

**SYNTHESIS OF Cu-BASED MIXED
METAL OXIDES CATALYSTS FOR
SELECTIVE CO₂ HYDROGENATION TO
OXYGENATES**

BY

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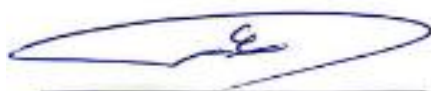
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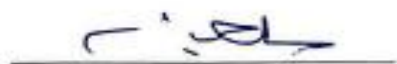
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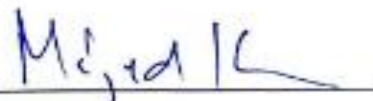
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[Dedication]

This work is dedicated to my beloved parents, brothers, sisters, and my entire family.

May Allaah Ta’ala continue blessing their lives.

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Allaah, Subhanahu Wa Ta'ala, the creator and sustainer of the universe, deserves all the credit for guiding me and providing me with the strength to achieve yet another milestone in my life. I am deeply appreciative of the assistance and guidance provided by my mentor and thesis committee during the course of my research. I am grateful to all those who assisted in this achievement and would like to take this opportunity to express my gratitude. I am particularly grateful to Dr. Saheed Ganiyu, my advisor, who has been a mentor and advisor to me during my time at KFUPM. His hospitality and generosity are truly commendable. He provided logistical support, valuable suggestions, and other contributions to this project that were substantial. I am appreciative of your steadfast support and direction. Furthermore, I would like to express my appreciation to Dr. Muhammad Tahir for his unwavering support and guidance during the course of my project. In addition, the substantial and generous contributions of Dr. Majad Khan to this project are greatly appreciated. I would like to take this opportunity to wholeheartedly express my deepest gratitude to Dr. Khalid Alhooshani for his exceptional mentorship, unwavering encouragement, and invaluable guidance throughout the duration of my project. His profound expertise, patience, and dedication have been instrumental in shaping my work, and I am truly grateful for the time and effort he has invested in my academic growth. I am deeply grateful to Dr. Babar Ali, my mentor, for his unwavering support and collaborative spirit during this academic endeavor. I would like to extend my deepest and most sincere appreciation to Dr. Aniz Ummer for his exceptional mentorship, steadfast encouragement, and collaborative approach throughout this academic journey. This project would not have reached its full potential without invaluable contributions from Dr. Basiru

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LIST OF ABBREVIATIONS

BET	:	Brunauer–Emmett–Teller
BJH	:	Barrett–Joyner–Halenda
CCS	:	Carbon capture and storage
CCU	:	Carbon capture and utilization
CO₂-TPD	:	CO ₂ -temperature programmed desorption
DME	:	Dimethyl ether
SEM	:	Scanning Electron Microscopy
FTIR	:	Fourier transformation infrared
GC	:	Gas chromatograph
GHGs	:	Greenhouse gases
H₂-TPR	:	H ₂ -temperature-programmed reduction
NH₃-TPD	:	NH ₃ temperature-programmed desorption
RWGS	:	Reverse water gas shift
TCD	:	Thermal conductivity detector
TEM	:	Transmission electron microscopy

ABSTRACT

Full Name : Jamilu Nura Musa

Thesis Title : Synthesis of Cu-based mixed metal oxides catalysts for selective CO₂ hydrogenation to oxygenates

Major Field : Chemistry

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Thermocatalytic CO₂ hydrogenation has emerged as a promising approach for synthesizing valuable oxygenates, offering a dual benefit of mitigating anthropogenic CO₂ emissions while producing industrially relevant chemicals. This study focuses on engineering multicomponent Cu-Fe-Zn oxide catalysts to enhance CO₂ conversion into oxygenated products, including methanol (CH₃OH), ethanol (CH₃CH₂OH), higher alcohols and dimethyl ether. The work introduces surfactant-assisted co-precipitation strategy to synthesize a Cu-Fe-Zn catalyst capable of selectively producing oxygenates, notably C₂+ alcohols, under optimized conditions. Catalysts were characterized using N₂ physisorption, FTIR spectroscopy, XRD, H₂-TPR, CO₂-TPD, SEM-EDX, and TEM to correlate structural and acidic properties with performance to be evaluated using fix-bed reactor. Beyond immediate applications, this research provides foundational insights for designing advanced catalysts to address carbon neutrality goals through efficient CO₂ valorization.

Keywords: CO₂ hydrogenation; Oxygenates; Methanol; Ethanol; C₂+ alcohols; Dimethyl ether; Cu-based catalysts.

ملخص الرسالة

الاسم الكامل: جميلو نورا موسي

عنوان الرسالة: تخليق محفزات أكاسيد المعادن المختلطة القائمة على النحاس لعملية الهدرجة الانتقائية لثاني أكسيد الكربون إلى مؤكسجات

التخصص: الكيمياء

تاريخ الدرجة العلمية: مايو / 2025

ظهرت الهدرجة الحرارية التحفيزية لثاني أكسيد الكربون كنهج واعد لتخليق مركبات مؤكسجة ذات قيمة، موفرة فائدة مزدوجة تتمثل في الحد من انبعاثات ثاني أكسيد الكربون الناتجة عن النشاط البشري، مع إنتاج مواد كيميائية ذات أهمية صناعية. تركز هذه الدراسة على هندسة محفزات متعددة المكونات من أكاسيد النحاس والحديد والزنك لتعزيز تحويل ثاني أكسيد الكربون إلى منتجات مؤكسجة، تشمل الميثانول، والإيثانول، والكحولات الأعلى، وثنائي ميثيل الإيثر. يقدم هذا العمل إستراتيجية ترسيب مشترك بمساعدة مادة خافضة للتوتر السطحي لتصنيع محفز قادر على إنتاج المركبات المؤكسجة بشكل انتقائي، ولا سيما الكحولات ذات السلسلة الكربونية الأطول تحت ظروف مثلى. وقد تم توصيف المحفزات باستخدام تقنيات الامتزاز الفيزيائي للنيتروجين، والأطياف تحت الحمراء، والحيود بالأشعة السينية، والاختزال المبرمج لدرجة الحرارة باستخدام الهيدروجين، وتحليل البرمجة الحرارية لثاني أكسيد الكربون، والمجهر الإلكتروني الماسح، والمجهر الإلكتروني النافذ، بهدف ربط الخصائص البنوية والحامضية بالأداء، والذي سيتم تقييمه باستخدام مفاعل ثابت السرير. وبالإضافة إلى التطبيقات المباشرة، توفر هذه الدراسة رؤى أساسية لتصميم محفزات متقدمة تساهم في تحقيق أهداف الحياد الكربوني من خلال تحويل فعال لثاني أكسيد الكربون

CHAPTER 1

INTRODUCTION

1.1 Background

High demand for energy supplements has resulted in massive emissions of carbon dioxide (CO₂), a serious environmental risk strongly associated with global warming and climate instability [1]. This escalating concern remains one of the most critical threats to human civilization and ecological systems. In response, the Paris Agreement, established in 2015, set a global objective to limit the average temperature rise to well below +2 °C above pre-industrial levels (circa 1850), with a more ambitious target of 1.5 °C by 2050 [2]. To achieve this ambitious goal and transition toward a net-zero carbon economy, considerable attention has been given to technologies that either prevent CO₂ emissions or repurpose them in sustainable ways. These strategies aim not only to reduce atmospheric CO₂ levels but also to shift toward a circular carbon economy, where carbon is continuously recycled into useful products. One such promising approach is catalytic CO₂ hydrogenation, which enables the conversion of CO₂ into energy-rich fuels and industrial chemicals, thereby integrating emissions reduction with resource recovery.

1.2. CO₂ emissions Mitigation Technologies

A range of innovative technologies have emerged and undergone extensive research in efforts to mitigate escalating global CO₂ emissions (Figure 1). Prominent among these are carbon-capture-and-storage (CCS), a concept with historical roots dating back centuries [3], and carbon-capture and utilization (CCU), a complementary strategy gaining traction in recent decades [4]. Despite gradual implementation of CCS infrastructures, barriers such as cost inefficiencies and complex logistical demands continue to limit their scalability [5]. These frameworks align with the two overarching paradigms for managing CO₂ : CCS, which prioritizes long-term isolation of gas, and CCU, which repurposes it for industrial applications [6], CCS systems enable CO₂ capture via adaptable processes, including the aforementioned combustion techniques, which can be customized to align with emission source characteristics, such as industrial flue gases or energy production facilities [7]. An alternative CCS pathway involves injecting compressed CO₂ into geologically stable reservoirs; however, this method faces criticism due to significant operational expenses and the underutilization of CO₂'s potential as a carbon feedstock. Irrespective of the method employed, the central tenet of CCS remains consistent: intercepting and compressing CO₂ at its emission source to prevent atmospheric release [8].

Different CO ₂ sources:	Different CO ₂ capture alternatives:	CCUS:
❑ Energy sector (73.2 %) • Transportation, Paper, Iron, Machinery, Steel ❑ Agriculture, forestry & land use sector (18.4 %) • Livestock manure, Deforestation ❑ Industry (5.2 %) • Cement & Chemicals production ❑ Waste (3.2 %) • Landfills & Wastewater	❑ Chemical Looping • Reforming, Combustion ❑ Membrane • Inorganic, Polymeric, Facilitated-transport ❑ Absorption • Amine based, Ionic-liquids, Ammonia ❑ Adsorption • Carbon based, Metal-oxides, Zeolites, MOFs	❑ Carbon Capture & Storage (CCS) • Geological storage, Ocean storage ❑ Carbon Capture & Utilization (CCU) • Enhanced Oil Recovery (EOR), Fuels, Chemical feedstock for methanol, alkanes, and syngas production

Figure 1 Existing technology for CCUS

The technology for CCU offers greater advantages compared to CCS, as products generated through CO₂ utilization can serve as a source of revenue while addressing CO₂ mitigation efforts. Moreover, in contrast to CCS, CCU eliminates the risk of CO₂ leakage, positioning this technology as both environmentally friendly and sustainable. Figure 2 illustrates distribution of documents by subject area concerning CO₂ CCU from 2011 to 2025, with chemistry accounting for the largest share at 35.7 %.

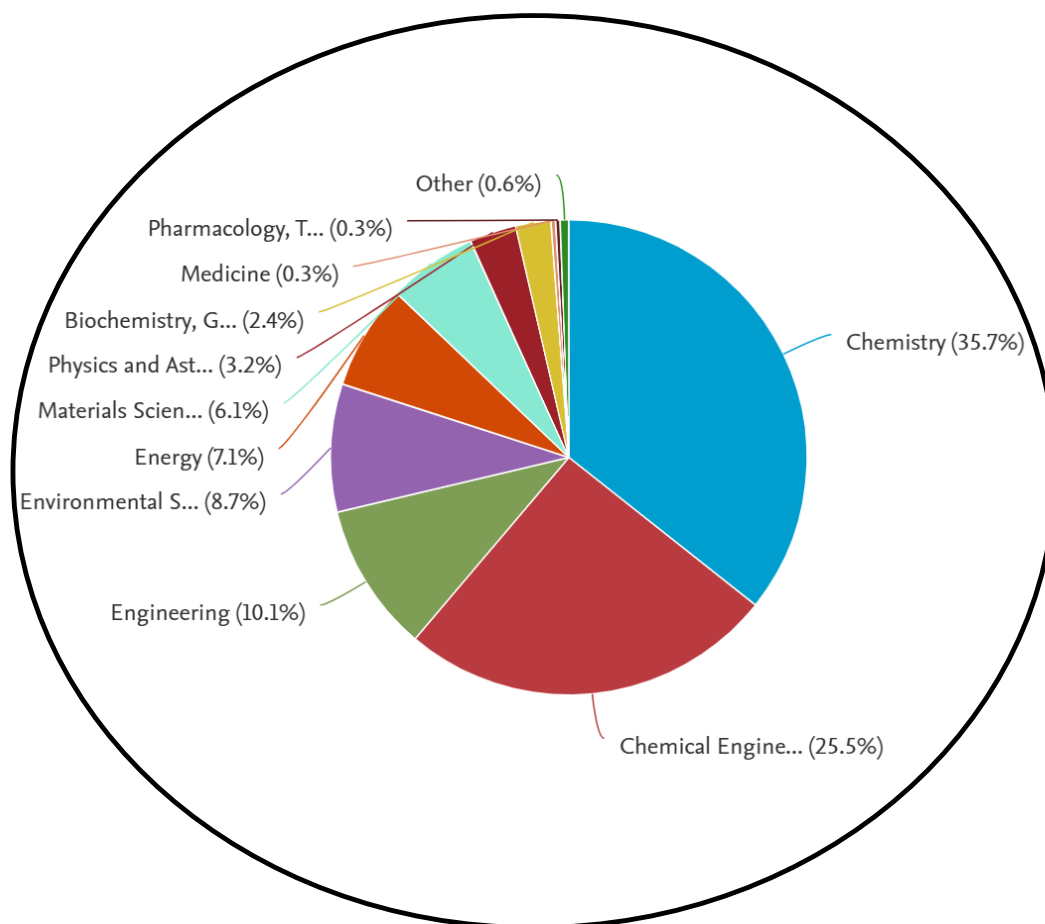


Figure 2 Illustration of the distribution of documents categorized by subject area related to CO₂ CCU from 2011 to 2025 (Source: www.scopus.com)

While photocatalytic-reactions have predominantly been reported for CO₂ utilization, electrochemical-reduction, on the other hand, suggests that catalytic CO₂ hydrogenation presents a more promising alternative compared to other methods of utilizing CO₂. For instance, the electrocatalytic-reduction of CO₂ is heavily influenced by pH and electrode-voltage. Although it has traditionally been performed at ambient temperature and pressure [9], activating the highly stable CO₂ molecule requires a considerable overpotential. A fundamental distinction between photocatalytic and electrochemical CO₂ reduction lies in their electron sources: the former relies on light-induced electron-hole pairs in

semiconductors, whereas the latter depends on externally supplied electrical currents. Despite their promise, photocatalytic systems remain constrained by suboptimal efficiency, poor product selectivity, and narrow product diversity challenges exacerbated by their dependence on photon absorption dynamics [10]. A growing interest which has been shown in the newly developed CO₂ catalytic-conversion approach came as potential and promising-solution for excessive-CO₂-emissions in industrial-production-processes[11], and addressing this issue is now essential due to a rapid increase in CO₂ emissions and associated environmental risks [12]. This catalytic CO₂ conversion has also occupied an important spot in highly applicable "carbon neutral" approach to sustainable development, which has drawn a lot of interest from researchers [1,11,13] proving heterogeneous catalysis to be an essential approach to deal with global warming as it lowers carbon emissions, increases energy efficiency, lowers energy demand, and substitutes renewable energy for fossil fuels in decarbonization strategies[14–16]. However, it is now more imperative to capture, store, and use CO₂ (a greenhouse gas) to address the issue of CO₂ emissions. As a result, catalytic CO₂ hydrogenation as an effective route to convert CO₂ into value-added products like oxygenates (e.g. methanol [17–19], dimethyl-ether (DME) [28]), and jet fuel [21] is progressively attracting humans' attention. This approach not only contributes to CO₂ mitigation but also aligns with broader sustainability goals by enabling the production of clean fuels and industrial chemicals from waste carbon. Given the critical role of catalyst design in determining activity and selectivity, current research continues to focus on the development of highly efficient and stable catalytic systems that can drive this transformation under practical conditions. This growing interest underscores

the urgent need for advanced catalysts capable of facilitating selective CO₂ hydrogenation to oxygenates, forming the foundation of the present research.

1.3. Research Objectives

Conversion of carbon dioxide (CO₂) into value-added oxygenates via heterogeneous catalysis represents a promising pathway to address both environmental and energy-related challenges. Among potential catalysts, Cu-based mixed metal oxides exhibit significant promise due to their tunable redox properties, cost-effectiveness, and ability to facilitate CO₂ activation and hydrogenation. The overall aim of this research is to design and evaluate a series of Cu-Zn-Fe (CZF) catalysts synthesized via surfactant-assisted co-precipitation, and to investigate their structure–activity relationships for selective CO₂ hydrogenation to oxygenates.

The specific objectives of this study are

1. To synthesize a series of Cu-Zn-Fe-based mixed metal oxide catalysts (CZF-x) by varying the molarity of the precipitating agent (Na₂CO₃) using a surfactant-assisted co-precipitation method, while keeping the metal loadings constant.
2. To thoroughly characterize the structural, textural, and surface properties of the synthesized catalysts using techniques such as XRD, BET, H₂-TPR, CO₂-TPD, FTIR, SEM-EDX, and TEM, to understand their crystalline phases, reducibility, basicity, morphology, and particle dispersion.
3. To evaluate the catalytic performance of the CZF-x catalysts in a fixed-bed reactor system under controlled conditions (280 °C, 30 bar, H₂/CO₂ = 3) for the

hydrogenation of CO₂ to oxygenated products, focusing on CO₂ conversion, product selectivity, and productivity.

4. To correlate catalyst properties (e.g., crystallinity, surface area, reducibility, basicity, and morphology) with catalytic activity and selectivity, thereby elucidating structure–activity relationships.
5. To identify the optimal synthesis parameters (particularly Na₂CO₃ concentration) that result in superior catalytic activity and oxygenate selectivity, and to provide mechanistic insight for future catalyst design.

CHAPTER 2

LITERATURE REVIEW

2.1. CO₂ hydrogenation

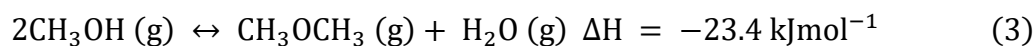
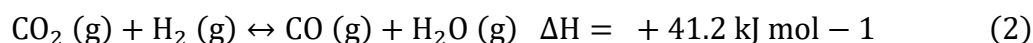
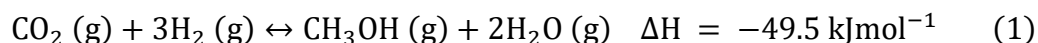
The hydrogenation of CO₂ to oxygenates, particularly methanol, presents a promising and sustainable strategy for mitigating CO₂ emissions while addressing energy shortages [22]. Methanol serves not only as a hydrogen carrier but also as a versatile precursor for synthesizing high-value chemical products [23]. Among various catalysts, the co-precipitation-derived Cu/ZnO/Al₂O₃ (CZA) system is widely employed for CO₂-to-methanol conversion because of its cost-effectiveness, favorable catalytic performance, and compatibility with moderate reaction conditions [24]. However, CZA catalysts face challenges such as limited lifespan and poorly understood deactivation mechanisms [25]. Studies attribute this deactivation to water adsorption on the hydrophilic Al sites during methanol synthesis, as well as ZnO recrystallization—which disrupts critical Cu-ZnO interfaces [22]. To enhance catalyst durability and activity, the incorporation of promoters like Zr, Ce, or La has been explored [26]. Methanol, as a pivotal C₁ oxygenate derived from CO₂ hydrogenation, acts as a key industrial platform chemical for downstream syntheses [27]. Consequently, decades of research have focused on optimizing catalytic systems for efficient methanol production [28]. While elevated reaction temperatures boost CO₂ conversion rates, they concurrently diminish methanol selectivity and escalate energy demands [29]. This trade-off underscores the need for mechanistic studies to guide the design of advanced catalysts. Recent progress in CO₂ hydrogenation has been achieved

with metal-support-systems like CuZnAl and CuZnZr [30]. Notably, Cu-based-catalysts dominate research efforts owing to their exceptional cost-performance ratio and catalytic efficacy, where Cu sites facilitate H₂ adsorption while CO₂ activation occurs at support interfaces [31]. Another valuable oxygenate is DME. It is plain ether that contains no C-C bonds [32]. DME has gained potential to be used as an alternative fuel to gasoline and diesel because of its high-cetane-number, cleanliness nature, safety, and non-corrosiveness energy source nature [33]. It readily liquefies at 20 °C under a vapor pressure of 5.1 bar, thus, it is a gas at atmospheric conditions [34]. DME is regarded as an excellent circulating hydrogen carrier, providing solutions for both transportation and storage of hydrogen [33,35], and has been in use as an aerosol-propellant that alternated the known but forbade ozone-destroying CFC-compounds [33]. DME has been a crucial raw ingredient for production of aviation fuel and low-carbon-olefins [36–39].

2.1.1. Thermodynamics and kinetics of the reactions

Thermodynamic analysis plays fundamental role in assessing viability and predicting outcomes of CO₂ hydrogenation processes under varying operational conditions. Critical thermodynamic parameters - including enthalpy changes, entropy variations etc. provide essential-discernments in energy-landscape and reaction pathways [40]. Systematic evaluation of these thermodynamic properties enables optimization of reaction parameters to enhance product yield, selectivity, and overall process efficiency. The Gibbs-free-energy change (ΔG) serves as a particularly crucial indicator for assessing reaction

spontaneity. In CO₂ hydrogenation systems, elevated temperatures generally increase ΔG values for most reactions, thermodynamically disfavoring the formation of desired products [41]. Thermodynamic calculations suggest that lower reaction temperatures or higher system pressures should promote dimethyl ether (DME) synthesis. However, kinetic analysis reveals that effective CO₂ activation requires temperatures exceeding 220°C, despite the thermodynamic preference for lower temperatures. This temperature-dependent behavior leads to competing reaction pathways, with DME production occurring alongside methanol formation (1) and carbon monoxide generation (2) [42]:



Subsequently, DME is generated through the process of methanol dehydration/condensation utilizing an acid catalyst, which serves to promote the forward reaction while restricting CO₂ consumption through the RWGS reaction (Equation 3) [42]. Direct production of DME from CO₂ is improved with increased pressure because of decrease in number of moles [43] and at lower temperatures, as elevated temperatures promote endothermic side-reactions, including RWGS, which deplete CO₂ and H₂. But operating at low temperatures calls for optimization of reactor designs and developments, including in-situ water-removal methods (such as distillation or membranes) [44] and advancement of more effective CO₂-hydrogenation catalysts. In a study evaluating

equilibrium product distributions during CO₂ hydrogenation, Shen et al. [45] quantified the theoretical yields of dimethyl ether (DME), carbon monoxide (CO), and methanol. Their analysis demonstrated that under consistent reaction parameters, DME exhibits a thermodynamically favored equilibrium that yields significantly surpassing that of methanol in this process, as graphically represented in Figure 3 [46].

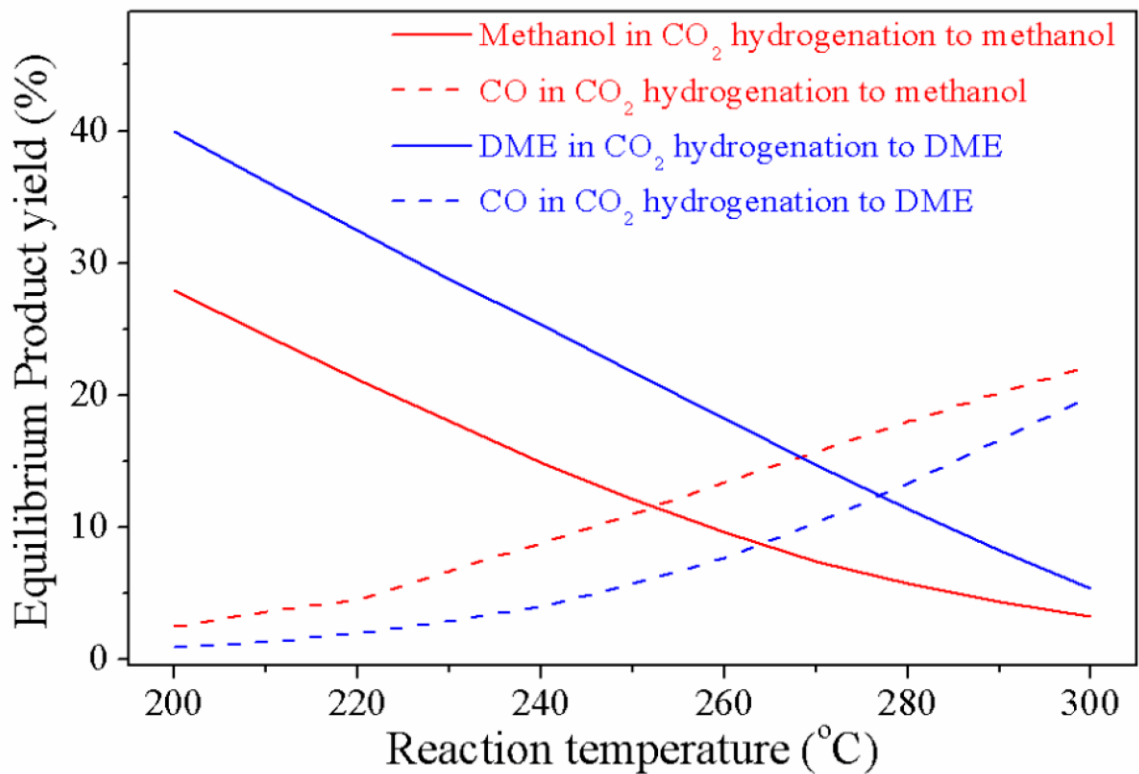


Figure 3 Product equilibrium-yields

2.2 Catalyst Development for CO₂ Hydrogenation

Catalyst development for hydrogenating CO₂ to oxygenates, notably methanol and dimethyl ether (DME), has evolved significantly over time. The earliest catalytic systems for methanol synthesis employed zinc-chromium-oxide formulations [47]. A breakthrough emerged in 1966 with the introduction of copper-based catalysts, which were developed to enhance methanol yields via CO/CO₂ hydrogenation. For DME synthesis, integrated catalytic systems combining methanol synthesis and dehydration phases were designed to mitigate challenges such as mass-transfer limitations, uneven active-site distribution, and inefficient interaction between intermediate methanol and acid sites responsible for dehydration [48].

2.2.1 Active Metals for CO₂ Hydrogenation

In light of their high-activity and selectivity, transition-metals are in-use as active-metals aimed at hydrogenation of carbon dioxide. As demonstrated in Table 1, researchers have designed and assessed many combinations of catalysts throughout the years to identify the reaction-promoting properties of each element. Despite the fact that Cu-based systems, like bimetallic Cu-ZnO composites, have been used in a number of studies and shown promising activity for CH₃OH synthesis, researchers have also investigated other bimetallic combinations [49].

Table 1 Probable Elements (oxide) for Methanol-synthesis

Sr. No	Element (Oxide)	Composition in Catalyst (wt%)	Justification	Ref.
1	CuO	50–70 atomic % < 35	Active-site for H ₂ -dissociation. Moreover, copper is more economical in comparison to other elements.	[50]
2	ZnO	20–50	Cu mixed with ZnO has improved catalytic activity in methanol production process.	[51]
3	Alumina, Al ₂ O ₃ (Promoter / Support)	5–20	Al ₂ O ₃ enhances stability of catalysts. Acidity of Al ₂ O ₃ surface concurrently influences the selectivity of by-products.	[52]
4	Zirconium Oxide	1 (atomic ratio)	ZrO ₂ will increase dispersion of Cu while decreasing its surface and particle size. ZrO ₂ 's hydrophobic characteristic,	[53]

which allows it to reject water
produced during reaction.

5	Indium Oxide, In ₂ O ₃ (Support)	10	In ₂ O ₃ has the capacity to inhibit RWGS-reaction, which competes with methanol- synthesis via CO ₂ hydrogenation.	[54]
6	Magnesium Oxide, MgO (Support)	20	MgO improves Cu dispersion, which boosts CO ₂ hydrogenation.	[55]
7	Palladium, Pd	≤ 5	Pd activates H ₂ gas into H-atoms that overflow metallic oxide supports and produce formate ions.	[56]
8	Iridium, Ir	1–10	Ir can enhance the creation of oxygen vacancies.	[57]

2.2.2 Promoters

Promoters are known to contribute to increasing metal dispersion, enlarging surface area, lowering reduction temperatures, and reducing crystallite size [58]. They also improve interactions between catalytic-components and change active-sites. Promoters boost metal-dispersion and specific surface area of catalysts, while doping ZnO strengthens Cu-ZnO interaction and produces defects in Cu-phase, improving catalytic-activity. ZnO promoters occupy interstices between Cu, maintaining optimal Cu-dispersion in Cu/ZnO catalysts and achieving 65 % DME selectivity. ZrO₂ has been identified as more effective-promoter than ZnO for enhancing CO₂ hydrogenation. Cu-Zr interaction further stabilizes Cu-sites, which explains increased Cu-dispersion and enhanced Cu-ZnO contact [59]. Increasing calcination temperature promotes monoclinic-form of ZrO₂ [60]. The Pd/In-catalyst achieves methanol synthesis efficiency of around 70 %, though it produces significant amounts of CO during hydrogenation and favors methane-formation over methanol [61]. Moreover, Fan *et al.* found that Pd/CeO₂ exhibits exceptional activity and durability [62]. Conversely, Pd-based-catalysts generally demonstrate lower-activity compared to Cu-based-catalysts. Addition of silver to copper-based-catalyst has shown improved catalytic-performance in CO₂ hydrogenation to methanol [63]. Koppel *et al.* demonstrated that Ag/ZrO₂ achieves higher methanol-selectivity compared to Cu/ZrO₂ [64]. While modifying Cu/ZrO₂ with Ag enhances methanol selectivity, it is crucial to note that excessive Ag dispersion may reduce selectivity, which can be attributed to relationship between Ag-dispersion and rate of RWGS-reaction [65].

Zirconium (Zr) is frequently used as a promoter in catalytic applications. Adding 7.5 % Zr to activated carbon reduces the specific surface area from 1,280 m²/g to 1,132 m²/g and decreases the pore volume from 0.95 cm³/g to 0.86 cm³/g, indicating micropore occlusion [66]. Similarly, incorporating Zr into Cu/ γ -Al₂O₃ reduces the specific surface area from 234.3 m²/g to 224.8 m²/g, while the pore volume remains unchanged at 0.45 cm³/g [67]. For Cu-Fe/ZSM5 catalysts, adding 1 % Zr increases the specific surface area from 94.24 m²/g to 107.22 m²/g, but raising the Zr concentration to 3 % reduces it to 92.62 m²/g [68]. Incorporating 5.25 % Zr into H₃PO₄-impregnated activated carbon increases weak acid sites from 125 to 175 mol/g due to Zr-O-P bond formation. Higher Zr concentrations, from 0.25 % to 7.5 %, correlate with improved methanol conversion by generating additional weak acid sites that act as active sites for dimethyl ether (DME) formation [69]. Adding Zr to the CuO/ZnO/Al₂O₃ (CZA) catalyst improves stability by leveraging Zr's hydrophobic properties, which repel water (a methanol synthesis by-product) from the active site, thus preventing deactivation [70]. The inclusion of ZrO₂ in Cu-ZnO catalysts enhances catalytic performance compared to ZnO alone. A Cu-ZnO-ZrO₂ catalyst achieves a CO₂ conversion rate of 23 % and methanol productivity of 331 g CH₃OH kg_{aCat}⁻¹ h⁻¹ under mild conditions (280°C, 50 bar, GHSV of 10,000 h⁻¹) [71]. The improved performance of Cu-ZnO-ZrO₂ is attributed to ZrO₂'s hydrophobicity, which minimizes water adsorption, increases surface alkalinity, and promotes CO₂ adsorption and methanol production. ZrO₂ activates adsorbed CO₂ to form CO₂^{*} species, which can react with H₂^{*} species to generate intermediates (e.g., formate, dioxoethylene, methoxy) crucial for methanol synthesis [71]. Additionally, ZrO₂ promotes oxygen vacancy formation during reduction, enhancing Cu dispersion and Cu-ZnO interaction. The stabilization of Cu^{δ+} sites through zirconia interaction further

improves Cu dispersion and Cu-ZnO contact [72]. The addition of magnesium (Mg) as a promoter to the Cu/ZnO/ γ -Al₂O₃ catalyst improves Cu dispersion, as evidenced by a shift in the malachite XRD peak due to the incorporation of Mg²⁺ into the malachite structure [73]. This modification also increases the surface area of γ -Al₂O₃ from 79.2 m²/g to 95.9 m²/g when combined with ZnO/ γ -Al₂O₃. Furthermore, incorporating MgO into the Cu/ γ -Al₂O₃ (CA) catalyst results in better Cu dispersion and a higher surface area compared to the inclusion of ZnO or ZrO₂ [67]. Din *et al.* (2020) reported that adding Mg to a Cu/Mordenite catalyst increased its surface area by 6.4 % with the incorporation of 0.3 wt % Mg [74,75]. Similarly, Mao and Guo integrated alkaline earth metals (MgO, BaO, and CaO) into ZSM5, finding that MgO yielded the highest ZSM5 surface area at 274.1 m²/g. MgO/ZSM5 also exhibited the highest concentration of acid sites (8.80×10^{-4} mol g⁻¹) compared to BaO/ZSM5 (7.52×10^{-4} mol g⁻¹) and CaO/ZSM5 (8.66×10^{-4} mol g⁻¹). Among these, MgO had the lowest basicity but reacted only to strong acid sites, whereas BaO and CaO reacted at both weak and strong acid sites. As a result, MgO/ZSM5 demonstrates greater overall basicity than BaO/ZSM5 and CaO/ZSM5 [75]. Adding MgO to the Cu/ZnO/ γ -Al₂O₃ catalyst reduces its overall acidity due to MgO's pronounced basicity. MgO interacts with strong acid sites, transforming them into moderate or weak acid sites [66]. Mao *et al.* [76] utilized MgO as a neutralizing agent to convert strong acid sites into weak acid sites. Strong acid sites can promote the excessive decomposition of dimethyl ether (DME) into hydrocarbons with shorter carbon chains [77]. Incorporating Mg into bifunctional catalysts also affects their catalytic performance. For instance, adding 20 % Mg to the Cu/ZnO/ γ -Al₂O₃ catalyst demonstrated superior activity compared to 0 %, 5 %, 10 %, and 30 % Mg. The increase in DME selectivity from 50 % to 83 % was observed

with the addition of 20 % Mg, attributed to the higher concentration of medium-strength acid sites created by this incorporation [78]. These acid sites play a crucial role in the methanol-to-DME dehydration reaction while suppressing the formation of by-products such as coke and other hydrocarbons [79].

2.2.3 Supports

The primary purpose of support in catalysis, particularly in catalyst-design, is to evenly distribute active-sites on-the surface, while maintaining thermal-stability, and preventing sintering of metal-oxides [80]. By controlling porosity of catalyst, support increases mechanical-strength and improve the surface-to-volume ratio. Moreover, support plays critical role in influencing selectivity and activity of DME during CO₂-hydrogenation [81]. In addition to fulfilling these roles, acidity of support is a crucial parameter in designing efficient-catalysts for methanol dehydration to DME [41]. In 1923, BASF introduced ZnO-Cr₂O₃ as its first-catalyst for converting syngas to methanol under high-pressure [41]. However, syngas-contaminants such as sulfur, chlorine, and heavy metals adversely impact catalyst performance. Thus, Imperial Chemical Industry (ICI) developed Cu/ZnO-catalysts in 1966, which operate at 5–10 MPa and 200–300 °C, with ZnS added to protect against poisoning [82]. ZnO's active lattice electron pair facilitates methanol synthesis [83]. Acidic solids used for methanol dehydration to DME include crystalline aluminosilicates, γ -Al₂O₃ [84], H-form-zeolites, sulfated zirconia, and [85].

2.2.4. Cu-based catalyst

Ternary Cu-based-catalysts, specifically Cu/ZnO/Al₂O₃, remain the most widely employed in industrial methanol-synthesis from CO and CO₂ due to their exceptional activity and selectivity. BASF pioneered methanol-production from syngas [86]. Later, Cu/ZnO/Al₂O₃-catalyst, introduced by Imperial-Chemical-Industries, enabled industrial-methanol-synthesis under trivial reaction-conditions [87]. Multiple studies have established the efficiency of Cu as an active catalyst, particularly when combined with other metal and non-metal promoters. Catalyst performance is also influenced by factors such as composition, preparation methods, and reaction-conditions, all of which affect surface-structure and catalytic behavior [88]. Since 1921, copper-based catalysts have been employed in methanol synthesis [52]. ZnO recognized as an ideal partner for Cu improves dispersion and stability of active-Cu-sites through its strong-interaction with Cu-phase [89]. Moreover, the specific ZnO phase that interfaces with Cu portrays key-role in regulating catalytic-performance of Cu/ZnO-system [90]. CeO₂ has emerged as promising support-material due to its remarkable oxygen-storage-capability [91].

Liu *et al.* synthesized Cu/Ga₂O₃/ZrO₂ and CuO/B₂O₃/ZrO₂ catalysts, studying effect of nanocrystalline-zirconia on catalytic-performance. The nanoscale Zr component significantly modified the catalyst's electronic structure, metal-support interaction, and surface properties, leading to increased corner defects, enhanced reducibility, and a higher density of oxygen vacancies, all of which promoted methanol synthesis [92]. Lei *et al.* explored morphological-effects of ZnO, identifying that (002)-facet significantly promoted CH₃OH-synthesis due to its high-concentration of oxygen-vacancies [90]. Efforts to

improve performance of Cu/ZnO-systems have focused on designing advanced catalyst-structures, including core-shell Cu-ZnO-configurations, graphitic-ZnO, and Cu-Zn-nano alloy-layers [93]. Enhancements in Cu-ZnO-based catalysts have also been achieved through addition of promoters and stabilizers, which boosts both activity and stability [94]. For instance, Al₂O₃ has been shown to stabilize the active Cu sites effectively [95]. Another strategy to optimize catalyst performance lies in refining the synthesis process.

Extensive research on mechanisms over Cu-based-catalysts has consistently identified formate-species as key-reaction-intermediates [96,97]. Although, debates continue regarding the precise nature of active-sites and rate-limiting-steps in reaction-pathway. Bowker et al. [98] examined Cu(60 %)/ZnO(30 %)/Al₂O₃ and polycrystalline copper catalysts using TPR, temperature-programmed desorption (TPD), and microreactor kinetic studies. Following formation of methanol from CO₂ and H₂ at 500 K, they noticed that Cu-surface was largely saturated with oxygen and formate-species, while ZnO contained interstitial-hydrogen. In accordance with these observations, the authors postulated that rate-limiting-phase includes hydrogenation of formate-intermediates generated on copper-surface through coadsorption of CO₂ and H₂ [99]. Influencing operating-temperature on CO₂-hydrogenation over Cu-based-catalysts reveals consistent-trend: higher-temperatures generally enhance CO₂-conversion and CO-selectivity while reducing methanol-selectivity. This behavior has been observed across various systems, including Cu/Al₂O₃ (453–533 K) [100], Cu/TiO₂ (493–553 K), Cu/ZrO₂ (493–553 K) [101], Cu/ZnO/La₂O₃ (523–673 K) [102], Cu/SiO₂ (523–623 K) [103], and Cu/ZnO/Al₂O₃/Cr₂O₃ (463–553 K) [104]. In some cases, rising temperatures have also been associated with an increase in selectivity toward light hydrocarbons, such as CH₄ [102]. Support materials

play a critical role in catalyst performance. Denise and Sneed [105] demonstrated that Cu supported on MgO, La₂O₃, and Sm₂O₃ produced fewer active catalysts, while ZnO, Al₂O₃, ZrO₂, ThO₂-K, and Cu/ZnO/Al₂O₃ systems exhibited higher activity. Amenomiya [101] ranked the activity and methanol selectivity of Cu catalysts as CuO/ZrO₂ > CuO/ZnO > CuO/TiO₂ > CuO/Cr₂O₃-Al₂O₃ > CuO/Al₂O₃ > CuO/SiO₂, with CuO/SiO₂ being inactive. Their findings suggested that catalyst performance is governed more by the nature of the Cu-support interaction than by surface area. Fujitani *et al.* [106] further noted that specific methanol formation activity varied as Cu/Ga₂O₃ > Cu/ZnO > Cu/Cr₂O₃ > Cu/ZrO₂ ≈ Cu/Al₂O₃ > Cu/SiO₂. They attributed this variation to the formation of Cu⁺ sites at the interface of Cu particles and the supporting oxide, either on the Cu surface or near the Cu particle perimeter. These studies collectively highlight the interplay between temperature, support material, and Cu interactions in determining the efficiency and selectivity of CO₂ hydrogenation. The rate-determining step in the direct conversion of CO₂ to DME remains a contentious topic. Methanol dehydration to DME is widely accepted to proceed through two distinct mechanisms: (a) the associative mechanism, where two adsorbed methanol molecules directly interact to form DME, and (b) the dissociative mechanism, in which adsorbed methanol dissociates into a surface methoxy species before combining with another methanol molecule to produce DME [107]. Both pathways depend on the synergistic activity at Brønsted acidic sites. Furthermore, methanol synthesis from CO₂ involves two primary reaction routes on Cu (111): the formate pathway and CO hydrogenation facilitated by the reversible water-gas shift (RWGS) reaction [107]. The formate mechanism is initiated by hydrogen spillover from metallic Cu (111) to preactivated CO₂, generating monodentate (m-HCOO^{*}) or bidentate (b-HCOO^{*}) formate

species [108]. The subsequent hydrogenation of these formate species to oxy-intermediates is identified as the rate-limiting step, eventually leading to methanol formation through methoxy (CH_3O^*) and other intermediates. In contrast, the RWGS mechanism begins with the formation of HOCO^* species, which undergo further hydrogenation to form CH_3O^* . The generation of HOCO^* is the rate-limiting step in the RWGS pathway, with a significant energy barrier of approximately 161.67 kJ/mol. Methanol synthesis predominantly occurs through the formate pathway, as only a small fraction of CO^* contributes to methanol formation. Most CO is released as a gaseous byproduct through the decomposition of HOCO^* or HCO^* species, thereby limiting methanol selectivity. However, doping and promotional effects on Cu catalysts can enhance the hydrogenation of CO_2 to methanol by improving CO binding and stabilizing intermediates [107]. This underscores the importance of optimizing catalytic properties to improve efficiency in CO_2 hydrogenation processes. Bonura *et al.* conducted operando spectroscopic studies under relevant CO_2 hydrogenation conditions (3 MPa, 200–260 °C), identifying key intermediates such as adsorbed CO^* , formate (HCOO^*), carbonate (CO_3^{2-}), and methoxy (CH_3O) involved in the DME synthesis pathway [48]. Their findings demonstrated that methanol formation proceeds via either the formate or reverse water-gas shift (RWGS) mechanisms on $\text{CuO-ZnO-ZrO}_2/\text{H-ZSM-5}$, while a distinct carbonate mechanism is activated on the oxidized $\text{Cu}(\delta^+)$ surface. Specifically, CO_2 dissociatively adsorbs as CO^* and O^* on $\text{Cu}^{\delta+}$, followed by further interaction with CO_2 to form carbonate intermediates. These intermediates undergo sequential hydrogenation steps to yield methoxy, highlighting the role of $\text{Cu}^{\delta+}$ in the reaction. Optimal conditions near 200 °C and 3 MPa resulted in 90 % DME selectivity and robust catalyst stability. However, higher pressures (>3 MPa) may accelerate DME

production but risk catalyst deactivation due to increased water partial pressure, which can oxidize active Cu sites [109]. Methanol synthesis was shown to rely on Cu^0 as the active site, with lower metal reduction temperatures preventing the formation of large Cu crystals. Liu *et al.* explored the effect of Zr doping on the reducibility and performance of CuO in the bifunctional $\text{CuO-Fe}_2\text{O}_3\text{-ZrO}_2/\text{H-ZSM-5}$ catalyst [73]. They found that adding 1 wt % ZrO_2 improved the dispersion and reducibility of CuO at lower temperatures while increasing the catalyst's surface area. Zr species were observed to interact with CuO and Fe_2O_3 , reducing the outer shell electron density of Cu^{2+} . This modification enhanced CO_2 conversion (28 %) and DME selectivity (64 %) at 260 °C and 3 MPa with a GHSV of 1500 $\text{mL g cat}^{-1} \text{h}^{-1}$ compared to undoped $\text{CuO-Fe}_2\text{O}_3/\text{H-ZSM-5}$. The strategic incorporation of ZrO_2 emerges as a promising approach for improving catalyst properties, including surface area, active site distribution, low-temperature reducibility, and high-temperature stability [110].

Fan *et al.* recently utilized atomic layer deposition (ALD) to develop an ultrathin ZrO_2 film on $\text{CuO/ZnO/Al}_2\text{O}_3$ and examined its impact on the catalytic performance of the $\text{CuO/ZnO/Al}_2\text{O}_3/\text{H-ZSM-5}$ system [111]. The catalyst achieved a maximum DME yield of 17.2 % at 240 °C and 2.8 MPa, which was attributed to the ZrO_2 -induced enhancement of oxygen vacancies, improved Cu thermal stability, and suppression of the RWGS reaction. Similarly, An *et al.* explored a simulated CO_2 hydrogenation process to optimize DME yield [112]. By integrating a physical mixture of $\text{CuO-ZnO-Al}_2\text{O}_3\text{-ZrO}_2$ and H-ZSM-5 catalysts with a recognized kinetic model, they demonstrated that CO recycling at the reactor inlet significantly boosted DME production while yielding a CO-free product by enhancing the space-time yield of DME. Frusteri *et al.* suggested that ZrO_2 plays a vital

role in activating adsorbed CO_2 , leading to the formation of CO_2^* species, which react with H_2^* to form intermediates such as formate, dioxomethylene, and methoxy, ultimately converting to methanol [76]. Additionally, Witoon *et al.* proposed that bicarbonate species derived from CO_2^* interact with H_2^* to produce methanol [113]. Catalysts such as CuO-ZnO-MnO and CuO-ZnO-ZrO₂ have demonstrated superior performance compared to CuO-ZnO-Al₂O₃ for hydrogenation of $\text{H}_2 + \text{CO} + \text{CO}_2$ feedstocks. While the CuO-ZnO-MnO catalyst is more cost-effective for hydrogenation of CO/CO₂ mixtures, CuO-ZnO-ZrO₂ excels in pure CO₂ hydrogenation applications [69]. Li and Chen further conducted an in-depth study of the synergistic effects of ZrO₂ and proposed strategies for enhancing the catalytic efficiency of ZrO₂-based catalysts in CO₂ hydrogenation to methanol [114].

2.3. Catalyst Properties Influencing DME Synthesis

2.3.1. Acidity

The acidity of the catalyst plays a pivotal role in the synthesis of DME, particularly in the methanol dehydration step. Both Bronsted and Lewis acid sites are instrumental in this process. Bronsted acid sites, which provide protons, facilitate the protonation of methanol, leading to the formation of reactive intermediates that are essential for the dehydration reaction. Meanwhile, Lewis's acid sites contribute by accepting electron pairs, thereby polarizing methanol molecules, and making them more susceptible to dehydration [115]. The strength and density of acid sites also significantly impact the yield of DME. Strong acid sites are effective in promoting dehydration reactions; however, they can also catalyze side reactions that lead to the formation of undesirable by-products [116].

Therefore, an optimal balance of acid strength is necessary to maximize DME yield while minimizing the formation of by-products.

Viscardi R. *et al.* (2020) investigated how surface acidity influences methanol dehydration to DME. Their findings demonstrated that a higher Brønsted acid site concentration leads to an increased DME yield, highlighting the importance of acid sites in the catalytic process. Since these catalysts exhibit comparable surface areas, variations in their performance are attributed to differences in surface acidity. At lower acidity levels, the DME yield rises gradually, whereas at higher acidity, especially at elevated temperatures, the yield increases more sharply. This trend is likely due to enhanced acid strength [117].

2.3.2. Metal Content and Dispersion

The metal content and dispersion within a catalyst significantly affects CO₂ activation during DME synthesis. The amount of metal loaded onto the catalyst surface influences the number of active sites available for the adsorption and activation of CO₂ [118]. Although high loading of copper (50–70 wt.%) is generally used in methanol synthesis processes, where the high metal loading can increase catalytic activity; however, it must be carefully controlled, as excessive loading may lead to particle agglomeration, reducing the effective surface area and, consequently, the overall catalytic performance [119]. Uniform dispersion of metal particles is essential to maximize the exposure of active sites and enhance the interaction between CO₂ and the catalyst surface. To ensure sustained catalytic activity, preventing metal sintering is crucial. Sintering leads to the growth of metal particles, which diminishes the active surface area and deactivates the catalyst over

time [120]. This challenge can be addressed by employing high-surface-area supports that stabilize the metal particles and inhibit their mobility. Additionally, using promoters that strengthen metal-support interactions can further mitigate sintering [121]. Optimized catalyst preparation methods, such as controlled calcination and reduction processes, also play a significant role in maintaining metal dispersion and preventing sintering, ensuring long-term catalyst stability and efficiency in DME synthesis. Frusteri *et al.* (2015) investigated the synthesis of DME through CO₂ hydrogenation. Their findings indicate that the catalyst composition (CuZnZr) influences both DME selectivity and overall catalytic activity [76]. The study examined CuO metal loadings ranging from 28 to 57 wt %. The catalyst's characteristics revealed that as CuO loading increased, the BET surface area declined from 158 to 145 m²/g, while the Cu surface area improved from 17 to 28 m²/g. Additionally, Cu dispersion decreased from 12.0 % to 9.5 %, leading to Cu particle growth from 85 to 110 Å. At a reaction temperature of 240 °C, CO₂ conversion increases with increase in loading within the range of 14.7 % to 18 %, depending on CuO loading, while methanol selectivity varied from 44.3 % to 51.1 %. These variations are attributed to differences in copper content, which also influence the metal surface area.

2.4. Process Conditions and Optimization

2.4.1. Temperature, Pressure & H₂/CO₂ Feed Ratio

The process conditions, particularly temperature and pressure, play a critical role in the efficiency and selectivity of CO₂ hydrogenation to DME. The reaction is overly sensitive to temperature, where an optimal range must be maintained to balance the kinetics of the reaction and the thermodynamic equilibrium [122]. Elevated temperatures generally favor the forward reaction of CO₂ hydrogenation, enhancing the conversion rate [123];

however, excessively elevated temperatures can lead to the formation of unwanted by-products, reducing DME selectivity [124]. Therefore, identifying an optimal temperature range is essential to maximize DME yield while minimizing side reactions.

Pressure is another significant factor that affects the reaction dynamics. Higher pressures typically increase the solubility of gases, thereby improving the contact between CO₂ and hydrogen with the catalyst surface. This leads to higher reaction rates and improved conversion efficiency [125]. However, operating at exceedingly high pressures can pose engineering challenges and may accelerate catalyst deactivation through sintering and coking.

The ratio of hydrogen to carbon dioxide (H₂/CO₂) is a critical parameter that significantly impacts the reaction efficiency and selectivity towards DME in the hydrogenation process. A higher H₂/CO₂ ratio generally enhances reaction efficiency by providing an excess of hydrogen, which drives the reaction towards the formation of methanol and subsequently DME. This ensures that CO₂ conversion is maximized, and the reaction equilibrium shifts favorably towards the desired product. However, an excessively high H₂/CO₂ ratio can lead to over-hydrogenation, producing unwanted by-products such as methane, thereby reducing the selectivity for DME.

CHAPTER 3

EXPERIMENTAL

This chapter outlines the materials, methods, and procedures employed to synthesize, characterize, and evaluate the catalytic performance of Cu-based mixed metal oxide catalysts for selective CO₂ hydrogenation. The catalysts were prepared using a surfactant-assisted co-precipitation technique, followed by comprehensive physicochemical characterization using various analytical tools. The catalytic activity was subsequently assessed in a fixed-bed reactor under controlled reaction conditions.

3.1. Materials and method

3.1.1. Chemicals

Cu(NO₃)₂·3H₂O (MW: 241.60 g/mol, assay: 98.0-103 %), Zn(NO₃)₂·6 H₂O (MW: 297.49 g/mol, assay: ≥ 99.0 %), CTAB (MW: 364.45 g/mol, assay: ≥ 99.0 %), and Na₂CO₃ (MW: 105.99 g/mol, assay: ≥ 99.0 %), all from Sigma-Aldrich, while CH₂OH.CH₂OH (ethylene glycol) (MW: 62.07 g/mol, assay: min. 95 %) from Ajax Chemicals, FeCl₂·4H₂O (MW: 198.81 g/mol, assay: ≥ 99.0 %) from Fluka, were purchased and kept in our lab. Each reagent was used exactly as received and was of analytical reagent excellence.

3.1.2. Catalyst preparation

Cu-based mixed metal-oxides catalysts were prepared using surfactant-assisted co-precipitation-method. First, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, in different specific molar ratio, were measured and combined in mixture of deionized water (60 mL) and ethylene glycol (20 mL). The mixture (each) was kept under stirring at 650 rpm (at 80 °C) for 60 min, after which a CTAB (0.7 %w/v) was gently added to each solution and allowed to stay for half an hour. Na_2CO_3 solution (prepared at different molarity, 0.10, 0.25, 0.40, 0.70, and 1.00 M) serving as a precipitating agent, was gently added dropwise. The precipitated solutions were variously obtained after a good 2 hrs. They were centrifuged and washed, dried in hot-oven at 105 °C overnight, and then calcined at 450 °C for 4 h, with 2 °C/min as the heating-rate. The catalyst (each) was denoted as CZF-x. While we kept the Cu, Zn, and Fe loadings to be constant, we assigned x to represent the molarity of the Na_2CO_3 (precipitating agent). Fig. 1 displayed how the synthesis was carried out.



Figure 4 Schematic representation of the catalyst preparation

3.2. Catalyst characterization

The catalysts were fully and well characterized, and explored by means of XRD, N_2 -sorption technique, H_2 -TPR, CO_2 -TPD, FTIR, SEM-EDS, and TEM.

3.2.1. X-Ray diffraction (XRD) analysis

XRD analyses were conducted to analyze crystalline-phases and diffraction-patterns of CZF-x catalysts. Analyses were carried out at ambient temperature using monochromatic Cu K_α radiation as the source ($\lambda = 1.5418 \text{ \AA}$), voltage of 40 kV, current of 40 mA, and scan rate of 3 °/min. The diffraction patterns were gradually recorded between a scan angle (2θ °) range of 5-80 °. Bruker-D2-Phaser 2nd Generation (Advanced diffractometer, Bruker, Karlsruhe, Germany) was used to record the XRD data.

3.2.2. Nitrogen adsorption-desorption analysis

Quantachrome instruments (Autosorb iQ-XR-XR (2 Stat.) Viton) were employed to analyze surface-area and porosity of catalysts using N₂-adsorption-desorption analysis at -196 °C. While determining pore-size and specific-surface-area, two-models were utilized, i.e., BJH and BET, respectively. Before the analysis, each catalyst was fully pretreated at 250 °C for 180 min.

3.2.3. SEM-EDX analysis

SEM analysis was performed to know morphologies of the catalysts. Quattro ESEM (Thermo-Fisher-Scientific, Oxford Inc.) was utilized while obtaining micrographs of the catalysts. The catalysts were sprinkled on top of carbon tape to obtain the SEM micrographs. Energy-dispersive X-ray spectroscopy (EDX) for elemental compositional mapping was also conducted.

3.2.4. TEM analysis

While studying catalyst morphology and structure, TEM (Transmission Electron Microscopy), a power imaging technique, was used. Specifically, JEOL JEM-F200 (200 kV, FE-TEM), a multi-purpose electron microscope was employed.

3.2.5. FT-IR analysis

FT-IR analysis was conducted at ambient temperature to determine catalysts' structural-and-compositional properties. FT-IR spectrometer (NICOLET iS10) was used after the samples were well prepared and subsequently compacted into disc for analysis.

3.2.6. H₂-TPR analysis

Catalysts-reduction-temperature was examined via H₂-TPR (MicrotracBEL, Catalyst analyzer BELCAT II). Each catalyst (50 mg) was put in U-shaped glass-tube reactor and pretreat under an argon (Ar) flow-rate of 50 mL min⁻¹ at 250 °C for 56 min. After treatments, catalysts were cooled-down to room-temperature, and 10 % (v/v) H₂ in Ar was then delivered to reactor at flow-rate of 50 mL min⁻¹. The catalysts were heated-up to 600 °C at a ramp rate of 10 °C min⁻¹. TCD was used to monitor amount of H₂-consumption.

3.2.7. CO₂-TPD analysis

Using BELCAT-device (MicrotracBEL, Catalyst analyzer BELCAT II), CO₂-TPD-analysis was undertaken in order to assess basicity and surface-properties of the catalysts. Before the analysis, 50 mg of catalyst, each, was pretreated at 250 °C for 56 min using He at 50 mL/min flow-rate, later cooled to 50 °C before introducing a stream of CO₂ (10 mL/min) and sustained for 46 min. Flow of He (40 mL/min) gas was injected while slowly decreasing temperature to 50 °C to remove remaining-CO₂. Catalysts were heated up to 600 °C at a ramp-rate of 10 °C min⁻¹, while continuously recording TCD-signal.

3.3. Catalyst test and performance evaluation

Catalytic-performances of catalysts were evaluated for CO₂ hydrogenation to oxygenates after they been assessed using fixed-bed-flow-reactor with internal-diameter of 9 mm. The reactor is fitted with gas chromatograph (Agilent 8890 GC) for an online analysis of the catalyst. Typically, in the experiment, 0.5 g (each) of the catalysts were loaded into reaction-tube and secured with quartz wool. Prior to the reaction, a mixture of N₂/H₂ = 9 was used to pretreat and reduce the-catalyst under ambient-pressure at 350 °C

for 2 h with a H_2 flow-rate of 50 mL min^{-1} . The reactor was then cooled to the reaction-temperature, 280°C , and feed gas was introduced at pressure of 30 bar and a space-velocity of $3000 \text{ mL g}^{-1} \text{ h}^{-1}$. The feed gas consisted of a mixture of CO_2 and H_2 in a molar-ratio of 3.

For the product-analysis, Agilent 8890 GC-online gas-chromatograph was employed. The reactor product-stream flushed through GC's loop after passing fully-through heated transfer-line that was kept-at 120°C and led to gas-chromatograph. 2 FIDs and 2 TCD, calibrated for every component under analysis, were installed on the four independent channels that made up the GC. The FIDs were set up for independent analysis of hydrocarbons and oxygenates. While the TCDs were used to analyze permanent gases. Product selectivity was evaluated, frequently, for minimum of 3 h. The equations (1, 2, and 3) shown below were used to evaluate CO_2 -conversion, CO-selectivity, and hydrocarbon-selectivity, respectively [126].

$$CO_2 \text{ conversion (\%)} = \frac{CO_{2in} - CO_{2out}}{CO_{2in}} * 100 \quad (1)$$

$$CO \text{ selectivity (\%)} = \frac{CO_{2out}}{CO_{2in} - CO_{2out}} * 100 \quad (2)$$

$$Hydrocarbon \text{ selectivity (\%)} = \frac{\text{mole of } Ci \text{ produt} * i}{\sum_{i=1}^n \text{mole of } Ci \text{ produt} * i} * 100 \quad (3)$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Catalyst characterization

4.1.1. XRD analysis

The crystalline phases of the synthesized Cu/Zn/Fe (CZF) catalysts prepared using varying concentrations of the precipitating agent were analyzed by X-ray diffraction (XRD), as shown in Figure 5. The XRD patterns reveal the presence of distinct reflections corresponding to CuO (JCPDS No. 45-0937), ZnO (JCPDS No. 36-1451), [127], and α -Fe₂O₃ (JCPDS No. 33-0664) [128] confirming the formation of mixed metal oxide phases in all samples. All the catalysts exhibit diffraction peaks at 2θ values of approximately 31.8 °, and 36.3 °, which are characteristic of the (100), and (101) planes of hexagonal wurtzite ZnO. Peak at 38.7 ° is attributed to the (111) planes of monoclinic CuO [129], whereas reflections at 33.0 °, 49.5 °, and 64.1 ° correspond to α -Fe₂O₃. The presence of these phases across all samples indicates the successful incorporation of the three metal components. In response to incorporating Cu to the ZnO lattice, ZnO diffraction peaks shifted towards higher angles, suggesting lattice contraction [130].

However, significant differences in peak intensity and sharpness were observed as a function of the precipitating agent concentration. As the concentration increased from 0.10 M to 1.00 M, a gradual sharpening and intensification of the CuO and ZnO diffraction peaks were observed. This indicates an enhancement in crystallinity and possibly an

increase in crystallite size. The CZF-1.00 catalyst, prepared using 1.00 M precipitating agent, displayed relatively intense and well-defined peaks, suggesting a high degree of crystallinity and better phase segregation compared to other samples. In contrast, the CZF-0.10 catalyst exhibited relatively less intense peaks, indicative of lower crystallinity and possibly amorphous or poorly developed phases.

The improved crystallinity in CZF-1.00 may be attributed to the higher concentration of hydrogencarbonate ions during precipitation, which promotes faster nucleation and crystal growth. Enhanced crystallinity is often associated with improved thermal stability and structural integrity of the active phase, which are critical for catalytic performance. Moreover, the prominent CuO peaks observed in CZF-1.00 suggest better dispersion and availability of the active Cu species, which play a crucial role in redox-based catalytic reactions. The increased intensity of ZnO reflections further implies a supportive role in stabilizing CuO dispersion and maintaining the structural framework of the catalyst. These structural improvements are likely to contribute to the superior catalytic activity of the CZF-1.00 catalyst. The strong metal–support interaction, optimal crystallite size, and well-defined phase composition enhance the redox behavior and facilitate the accessibility of active sites, thereby improving overall catalyst performance.

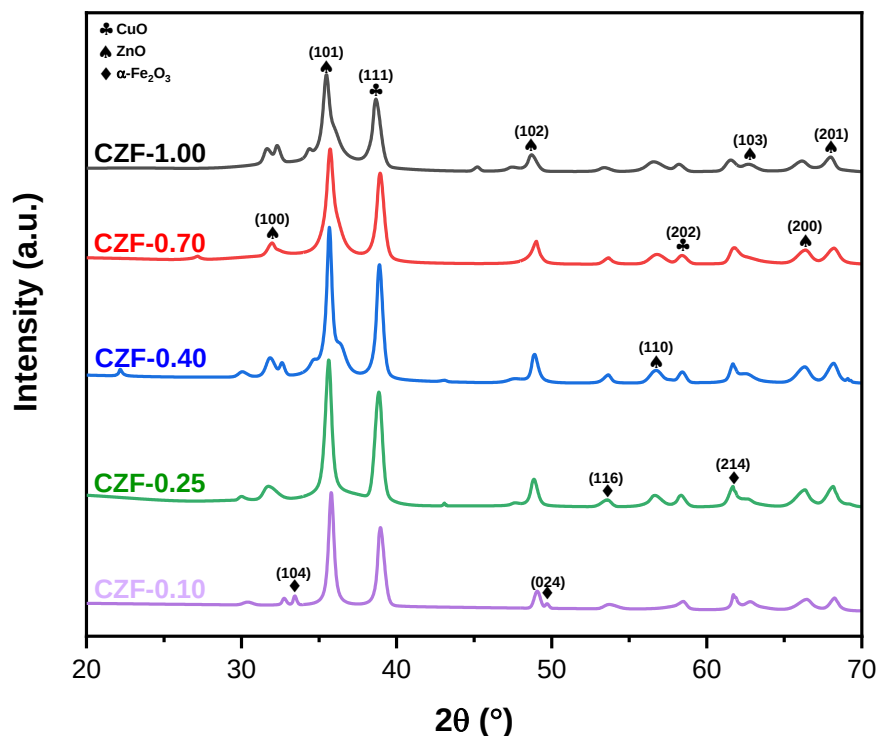


Figure 5 XRD pattern of the catalysts

4.1.2. N₂-adsorption-desorption analysis

The textural characteristics of the CZF (Cu/Zn/Fe) catalysts synthesized using varying concentrations of the precipitating agent were investigated by nitrogen adsorption–desorption isotherms and are summarized in Table 2. The corresponding isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution plots are presented in Figure 6(a) and 6(b), respectively.

All the catalysts exhibit type IV isotherms (Figure 6a) with H₃-type hysteresis loops, characteristic of mesoporous materials with slit-like pores. The pore size distribution

curves (Figure 6b) reveal that all samples possess a dominant mesopore structure, with average pore diameters ranging from approximately 8.91 to 10.43 nm. These mesoporous features are essential for facilitating effective mass transfer during catalytic reactions, especially for reactions involving bulky molecules.

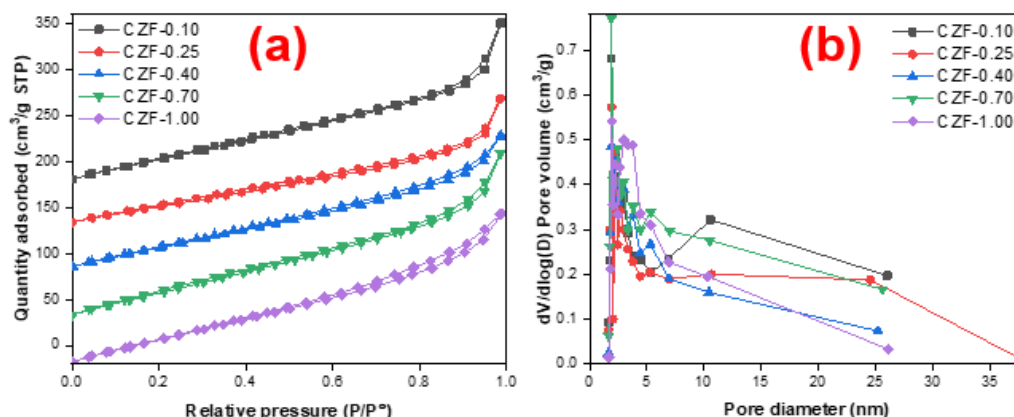


Figure 6 N₂-adsorption-desorption isotherms (b) pore-size-distribution

The surface area, total pore volume, and average pore diameter show noticeable variations as a function of the precipitating agent concentration. The CZF-0.25 catalyst exhibited the lowest surface area (81 m²/g) and smallest pore volume (0.211 cc/g), indicating a less porous structure and a possible collapse or blocking of pores during synthesis. On the other hand, the CZF-0.70 catalyst, prepared using 0.70 M concentration of the precipitant, exhibited the highest surface area (114 m²/g), followed closely by CZF-1.00 (113 m²/g). Both catalysts also presented relatively high pore volumes (0.275–0.253 cc/g) and smaller average pore diameters (~9.7–8.9 nm), suggesting a well-developed mesoporous network with more accessible active sites.

Table 2 N₂ adsorption-desorption surface analysis summary

Catalyst	Surface	Total Pore	Average
	Area (m ² /g)	Volume (cc/g)	Pore Diameter (nm)
CZF-0.10	103	0.266	10.33
CZF-0.25	81	0.211	10.43
CZF-0.40	100	0.225	9.03
CZF-0.70	114	0.275	9.65
CZF-1.00	113	0.253	8.91

These observations suggest that a higher concentration of precipitating agent promotes better pore formation and prevents collapse or blockage of the porous framework, likely due to more rapid and uniform nucleation during co-precipitation. Furthermore, the slightly lower average pore diameter in CZF-1.00 could imply tighter pore distributions, which may enhance surface reactivity and diffusion-controlled processes during catalysis.

The superior catalytic activity observed for CZF-1.00 can be linked to its optimized textural properties. A high surface area increases the number of accessible active sites for the catalytic reaction, while an appropriate pore size ensures efficient reactant and product diffusion. The synergistic combination of high surface area, moderate pore volume, and narrower pore size distribution in CZF-1.00 provides an ideal environment for catalytic

performance, particularly in reactions involving redox or acid–base surface mechanisms. In contrast, the reduced surface area and broader pore size of CZF-0.25 and CZF-0.10 likely hinder active site accessibility and diffusion, thereby explaining their relatively lower catalytic performance. Notably, CZF-0.70 also displayed a comparable surface area to CZF-1.00; however, the slight differences in pore diameter and volume, in conjunction with possibly different crystallinity and metal dispersion (as seen from XRD), may contribute to its slightly reduced activity compared to CZF-1.00. These results underscore the fact that catalytic performance is a multifactorial outcome, dependent on a combination of textural, structural, and compositional factors.

4.1.3. SEM-EDX analysis

The surface morphology and nanostructure of Cu/Zn/Fe (CZF) catalysts synthesized via co-precipitation using varying concentrations of Na_2CO_3 (1.00–0.10 M) were investigated using scanning electron microscopy (SEM). These catalysts, labeled CZF-x (where x denotes the molar concentration of Na_2CO_3), displayed dramatic morphological evolution with changing precipitation conditions, directly influencing their catalytic activity in CO_2 hydrogenation to value-added products.

Among all, CZF-1.00 (Figure 7a), synthesized using 1.00 M Na_2CO_3 , exhibited the most favorable morphology, a well-defined hierarchical structure composed of densely packed nanosheets and nanorods, radiating outward in a flower-like architecture. This type of morphology is generally formed under high supersaturation conditions that favor anisotropic growth and high nucleation density, producing uniform nanostructured aggregates with enhanced surface area and porosity. Such intricate structures are beneficial for catalysis because they increase the number of accessible active sites, enhance reactant

diffusion, and potentially stabilize active phases during reaction [131]. The high surface area of CZF-1.00, together with the intimate contact between Cu, ZnO, and FeO_x phases, facilitates synergistic interactions among the metal components. Copper is known for its key role in CO₂ activation and hydrogenation to methanol, ZnO enhances Cu dispersion and electronic interaction, while iron can promote C–C coupling reactions necessary for the formation of C₂ products [132–134]. The architecture of CZF-1.00 enhances these interfacial interactions, which explains its superior performance in converting CO₂ to mixed alcohols and DME.

In contrast, CZF-0.70 (Figure 7b) displayed more amorphous and aggregated morphologies, indicating insufficient nanostructure development. The irregular, bulky particles lack porosity and textural uniformity, limiting the exposure of active sites and reducing diffusion pathways for gaseous reactants. Such morphologies typically result from lower nucleation rates and less controlled precipitation, leading to catalyst deactivation through sintering and poor metal dispersion [135]. CZF-0.40 (Figure 7c) retained some degree of particle dispersion but primarily featured irregular, spherical nanoparticles loosely aggregated without any observable structural hierarchy. The reduced particle uniformity and low porosity suggest diminished accessibility of active centers, which is detrimental for sustained CO₂ conversion [136]. CZF-0.25 (Figure 7d) presented larger granular structures with few isolated needle-like features, indicating a mixed and partially phase-separated morphology. This can limit contact between Cu and Zn/Fe phases, weakening the synergistic effects essential for high activity and selectivity in CO₂ hydrogenation.

Also, CZF-0.10 (Figure 7e) exhibited densely packed spherical particles with severe agglomeration and minimal surface texturing. These particles likely suffered from poor metal dispersion and minimal porosity, both of which drastically reduce catalytic efficiency and stability. This morphology is typical when precipitation occurs under low carbonate concentrations, where the driving force for homogeneous nucleation is insufficient. As expected, CZF-0.10 demonstrated the poorest performance in the series. The strong correlation between morphology and catalytic performance confirms the importance of morphological control via synthesis parameters. High carbonate concentrations promote the formation of nanostructured, porous frameworks with high metal dispersion, which are essential for efficient CO₂ hydrogenation. In particular, the flower-like nanostructure of CZF-1.00 provides not only high surface area but also thermally robust architecture that prevents catalyst deactivation during prolonged reactions. These findings highlight the crucial role of precipitant concentration in tailoring catalyst nanostructure and functionality for CO₂ valorization.

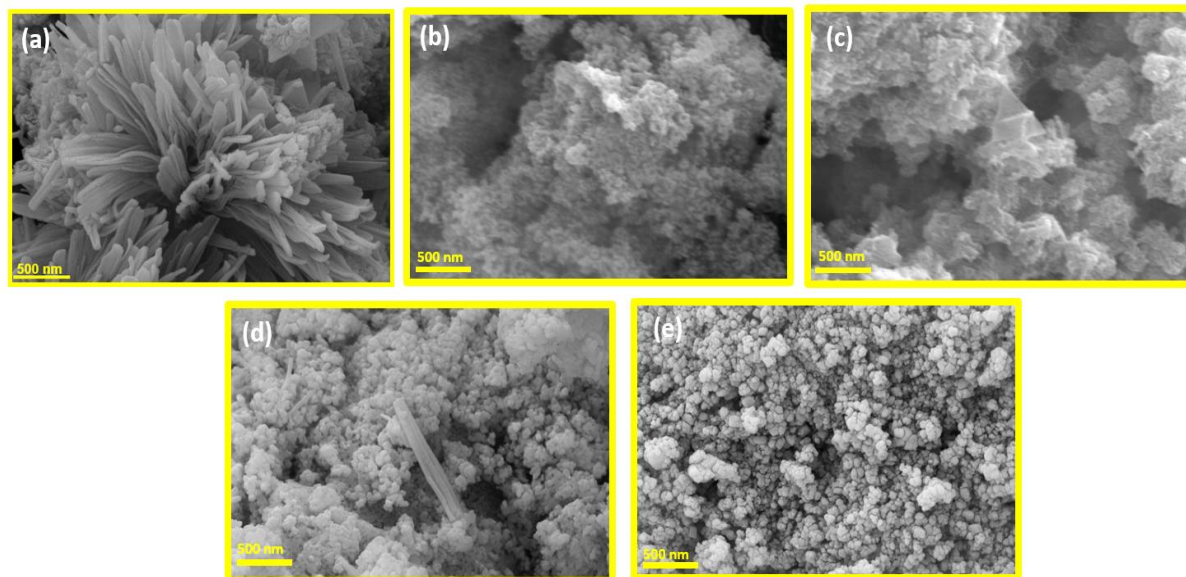


Figure 7 SEM images of Cu/Zn/Fe (CZF-x) catalysts synthesized via co-precipitation using varying concentrations of Na_2CO_3 as precipitant: (a) CZF-1.00, (b) CZF-0.70, (c) CZF-0.40, (d) CZF-0.25, and (e) CZF-0.10

Furthermore, Figure 8a–e displays the energy-dispersive X-ray (EDX) spectrum and elemental mapping results (Figure 9a–o) for the prepared catalysts, CZF-1.00 (Figure a–c), CZF-0.70 (Figure d–f), CZF-0.40 (Figure g–i), CZF-0.25 (Figure j–l), and CZF-0.10 (Figure m–o). The EDX spectrum clearly shows characteristic peaks corresponding to copper (Cu), zinc (Zn), and iron (Fe) in all samples, confirming the absence of any other detectable elemental impurities. The elemental mapping analysis further supports these findings, revealing a highly uniform and well-dispersed distribution of Cu, Zn, and Fe throughout the nanocomposite structures. This homogeneous dispersion of elements is critical for ensuring consistent catalytic performance and highlights the effectiveness of the synthesis method in achieving a well-integrated composite material.

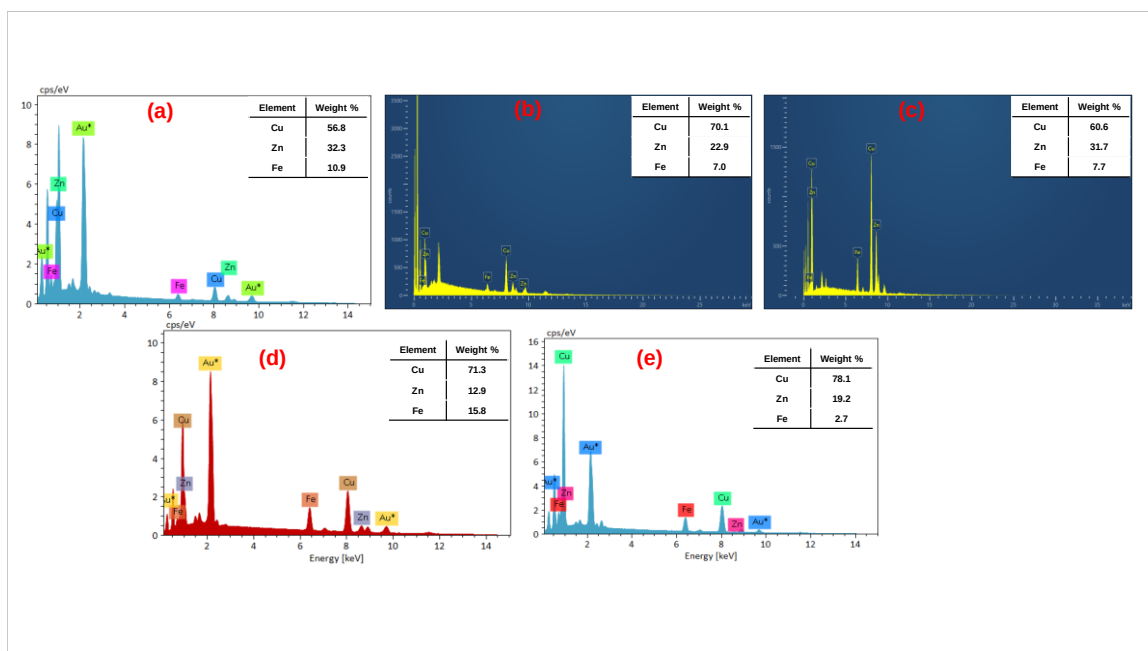


Figure 8 EDX analyses of Cu/Zn/Fe (CZF-x) catalysts synthesized via co-precipitation using varying concentrations of Na_2CO_3 as precipitant: (a) CZF-1.00, (b) CZF-0.70, (c) CZF-0.40, (d) CZF-0.25, and (e) CZF-0.10

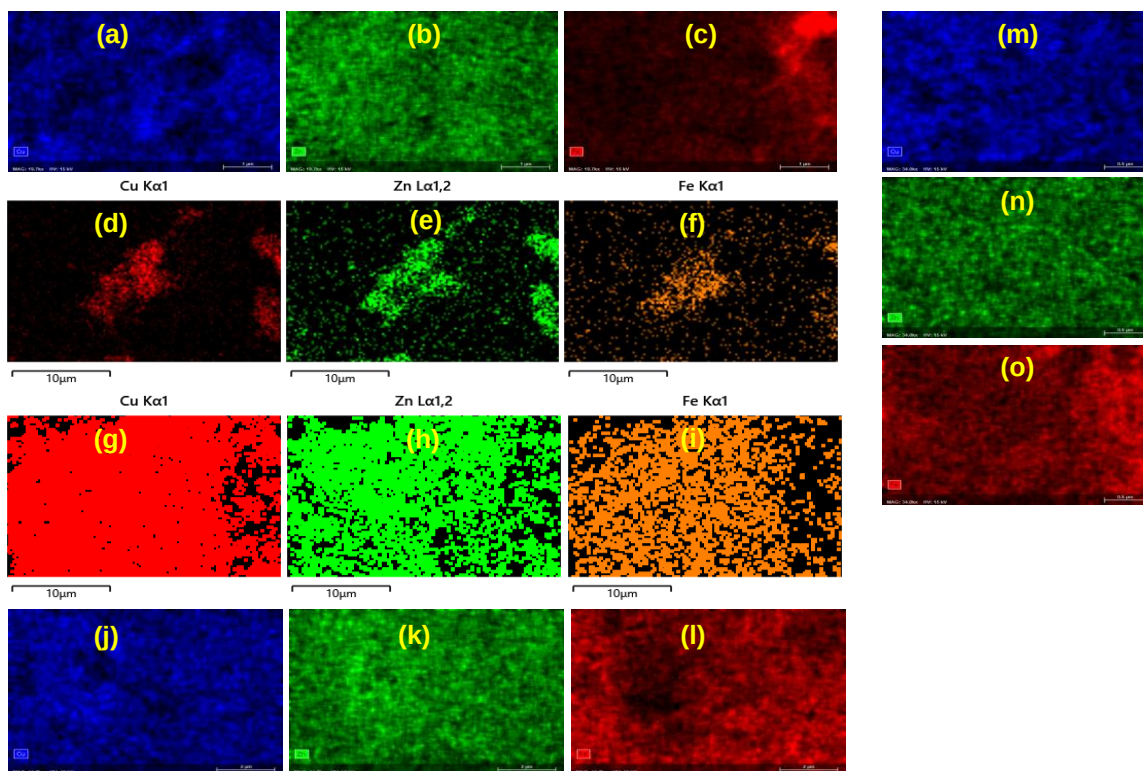


Figure 9 EDX mapping analyses of the prepared catalysts. (a-c) CZF-1.00, (d-f) CZF-0.70, (g-i) CZF-0.40, (j-l) CZF-0.25, and (m-o) CZF-0.10

4.1.4. TEM analysis

Transmission electron microscopy (TEM) analysis offers valuable insights into the morphology, particle size, and dispersion behavior of the CZF (Cu/Zn/Fe) catalysts synthesized using different Na_2CO_3 precipitant concentrations (Figure 10). CZF-1.00 (Figure 10a–c) exhibits uniformly dispersed nanoparticles with excellent structural homogeneity and minimal aggregation. The histogram in Figure 10c reveals an average particle size of 5.50 ± 0.17 nm, indicating tight control over nucleation and growth. This nanoscale dimension, combined with good dispersion, facilitates a higher density of accessible active sites—crucial for enhanced CO_2 hydrogenation activity [95].

CZF-0.70 (Figure 10d–f) shows a moderate increase in particle size, averaging 7.02 ± 1.10 nm as per panel (f). While the nanoparticles remain relatively well-dispersed, the broader distribution and slightly larger size suggest reduced control over the precipitation process. These features could reduce surface-active area and impair catalytic uniformity compared to CZF-1.00 [133]. CZF-0.40 (Figure 10g–i) displays a similar size range, with an average diameter of 7.59 ± 0.69 nm (Figure 10i). Despite comparable particle dimensions to CZF-0.70, the dispersion appears somewhat inferior, and certain regions show incipient aggregation. These structural imperfections may translate into less consistent catalytic performance [133].

In CZF-0.25 (Figure 10j–l), the particle size increases dramatically, reaching 9.08 ± 0.81 nm (Figure 10l). The micrographs show dense clustering and poor nanoparticle separation, indicating substantial agglomeration. Such a large particle size reduces the surface-to-volume ratio and limits exposure of catalytic sites, often resulting in reduced activity and selectivity for CO_2 hydrogenation [41]. Interestingly, CZF-0.10 (Figure 10m–o) shows a

return to a smaller average size of 5.01 ± 0.39 nm (Figure 10o), similar to CZF-1.00. However, despite the small particle size, the TEM images show non-uniformity in distribution and a tendency toward localized agglomeration. This suggests that while size control may be achievable at low carbonate concentrations, uniformity and stabilization of particles remain challenges, likely due to insufficient carbonate availability during precipitation. These observations clearly illustrate that both particle size and dispersion are sensitive to the carbonate concentration used during synthesis. Among all samples, CZF-1.00 not only achieved small and most uniform particles but also shows superior dispersion. This microstructural quality is strongly correlated with its enhanced catalytic performance in CO₂ hydrogenation to value-added products.

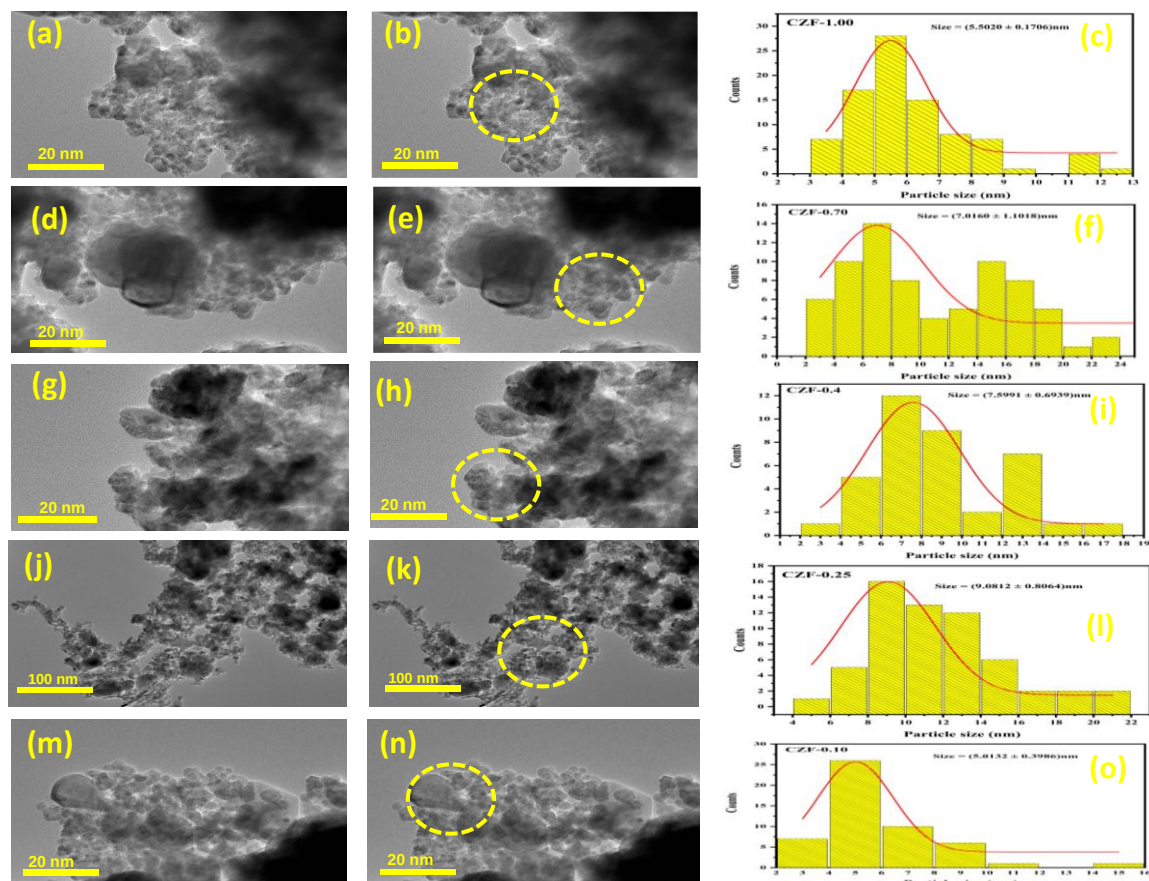


Figure 10 TEM image of the prepared catalysts. (a-c) CZF-1.00, (d-f) CZF-0.70, (g-i) CZF-0.40, (j-l) CZF-0.25, and (m-o) CZF-0.10

4.1.5. FT-IR analysis

- The functional groups of the catalysts were characterized using FT-IR spectroscopy in the $1500\text{--}500\text{ cm}^{-1}$ range (Figure 11). Distinct bands at 875 cm^{-1} and 595 cm^{-1} were assigned to the stretching vibrations of Cu–O and Zn–O bonds, respectively [137]. Additionally, an absorption peak near 570 cm^{-1} corresponded to $\text{Fe}^{2+/3+}\text{--O}^{2-}$ stretching modes, confirming the presence of a magnetite (Fe_3O_4) phase [138]. This finding aligns with XRD results, where the 570 cm^{-1} band was specifically attributed to $\text{Fe}^{3+}\text{--O}^{2-}$ stretching in the crystalline phase. Beyond the metal-oxygen vibrations, a broad O–H stretching band (centered at $\sim 3450\text{ cm}^{-1}$, range: $2900\text{--}3650\text{ cm}^{-1}$) was observed.

Notably, the CZF-1.00 catalyst exhibited weaker O–H intensity compared to others, likely due to dehydroxylation or neutralization by residual Na^+ ions from Na_2CO_3 during calcination. Furthermore, vibrational peaks between $1200\text{--}1700\text{ cm}^{-1}$ indicated carbonate species formed via CO_2 chemisorption on the catalyst surface [128]. Such carbonates typically exist as unidentate, bidentate, bicarbonate, or free carbonate structures on basic solids [139].

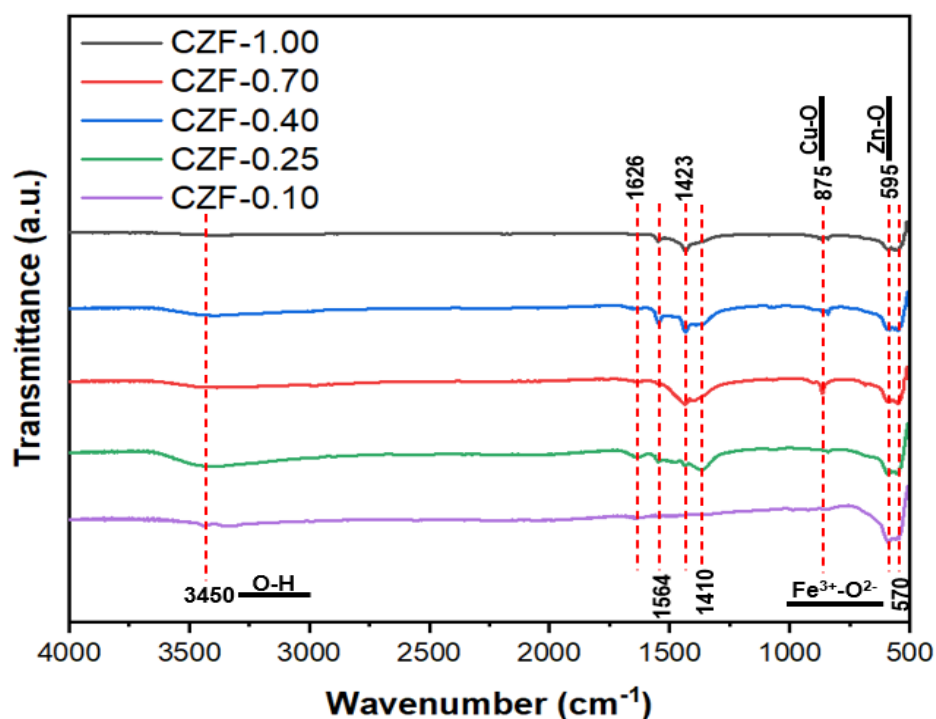


Figure 11 FT-IR spectra of the catalysts

5.1.1. H_2 -TPR analysis

The temperature-programmed reduction (H_2 -TPR) profiles of the CZF catalyst series ($\text{Cu}:\text{Zn}:\text{Fe} = 60:30:10$) synthesized with varying concentrations of sodium carbonate (Na_2CO_3) as the precipitating agent are shown in Figure 12. The corresponding reduction peak temperatures (T_{max}) and quantitative H_2 uptake values are tabulated in Table 3. All

catalysts exhibit multiple reduction peaks, indicating the stepwise reduction of metal oxide species. These are attributed to the sequential reduction of $\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$ and possible partial reduction of Fe and Zn species. Notably, the position, intensity, and quantity of H_2 consumed vary significantly with the Na_2CO_3 concentration, highlighting the influence of synthesis conditions on the reducibility and metal dispersion.

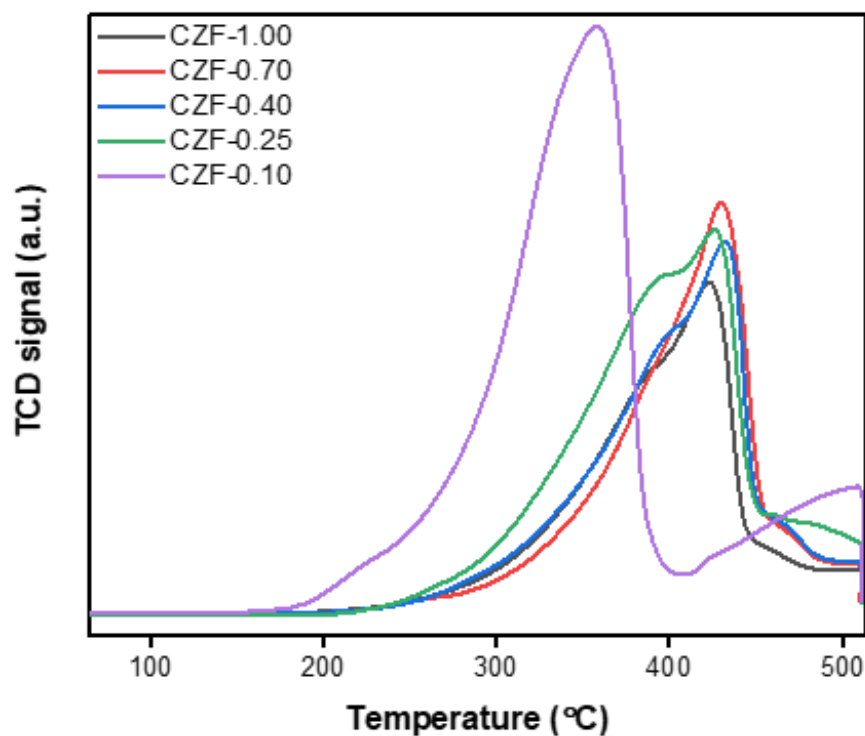


Figure 12 H_2 TPR profile of the catalysts

CZF-1.00 displays well-resolved reduction peaks centered at 396 °C and 425 °C, with minor peaks at 446 °C and 508 °C, indicating a relatively moderate-to-strong metal–

support interaction. The total H₂ consumption is 1.205 mmol/g, mainly dominated by the low-temperature peak at 396 °C (0.858 mmol/g). This suggests the presence of highly dispersed and readily reducible CuO species, which are beneficial for H₂ activation [140]. The moderate temperatures and sharper profiles imply a good balance between metal accessibility and stability, which likely contributes to the superior catalytic activity observed in this catalyst.

While in the case of CZF-0.70 and CZF-0.40, the catalysts exhibit similar TPR behavior with dominant peaks at ~ 429 °C (CZF-0.70) and ~ 404 °C (CZF-0.40). Both catalysts show higher total H₂ uptakes (1.464 and 1.553 mmol/g, respectively) than CZF-1.00. However, the major reduction peaks appear at higher temperatures, suggesting stronger metal–support interactions or agglomerated CuO species. Although the hydrogen uptake is high, the delayed reducibility could hinder the timely formation of active Cu⁰ species under reaction conditions, possibly explaining their inferior performance compared to CZF-1.00.

Table 3 Total H₂ consumption on various peak position

Catalyst	T _{max} (°C)	Total H ₂ consumed (mmol/g)
CZF-1.00	396	0.858
	425	0.299
	446	0.043
	508	0.005
CZF-0.70	429	1.464
	508	0.014
CZF-0.40	404	1.234
	434	0.312
	465	0.007
	508	0.007
CZF-0.25	405	1.713
	429	0.238
	451	0.004
	506	0.025
CZF-0.10	237	0.116
	357	2.707
	406	0.005
	483	0.029

Moreover, CZF-0.25 catalyst exhibits a sharp peak at 405 °C with the high total H₂ consumption (1.980 mmol/g). While this indicates a high metal loading or increased reducibility, the elevated reduction temperature implies strong metal–support interactions that may inhibit full reduction during actual reaction temperatures. Moreover, the presence of a shoulder peak at 429 °C and additional minor peaks at 451 °C and 506 °C hints at a

heterogeneity in the metal oxide phases, potentially leading to less uniform active sites. Unlike CZF-0.10 catalyst, which interestingly presents a unique low-temperature reduction feature at 237 °C and a prominent peak at 357 °C, with a notably high H₂ uptake of 2.857 mmol/g, the highest among all samples. However, this sample showed the poorest catalytic performance, which suggests that mere hydrogen consumption capacity is not directly proportional to activity. The low-temperature peaks likely correspond to bulkier or less stable CuO particles, which may be prone to sintering or poor metal-support contact. Additionally, weakly bound Cu species might lead to poor catalytic stability.

5.1.2. CO₂-TPD analysis

The CO₂-temperature programmed desorption (CO₂-TPD) analysis was conducted to probe the surface basicity of the CZF catalyst series, comprising Cu, Zn, and Fe in a fixed molar ratio (6:3:1), synthesized using varying concentrations (0.10–1.00 M) of Na₂CO₃ as the precipitating agent. This technique is vital for elucidating nature, strength, and distribution of basic-surface sites, which are known to significantly influence catalytic performance in reactions involving CO₂ activation or intermediate stabilization, such as methanol synthesis, WGS (water-gas shift), or dry reforming. CO₂ adsorption is important for the hydrogenation reaction of CO₂. Figure 13 displays the CO₂-TPD profiles of the catalysts, and Table 4 summarizes the desorption maxima and the corresponding CO₂ quantities desorbed. All samples exhibited multiple desorption peaks, indicating the presence of a distribution of basic sites of different strengths. The Low-temperature peaks, 100–200 °C, correspond to weak basic sites, typically for surface hydroxyls and bicarbonates. Medium-temperature peaks 200–350 °C are associated with moderate basic

sites, such as metal–oxygen pairs, whereas high-temperature peaks $> 350\text{ }^{\circ}\text{C}$ are indicative of strong basic sites, often attributed to lattice oxygen or less-coordinated oxide ions (O_2^-) species [141].

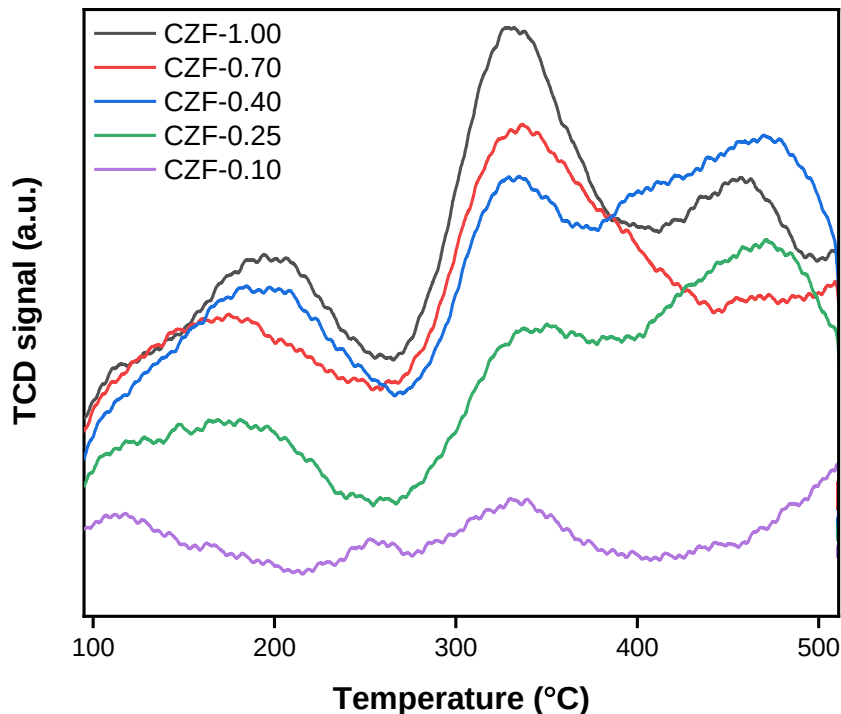


Figure 13 CO_2 TPD profile of the catalysts

The concentration of Na_2CO_3 during co-precipitation had a pronounced effect on the nature and density of basic sites: for catalyst CZF-1.00 (1.00 M Na_2CO_3), exhibited three distinct desorption peaks at $193\text{ }^{\circ}\text{C}$, $326\text{ }^{\circ}\text{C}$, and $462\text{ }^{\circ}\text{C}$, corresponding to weak, moderate, and strong basic sites, respectively. Although the total CO_2 desorbed (0.009 mmol/g) is slightly lower than CZF-0.70 (0.014 mmol/g), CZF-1.00 has a higher intensity of medium-strength

basic sites (0.006 mmol/g at 326 °C), which are typically the most catalytically relevant for CO₂ activation.

Table 4 CO₂-TPD data

Catalyst	T _{max} (°C)	Total CO ₂ desorbed (mmol/g)
CZF-1.00	193	0.002
	326	0.006
	462	0.001
CZF-0.70	141	0.007
	335	0.007
CZF-0.40	183	0.004
	325	0.002
	469	0.003
CZF-0.25	145	0.006
	332	0.002
	470	0.002
CZF-0.10	111	0.002
	329	0.001

While in the case of CZF-0.70 (0.70 M) catalyst, it also shows two strong desorption peaks at 141 °C and 335 °C, with the highest total CO₂ desorption (0.014 mmol/g), primarily due to high weak-to-moderate basic site content. However, the absence of a high-temperature peak suggests a lack of strong basic sites, which may limit stability or activity in reactions requiring stronger adsorption energies. But on the other hand, catalysts CZF-0.40 and CZF-

0.25 displayed broader and less intense desorption peaks, indicating reduced basicity. The total CO₂ desorption decreased progressively with lower Na₂CO₃ concentrations, suggesting incomplete precipitation or reduced formation of surface-active phases. Similarly, CZF-0.10 catalyst showed the weakest basic site distribution with low-intensity desorption peaks centered around 111 °C and 329 °C. The total desorbed CO₂ (0.003 mmol/g) confirms that low Na₂CO₃ concentrations yield poorly structured or underdeveloped basic surfaces.

In contrast, CZF-1.00, despite not having the absolute highest total CO₂ desorption, clearly demonstrates the most balanced distribution of weak, moderate, and strong basic sites, particularly the prominent moderate basic site peak at 326 °C. This is significant because moderate basic sites strike the best compromise between CO₂ adsorption strength and surface reactivity, thereby facilitating improved CO₂ activation via reversible adsorption, stabilization of key intermediates (e.g., formate) without site blocking, enhanced metal-support synergy, particularly with dispersed Zn species. Furthermore, CZF-0.70's basicity is skewed toward weaker sites, which, although abundant, may lead to insufficient activation energy for certain reactions, explaining its lower catalytic activity compared to CZF-1.00. The poor basicity and lack of well-defined medium/strong sites in CZF-0.40, CZF-0.25, and CZF-0.10 are consistent with their inferior catalytic performance, reinforcing the importance of optimal precipitation conditions (i.e., 1.00 M Na₂CO₃) in generating a highly basic, catalytically active surface.

5.2. Catalyst test and performance evaluation

CO₂-hydrogenation-process was performed on the catalysts and results have been portrayed in Figure 14-15. CO₂-conversion, product-selectivity, and hydrocarbon-distribution of different catalysts are tabulated (summarized) in Table 5. Principal-output comprises predominantly of oxygenates (ethanol, C₂+ alcohol, and methanol), which are highly valuable products. Other valuable oxygenates obtained include DME and diethyl ether. CO and some hydrocarbons were also being obtained. When employing the CZF-1.00 catalyst, total oxygenates-selectivity reaches 83.7 % with a CO₂-conversion rate of 17.7 %. CZF-1.00 based on precipitant concentration (1.00 M) demonstrates reasonable-level of performance. This observation corresponds with recent studies suggesting low-catalytic performance in turning CO₂ into oxygenates [142,143]. However, CO₂ conversion and total oxygenates selectivity decreased evidently as the precipitant-concentration was changed from 1.00 M in CZF-1.00 to 0.70 M in CZF-0.70 as can vividly be seen in Table 5.

Furthermore, we notice that further changes in precipitant concentration in CZF-0.40 and CZF-0.25 came with an improved CO₂ conversion and total oxygenates selectivity in comparison with CZF-0.70, though they were lower than CZF-1.00 in terms of both the conversion and selectivity. And as we decreased the precipitant concentration again, we clearly observed another change in CO₂ conversion rate, a decrease, to be specific. Although CZF-0.10 has the lowest CO₂ conversion rate, the catalyst, CZF-0.10, displayed an outstanding total oxygenates selectivity and very minimal CO selectivity as clearly tabulated in Table 5.

Moreover, the CO₂ conversion and product selectivity observed throughout this CO₂ hydrogenation process were attributed to many different contributory factors. Looking at CZF-1.00, having the highest CO₂ conversion percentage and a second-position in terms of total oxygenates selectivity, we can confidently claim some important attributes were behind the observed selectivity from methanol, 18.1 %, ethanol, 36.7 %, and higher alcohols, 22.8 %. First, the selectivity toward methanol may be attributed to the formation of methanol at Cu (111) phase as it has been reported that methanol formation is predominantly occurring at copper phase (111) [144]. And this can also be proven from the XRD pattern we have shown, which clearly displayed the presence of Cu (111) in our catalysts. Secondly, while methanol formation was successfully achieved, CO formation was also observed. Having the CO in this process has played a significant role in the formation of both ethanol and C₂₊ alcohols as susceptible C-C coupling was taken place within the reaction. And this can be attributed to the presence of Fe component in the catalyst that susceptible transform into metallic Fe and iron-carbide phases during the reaction. Presence of Fe-carbide will significantly facilitate C-C coupling [145]. CO is serving as an intermediate to both ethanol and higher alcohols [146], so, we can probably say that the CO formed within this reaction was utilized in C-C coupling to form ethanol and C₂₊ alcohols. In addition, DME and diethyl ether were also being obtained, though not significantly high. This could be due to the insufficient acidic functionality that can dehydrate the methanol form. Acidic function facilitates methanol dehydration to obtain DME [41] before achieving diethyl ether through C-C coupling by CO-insertion. Nevertheless, maintaining an appropriate proportions of Cu and Fe not only resulted in

oxygenates selectivity, but also in their yields as well displayed in Table 6. For example, C₂₊ alcohols and ethanol were 15.3 and 24.8 %, respectively.

Interestingly, the highest selectivity toward oxygenates was observed from CZF-0.10, amounting to 92.5 % as vividly shown in Table 5. However, the conversion of CO₂ was not significantly high, which may be due to the poor CO₂ activation associated with the fewer basic sites of the catalyst as clearly indicated by CO₂-TPD analysis we conducted. Despite the poor CO₂ activation from this catalyst, still, a reasonable amount of methanol was yielded, around 9.4 %, resulting in notable methanol selectivity of 30.7 %, which happen to be the highest methanol selectivity among all methanol selectivity from all the catalysts series. And this can be attributed to the reduction-temperature (350 °C, which correlates with its H₂ TPR profile) used while trying to reduce the main active metal (i.e Cu) into its metallic form of Cu (111) which is known for methanol formation as already highlighted. Similarly, from this same catalyst, CZF-0.10, the highest selectivity towards oxygenates was observed with C₂₊ alcohols, amounting to 51.6 % as clearly tabulated in Table 5. And this highest selectivity observed can also be associated with reduction-temperature used during the catalyst reduction. Reduction of Cu/Zn/Fe catalyst is highly recommended at 350 °C when the target products include C₂₊ alcohols [147].

Apart from the aforementioned products, hydrocarbons (HC) selectivity was also being realized, and was evenly distributed as illustrated in Figure 15 and tabulated in Table 7. Using 280 °C as our reaction temperature, a notable hydrocarbon selectivity was also achieved with CZF-0.70. It amounted to 30.2 % selectivity towards hydrocarbons. Specifically, CH₄ contribution from this selectivity (30 %) was the highest among all the hydrocarbons as clearly shown in Table 7. Although the conversion of CO₂ was not

significant from this catalyst, but still the catalyst gave a good hydrocarbons selectivity, which may be attributed to the fact that sometimes CO₂ methanation takes place at lower temperature as this highest selectivity was majorly contributed by CH₄ [148]. Moreover, the hydrocarbons selectivity of CZF-1.00 was lower than that of CZF-0.70, but its CO₂ conversion is far better. Therefore, 280 °C as the reaction temperature is deemed to be favoring more CO₂ activation in CZF-1.00 than in the other catalysts. However, it is favoring more hydrocarbons selectivity in CZF-0.70 than in the other catalysts.

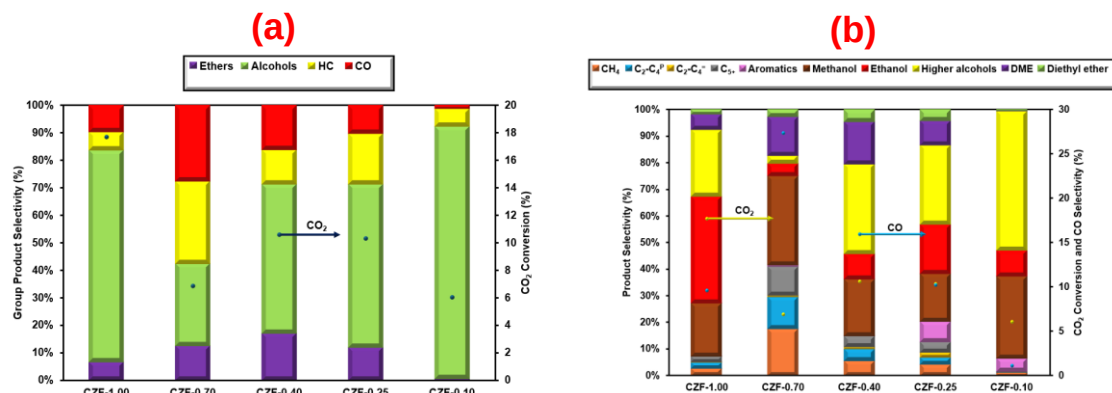


Figure 14 CO₂ hydrogenation on different Cu-based mixed metal oxides catalysts. Reaction conditions: Temperature = 280 °C, n (H₂)/n (CO₂) = 3 (molar ratio), Pressure = 30 bar, 0.5 g catalysts loading, and a space velocity of 3000 mL g⁻¹ h⁻¹. (a) group product selectivity (b) individual product selectivity

Table 5 Catalysts' performance and productivity

Catalyst	CO ₂ Conv. (%)	Oxygenate Sel. (%)					Total Sel. (%)	HC Sel. (%)	CO Sel. (%)
		Ethers		Alcohols					
		DME	Diethyl ether	MeOH	EtOH	C ₂ + alcohols	Oxygenates		
CZF-1.00	17.71	5.17	1.44	18.13	36.17	22.83	83.74	6.66	9.59
CZF-0.70	6.87	10.57	1.85	24.41	3.39	2.23	42.45	30.21	27.35
CZF-0.40	10.60	13.34	3.76	17.86	8.13	28.28	71.37	12.69	15.96
CZF-0.25	10.30	8.31	3.61	16.17	16.59	26.70	71.38	18.42	10.21
CZF-0.10	6.04	0.18	0.30	30.74	9.59	51.65	92.46	6.44	1.11

Table 6 Product yield obtained via the catalytic hydrogenation of CO₂

Catalyst	CO ₂ Conv. (%)	Oxygenate Yield (%)					HC Yield (%)	CO Yield (%)
		Ethers		Alcohols				
		DME	Diethyl ether	MeOH	EtOH	C ₂ + alcohols		
CZF-1.00	17.71	3.45	0.97	12.12	24.18	15.26	4.46	6.41
CZF-0.70	6.87	2.21	0.39	5.1	0.71	0.47	6.31	5.71
CZF-0.40	10.60	4.84	1.36	6.47	2.95	10.25	4.61	5.78
CZF-0.25	10.30	3.6	1.57	7.02	7.20	11.59	7.99	4.43

Table 7 Product distribution after catalyst evaluation

Catalyst	CO ₂ Conv. (%)	Oxygenate Distr. (%)					HC Distr. (%)				
		Ethers		Alcohols							
		DME	Diethyl ether	MeOH	EtOH	C ₂ + alcohols	CH ₄	C ₂ - C ₄ ^P	C ₂ - C ₄ ⁼	C ₅ +	Arom atics
CZF-1.00	17.71	6.17	1.72	21.65	43.19	27.26	39.64	28.53	2.55	28.08	1.20
CZF-0.70	6.87	24.91	4.36	57.52	7.99	5.25	42.40	28.90	1.46	26.22	1.03
CZF-0.40	10.60	18.70	5.27	25.03	11.39	39.64	37.35	29.79	4.73	27.34	0.79
CZF-0.25	10.30	11.64	5.06	22.66	23.25	37.41	20.74	13.46	8.47	19.54	37.79
CZF-0.10	6.04	0.19	0.32	33.25	10.37	55.87	22.05	2.33	0.00	2.33	73.29

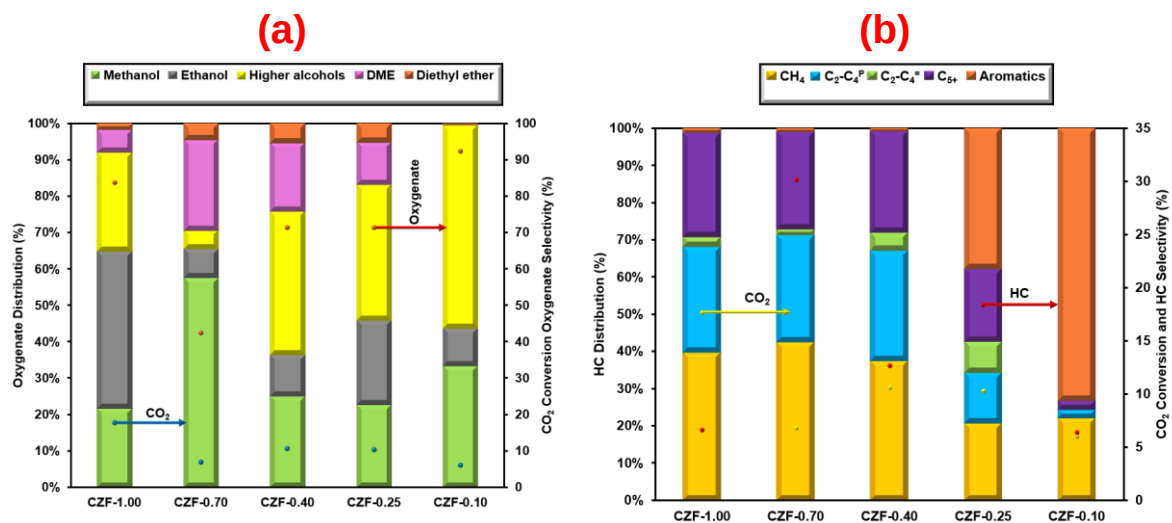


Figure 15 CO₂ hydrogenation on different Cu-based mixed metal oxides catalysts. Reaction conditions: Temperature = 280 °C, n (H₂)/n (CO₂) = 3 (molar ratio), Pressure = 30 bar, 0.5 g catalysts loading, and a space velocity of 3000 mL g⁻¹ h⁻¹. (a) oxygenate distribution (b) hydrocarbons (HC) distribution

CHAPTER 5

CONCLUSIONS

In this research-work, we designed a streamlined method of catalysts synthesis where we successfully synthesized a series of Cu-based mixed metal oxides catalysts specifically to convert CO₂ into valuable products via catalytic-hydrogenation. We systematically varied the concentration of precipitant, and we explored its impact on the catalytic performance of our catalysts. The addition of Na₂CO₃, our precipitant, at different molarity facilitated the coprecipitation of the metal ions thereby forming mixed hydroxycarbonates. The gentle addition of this precipitant has led to achieving proper pH and precipitation kinetics, which was in turn has led to achieving excellent surface area and porosity, smaller particle size, adequate surface basicity, and distinctive morphology from our catalysts. Cu-based catalyst has been proven to be among the prominent catalysts for CO₂ hydrogenation reaction due to its cost-effectiveness, which is relatively economical. Typically, H₂ dissociation occurs on Cu-Zn interface. Presence of Fe in the catalysts has facilitated C-C coupling while CO₂ activation takes place on the Cu-Fe interface. The synthesized catalysts demonstrated distinctive CO₂ conversion and product selectivity. While evaluating the performance of catalysts, CZF-1.00 having the highest precipitant concentration displayed a significant CO₂ conversion of 17.7 % and an exceptional oxygenates selectivity of 83.7 %, which demonstrated that really C-C coupling has significantly occurred as ethanol and C₂+ alcohols were dominantly high in selectivity when compared to methanol and DME. The proper Cu, Zn, and Fe proportion together with the ideal precipitant concentration under

the right reduction and reaction conditions have proven that the catalyst, CZF-1.00, selectively favored the production of oxygenates while suppressing the production of CO and CH₄.

While progress has been made, critical knowledge gaps persist regarding the reaction mechanisms and kinetics of CO₂ hydrogenation. These uncertainties currently limit the ability to precisely engineer catalysts and optimize reactor systems for industrial-scale deployment. To address these challenges, future studies should prioritize:

1. Structure-Activity Relationships: Delving deeper into how atomic-scale structure of Cu-based catalysts governs their performance, enabling the rational design of tailored active sites.
2. Reactor Engineering: Developing scalable reactor configurations that maximize efficiency and selectivity under practical operating conditions.

Advancing these areas is essential to realize full potential of CO₂ hydrogenation, bridging the gap between laboratory-scale breakthroughs and industrial adoption.

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Vitae

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EDUCATION

- **King Fahd University of Petroleum and Minerals (2022 till date)**
MS Analytical Chemistry (Defended and passed)
- **Bayero University, Kano (2014 - 2019)**
B.Sc. Chemistry (First Class Honors)
- **Maitama Sule Science College, Gaya (2011 - 2014)**
- **Model Primary School, Dawakin Kudu (2002 - 2008)**
Certificate of primary education

SKILLS AND ABILITIES

- Currently, I am independently working with different analytical instruments inside and outside Chemistry Department, KFUPM
- Well, I am acquainted with laboratory-research work and procedures
- Experienced in writing term-projects and review article
- Organizational and planning skills
- Proven leadership skills and ability to motivate
- Ability to work independently or as part of a team
- Experience in barbing saloon
- Outgoing, friendly personality, confident dealing with customers

- Attention to detail
- Responsible, honest, adaptable, and well presented

PUBLICATIONS

- Basiru O Yusuf, Mustapha Umar, Mansur Aliyu, Aliyu M Alhassan, Mohammed Mosaad Awad, Omer A Taialla, Abdulhakam Shafiu Abdullahi, **Jamilu Nura Musa**, Khalid R Alhooshani, Saheed A Ganiyu, “Recent advances and future prospects of MXene-based photocatalysts in environmental remediations.” Journal of Environmental Chemical Engineering. (Published, 2024)
- Babar Ali, Muhammad Tahir Arslan, Ijaz Hussain, Shamraiz Hussain Talib, Ahmad Salam Farooqi, Aliyu Musa Alhassan, **Jamilu Nura Musa**, Basiru O Yusuf, Khalid R Alhooshani, Saheed A Ganiyu, “Catalyst engineering strategies for the direct hydrogenation of CO₂ into aromatics: A state-of-the-art review.” International Journal of Hydrogen Energy. (Published, 2025)

ACHIEVEMENTS/RESPONSIBILITIES

- Poster presentation on “CO₂ hydrogenation catalyst to dimethyl ether synthesis approach: role of support and promoter” at Chemistry Department, KFUPM, April 2024
- Competency training in effective communication skills organized by Student Excellence and Success in cooperation with the Department of Global Studies, KFUPM, February 2024
- Certificate of achievement with Al Fozan Academy on community work principles and fundamentals course (Raed Basis) as part of Saudi Aramco initiative to promote volunteering work in Saudi Arabia, January 2024
- Deputy Production/Process Officer at Dangote Fertilizer Limited, Nigeria
- Assistant Presiding Officer, 2019 General elections (Nigeria)
- Speaker, Model Primary School Old Boys, Dawakin Kudu (Class 2008)
- School Prefect, Model Primary School, Dawakin Kudu (2008)

WORK AND EXPERIENCE

- Freshmen laboratory teaching assignment and grading activities at King Fahd University of Petroleum and Minerals (2022 till date)
- SATORP Company Visit in Al – Jubail, April 2024
- Worked with Dangote Fertilizer Limited, Nigeria (2021-2022)
- National Youth Service, NYSC, Nigeria (2019-2020)
- Worked at Kano State Drugs and Medical Consumables Supply Agency for six(6) months SIWES
- Extra Mural lesson on Science and Technical Examination for Junior Secondary School Students at Dawakin Kudu
- May 2019 - June 2019, Al-Hidaya Primary School, Dawakin Kudu. Assist in teaching and general administrative work