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of Cu/ZnO/CeO₂ nanoparticles for the hydrogenation
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Marc Capdevila Cardona

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Antoni Sánchez

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UIO66 metal-organic framework as a support material of Cu/ZnO/CeO₂ nanoparticles for the hydrogenation of carbon dioxide to produce methanol.

Marc Capdevila Cardona*, Seyed Alireza Vali and Antoni Sánchez

*Marc Capdevila: marc.capdevila@uab.cat

Composting Research Group (GICOM),
Department of Chemical, Biological and Environmental Engineering,
Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Abstract

A series of catalysts were tested for the hydrogenation of carbon dioxide to methanol. The six experiments conducted utilized the following catalysts: CuZnO, CuZnOAl₂O₃, CuZnOCeO₂, CuZnOTiO₂, CuZnOAl₂O₃CeO₂, and CuZnOCeO₂Al₂O₃. Subsequently, four catalysts exhibiting the most promising results underwent additional synthesis, incorporating a metal-organic framework (UIO66) as a support. The catalysts combined with the MOF included CuZnO, CuZnOCeO₂, CuZnOAl₂O₃, and CuZnOAl₂O₃CeO₂. Utilizing UIO66 as a support yielded exceptionally favorable outcomes in terms of selectivity (%) and Space-Time Yield (STY) (mg g⁻¹cat h⁻¹), resulting in a production increase of methanol exceeding two times that of catalysts without MOF support. Notably, CuZnO@UIO66 demonstrated the best performance, achieving an STY of 80 mg g⁻¹cat h⁻¹ and 90% selectivity. Despite comparatively lower results, CuZnOCeO₂@UIO66 emerged as a novel material with promising outcomes, producing a methanol rate of 50 mg g⁻¹cat h⁻¹ and 100% selectivity. In conclusion, the main results of this paper was the use of CuZnOCeO₂@UIO66 due to its excellent performance. Future studies are proposed to further evaluate this catalyst. Primary objectives include catalyst characterization using X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). Additionally, investigations into the impact of varying pressure and temperature conditions on performance will be conducted. Lastly, the catalyst's long-term stability will be assessed to determine its operational lifespan without a substantial decrease in activity.

Keywords: MOF, space-time Yield, selectivity, nanoparticles, UIO66

1. Introduction

In the 21st century, contemporary society faces two critical challenges: mitigating global warming, which is beginning to impact all countries universally, and seeking alternatives to traditional energy sources such as fossil fuels, which are expected to deplete in the coming decades. Decisions must be made for the transition towards a world where energy is derived from renewable sources, thereby reducing carbon dioxide emissions.

Various approaches can be employed to address these challenges, including waste valorization, renewable energy production and enhancing the efficiency of existing processes to optimize energy utilization and minimize waste.

Carbon dioxide and hydrogen play pivotal roles in the potential solutions to these issues. Carbon dioxide is a primary byproduct of combustion processes, responsible for global warming, while hydrogen serves as an efficient and clean energy source obtainable from renewable sources like solar or wind power. This article focuses on the valorization of carbon dioxide in conjunction with hydrogen to produce methanol, a high-value precursor used in the synthesis of various products and fuels [1].

This process has been well-established for over a century, utilizing conventional catalysts such as Cu/ZnO/Al₂O₃ [2-4]. However, these catalysts encounter challenges under reaction conditions. As the reaction proceeds over time, the agglomeration of Cu nanoparticles intensifies, leading to their separation from ZnO. This phenomenon results in a reduction of the Cu/ZnO_x interfaces, consequently causing a decline in catalytic activity [5]. Therefore, it becomes imperative to prevent the disappearance of Cu/ZnO_x interfaces to avert the loss of catalytic activity.

To address this issue, strong metal-support interactions (SMSIs) have been employed to stabilize Cu nanoparticles. Notably, the use of zirconia as a catalyst has demonstrated an exceptionally strong interaction with Cu nanoparticles, enhancing both their stability and dispersion [6]. Additionally, mesoporous zeolites have been utilized to confine Cu, effectively preventing agglomerations [7].

In this context, Metal-Organic Frameworks (MOFs), characterized by regular pores and cavities facilitating the encapsulation of Nanoparticles (NPs), offer a promising approach. By combining the effects of Strong Metal-Support Interactions (SMSIs) and the use of mesoporous zeolites, MOFs can effectively prevent the agglomeration of Cu

nanoparticles over time. This synergistic strategy aims to maintain the stability of Cu nanoparticles and mitigate the decrease in catalytic activity, ultimately achieving a high selectivity in the hydrogenation of carbon dioxide [8].

In this study, six catalysts, namely CuZnO, CuZnOAl₂O₃, CuZnOCeO₃, CuZnOTiO₃, CuZnOAl₂O₃CeO₂, and CuZnOCeO₂Al₂O₃, were synthesized for use in the hydrogenation of carbon dioxide. The experiments were conducted under mild conditions of pressure and temperature when compared to traditional catalysts. Subsequently, the four catalysts demonstrating the best results in terms of Space-Time Yield (STY) and selectivity underwent a secondary synthesis, incorporating a commercial MOF (UIO66) as a support material. These catalysts were tested again under the same aforementioned reaction conditions.

2. Experimental

2.1 Materials

Zinc nitrate hexahydrate, aluminum nitrate nonahydrate, copper nitrate trihydrate, cerium nitrate hexahydrate, and sodium carbonate were employed as reactants in the synthesis of the catalysts. These chemicals were procured from Sigma-Aldrich (Barcelona) with a purity exceeding 98%.

For the synthesis of UIO66, zirconium chloride (IV), terephthalic acid, chlorohydric acid (37%), and N, N-dimethylformamide were utilized. These reagents were also sourced from Sigma Aldrich (Barcelona).

The gas mixture consisting of 25% carbon dioxide and 75% hydrogen, employed in the catalytic tests, was obtained from Carbueros Metalicos (Barcelona).

2.2 Synthesis of CuZn/Al₂O₃/CeO₂/TiO₂/CeO₂TiO₂/Al₂O₃CeO₂ nanoparticles

In the synthesis of the six catalysts, the procedure closely follows the methodology outlined in reference [7]. 2.416 g of copper nitrate trihydrate and 1.487 g of zinc nitrate hexahydrate were accurately weighed and dissolved in 200 mL of Milli-Q (MQ) water. For each catalyst, the precise amounts of the respective compounds are detailed in Table 1.

Table 1: Amount of reactives used for the synthesis of **a** CuZnO **b** CuZnOAl₂O₃ **c** CuZnOCeO₂ **d** CuZnTiO₂ **e** CuZnOCeO₂TiO₂ **f** CuZnOCeO₂Al₂O₃.

| | a | b | c | d | e | f |
|---|----------|----------|----------|----------|----------|----------|
| Cu(NO₃)₂ (g) | 2.416 | 2.416 | 2.416 | 2.416 | 2.416 | 2.416 |
| Zn(NO₃)₂ (g) | 1.487 | 1.487 | 1.487 | 1.487 | 1.487 | 1.487 |
| Ce(NO₃)₂ (g) | - | - | 0.723 | - | 0.723 | 0.723 |
| Al(NO₃)₂ (g) | - | 0.625 | - | - | - | 0.625 |
| TiO₂ (g) | - | - | - | 0.133 | 0.133 | - |

Following dissolution with a magnetic stirrer, the solution was transferred to a 500 mL Scharlau Minireactor HME -R/500. Subsequently, the pH was adjusted to 8 using a 0.25M sodium carbonate solution. Once the correct pH was attained, the mixture was agitated for 2 hours at 120 rpm and 60°C. Following this, the solution underwent centrifugation three times for 5 minutes at 7000 rpm, followed by washing with Milli-Q (MQ) water. The obtained nanoparticles were then placed in an oven at 105°C overnight and subsequently calcinated using a muffle for 3 hours at 250°C. In the case of nanoparticles containing titanium, titanium oxide was initially dissolved in 100 mL of MQ water and subjected to ultrasonication for 90 minutes. This entire procedure was repeated for all catalysts without UIO66.

2.3 Synthesis of UIO66 MOF

Initially, 250 mg of zirconium chloride and 246 mg of terephthalic acid were weighed and dissolved in 30 ml of N, N-dimethylformamide, along with 2 ml of 37% chlorohydric acid. The solution was then introduced into an ultrasonic bath for 90 minutes. Subsequently, the mixture was transferred to a flask and subjected to magnetic agitation at 80°C for 24 hours, allowing for the observation of an increase in turbidity.

Upon completion of this reaction, the solution underwent centrifugation three times at 7000 rpm for 5 minutes and was cleaned using a mixture of methanol and DMF (dimethylformamide). The resulting solid material was then placed in an oven at 70°C overnight. Finally, the material underwent calcination for 3 hours at 250 °C.

2.4 Synthesis of CuZnO@UIO66, CuZnOAl₂O₃@UIO66 and CuZnOCeO₂@UIO66 catalysts

For the synthesis of the catalyst with UIO66 incorporation, the procedure is as follows: 1.208 g of copper nitrate trihydrate and 0.743 g of zinc nitrate hexahydrate are dissolved in 100 mL of Milli-Q (MQ) water, and the solution is agitated for 30 minutes. Separately, 0.45 g of UIO66 is dissolved in 100 ml of water, and the mixture is magnetically stirred and then subjected to ultrasonication for 90 minutes.

Subsequently, the two solutions are combined, and the pH is adjusted to 8 by adding a 0.25M sodium carbonate solution. The reactor is then agitated for 2 hours and heated to 60°C. The resulting mixture is centrifuged three times at 7000 rpm for 6 minutes and cleaned with MQ water. The solid obtained is placed in an oven at 105 °C overnight and finally calcinated for 3 hours at 250°C. Table 2 provides a detailed list of the quantities of reactants used for all the synthesis steps.

Table 2: Amount of reactive used for the synthesis of a CuZnO@UIO66 b CuZnOAl₂O₃@UIO66 c CuZnOCeO₂@UIO66 d CuZnTiO₂@UIO66 e CuZnOCeO₂TiO₂@UIO66 f CuZnOCeO₂Al₂O₃@UIO66.

| | a | b | c | d | e |
|---|-------|--------|--------|--------|-------|
| Cu(NO₃)₂ (g) | 1.208 | 1.208 | 1.208 | 1.208 | 1.208 |
| Zn(NO₃)₂ (g) | 0.743 | 0.743 | 0.743 | 0.743 | - |
| Ce(NO₃)₂ (g) | - | - | 0.3615 | 0.3615 | - |
| Al(NO₃)₂ (g) | - | 0.3125 | - | 0.3125 | - |
| TiO₂ (g) | 0.45 | 0.45 | 0.45 | 0.45 | 0.45 |

2.5 Catalytic tests

Catalytic tests involve using a stainless-steel reactor with dimensions of 8.9 cm in length and 5.25 mm in diameter, resulting in a total volume of 1.92 cm³. Weighing 10 mg of the catalyst, it is packed in the middle of the reactor between two layers of glass wool that act as a support for the catalyst.

The reactor, acting as an oven, is placed inside a gas chromatograph (5890 series II) to achieve the desired temperature of 250 °C. The temperature is increased at a rate of

5°C/min, and the pressure is set to 11.5 bar. The gas mixture introduced into the reactor comprises 25% carbon dioxide and 75% hydrogen, with a flow rate of 11 mL/min.

The reaction time is set at 1 hour, the reason is that it's a typical time set in experiments of other papers about this reaction is from 1 to 3 hours, in this case is carried out for one hour to have time to finish all the tests. After this period, the outlet gas is collected in a Flex Foil PLUS Sample Bag, which has been previously purged with nitrogen.

Methanol samples were analyzed on a gas chromatograph (Shimadzu GC-2010) with a flame ionization detector (FID) and helium as the carrier gas. The software used was Chromeleon to determine the concentrations of chemical compounds, with the inlet temperature of 260 °C and the flow of 50 mL/min, and the detector temperature was 280 °C.

An Agilent 7890B GC System chromatograph was employed to measure carbon monoxide and carbon dioxide and methane, using a thermal conductivity detector (TCD), and helium as the carrier gas with an inlet temperature of 120 °C, an inlet flow of 20 mL/min, and a detector temperature of 150 °C. The software employed was Agilent OpenLAB CDS ChemStation (Version A.01.04).

To study the catalytic activity the space time yield and selectivity were calculated. For selectivity only carbon monoxide has been considered as by product formed. Equations 1 and 2 shows how the STY and selectivity were calculated:

$$CH_3OH\ STY\ \left(\frac{mg}{g_{cat} * h}\right) = \frac{Mass\ of\ methanol\ (mg)}{Mass\ of\ catalyst\ (g) * Hour} \quad (1)$$

$$CH_3OH\ Selectivity\ (\%) = \frac{Area\ methanol}{Area\ methanol + Area\ carbon\ monoxide} \quad (2)$$

The areas that appear in equation 2, are the ones obtained from the chromatographer analysis.

3. Results

3.1 Catalytic performance

In the analysis of the catalytic performance of various catalysts, two pivotal factors will be scrutinized: Space Time Yield (STY) and selectivity. STY serves as a crucial metric to evaluate the efficiency of the reaction, quantifying the methanol production rate per gram

of catalyst. Selectivity, on the other hand, is a vital parameter indicating the generation of by-products in the reactions, beyond methanol. This bears significance for downstream processes, influencing the ease of subsequent procedures within the facility.

The first results are in order of relevance like the STY that can be seen in Fig 1.

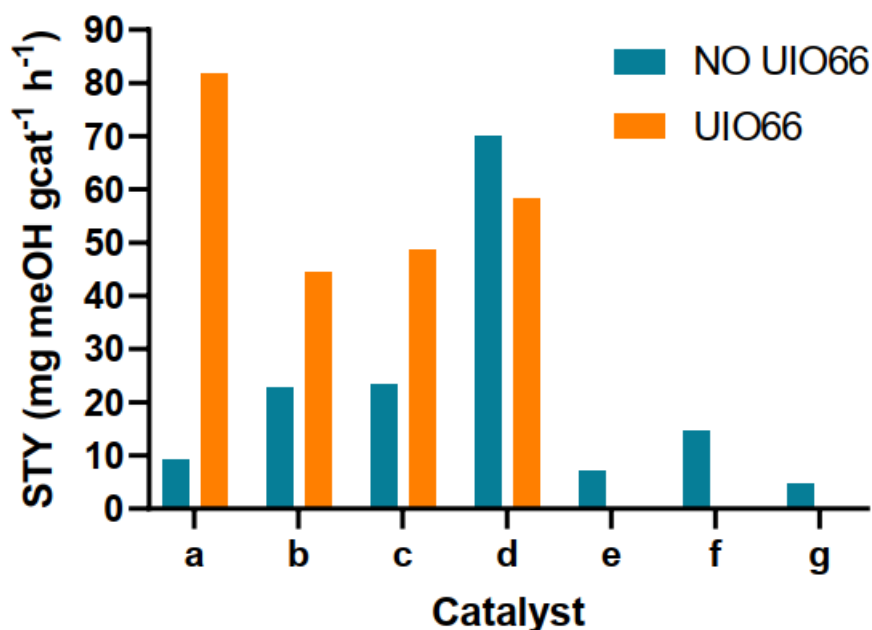


Fig 1: STY results of the catalyst samples of **a** CuZnO **b** CuZnOAl₂O₃ **c** CuZnOCeO₂ **d** CuZnOCeO₂Al₂O₃ **e** UIO66 **f** CuZnOTiO₂ and **g** CuZnOCeO₂TiO₂, at 250°C, 11.5 bar and 11mL min⁻¹.

In Figure 1, the STY for the different catalysts is represented, first without using UIO66 as a support, and then for the four catalysts that were combined with UIO66. As can be seen, the blue lines represent the catalysts without MOF. The ones that obtained the best results are in the following order: CuZnOAl₂O₃CeO₂ > CuZnOCeO₂ > CuZnOCeO₂ >

$\text{CuZnOTiO}_2 > \text{CuZnO} > \text{CuZnOCeO}_2\text{TiO}_2$ In the case of the selectivity results that are shown in Fig 2 are quite different compared with the STY:

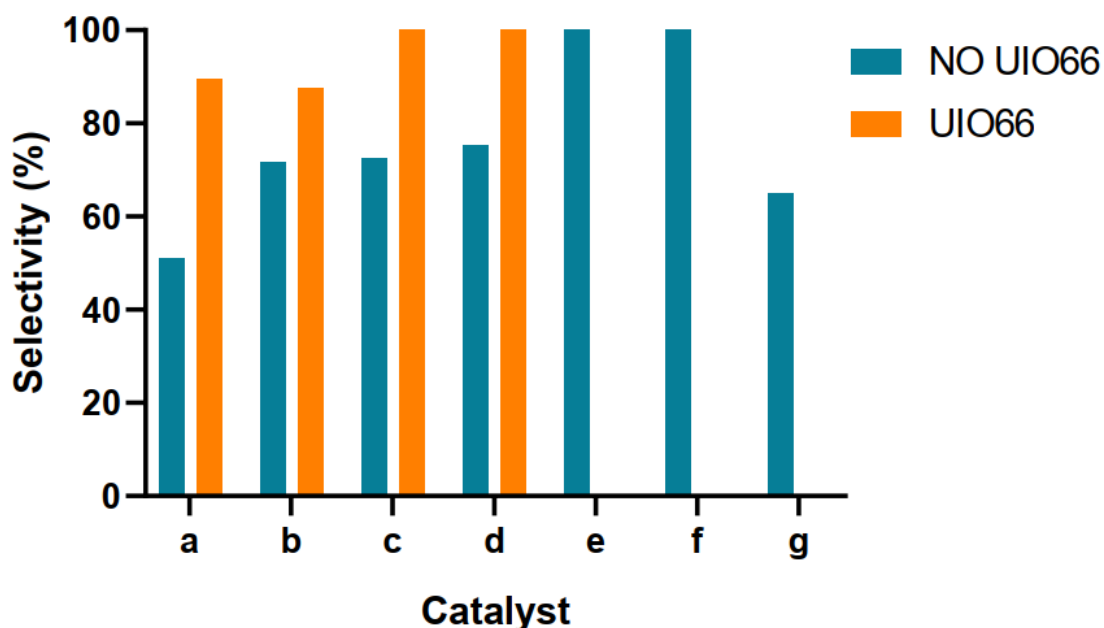


Fig 2: Selectivity results of the catalyst samples of **a** CuZnO **b** CuZnOAl₂O₃ **c** CuZnOCeO₂ **d** CuZnOCeO₂Al₂O₃ **e** UIO66 **f** CuZnOTiO₂ and **g** CuZnOCeO₂TiO₂, at 250°C, 11.5 bar and 11 mL min⁻¹.

In this case, the catalyst that exhibited the best selectivity is CuZnOTiO₂. However, despite this fact, this catalyst will not be selected for combination with MOF, as the STY obtained is too low, around 15 mg g⁻¹ cat h⁻¹. Considering this, the ones that demonstrated the best performance in terms of selectivity follow the next order: CuZnOCeO₂Al₂O₃ > CuZnOCeO₂ > CuZnOAl₂O₃ > CuZnO. Based on these results, the four catalysts selected to be combined with UIO66 are CuZnOCeO₂Al₂O₃, CuZnOCeO₂, CuZnOAl₂O₃ and CuZnO.

Focusing now on the results of the supported catalysts, represented by the orange lines in Figure 1 and 2, the use of MOF as a support yields very positive results in almost all cases. For example, CuZnO@UIO66 obtained eight times the STY of the same catalyst without MOF, and the selectivity was also close to 90%, instead of the initial 50%.

In the case of the other materials, the results are also good but not as significant as in the case of CuZnO@UIO66. The catalysts CuZnOAl₂O₃@UIO66 and CuZnOCeO₂@UIO66 showed a twofold increase in STY compared to the original ones, reaching values of 43 and 50 mg g⁻¹ cat h⁻¹ respectively. In terms of selectivity, these two catalysts also

exhibited an increase of 15% in the case of CuZnOAl₂O₃@UIO66 and 30% for CuZnOCeO₂@UIO66, approaching a selectivity of 100%.

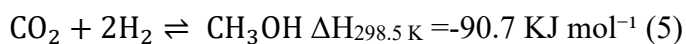
The last catalyst to mention is CuZnOAl₂O₃CeO₂@UIO66, which is the only material that, after being synthesized with the MOF and tested, exhibited worse results in terms of STY compared to the catalyst without UIO66.

4. Discussion

Examining the acquired results, particularly focusing on the initial round of experiments concerning the catalyst without MOF support, it is evident that the incorporation of various materials, particularly CeO₂ and Al₂O₃, leads to an increase in both STY and selectivity.

In the instance of CuZnOCeO₂, the STY is 23 mg g⁻¹ cat h⁻¹ compared to 9 mg g⁻¹ cat h⁻¹ in the case of CuZnO, with a concurrent 20% increase in selectivity. This enhancement is attributed to the hydrophobic nature of CeO₂, which facilitates copper dispersion and surface basicity [14]. Additionally, the facile transition from Ce³⁺ to Ce⁴⁺ generates numerous oxygen vacancies on the cerium surface, promoting the adsorption and conversion of carbon dioxide [15].

Contrastingly, CuZnOAl₂O₃, the typical catalyst employed in the industry for this process, exhibits an STY of 20 mg g⁻¹ cat h⁻¹ and a selectivity near 70%, yielding inferior results compared to the cerium catalyst. This discrepancy can be attributed to the hydrophilic nature of Al₂O₃ in contrast to CeO₂. Moreover, one of the reactions in this process generates water, as can be observed in reaction (4):



The presence of water promotes the aggregation of copper producing a deactivation of the catalyst, and the last case the loss of activity.

Examining Figure 1, it is evident that CuZnOAl₂O₃CeO₂ stands out as the catalyst presenting the most favorable results. This catalyst harnesses the advantageous properties of Al₂O₃, such as thermal stability, surface area augmentation, and enhanced dispersion

of Cu and Zn. The combination of these characteristics with the properties imparted by the addition of CeO₂ yields highly promising outcomes in terms of both Space Time Yield (STY) and selectivity.

In light of the results from the initial six syntheses, four catalysts were subjected to a subsequent round of synthesis, incorporating the molecular-organic framework UIO66 as a support. The outcomes for these catalysts are depicted in the orange columns in Figures 1 and 2.

Upon initial assessment, the results of the materials combined with UIO66 exhibit generally positive trends. In three instances, the Space Time Yield (STY) increases for the materials supported by the MOF. Notably, the most notable improvement in STY is observed in CuZnO@UIO66, reaching 80 mg g⁻¹cat h⁻¹. This is a significant observation, especially considering that the catalyst without MOF performs worse than CuZnOCeO₂, CuZnOAl₂O₃, and CuZnOAl₂O₃CeO₂. However, when UIO66 was introduced, CuZnO surpasses the others in terms of STY. This phenomenon may be attributed to interactions between the MOF and the added materials such as CeO₂ and Al₂O₃, which could either decrease the catalyst's activity or hinder the adsorption of carbon dioxide. In the cases of CuZnOCeO₂@UIO66 and CuZnOAl₂O₃@UIO66, the results with the addition of MOF show substantial improvement, as evident in Figures 3 and 4. This underscores the MOF's efficacy as an excellent material that enhances the catalyst's surface area, a essential factor for optimal performance in reactions. Additionally, the MOF facilitates the dispersion of nanoparticles, preventing agglomeration and ensuring more active sites remain available for interaction with reactants [8,10]. Notably, the achievement of 100% selectivity in the case of CuZnOCeO₂@UIO66 is particularly noteworthy, as it simplifies downstream processes by minimizing the production of by-products.

In the context of methanol synthesis through carbon dioxide hydrogenation, the interaction between metals and MOFs has proven to be a highly effective active site [8, 10]. The encapsulation of nanoparticles between the bonds of Cu-Zr, established due to the presence of MOF, plays a crucial role in carbon dioxide absorption and activation [11]. Comparing the results with different types of catalysts, CuZnOCeO₂, with and without UIO66, outperforms the commercial catalyst CuZnOAl₂O₃ in terms of both selectivity and STY. This behavior can be attributed to the fact that Al₂O₃ is a

hydrophobic molecule, leading to a decrease in activity [12], particularly as the hydrogenation reaction generates water, as seen in reactions (3) and (4).

5. Further works

Due to the promising results that has been obtained in the catalytic tests of $\text{CuZnOCeO}_2@\text{UIO66}$, in terms of average between the STY and the selectivity, and the fact that is a novel material, a continuation in the evaluation in other terms of the catalytic performance can be an effective way for futures investigations.

Is for this reason that here will be proposed different test and characterization methods to do a maximum accurate evaluation of the catalyst, that due to the lack of time haven't been done in this paper.

The suggested procedure will follow the following steps.

- Replicate the catalyst synthesis but varying the proportion of the elements Cu/Zn/Ce.
- Perform a characterization of the catalyst with a x ray diffraction (XRD), BET analysis, SEM (scanning electron microscopy), TEM (transmission electron microscopy) and EDS (energy dispersion spectroscopy).
- Carry out the catalytic test and determine which of the three samples with the different elements proportion has the better results.
- Perform the catalytic test at different pressures and temperatures to see find the best reaction conditions.
- Analyze the catalyst stability to determine the variation of the catalytic activity through the time.
- Change the reactor configuration, in this case, distribute the 10 mg of catalyst in two layers in the reactor.

6. Conclusions

Six catalysts, CuZnO, CuZnOAl₂O₃, CuZnOCeO₂, CuZnOTiO₂, CuZnOAl₂O₃CeO₂, and CuZnOCeO₂Al₂O₃, were synthesized and assessed for methanol production and selectivity. Subsequently, the top-performing four catalysts were selected for combination with a metal-organic framework, UIO66. The resulting catalysts CuZnO@UIO66, CuZnOAl₂O₃@UIO66, CuZnOCeO₂@UIO66, and CuZnOAl₂O₃CeO₂@UIO66 exhibited improvements in both selectivity and Space Time Yield (STY). Among these, particular attention has been given to CuZnOCeO₂@UIO66, a novel material demonstrating exceptional results, with a STY of 50 mg g⁻¹ cat h⁻¹ and a selectivity of 100%.

Considering the promising outcomes of CuZnOCeO₂@UIO66, a series of proposed experiments aims to further evaluate the catalyst through various characterizations. These experiments will explore optimal working conditions to enhance methanol production. This systematic approach seeks to uncover the catalyst's potential and refine its performance for future applications in large scale methanol synthesis.

Author Contributions MCC: Formal analysis, Investigation, Writing-review & Editing. SAV: Conceptualization, Supervision, Writing-review. AS: Writing-review & editing, Supervision, Funding acquisition

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