123 K (Figures 11 and 12), lower selectivity to H₂ was observed (approximately 60%), with moderate elevations in the CO₂ content, typically between 20% and 30%, after complete combustion.

With regard to syngas production, its selectivity is showed in Figures 13 and 14. Its composition, expressed in terms of the H₂/CO ratio, is shown in Figures 15 and 16.

Selectivities around 80% were reached at the operations of steam reforming processes in both temperatures tested, with higher levels than those obtained in the autothermal reforming operations. Interestingly, high H₂/CO ratios were observed during the autothermal reforming operations. As a result, this process significantly emphasizes hydrogen production constituting the generated syngas. Minimal amounts of carbon monoxide contributed to the high H₂/CO ratios attained.

4. CONCLUSIONS
Considering the autothermal reforming of natural gas process as an alternative to produce synthesis gas and/or hydrogen, industrially operated through steam reforming, a
comparative experimental research was proposed and carried out, seeking the appropriate methane reforming method in fixed-bed reactors in the presence of the Ni(5.75 wt.%)/γ-Al₂O₃ catalyst.

Higher conversion rates through steam reforming, at a level of 80%, conducted to yields around 72% in H₂, 28% in CO and 50% in CO₂. Higher selectivities in hydrogen (around 80%), obtained during the operations of steam and autothermal reforming processes, occurred according to synthesis gas production with significant content of this gas and minimal contents of carbon monoxide, representing higher orders of magnitude in terms of the H₂/CO molar ratios.

Compared to the steam reforming process, the autothermal reforming process, in the presence of Ni(5.75 wt.%)/γ-Al₂O₃ catalyst, is recommended for hydrogen production with a reduced content of carbon monoxide.

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