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HYDROGEN PRODUCTION FROM STEAM REFORMING OF BIOMETHANE AND BIOETHANOL

Felipe Antonio Dela Rosa
Universidade Tecnológica Federal do Paraná
Apucarana – Paraná
http://lattes.cnpq.br/9828598156726505

Jeferson Rocha Queiroz
Universidade Tecnológica Federal do Paraná
Apucarana – Paraná
http://lattes.cnpq.br/0214620995806404

Fernando Alves da Silva
Universidade Tecnológica Federal do Paraná
Apucarana – Paraná
http://lattes.cnpq.br/4913976138341762

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Abstract: Hydrogen has stood out as a sustainable alternative for energy production, especially when derived from biofuels. In this study, a nickel-alumina catalyst was evaluated to obtain hydrogen from biomethane and bioethanol. The tests indicated high selectivity for H2, but with the formation of coke in the catalyst, limiting its industrial application due to deactivation. However, the catalyst showed greater selectivity in producing hydrogen from biomethane, a simpler reaction free of byproducts. This suggests biomethane's potential as a viable source of hydrogen, despite challenges with the catalyst. The research highlights the importance of finding solutions to extend the useful life of the catalyst and promote the production of hydrogen from renewable and sustainable sources.

Keywords: Catalyst; Hydrogen; Remodeling.

INTRODUCTION

The search to replace unsustainable energy matrices with more environmentally friendly sources is a global priority due to the climate challenges that society currently faces. The increase in demand for energy, driven by population growth and economic development, has put pressure on finite natural resources and caused negative impacts on the environment. In this context, the transition to a sustainable energy matrix is essential to reduce greenhouse gas emissions and preserve the planet for future generations (Dupont; Grassi; Romitti. 2023).

One of the promising solutions in this search is the use of hydrogen as an alternative energy source. Hydrogen, when produced in a clean way, for example, through the electrolysis of water with renewable energy, has low or no carbon emissions. Furthermore, it has high energy density, which makes it viable for large-scale storage and efficient distribution. Combined with advanced technologies such as fuel cells, hydrogen can be transformed into electricity and heat, meeting the energy needs of various sectors (Ribeiro et al. 2017).

A possible source of hydrogen production that can replace natural gas is biogas, where it arises from the decomposition of organic matter, such as agricultural waste, animal waste and sewage while natural gas is a fossil fuel originating from the decomposition of organic matter. underground over thousands of years under high temperature and pressure. This distinction in relation to natural gas is important to analyze economic and environmental viability (Paini, 2017).

The use of biogas not only presents economic benefits by reducing greenhouse gas emissions, but also contributes to the achievement of environmental goals. By preventing the release of methane (CH4) during the organic matter degradation process, biogas helps industries adapt to current environmental regulations, reducing their carbon footprints (Lins et al. 2022).

A technique that can be used to produce hydrogen from biogas is steam reforming of biomethane, obtained through the purification of biogas. This approach turns biogas into hydrogen, capturing and utilizing the resulting carbon dioxide, which reduces greenhouse gas emissions and helps mitigate climate change (Khamhaeng et al. 2021). Biogas steam reforming is described in Equations 1 and 2 which occur simultaneously.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

In addition to biogas as a raw material for hydrogen production, another important route to be studied is ethanol steam reforming. This alcohol can also contribute to the hydrogen energy matrix in a renewable way, as it can be obtained from the fermentation of biomass, such as sugar cane.

When steam reforming of bioethanol occurs completely, it occurs according to the reaction described by Equation 3.

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{3}$$

In this specific study, activities were carried out to synthesize a nickel-alumina-based catalyst and, subsequently, analyze its activity in the biomethane and bioethanol reforming reaction with the objective of producing hydrogen. The entire process took place in a controlled reactor, where the parameters of temperature, pressure and feed proportions used were adjusted and monitored. The purpose of this investigation was to understand the behavior of the catalyst and its efficiency in favoring the transformation of biomethane or bioethanol into hydrogen, thus contributing to progress in the search for more sustainable and renewable energy sources.

MATERIALS AND METHODS

CATALYST SYNTHESIS

To obtain the nickel-alumina catalyst, the wet impregnation route was used. A quantity of hexahydrate (97% purity) was subjected to a desiccator with a vacuum pump for one hour, with the aim of eliminating any trace of moisture present in the . The impregnation procedure was conducted to obtain a molar ratio of 1.5 Ni/Al at the end of the synthesis. To this end, based on the molar ratio, the mass fractions that the precursors represent were determined, according to Equations 4 and 5.

$$1\,mol\,Ni \rightarrow \frac{1\,mol\,Ni(NO_3)_2.6H_2O}{1\,mol\,de\,Ni}\,\frac{298{,}81g}{1\,mol\,Ni(NO_3)_2.6H_2O}\,\frac{1}{0{,}97} = 308{,}05g\,Ni(NO_3)_2 \tag{4}$$

$$5\,mol\,Al \rightarrow \frac{1\,mol\,Al_2O_3}{2\,mol\,de\,Al}\,\frac{101{,}96g}{1\,mol\,Al_2O_3} = 254{,}9g\,Al_2O_3 \tag{5}$$

From the molar ratio of 5, the added masses of the salts would represent a total of 562.95 g of precursors, composed of 45.28% by mass of and 54,72% of . From the fractions, it was possible to determine the masses to be weighed.

The materials were then dried and then homogenized in a flask, using distilled water as a solvent. The flask was subsequently placed in a vacuum evaporator in a water bath, establishing a temperature of 80ºC to eliminate the solvent. Next to the rotary evaporator, a condenser operating at 9°C was responsible for recovering the evaporated water. After evaporation, the material was scraped from the flask and transferred to a porcelain container, and subjected to a calcination process in a muffle furnace. The temperature schedule was as described below:

1) Heating at a rate of 10ºC/min from room temperature to 100ºC;

2) Isothermal maintenance for 30 minutes at 100ºC.

3) Heating at 10ºC/min from 100ºC to 250ºC.

4) Isothermal maintenance for 30 minutes at 250ºC.

5) Heating at 10ºC/min from 250ºC to 500ºC.

6) Isothermal maintenance for 5 hours at 500ºC.

At the end of the process, the total mass of the catalyst produced was 11.4412g, with a molar ratio of 5 Ni/Al.

CATALYST CHARACTERIZATION

The catalyst sample was subjected to N2 adsorption-desorption at -196°C for textural characterization on Quatachrome NOVA 1200 series equipment. The sample was previously activated in vacuum to remove possible adsorbates, at 300 °C, for 4 h. The isotherm was used to determine the pore size distribution, average size, specific area and pore volume using the DFT (Density Function Theory) method.

In order to identify the crystalline state in the catalyst structure, XRD (X-ray diffraction) analyzes were used using the powder method. The diffractograms of the calcined samples (pure alumina, nickel oxide and catalyst) were obtained using Bruker equipment, model D8 Advanced equipped with an XRK 900 furnace, with 2θ varying between 5° and 80º, with a step of 0.019º, 0.58 °/ min goniometer speed, and Cu-Kα radiation source (40 kV and 35 mA).

CATALYTIC TESTS

The next phase consisted of the biomethane or bioethanol steam reforming reaction, where a 0.116g sample of catalyst was separated and weighed for Test 1. The biogas feed flow rate was adjusted to 1.26mL/s and the water flow rate to 0.0999g/s, where the biogas feed flow was obtained by the time the bubbles traveled 10mL inside a bubble meter and the water was weighed and timed, dividing the mass of water obtained by the temperature range that was deposited in the container. The feed ratio was calculated based on the general gas equation, converting the volumetric or mass flow rates to molar flow rates through the molar masses of water and methane, and finally, the feed ratio was determined using Equation 6.

$$1\,atm.\ \frac{1{,}88mL}{s}.\frac{1s}{1000mL}.\,\dot{n}CH_4.\,0{,}082\frac{atm.L}{mol.K}.\,298\mathrm{K} \rightarrow\ \dot{n}CH_4 = FCH_4 = 5{,}26x10^{-5}mol/s \tag{6}$$

where the feed flow resulted in a water: biomethane molar ratio of $\frac{F_{H_2O}}{F_{CH_4}} = 105{,}44$.

The reactor had a temperature setpoint of 600ºC, and a pre-evaporator oven with a setpoint of 250ºC to vaporize the water and heat the mixture. After the flow rates were stabilized, the reaction occurred for 4h, and gaseous ampoules were used to capture the gaseous products generated by the reactor; Samples were collected at the beginning (activation) and at the end of the reaction, and an arithmetic mean was used as the average selectivity for the catalytic test.

For the test with ethanol, 0.1135g of the catalyst was used, a solution of 20% ethanol in 1L of water. The reactor had a temperature setpoint of 500ºC, and gaseous ampoules were placed at the reactor outlet to capture the products from the beginning and end of the reaction.

In all tests, the gaseous product was collected using a 37 mL glass gasometric ampoule, with the aid of a stainless steel transfer kit, and injected into a Trace Thermo Finnigan chromatograph (3 m × 1/8" stainless steel column with Poropak N 80/100 mesh in series with a 13X molecular sieve, with DCT in the mobile phase); the liquid fraction was also analyzed on a gas chromatograph, Varian 3300 (10% Carbowax 20M column in CHR Chromosorb W HP, 3 m × 1/8", equipped with DCT and mobile phase He).

RESULTS AND DISCUSSIONS

The structure of the catalyst was analyzed by comparing the diffractograms of samples of pure alumina, nickel oxide and the catalyst formed, as shown in Figure 1.

Pure alumina does not have a 100% crystalline structure, as noises were observed in the graph generated by XRD, which confirm amorphous portions in this material.

Using alumina as a vehicle for nickel to be deposited inside, it is expected that a greater dispersion of nickel will occur on its surface, and thus generates a larger area in which the catalyst participates in the reaction.

Unlike alumina, nickel has a more crystalline structure, a fact confirmed by the peaks found in the graph generated by XRD.

As for the synthesized catalyst, impregnation followed by heat treatment in the muffle furnace allowed the formation of a more crystalline structure compared to the pure support (alumina), which can be observed by comparing the XRD graphs shown in Figure 1 below.

The results of the catalyst's XRD tests found three peaks that stand out among its components. Knowing that the DRX test only finds particles smaller than 5 nanometers, it can be considered that the catalyst has good nickel dispersion (larger contact surface). The last peak observed suggests the formation of a new phase, where nickel integrated into the alumina structure, a fact possible due to the interaction between nickel and alumina during heat treatment in the muffle furnace at 250ºC to 500ºC.

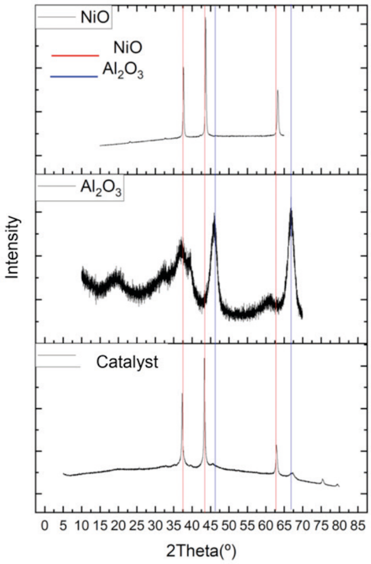

Figure 1 - DRX Catalyst.

Source: Own Authorship (2023).

Nitrogen physisorption analysis was carried out and its isotherm was obtained as shown in Figure 2 below.

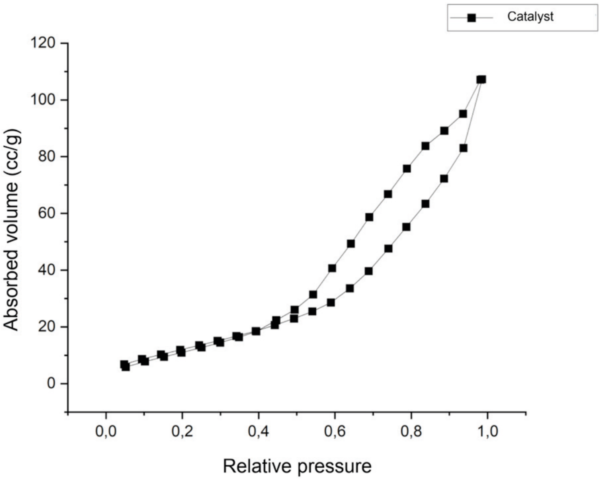

Figure 2 - Nitrogen Isotherm.

Source: Own Authorship (2023).

The isotherm is similar to the curves of mesoporous materials and presents hysteresis between the adsorption and desorption curves, a characteristic behavior of this type of morphology.

From the isotherm data, the pore size distribution of the catalyst was performed as shown in Figure 3.

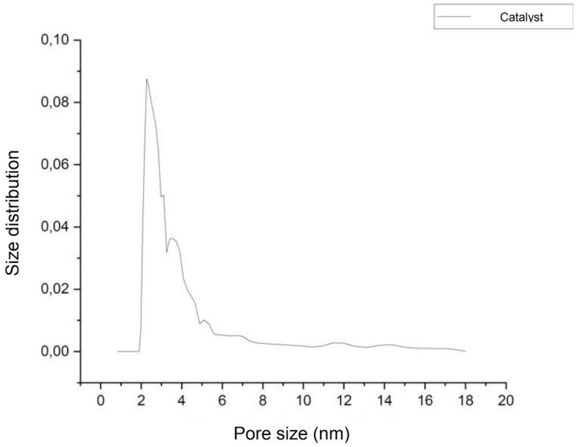

Figure 3 - Pore Size Distribution

Source: Own Authorship (2023).

From the distribution obtained in Figure 3, the average pore size value was 6.5nm, which confirms that the catalyst is in the mesoporous range, as already predicted by the isotherm in Figure 2. Therefore, it can be considered that the catalyst is suitable for this type of reforming reaction, since the diffusion effects of methane and water, or bioethanol, can occur inside the pores, coming into contact with the nickel inside. Furthermore, based on the isotherm data and the DFT model used, a specific area of 51.04 m^2/g was obtained, and a total pore volume of 0.166 cm^3/g.

Regarding catalytic tests, Table 1 presents the average selectivity obtained during the biomethane and bioethanol steam reforming tests.

Selectivity		
Sample / Component	Ref. Methane	Ref. Ethanol
H_2	98,56%	88,13%
*N_2	0,00%	10,59%
O_2	0,00%	0,00%
CH_4	0,00%	0,15%
CO	1,43%	0,02%
CO_2	0,01%	0,01%
C_2H_4	0,00%	0,32%
C_2H_6	0,00%	0,78%
Total:	100,00%	100,00%

Table 1 - Average component selectivity.

* Inert gas

Source: Own Authorship (2023).

The biomethane reforming showed a higher yield for hydrogen when compared to the ethanol reforming, as observed by the average selectivity to hydrogen in Table 1. This occurred because its reforming reaction is summarily simpler than the ethanol reforming.

However, the low selectivity to CO or CO2 suggests that the reforming reaction, as presented by Equations 1 and 3, did not occur completely, which indicates that part of the carbon remained adsorbed on the catalyst surface as coke. This behavior is common in nickel alumina catalysts due to the high acidity of this support, which makes carbon gasification difficult.

For the bioethanol reforming test, by-products such as ethylene and ethane were also observed, arising from possible dehydration reactions followed by hydrogenation, which contribute to the reduction of the hydrogen yield. Such byproducts are favorably obtained in the reforming of this alcohol due to the greater number of bonds contained in its molecule, which are heterogeneous, compared to the biomethane molecule.

However, it is worth highlighting that ethanol has a majority access in Brazil, being a closed carbon cycle renewable fuel that has a well-defined structure, market and industry in Brazil, which would facilitate the production of hydrogen from bioethanol compared to biomethane.

CONCLUSIONS

The catalyst presented a structure containing nickel oxides dispersed on the alumina surface, in addition to a morphology containing mesopores in a distribution with an average size of 6.5nm.

Catalytic tests indicated good selectivity, being greater for biomethane. In this case, biomethane reforming would be more suitable due to greater selectivity and the absence of subcomponents originating from the reforming reaction. However, taking into consideration, that ethanol is more accessible, more commonly produced from renewable raw materials, with a closed carbon cycle and a well-defined structure in the country, it also becomes an option for reform.

From an industrial point of view, the catalyst is not viable as its activity time is reduced due to the formation of coke. New studies and applications can be developed or even new techniques for manufacturing the catalyst to delay the formation of coke and prolong its longevity.

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