Niobium Catalysts: Synthesis, characterization and evaluation for CO₂ conversion to methanol

Yara M. G. Lucas[a], Maria R. A. Arcanjo[a], Rafaelle G. Santiago[a], Diana C. S. de Azevedo[a], Moises Bastos-Neto[a]

[a]Laboratório de Pesquisa em Adsorção e Captura de CO₂ – Federal University of Ceará, Fortaleza, Brazil

Abstract

Under the current climate context, the application of CCUS methods is increasingly necessary as the constant emission of CO_2 is responsible for the increase of the greenhouse effect. Therefore, it is extremely favorable to transform this gas into raw material to obtain valuable chemical products, such as methanol. In this sense, this preliminary study aimed to evaluate different compositions of six catalysts for the CO_2 conversion to methanol. The catalysts were Cu-ZnO based, supported on Al_2O_3 or Nb_2O_5 and synthesized in defined proportions by the physical mixing method. The characterization was initially carried out by two different methods, XRD and thermogravimetric analysis. The catalytic tests were performed in a fixed-bed reactor, at 25 bar, 200 °C with a $H_2:CO_2$ ratio of 3 using two catalysts under the same proportion. The best catalytic performance was presented by the niobium supported catalyst, exhibiting a maximum concentration of 360.9 µmol L^{-1} in the 30 hours reaction studied. Other tests will be conducted in remaining proportions to evaluate the composition of the catalysts in the CO_2 conversion.

Keywords: CO_2; Methanol; Catalysis; Niobium oxide; Aluminum oxide.

1. Introduction

Rising greenhouse gas emissions underscore the need for carbon capture and utilization. CO_2 hydrogenation to methanol is promising due to its value in producing essential compounds like plastics and paints. However, CO_2 is low reactivity requires high activation temperatures. Research in heterogeneous catalysis explores methods for conversion under milder conditions [1, 2].

In CO_2 hydrogenation to methanol, copper is widely used as the active phase for its superior performance [3, 4]. The Cu-ZnO combination is common, as zinc enhances activity and prevents copper sintering by acting as a geometric spacer [5-8]. Al_2O_3 is commonly used as a support with Cu-Zn catalysts for its stability [9]. Niobium is a promising alternative, offering similar properties to alumina while enhancing catalytic activity [10-11].

The present work preliminarily evaluated the performance of different Cu-ZnO catalysts supported on similar materials (Al_2O_3 or Nb_2O_5) synthesized in different proportions for comparison purposes.

2. Material and methods

2.1 Catalysts synthesis

The catalysts were prepared by physical mixture of the selected reagents, using an adaptation of the methodology reported by Santiago et al. (2022) [12]. The metallic precursors were aqueous solutions of copper (II) oxide (Sigma Aldrich), zinc oxide (Sigma Aldrich), aluminum oxide (Sigma Aldrich) and niobium oxide, which was kindly supplied by CBMM. Thus, the solutions were mixed and heated to 70 °C for 1 hour under stirring. Then, the precipitated solid was separated, washed to neutralize the pH and dried at 70 °C for 24 hours. Finally, the solid was calcined at 300 °C for 2 hours following a ramp of 5 °C min⁻¹. Each mixture was estimated to produce 3 g of catalyst, with different proportions, illustrated in Table 1.

Table 1. Selected proportions of the synthesized catalysts.

Catalysts	CuO	ZnO	Al_2O_3	Nb_2O_5
CZA21	2	1	1	-
CZA31	3	1	1	-
CZA32	3	2	1	-
CZN21	2	1	-	1
CZN31	3	1	-	1
CZN32	3	2	-	1

2.2 Catalysts Characterization

X-ray diffraction patterns were performed on a Panalytical X'Pert PRO-LRX diffractometer equipped with a Cu-Kα radiation in the 2θ range 0-100°.

Thermogravimetric analysis was obtained in a thermal analyzer Skimmer™ QMS STA 309 CD/403/5/G (Netzsch, Germany) using a 30 mL min⁻¹ flow rate of synthetic air to simulate non-inert atmosphere. The analysis was conducted at temperatures ranging from 25 °C to 850 °C following a heating ramp of 10 °C min⁻¹.

2.3 Adsorption Isotherms

Carbon dioxide adsorption isotherms were measured using a magnetic suspension balance (Rubotherm, Germany) at 100, 150, and 200°C, in order to understand the behavior of the materials in relation to the adsorption phenomena involved and associate them with the mechanisms studied in the reaction.

2.4 Catalytic Tests

The catalysis reaction was conducted in a fixed-bed flow reactor. Thus, initially the catalysts were subjected to a H_2 flow (15 mL min⁻¹, 250 °C, 1 h) aiming to reduce the copper oxide to Cu^0. Then, the system was pressurized to 25 bar with H_2 and the reaction was started after reaching equilibrium, occurring for 30 h, under a total gas flow of 60 mL min⁻¹ in a molar ratio of 1 CO_2 to 3 H_2 at 200 °C. For the analysis, products samples were collected at the column exit and inserted into an Agilent 7820 gas chromatograph equipped with thermal conductivity (TCD) and flame ionization (FID) detection methods.

The equations of CO_2 conversion (X_{CO_2}) and methanol yield (Y) were defined in the equations 1 and 2, respectively.

$$X_{CO_2} = \frac{n_{in} - n_{out}}{n_{in}} \qquad (1)$$

$$Y = \frac{y \cdot n_m}{n_{in}} \qquad (2)$$

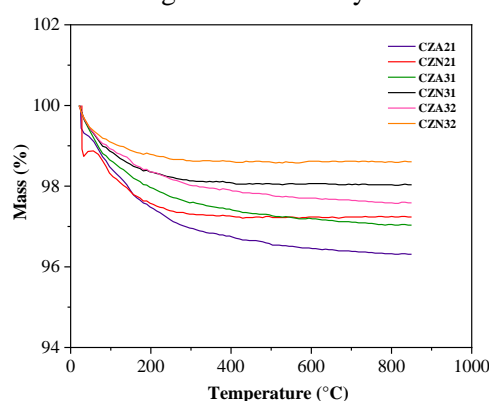Where n_{in}/n_{out} is the amount of CO_2 in the inlet/outlet stream, n_m is the amount of methanol in the outlet stream, and y is the stoichiometric coefficient of methanol.

3. Results and Discussion

3.1 Catalysts Characterization

The graph for the thermogravimetric analysis is shown in figure 1.

Figure 1. Thermogravimetric analysis.

All the catalysts, supported on alumina or niobium, showed greater mass loss in the initial temperature range, up to 200 °C by around 2 to 2.5% of loss, corresponding to the water contained in the compounds. After this temperature the mass loss becomes even smaller, by around 1% up to 850 °C. Therefore, considering the reaction temperature, there is no significant loss of mass in the catalysts.

The XRD patterns for the alumina and niobium supported catalysts are shown in Figures 2 and 3, respectively.

Figure 2. XRD patterns for the Al_2O_3 (A1) and Nb_2O_5 (A2) supported catalysts.
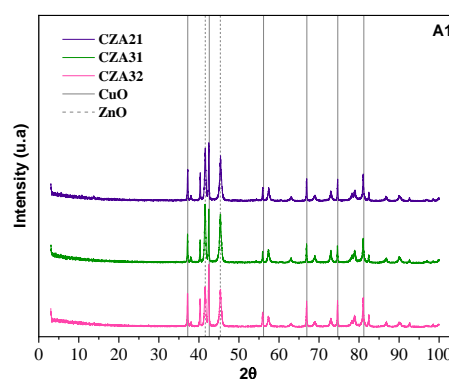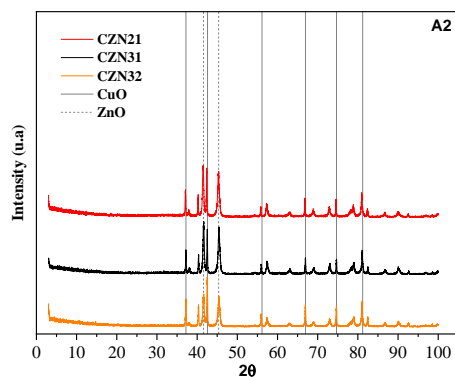
The patterns mainly feature characteristics peaks of copper, as seen in the oxide patterns, which may indicate a favorable active phase. Although there are zinc peaks at its characteristic angles, the intensity is more similar to copper patterns, which may be explained by the geometric spacer function associated with zinc, helping to disperse the component [5-8].

It was not possible to find characteristic peaks of the support for the niobium catalysts, since the calcination temperature was too low to obtain a crystalline structure, which only occurs in the range of 400 °C [13-14].

3.2 Adsorption Isotherms

Figure 3 (A1 and A2) shows the amounts of CO_2 adsorbed at different pressures in isothermal experiments for the catalysts studied.

The CZA31 and CZN31 catalysts exhibit similar behavior in CO_2 adsorption, with the amount adsorbed decreasing as the temperature increases, suggesting that the process is primarily physical and exothermic under the studied conditions. The amount of CO_2 adsorbed is higher for both the CZA31 and CZN31 catalysts at higher pressures. This indicates a direct correlation between the applied pressure and the amount of CO_2 adsorbed. The CZN31 catalyst shows a greater amount of CO_2 adsorbed compared to the CZA31 at almost all pressures and temperatures studied, suggesting that CZN31 may have a slightly better efficiency for CO_2 capture.

Figure 3. CO_2 isotherms on (A1) CZA31 and (A2) CZN31 catalysts.
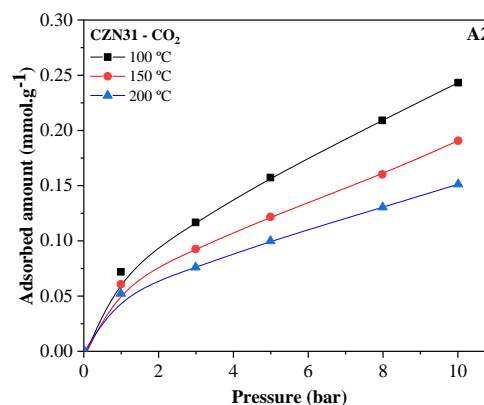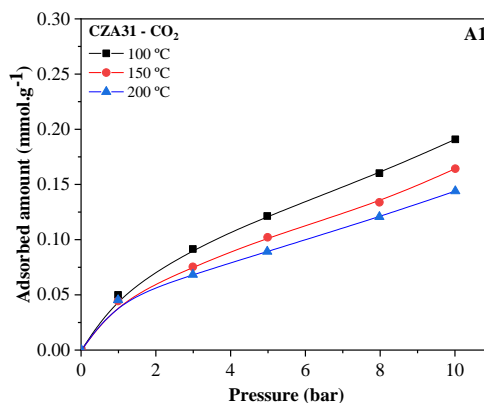
The CO_2 adsorption capacity of the CZA31 and CZN31 catalysts is crucial as it determines the amount of CO_2 available on the surface for the hydrogenation reaction. Catalysts with higher adsorption capacity, such as CZN31, can ensure a higher concentration of CO_2 on the active surface, potentially increasing the reaction rate. Although the data are for other temperatures and pressures, the trend of decreasing adsorption capacity with increasing temperature suggests that at 200 ℃, CO_2 adsorption is less effective. However, the high pressure (25 bar) can compensate for this decrease, increasing the amount of CO_2 adsorbed and available for the reaction.

3.3 Reaction Tests

The CO_2 conversion and the methanol concentration at the outlet of the reactor for the alumina and niobium-supported catalysts in the 3:1:1 ratio are shown in Figures 4 (A1 and A2), respectively. Based on the results presented, in the alumina supported catalyst there is no manifestation

of methanol production until around 4 hours of reaction.

Figure 4. CO_2 conversion using the 3:1:1 catalyst (A1) and methanol concentration at the outlet of the reactor using the 3:1:1 catalyst (A2).
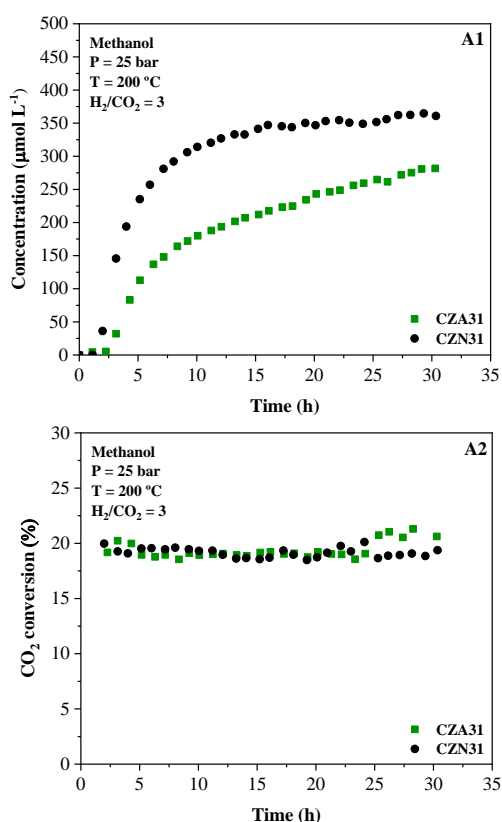
Furthermore, the catalyst presented a slow growth, presenting a maximum concentration of 281.6 µmol L^{-1} and a 20.6% CO_2 conversion at the end of the 30 hours reaction studied. In contrast, the niobium catalyst starts methanol production about an hour earlier, in addition to presents noticeably greater and faster production. In this context, the maximum concentration presented by the CZA catalyst is reached around 7 hours reaction of the CZN. Moreover, at the end point of reaction, the conversion was 19.4% and the concentration was 360.9 µmol L^{-1}, almost 30% higher than the alumina catalyst. The catalytic performance presented in this preliminary study is comparable to that reported in other studies of synthesized CZA catalysts, such as Santiago et al. (2022), when observed the first 30 hours of reaction [12]. Regarding niobium catalysts,

the results seem promising, as they are more favorable when compared to some results reported in the literature, such as Silva et al. (2016) [15], where niobium oxide catalysts tested under similar conditions showed less than 1% conversion. This study is preliminary, and further research on the other proportions listed in Table 1 is still needed.

4. Conclusion

The studied catalysts showed catalytic performance comparable or superior to other catalysts reported in the literature. The niobium-supported catalyst yielded the best methanol concentrations. The reaction temperature of 200 °C did not cause significant material degradation. The catalysts exhibited characteristics of Cu-ZnO interactions, crucial for component dispersion. The CZN31 catalyst outperformed in CO_2 adsorption. High pressure (25 bar) at 200 °C compensates for lower adsorption at elevated temperatures, ensuring adequate CO_2 for hydrogenation. Further studies on different proportions are needed for more insights into catalyst composition.

5. Acknowledgements

6. References

[1] Methanol Applications. Methanol Institute, 2024.
[2] Song, C., 2006, Catalysis Today 115, 2-32.
[3] Dasireddy, V.D.B.C., Likozar, B., 2019, Renew. Energ. 140, 452–460.
[4] Behrens, M., Kasatkin, I. et al, 2012, Science 336, 893–897.
[5] Aguayo, A.T., Ereña J. et al, 2007, Ind. Eng. Chem. Res. 46, 5522-5530.
[6] Behrens, M., Schlogl, R., 2013, Zeitschrift fur Anorganische and Allgemeine Chemie 639, 2683-2695.
[7] Nakamura, J., Nakamura, I. et al, 1995, Catal. Lett. 31, 325-331.
[8] Liao, F., Huang, Y. et al, 2011, Angew. Chem. 123, 2210-2213.
[9] Catizzone, E., Bonura, G. et al, 2018, Molecules 23, 31.
[10] Tanabe, K., Okazaki, S., 1995, Applied Catalysts A: General 133, 191-218.
[11] Tanabe, K., 2003, Catalysis Today 78, 65-77.
[12] Santiago, R.G., Coelho, J.A. et al, 2022, Frontiers in Chemistry 10:903053.
[13] Chai, S-H., Wang, H-P. et al, 2007, Journal of Catalysis 250, 342–349.
[14] Ko, E.I., Weissman, J.G., 1990, Catalysis Today 8, 27-36.
[15] Silva, R.J., Pimentel, A.F. et al, Journal of CO_2 Utilization 15, 83-88.