|  |
| --- |
|  |

Cobalt supported on mesoporous Nb2O5 in the the Fischer- Tropsch Synthesis

\*Hídila Souza Teixeira da Silva¹; Diogo Pimentel de Sá da Silva¹; Gabriel Garcia Silva²; Ana Gabriela Martins Silva¹; Ricardo Reis Soares¹

¹ Faculty of Chemical Engineering – Federal University of Uberlandia – Uberlândia. MG. ²Institute of Chemistry – Federal University of Uberlandia – Uberlândia. MG.

\*Corresponding author: hidila2@gmail.com

|  |
| --- |
| Abstract |

ABSTRACT - In this work, we report the reaction of Fischer-Tropsch synthesis using a mesoporous niobium-based support for cobalt catalyst. A porous niobium metal oxide with a BET surface area of 195.59 m2.g-1 was tested with 15% by weight of cobalt for FT reactions and compared with a commercial catalyst. The results obtained indicated that the catalyst containing the mesoporous niobium achieved high selectivity for C9+ products and low methane production when compared to commercial FT catalysts under the same operating conditions. This study found that the prepared support was efficient and a competitive option for the development of commercial FT catalyst supports.

*Keywords: Selectivity, Commercial catalyst, Low CO2, Hydrocarbons.*

## Introduction

The Fischer-Tropsch Synthesis (FTS) is a chemical process for producing liquid hydrocarbons from synthesis gas, which consists mainly of carbon monoxide and hydrogen. This process was developed by German chemist Franz Fischer and German engineer Hans Tropsch in 1925 and has been widely used in the synthetic fuel industry. [1].

The FTS process involves the reaction of synthesis gas (a mixture of H2 and CO, derived from the pyrolysis/gasification/combustion of plant substrates) with an iron, cobalt or nickel catalyst under conditions of high pressure and temperature. The reaction produces hydrocarbons of different molecular weights, ranging from methane to long-chain hydrocarbons, which are liquid at room temperature [2-3].

However, FTS is a complex process, in which the development of a highly efficient catalyst remains a challenge nowadays. Iron and Cobalt catalysts are widely used but have disadvantages such as easy deactivation and high costs. Supporting these materials can improve the activity, selectivity, and stability of catalysts, making them more efficient and effective in industrial applications [3-5].

The most common supports for FTS catalysts are silicas, alumina, and zeolites. The type of support used depends on the specific application of the catalyst as well as the desired properties of the catalyst. In some studies, crystalline niobium pentoxide (Nb2O5) has been shown to be a promising alternative for supporting FTS catalysts, due to its high surface area, thermal and chemical stability, and acidic and redox properties, which can improve the activity, selectivity, and stability of the catalyst. Additionally, mesoporous niobium-based supports have also shown to be a competitive option for the preparation of commercial FTS catalyst supports, as mentioned earlier. The type of support used should be chosen based on the specific application of the catalyst and desired properties [6–8].

Therefore, we report here the FTS reaction using a mesoporous Nb2O5 that was used as a support for cobalt catalyst. This catalyst showed excellent catalytic activity, good selectivity for C9+ products, and excellent dispersion of the active phase over the support structure due to the good textural properties obtained. Making it a competitive option for commercial catalyst supports.

## Experimental

*Catalyst preparation for Fischer-Tropsch reactions*

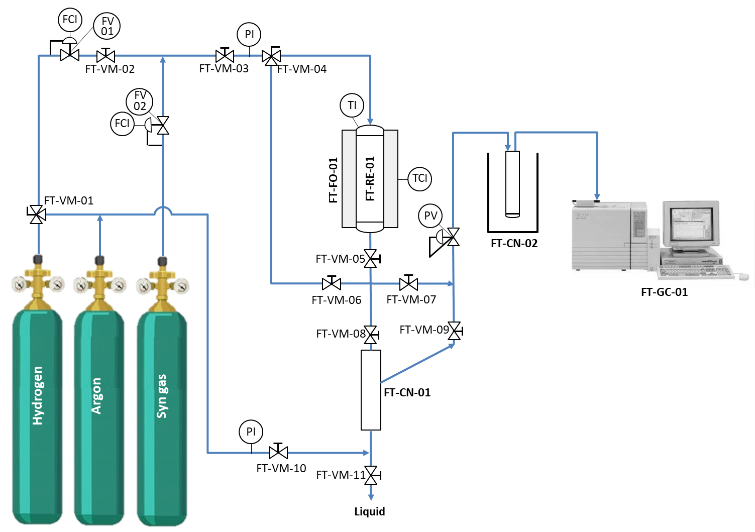
Cobalt catalysts were prepared by co-precipitation method used by Tarka. et al., 2017 and Karolewska et. al., 2012 [9,10].

For preparation 15Co/Nb2O5m catalyst, the appropriate amounts of a mixture of Co(NO3)2·6H2O was solubilized the water and warmed to approximately 90 ºC. The support Nb2O5m was added and stirring for 10 minutes. The K₂CO₃ (analytical purity) was used as a precipitating agent. The Potassium carbonate was solubilized in water and slowly added to the mixture containing cobalt and support until a pH of 9.0 was obtained. The final mixture was stirred for 10 minutes, and vacuum filtered and washed with deionized water to remove potassium. The precipitate was then dried at 100ºC for 12h and calcined in a muffle furnace overnight at 500ºC with air flow. After sieving (200 mesh) a black powder 15Co/Nb2O5mwas obtained.

The preparation of the 15Co/Nb2O5 catalyst, the (HY-340) supplied by CMBB, was calcined at 500ºC for 4 hours, the white powder as denominated Nb2O5 was obtained. After that, the same steps mentioned above were followed.

*Catalytic performance*

The Fischer-Tropsch reaction was carried out in a fixed-bed stainless steel reactor. The catalyst (400 mg) was mixed with quartz sand (400 mg) and then reduced in situ using high purity H2 at 400 °C, gas hourly space velocity (GHSV) = 1200 h-1, flow time = 12 h and atmospheric pressure. After reduction, the reaction conditions were set as 20 bar, temperature ranging between 220-280°C, GHSV 600 h-1, run time 30 h and H2/CO ratio = 2:1. The gaseous products were analyzed by online gas chromatography (GC-17A - Shimadzu), equipped with a packed column - Hayesep (TCD-FID). As shown in the figure, 1.

**Figure 1.** Flowchart of the Fischer-Tropsch Synthesis unit.  


The equipment was tagged as follows: VM: Manual Valve, FV: Flow Controller Valve, FCI: Flow Controller Indicator, PI: Pressure Indicator, TI: Thermocouple, TCI: Temperature Controller Indicator, FT-FO-01: Oven, FT-RE-01: Fixed Bed Reactor, FT-CN-01: Ambient Temperature Condenser, FT-CN-02: Low Temperature Condenser, FT-GC-01: Gas Chromatogram.

The collected wax and oil products were weighted after separation from water. The wax was dissolved in Carbon disulfide (Sigma Aldrich). The liquid samples were analyzed by a GC (Shimadzu GC-2010) equipped with an FID detector and auto injector AOC-20i and Zebron Inferno capillary column (ZB-5 HT). The selectivity of CO2, CH4, C2-C4 in the tail gas was calculated according to these formulas and C5+ was obtained on a molar carbon basis.

|  |  |
| --- | --- |
|  | (1) |
|  | (2) |
|  | (3) |
|  | (4) |
|  | (5) |

Where, X refers to conversion; S refers to Selectivity; F refers to molar flow; n refers to number of carbons.

The liquid product distribution was calculated by the following formula based on GC analysis results for oil and wax. For FID detector, the peak area of hydrocarbon was proportional to the weight concentration.

|  |  |
| --- | --- |
|  | (6) |

Where, refers to peak area of the hydrocarbon in the chromatograms; refers to response factor; refers to molecular weight of the hydrocarbon.

## Results and discussion

The designed catalyst was tested at 220-280°C under the condition of FTS with a pressure of 20 bar, as shown in Table 1. The temperature of 220°C provided a conversion of approximately 36%, being the temperature that produced the most CO2. The conversion of 48.90% was achieved at 250°C, which was the temperature that produced the most C5+ long-chain hydrocarbons, also resulting in the lowest selectivity for CO2 production. The iso/n-alkane production ratio for light hydrocarbons, C1-4, decreased at 280°C, indicating that more n-alkanes are produced, while at lower temperatures the production ratio did not change significantly. The selectivity for hydrocarbons was best represented at 280°C.

**Table 1.** Catalytic performance of the Co/Nb2O5m catalyst and product distribution in the Fischer–Tropsch synthesis in different temperature, TOs = 35h, WHSV= 600 h-1, H2:CO =2:1.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temperature (ºC) | CO Conversion (%) | Selectivity (%) | | | |
| CO2 | CH4 | C2-C4 | C5+ |
| 220 | 35.82 | 6,99 | 13.95 | 8.33 | 70.73 |
| 250 | 48.90 | 4.01 | 11.73 | 6.65 | 77.61 |
| 280 | 33.87 | 5.56 | 16.96 | 8.64 | 68.84 |

This work presents a meticulous comparison and study to evaluate the competitiveness of the synthesized catalyst for commercial purposes. A commercial catalyst **[[1]](#endnote-1)** was tested under the same operational conditions in the best temperature obtained in the FTS. In order to compare, a catalyst with the same weight loading of cobalt supported on low surface area niobia, obtained from the calcination of niobic acid (HY-340) provided by CBMM, (15Co/Nb2O5) was synthesized and tested in the FTS, following the same impregnation conditions of the active phase reported here.

The reactions were carried out in a fixed-bed reactor at 20 bar and a temperature of 280°C. The results are observed in Figure 2 (a), where the CO conversion for the 15Co/Nb2O5 catalyst showed values close to the commercial catalyst. The 15Co/Nb2O5 catalyst presented low conversion values, which can be attributed to pore saturation due to the higher loading of the active phase deposited. As seen in previous works, this material presents low textural properties [7-8], and it is believed that the higher loading of the active phase caused pore obstruction, interfering in the mass transfer, and influencing the catalyst conversion. The formation hydrocarbons (C5+) were slightly higher in the synthesized catalyst, which can be attributed to the temperature range used since cobalt catalysts tend to deactivate at high temperatures.

**Figure 2.** (a) distribution of hydrocarbons FTS; (b) CO conversion with time on stream (h) on the catalyst. Results on different catalysts at reaction temperature 250 ºC. TOs = 35h, WHSV= 600 h-1, H2:CO = 2:1



## Conclusions

Based on the evaluation of the Fischer-Tropsch reaction carried out in this work, it can be concluded that the synthesized catalyst showed a competitive performance compared to commercial catalysts already present in the market. Thus, the results are consistent with the literature attesting that catalysts supported on mesoporous materials allow for the improvement of catalytic activity, making them more efficient and effective in industrial applications.

## Acknowledgments

EMBRAER, SUZANO, KLABIN, PETROBRAS e FAPEMIG for the funding of the BioValue project, we would like to thank CAPES and CNPQ for supporting the scholarship recipients, and CBMM for providing the niobium oxides.

## Referênces

1. Khodakov, A. Y.; Chu, W.; & Fongarland, P. Advances in the Development of Novel Cobalt Fischer−Tropsch Catalysts for Synthesis of Long-Chain Hydrocarbons and Clean Fuels. *Chem. Rev*, **2007**, 107(5), 1692–1744.
2. Wentrup, J.; Pesch, G. R.; & Thöming, J. Dynamic operation of Fischer-Tropsch reactors for power-to-liquid concepts: A review. *Renew. Sustain. Energy Rev*, **2022**, 162, 112454.
3. Steynberg, A.; & Mark, D. *Fischer-Tropsch Technology,* **2004** (1ST ed., Vol. 152). Elsevier.
4. Opeyemi Otun, K., Yao, Y., Liu, X., & Hildebrandt, D. Synthesis, structure, and performance of carbide phases in Fischer-Tropsch synthesis: A critical review. *Fuel*, **2021**, 296, 120689.
5. Pratt, J. W. *A Fischer-Tropsch Synthesis Reactor Model Framework for Liquid Biofuels Production,* **2012.**
6. Frydman, A.; Soares, R.R.; Schmal, M. High Selectivity of Diesel Fraction in Fischer-Tropsch Synthesis with Co/Nb2O5. *Stud. Surf. Sci. Catal.,* **1993**, pp. 2797–2800.
7. Soares, R.R.; Frydman, A.; Schmal, M Effect of preparation method on 5% Co/Nb2O5 in Fischer-Tropsch Syntesis (FTS), *Catal. Today,* 1993, 16, 361–370.
8. Silva, R.R.C.M.; Schmal, M.; Frety, R.; Dalmon, J.A.; Effect of the support on the fischer–tropsch synthesis with Co/Nb2O5 catalysts. *J. Chem. Soc., Faraday Trans*, **1993**, 89, 3975–3980.
9. Karolewska, M.; Truszkiewicz, E; Mierzwa, B.; Kępiński, L.; Raróg-Pilecka, W. Ammonia synthesis over cobalt catalysts doped with cerium and barium. Effect of the ceria loading, *Appl Catal A Gen*. 445–446, **2012**, 280–286.
10. Tarka, A.; Zybert, M.; Kindler, Z.; Szmurło, J.; Mierzwa, B.; Raróg-Pilecka, W. Effect of precipitating agent on the properties of cobalt catalysts promoted with cerium and barium for NH 3 synthesis obtained by co-precipitation, *Appl Catal A Gen.*, **2017**, 532 19–25.

1. Information about the commercial catalyst cannot be disclosed. [↑](#endnote-ref-1)