CO₂ UTILIZATION VIA BIOGAS REFORMING USING NICKEL-ALUMINA AEROGEL AND XEROGEL CATALYSTS

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ABSTRACT – Biogas reforming is a process of great environmental and industrial appeal that aims the production of syngas. During the reforming processes, the commercial catalyst suffers with excessive coke deposition. To increase the catalytic performance and to minimize the coke formed, Ni10-Al₂O₃ (10% in weight) aerogel and xerogel catalysts were synthesized. The production of syngas and coke were investigated at 700 °C in the biogas reforming. Nanoscale and mesoporous with high surface area aerogel and xerogel catalysts were obtained. The aerogel catalyst showed higher H₂ and CO production than xerogel. Aerogel catalyst is a promising alternative to increase syngas production and to minimize carbon deposition in the biogas reforming.

1. INTRODUCTION

Biogas is mainly formed by CH₄ and CO₂ that can be used as feedstock in dry reforming of methane, biogas reforming, to generate syngas. Methane and carbon dioxide are the major components of greenhouse gases. The biogas reforming is part of the technologies that goals the utilization of CO₂ and the reduce polluting and nocives gases. The syngas (H₂ and CO) is used in metanol production and Fischer-Tropsch to obtain liquid fuels (Usman et al., 2015).

Due to high activity, stability and economic advantages, Ni supported in ceramic material with or without promoters is the catalyst most used in methane reforming processes. The noble metals are economically unvaible when applied on industrial scale (Gurav et al., 2017). The main difficulty of Ni catalysts is the carbonaceous deposition on the surface of the catalyst. To resist to deactivation is one of the most important properties, in addition to high activity and stability (Alipour et al., 2014).

Active phase, support, promoters and preparation methods are the mainly factors studied to increase the catalytic performance and to minimize the effects of coke. The catalysts developed in sol-gel route, particularly aerogel, exhibited better catalytic performance, higher metal-support interaction, metallic dispersion, surface area and smaller particle size and carbonaceous deposition than several preparation methods (Rad et al., 2016; Song et al., 2016). Among the methods of preparing the aerogel and xerogel, the use of propylene oxide as a gelling agent is a simple and more efficient route (Bang et al., 2012) being also selected in this study.
In this scenario, the aims of this work were evaluate syngas production and coke deposition in the biogas reforming reaction using nickel-alumina aerogel and xerogel catalysts.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Ni10-Al2O3 (10% in weight) aerogel catalyst (NA) was prepared by sol-gel method with supercritical drying using CO2. The precursors salts Ni(NO3)2.6H2O and Al(NO3)3.9H2O (Sigma Aldrich), were dissolved in ethanol (Neon), mixed at room temperature for 20 min at 500 rpm, until a uniform solution was obtained. Propylene oxide (Sigma Aldrich) was added as a gelling agent. After 6 min, without stirring, the gel was formed. Gel maturation occurred at room temperature for 48 h, then was washed with ethanol. The gel was then dried with supercritical CO2 (White Martins) at 50 °C and 100 bar for 4 h. The same previous steps were performed to Ni10-Al2O3 xerogel catalyst (NX). The exception was the supercritical drying that replaced by drying oven model SP-100/A (SPLabor) at 80 °C for 3 days. Calcination was performed at 700 °C with a heating rate of 10 °C·min⁻¹ for 5 h to both catalysts.

2.2. Catalyst Characterization

The BET surface area, pore volume and average pore diameter of the catalysts were obtained by the Autosorb-1 equipment (Quantachrome Instrument). The catalysts were subjected to the vacuum degassing pretreatment at 200 °C for 2 h.

2.3. Biogas Reforming Reactions

Biogas reforming reactions were conducted in the Dyntherm HP-ST Pressurized Thermobalance (Rubotherm), which operates as a differential reactor, enabling quantification of the mass of coke formed throughout the reaction. The mass of catalyst used in each reaction was 50 mg. Before the reaction, the catalysts were reduced in situ under H2 flow of 25 mL·min⁻¹ and Ar 100 mL·min⁻¹ at the heating rate of 20 °C·min⁻¹ until the temperature of 800 °C for 1h. The reactions were performed at 700 °C, atmospheric pressure, with the gas flow being: 20 mL·min⁻¹ CH4, 20 mL·min⁻¹ CO2 and 100 mL·min⁻¹ Ar. The reaction products were identified and quantified in GC-2014ATFSPL gas chromatograph (Shimadzu) with TCD/FID detectors and coupled MTN-1 methanizer (Shimadzu). The gases used were provided by White Martins.

3. RESULTS AND DISCUSSIONS

Table 1 shows the values of specific surface area, volume and average pore diameter for the catalysts. The change in the drying method (aerogel to xerogel) resulted in a decrease in the specific surface area, pore volume and average pore diameter. The catalysts NA and NX presented high specific surface area as expected for catalysts prepared by sol-gel method.
Table 1 – Physicochemical properties of NA and NX catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(V_p) (cm(^3)/g)</th>
<th>(D_p) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>240.4</td>
<td>1.16</td>
<td>19.28</td>
</tr>
<tr>
<td>NX</td>
<td>199.3</td>
<td>0.23</td>
<td>4.84</td>
</tr>
</tbody>
</table>

Biogas reforming reactions were performed at a space velocity of 168,000 mL·h\(^{-1}\) g\(^{-1}\)cat and CH\(_4\)::CO\(_2\) molar ratio of 1:1. Methane and carbon dioxide conversions were less than 15% according to the limit established for differential reactor. Figure 1 shows the production of hydrogen and carbon monoxide during the biogas reforming reactions using NA and NX catalysts.

![Figure 1](image.png)

Figure 1 – Production of hydrogen and carbon monoxide in the biogas reforming using NA and NX catalysts at 700 °C.

According to Figure 1, syngas production was higher using NA than NX. Both catalysts remained active and stable. After 5 h, \(H_2\) and CO production were 0.848 and 0.868 μmol (\(H_2/CO\) 0.976) for NA and 0.015 and 0.071 μmol (\(H_2/CO\) 0.210) for NX respectively. The amount of carbon deposited in the end of the biogas reforming measured from Thermobalance were 4.42 mg (NA) and 3.00 mg (NX). The least coke formation on xerogel catalyst does not justify the utilization of NX to the process. NX did not reach the expected \(H_2/CO\) ratio and did not satisfactorily produce the syngas. The low syngas production explains the least amount of coke deposited on this catalyst.
4. CONCLUSIONS

In this work, the syngas production and coke formed in the biogas reforming using nickel-alumina aerogel and xerogel catalysts were studied. The sol-gel preparation method using propylene oxide as gelling agent was effective in obtaining NA and NX catalysts. The physical nitrogen adsorption technique proved the efficiency of method in to develop catalysts with high specific surface area, mesoporous and in nanoscale dimension. NA aerogel catalyst presented the largest surface area and the highest syngas production, being also the most selective for hydrogen. Both catalysts remained active and stable at the end of the reaction. The least coke formation occurred with NX. However, NA conducted the highest syngas production per coke formed. The aerogel catalyst is the most promising alternative for syngas production and minimization of carbon deposition in the biogas reforming.

5. REFERENCES

ALIPOUR Z, REZAEI M, MESHKANI F, Ni$_{0.05}$Mn$_{0.95}$O catalysts for the dry reforming of methane. *Fuel*, v. 129, p. 197-203, 2014.


