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Evaluation of feeding molar rate in mini fixed bed reactor for methanol steam reforming with pre-optimized composition of $CuO/ZnO/Al_2O_3$ catalyst

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ABSTRACT. Hydrogen gas is an ideal fuel due to its higher calorific value among fuels and minimal environmental impact on their energy applications. However, the high cost around high reactivity, explosion risks and extremely low energy density, make it unfeasible to be used as fuel in large quantities scale. There are some possibilities to circumvent these limitations, including obtaining and converting energy through fuel cells, which is very promising. Research in this field has been summarized in recent decades, motivated by the environmental problems faced due to the dependence on non-renewable energy matrices. From this, this study aimed to improve the steam methanol reforming using $CuO/ZnO/Al_2O_3$ catalyst. The catalyst was characterized by atomic absorption spectroscopy, N_2 physisorption and XRD. Catalytic tests were carried out in a laboratory scale fixed bed reactor at 300°C, atmospheric pressure and in differential conditions (methanol conversion < 10%); a previous run for catalyst synthesis validation in relation to the results obtained in the literature for the same conditions was evaluated. Subsequently, it was found that the thermal degradation of methanol at 300°C without the presence of the catalyst was negligible, and then operational conditions were established to obtain methanol conversions lower than 10%. Then, the initial deactivation of the catalyst over 31h. Also identifying the stability after 7 h in reaction with average conversion into 9.7% of methanol, showing high stability, in addition to good reproducibility on the part of synthesis in optimal composition. Then, experiments were carried out for the molar ratios 2:1 and 4:1 with methanol conversions of 15.5% and 6.6%, respectively. Note that performing the average of the 4:1 and 2:1 methanol conversion in 14.6% obtained at indicating that the upper boundary molar ratios (4:1) compensates for the conversion reduction in 2:1, achieving a result superior to the reference 3:1.

Keywords: fuel cells; heterogeneous catalysis; $CuO/ZnO/Al_2O_3$ catalyst in composition optimized; fixed bed reactor.

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Introduction

Planet Earth has reached the limit of natural resources that could be renewed in a year without causing any burden to the environment in July 2019, which indicates that around 1,75 planets are needed to maintain the world consumption pattern (Global Footprint Network, 2019). Energy obtained from non-renewable sources is one of the main causes of this scenario, with emphasis on oil and its derivatives, coal and natural gas. A solution to reverse this framework and ensure sustainable development for future generations is the use of renewable energy sources, including hydroelectric, solar, wind, fuel cell, biomass, among others.

The Earth Overload Day in 2020 was delayed by 3 weeks from the previous year; this was the most significant reduction in over 40 years (Global Footprint Network, 2020). The reason for this "breathing" of the planet was the pandemic caused by the Covid-19 virus; although tragic due to the death of millions of people, the measures of social distancing and lockdown that occurred in several countries have caused a reduction in carbon emissions (Global Footprint Network, 2020). In this way, a direct relationship between the reduction of global pollution and positive environment effects was observed.

It is known that since 1970 it takes more than one planet Earth to support consumption and other habits of human beings. The global public health crisis that started in 2020 demonstrated that it is possible to establish a change in this trend in a short period of time. However, this sustainability must be achieved through projects, consumer education and technological alternatives.

Brazil consumes more renewable energy than countries belonging to the Organization for Economic Cooperation and Development (OECD) and the world average (EPE, 2020). However, oil and derivatives still contribute about 34.4% of its national energy matrix, within 53.9% of non-renewable energy sources considering the country's Internal Energy Offer (OIE) (EPE, 2020).

From this, the use of fuel cells that operate with hydrogen for the production of electric energy has a great potential for increasing the share of renewable energy compared to fossil sources, so that the impacts of pollutant emissions are significantly reduced, thus being able to bring cleaner and cheaper energy to remote locations with difficult access to conventional ones.

However, it is notable that cells based on hydrogen obtained through fuels – such as methanol, ethanol, methane, natural gas – have several practical implications that make their application on a large scale difficult. Among them, there are parallel (or consecutive) reactions that compete in the hydrogen yield; the high temperatures and pressures for converting fuels into H_2; the deactivation of the catalyst through carbon monoxide and coke poisoning.

The fuel used to power the cells must be renewable, technically and economically attractive to make the energy source clean and viable. A potential generator of hydrogen is methanol, which steam reforming process catalyzed by $CuO/ZnO/Al_2O_3$ is consolidated in the chemical industry, due to its low-cost catalyst, operating at temperatures in the range of 200 to 300°C and pressures of 1 atm, with low formation of carbon monoxide (which increases cell life), lower emission of pollutants, reduced number of parallel and consecutive reactions and higher carbon-hydrogen ratio, when compared to hydrocarbons and other alcohols.

In Brazil, a large part of the methanol supply is of fossil origin or is imported. However, it can easily be produced from biomass under anaerobic conditions. The great advantages of methanol over ethanol (a less toxic biofuel, with a visible flame and favorable infrastructure in the Brazilian scenario) is the fact that there are catalysts in the commercially consolidated steam reforming process (Rodrigues, 2012).

The use of methanol is a potentially favorable source for obtaining hydrogen by reforming processes compared to other hydrocarbon and alcohol fuels, mainly due to its operation at relatively low temperature, high carbon-hydrogen ratio, low CO formation, zero NO_X emission and SO_X, in addition to overcoming many of the problems associated with transporting and storing hydrogen. According to Neto, Santos and Jorge (2014) and Purnama et al. (2004) the most common route to obtain hydrogen through methanol is by steam reforming, represented by Equation 1.

$$CH_3OH_{(g)} + H_2O_{(g)} \rightarrow 3H_2 + CO_2 \quad (1)$$

The maximum yield in hydrogen production via this route is 75%, however, an energy source is required due to the endothermic nature of this reforming reaction. Other ways to obtain hydrogen through methanol reforming are the decomposition (Equation 2) and partial oxidation reactions (Equation 3),

$$CH_3OH \rightarrow CO + 2H_2 \quad (2)$$

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CO_2 + 2H_2 \quad (3)$$

According to Purnama et al. (2004), there is still water-gas shift reaction (Equation 4), which contributes to H_2 yield.

$$CO + H_2O_{(g)} \rightleftarrows CO_2 + H_2 \quad (4)$$

It is possible to verify that the methanol steam reforming presents a higher stoichiometric hydrogen production. In addition, the purity of hydrogen is essential for fuel cells, which can use the steam reforming of methanol by a consolidated process and at relatively low temperature, resulting in greater energy efficiency and lower costs of production compared to other reforming processes and other fuels (Hoogers et al., 2003).

There are several types and variations of catalysts used in methanol steam reforming. Group VIII metals such as Pd, Pt and Ni favor the water-gas shift reaction from methanol, while Cu-based catalysts favor the production of H_2 with high selectivity in relation to CO (Yong, Ooi, Chai, & Wu, 2013). Commercial catalysts, applied on a large scale, are generally composed of $CuO/ZnO/Al_2O_3$. The ZnO has the function of promoting agent, responsible for reducing sintering and promoting the reducibility of Cu.

The composition of Cu, Zn and Al can vary the way the metals are structurally arranged, and their textural properties depend mainly on the method by which the metals (Cu and Zn) are incorporated into the support (aluminum oxide - Al_2O_3). This catalyst has been extensively studied in the literature due to its good results

in hydrogen and carbon dioxide selectivity, high stability and catalytic activity, low carbon monoxide formation and low cost of the metals used against noble metals as Pt; furthermore, it is a consolidated catalyst for this process (Amphlett, et al., 1994; Agrell, Birgersson, & Boutonnet, 2002, Choi & Stenger, 2003; Purnama et al., 2004; Patel & Pant, 2006; Ahmadi, Haghighi, & Ajamein, 2016; Fornari, Neto Menechini, Lenzi, Santos, & Jorge, 2017).

Although the industrial MSR process has been consolidated with catalysts based on $CuO/ZnO/Al_2O_3$ some researchers have developed studies to solve the problem of CO selectivity and catalytic stability, evaluating catalysts containing other metals and/or supports in the reaction.

In this work, the synthesized catalyst was therefore also based on $CuO/ZnO/Al_2O_3$. On the other hand, given the several compositions presented by literature (Amphlett, et al., 1994; Agrell, et al., 2002, Choi & Stenger, 2003; Purnama et al., 2004; Patel & Pant, 2006; Ahmadi et al., 2016; Fornari et al., 2017), the synthesis of the catalyst was carried out from an optimized statistical composition that leads to maximum H_2 selectivity by MSR (Fornari et al., 2017).

In this context, the methanol steam reforming process was aim of study in this work. The $CuO/ZnO/Al_2O_3$ catalyst was synthesized and characterized by metallic composition, morphology and structure. Subsequently, catalytic tests were carried out in a continuous mini fixed-bed reactor. This work was based on an unprecedented study for the methanol steam reforming process, after validation of the catalyst and characterizations, using a $CuO/ZnO/Al_2O_3$ catalyst in a pre-optimized composition to evaluate the effects of the molar ratio on the conversion of methanol.

Materials and methods

Catalyst Synthesis

The selection of the $CuO/ZnO/Al_2O_3$ catalyst prepared by wet impregnation was carried out according to the methodology proposed by Badmaev, Pechenkin, Belyaev, and Sobyanin (2015) and with the specific objectives of evaluating the catalytic tests of optimized composition of Fornari et al. (2017).

Copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$ – Synth, 101,65%), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$ – Sigma-Aldrich, 99,6%) and commercial alumina (Al_2O_3 – Merck) were added in the amounts necessary to obtain the compositions obtained by Fornari et al. (2017), in an Erlenmeyer flask with 300 mL of deionized water. This mixture was left under magnetic stirring for about 24 h. Subsequently, the mixture was transferred to a round-bottomed flask and dried by means of a rotary vacuum evaporation at 80°C until excess water removing. The paste obtained was dried in an oven at 100ºC for 72h. After that, the obtained powder was calcined at 400ºC, for 5h, with a heating ramp of 2ºC min^{-1} (Badmaev et al., 2015).

Finally, the catalyst was crushed with a pressure of 147 kgf cm^{-2}, macerated in a mortar with a pistil and sieved in Granutest sieves in particle sizes between Tyler 35 mesh (0,42 mm) and 200 mesh (0,075 mm), for the purpose of classifying the diameter of the catalyst particles for the catalytic tests to ensure less or no-diffusional internal effects.

Catalyst Characterization

Metallic compositions of the catalyst were obtained by means of atomic absorption spectrometry in the SpectrAA 50B equipment from VARIAN (DEQ/UEM), after acid digestion of the samples with heating, by3eflon0.5 mL of HNO_5:HCl with 1:3 v:v, and 3 mL of hydrofluoric acid until the volume of the liquid significantly decreased; after cooling, 10 mL of deionized water, 5 mL of 4% H_3BO_3 and 1 mL of concentrated HCl were added to obtain a clear solution under heating. After cooling, the solution was transferred to a 100 mL volumetric flask with some deionized water and then made up to volume.

The specific area, pore volume and pore size distribution were determined by nitrogen physisorption analysis (Linde, purity > 99,999%) at 77 K and pressures from $1,2x10^{-3}$ MPa to 0,092 MPa using the Micromeritics ASAP 2020 analyzer (LATI/DEQ/UEM). Prior to analysis, the sample was degassed at $1,3x10^{-4}$ MPa and 200°C, with a heating rate of 10°C min^{-1}, for 2h. The specific area was determined using the BET method, and pore volume was calculated using the single point adsorption isotherm at $P/P_0 = 0,98$. For pore size distribution, BJH method was used.

In order to identify the crystalline states in the catalyst structure, the analysis by XRD (X-ray diffraction) by the powder method was performed. XRD analyzes were performed in a Shimadzu LabX 6000 diffractometer (LATI/DEQ/UEM) using CuKα radiation. The measurements were determined with a voltage of 40 kV and a

current of 30 mA using a Cu tube, with a rate of 2θ° min^{-1}, acquisition time of 1 s and an interval of 10º ⩽ 2θ ⩽ 70º. X-ray diffractograms were obtained in vacuum and the peaks were identified from the ICDD (International Conference on Diffraction Data) database and analyzed using the Xpert HighScore Philips Plus software, version 1.0.

Experimental Tests

For the catalyst to be added to the reactor, it was necessary to use a stainless-steel screen supporting the catalyst and glass spheres. The support welded on the outside of the reactor served to fix the thermocouple, ensuring the monitoring of the temperature in the catalytic bed throughout the test. A mass of 200 mg^{-1} of catalyst was placed on top of the screen, and then a layer with 200 mg^{-1} of inert glass spheres (Sigma-Aldrich) was placed to homogenize the flow of reagents.

Previous to each catalytic runs, in situ drying of the catalyst was carried out, with a constant flow rate of N_2 (99,996%, White Martins) at 50 $mL.min^{-1}$, heated from room temperature to 100°C at a 5°C $min.^{-1}$ heating rate, and kept at this temperature for 1h.

After drying, a 60 mL $min.^{-1}$ of 5% mol H_2/ N_2 mixture flow was used to obtain the active phase by reducing CuO to Cu metallic, with a heating up from 100°C to 200ºC (5ºC $min.^{-1}$) and maintained for 30 min. at this temperature. Afterwards, it was heated again from 200 to 300ºC (at 5ºC $min.^{-1}$) and the kept at 300ºC under the reducing mixture flow for 1h.

Firstly, it was carried out preliminary tests to validate the catalyst and evaluate the experimental conditions to obtain conversions close to 10% (differential operation). The flow conditions found to obtain the adopted differential methanol conversion were repeated and replicated for the catalytic tests in in molar methanol:water ratios of 2:1, 3:1 and 4:1. All catalytic tests were evaluated at 300ºC at atmospheric pressure (100,7 kPa).

Results and discussions

Catalyst Characterization

The chemical composition of the catalyst was obtained to verify if the impregnation process was effective in the synthesis. Table 1 shows the values obtained for weight composition of the Cu and Zn, compared to the results of Fornari et al. (2017), adopted as the nominal composition after optimization.

Table 1. Results obtained from the composition by atomic absorption of the Self-Authored catalyst (2021) and by Fornari et al. (2017).

Authors	Cu (%)	Relative deviation of Cu[c] (%)	Zn (%)	Relative deviation of Zn[c] (%)
Fornari et al. (2017)[a]	20,7	-	13.4	-
Fornari et al. (2017)[b]	19.4 ± 0.6	6.3 ± 0,6	15.5 ± 0.9	15.7 ± 0.9
Authors themselves	19.2	7.8	11.2	16.4

[a]Nominal value of the optimized composition. [b]Value obtained experimentally. [c]Deviation using the work of Fornari et al. (2017)[a] (nominal) as reference.

There was a variation of 7,8% of Cu and 16,4% of Zn in relation to the value of the optimized nominal composition for the reference catalyst, but they are close to the values obtained experimentally by Fornari et al. (2017), with similar deviations. Such results indicated catalyst reproducibility. The deviations presented in the catalyst synthesis of this work may occurred from the absorption of moisture by the hygroscopic salts or caused by the loss of mass in the material transfer stages during the preparation of the catalyst.

Textural characteristics, as BET surface area, pore volume and average pore size are shown in Table 2, which also contains the results found by Fornari et al. (2017) in their catalyst.

Table 2. Texture properties for catalysts synthesized by impregnation.

Authors	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (Å)
Fornari et al. (2017)	69	0.061	18
Authors themselves	81.7	0.191	68.2

In Figure 1, the pore size distribution of the synthesized catalyst is shown. The profile obtained is similar to that obtained by Fornari et al. (2017), except for peaks in an order lower than 25 Å, also demonstrating the presence of micropores, although in a smaller quantity than mesopores; the bimodal pore size distribution

profile in Figure 1 is in agreement with the isotherm profile (Figure 2), in which the small amount of adsorbed nitrogen (forming a plateau) at low relative pressure values indicates the presence of micropores in the catalyst morphology.

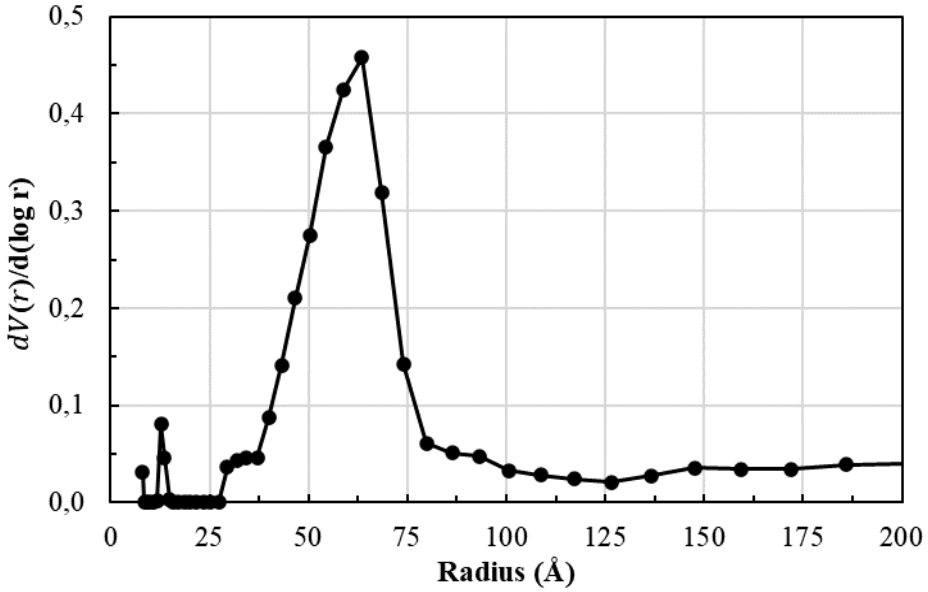

Figure 1. Pore size distribution of the synthesized catalyst.

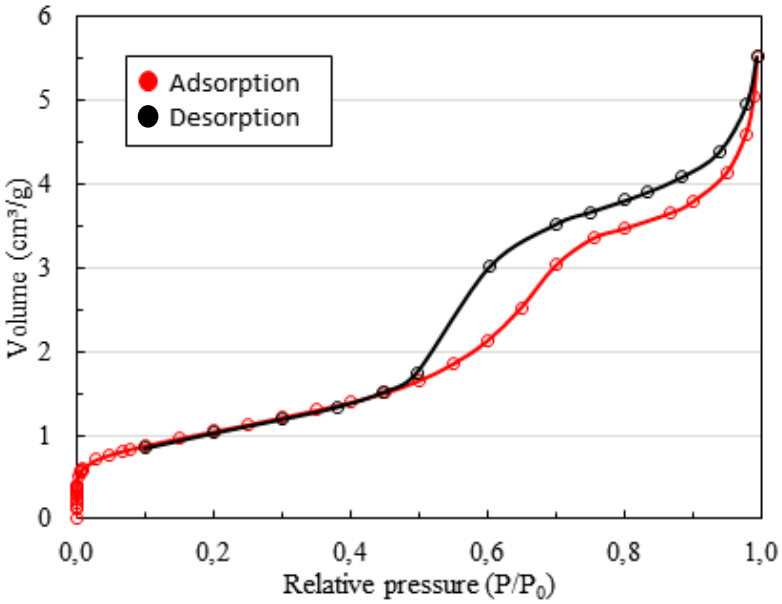

Figure 2. N_2 adsorption-desorption isotherm for the $CuO/ZnO/Al_2O_3$ catalyst.

The adsorption-desorption profile of N_2 is shown in Figure 2. According to the IUPAC classification, the isotherm has a type IV shape with a plateau at the beginning (monolayer adsorption, associated with the filling of micropores), with an increase in the adsorbed volume for higher values of relative pressure, which represents the adsorption in larger pores (mesopores). There was formation of hysteresis, which seems like a H4 type, characterizing a possible heterogeneity of the mesopores in relation to different shapes and openings and capillary condensation.

The diffractogram obtained for catalyst obtained in this work is shown in Figure 3.

The diffractogram indicates that the material is crystalline. The presence of the peak referring to copper aluminate ($2\theta = 44.9°$) is highlighted as the most intense, thus demonstrating greater crystallinity. However, the presence of smaller peaks throughout the diffractogram indicates the presence of smaller crystallites dispersed on the alumina support.

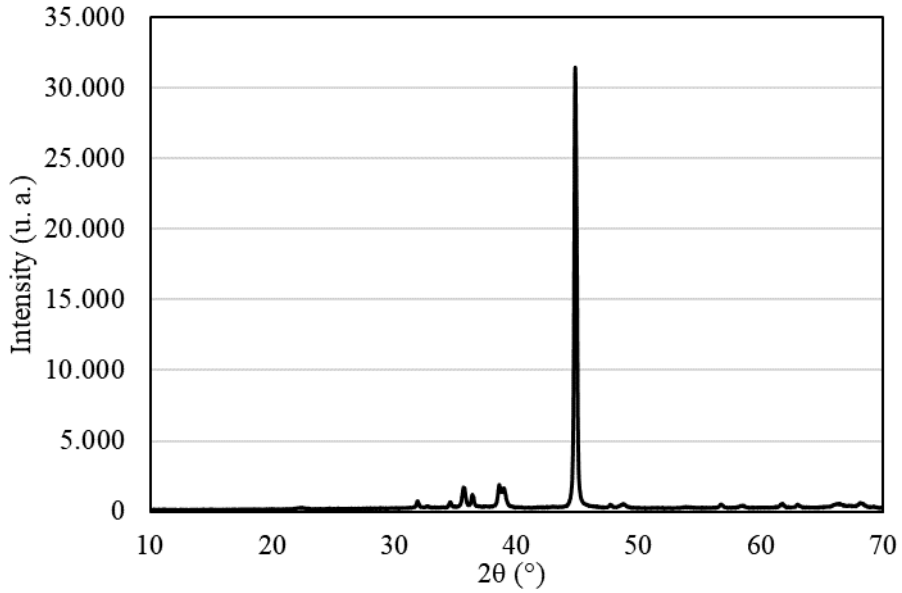

Figure 3. Diffractogram of the CuO/ZnO/Al_2O_3 catalyst.

The presence of crystallites that diffract X-rays with less intensity, and consequently of reduced sizes, indicate that the synthesis process led to a homogeneous distribution of the active phases on the support (large dispersion). Furthermore, the presence of mixed oxides (copper aluminate, 2θ = 44.9°; and aluminum-zinc oxide, 2θ = 53.9°) also indicates a high interaction of the active phase with alumina. Therefore, such effects may contribute to a better stability and activity of the catalyst.

Catalytic tests

Synthesized catalyst validation test

The conversion of methanol for the catalyst in this work and that found by Fornari et al. (2017) for the optimized catalyst are shown in Figure 4.

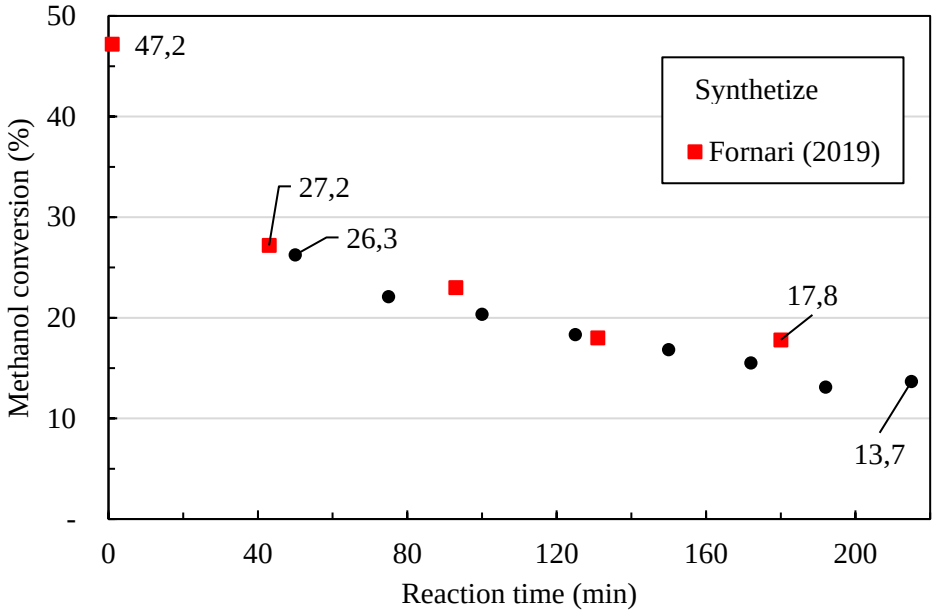

Figure 4. Catalyst comparison with reference data (validation).

It is possible to observe that the results were similar to each other, validating the synthesis of the catalyst, showing the reproducibility of the methodology and catalytic activity of the catalyst synthesized by Fornari et al. (2017).

Test to determine the differential condition

To determine the differential operating conditions, preliminary catalytic tests were carried out, varying only the mass flow rates of the water-methanol mixture flow from 0.86 to 0.41 g min.$^{-1}$. The flow rate of 0.41 g min.$^{-1}$ led the system to a 7.6% methanol conversion, as shown in Figure 5. So, this feeding flow was adopted as the operational reference condition to evaluate the methanol:water molar feed composition at differential conditions.

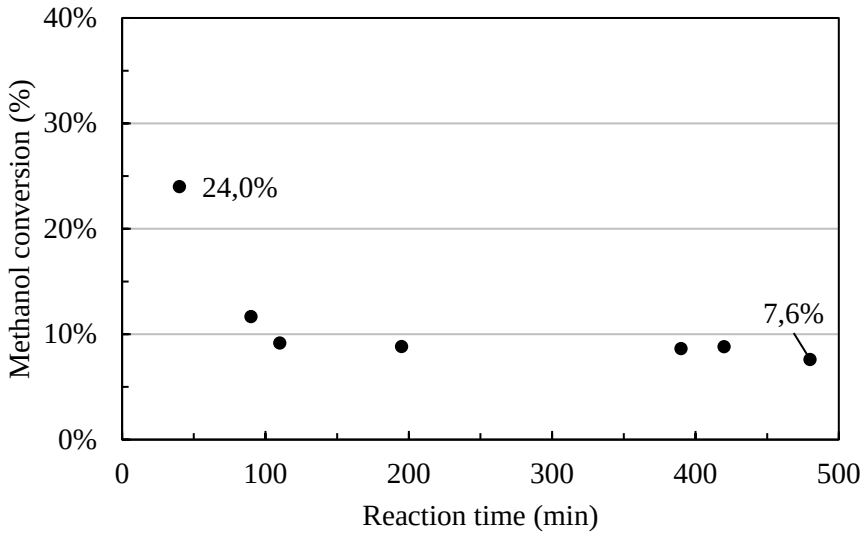

Figure 5. Experimental evaluation with a 3:1 molar ratio and a mass flow rate of 0.41 g.min^{-1}.

Catalytic tests

Figure 6 was obtained reproducing the differential experimental conditions with methanol:water molar ratios of 4:1, 3:1 and 2:1. The reactions was evaluated for 450 min in running.

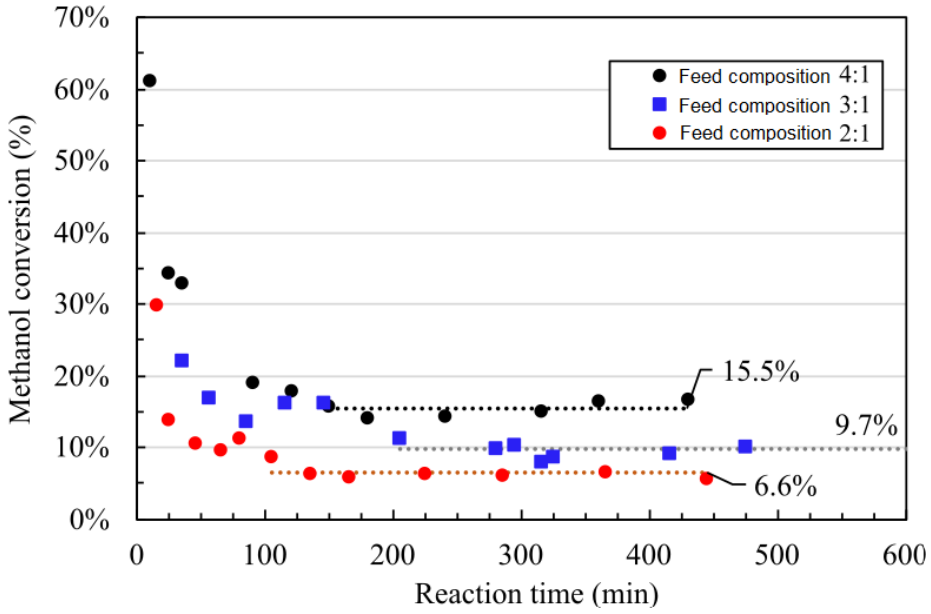

Figure 6. Methanol conversion stability test of the pre-optimized catalyst in molar ratios of 2:1, 3:1 and 4:1 of MeOH:H_2O.

From Figure 6, it can be concluded that the catalyst has an initial drop in conversion associated with the effects of initial deactivation. In addition, it is observed that the catalyst remained stable after the initial deactivation which occurred up to about 7h of reaction.

It was observed that the catalyst remained stable in all tests. For the 4:1 molar ratio, the drop in conversion was greater when compared to the other two feed molar ratios; after the total reaction period, an average methanol conversion of 6.6, 9.7 and 15.5% was obtained for the molar ratios 2:1, 3:1 and 4:1, respectively.

One can note that changing the volumetric flow to keep the methanol contact time constant implies changing the residence time between the analyzed reactions. For this, it was verified that although it has a longer residence time, the reaction in molar ratio 4:1 has the lowest methanol conversion observed. On the other hand, the 4:1 reaction has the highest methanol conversion and the shortest residence time. This association indicates that, for the conditions evaluated, the MSR reaction has greater influence by increasing the feed molar ratio.

On the other hand, Figures 4 and 6 show a reduction in conversion as long the time. This was expected since a slow initial deactivated may occur from partial cooper oxidation. This deactivation becomes less expressive when a stabilization occurs, reinforcing that in all the experiments, there was only an initial deactivation of the catalyst based on $CuO/ZnO/Al_2O_3$, which does not accompany all the catalytic run.

Table 3. Evaluation of conversions as a function of molar feed ratio.

Operation	Molar Ratio	Methanol Conversion (%)	Deviation[a] (%)
1	3:1	9.7	-
2	4:1	15.5	61.5
3	2:1	6.6	31.2 (*negative*)
4[b]	4:1 and 2:1	11.0	14.6

[a]Deviation from feed composition 3:1 operation. [b]simple average of the conversions obtained by conventional operations in 4:1 and 2:1.

From the data contained in Table 3, an increase of about 61.5% in methanol conversion was observed when the feed molar ratio was changed from 3:1 (reference) to 4:1; this result was expected due to the greater presence of water, which contributes to increases the reaction rate. On the other hand, a reduction of about 31.2% in methanol conversion was observed when the molar ratio was changed from 3:1 to 2:1.

Despite the reduction in conversion observed for the catalytic test with 2:1 molar ratio, when evaluating the average conversion of Operations 2 and 3, there is a gain in this mean conversion compared to the reference condition (Operation 1). This average conversion gain was 14.6%. Thus, despite a reduction in the conversion for a given condition (2:1 ratio), the gain obtained at the other one (4:1 ratio) is higher and, therefore, the average is shifted to a value higher than the reference. This gain in average conversion by 4:1 and 2:1 compared to 3:1 feed molar rate indicates that a periodic (*i.e.* temporally changes in feed composition) may contribute to higher methanol conversion than only one steady-state condition.

Conclusion

The catalytic tests with different feed molar rates indicated high stability of the $Cu/ZnO/Al_2O_3$ catalyst, since only initial deactivation was observed. The structural and morphological properties evaluated showed the catalyst has strong metal-support interactions due to $Cu\text{-}Al_2O_3$ and $Zn\text{-}Al_2O_3$ well-dispersed mixed oxides, observed by XRD, besides a mesoporous morphology which contributed to the large surface area. In addition, it was obtained that the simple average of methanol conventional with feed molar ratios of 4:1 and 2:1 was 14.6% superior to the 3:1 molar ratio. Also, highest conversion was obtained for a feed molar rate of 4:1 was observed, which confirms that an excess of water contributes to methanol conversion.

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References

Agrell, J., Birgersson, H., & Boutonnet, M. (2002). Steam reforming of methanol over a $Cu/ZnO/Al_2O_3$ catalyst: a kinetic analysis and strategies for suppression of CO formation. *Journal of Power Sources*, *106*(1), 249-257. DOI: https://doi.org/10.1016/S0378-7753(01)01027-8

Ahmadi, F., Haghighi, M., & Ajamein, H. (2016). Sonochemically coprecipitation synthesis of $CuO/ZnO/ZrO_2/Al_2O_3$ nanocatalyst for fuel cell grade hydrogen production via steam methanol reforming. *Journal of Molecular Catalysis A: Chemical, 421*(1), 196-208. DOI: https://doi.org/10.1016/j.molcata.2016.05.027

Amphlett, J. C., Creber, K., Davis, J. M., Mann, R. F., Peppley, B., & Stokes, D. M. (1994). Hydrogen production by steam reforming of methanol for polymer electrolyte fuel cells. *International Journal of Hydrogen Energy*, *19*(2), 131-137. DOI: https://doi.org/10.1016/0360-3199(94)90117-1

Badmaev, S. D., Pechenkin, A. A., Belyaev, V. D., & Sobyanin, V. A. (2015). Hydrogen production by steam reforming of dimethoxymethane over bifunctional CuO-ZnO/γ- Al_2O_3 catalyst. *International Journal of Hydrogen Energy, 40(*40), 14052-14057. DOI: https://doi.org/10.1016/j.ijhydene.2015.05.188

Choi, Y., & Stenger, H. G. (2003). Water gas shift reaction kinetics and reactor modelling for fuel cell grade hydrogen. *Journal of Power Sources*, *124*(2), 432-439. DOI: https://doi.org/10.1016/S0378-7753(03)00614-1

Empresa de Pesquisa Energética [EPE]. (2020). *Balanço energético nacional 2020: relatório síntese/ ano base 2019*. *Maio, 2020*. Retrieved on June 21, 2020 from https://www.epe.gov.br/pt/publicacoes-dados-abertos/publicacoes/balanco-energet ico-nacional-2020.

Fornari, A. C., Neto Menechini, R., Lenzi, G. G., Santos, O. A. A., Jorge, L. M. M. (2017). Utilization of sol-gel CuO-ZnO-Al_2O_3 catalysts in the methanol steam reforming for hydrogen production. *Canadian Journal of Chemical Engineering, 95*(1), 2258-2271. DOI: https://doi.org/10.1002/cjce.23005

Global Footprint Network. (2019). *Earth Overshoot Day 2019 is July 29th, the earliest ever*. Oakland, CA: Global Footprint Network. Retrieved on Sep. 15, 2019 from https://www.footprintnetwork.org/2019/06/26/press-release-june-2019-earth-overshoot-day/

Global Footprint Network. (2020). *Earth Overshoot Day is August 22, more than three weeks later than last year*. Oakland, CA: Global Footprint Network. Retrieved on Jan. 9, 2021 from https://www.overshootday.org/newsroom/ press-release-june-2020-english/

Hoogers, G. (2003). *Fuel Cell Technology Handbook*. Boca Raton, FL: CRC Press. DOI: https://doi.org/10.1201/9781420041552

Neto, R. M., Santos, O. A. A., & Jorge, L. M. M. (2014). Modelagem e simulação de um reator isotérmico de reforma a vapor de metanol. *Acta Scientiarum. Technology*, *36*(2), 295-301. DOI: https://doi.org/10.4025/actascitechnol.v36i2.18850

Patel, S., & Pant, K. K. (2006). Production of hydrogen with low carbon monoxide formation via catalytic steam reforming of methanol. *Journal of Fuel Cell Science and Technology*, *3*(4), 369-374. DOI: https://doi.org/10.1115/1.2349514

Purnama, H. Ressler, T., Jentoft, R. E., Soerijanto, H., Schlögl, R., & Schomäcker, R. (2004). CO formation/selectivity for steam reforming of methanol with a commercial CuO/ZnO/ Al_2O_3 catalyst. *Applied Catalysis A: General*, *259*(1), 83-94. DOI: https://doi.org/10.1016/j.apcata.2003.09.013

Rodrigues, F. (2012). Mesmo sem receber o mesmo nível de interesse do óleo vegetal: o discreto metanol consolidou-se como ingrediente fundamental para o biodiesel brasileiro. Retrieved on Sep. 10, 2019 from https://www.biodieselbr.com/reVista/022/mercado-metanol-1

Yong, S.T., Ooi, C. W., Chai, S. P., & Wu, X. S. (2013). Review of methanol reforming-Cu-based catalysts, surface reaction mechanisms, and reaction schemes. *International Journal of Hydrogen Energy*, *38*(22), 9541-9552. DOI: https://doi.org/10.1016/j.ijhydene.2013.03.023