Tutor/s

Dr. Jordi Guilera Sala
Departament d'Enginyeria Química i Química Analítica

Sra. Cippora Magagnin
Institut de Recerca en Energia de Catalunya (IREC)

Grau de Química

Treball Final de Grau

Evaluation of Advanced Catalysts for Green Methanol Synthesis.
Avaluació de Catalitzadors Avançats per a la Síntesi de Metanol Verd.

Nahuel Ignacio Trigo

January 2026

Universitat de Barcelona

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

Aquesta obra esta subjecta a la llicència de:
Reconeixement–NoComercial-SenseObraDerivada

http://creativecommons.org/licenses/by-nc-nd/3.0/es/

Quiero agradecer a mis tutores que he tenido a lo largo de la investigación: A Cippora Magagnin por la supervisión y apoyo que me ha brindado durante todo el proyecto y a Jordi Guilera, por la confianza y sus consejos para afrontar los avances del desarrollo del trabajo.

También agradecer a los compañeros con los que he compartido estos meses dentro del IREC, especialmente a Amine Lwazzani y a Jesús Díaz Del Campo, quienes su ayuda y consejos han sido de gran utilidad a lo largo de este proyecto. Ha sido un grato gusto haber sido parte de este proyecto.

No dejar de lado a mis amigos y quienes se han tomado el tiempo en escucharme. Eva, Lorena, Estel, por esos momentos en los que conversar entre nosotros funcionaba como apoyo mutuo para seguir adelante.

Por último, agradecer a mi familia, que sin el apoyo de ellos habría sido imposible estar donde estoy aquí. Han sido un pilar fundamental para mí desde que tengo uso de razón.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

The synthesis and performance assessment of $Cu/ZnO/Al_2O_3$ (CZA) catalysts for green methanol synthesis is closely aligned with several United Nations Sustainable Development Goals (SDGs), particularly those related to clean energy, industrial innovation, and climate action.

By exploring strategies to reduce copper oxide content through conventional wet impregnation while simultaneously minimizing and precisely controlling zinc oxide loading via Atomic Layer Deposition (ALD), this research addresses key challenges associated with the efficient and sustainable production of methanol from renewable hydrogen and captured carbon dioxide—an essential pathway for future low-carbon energy systems. Based on this objective, the related SDGs are:

SDG 7: Green methanol is a versatile energy carrier and chemical feedstock. Its liquid nature, compatibility with existing infrastructure, and potential for carbon recycling make it a promising alternative to fossil-derived fuels and chemicals. Improving the efficiency and selectivity of green methanol synthesis using optimized CZA catalysts aims to ensure access to affordable, reliable, sustainable, and modern energy.

SDG 9: the combined use of wet impregnation and ALD represents a complementary synthesis strategy which promotes resilient infrastructure, sustainable industrialization, and technological innovation. Wet impregnation offers a scalable and industrially established route for tailoring copper content, while ALD provides atomic-level precision in zinc oxide deposition, enabling fine control over promoter distribution, metal–support interactions, and material efficiency. This hybrid approach allows for more effective utilization of active copper sites while reducing excess metal usage and associated material waste.

SDG 13: From a climate perspective, this research contributes to greenhouse gas mitigation by supporting carbon dioxide utilization in the production of value-added fuels. The reduction of both Cu^0 and ZnO contents —achieved through distinct yet complementary synthesis methods—enhances resource efficiency while maintaining catalyst performance, thereby lowering the environmental footprint associated with catalyst production and green methanol synthesis processes.

CONTENTS

1. SUMMARY

Methanol is of significant interest for integrated hydrogen production systems, both for transportation fuels and industrial uses, due to the advantageous properties of methanol as a hydrogen carrier. On this context, green methanol has emerged as a promising liquid fuel capable of substantially reducing carbon emissions and supporting the transition of the transport sector toward carbon neutrality. While conventional $Cu/ZnO/Al_2O_3$ (CZA) catalysts have been widely employed in methanol production, recent advances such as Atomic Layer Deposition (ALD) offers innovative approaches to catalyst synthesis. Evaluating this fabrication method can yield valuable insights into enhancing catalytic performance and sustainability.

This study explores the synthesis and performance of $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis, with a particular focus on minimizing CuO content and studying the effects of the addition of ZnO, assessing ALD as an alternative to traditional preparation techniques. The main objective of this project is to review the best alternative of CuO precursor to synthetize the catalyst using the wet impregnation method, and once determined, compare and assess the catalytic activity of methanol synthesis catalysts prepared via ALD and conventional impregnation method. Through laboratory-scale experiments, the study aims to identify the most effective synthesis method in terms of activity, selectivity, and long-term stability.

Catalysts with a varying CuO content were prepared using wet impregnation and those catalysts containing ZnO were deposited using ALD methods. Samples were studied by common analytical techniques. The catalytic activity of catalysts was evaluated in methanol synthesis reactions conducted at temperatures between 200-300ºC.

This research has determined that copper nitrate is the best option as a CuO precursor for synthesizing the catalyst using the wet impregnation method. Furthermore, it demonstrated the importance of the presence of ZnO in the catalyst, resulting in better methanol productivity compared to catalysts without ZnO. Finally, it was determined that catalysts impregnated with 10% wt of Cu^0 performed better than the catalysts impregnated with 20% and 30% wt of Cu^0, obtaining a methanol production of 26.5 mmol g^{-1} h^{-1} and a carbon conversion of 10.25%.

Keywords: ALD, CZA, wet impregnation.

2. RESUMEN

El metanol es de gran interés para los sistemas integrados de producción de hidrógeno, tanto para combustibles de transporte como para usos industriales, debido a las propiedades ventajosas del metanol como portador de hidrógeno. En este contexto, el metanol verde ha surgido como un combustible líquido prometedor, capaz de reducir de forma sustancial las emisiones de carbono y de apoyar la transición del sector del transporte hacia la neutralidad de carbono. Aunque los catalizadores convencionales de $Cu/ZnO/Al_2O_3$ (CZA) han sido ampliamente empleados en la producción de metanol, avances recientes como la Deposición de Capas Atómicas (Atomic Layer Deposition, ALD) ofrecen enfoques innovadores para la síntesis de catalizadores. La evaluación de este método de fabricación puede aportar información valiosa para mejorar el rendimiento catalítico y la sostenibilidad.

Este estudio explora la síntesis y el rendimiento de catalizadores de $Cu/ZnO/Al_2O_3$ para la síntesis de metanol, con un énfasis particular en la minimización del contenido de CuO y en el estudio de los efectos de la adición de ZnO, evaluando la ALD como una alternativa a las técnicas de preparación tradicionales. El objetivo principal de este proyecto es revisar la mejor alternativa de precursor de CuO para sintetizar el catalizador mediante el método de impregnación húmeda y, una vez determinado, comparar y evaluar la actividad catalítica de los catalizadores de síntesis de metanol preparados mediante ALD y mediante el método convencional de impregnación. A través de experimentos a escala de laboratorio, el estudio pretende identificar el método de síntesis más eficaz en términos de actividad, selectividad y estabilidad a largo plazo.

Se prepararon catalizadores con un contenido variable de CuO mediante impregnación húmeda, y aquellos catalizadores que contenían ZnO se depositaron utilizando métodos de ALD. Las muestras se estudiaron mediante técnicas analíticas comunes. La actividad catalítica de los catalizadores se evaluó en reacciones de síntesis de metanol realizadas a temperaturas comprendidas entre 200 y 300 ºC.

Esta investigación ha determinado que el nitrato de cobre es la mejor opción como precursor de CuO para la síntesis del catalizador mediante el método de impregnación húmeda. Asimismo, se demostró la importancia de la presencia de ZnO en el catalizador, lo que dio lugar a una mayor productividad de metanol en comparación con catalizadores sin ZnO. Finalmente, se determinó que los catalizadores impregnados con un 10 % en peso de CuO presentaron un mejor desempeño que aquellos impregnados con un 20 % y un 30 % en peso de CuO, obteniéndose una producción de metanol de 26,5 $mmol \cdot g^{-1} \cdot h^{-1}$ y una conversión de carbono del 10,25 %.

Palabras clave: ALD, CZA, Impregnación húmeda.

3. INTRODUCTION

3.1. METHANOL AS SUSTAINABLE FUEL

Methanol has attracted increasing attention as a sustainable energy carrier due to its versatility, high energy density in liquid form, and compatibility with existing infrastructure. As a liquid fuel, methanol can be easily stored, transported, and distributed, overcoming several limitations associated with gaseous hydrogen[1]. Moreover, methanol can act as a hydrogen carrier, enabling its indirect use in fuel cells and other hydrogen-based energy systems.[1 2]

In the context of climate change mitigation, green methanol, produced from renewable hydrogen and captured carbon dioxide, has emerged as a promising alternative to fossil-based fuels[2]. Its use can significantly reduce greenhouse gas emissions, particularly in hard-to-abate sectors such as maritime transport, aviation, and chemical manufacturing[3]. As a result, methanol synthesis plays a central role in Power-to-Liquid (P2L) strategies aimed at closing the carbon cycle and promoting a circular economy[4].

3.2. FUNDAMENTALS OF METHANOL SYNTHESIS

Industrial methanol synthesis is typically carried out through the catalytic hydrogenation of carbon monoxide and carbon dioxide with a stochiometric ratio of syngas of 2.1-2.2 according to the following reactions[5]:

$CO + 2H_2 \rightleftharpoons CH_3OH$ ΔH^o= -90.6 kJ mol^{-1} Eq[1]

$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ ΔH^o= -49.6 kJ mol^{-1} Eq[2]

These reactions are exothermic and are commonly performed at moderate temperatures (200–300 °C) and high pressures (30–100 bar) in the presence of heterogeneous catalysts[6]. Under reaction conditions, side reactions such as the water–gas shift (WGS) and reverse water–gas shift (rWGS) may also happen, influencing product distribution and catalyst performance.[7]

$CO + H_2O \rightleftharpoons CO_2 + H_2$ ΔH^o= -41.3 kJ mol^{-1} Eq[4]

$CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH^o= 41.3 kJ mol^{-1} Eq[3]

For green methanol production, the use of CO_2-rich feeds combined with renewable hydrogen has gained relevance. In this context, catalyst efficiency, selectivity toward methanol, and long-term stability become critical parameters, especially when operating under milder conditions to reduce energy consumption and improve process sustainability[8].

3.3. CATALYSTS FOR METHANOL SYNTHESIS

Conventional and commercial methanol synthesis catalysts are typically based on Cu/ZnO/Al_2O_3 (CZA) systems with an atomic ratio Cu:Zn:Al equal to 6:3:1, synthetized by coprecipitation at controlled pH using a mixture of all metal precursors required, which have been extensively studied and industrially implemented due to their high activity and selectivity[9 10]. In these catalysts, copper is generally considered the primary active phase for methanol formation, while ZnO and Al_2O_3 act as structural and electronic supports.

Copper-based species play a central role in methanol synthesis catalysts. Under reaction conditions, CuO is reduced to metallic Cu^0, which is widely accepted as the active phase responsible for CO and CO_2 hydrogenation. The catalytic performance of copper strongly depends on particle size, dispersion, and reducibility, as well as on its interaction with the surrounding oxide phases.

High copper loadings are commonly employed to ensure sufficient activity; however, excessive Cu content can lead to particle agglomeration and sintering, negatively affecting long-term stability[11]. Therefore, optimizing copper loading and precursor selection is essential to maximize methanol productivity while maintaining catalyst durability[17]. Meanwhile, zinc oxide plays a crucial promotional role in Cu-based methanol synthesis catalysts. Although ZnO is not considered catalytically active on its own, its presence significantly enhances copper performance through strong metal–support interactions. ZnO has been shown to improve copper dispersion, modify electronic properties of Cu sites, and stabilize active copper species during operation.

Furthermore, the Cu–ZnO interface is widely recognized as a key structural feature governing catalytic activity and selectivity. The controlled presence of ZnO can enhance methanol formation rates while suppressing undesired side reactions[7]. Consequently, precise control over ZnO content and distribution is of great importance in catalyst design.

Despite their widespread use, traditional commercial CZA catalysts present several challenges, including sintering of copper particles, loss of active surface area, and gradual deactivation under prolonged operation. These issues are often exacerbated by high metal loadings and insufficient control over metal dispersion and metal–support interactions[11 12].

Consequently, significant research efforts have focused on developing advanced catalyst preparation strategies capable of improving metal dispersion, enhancing catalyst stability, and reducing the overall metal content without compromising catalytic performance[13 13 14 15 16].

3.4. Principles of WI, ALD and Application to Catalysts

3.4.1. Wet Impregnation and Incipient Wetness Impregnation

Wet impregnation (WI) is one of the most widely used methods for the preparation of heterogeneous catalysts due to its simplicity, scalability, and low cost. In this technique, a metal precursor solution with excess of solvent is contacted with a porous support, followed by solvent evaporation, drying, and calcination to obtain the desired oxide phase[17].

On the other hand, incipient wetness impregnation (IWI) is a method in catalyst synthesis where a highly concentrated solution of a soluble precursor solution, commonly composed of water and a highly soluble metal salt, precisely fills the pores of a porous support until just saturated, allowing capillary action to distribute the active metal evenly for highly dispersed, efficient catalysts after drying and calcining. It's crucial for creating catalysts with high active site density, preventing agglomeration, and achieving high loading efficiency.

Despite their advantages, WI and IWI often result in limited control over metal dispersion and particle size distribution, particularly at low metal loadings[11 17]. The final catalyst properties are strongly influenced by factors such as precursor chemistry, solvent choice, and calcination conditions. These limitations can lead to heterogeneous metal distribution and reduced reproducibility, motivating the exploration of alternative methods that, in combination with the WI or IWI method, can overcome its shortcomings and reach a good alternative compared to the well-known coprecipitation method.

3.4.2. Atomic Layer Deposition

Atomic Layer Deposition (ALD) is an advanced thin-film deposition technique based on sequential, self-limiting surface reactions, enabling atomic-scale control over the composition, thickness, and dispersion of deposited materials. Due to these characteristics, ALD has emerged as a powerful tool for the rational design of heterogeneous catalysts, particularly in applications where surface properties and metal–support interactions play a critical role.

In a typical ALD process on thin films, as shown in Figure 1, the substrate is alternately exposed to gaseous precursors separated by inert gas purging steps. Each precursor reacts selectively with surface functional groups until saturation is achieved, preventing

uncontrolled growth. As a result, each ALD cycle deposits a well-defined amount of material, allowing precise control over metal loading even at very low concentrations[18].

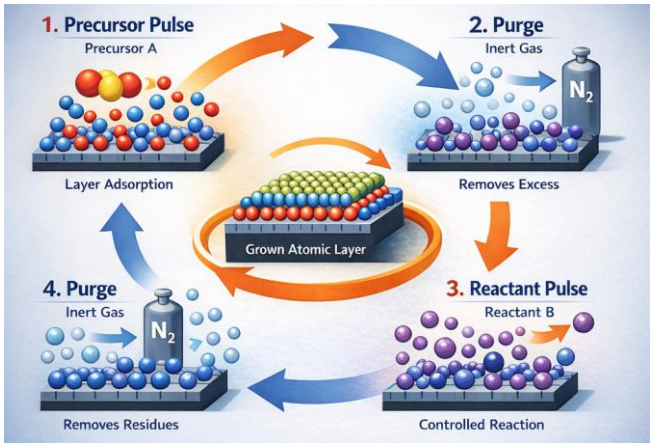

Figure 1: Schematic diagram of a traditional ALD cycle.

In the context of methanol synthesis catalysts, ALD offers significant advantages over conventional preparation methods. Traditional commercial $Cu/ZnO/Al_2O_3$ catalysts rely on relatively high metal loadings to achieve sufficient activity, often leading to particle sintering, loss of dispersion, and catalyst deactivation under reaction conditions[11 12]. ALD enables the deposition of ultrathin ZnO layers or highly dispersed ZnO species onto pre-formed CuO/Al_2O_3 supports, thereby minimizing ZnO content while preserving or enhancing catalytic performance.

One of the key benefits of ALD in Cu-based methanol synthesis catalysts is the controlled modification of the Cu–ZnO interface, which is widely recognized as a critical factor governing catalytic activity and selectivity. The conformal nature of ALD allows ZnO to be uniformly distributed over the catalyst surface and within porous supports, promoting intimate contact between Cu and ZnO phases. This controlled interfacial engineering can enhance copper reducibility, stabilize active Cu^0 sites, and improve resistance to sintering during long-term operation.

Furthermore, ALD facilitates the preparation of model catalytic systems, where the effect of ZnO presence or absence can be systematically studied while maintaining constant Cu loading. This level of control is particularly valuable for fundamental studies aimed at establishing structure–performance relationships in methanol synthesis and related reactions such as the reverse water–gas shift (rWGS).

Despite its advantages, ALD presents certain limitations, including relatively low deposition rates and the requirement for volatile, thermally stable precursors. However, for applications focused on catalyst optimization rather than large-scale production, these limitations are outweighed by the technique's exceptional precision and reproducibility.

In summary, Atomic Layer Deposition represents an innovative and effective approach for the development of advanced $Cu/ZnO/Al_2O_3$ catalysts for green methanol synthesis, enabling reduced metal loadings, enhanced interfacial control, and improved catalytic performance compared to conventional synthesis methods[18 19].

3.5. Background and Scope

This study is part of the COMECOCO2 project, which aims to develop a catalyst for methanol synthesis based on commercial CZA that can optimize the problems associated with hydrogen transport and distribution.

4. OBJECTIVES

The main objective of this study consists of the developing a catalyst for methanol synthesis based on co-precipitation synthesis of commercial $Cu/ZnO/Al_2O_3$, optimizing the metal loading using the classic method of wet impregnation to reduce the amount of CuO and, on other side, use the conformal thin-film deposition technique Atomic Layer Deposition (ALD) to minimize the ZnO amount to use in an innovative P2L system for efficient production of green methanol.

To achieve this objective, catalysts with varying copper loadings were prepared and deposited with ZnO by a fixed ALD procedure. The properties and behavior of the catalysts with and without ZnO will be correlated to study the presence of ZnO.

A series of traditional characterization techniques will be provided to determine the best choice for the CuO precursor and also to determine the best amount of itself in order to improve the methanol synthesis, based on productivity, stability and selectivity.

5. EXPERIMENTAL SECTION

5.1. CATALYST SYNTHESIS

5.1.1. Precursor Synthesis

The following table shows the materials and their respective quantities used for the synthesis explained below.

Precursor	Support	Weight (g)	H_2O Weight (g)	CuO (%Wt)	Method
$Cu(NO_3)_2 \cdot 2.5H_2O$	Al_2O_3	2.035	12.81	10	Wet Impregnation
$Cu(OAc)_2 \cdot H_2O$	Al_2O_3	1.747	50.93	10	Wet Impregnation

Table 1: Reactives used for Copper Precursor Investigation

5g of 0.5mm diameter mesoporous γ-Al_2O_3 Accu-Spheres Saint-Gobain Norpro® were placed into a round bottom flask and then attached to a BUCHI Rotavapor® R-300 rotary evaporator system. The precursor copper solution was placed into a 60 mL bottle and connected to the feeder valve of the rotary evaporator as shown in figure 2. Then, the solution was added dropwise into the support and left to stir for 45 minutes at 75ºC and 800 mbar. Maintaining the same stirring and temperature conditions, the pressure was decreased to 150 mbar until complete solvent evaporation. The resulting pellets were calcined at 350ºC for 4 hours with a 3ºC/min ramp.

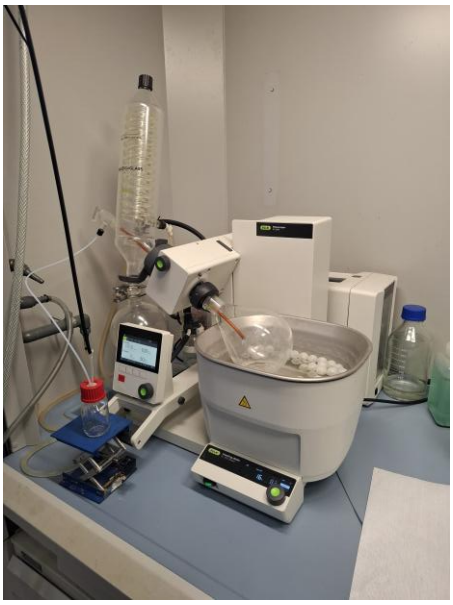

Figure 2: Wet Impregnation Setup

Figure 3: Picosun™ R-150 ALD System

5.1.2. Atomic Layer Deposition Synthesis

ZnO catalysts were synthesized from the different batches of $CuO–Al_2O_3$ catalyst using Atomic Layer Deposition (ALD). For the ALDZnO–(X%)$CuO–Al_2O_3$ catalyst, 0.35 g of $CuO–Al_2O_3$ was weighed. Diethylzinc (DEZ) was used as ZnO precursor and water (H_2O) as the oxidizing agent, using N_2 as the inert gas for purging. The process was conducted at 200 °C for 100 cycles.

Each cycle, as shown in Figure 4, involved a pulse of 10 seconds of low flow (40 sccm) followed by a 0.1 second water pulse and 60 seconds of superficial contact. Once superficial contact was completed, a nitrogen purge (45 seconds, 150 sccm) was performed. The same pulse procedure was repeated, with a pulse of DEZ.

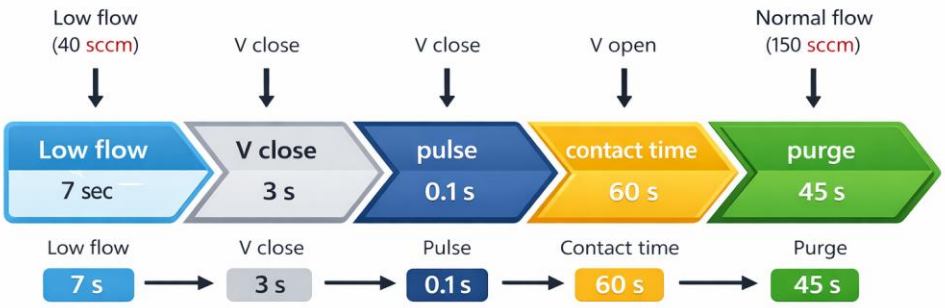

Figure 4: A representative image of the ALD cycle

5.2. CHARACTERIZATION

5.2.1. TGA

To determine the calcination temperature of each precursor, 25mg of $Cu(NO_3)_2$•$2.5H_2O$, $Cu(OAc)_2$•H_2O and CuSO4•$5H_2O$ were analysed in a PerkinElmer Thermogravimetric Analyzer TGA 4000 using a programmed temperature from 40°C to 800°C with a 5°C/min ramp. A 20 ml/min N_2 flow was used to create a controlled atmosphere.

5.2.2. XRD

The determination of the crystalline structure and phase composition of the analysed materials was carried out using X-ray diffraction (XRD). Sample preparation involved grinding into fine powder and then depositing into a zero background XRD sample holder. A few drops of ethanol were added to the powder and dried under ambient conditions to gain better surface distribution. XRD patterns were collected within the 2θ range of 20-80° in a Bruker type XRD D8 Advance A25 diffractometer using a Cu Kα radiation (λ = 1.5406 Å), a voltage of 40 kV, a current of 40 mA and a step size of 0.02°, with 2 seconds of duration at each step. The average crystal sizes of CuO were estimated using the Scherrer's equation at 2θ = 32.5º, 35.5° and 38.7º for (110), (-111) and (111), respectively:

$$D = \frac{K\lambda}{\beta \cos\theta} \; Eq[5]$$

The values of X-ray wavelength and Scherrer constant are λ = 1.5406 Å and K = 0.9.

5.2.3. Brunauer-Emmett-Teller

The specific surface area and pore size distribution of the analysed materials were determined by nitrogen physisorption. Measurements were conducted using a Micromeritics FlowPrep 060 for sample preparation and a Micromeritics TriStar II analyser, both operated with dedicated software that enabled precise temperature control and continuous monitoring of gas volume and system pressure.

Prior to the physisorption measurements, the samples were degassed under a nitrogen flow to remove adsorbed species. The degassing procedure involved an initial heating step at 90 °C for one hour, followed by further heating and a final treatment at 250 °C for five hours to ensure complete removal of volatile components.

After degassing, nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature. Vacuum was applied to the system, and a precisely known volume of nitrogen gas was introduced while continuously monitoring pressure variations. Once the maximum relative pressure was reached, vacuum was reapplied. The resulting isotherms were analysed to determine the BET specific surface area (SA_{BET}), total pore volume, and pore size distribution.

5.2.4. H_2-TPR

The determination of the oxidation states of the current metals in the analysed materials was carried out using Temperature Programmed Reduction (H_2-TPR). These analyses were performed with an Autochem 2890 (Micromeritics) using a 50 NmL/min flow of H_2 (10% H_2 in Ar). With this technique, the temperatures at which the samples are reduced in the presence of hydrogen were measured for the respective synthesized catalysts.

5.2.5. SEM-EDX

The cross section of the commercial CZA and the Cu(X%)ZnO(ALD) catalysts was performed to determine the amount of CuO and ZnO of the catalysts using a Zeiss Gemini Auriga® equipped with energy dispersive X-ray spectroscopy (EDX). To prepare the sample for the measurements, a resin was prepared by mixing Struers® EpoFix Resin and Struers ® EpoFix Hardener in a ratio of 21:3 (7:1). The resin, once mixed, was transferred to a mold previously coated in high vacuum grease with a small amount of pellets from the sample and it was left to harden for 24 hours. The resin piece with the sample was then partially sanded with a polishing machine until the cross-section of the pellets was obtained. Due to the resin is non-conductive, the sample was gold-coated using the Emitech® k575X Peltier cooled sputtering system. Energy dispersive X-ray spectroscopy was carried out.

5.3. Methanol Synthesis Catalytic Tests

5.3.1. Catalytic Reaction

The following table shows the analysed catalysts, including the metal composition and the synthesis method performed.

Sample	Support	ZnO (%Wt)	CuO (%Wt)	Method
Commercial CZA	–	31.6	61.8	Co-Precipitation
Cu 10%	Al_2O_3	–	10	WI
Cu 20%	Al_2O_3	–	20	WI
Cu 30%	Al_2O_3	–	30	WI
Cu(10%)ZnO(ALD)*	CuO-Al_2O_3	<1	10	ALD
Cu(20%)ZnO(ALD)*	CuO-Al_2O_3	<1	20	ALD
Cu(30%)ZnO(ALD)*	CuO-Al_2O_3	<1	30	ALD

Table 2: Composition of the oxides of Catalysts

*Used $Cu(NO_3)_2 \cdot 2.5H_2O$ as a precursor

The catalytic methanol synthesis reactions were performed in a Microactivity Reference PID Eng&Tech fixed-bed reactor, with a total mass flow composed of 66% H2, 5% of N2, 22% of CO and 7% of CO2 in order to achieve a stochiometric ratio of syngas of 2.1-2,2; as described in section 3.2.

Figure 5: Interior of the Microactivity Reference PID Eng&Tech

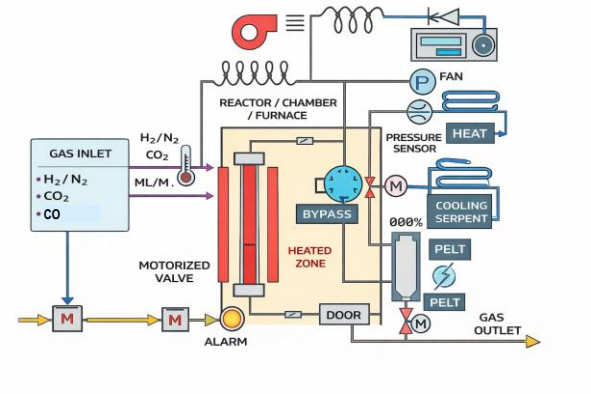

Figure 6: Reactor Scheme

0.3g of catalyst were mixed with 3g of SiC to prevent hot spots and placed as showed in Figure 1. Then, to reduce the CuO to Cu^0, the system was conducted with a mass flow of 90% of N_2 and 10% of H_2 at 1bar, 300ºC for 2 hours, using a 3ºC/min ramp. After that, the reactions were conducted at 38 bar at 300ºC, 250ºC and 200ºC for 4 hours each experiment, using a 1 bar/min ramp to pressurize and a 1ºC/min ramp to increase/decrease the temperature.

The catalysts that yielded the best results were selected and, with the commercial catalyst as a reference, stability tests were performed for each of them.

For these analyses, the same reactor setting, reduction and conditions were performed, but with the difference that this series of experiments were carried only at 250ºC for 120 hours.

5.3.2. Analytics

The resulted gas output was measured with an Agilent Technologies 490 Micro GC300 to determine carbon conversion and methanol productivity.

$$\%C = \frac{mol/minMeOH}{mol/minCO_2 + mol/minCO} \qquad Eq[6]$$

$$MeOH\ productivity\ \left(mol\ g_{catalyst}^{-1}\ h^{-1}\right) = \frac{mol/minMeOH}{g_{catalyst}\ 60min} \qquad Eq[7]$$

In order to determine the methanol selectivity and concentration of methanol of the collected liquid samples for the previous experiments, 1 µl of methanol collected in each analysis was injected into a Shimadzu GC-2010 gas cromatography.

Figure 7: Shimazdu GC-2010

To obtain these results, an external calibration curve of methanol, ethanol, propanol and isopropanol were performed in order to determine the concentration.

The selectivity was calculated with the following equation:

$$S_{MeOH}(\%) = \frac{nMeOH}{nMeOH+nEtOH+nPrOH+niPrOH} \quad Eq\ [8]$$

6. Results and Discussion

6.1. Materials Structural Characterization and Properties

6.1.1. Precursor Synthesis

The TGA of the copper precursors and their respective derivatives are presented in Figure 8 and Figure 9, respectively.

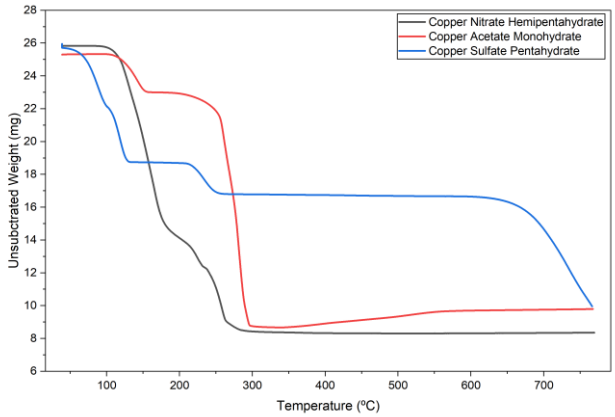

Figure 8 TGA results of the copper precursors

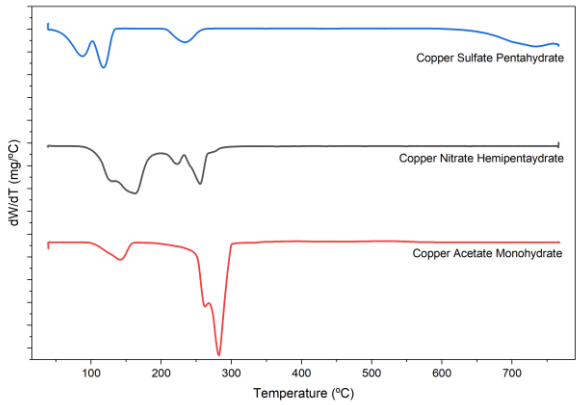

Figure 9: 1st derivative of the TGA results

The results show that for both the $Cu(NO_3)_2$•$2.5H_2O$ and $Cu(OAc)_2$•H_2O, there is no mass loss from approximately 300ºC onwards. However, the same does not occur with the CuSO4•$5H_2O$ sample, where mass loss is also detected above 650ºC, reflecting that the calcination temperature is much higher, making it more prone to generating unwanted structures such as Cu-Al spinel, whose formation can be initiated at 500ºC getting as result a catalyst that is more efficient in rWGS reactions[20].

The XRD of the copper precursors are presented in Figure 10. A measurement was taken before and after each sample was calcined. For CuO monoclinic structure, the most significant peaks at 2θ are 32.5º (-1 1 0), 35.5º (-1 1 1), 38.7º (1 1 1), 48.7º (-2 0 2), 53.5º (0 2 0), 58.3º (2 0 2) and 61.5º (-1 1 3).

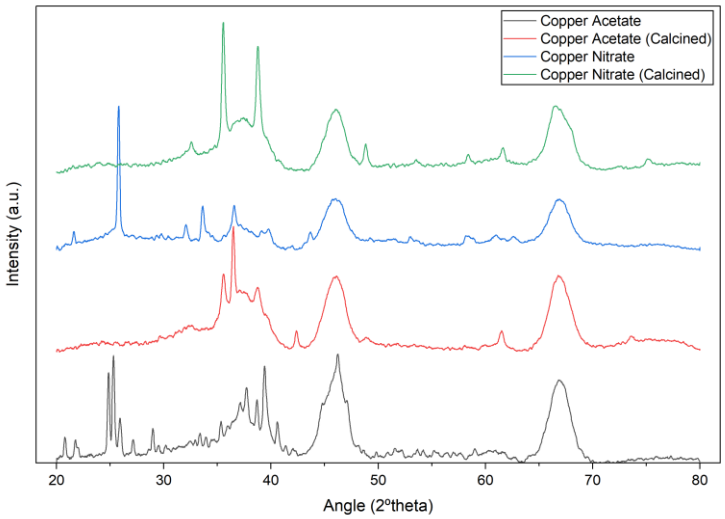

Figure 10: XRD Patterns of Cu Precursors

Estimating crystallite size using the Scherrer equation, with the three main CuO peaks at 32.5º, 35.5º and 38.7º, indicates that CuO derived from copper acetate has crystallite sizes of 9.12 nm, while that obtained from copper nitrate shows crystallites of 15.8 nm. This suggests that acetate promotes greater CuO dispersion after calcination, with a larger interfacial area of CuO-Al_2O_3.

Figure 11 presents the H_2-TPR profiles of copper nitrate hemipentahydrate and copper acetate monohydrate. Clear differences in the thermal response and gas evolution behavior are observed between the two precursors, reflecting their distinct decomposition pathways and thermal stabilities.

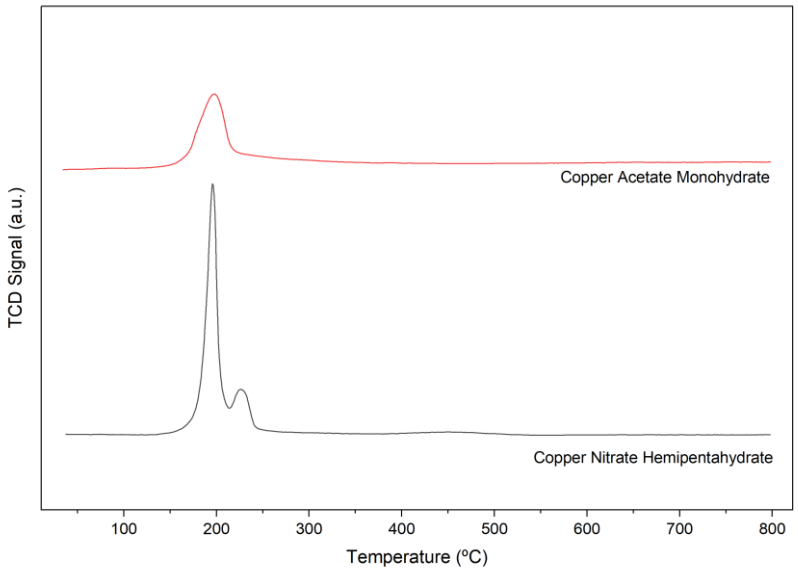

Figure 11: H_2-TPR Profile for Copper Precursors

The profile of copper nitrate hemipentahydrate is dominated by a sharp and intense peak centred at approximately 180–200 °C, accompanied by a weaker secondary feature at slightly higher temperature. The narrow and high-intensity nature of the primary peak indicates a rapid and energetically favourable decomposition process. This behaviour is consistent with the thermal instability of nitrate ligands, which readily decompose to release NO_x and oxygen-containing species, leading to abrupt structural rearrangement and formation of copper oxide phases. The presence of a secondary peak suggests the completion of nitrate decomposition. Beyond 300 °C, no additional features are observed, indicating that the precursor is fully decomposed at relatively low temperature.

In contrast, copper acetate monohydrate exhibits a markedly different response. An only low-intensity peak centred around 200–230 °C is observed. The broadened profile reflects a slower and more progressive decomposition process, characteristic of organic acetate ligands, which undergo stepwise decarboxylation and fragmentation over a wider temperature window. The absence of sharp features suggests a more controlled conversion to copper oxide species. No significant thermal events are detected at higher temperatures, indicating the completion of decomposition within this temperature range.

The comparison between the two precursors highlights the strong influence of ligand chemistry on thermal behaviour. Copper nitrate undergoes rapid decomposition at lower temperatures, resulting in abrupt gas release and fast oxide formation, whereas copper acetate decomposes more gradually and over a broader temperature interval. These differences are expected to have important implications for catalyst preparation, as fast nitrate decomposition may induce localized sintering, while acetate precursors can improve dispersion and controlled nucleation due to their softer decomposition kinetics.

6.1.2. Catalysts Synthesis

The XRD of the catalysts that were used to perform methanol synthesis are represented in Figure 12 and Figure 13. For CuO monoclinic structure, the most significant peaks were mentioned in 6.1.1.

For ZnO hexagonal wurtzite structure, the common diffraction peaks at 2θ are 31.8º (1 0 0), 34.4º (0 0 2), 36.2º (1 0 1), 47.5º (1 0 2), 56.6 (1 1 0), 62.9º (1 0 3) and 66.4º (2 0 0).

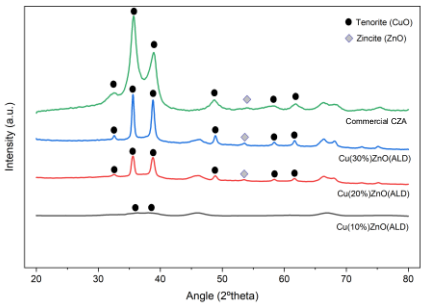

Figure 12: XRD patterns of CZA catalysts with ZnO

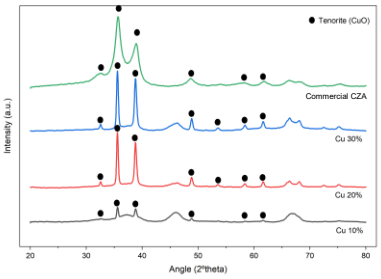

Figure 13: XRD pattens of catalysts without ZnO (except commercial one)

Due to the overlapping peaks between both oxides and the low ZnO content of non-commercial catalysts, no detectable ZnO peaks were found in the Cu(30%)ZnO(ALD), Cu(20%)ZnO(ALD) and Cu(10%)ZnO(ALD). Also, significative diffraction peaks corresponding to γ-Al_2O_3 are at 66.8º (4 4 0)[21]. Therefore, we cannot assume that this peak could belong to ZnO, especially considering this low oxide content.

The crystallite size of CuO in the catalyst was estimated using the Scherrer equation. The crystallite sizes obtained remained in the range between 22.9 and 29.0 nm, except for both catalysts that had 10% of Cu^0. Also, both catalysts follow different trend. Adding ZnO decreased the crystallite size meanwhile in the 20% and 30% of Cu^0 the sizes increased a few nanometres by the addition of ZnO.

The nitrogen adsorption–desorption isotherms of the catalysts are classified as Type IV, representative of mesoporous materials with pore diameters between 2 and 50 nm[22]. The key textural parameters obtained from these measurements, including $_{SA}$BET, pore volume, average pore diameter and crystallite size, are summarized in Table 3.

Sample	$_{SA}$BET (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	Crystallite Size (nm)
Commercial CZA	51.7	0.22	16.0	25.3
Cu 10%	–	–	–	15.8
Cu 20%	–	–	–	25.0
Cu 30%	–	–	–	22.9
Cu(10%)ZnO(ALD)	170.1	0.55	12.7	6.2
Cu(20%)ZnO(ALD)	152.0	0.49	12.6	27.1
Cu(30%)ZnO(ALD)	130.7	0.40	12.0	29.0

Table 3: CZA catalysts crystallographic and surface properties

The nitrogen adsorption–desorption study confirms that all synthesized CZA catalysts possess a mesoporous structure with significantly higher surface area and pore volume than the commercial CZA catalyst. Increasing Cu loading leads to a gradual reduction in textural properties, likely due to pore blockage and metal oxide agglomeration.

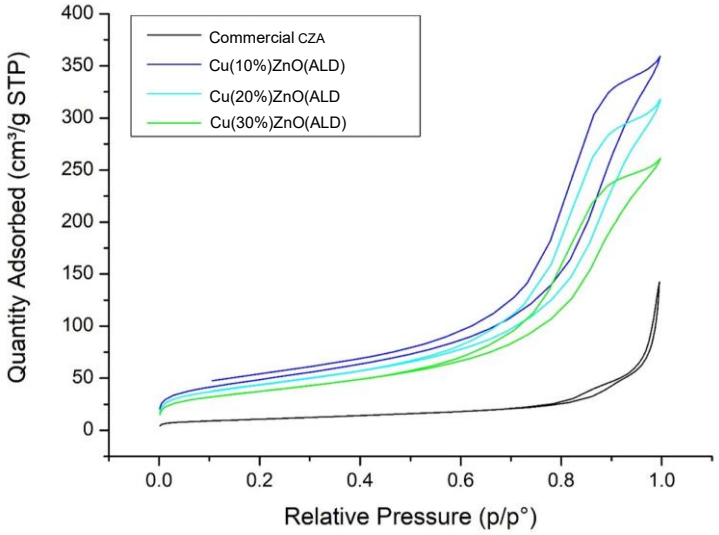

Figure 14: Catalysts BET Isotherms

Overall, the Cu(10%)ZnO(ALD) and Cu(20%)ZnO(ALD) catalysts offer the most favorable balance between **high surface area and preserved mesoporosity**, which is consistent with their improved reducibility observed in H_2-TPR experiments. These results demonstrate that textural properties play a crucial role in determining the structural and catalytic behavior of Cu-based catalysts.

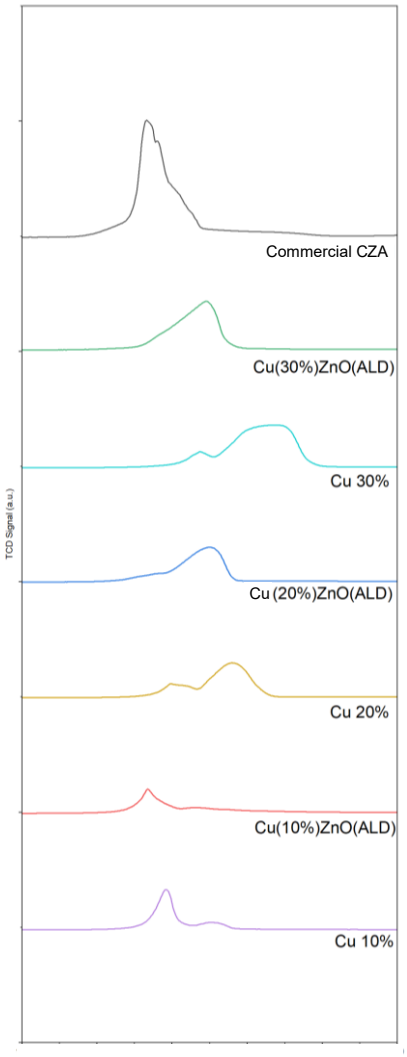

Figure 15: H2-TPR Profiles of Catalysts Analyzed

To analyse the reducibility of all catalysts used, H_2-TPR was performed, with their respective results presented in Figure 11. For that analysis, the peaks were detected in a range of 170-280ºC. The unmodified copper catalysts without ZnO showed a strong dependence of reducibility on Cu^0 loading. At low Cu^0 content (10 wt%), the reduction occurs at relatively low temperatures, indicating the presence of well-dispersed CuO species. However, as the Cu loading increases to 20 and 30 wt%, the reduction peaks broaden and shift toward higher temperatures. This behavior suggests progressive CuO particle growth and the formation of bulk-like CuO species, which are more difficult to reduce. These results highlight the limitations of Cu-only systems, where increasing metal loading negatively affects dispersion and reducibility.

In contrast, the **Cu(x%)ZnO(ALD)** catalysts exhibit markedly improved reduction behavior at all Cu loadings. Compared to their unmodified counterparts, the reduction peaks are systematically narrower and shifted to lower temperatures. This indicates a more homogeneous distribution of CuO species and enhanced reducibility. The effect of ZnO introduced by ALD is particularly significant at intermediate and high Cu loadings, where it effectively suppresses the high-temperature reduction features associated with poorly dispersed or bulk CuO. These observations demonstrate that ZnO deposited by ALD plays a key role in stabilizing finely dispersed CuO species and assessing favorable Cu–ZnO interactions.

When benchmarked against the commercial CZA catalyst, the Cu(x%)ZnO(ALD) samples show notable similarities. The **Cu(10%)ZnO(ALD)** and **Cu(20%)ZnO(ALD)** catalysts exhibit reduction temperatures and peak shapes approaching those of the commercial reference, indicating that Cu(x%)ZnO(ALD) can partially replicate the beneficial structural and electronic effects of conventional ZnO and Al_2O_3 promoters. The results demonstrate that ZnO, when precisely deposited by ALD, is sufficient to significantly improve Cu reducibility.

Overall, the comparative analysis confirms that ZnO ALD modification bridges the performance gap between simple Cu catalysts and industrial CZA formulations, particularly at low Cu loading.

On the other hand, the results show that performing the reduction reaction at 300ºC will guarantee complete reduction of CuO species.

The cross section was performed to determine the amount of CuO and ZnO of Cu(10%)ZnO(ALD), Cu(20%)ZnO(ALD) and Cu(30%)ZnO(ALD). It can be observed, specifically in catalyst **Cu(30%)ZnO(ALD)**, that the CuO present agglomerates on the surface, coinciding with the studies presented in the BET isotherms.

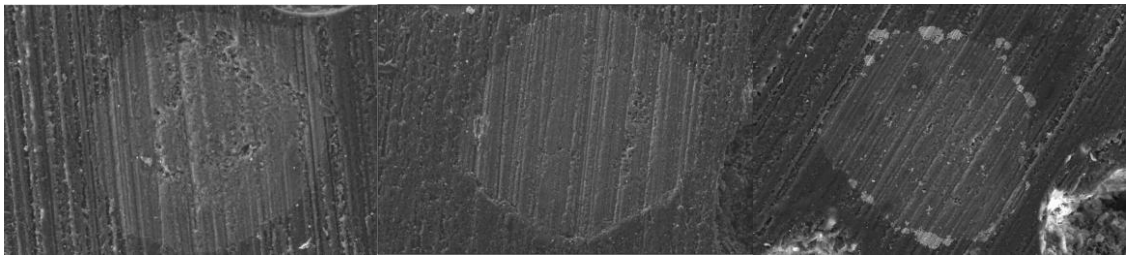

Figure 16: From left to right: EDX cross section of Cu(10%)ZnO(ALD), Cu(20%)ZnO(ALD) and Cu(30%)ZnO(ALD) in a 200µm scale.

The mapping results showed the composition of each catalyst represented in table 4:

Sample	Cu (%wt.)	Zn (%wt.)	Al (%wt.)
Commercial	62.8	32	5.2
Cu(10%)ZnO(ALD)	8.6	-	91.2
Cu(20%)ZnO(ALD)	19.3	-	80.7
Cu(30%)ZnO(ALD)	27.9	-	72.1

Table 4: Catalysts Composition (%wt)

Given that the amount of ZnO is less than 1%, it is understandable that the mapping did not detect enough ZnO to be counted. The composition of each catalyst seems to be under the expected weight percentage, probably due to a loss of precursor solution in the wet impregnation. Nevertheless, it is still useful information to confirm that the impregnations have been carried out correctly.

6.2. Catalytic Activity, Stability and Selectivity Under Methanol Synthesis

6.2.1. Catalytic Activity

To determinate the effect of different Cu^0 loadings and the effect of ALD deposition and the amount of ZnO on the performance of the catalyst in the methanol synthesis, catalytic tests were done for the catalysts mentioned in 5.3.1. All catalytic activity tests were performed under the same operating conditions, detailed in the Experimental Section 5.3.1.

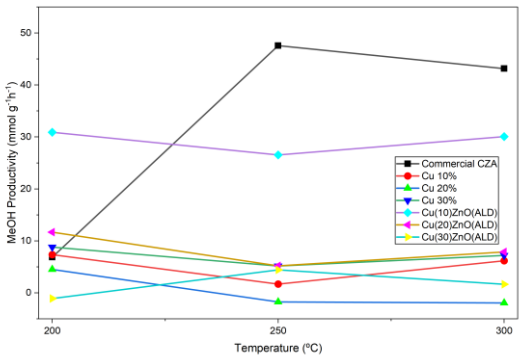

Figure 17: MeOH production of all catalyst analyzed

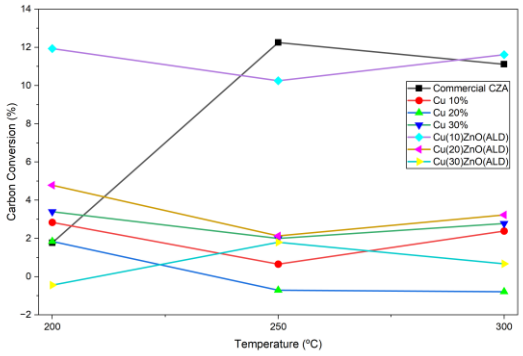

Figure 18: Carbon Conversion of all catalysts analyzed

Most of the catalysts present have low performance compared to the commercial catalyst, with the exception of **Cu(10%)ZnO(ALD)** catalyst, which notably has even better performance at low temperatures. This behavior can be explained with the previous characterization results, which yield a better dispersion of CuO at lower amounts of impregnation. Also, the presence of ZnO improves the CuO dispersion, generating more active sites.

The second best catalytical performance could be attributed to **Cu(20%)ZnO(ALD)**, as shown in Table 5. **Cu(20%)** results were under the quantification limits of the micro GC device.

Sample	MeOH Productivity (mmol g^{-1} h^{-1})	Carbon Conversion (%)
Commercial CZA	47.6	12
Cu 10%	1.7	<1
Cu 20%	–	–
Cu 30%	5.1	2
Cu(10%)ZnO(ALD)	26.5	10
Cu(20%)ZnO(ALD)	5.2	2
Cu(30%)ZnO(ALD)	4.4	2

Table 5: Catalytic Activity of Analized Catalysts at 250ºC

6.2.2. Catalytic Selectivity

The results showed in the GC are the presented-on Table 6:

Sample	MeOH (%)	EtOH (%)	PrOH (%)	iPrOH(%)	[MeOH] (%Wt)
Commercial	>99	<1	<1	<1	72.5
Cu(10%)ZnO(ALD)	97.5	<1	<1	<1	11.5
Cu(20%)ZnO(ALD)	>99	<1	<1	<1	62.5

Table 6: Results of Selectivity Analysis for Selected Catalysts

For **Cu(10%)ZnO(ALD),** despite the methanol concentration being almost 6 times lower than the obtained with the commercial one, the selectivity displays a higher value than the other alcohols, approaching the results obtained in the commercial catalyst.

The results were better for **Cu(20%)ZnO(ALD)**, having a remarkable approximation to the behavior exhibited by the commercial catalyst in question.

7. CONCLUSIONS

This study was divided into two main topics: the investigation and determination of the most suitable copper precursor for the synthesis of catalysts by wet impregnation; and the optimization of CZA catalyst, reducing the amount of CuO by WI and the amount of ZnO using ALD methods.

For the precursor investigation, the TGA analysis has shown that copper sulfate pentahydrate will not be useful to perform WI techniques using γ-Al_2O_3 as a support due to its high calcination temperature, where various unwanted structures can be generated, favoring rWGS reactions that are not our focus in this research.

Once reviewed the results of copper acetate monohydrate and copper nitrate hemipentaydrate, most of the characterization analysis suggest that the ideal precursor in this case would be $Cu(OAc)_2 \cdot H_2O$, because it promotes better CuO dispersion. The main problem remains in creating a homogeneous catalyst: due its low solubility, the precursor precipitates before full impregnation, resulting in a highly heterogeneous catalyst that will lose stability and performance during time. For that reason, sacrificing dispersion but taking into account better results in terms of stability and homogeneity, **$Cu(NO_3)_2 \cdot 2.5H_2O$** was selected as the best precursor to perform wet impregnation of CuO to the Al_2O_3 support.

For the catalytical analysis, the ZnO showed a very important role in CZA catalysts. Carbon conversion and methanol productivity were far superior in every aspect compared to their ZnO-free counterparts, getting the importance of ZnO to generate more dispersion and active sites. Also, lower amounts of Cu^0 demonstrated better dispersion, avoiding surface bulking and offering more active sites to perform the reaction.

In summary, this investigation underscores the complex interplay between catalyst composition, weight optimization, and different properties in determining methanol synthesis performance. The ALD technique offers a lot of advantages for further catalyst optimization to achieve better balance and results between activity, stability and selectivity performing.

8. REFERENCES AND NOTES

1. Zhang, M.; Liu, D.; Wang, Y.; Zhao, L.; Xu, G.; Yu, Y.; He, H. Recent Advances in Methanol Steam Reforming Catalysts for Hydrogen Production. Catalysts. Multidisciplinary Digital Publishing Institute (MDPI) January 1, 2025. https://doi.org/10.3390/catal15010036.
2. Zhang, W.; Wen, C.; Zhang, X.; Chen, L.; Zhang, Q.; Ma, L. A Review of Green Methanol Production: Technologies, Economic Evaluation and Carbon Emission Analysis. Energy & Fuels 2025, 39, 39, 18733-18750. https://doi.org/10.1021/acs.energyfuels.5c03278.
3. Cui, X.; Hou, D.; Bing, Q.; Hu, J.; Deng, D. Shaping the Future of Green Methanol. Chem Catalysis 2025, 5, 9, 101515. https://doi.org/10.1016/j.checat.2025.101515.
4. Harris, C.; Onode, H.; Delage, R.; Nakata, T. P2G and P2L System Design for the Hard-to-Abate Sector With Logistic Considerations in Japan. Energy Conversion and Management: X 2026, 29, 101469. https://doi.org/10.1016/j.ecmx.2025.101469.
5. Zhu, J.; Su, Y.; Chai, J.; Muravev, V. Mechanism and Nature of Active Sites for Methanol Synthesis from CO/CO2 on Cu/CeO2. ACS Catalysis 2020, 10, 19, 11532-11544. https://doi.org/10.1021/acscatal.0c02909.
6. Liu, G.; Hagelin.Weaver, H.; Welt, B. A Concise Review of Catalytic Synthesis of Methanol from Synthesis Gas. Waste 2023, 1, 1, 228-248. https://doi.org/10.3390/waste1010015.
7. Dehimi, L.; Alioui, O.; Benguerba, Y.; Yadav, K.; Bhutto, J.; Fallatah, A.; Shukla, T.; Alreshidi, M.; Balsamo, M.; Badawi, M.; Erto, A. Hydrogen Production by the Water-Gas Shift Reaction: A Comprehensive Review on Catalysts, Kinetics, and Reaction Mechanism. Fuel Processing Technology 267 (2025). https://doi.org/10.1016/j.fuproc.2024.108163.
8. Zhang, P.; Chen, Q.; Geng, I.; Wu, H.; A New Transportation Energy Review: Methanol Catalytic Synthesis From CO2 Green Hydrogenation. Renewable and Sustainable Energy Reviews 2025, 218, 115819. https://doi.org/10.1016/j.rser.2025.11.5819.
9. Kasatkin, I.; Kurr, P.; Kniep, B.; Trunschke, A. Role of Lattice Strain and Defects in Copper Particles on the Activity of Cu/ZnO/Al2O3 Catalysts for Methanol Synthesis. Angewandte Chemie International Edition 2007, 46, 38, 7324-7327. https://doi.org/10.1002/anie.200702600.
10. Behrens, M.; Schlögl, R. How to Prepare a Good Cu/ZnO Catalyst or the Role of Solid State Chemistry for the Synthesis of Nanostructured Catalysts. Zeitschrift für anorganische und allgemeine Chemie 2013, 639, 15, 2683-2695. https://doi.org/10.1002/zaac.201300356.
11. Kamsuwan, T.; Guntida, A.; Praserthdam, P.; Jongsomjit, B. Differences in Deterioration Behaviors of $Cu/ZnO/Al_2O_3$ Catalysts with Different Cu Contents toward Hydrogenation of CO and CO2. ACS Omega 2022, 7 (29), 25783–25797. https://doi.org/10.1021/acsomega.2c03068.
12. Sun, J.; Metcalfe, I.; Sahibzada, M. Deactivation of Cu/ZnO/Al2O3 Methanol Synthesis Catalyst by Sintering. Industrial & Engineering Chemistry Research 1999, 38, 10, 3868-3872. https://doi.org/10.1021/ie990078s.
13. Liu, H.; Zhu, W.; Zhou, X.; Wei, B.; Bing, L.; Han, D.; Wang, G.; Wang, F. Fabrication of Cu-Based Catalysts for the Synthesis of Neopentyl Glycol from Hydroxypivalaldehyde Hydrogenation: Studies on the Role of Zr Promoter. Reaction Kinetics, Mechanisms and Catalysis 2024. https://doi.org/10.1007/s11144-024-02768-x.
14. García, A.; Lwazzani, M. A.; Biset-Peiró, M.; Guilera, J.; Efficient CeO_2 decoration of Fischer-Tropsch Catalysts Through Atomic Layer Deposition. Catalysis Today 459 (2025). https://doi.org/10.1016/j.cattod.2025.115400.
15. Arandia, A.; Yim, J.; Warraich, H.; Leppäkangas, E.; Bes, R.; Lempelto, A.; Gell, L.; Jiang, H.; Meinader, K.; Viinikainen, T.; Huotari, S.; Honkala, K.; Puurunen, R. Effect of Atomic Layer Deposited Zinc Promoter on the Activity of Copper-on-Zirconia Catalysts in the Hydrogenation of Carbon Dioxide to Methanol. Applied Catalysis B: Environmental 321 (2023). https://doi.org/10.1016/j.apcatb.2022.122046.
16. Oneill BJ, Jackson DHK, Lee J, Canlas C, Stair PC, Marshall CL, et al. Catalyst design with atomic layer deposition. ACS Catalysis 2015;5:1804–25. https://doi.org/10.1021/cs501862h.
17. Hadi, M.; Alavi, S. M.; Rezaei, M.; Akbari, E.; Tabarkhoon, F. Methanol Steam Reforming Over $CuO/Mg/Al_2O_4$ Nanocatalysts: Influence of Copper Oxide Loading and Process Parameters on Hydrogen Production. Fuel 2025, 399. https://doi.org/10.1016/j.fuel.2025.135678

18. George, S. Atomic Layer Deposition: An Overview. Chem. Rev. 2010, 110, 1, 111–131. https://doi.org/10.1021/cr900056b
19. Li, D.; Xu, F.; Tang, X.; Dai, S.; Pu, T.; Liu, X.; Tian, P.; Xuan, F.; Xu, Z.; Wachs, I. E.; Zhu, M. Induced Activation of the Commercial Cu/ZnO/Al_2O_3 Catalyst for the Steam Reforming of Methanol. Nat Catal 2022, 5 (2), 99–108. https://doi.org/10.1038/s41929-021-00729-4.
20. Bahmanpour, A. M.; Héroguel, F.; Kiliç, M.; Baranowski, C. Cu-Al Spinel as a Highly Active and Stable Catalyst for the Reverse Water Gas Shift Reaction. ACS Catalysis 2019, 9, 76243-6251. https://doi.org/10.1021/acscatal.9b01822.
21. Rahmanpour, O.; Shariati, A. New Method for Synthesis Nano Size γ-Al2O3 Catalyst for Dehydration of Methanol to Dimethyl Ether. International Journal of Chemical Engineering and Applications 2012, 125-128. https://doi.org/10.7763/IJCEA.2012.V3.172.
22. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). Pure and Applied Chemistry 1985. https://doi.org/10.1351/pac198557040603.
23. Zuo, Z.; Wang, L.; Yu, L.; Han, P.; Huang, W. Experimental and Theoretical Studies of Ethanol Synthesis from Syngas over CuZnAl Catalysts without Other Promoters. J. Phys. Chem. C 2014, 118, 24, 12890–12898. https://doi.org/10.1021/jp502828c.

9. ACRONYMS

- ALD: Atomic Layer Deposition.
- BET: Brunauer-Emmett-Teller.
- CZA: $Cu/ZnO/Al_2O_3$.
- DEZ: Diethylzinc.
- EDX: Energy-Dispersive X-ray Spectroscopy.
- EtOH: Ethanol.
- H_2-TPR: Hydrogen-Temperature Programmed Reduction.
- IREC: Institut de Reserca en Energia de Catalunya.
- IWI: Incipient Wetness Impregnation.
- MeOH: Methanol.
- P2L: Power-to-Liquid
- PrOH: Propanol.
- iPrOH: Isopropanol.
- SA_{BET}: BET Surface Area.
- SEM: Scanning Electron Microscopy.
- TGA: Thermogravimetric Analysis.
- XRD: X-Ray Diffraction.
- rWGS: Reverse Water Gas Shift.
- WGS: Water Gas Shift.
- WI: Wet Impregnation.

APPENDICES

APPENDIX 1: SEM-EDX MAPPING OF SAMPLES ANALYZED

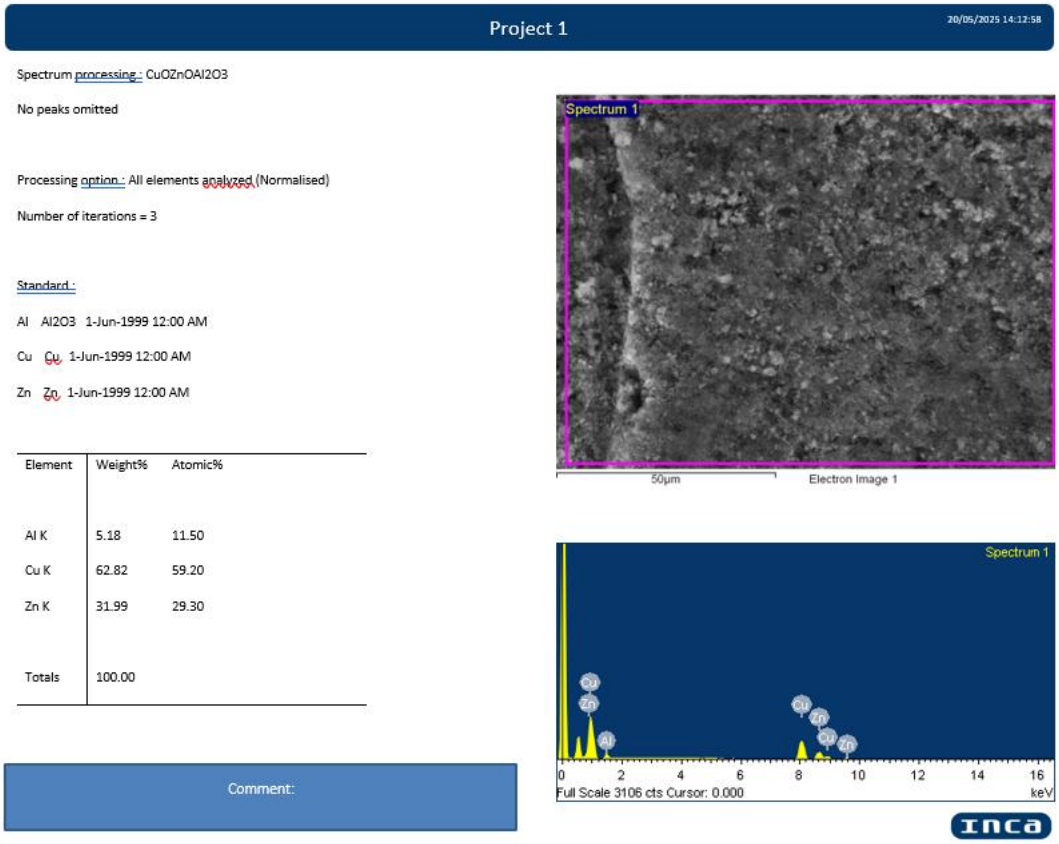

Figure A1: Mapping of Commercial CZA

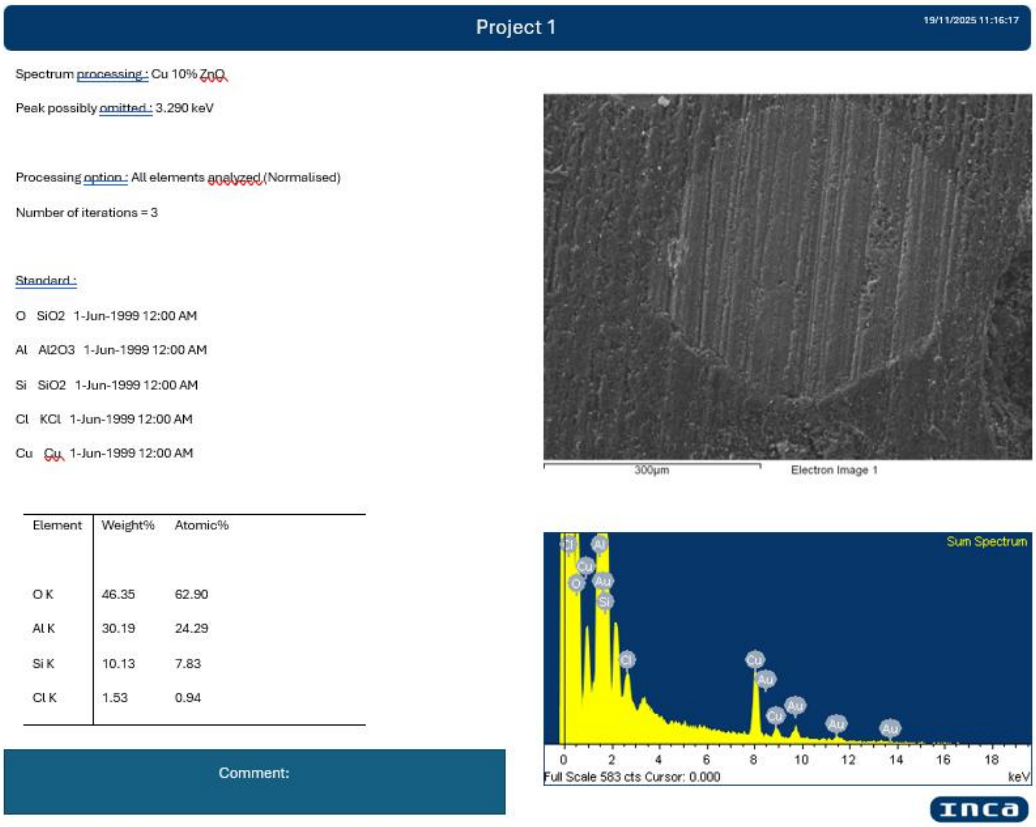

Figure A2: Mapping of Cu(10%)ZnO(ALD)

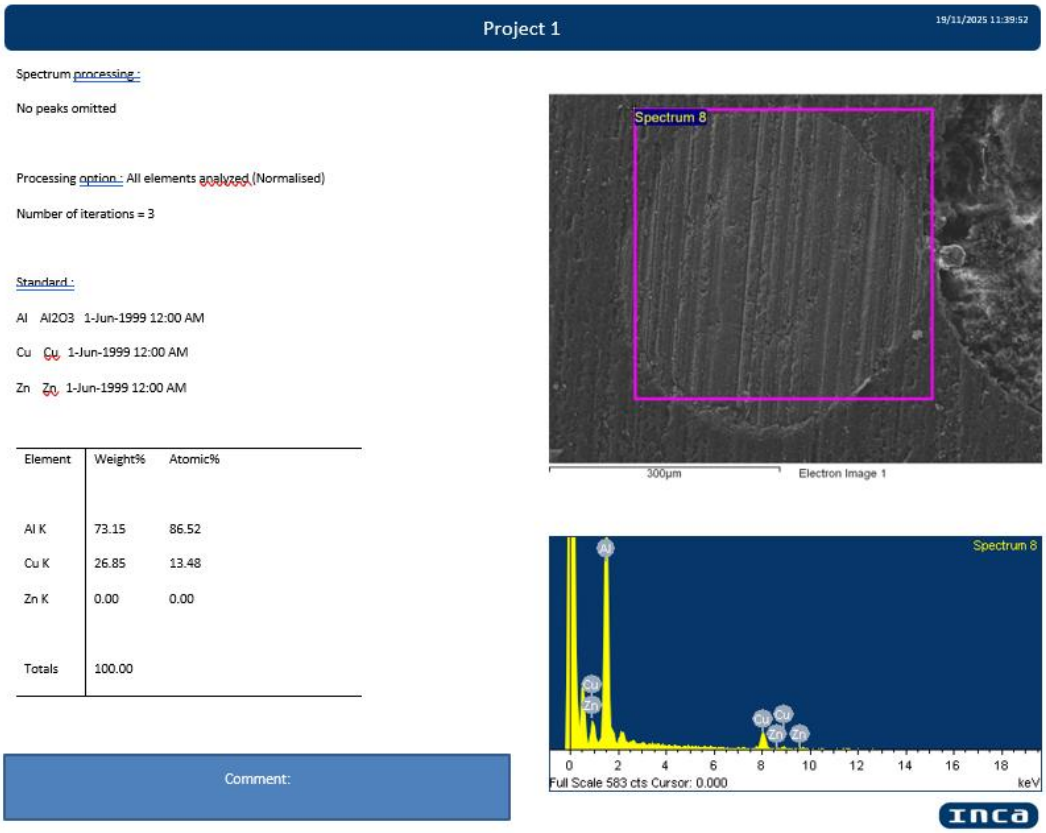

Figure A3: Mapping of Cu(20%)ZnO(ALD)

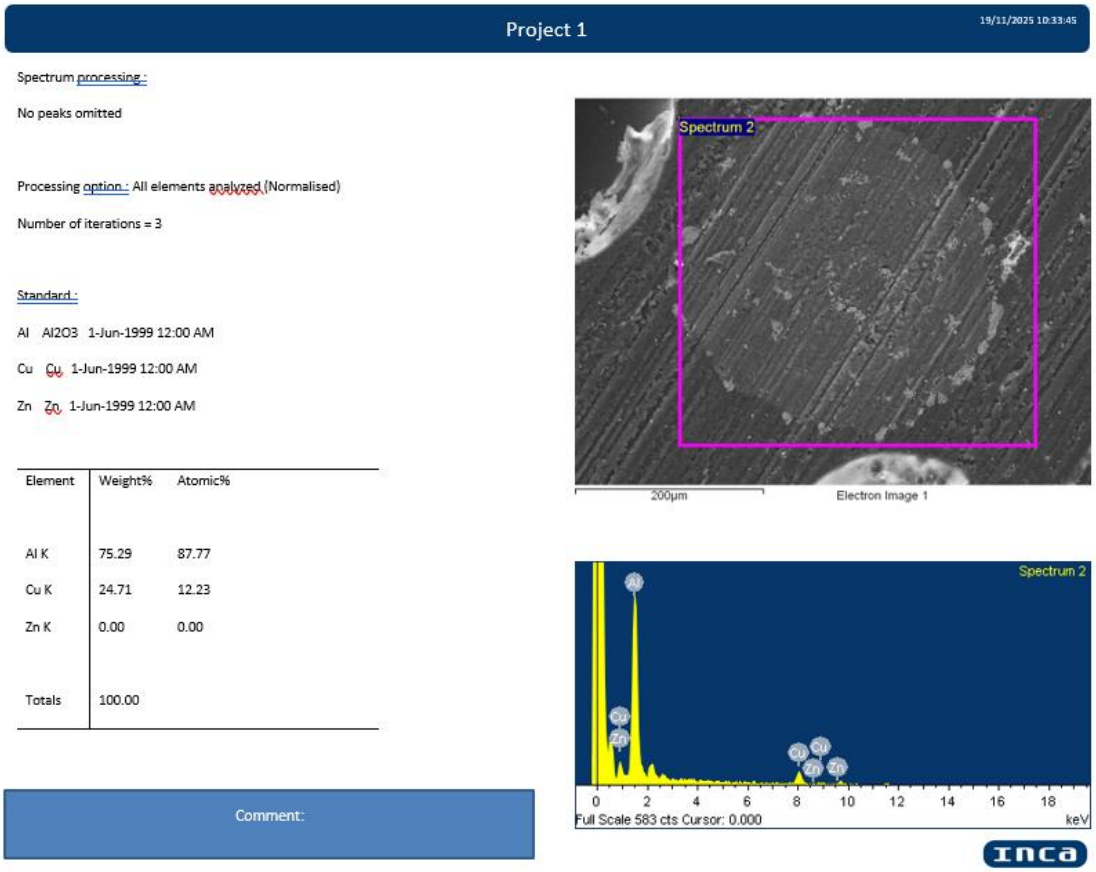

Figure A4: Mapping of Cu(30%)ZnO(AL