Thermo-catalytic Reduction of CO₂ to Value-Added Products on Supported Cu Nanostructures and Bimetallic Cu Nanoalloys M.Sc. Thesis

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Thermocatalytic** Reduction of CO₂ to Value-Added Products on Supported Cu Nanostructures and Bimetallic Cu Nanoalloys, is an authentic record of my own work carried out during the period from August 2023 to May 2024 under the supervision of Prof. Dr. Venkatesh Chelvam, Department of Chemistry, IIT Indore and Dr. Ali Mohamed Abdel-Mageed, Leibniz Institute for Catalysis, University of Rostock, Rostock, Germany.

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> Riya Sehrawat M.Sc. Student

ABSTRACT

In the wake of industrialization, humanity has faced the daunting challenge of mitigating the environmental repercussions of harmful pollutant emissions. Among these, the rise in carbon dioxide (CO_2) levels is a pivotal concern. The alarming shift in climate patterns brings forth an array of issues. Negative emission technologies like Carbon Capture, Utilization, and Storage (CCUS) are imperative.

Our research focuses on the thermocatalytic reduction of CO_2 to generate value-added chemicals and/or hydrogen carriers, a fundamental component of artificial CO_2 utilization. Through thermo-catalysis, CO_2 captured from the air can be converted into valuable compounds, such as organic chemicals, hydrocarbon fuels, and polymers. Among these, methanol production holds promise due to its ease of storage and transport, and its role in synthesizing essential chemicals and fuels.

Considering the above aspects, this research aims to develop an advanced heterogeneous catalyst for CO_2 hydrogenation to methanol by optimizing catalyst properties, feed gas composition, and use of water as solvent. The present research is poised to significantly contribute to the field of catalysis, steering us closer to a greener and more sustainable future, in alignment with global efforts to combat climate change and reduce our carbon footprint.

TABLE OF CONTENTS

	LIST OF FIGURES	viii-ix
	SYMBOLS/UNITS	X
	ACRONYMS	xi-xii
Chapter 1.	INTRODUCTION	1-3
Chapter 2.	LITERATURE REVIEW	4-6
Chapter 3.	EXPERIMENTAL SECTION	7-23
3.1	General Methods and Information	7-8
3.2	Synthesis of Support	8-10
3.3	Synthesis of Low Metal Loading Catalyst	10-18
3.4	Synthesis of High Metal Loading Catalyst	18-22
3.5	Catalytic Activity Measurement	22-23
Chapter 4.	RESULTS AND DISCUSSION	24-93
4.1	Characterization of ZnO Crystallites	24-30
4.2	Characterization of Cu/ZnO Monometallic	31-38
	Catalyst	
4.3	Characterization of Cu ₉₀ Ag ₁₀ /ZnO Bimetallic	39-46
	Catalyst	
4.4	Characterization of Cu ₉₀ Pt ₁₀ /ZnO Bimetallic	47-53
	Catalyst	
4.5	Characterization of Ni ₉₀ Pt ₁₀ /ZnO Bimetallic	54-61
	Catalyst	
4.6	Characterization of Ni ₉₀ Ag ₁₀ /ZnO Bimetallic	62-67
	Catalyst	
4.7	Characterization of 5 Wt% Cu/ZnO Monometallic	67-75
	Catalyst	
4.8	Characterization of 6 Wt% Au/ZnO Monometallic	75-83
	Catalyst	
4.9	Characterization of Cu ₉₀ Au ₁₀ /ZnO Bimetallic	83-92
	Catalyst	

4.10	Comparison of Catalytic Activity	93
93Chapter 5.	CONCLUSION	94
	REFERENCES	95-98

LIST OF FIGURES

Figure 1.	[A] PXRD of ZnO crystallites	24
	[B] Williamson-Hall (WH) plot of ZnO crystallites	
Figure 2.	FE-SEM image of ZnO crystallites	25
Figure 3.	EDX spectrum of ZnO crystallites	26
Figure 4.	TGA analysis of ZnO crystallites	27
Figure 5.	FTIR spectrum of ZnO crystallites	28
Figure 6.	[A] N_2 adsorption-desorption isotherm at -196 °C	29
	of ZnO	
	[B] Pore size distribution of ZnO crystallites	
Figure 7.	[A] PXRD of Cu/ZnO	31
	[B] Williamson-Hall (WH) plot of Cu/ZnO	
Figure 8.	FE-SEM image of Cu/ZnO	33
Figure 9.	EDX spectrum of Cu/ZnO	34
Figure 10.	EDX mapping of Cu/ZnO	35
Figure 11.	[A] N_2 adsorption-desorption isotherm at -196 °C of Cu/ZnO	37
	[B] Pore size distribution of Cu/ZnO	
Figure 12.	[A] PXRD of Cu ₉₀ Ag ₁₀ /ZnO	39
	[B] Williamson-Hall (WH) plot of Cu ₉₀ Ag ₁₀ /ZnO	
Figure 13.	FE-SEM image of Cu ₉₀ Ag ₁₀ /ZnO	41
Figure 14.	EDX spectrum of Cu ₉₀ Ag ₁₀ /ZnO	42
Figure 15.	EDX mapping of Cu ₉₀ Ag ₁₀ /ZnO	43
Figure 16.	[A] N_2 adsorption-desorption isotherm at -196 °C of $Cu_{90}Ag_{10}/ZnO$	45
	[B] Pore size distribution of Cu ₉₀ Ag ₁₀ /ZnO	
Figure 17.	[A] PXRD of Cu ₉₀ Pt ₁₀ /ZnO	47
	[B] Williamson-Hall (WH) plot of Cu ₉₀ Pt ₁₀ /ZnO	
Figure 18.	FE-SEM image of Cu ₉₀ Pt ₁₀ /ZnO	49
Figure 19.	EDX mapping of Cu ₉₀ Pt ₁₀ /ZnO	50

Figure 20.	[A] N_2 adsorption-desorption isotherm at -196 °C of $Cu_{90}Pt_{10}/ZnO$	52
	[B] Pore size distribution of Cu ₉₀ Pt ₁₀ /ZnO	
Figure 21.	[A] PXRD of Ni90Pt10/ZnO	54
	[B] Williamson-Hall (WH) plot of Ni90Pt10/ZnO	
Figure 22.	FE-SEM image of Ni ₉₀ Pt ₁₀ /ZnO	56
Figure 23.	EDX spectrum of Ni ₉₀ Pt ₁₀ /ZnO	57
Figure 24.	EDX mapping of Ni ₉₀ Pt ₁₀ /ZnO	58
Figure 25.	[A] N_2 adsorption-desorption isotherm at -196 °C of $Ni_{90}Pt_{10}/ZnO$	60
	[B] Pore size distribution of Ni ₉₀ Pt ₁₀ /ZnO	
Figure 26.	[A] PXRD of Ni ₉₀ Ag ₁₀ /ZnO	62
	[B] Williamson-Hall (WH) plot of Ni ₉₀ Ag ₁₀ //ZnO	
Figure 27.	FE-SEM image of Ni ₉₀ Ag ₁₀ /ZnO	64
Figure 28.	EDX spectrum of Ni ₉₀ Ag ₁₀ /ZnO	65
Figure 29.	EDX mapping of Ni ₉₀ Ag ₁₀ /ZnO	66
Figure 30.	PXRD of 5 Wt% Cu/ZnO	67
Figure 31.	FE-SEM image of 5 Wt% Cu/ZnO	68
Figure 32.	EDX mapping of 5 Wt% Cu/ZnO	69
Figure 33.	ICP-OES of 5 Wt% Cu/ZnO	70
Figure 34.	Zeta Potential of 5 Wt% Cu/ZnO	71
Figure 35.	[A] GC after catalysis with Cu/ZnO	72
	[B] GC-MS after catalysis with Cu/ZnO	
Figure 36.	¹ H NMR after catalysis with Cu/ZnO	73
Figure 37.	[A] N_2 adsorption-desorption isotherm at -196 °C ofCu/ZnO	74
	[B] Pore size distribution of Cu/ZnO	
Figure 38	PXRD of 6 Wt% Au/ZnO	75
Figure 39.	FE-SEM image of 6 Wt% Au/ZnO	76

Figure 40.	EDX Mapping of 6 Wt% Au/ZnO	77
Figure 41.	ICP-OES of 6 Wt% Au/ZnO	78
Figure 42.	Zeta Potential of 6 Wt% Au/ZnO	79
Figure 43.	[A] GC after catalysis with Au/ZnO	80
	[B] GC-MS after catalysis with Au/ZnO	
Figure 44.	¹ H NMR of reaction solution in DMSO-d6 after catalysis with Au/ZnO	81
Figure 45.	[A] N_2 adsorption-desorption isotherm at -196 °C of Au/ZnO	82
	[B] Pore size distribution of Au/ZnO	
Figure 46.	PXRD of 5 Wt% Cu ₉₀ Au ₁₀ /ZnO	83
Figure 47.	FE-SEM image of 5 Wt% Cu ₉₀ Au ₁₀ /ZnO	84
Figure 48.	EDX mapping of 5 Wt% Cu ₉₀ Au ₁₀ /ZnO	86
Figure 49.	ICP-OES of 5 Wt% Cu ₉₀ Au ₁₀ /ZnO	87
Figure 50.	Zeta Potential of 5 Wt% Cu ₉₀ Au ₁₀ /ZnO	88
Figure 51.	[A] GC after catalysis with Cu ₉₀ Au ₁₀ /ZnO	89
	[B] GC-MS after catalysis with Cu ₉₀ Au ₁₀ /ZnO	
Figure 52.	¹ H NMR of reaction solution in DMSO-d6 after	90
	catalysis with Cu ₉₀ Au ₁₀ /ZnO	
Figure 53.	[A] N_2 adsorption-desorption isotherm at -196 °C of Cu ₉₀ Au ₁₀ /ZnO	91
	[B] Pore size distribution of Cu ₉₀ Au ₁₀ /ZnO	
Figure 54.	CO ₂ conversion, selectivity of MeOH and,	93
	selectivity of CO using different catalysts	

SYMBOLS/ UNITS

Cubic Centimeter сс °C Degree Celsius G Gram h Hours Milli gram mg Milliliter mL Mt Million Metric Ton Μ Molarity

ACRONYMS

Ar	Argon
BJH	Barrett-Joyner-Halenda
BET	Brunauer-Emmett-Teller
CCUS	Carbon Capture, Utilization and Sequestering
CO_2	Carbon Dioxide
СО	Carbon Monoxide
Cu	Copper
Cu(NO ₃) ₂ .3H ₂ O	Copper Nitrate Trihydrate
DMSO	Dimethyl Sulfoxide
EDX	Energy Dispersive X-ray
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
Ga	Gallium
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectroscopy
Au	Gold
H_2	Hydrogen
MeOH	Methanol
Ni	Nickle
Ni(NO ₃) ₂ .6H ₂ O	Nickel Nitrate Hexahydrate
N_2	Nitrogen
NMR	Nuclear Magnetic Resonance
Pd	Palladium
Pt	Platinum
PtCl ₄	Platinum Tetrachloride
K_2PdCl_4	Potassium Tetrachloropalladate
PXRD	Powder X-Ray Diffraction

RWGS	Reverse Water Gas Shift
RPM	Revolutions Per Minute
AgNO ₃	Silver Nitrate
Na ₂ CO ₃	Sodium Carbonate
NaOH	Sodium Hydroxide
NaNO ₃	Sodium Nitrate
STY	Space-Time Yield
HAuCl ₄ .3H ₂ O	Tetrachlorogold Trihydrate
TGA	Thermogravimetric Analysis
ZnCO ₃	Zinc Carbonate
$Zn(NO_3)_2$	Zinc Nitrate
ZnO	Zinc Oxide

Chapter 1

INTRODUCTION

Industrialization has always been considered as a boon for mankind moder civilization. It came, however, with several undesired consequences. One of which is the deterioration of the environment by releasing harmful pollutants contributing to the global warming, particularly the everincreasing CO₂ emission. There are abundant sources of CO₂ emission in nature, ranging from natural to manmade. The worst of all sources is burning fossil fuels for human benefitting activities. Electricity, transportation, and industry sectors are the primary consumers of fossil fuels and, hence, the significant producers of Green House Gases (GHGs) [1]. The indiscriminate use of fossil fuels has accumulated a large quantity of CO₂ in the atmosphere, disrupting the planet's natural greenhouse effect. Intensification of this effect leads to a rise in the earth's temperature causing global warming. Other related effects include more frequent and severe heatwaves, altered weather patterns, melting ice caps, and rising sea levels, which have widespread environmental, economic, and societal impacts [2]. Changing the energy source from fossil fuels to renewable resources seems suitable. However, relying solely on renewable energy may not be sufficient to address the challenge of global warming as it does not account for the already existing CO_2 in the atmosphere. Thus, negative emission technologies, such as CCUS, are essential [3].

Chemical conversion of CO_2 is the most essential method for its artificial utilization. The captured CO_2 from the air, from industrial furnaces or from power plants can be converted into valuable added chemicals such as organic compounds, hydrocarbon fuels, and polymers by thermocatalytic, electrocatalytic, or photocatalytic reduction reactions [4]. H₂ gas obtained from photocatalytic water splitting using direct sunlight or water

electrolysis using electricity generated by a renewable source can be used as a reduction source [5]. Reduction and conversion of CO₂ to methanol can be enormously beneficial as it is an easily stored and transported liquid, unlike gaseous products. With more than 110 million Metric tons/year of production, methanol is undoubtedly a critical compound of C1 chemistry. Many chemicals, namely, formaldehyde, acetic acid, methyl tert-butyl ether (MTBE), and gasoline (Methanol to Gasoline process, MTG), are synthesized with methanol as a chemical intermediate. Methanol's highoctane rating makes it an excellent substitute or an additive for fuel [6,7]. Currently, industrially, gas-solid catalytic reactors are used in methanol synthesis from synthesis gas over copper-based catalysts Cu/ZnO/Al₂O₃ at 250 °C-300 °C and 50-100 bar [8]. Such high-temperature conditions act as an inhibitor to facile conversion. CO₂ to methanol conversion is exothermic, so low temperature is favoured for the forward reaction. The catalyst also suffers from performance reduction due to agglomeration of Cu and high activity for competing reactions, namely, reverse water-gas shift (RWGS), which is endothermic and favourable at lower temperatures [9].

Research shows that Au supported on ZnO is a promising catalyst for this reaction (5-50 bar at 240 °C) with better selectivity, yield, and enhanced CO₂ hydrogenation to MeOH rates [10,11]. However, the high cost of Au limits its application. Traditionally, Ni-based catalysts produce methane instead of methanol. On the contrary, when Ga is introduced, due to changes in the electronic structure of Ni, the main product is methanol. The Ni-Ga catalyst reduces CO₂ to methanol at ambient pressure and exhibits the same or better methanol synthesis activity than conventional Cu/ZnO/Al₂O₃ catalysts. Furthermore, the Ni-Ga catalyst produces considerably lower amounts of CO [12,13]. Thus, we can tune the properties of Cu or other metal-based catalysts by introducing a new metal by forming an alloy. With this budding topic of bimetallics, we can also use the valuable properties of expensive metal catalysts without compromising cost.

Other helpful tunable properties include capturing CO_2 in the liquid phase (e.g., using liquid amines) to carry out reduction using an indirect route, which helps with the temperature and energy constraints [14,15]. Water as a solvent will be used to avoid any non-environment-friendly solvents. Thus, combining all the above factors, we aim to develop a better novel optimized heterogeneous catalyst for CO_2 hydrogenation to methanol in water.

Chapter 2

LITERATURE SURVEY

With regeneration, recovery and process scale up to dimensions relevant for industrial production as the main difficulties in using homogeneous catalysts, the preference for heterogeneous catalysts is due to their stability, separation, handling, and reuse advantages. Using heterogeneous catalysts can help to fulfill large-scale production at lower cost. Homogeneous catalysts also have a limited lifetime in harsh conditions thus, the feasibility of heterogeneous catalysts in the catalytic hydrogenation of CO_2 into methanol can fulfill industrial applications [16].

The emissions from highly energy-intensive industrial processes don't just contain CO_2 ; they also include other elements resulting from combustion that can rapidly deactivate CO_2 hydrogenation catalysts. In industry, amine scrubbers are commonly used for capturing CO_2 after combustion. However, this method involves a significant energy cost for removing CO_2 from the liquid solution [17]. The rate-limiting step in gaseous phase CO_2 hydrogenation reaction is the activation of CO_2 but capture and activation are simultaneous in liquid phase CO_2 conversion reactions. Thus, we can skip this expensive desorption process and use these CO_2 -derived activated species. This would significantly reduce cost and functional temperature, which is essential for an exothermic reaction like CO_2 hydrogenation to methanol [9,18]. However, the currently used solvents are organic, which are hazardous to the environment.

Ali et al. demonstrated that the feed gas composition significantly impacts the activation and catalytic performance of Au/ZnO catalysts in methanol production from CO_2 and H_2 . The presence of CO plays a crucial role, whether it's present as a reactant in CO-containing gas mixtures, generated from side reactions, or a mix of both. When the catalyst is exposed to CO/H_2 , it initially exhibits high methanol formation activity, but this diminishes when the gas is switched to CO₂/H₂ [14,19]. These trends may apply to metal/ZnO catalysts like Cu/ZnO and Pd/ZnO to improve their activation.

Industrially, Cu on ZnO support is used for methanol synthesis from syngas [20]. Zinc oxide (ZnO) has garnered significant interest as a prospective material because of its non-toxic nature, stability, favorable electrical and optical characteristics, and affordability [21]. The exceptional catalytic characteristics of ZnO-based materials are linked to their surface structure, nanoarchitecture, defects, and electron transport capabilities. Deliberately introducing defects and doping with metals enhances catalyst activity, making these materials vital for industrial applications. ZnO-based materials play a crucial role as constituents in heterogeneous catalysts, with their effectiveness closely tied to the density of active sites on the surface [22]. The substantial surface area of copper in industrial catalysts is due to ZnO acting as a structural intermediary between copper nanoparticles (Cu NPs), aiding in the even distribution of the copper phase during catalyst creation. ZnO's presence also enhances the inherent activity of methanol synthesis catalysts based on copper, resulting in what is referred to as the Cu-ZnO synergy [23]. Also, reducible oxides like ZnO, because of their excellent redox properties and O vacancy formation, are promising support for Au catalysts as initial activation of Au/ZnO catalyst goes hand in hand with O vacancy formation [24].

Although methanol synthesis is thermodynamically more favoured at lower temperatures, copper-based catalysts exhibit diminished performance under such conditions. Furthermore, Cu-based catalysts are susceptible to substantial deactivation over time. Consequently, supported metal-based catalysts like Pd, Pt, Au, and Ag excel in delivering remarkable methanol selectivity [26]. When subjected to high temperatures in a reducing environment, Pd strongly tends to create alloy structures with ZnO, a phenomenon closely linked to catalytic performance and methanol selectivity. Consequently, Pd supported on ZnO has exhibited the highest activity and selectivity for methanol synthesis compared to other metal oxides such as Ga₂O₃, In₂O₃, SiO₂, MgO, and ZrO, as shown by Iwasa et. al [27]. Additionally, the combination of Pd and Cu is intriguing, as stable Pd-Cu alloys can form after reduction, potentially enhancing methanol formation. It has also been found that supported gold catalysts, particularly Au/ZnO, exhibit comparable or even superior activity to commercial Cu/ZnO catalysts and demonstrate higher selectivity for methanol production over the competing reverse water gas shift (RWGS) reaction at pressures up to 50 bar [28]. Exploring Ag catalysts in the context of methanol synthesis from CO₂ hydrogenation has received relatively limited attention. Yet, including Ag as a promoter in catalysts is pivotal in enhancing the process of CO₂ conversion into methanol [29].

Bimetallic catalysts on oxide supports have started to gain attention, and one of the prominent examples is the discovery of Ni-Ga catalysts. Ni-based catalysts usually hydrogenate CO_2 to methane, but adding Ga produces methanol with a better synthesis activity than the commercial Cu-based catalyst. Harnessing the capacity to create bimetallic compounds allows for the design of catalysts that outperform single metals in terms of activity, selectivity, and long-term stability [30]. Incorporating gallium into the Cu/ZnO catalyst resulted in a 1.5-fold increase in the methanol Space-Time Yield (STY) compared to Cu/ZnO alone [31]. Moreover, unlike the traditional Cu/ZnO/Al₂O₃ catalysts, the bimetallic Cu-M (M = Ag, Au, Pt, and Pd) catalysts demonstrate enhanced activity and methanol selectivity due to their ability to prevent particle size aggregation and modulate the electronic structure.

Chapter 3

EXPERIMENTAL SECTION

3.1 General Methods and Information

This study employed a comprehensive suite of analytical techniques to characterize synthesized catalysts. The the starting materials Zn(NO₃)₂.6H₂O, Ni(NO₃)₂.6H₂O, and Na₂CO₃ were procured from Avra Synthesis Pvt. Ltd. and LIT, respectively. AgNO3 was procured from Spectrochem Pvt. Ltd., NaOH from Finar Limited, and PtCl₄ and K₂PdCl₄ from BLD Pharmatech Ltd. Cu(NO₃)₂.3H₂O and HAuCl₄.3H₂O were procured from Sigma Aldrich. An Ultrasonic Cleaner from Labman was used to disperse ZnO in distilled water at 60 °C. Eco tester pH1 pH meter and WTW pH 526 were used to measure the pH. The Powder X-ray Diffraction (PXRD) analysis was conducted using a Rigaku SmartLab Automated Multipurpose X-ray Diffractometer and Philips PANalytical X'Pert diffractometer, providing valuable insights into the crystal structure of the material. The use of a method called the pseudo-Voigt function was made to analyze the peak positions and shapes. This was performed the help of the HighScore Plus software package from Panalytical, located in Almelo, The Netherlands. To identify the different phases, the PDF-2 database provided by the International Center of Diffraction Data (ICDD) was consulted. The Field Emission Scanning Electron Microscopy (FE-SEM) imaging was performed with a Carl Zeiss Supra 55 instrument, facilitating the examination of the material's morphology. Energy Dispersive X-ray (EDX) data was collected using an Oxford AZtec X-MAX 20, offering compositional information. Thermogravimetric Analysis (TGA) was carried out utilizing a METTLER TOLEDO TGA/DSC 1 STARe System to assess thermal stability. The Fourier Transform Infrared (FTIR) spectroscopy of ZnO was conducted with a Bruker TENSOR 27 instrument. BET analysis was conducted using Quanta chrome, and Autosorb iQ2 by Anton Paar and MicrotracBELL Japan, BELSORP-Max.

Additionally, Ants-i Tube Furnace was used to reduce the sample at 500 °C in the flow of 10% H₂/N₂. A hot air oven at 80 °C was used for drying precipitate, and a muffle furnace set at 500 °C was employed for its calcination. The high vacuum pump aided in washing the precipitate. GCMS-GP2010 Ultra, Shimadzu was used for the analysis of liquid products directly after the reaction. GC, 8860 Gas Chromatograph Plus, Agilent, was used to analyze the gaseous products. NMR spectral data were recorded in AV-III HD 400 (Bruker), ICP-OES elemental analysis using Varian/Agilent 715-ES, and zeta potential of the samples in Malvern Zeta Sizer Ultra MPT-3 instruments. These procedures and instruments collectively formed the foundation for comprehensively characterizing the synthesized material, enabling a detailed understanding of its structural, morphological, and compositional properties.

3.2 Synthesis of Support

3.2.1 Synthesis of ZnO Crystallites

Several physical and chemical methods have been employed to craft nanoparticles from various materials. For instance, creating ZnO nanoparticles can be achieved through multiple techniques, including chemical precipitation, sol-gel synthesis, thermal decomposition, and hydrothermal processes [32]. The precipitation method stands out for its significance and utility due to its numerous merits, such as operating at low temperatures, cost-effectiveness, environmental friendliness, and the minimal need for expensive equipment. Further, two distinct washing procedures were employed to purify the precipitate. The first method involves utilizing a fritted glass funnel in conjunction with Whatman filter paper, while the second method uses centrifugation at 1200 rpm for 8 minutes. It was observed that the latter approach led to increased agglomeration of particles, resulting in its dismissal as the chosen washing technique.

$$Zn(NO_{3})_{2} + Na_{2}CO_{3} \xrightarrow{70 \text{ °C, 1h}} ZnCO_{3} + 2NaNO_{3} \dots Eq^{n}(1)$$

$$Mol. wt.$$

$$(125.39 \text{ g/mol})$$

$$ZnCO_{3} \xrightarrow{500 \text{ °C, 4h}} ZnO + CO_{2} \dots Eq^{n}(2)$$

$$Mol. wt.$$

$$(81.38 \text{ g/mol})$$

The synthesis of ZnO crystallite begins with a double displacement reaction between Zn(NO₃)₂ and Na₂CO₃. The reaction yields ZnCO₃ as a solid precipitate (Eq. 1), while the NaNO₃ remains solvated in the reaction mixture. The obtained ZnCO₃ precipitate, crucial to the synthesis, undergoes a subsequent transformation through calcination. After subjecting it to high temperatures for 4 hours at 500 °C, the ZnCO₃ decomposes, releasing CO₂ (Eq. 2). This calcination step is fundamental as it leads to the formation of the desired ZnO crystallite, making it available for further applications in various fields.

Preparation of Solutions

- Preparation of 150 mL, 0.1 M Zn(NO₃)₂.6H₂O solution
 4.46 g of Zn(NO₃)₂.6H₂O was dissolved in distilled water (150 mL) taken in a round bottom flask (500 mL).
- Preparation of 150 mL, 0.12 M Na₂CO₃ solution
 1.91 g of Na₂CO₃ was dissolved in distilled water (150 mL) taken in a beaker (250 mL).

Procedure for the Synthesis of ZnCO₃ and ZnO

0.1 M Zn(NO₃)₂.6H₂O solution (150 mL) was taken in a round bottom flask (500 mL) with a magnetic pellet and heated at 70 °C in an oil bath for 10 minutes with constant stirring. Next, 0.12 M Na₂CO₃ (150 mL) solution was added dropwise over a period of 10 minutes using a Pasteur pipette. The reaction mixture was further stirred for 1 hour at 70 °C to obtain a white

precipitate of ZnCO₃. After 1 hour, the reaction mixture was cooled, and the ZnCO₃ precipitate was transferred to a fritted glass funnel with Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water (5 × 100 mL) using a vacuum pump. The white precipitate in the Whatman filter paper was dried overnight for 12 h in a hot air oven at a temperature of 80 °C to obtain dry ZnCO₃ in 93% yield (1.56 g). The dried precipitate was then transferred to an alumina crucible boat (10 mL) and calcined in an oven at 500 °C for 4 h in an atmosphere of air to obtain ZnO white solid (1.08 g). The calcined sample was then transferred to a mortar and grinded using a pestle to obtain a homogeneous white powder and characterized using PXRD, FE-SEM, EDX, TGA, and FTIR techniques.

3.3 Synthesis of Low Metal Loading Catalysts

Both the monometallic (Cu) and bimetallic (Cu-Ag, Cu-Pt, Ni-Ag, Ni-Pt) catalysts are synthesized using the Deposition-Precipitation method. In the Deposition-Precipitation method, an aqueous medium is prepared to contain a vigorously agitated suspension of finely divided solid ZnO particulates. These particulates serve as stable nucleating surfaces, preferably thermally stable, and act as supporting or carrier materials that remain insoluble under the deposition precipitation conditions. This method facilitates the deposition of very finely divided metallic particles of monometallic or bimetallic catalysts on the surface of the supporting material, ZnO. The precise and spaced-apart positioning of these metallic particles on the surface allows for maintaining their fine division and separation during subsequent operations such as calcination, oxidation, reduction, and heat treatments. These treatments are necessary to convert the initially deposited metal hydroxides into the required monometallic (Cu) and bimetallic (Cu-Ag, Cu-Pt, Ni-Ag, Ni-Pt) catalysts for its intended application.

3.3.1 Synthesis of Cu/ZnO Monometallic Catalyst

Preparation of Solutions

- Preparation of 100 mL, 0.37 M ZnO suspension
 3 g of ZnO was dissolved in warm distilled water (100 mL) taken in a round bottom flask (250 mL).
- 2. Preparation of 55.5 mL, 0.5 M NaOH solution

Preparation of 10 mL, 0.006 M Cu(NO₃)₂.3H₂O solution
 14.49 mg of Cu(NO₃)₂.3H₂O was dissolved in distilled water (10 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Cu/ZnO Catalyst

Distilled water (100 mL) was taken in a round bottom flask (250 mL) and heated at 60 °C for 10 minutes and ZnO (3 g, 36.9 mmol) was added to the reaction flask. For 1 h, the ZnO suspension was sonicated in a sonicator at 60 °C. After an hour, using a pH meter, the pH of the suspension was constantly monitored, and increased slowly by addition of 0.5 M NaOH solution dropwise to a pH 8–9. Further, the ZnO suspension was constantly stirred with the help of a magnetic pellet and magnetic stirrer. After 2 minutes, alongside stirring, to the above suspension, 0.006 M of Cu(NO₃)₂.3H₂O solution (10 mL) was added dropwise over a period of a minute using a Pasteur pipette. Again, with the help of pH meter, the pH of the resulting solution was measured and found to be at pH = 7. If the pH is less than 7, then adjust the pH to 7 using 0.5 M NaOH solution. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate formed was transferred to a fritted glass funnel with a Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water (5 \times 50 mL) using a vacuum pump. The light green precipitate in the Whatman

^{1.11} g of NaOH was dissolved in distilled water (55.5 mL) taken in a beaker (100 mL).

filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the resulting catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed vial until reduction experiment was carried out. The prepared catalyst was then reduced by transferring the catalyst to a crucible and placed in a tube furnace. N₂ gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of N₂ gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of N₂ gas. The resulting Cu/ZnO light green solid (2.565 g, 86%) was grinded using a mortar and pestle, weighed, and stored in dark vials sealed with parafilm in a desiccator.

3.3.2 Synthesis of Cu₉₀Ag₁₀/ZnO Bimetallic Catalyst

Preparation of Solutions

- Preparation of 100 mL, 0.37 M ZnO suspension
 3 g of ZnO was dissolved in warm distilled water (100 mL) taken in a round bottom flask (250 mL).
- Preparation of 29.8 mL, 0.5 M NaOH solution
 0.596 g of NaOH was dissolved in distilled water (29.8 mL) taken in a beaker (100 mL).
- Preparation of 10 mL, 0.006 M Cu(NO₃)₂.3H₂O solution
 14.49 mg of Cu(NO₃)₂.3H₂O was dissolved in distilled water (10 mL) taken in a beaker (25 mL).
- Preparation of 5 mL, 0.0012 M AgNO₃ solution
 1.02 mg of AgNO₃ was dissolved in distilled water (5 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Cu₉₀Ag₁₀/ZnO Catalyst

Distilled water (100 mL) was taken in a round bottom flask (250 mL) and heated at 60 °C for 10 minutes and ZnO (3 g, 36.9 mmol) was added to the reaction flask. For 1 h, the ZnO suspension was sonicated in a sonicator at 60 °C. After an hour, using a pH meter, the pH of the suspension was constantly monitored, and increased slowly by addition of 0.5 M NaOH solution dropwise to a pH 8–9. Further, the ZnO suspension was constantly stirred with the help of a magnetic pellet and magnetic stirrer. After 2 minutes, a premixed solution of Cu(NO₃)₂.3H₂O (10 mL, 0.006 M) and AgNO₃ (5 mL, 0.0012 M) was added to the ZnO suspension dropwise over a period of a minute using a Pasteur pipette. Again, with the help of pH meter, the pH of the resulting solution was measured and found to be at pH = 7. If the pH is less than 7, then adjust the pH to 7 using 0.5 M NaOH solution. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate formed was transferred to a fritted glass funnel with a Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water (5 \times 50 mL) using a vacuum pump. The light grey precipitate in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the resulting catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed vial until reduction experiment was carried out. The prepared catalyst was then reduced by transferring the catalyst to a crucible and placed in a tube furnace. N2 gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of N2 gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of N₂ gas. The resulting $Cu_{90}Ag_{10}/ZnO$ light grey solid (2.820 g, 94%) was grinded using a mortar and pestle, weighed, and stored in dark vials sealed with parafilm in a desiccator.

3.3.3 Synthesis of Cu₉₀Pt₁₀/ZnO Bimetallic Catalyst

Preparation of Solutions

- Preparation of 100 mL, 0.37 M ZnO suspension
 3 g of ZnO was dissolved in warm distilled water (100 mL) taken in a round bottom flask (250 mL).
- 2. Preparation of 14.25 mL, 0.5 M NaOH solution

0.258 g of NaOH was dissolved in distilled water (14.25 mL) taken in a beaker (25 mL).

- Preparation of 10 mL, 0.006 M Cu(NO₃)₂.3H₂O solution
 14.49 mg of Cu(NO₃)₂.3H₂O was dissolved in distilled water (10 mL) taken in a beaker (25 mL).
- 4. Preparation of 5 mL, 0.0012 M PtCl₄ solution

15 mg of PtCl₄ was dissolved in distilled water (10 mL) to form 0.0029 M stock solution. Stock solution (2.02 mL) was added to distilled water (2.98 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Cu₉₀Pt₁₀/ZnO Catalyst

Distilled water (100 mL) was taken in a round bottom flask (250 mL) and heated at 60 °C for 10 minutes and ZnO (3 g, 36.9 mmol) was added to the reaction flask. For 1 h, the ZnO suspension was sonicated in a sonicator at 60 °C. After an hour, using a pH meter, the pH of the suspension was constantly monitored, and increased slowly by addition of 0.5 M NaOH solution dropwise to a pH 8–9. Further, the ZnO suspension was constantly stirred with the help of a magnetic pellet and magnetic stirrer. After 2 minutes, a premixed solution of Cu(NO₃)₂.3H₂O (10 mL, 0.006 M) and PtCl₄ (5 mL, 0.0012 M) was added to the ZnO suspension dropwise over a period of a minute using a Pasteur pipette. Again, with the help of pH meter, the pH of the resulting solution was measured and found to be at pH = 7. If the pH is less than 7, then adjust the pH to 7 using 0.5 M NaOH solution.

The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate formed was transferred to a fritted glass funnel with a Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water (5×50 mL) using a vacuum pump. The light grey precipitate in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed vial until reduction experiment was carried out. The prepared catalyst was then reduced by transferring the catalyst to a crucible and placed in a tube furnace. N₂ gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of N₂ gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of N₂ gas. The resulting Cu₉₀Pt₁₀/ZnO light grey solid (2.698 g, 90%) was grinded using a mortar and pestle, weighed, and stored in dark vials sealed with parafilm in a desiccator.

3.3.4 Synthesis of Ni90Pt10/ZnO Bimetallic Catalyst

Preparation of Solutions

3Preparation of 100 mL, 0.37 M ZnO suspension

3 g of ZnO was dissolved in warm distilled water (100 mL) taken in a round bottom flask (250 mL).

- Preparation of 14.25 mL, 0.5 M NaOH solution
 0.258 g of NaOH was dissolved in distilled water (14.25 mL) taken in a beaker (25 mL).
- Preparation of 10 mL, 0.006 M Ni(NO₃)₂.6H₂O solution
 17.44 mg of Ni(NO₃)₂.6H₂O was dissolved in distilled water (10 mL) taken in a beaker (25 mL).
- 3. Preparation of 5 mL, 0.0012 M PtCl₄ solution

15 mg of PtCl₄ was dissolved in distilled water (10 mL) to form 0.0029 M stock solution. Stock solution (2.02 mL) was added to distilled water (2.98 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Ni90Pt10/ZnO Catalyst

Distilled water (100 mL) was taken in a round bottom flask (250 mL) and heated at 60 °C for 10 minutes and ZnO (3 g, 36.9 mmol) was added to the reaction flask. For 1 h, the ZnO suspension was sonicated in a sonicator at 60 °C. After an hour, using a pH meter, the pH of the suspension was constantly monitored, and increased slowly by addition of 0.5 M NaOH solution dropwise to a pH 8–9. Further, the ZnO suspension was constantly stirred with the help of a magnetic pellet and magnetic stirrer. After 2 minutes, a premixed solution of Ni(NO₃)₂.6H₂O (10 mL, 0.006 M) and PtCl₄ (5 mL, 0.0012 M) was added to the ZnO suspension dropwise over a period of a minute using a Pasteur pipette. Again, with the help of pH meter, the pH of the resulting solution was measured and found to be at pH = 7. If the pH is less than 7, then adjust the pH to 7 using 0.5 M NaOH solution. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate formed was transferred to a fritted glass funnel with a Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water $(5 \times 50 \text{ mL})$ using a vacuum pump. The light grey precipitate in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed vial until reduction experiment was carried out. The prepared catalyst was then reduced by transferring the catalyst to a crucible and placed in a tube furnace. N₂ gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of N₂ gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H_2/N_2 for 2 h, cooled to room temperature under a flow of N_2 gas. The resulting Ni₉₀Pt₁₀/ZnO light grey solid (2.741 g, 91%) was grinded using a

mortar and pestle, weighed, and stored in dark vials sealed with parafilm in a desiccator.

3.3.5 Synthesis of Ni₉₀Ag₁₀/ZnO Bimetallic Catalyst

Preparation of Solutions

1. Preparation of 100 mL, 0.37 M ZnO suspension

3 g of ZnO was dissolved in warm distilled water (100 mL) taken in a round bottom flask (250 mL).

- Preparation of 15.35 mL, 0.5 M NaOH solution
 0.305 g of NaOH was dissolved in distilled water (15.35 mL) taken in a beaker (25 mL).
- Preparation of 10 mL, 0.006 M Ni(NO₃)₂.6H₂O solution
 17.44 mg of Ni(NO₃)₂.6H₂O was dissolved in distilled water (10 mL) taken in a beaker (25 mL).
- 4. Preparation of 5 mL, 0.0012 M AgNO₃ solution

11 mg of AgNO₃ was dissolved in distilled water (10 mL) to form 0.007 M stock solution. Stock solution (0.9 mL) was added to distilled water (4.1 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Ni₉₀Ag₁₀/ZnO Catalyst

Distilled water (100 mL) was taken in a round bottom flask (250 mL) and heated at 60 °C for 10 minutes and ZnO (3 g, 36.9 mmol) was added to the reaction flask. For 1 h, the ZnO suspension was sonicated in a sonicator at 60 °C. After an hour, using a pH meter, the pH of the suspension was constantly monitored, and increased slowly by addition of 0.5 M NaOH solution dropwise to a pH 8–9. Further, the ZnO suspension was constantly stirred with the help of a magnetic pellet and magnetic stirrer. After 2 minutes, a premixed solution of Ni(NO₃)₂.6H₂O (10 mL, 0.006 M) and AgNO₃ (5 mL, 0.0012 M) was added to the ZnO suspension dropwise over a period of a minute using a Pasteur pipette. Again, with the help of pH meter, the pH of the resulting solution was measured and found to be at pH = 7. If the pH is less than 7, then adjust the pH to 7 using 0.5 M NaOH solution. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate formed was transferred to a fritted glass funnel with a Whatman filter paper fitted to a round bottom flask (250 mL) and washed with distilled water (5 \times 50 mL) using a vacuum pump. The light grey precipitate in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed glass vial until the reduction experiment was carried out. The prepared catalyst was transferred to a crucible and placed in a tube furnace for reduction. N2 gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of N₂ gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of N₂ gas. The resulting Ni₉₀Ag₁₀/ZnO light grey solid (2.762 g, 92%) was grinded using a mortar and pestle, weighed, and stored in dark vials sealed with parafilm in a desiccator.

3.4 Synthesis of High Metal Loading Catalysts

Both the monometallic (Cu and Au) and bimetallic (Cu-Au) catalysts are using the Deposition-Precipitation method as described above.

3.4.1 Synthesis of 5 wt% Cu/ZnO Monometallic Catalyst

Preparation of Solutions

1. Preparation of 250 mL, 0.24 M ZnO suspension

5 g of ZnO was dissolved in warm distilled water (250 mL) taken in a round bottom flask (250 mL).

Preparation of 100 mL, 1 M NaOH solution
 4 g of NaOH was dissolved in distilled water (100 mL) taken in a beaker (250 mL).
Preparation of 4 mL, 0.98 M Cu(NO₃)₂.3H₂O solution
 943.8 mg of Cu(NO₃)₂.3H₂O was dissolved in distilled water (4 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of 5wt% Cu/ZnO Catalyst

In a round bottom flask (250 mL), ZnO (5 g, 61.44 mmol) was taken, and distilled water (250 mL) was added to the reaction flask. The ZnO suspension was stirred using a magnetic pellet and heated at 60 °C for 20 minutes. The pH of the suspension was constantly monitored and increased slowly by the addition of 1 M NaOH solution dropwise until the pH reached 8-9. After 2 minutes, 0.98 M of Cu(NO₃)₂.3H₂O solution (4 mL) was added dropwise to the suspension using a 5 mL syringe needle while maintaining pH ~7 by addition of 1 M NaOH dropwise using another 5 mL syringe needle. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate was transferred to a glass funnel with a Whatman filter paper fitted to a flask (1 L) and washed with distilled water $(3 \times 100 \text{ mL})$ at 40 °C. The grey-brown precipitate (5.08 g) in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the dried catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed glass vial until the reduction was carried out. The catalyst (3 g) was transferred to a glass crucible and placed in a tube furnace for reduction. Argon gas flow was switched on, and after 2 minutes, the temperature was ramped 10 °C/min to 500 °C with constant flow of argon gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of argon gas. The resulting Cu/ZnO maroonbrown solid (2.83 g) was grinded using a mortar and pestle, weighed, and stored in dark glass vials sealed with parafilm in a desiccator.

3.4.2 Synthesis of 6wt% Au/ZnO Monometallic Catalyst

Preparation of Solutions

1. Preparation of 250 mL, 0.25 M ZnO suspension

5 g of ZnO was dissolved in warm distilled water (250 mL) taken in a round bottom flask (250 mL).

2. Preparation of 100 mL, 1 M NaOH solution

4 g of NaOH was dissolved in distilled water (100 mL) taken in a beaker (250 mL).

Preparation of 5 mL, 0.3 M HAuCl₄.3H₂O solution
 599.7 mg of HAuCl₄.3H₂O was dissolved in distilled water (5 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of Au/ZnO Catalyst

In a round bottom flask (250 mL), ZnO (5 g, 61.44 mmol) was taken, and distilled water (250 mL) was added to the reaction flask. The ZnO suspension was stirred using a magnetic pellet and heated at 60 °C for 20 minutes. The pH of the suspension was constantly monitored and increased slowly by the addition of 1 M NaOH solution dropwise until the pH reached 8-9. After 2 minutes, 0.3 M HAuCl₄.3H₂O solution (5 mL) was added dropwise to the suspension using a 5 mL syringe needle while maintaining pH ~7 by addition of 1 M NaOH dropwise using another 5 mL syringe. The reaction mixture was further stirred for 3 h at 60 °C, cooled, and the precipitate was transferred to a glass funnel with a Whatman filter paper fitted to a flask (1 L) and washed with distilled water (3×100 mL) at 40 °C. The light-yellow precipitate (5.17 g) in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the dried catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed glass vial until the reduction was carried out. The catalyst (3 g) was transferred to a glass crucible and placed in a tube furnace for reduction. Argon gas

flow was switched on, and after 2 minutes, the temperature was ramped 5 °C/min to 500 °C with constant flow of argon gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H_2/N_2 for 2 h, cooled to room temperature under a flow of argon gas. The resulting Au/ZnO grey solid (2.91 g) was grinded using a mortar and pestle, weighed, and stored in dark glass vials sealed with parafilm in a desiccator.

3.4.3 Synthesis of 5wt% Cu₉₀Au₁₀/ZnO Bimetallic Catalyst

Preparation of Solutions

- Preparation of 250 mL, 0.25 M ZnO suspension
 5 g of ZnO was dissolved in warm distilled water (250 mL) taken in a round bottom flask (250 mL).
- Preparation of 100 mL, 1 M NaOH solution
 4 g of NaOH was dissolved in distilled water (100 mL) taken in a beaker (250 mL).
- Preparation of 5 mL, Cu(NO₃)₂.3H₂O and HAuCl₄.3H₂O solution 127.2 mg of HAuCl₄.3H₂O and 702.3 mg of Cu(NO₃)₂.3H₂O were taken in a beaker (25 mL) followed by the addition of distilled water (5 mL) taken in a beaker (25 mL).

Procedure for the Synthesis of 5wt% Cu₉₀Au₁₀/ZnO

In a round bottom flask (250 mL), ZnO (5 g, 61.44 mmol) was taken, and distilled water (250 mL) was added to the reaction flask. The ZnO suspension was stirred using a magnetic pellet and heated at 60 °C for 20 minutes. The pH of the suspension was constantly monitored and increased slowly by the addition of 1 M NaOH solution dropwise until the pH reached 8–9. After 2 minutes, the bimetallic solution (5 mL) of HAuCl₄.3H₂O and Cu(NO₃)₂.3H₂O as prepared above was added dropwise to the suspension using a 5 mL syringe needle while maintaining pH ~7 by addition of 1 M NaOH dropwise using another 5 mL syringe. The reaction mixture was

further stirred for 3 h at 60 °C, cooled, and the precipitate was transferred to a glass funnel with a Whatman filter paper fitted to a flask (1 L) and washed with distilled water (3 × 100 mL) at 40 °C. The grey precipitate (5.12 g) in the Whatman filter paper was dried overnight for 12 h in a hot air oven at 80 °C, and the dried catalyst was grinded using a mortar and pestle. The catalyst was stored in a sealed glass vial until the reduction was carried out. The catalyst (3 g) was transferred to a glass crucible and placed in a tube furnace for reduction. Argon gas flow was switched on, and after 2 minutes, the temperature was ramped 5 °C/min to 500 °C with constant flow of argon gas. After reaching 500 °C, the catalyst was exposed to a flow of 10% H₂/N₂ for 2 h, cooled to room temperature under a flow of argon gas. The resulting Cu₉₀Au₁₀/ZnO brown-violet solid (2.83 g) was grinded using a mortar and pestle, weighed, and stored in dark glass vials sealed with parafilm in a desiccator.

3.5 Catalytic Activity Measurement

The experiment was conducted in liquid phase batch reactors using 100 mL Parr stainless steel autoclave reactors. These autoclaves were furnished with magnetic stirrers to ensure continuous mixing of the reaction mixture and catalyst throughout the reaction process. The use of glass insert tubes was employed to avoid any potential contamination from impurities in the stainless steel, providing a controlled environment for the reaction. The procedure involves dispersing catalyst (200 mg) into distilled water (200 mL) within the glass tubing inside the autoclave reactors. The charged autoclaves underwent multiple purging cycles with Ar to eliminate residual oxygen, followed by purging with H₂ and pressurization with a CO_2/H_2 (1:3) gas mixture. Subsequently, the reactor was heated to 200 °C low-speed stirring (100 rpm), then the stirring speed was increased to 500 rpm to initiate the reaction. After completion, the reactor was filtered, and the gas was collected at the outlet for quantitative analysis of reactant gases and potential products. The catalyst was filtered, and the

liquid was collected for further analysis. Additionally, a blank measurement without a catalyst was conducted to correct for solvated CO₂ in water. Gas chromatography-mass spectrometry (GCMS) was used to analyze liquid products formed after the reduction process. Samples were diluted with DMSO to make analysis easier along with addition of an internal standard diethylene glycol dibutyl ether (0.5 mL). Using a gas chromatograph (GC), gas-phase products and changes in CO₂ partial pressure were examined. Calibration curves for CO_2 and other possible byproducts were built from measurements of the composition of the gas used in quantitative analysis. Pressure drop measurements made after catalyst measurements were used to calculate CO₂ conversion, which was then standardized against reactors that were blank of catalysts (Eq. 1). CO formation yield (X_{CO}) in the gas phase was measured to determine selectivity towards CO using calibration curves created within the expected concentration range that the reaction would produce (Eq. 2). Based on the determined methanol yield (Y_{MeOH}) in the liquid phase, methanol selectivity was calculated (Eq. 3).

$CO_2 Conversion = (Area1(CO_2) - Area2(CO_2)) X Response Factor (Eq. 1)$

Area1: CO_2 area in chromatogram without catalyst (blank measurement) using the same conditions to pressurize and heat as the reaction was done

Area2: CO_2 area in chromatogram with catalyst (after catalytic measurement)

$$CO Selectivity = \left(\frac{X_{CO}}{CO_2 Conversion}\right) X \ 100 \ (Eq. 2)$$

$$MeOH \ Selectivity = \left(\frac{Y_{MeOH}}{CO_2 \ Conversion}\right) X \ 100 \ (Eq. 3)$$

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterization of ZnO Crystallites

4.1.1 PXRD



Figure 1. [A] PXRD of ZnO crystallites [B] Williamson-Hall (WH) plot of ZnO crystallites

Powder X-ray diffraction (Figure 1 A) of ZnO crystallites provides valuable insights into their structural characteristics. The data obtained from PXRD analysis reveals essential information about the crystal structure of ZnO. In this case, it was determined that the ZnO crystallites exhibit a Wurtzite structure, which is a hexagonal phase. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hall plot (Figure 1 B). While the Scherrer equation gave a size of 21 nm, the WH plot yielded 37 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.0019, suggesting minimal lattice strain and structural integrity.

4.1.2 FE-SEM



Figure 2. FE-SEM of ZnO crystallites

The Field Emission Scanning Electron Microscopy analysis (Figure 2) of the synthesized ZnO crystallite revealed a combination of rod-like and spherical shapes with an average diameter of approximately 66.99 nm. These crystallites displayed an average rod length of 135 nm. Furthermore, the surface area of the ZnO crystallites was determined to be about 3525 nm². This microstructural characterization provides valuable insights into the morphology and dimensions of the ZnO crystallites, contributing to a comprehensive understanding of their physical properties and potential applications.

4.1.3 EDX



Figure 3. EDX spectrum of ZnO crystallites

The Energy Dispersive X-ray analysis (Figure 3) of the synthesized ZnO crystallite revealed an average Zn-to-O ratio of 1.37:1, indicating an excess of zinc in the composition. This imbalance can be attributed to oxygen vacancy defects within the crystalline structure. Oxygen vacancies occur when oxygen atoms are missing from their lattice positions, resulting in an increased concentration of zinc relative to oxygen. These defects can significantly influence the electrical and optical properties of the ZnO crystallite, making the EDX data essential for understanding the material's structural and compositional characteristics and its potential performance in various applications.

4.1.4 TGA



Figure 4. TGA analysis of ZnO crystallites

The Thermogravimetric Analysis (Figure 4) of ZnO crystallite exhibited an initial buoyancy effect, indicating a percentage weight gain during the initial stages of the analysis. This effect is typically observed when desorption or release of volatile compounds or gases from the sample, often due to adsorbed moisture or other low-temperature reactions. However, as the TGA analysis continued, the synthesized ZnO crystallites were stable at higher temperatures, suggesting that the material can withstand elevated thermal conditions without significant decomposition or weight loss. The observed weight loss can be attributed to the decomposition of precursors or other low-temperature processes, emphasizing the compound's thermal stability and suitability for various high-temperature applications.

4.1.5 FTIR



Figure 5. FTIR spectrum of ZnO crystallites

The Fourier Transform Infrared (Figure 5) analysis of the synthesized ZnO crystallite revealed several distinctive peaks. A strong band at 3717 cm⁻¹ indicates O–H stretching vibrations, likely associated with moisture present. The peak at 2330 cm⁻¹ corresponds to O=C=O vibration corresponding to CO₂ present in the atmosphere [33]. An 865 cm⁻¹ peak can be associated with deformations outside the plane vibrations in carbonate [34]. Moreover, the presence of peaks in the range of 500–800 cm⁻¹ is indicative of ZnO vibration [35]. These FTIR results provide valuable insights into the functional groups and compounds in the synthesized ZnO crystallite.



Figure 6. [A] N₂ adsorption-desorption isotherm at –196 °C of ZnO [B] Pore size distribution of ZnO crystallites

The physicochemical properties of ZnO were investigated by N₂ physisorption at -196 °C (Figure 6 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 2 to 50 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a spectrum of pore diameters ranging from 3 to 18 nm, with a predominant peak observed at a diameter of 3 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 32.282 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.494 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.

4.2.1 PXRD



Figure 7. [A] PXRD of Cu/ZnO [B] Williamson-Hall (WH) plot of Cu/ZnO

Powder X-ray diffraction (Figure 7 A) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The absence of discernible copper peaks in the PXRD pattern of the Cu/ZnO catalyst is attributed to a low concentration of copper within the sample. X-ray diffraction (PXRD) is typically more adept at detecting diffraction peaks associated with higher concentrations and larger crystallites. In cases where the copper concentration is below a certain threshold, the diffraction signals may fall below the detection limit of the instrument. Additionally, if copper is present in the form of small nanoparticles, the corresponding diffraction peaks might exhibit broadness and weakness. This phenomenon arises due to the reduced crystallite size, making it challenging to distinguish these signals from the background or the predominant ZnO peaks. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hall plot (Figure 7 B). While the Scherrer equation gave a size of 30.51 nm, the WH plot yielded 27.66 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.00116, suggesting minimal lattice strain and structural integrity.

4.2.2 FE-SEM



Figure 8. FE-SEM image of Cu/ZnO

The SEM images (Figure 8) of the Cu/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the morphological features observed. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX (Energy Dispersive X-ray) and EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.2.3 EDX



Figure 9. EDX spectrum of Cu/ZnO

The EDX analysis (Figure 9) was conducted to examine the elemental composition of the Cu/ZnO catalyst synthesized. As anticipated, the EDX data revealed the presence of peaks corresponding to zinc (Zn) and oxygen (O), consistent with the composition of ZnO. Notably, a peak of lower intensity corresponding to copper (Cu) was also observed, providing confirmation of the successful incorporation of copper into the catalyst. The presence of this Cu peak further supports the synthesis of the desired Cu/ZnO composite material, contributing to the characterization of its elemental composition.

4.2.4 EDX Mapping









Figure 10. EDX mapping of Cu/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 10). The results of EDX mapping clearly illustrate a uniform distribution of copper (Cu) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of copper within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Cu on the ZnO support.



Figure 11. [A] N₂ adsorption-desorption isotherm at -196 °C of Cu/ZnO [B] Pore size distribution of Cu/ZnO

The effect of deposition on the physicochemical properties of Cu/ZnO was investigated by N₂ physisorption at -196 °C (Figure 11 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 2 to 50 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a spectrum of pore diameters ranging from 3 to 18 nm, with a predominant peak observed at a diameter of 3.433 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 31.472 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.339 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.





Figure 12. [A] PXRD of Cu₉₀Ag₁₀/ZnO [B] Williamson-Hall (WH) plot of Cu₉₀Ag₁₀/ZnO

Powder X-ray diffraction ((Figure 12 A) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The absence of discernible copper and silver peaks in the PXRD pattern of the Cu₉₀Ag₁₀/ZnO catalyst is attributed to a low concentration of copper and silver within the sample. X-ray diffraction (PXRD) is typically more adept at detecting diffraction peaks associated with higher concentrations and larger crystallites. In cases where the copper and silver concentration is below a certain threshold, the diffraction signals may fall below the detection limit of the instrument. Additionally, if copper and silver are present in the form of small nanoparticles, the corresponding diffraction peaks might exhibit broadness and weakness. This phenomenon arises due to the reduced crystallite size, making it challenging to distinguish these signals from the background or the predominant ZnO peaks. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hall plot (Figure 12 B). While the Scherrer equation gave a size of 21.85 nm, the WH plot yielded 34.91 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.00164, suggesting minimal lattice strain and structural integrity.

4.3.2 FE-SEM



Figure 13. FE-SEM image of Cu₉₀Ag₁₀/ZnO

The SEM images (Figure 13) of the Cu₉₀Ag₁₀/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the morphological features observed. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX (Energy Dispersive X-ray) and EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.3.3 EDX



Figure 14. EDX spectrum of Cu₉₀Ag₁₀/ZnO

The EDX analysis (Figure 14) was conducted to examine the elemental composition of the Cu₉₀Ag₁₀/ZnO catalyst synthesized. As anticipated, the EDX data revealed the presence of peaks corresponding to zinc (Zn) and oxygen (O), consistent with the composition of ZnO. Notably, peaks of lower intensities corresponding to copper (Cu) and silver (Ag) have been observed, providing confirmation of the successful incorporation of copper and silver into the catalyst. The presence of these Cu and Ag peaks further supports the synthesis of the desired Cu₉₀Ag₁₀/ZnO composite material, contributing to the characterization of its elemental composition.

4.3.4 EDX Mapping



Figure 15. EDX mapping of Cu₉₀Ag₁₀/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 15). The results of EDX mapping clearly illustrate a uniform distribution of copper (Cu) and silver (Ag) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of copper and silver within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Cu and Ag on the ZnO support.



Figure 16. [A] N₂ adsorption-desorption isotherm at -196 °C of Cu₉₀Ag₁₀/ZnO [B] Pore size distribution of Cu₉₀Ag₁₀/ZnO

The effect of deposition on the physicochemical properties of Cu₉₀Ag₁₀/ZnO was investigated by N₂ physisorption at -196 °C (Figure 16 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 2 to 50 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a spectrum of pore diameters ranging from 3 to 18 nm, with a predominant peak observed at a diameter of 3.845 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 31.057 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.356 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.





Figure 17. [A] PXRD of Cu₉₀Pt₁₀/ZnO [B] Williamson-Hall (WH) plot of Cu₉₀Pt₁₀/ZnO

Powder X-ray diffraction (Figure 17 A) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The absence of discernible copper peaks in the PXRD pattern of the Cu₉₀Pt₁₀/ZnO catalyst is attributed to a low concentration of copper and platinum within the sample. X-ray diffraction (PXRD) is typically more adept at detecting diffraction peaks associated with higher concentrations and larger crystallites. In cases where the copper and platinum concentrations are below a certain threshold, the diffraction signals may fall below the detection limit of the instrument. Additionally, if copper and platinum are present in the form of small nanoparticles, the corresponding diffraction peaks might exhibit broadness and weakness. This phenomenon arises due to the reduced crystallite size, making it challenging to distinguish these signals from the background or the predominant ZnO peaks. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hal plot (Figure 17 B). While the Scherrer equation gave a size of 19.94 nm, the WH plot yielded 27.72 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.00125, suggesting minimal lattice strain and structural integrity.

4.4.2 FE-SEM



Figure 18. FE-SEM image of Cu₉₀Pt₁₀/ZnO

The SEM images (Figure 18) of the $Cu_{90}Pt_{10}/ZnO$ catalyst closely resemble those of pure ZnO, indicating a similarity in the morphological features observed. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX (Energy Dispersive X-ray) and EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.4.3 EDX Mapping



Figure 19. EDX mapping of $Cu_{90}Pt_{10}/ZnO$

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 19). The results of EDX mapping clearly illustrate a uniform distribution of copper (Cu) and platinum (Pt) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of copper and platinum within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Cu and Pt on the ZnO support.



Figure 20. [A] N₂ adsorption-desorption isotherm at -196 °C of Cu₉₀Pt₁₀/ZnO [B] Pore size distribution of Cu₉₀Pt₁₀/ZnO

The effect of deposition on the physicochemical properties of Cu₉₀Pt₁₀/ZnO was investigated by N₂ physisorption at -196 °C (Figure 20 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 2 to 50 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a spectrum of pore diameters ranging from 3 to 18 nm, with a predominant peak observed at a diameter of 3.059 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 28.640 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.341 cc/g.

4.5.1 PXRD



Figure 21. [A] PXRD of $Ni_{90}Pt_{10}/ZnO$ [B] Williamson-Hall (WH) plot of $Ni_{90}Pt_{10}/ZnO$
Powder X-ray diffraction (Figure 21 A) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The absence of discernible nickel and platinum peaks in the PXRD pattern of the Ni₉₀Pt₁₀/ZnO catalyst is attributed to a low concentration of nickel and platinum within the sample. X-ray diffraction (PXRD) is typically more adept at detecting diffraction peaks associated with higher concentrations and larger crystallites. In cases where the nickel and platinum concentrations are below a certain threshold, the diffraction signals may fall below the detection limit of the instrument. Additionally, if nickel and platinum are present in the form of small nanoparticles, the corresponding diffraction peaks might exhibit broadness and weakness. This phenomenon arises due to the reduced crystallite size, making it challenging to distinguish these signals from the background or the predominant ZnO peaks. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hall plot (Figure 21 B). While the Scherrer equation gave a size of 20.76 nm, the WH plot yielded 31.71 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.00151, suggesting minimal lattice strain and structural integrity.

4.5.2 FE-SEM



Figure 22. FE-SEM image of Ni₉₀Pt₁₀/ZnO

The SEM images (Figure 22) of the $Ni_{90}Pt_{10}/ZnO$ catalyst closely resemble those of pure ZnO, indicating a similarity in the morphological features observed. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX (Energy Dispersive X-ray) and EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst. 4.5.3 EDX



Figure 23. EDX spectrum of Ni₉₀Pt₁₀/ZnO

The EDX analysis (Figure 23) was conducted to examine the elemental composition of the $Ni_{90}Pt_{10}/ZnO$ catalyst synthesized. As anticipated, the EDX data revealed the presence of peaks corresponding to zinc (Zn) and oxygen (O), consistent with the composition of ZnO. Notably, peaks of lower intensities corresponding to nickel (Ni) and platinum (Pt) have been observed, providing confirmation of the successful incorporation of nickel and platinum into the catalyst. The presence of these Ni and Pt peaks further supports the synthesis of the desired $Ni_{90}Pt_{10}/ZnO$ composite material, contributing to the characterization of its elemental composition.

4.5.4 EDX Mapping



Figure 24. EDX mapping of $Ni_{90}Pt_{10}/ZnO$

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 24). The results of EDX mapping clearly illustrate a uniform distribution of nickel (Ni) and platinum (Pt) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of nickel and platinum within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Ni and Pt on the ZnO support.



Figure 25. [A] N_2 adsorption-desorption isotherm at -196 °C of $Ni_{90}Pt_{10}/ZnO$ [B] Pore size distribution of $Ni_{90}Pt_{10}/ZnO$

The effect of deposition on the physicochemical properties of Ni₉₀Pt₁₀/ZnO was investigated by N₂ physisorption at -196 °C (Figures 25 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 2 to 50 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a spectrum of pore diameters ranging from 3 to 15 nm, with a predominant peak observed at a diameter of 3.843 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 27.268 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.349 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.

4.6.1 PXRD



Figure 26. [A] PXRD of Ni₉₀Ag₁₀/ZnO [B] Williamson-Hall (WH) plot of Ni₉₀Ag₁₀/ZnO

Powder X-ray diffraction (Figure 26 A) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. The absence of discernible nickel and silver peaks in the PXRD pattern of the Ni₉₀Ag₁₀/ZnO catalyst is attributed to a low concentration of nickel and silver within the sample. X-ray diffraction (PXRD) is typically more adept at detecting diffraction peaks associated with higher concentrations and larger crystallites. In cases where the nickel and silver concentrations are below a certain threshold, the diffraction signals may fall below the detection limit of the instrument. Additionally, if nickel and silver are present in the form of small nanoparticles, the corresponding diffraction peaks might exhibit broadness and weakness. This phenomenon arises due to the reduced crystallite size, making it challenging to distinguish these signals from the background or the predominant ZnO peaks. The crystallite size was also calculated using two methods: the Scherrer equation and the Williamson-Hall plot (Figure 26 B). While the Scherrer equation gave a size of 21.79 nm, the WH plot yielded 31.79 nm, showcasing methodological differences. The WH plot also revealed a microstrain value of 0.00136, suggesting minimal lattice strain and structural integrity.

4.6.2 FE-SEM



Figure 27. FE-SEM image of Ni₉₀Ag₁₀/ZnO

The SEM images (Figure 27) of the Ni₉₀Ag₁₀/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the morphological features observed. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX (Energy Dispersive X-ray) and EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.6.3 EDX



Figure 28. EDX spectrum of Ni₉₀Ag₁₀/ZnO

The EDX analysis (Figure 28) was conducted to examine the elemental composition of the Ni₉₀Ag₁₀/ZnO catalyst synthesized. As anticipated, the EDX data revealed the presence of peaks corresponding to zinc (Zn) and oxygen (O), consistent with the composition of ZnO. Notably, peaks of lower intensities corresponding to nickel (Ni) and silver (Ag) have been observed, providing confirmation of the successful incorporation of nickel and silver into the catalyst. The presence of these Ni and Ag peaks further supports the synthesis of the desired Ni₉₀Ag₁₀/ZnO composite material, contributing to the characterization of its elemental composition.

4.6.4 EDX Mapping



Figure 29. EDX mapping of Ni₉₀Ag₁₀/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 29). The results of EDX mapping clearly illustrate a uniform distribution of nickel (Ni) and silver (Ag) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of nickel and silver within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Ni and Ag on the ZnO support.

4.7Characterization of 5 Wt% Cu/ZnO Monometallic Catalyst



4.7.1 PXRD

Figure 30. PXRD of 5 Wt% Cu/ZnO

Powder X-ray diffraction (Figure 30) exhibits a Wurtzite structure, which is a hexagonal phase as in pure ZnO. This conclusion was further supported by referencing the JCPDS database, which is a reliable resource for confirming the crystal structures of various materials. Notably, additional peaks indicative of Cubic Cu was observed along with ZnO peaks, suggesting the presence of Cu Cubic within the catalyst. No change in the phase of ZnO Wurtzite is indicative of the deposition of Cu on the surface without wrecking the lattice arrangement of ZnO Wurtzite.

4.7.2 FE-SEM



Figure 31. FE-SEM image of 5 Wt% Cu/ZnO

The SEM images (Figure 31) of the 5 Wt% Cu/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the observed morphological features. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.7.3 EDX Mapping





Figure 32. EDX mapping of 5 Wt% Cu/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 32). The results of EDX mapping clearly illustrate a uniform distribution of copper (Cu) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of copper within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Cu on the ZnO support.

4.7.4 **ICP-OES**

Name	Cu Wt% Theoretical	Cu Wt% Experimental	
Cu/ZnO	5	4.67	

Figure 33. ICP-OES of 5 Wt% Cu/ZnO

Initially, 5 weight percent Cu loading on ZnO was the theoretical calculation. Nevertheless, a measured Cu loading of 4.67 weight percent was found by experimental examination using inductively coupled plasma optical emission spectroscopy (ICP OES), which was less than the theoretical estimation. The obtained Cu loading is still within an acceptable range.

4.7.5 Zeta Potential



Figure 34. Zeta Potential of 5 Wt% Cu/ZnO

The Zeta Potential values (Figure 34) were measured at various pH ranges to comprehend the behaviour of the catalyst's surface. Zeta potential values ranged from -0.3094 mV at pH 2 to -28.5 mV at pH 9.6, according to the data. It was discovered that the catalyst's isoelectric point (pH_IEP) is 2.6. This indicates that the catalyst's surface charge becomes neutral at pH 2.6. These results provide insight into how the catalyst interacts with its environment and maintains stability at various pH levels. Knowing this information is essential to determining the catalyst's performance in different applications.

4.7.6 Catalytic Measurement



Figure 35. [A] GC after catalysis with Cu/ZnO [B] GC-MS after catalysis with Cu/ZnO



Figure 36. ¹H NMR of reaction solution in DMSO-d6 after catalysis with Cu/ZnO

A thorough examination of the liquid and gaseous products was used to gauge the catalytic activity of the prepared catalyst. The presence of CO was detected in the GC data (Figure 35 A), with a retention time of 1.704 min, suggesting the existence of catalytic conversion activities. The peak in the chromatogram at a retention time of 2.859 min indicated the production of MeOH, which was validated by liquid product analysis using GC-MS (Figure 35 B). The existence of MeOH in the reaction mixture was confirmed by ¹H NMR spectroscopy (Figure 36), with a peak at 3.18 ppm, which supported the catalyst's catalytic activity. Quantitative evaluations revealed that the CO₂ conversion was 1.78 but MeOH selectivity was found to be 91.53%.



Figure 37. [A] N₂ adsorption-desorption isotherm at -196 °C of Cu/ZnO [B] Pore size distribution of Cu/ZnO

The physicochemical properties of Cu/ZnO were investigated by N₂ physisorption at -196 °C (Figures 37 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 1 to 100 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a predominant peak observed at a width of 11.9994 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 19.1250 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.079040 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.

4.8 Characterization of 6 Wt% Au/ZnO Monometallic Catalyst



4.8.1 **PXRD**

Figure 38. PXRD of 6 Wt% Au/ZnO

Powder X-ray diffraction (Figure 38) analysis revealed the presence of a Wurtzite structure, characteristic of pure ZnO, in the sample. This conclusion was further supported by referencing the JCPDS database,

which is a reliable resource for confirming the crystal structures of various materials. Notably, an additional peaks indicative of Cubic Au was observed along with ZnO peaks, suggesting the presence of Au Cubic within the catalyst. No change in the phase of ZnO Wurtzite is indicative of the deposition of Au on the surface without wrecking the lattice arrangement of ZnO Wurtzite.

4.8.2 FE-SEM



Figure 39. FE-SEM image of 6 Wt% Au/ZnO

The SEM images (Figure 39) of the 6 Wt% Au/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the observed morphological features. Tiny nanoparticles can be evidently seen deposited on the surface of larger nanoparticles. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX mapping techniques were employed, providing a more detailed examination of the elemental composition and distribution within the catalyst.

4.8.3 EDX Mapping







Figure 40. EDX mapping of 6 Wt% Au/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 40). The results of EDX mapping clearly illustrate a uniform distribution of gold (Au) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of gold within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Au on the ZnO support.

4.8.4 ICP-OES

Name	Au Wt% Theoretical	Au Wt% Experimental
Au/ZnO	6	5.08

Figure 41. ICP-OES of 6 Wt% Au/ZnO

Initially, 6 weight percent Au loading on ZnO was the theoretical calculation. Nevertheless, a measured Au loading of 5.08 weight percent was found by experimental examination using inductively coupled plasma optical emission spectroscopy (ICP OES), which was less than the theoretical estimation. This disparity could result from a number of things, including insufficient precipitation, loss during the washing or drying process.

4.8.5 Zeta Potential



Figure 42. Zeta Potential of 6 Wt% Au/ZnO

Zeta potential measurements (Figure 42) were carried out at different pH levels for the Au-ZnO catalyst to evaluate the catalyst's surface charge properties. Zeta potential measurements were made at pH 2.1, -12.29 mV, and pH 10.09, -20.53 mV, respectively. Through the analysis of these data, we can see variations in the catalyst's surface charge under various conditions, as shown by fluctuations in the zeta potential as pH fluctuates. Since the isoelectric point is usually found by determining the pH value at which the zeta potential becomes zero, predicting the isoelectric point (pH_IEP) based only on the provided zeta potential values may not be simple. These measurements of zeta potential provide important information on the stability and electrostatic behaviour of the catalyst.

4.8.6 Catalytic Measurement



Figure 43. [A] GC after catalysis with Au/ZnO [B] GC-MS after catalysis with Au/ZnO



catalysis with Au/ZnO

A thorough examination of the liquid and gaseous products was used to gauge the catalytic activity of the produced catalyst. The presence of CO was detected in the GC data (Figure 43 A), with a retention time of 1.705 min, suggesting the existence of catalytic conversion activities. The peak in the chromatogram at a retention time of 2.858 min indicated the production of MeOH, which was validated by liquid product analysis using GC-MS (Figure 43 B). The existence of MeOH in the reaction mixture was confirmed by ¹H NMR spectroscopy (Figure 44), with a peak at 3.18 ppm, which supported the catalyst's catalytic activity. Quantitative evaluations revealed that the CO₂ conversion was 1.56 but the MeOH selectivity was found to be 96.56%.



Figure 45. [A] N₂ adsorption-desorption isotherm at -196 °C of Au/ZnO [B] Pore size distribution of Au/ZnO

The physicochemical properties of Au/ZnO were investigated by N₂ physisorption at -196 °C (Figures 45 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 1 to 100 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a predominant peak observed at a width of 6.4844 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 15.8500 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.039281 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.

4.9 Characterization of 5 Wt% Cu₉₀Au₁₀/ZnO Bimetallic Catalyst



4.9.1 PXRD

Figure 46. PXRD of 5 Wt% Cu₉₀Au₁₀/ZnO

Powder X-ray diffraction (Figure 46) analysis revealed the presence of a Wurtzite structure, characteristic of pure ZnO, in the sample. This conclusion was further supported by referencing the JCPDS database,

which is a reliable resource for confirming the crystal structures of various materials. Notably, additional peaks indicative of Cubic Cu and Au were observed alongside the ZnO peaks, suggesting the presence of Cu and Au Cubic within the catalyst. No change in the phase of ZnO Wurtzite is indicative of the deposition of Cu and Au on the surface without wrecking the lattice arrangement of ZnO Wurtzite.

4.9.2 FE-SEM



Figure 47. FE-SEM image of 5 Wt% Cu₉₀Au₁₀/ZnO

The SEM images (Figure 47) of the 5 Wt% Cu₉₀Au₁₀/ZnO catalyst closely resemble those of pure ZnO, indicating a similarity in the observed morphological features. Tiny nanoparticles can be evidently seen deposited on the surface of larger nanoparticles. Consequently, limited insights can be drawn solely from the SEM analysis. To gain a more comprehensive understanding, EDX mapping techniques were employed, providing a more

detailed examination of the elemental composition and distribution within the catalyst.

4.9.3 EDX Mapping







Figure 48. EDX mapping of 5 Wt% Cu₉₀Au₁₀/ZnO

The spatial distribution of elements within the catalyst was determined using EDX mapping (Figure 48). The results of EDX mapping clearly illustrate a uniform distribution of gold (Au) and Copper (Cu) across the ZnO support. This spatial analysis provides valuable insights into the homogeneous incorporation of gold and copper within the catalyst, contributing to the understanding of its elemental arrangement and confirming the even dispersion of Au and Cu on the ZnO support.

4.9.4 ICP-OES

Name	Au Wt%	Cu Wt%	Au Wt%	Cu Wt%
	Theoretical	Theoretical	Experimental	Experimental
CuAu/ZnO	1.3	3.7	1.21	3.59

Figure 49. ICP-OES of 5 Wt% Cu₉₀Au₁₀/ZnO

Initially, 1.3 weight percent and 3.7 weight percent Au and Cu loading, respectively, on ZnO was the theoretical calculation. Nevertheless, a measured Au and Cu loading of 1.21 weight percent and 3.59 weight percent, respectively, was found by experimental examination using inductively coupled plasma optical emission spectroscopy (ICP OES), which was slightly less than the theoretical estimation. The obtained Au and Cu loading is still within an acceptable range. Cu_xAu_y comes out to be Cu_{90.13}Au_{9.87}.

4.9.5 Zeta Potential



Figure 50. Zeta Potential of 5 Wt% Cu₉₀Au₁₀/ZnO

Zeta potential measurements (Figure 50) were carried out at different pH levels for the CuAu-ZnO catalyst to evaluate the catalyst's surface charge properties. Zeta potential measurements were made at pH 2.148, -4.268 mV, and pH 9.903, -11.37 mV, respectively. Through the analysis of these data, we can see variations in the catalyst's surface charge under various conditions, as shown by fluctuations in the zeta potential as pH fluctuates. Since the isoelectric point is usually found by determining the pH value at which the zeta potential becomes zero, predicting the isoelectric point (pH_IEP) based only on the provided zeta potential values may not be simple. These measurements of zeta potential provide important information on the stability and electrostatic behaviour of the catalyst.

4.9.6 Catalytic Measurement



Figure 51. [A] GC after catalysis with Cu₉₀Au₁₀/ZnO [B] GC-MS after catalysis with Cu₉₀Au₁₀/ZnO



A thorough examination of the liquid and gaseous products was used to gauge the catalytic activity of the produced catalyst. The presence of CO was detected in the GC data (Figure 51 A), with a retention time of 1.704 min, suggesting the existence of catalytic conversion activities. The peak in the chromatogram at a retention time of 2.863 min indicated the production of MeOH, which was validated by liquid product analysis using GC-MS (Figure 51 B). The existence of MeOH in the reaction mixture was confirmed by ¹H NMR spectroscopy (Figure 52), with a peak at 3.18 ppm, which supported the catalyst's catalytic activity. Quantitative evaluations revealed that the CO₂ conversion was 2.35 but the MeOH selectivity was found to be 94.20%.


Figure 53. [A] N₂ adsorption-desorption isotherm at -196 °C of Cu₉₀Au₁₀/ZnO [B] Pore size distribution of Cu₉₀Au₁₀/ZnO

The physicochemical properties of Cu₉₀Au₁₀/ZnO were investigated by N₂ physisorption at -196 °C (Figure 53 A and B), revealing a distinctive Type-IV pattern indicative of mesoporous structures with pore size ranging from 1 to 100 nm. The hysteresis behavior is attributed to the mechanism of capillary condensation, which becomes more pronounced at higher pressures as the adsorbate (N₂ gas) progressively fills the pores, culminating in an inflection point typically observed near the completion of the first monolayer adsorption. In conjunction with the adsorption isotherm, pore size distribution analysis was conducted, revealing a predominant peak observed at a width of 12.2512 nm. Furthermore, the surface area of the material, determined through multipoint BET analysis, was calculated to be 20.5222 m²/g, while the pore volume, as determined by the Barrett-Joyner-Halenda (BJH) plot, was measured to be 0.090017 cc/g. Thus, the parameters suggest favorable physical properties for catalysis.

4.10 Comparison of Catalytic Activity



Figure 54. CO₂ conversion, selectivity of MeOH and, selectivity of CO using different catalysts

Notable differences were found in the conversion, MeOH selectivity, and CO selectivity of the three catalyst types used in the quantitative investigation of CO₂ hydrogenation to methanol. All catalysts had experimental metal loading of about 5 weight percent, thus making them suitable for comparisons. Cu₉₀Au₁₀/ZnO showed the highest CO₂ conversion rate (2.35%) of all the catalysts examined. The Au/ZnO catalyst had the lowest conversion at 1.56%, while the Cu/ZnO catalyst followed closely with a conversion rate of 1.78%. In terms of CO selectivity, Cu/ZnO showed the highest value (8.47%), followed by Cu₉₀Au₁₀/ZnO (5.80%), and Au/ZnO (3.43%). On the other hand, the Au/ZnO catalyst had the highest methanol selectivity of 96.56%, followed by Cu₉₀Au₁₀ on ZnO at 94.20% and Cu/ZnO at 91.53%. These findings highlight the synergistic potential of bimetallics in generating methanol through CO₂ hydrogenation. It can be evidently seen that by adding Au to Cu/ZnO catalyst, the activity gets enhanced, giving us the desired results.

Chapter 5

CONCLUSION

In the present study, we have effectively carried out the synthesis and characterization of a variety of ZnO-based catalysts, including both monometallic (Cu) and bimetallic (Cu-Ag, Cu-Pt, Ni-Ag, Ni-Pt) formulations. The confirmation of the deposition of low concentrations of these monometals and bimetals onto the ZnO support was carried out with various characterization techniques like as PXRD, FE-SEM, EDX, Elemental Mapping, and BET analysis. After getting these interesting results, metal weight percentages were increased to 5% in catalysts such as Cu/ZnO, Au/ZnO, and CuAu/ZnO, which were synthesized and thoroughly characterized using PXRD, SEM, elemental mapping, and ICP-OES techniques. Moreover, surface properties were assessed using Zeta potential analysis, providing valuable insights into the surface charge characteristics of these catalysts. Notably, catalytic activity assessments revealed that the bimetallic CuAu/ZnO catalyst exhibited superior performance, demonstrating the highest CO₂ conversion along with better methanol selectivity compared to the monometallic Cu/ZnO catalyst. These findings highlight the synergistic effects of bimetallic catalysts, suggesting their potential for enhanced catalytic applications in CO₂ hydrogenation processes. Moving forward, further exploration and development of similar bimetallic catalyst systems hold promise for advancing the field of heterogeneous catalysis toward more sustainable and efficient methodologies.

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