

Cu-ZrO₂/multi-walled carbon nanotubes catalyst for the hydrogenation of carbon dioxide to methanol

By
Kamogelo Modisane

Student Number: 805354

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment for the degree of Master of Science in Chemistry.

Promoters: Dr Manoko S. Maubane-Nkadimeng, Prof. Neil J. Coville
and Dr John Moma

Mentor: Dr Tumelo Phaahlamohlaka

University of the Witwatersrand, Johannesburg. April 2021

DECLARATION

I declare that this dissertation, which is hereby submitted for a degree of Master of Science in the Faculty of Science, School of Chemistry, University of the Witwatersrand, Johannesburg is my unaided work under the supervision of Dr Manoko S. Maubane-Nkadimeng, Prof Neil J. Coville and Dr John Moma. This work has not been submitted for any degree or examination at any institution.

A handwritten signature in dark ink, appearing to read 'Kamogelo Modisane', is written over a horizontal line.

Kamogelo Modisane

On this day of April 2021

DEDICATIONS

I would like to dedicate this thesis to the following people:

To my mother Neo Rachel Modisane and brother Adv. Tshepo Modisane, for their outmost love, support, prayers, and motivation throughout my journey.

To my late father! Thank you for being my spiritual fortress.

To Magdeline Dolly Mati, Khomotso Modishane, and Godfrey Puni Modisane. I wish to thank you all for your support, love, and inspiration to give my best in everything I do.

*“Ke batla go rapela, **thata thata**” Gabriel Moliki Modisane*

ACKNOWLEDGEMENTS

The success of this thesis was deeply dependent on the generosity of others. I would like to show appreciation and acknowledge the following people for their contribution:

First and foremost, I would like to express my deepest gratitude to God Almighty for the grace, courage, strength, and all, He continuously provided me with. No amount of words can describe how grateful I am to my supervisors, Dr Manoko S. Maubane-Nkadimeng, Professor Neil J. Coville, and Dr John Moma for their gentle guidance, patience, financial support, and for granting me the opportunity to work under their guidance. To both Dr. Manoko S. Maubane-Nkadimeng and Dr Mahlaba A. Debeila, I would like to offer my sincere gratitude for all your efforts to guide, educate and motivate.

I am grateful to the Microscopy and Microanalysis Unit (MMU) led by Prof Alexander Ziegler, for instrument training and for allowing me to make use of the valuable facilities and instruments. I would also love to acknowledge Rhandzu Rikhotso for assisting with high-resolution transmission electron microscopy (HRTEM) analysis through the Council for Scientific and Industrial Research (CSIR) characterization facility. Special gratitude to Mr. Tshepo Mashoene for helping with the hydrogenation reactor set-up and for some technical work in the lab.

I would also thank the National Research Foundation (NRF) for the innovation scholarship and the DSI-NRF Centre of Excellence in Strong Materials (COE-SM) for funding my research consumables and equipment needs for my studies.

I will forever be grateful to the following lab colleagues: Dr Tumelo Phaahlamohlaka, Mr. Thomas Mongwe, Ms. Lebogang Mosiane, Mr. William Mokone, and Ms. Pumza Mente, for showing me around the lab, great inputs as well as their motivational guidance they offered throughout my journey. To the following colleagues for their impact and discussions; Dr Victor Mashindi, Alice Magubane, Bokome Shaku, Thuli Buthelezi, Lerato Mokoloko, and Thelma Majola.

I extend my warm gratitude to all the members of the CATMAT research group, for all their constructive criticism, valuable suggestions and for providing a vibrant and encouraging environment. I thank the School of Chemistry and the University of Witwatersrand for providing a sanctuary and support throughout my study period.

Finally, I would like to express my deepest gratitude to my family and friends (out of Wits) for their endless support, love, and encouragement from undergraduate to postgraduate studies. I owe a special thanks to my best friend, Mr Keoagile Matseke, for always being there for me. Thank you for the love, support, understanding, and encouragement throughout my studies.

“The race is not for the swift or the battle for the strong, nor does food come to the wise or favour to the learned; but time and chance happen to them all “-Ecclesiastes 9:11

PRESENTATIONS AND PUBLICATIONS

PRESENTATIONS

- “Multi-walled carbon nanotubes supported Cu-ZrO₂ Catalyst for hydrogenation of Carbon dioxide to methanol.” University of the Witwatersrand, CATMAT Seminar, August 2019 (**Oral presentation**).
- “Deposition of Cu/ZrO₂ Nanoparticles Inside and Outside Multi-Walled Carbon Nanotubes.” CATSA 2019 conference, Cape town (**Poster presentation**).
- “Deposition of Cu/ZrO₂ Nanoparticles Inside and Outside Multi-Walled Carbon Nanotubes.” SACI 2020 virtual conference (**Poster presentation**).

PUBLICATIONS

- 1) Kamogelo Modisane, John Moma, Neil J. Coville, Manoko S. Maubane-Nkadimeng: *“Effect of solvent on the properties of zirconia confined within the cavity carbon nanotubes.”* (to be submitted)
- 2) Kamogelo Modisane, John Moma, Neil J. Coville, Manoko S. Maubane-Nkadimeng: *“Physicochemical properties of Cu-ZrO₂ confined within the cavity of carbon nanotubes.”* (to be submitted)
- 3) Kamogelo Modisane, Tumelo N Phaahlamohlaka, John Moma, Neil J. Coville, Manoko S. Maubane-Nkadimeng: *“Effects of catalyst confinement within the CNTs on the hydrogenation of CO₂ to methanol”* (to be submitted).

ABSTRACT

Carbon dioxide, is known as a greenhouse gas (heat-absorbing and heat-radiating gas), is critical to the preservation of life and habitable environmental temperatures. However, human-caused increases in CO₂ concentrations in the atmosphere, such as deforestation, the industrial revolution, and the use of fossil fuels, have resulted in catastrophic climate changes. According to research, converting carbon dioxide to value-added fuels is one method that can play in reducing CO₂ emissions while also providing economic and environmental benefits.

In this study, an attempt has been made to investigate a specific catalytic system entailing the CO₂ conversion into fuels and chemicals like MeOH and DME. The system studied is a Cu-ZrO₂ catalyst supported in/on carbon nanotubes (CNTs). In particular, the impact of confinement utilizing the inner channels of CNTs as a nano-reactor for the encapsulation of Copper, Zirconia, and Cu-ZrO₂ for the conversion of CO₂ via the hydrogenation reaction has been studied. Encapsulation of copper, Zirconia, and Cu-ZrO₂ was accomplished using novel and new techniques and principles described in the literature. As a result, the synthesis, characterization, and application of the obtained catalyst with distinct properties were described.

The synthesis of carbon nanotubes using acetylene as a carbon source resulted in CNTs in high yields, multiple walls and a spaghetti-like nature, and with inner diameter ranges of approximately 27 ± 7 nm. Investigations revealed that purifying the materials in concentrated HNO₃ at 140°C was critical in producing MWCNTs with open-cut tips, which served as entry points of the metal nanoparticles.

A simple wetness impregnation technique assisted by sonication was used to selectively deposit the metal/metal oxide inside the tubes. Because of their low surface tensions, tetrahydrofuran and ethanol was used as solvents. The solvents allowed for easy wetting and penetration of the nanoparticles into the nanotube cavity. Water was used after the reaction to wash away and remove any metal/metal oxide residue from on the outside of the tube. The prepared Cu@CNTs, ZrO₂@CNTs, and Cu-ZrO₂@CNTs materials that were formed were analyzed and characterized using various analytical techniques such as powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, transmission electron microscopy (TEM), temperature programmed reduction (TPR) and thermo-gravimetric analysis (TGA) technique.

The analysis revealed that the synthesis methods were able to encapsulate the metals inside and to evaluate the amount placed inside/outside the MWCNT cavity as not all of the particles were encapsulated.

These techniques also revealed that the deposition produced small particles of varying sizes depending on the metal/metal oxide used and the location of the particles. According to the BET analysis, the presence of metal or metal oxide increased the specific surface area and pore volume, of the samples resulting in a mesoporous pore structure with surface areas ranging from 80-166 m²/g. TEM analysis displayed that an increase in loading led to more particles being located outside the tubes and also agglomeration, and this was confirmed by the pore blockage and the reduction temperatures observed in the TPR data. TEM data also revealed that confinement had an effect on the particles grown inside the tubes, resulting in differences in particle sizes and shapes between the particles found outside and inside the tube.

Because previous reports on confinement demonstrated an increase in activity with reference to the confined metals, the synthesized catalyst was used in the CO₂ hydrogenation to methanol in reactor studies which were performed at 250 – 300°C (p = 15 bar) and the results showed that all the materials were capable of acting as a catalyst at the lower temperatures. However, the Cu-ZrO₂@CNTs displayed better activities than studies performed on the MWCNTs (blank reaction) or the metal loaded MWCNTs. The CO₂ conversions for Cu-ZrO₂@CNTs ranged from 5 – 40%, and this catalyst had higher stability and activity, but lower selectivity as compared to the Cu@CNTs and ZrO₂@CNTs catalysts. The catalysts demonstrated minimal reverse gas shift reactions with formations of traces of methane and carbon monoxide. This could be attributed to the synergistic relationship between copper and zirconia, as well as the synergy of the Cu-ZrO₂ with the MWCNT inner walls.

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LIST OF ABBREVIATIONS AND NOMENCLATURE

a.u:	Arbitrary unit
AC:	Activated carbon
AFROX:	African oxygen
ACE:	Associated chemical enterprises
C₂H₂:	Acetylene
ca:	Approximately
CNF(s):	Carbon nanofiber(s)
CNT(s):	Carbon nanotube(s)
CO₂:	Carbon dioxide
CVD:	Chemical vapor deposition
DME:	Dimethyl ether
DWCNTs:	Double-walled carbon nanotubes
EDS:	Energy dispersive spectrometer
EtOH:	Ethanol
FCC:	Face-centered cubic
FID:	Flame ionization detector
g:	Gram(s)
GHG:	Green-house gases
GO:	Graphene oxide
h:	hour(s)

JEOL:	Japan electron optics laboratory(s)
min:	Minutes
mL:	Milliliters
mL/min:	Milliliters per minute
mm:	Millimeters
mol:	Moles
MSR:	Methanol steam reforming
MWNT:	Multi-walled carbon nanotubes
nm:	Nanometers
NPs:	Nanoparticles
Parts per million:	ppm
SWNT:	Single-walled carbon nanotubes
T:	Temperature
t:	Time
TCD:	Thermal conductivity detector
TEM:	Transmission electron microscope
THF:	Tetrahydrofuran
TGA:	Thermogravimetric analysis
TPR:	Temperature programmed reduction
wt. %:	Weight percentage
XRD:	X-Ray diffraction

Chapter 1

INTRODUCTION

This chapter introduces the aims and objectives together with the background and motivation of the study.

1.1.1 Study background and motivation.

In the last decades, the emission levels of carbon dioxide (CO₂) have increased due to the industrial revolution owing primarily to deforestation and the burning of fossil fuels. The drastic increase in CO₂ emissions leads to an increase in air pollution, thus leading to global warming, climate change, acid rain, and the degradation of human health [1]. It is widely acknowledged that the conversion of CO₂ into fuels will effectively reduce CO₂ and reduce our dependency on fossil fuels at the same time [2,3]. CO₂ conversion to methanol is a promising effective technology to achieve this because of its imperative role in the biological sector and sustainable energy fields [3].

Methanol is not only one of most essential fuel substitutes for renewable energy use, but is also an important energy storage medium, both in terms of volume and weight, due to its high energy density [3]. Currently, the conversion of CO₂ is most progressive for chemicals with one carbon molecule, the so-called C1-chemicals, which regarded as a low-cost green C1 resource that may be utilized either directly or indirectly [4]. CO₂ is often used as a reactant in indirect processes including the production of methanol and dimethyl ether (DME), etc. Methanol and DME can also be refined into high molecular weight hydrocarbons and renewable fuels [5], with the CO₂ hydrogenation process being one of the most reliable and cost-effective routes for CO₂ utilization [6].

One possible approach to methanol production is to firstly produce renewable hydrogen via a solar photochemical process or electrochemical process, and the hydrogen is then used to hydrogenate CO₂ in a catalysed process [7]. Catalysis occurs when the rate of a chemical reaction is increased due to the intermediate participation of a small amount of an additional substance known as a catalyst. The catalyst is at the core of the hydrogenation reaction;

however, it requires an efficient support material to enhance the dispersion of the catalyst particles and to ensure the efficient economic exploitation of the available metal. Catalysis is typically known as homogeneous when all of the reactions' components are in a single phase, or heterogeneous when at least two phases are present [2].

Support materials are frequently used in heterogeneous catalysis to enhance the active sites (often metal surfaces) through the dispersion of active metals on a nanometer scale [2]. Furthermore, supports are considered to play a significant role in catalytic processes by modifying the electronic configurations of the active metal, developing distinct active sites around the edges of the active metal and support, and improving the synergy of a reaction surface with that of the catalyst, all of which increase the reaction rate. A heterogeneous catalyst is usually in a solid form and the reactants are either in the liquid or gaseous phase. The catalytic reaction can be explained by collision theory [8].

In homogeneous catalysis, both the catalyst and the reactants exist in the same phase. Every single catalytic entity can act as a single active site since the catalyst atoms are dispersed within the reactant. Tuning of the electronic and steric properties on a metal can be easily done by varying the donor atoms in the ligands or by tuning the donating ability of the ligands [8]. This makes homogeneous catalysts intrinsically more active and selective. Homogeneous catalytic systems normally have higher catalytic activity than their heterogeneous catalyst counterparts. In industries, however, heterogeneous catalysts are preferred because of their simplicity in reaction outline, differentiation, conduct, stability, and the reusability of catalysts [1].

The catalytic activity of CO₂ hydrogenation to methanol in a heterogeneous reaction is well-known reaction [1]. The reaction has been found to be influenced by the following: (a) the metal catalyst, (b) the size of the particle, (c) the metal distribution on the support, (d) the surface area of the catalyst, (e) the active sites on the catalyst and (f) the kind of promoters and supports used in the reaction [9].

The catalytic hydrogenation of CO₂ to methanol is a key process in a sustainable methanol-based economy [10,11]. The CO₂ hydrogenation reaction was reliant on the advancement of an efficient catalyst and the methanol synthesis catalyst has been optimized for commercial processes and the catalysts are most useful in CO₂ hydrogenation under well-known operating conditions [12]. In order to convert carbon dioxide and hydrogen to methanol, a broad range of alternative heterogeneous catalysts has been investigated.

Methanol-based catalysts are commonly classified into three types namely: (a) a copper-based catalyst, which is usually a modified methanol catalyst previously used in the hydrogenation of CO where copper nanoparticles are the primary active constituents for the catalyst catalytic system; (b) a catalyst with rare-earth metals such as palladium and platinum as active components; and (c) oxygen-deficient materials with active sites [13].

Copper without a support cannot convert methanol from CO₂ when considering its selectivity to methanol, and its catalytic reactivity, and stability [13]. Copper-based catalysts are highly active for this transformation but its activity and selectivity strongly depend on the support and/or the promoter used [10]. The production and stability of the catalyst's active phase are greatly affected by the effectiveness of the support and its ability to tune the chemical properties between the main active material and the promoter [13]. ZrO₂ added to a Cu-based catalyst as support could potentially increase the surface area and improve the Cu particle dispersion. This may result in a Cu-ZrO₂ interfacial site containing oxygen vacancies for methanol formation derived from the enhanced Cu/ZrO₂ interaction. This interaction may very well improve the yield of and selectivity of methanol due to the ZrO₂ oxygen vacancy promoting the Cu species into the ZrO₂ lattice thus resulting in the formation of stable Cu⁺ ions [13].

In comparison to the MeOH formation from synthetic gas, a similar amount of H₂O is generated during CO₂ hydrogenation. Not only can the large amounts of H₂O reduce the MeOH yield but it can also speed up the crystallization of Cu and ZrO₂, which in most cases rapidly deactivates the composite used [3]. The use of hydrophobic carbon-based materials as both a support and promoters may be useful here, due to the surface's hydroxyl group on the support resulting in a synergistic effect with the metal and a positive influence on the reaction [14]. In particular, it has been noted that carbon materials provide a relatively inert support, which shows a low metal support interaction, suggesting that this system is useful for the study of the catalytic behaviour of metals [15].

Carbon materials such as carbon spheres, carbon nano-rods, activated carbon (AC) and carbon nano-fibers (CNFs) are frequently utilized as catalyst supports because of their physicochemical and thermal properties. These properties include high surface area, inert graphitic surface, and high thermal stability. However, CNFs and AC have a lower specific surface area when compared with carbon nanotubes (CNTs) [16,17]. CNTs have emerged as both a support and a promoter for the preparation of various composites. The key benefit of using CNTs as a substrate for the formation of a nano-composite is their large surface to volume ratios, optical properties, and excellent mechanical and electrical conductivity [18].

An enticing opportunity to manipulate the inner cavity of a CNT for chemical reactions is provided by the unique morphological features of the CNTs. These reactions are either catalysed by individual tubes that serve as both catalysts and nano-reactors or by additional catalytic species confined within the channel. Encapsulation of various metal phases inside the CNT channels has been documented to achieve what has been termed **confinement** [18].

Modification of the CNTs can reduce the affinity between CNTs and metal nanoparticles (NPs), and promote NP encapsulation. Nitric acid functionalization of the CNT's external surface purified CNTs (*n*-CNTs) generated a useful CNT support as the new different surface species induce weak attractive or repulsive interaction between the NPs and the CNT external surface. As a result, the acidic treatment permits the incorporation of a polar hydrophilic surface group by the addition of the carboxylic acid group onto the surface of a CNT [17]. In another approach, Castillejos *et al.* [19] oxidised MWCNTs before attaching long alkylic chains to the MWCNTs via an amide coupling reaction. The hydrophobic chains covered the MWCNTs and provided an interaction with an NP stabilizer (i.e. 4-(3-phenyl propyl)pyridine), which guided the NPs towards the inner cavity of the MWCNTs [19]. The final properties of the composite may be influenced by many factors relating to the characteristics of CNTs (purity, flexibility, absorptivity, etc.) and their confinement properties [17].

Pan *et al.* [20] investigated the impacts of internalization of iron nanoparticles within the channels of carbon nanotubes on catalysis. They represented their efforts in the study to better understand the fundamental effects of confining metal nanoparticles within CNT channels. To achieve this, they developed strategies for the homogeneous dispersion of nanoparticles inside nanotubes. They concentrated on double-walled carbon nanotubes (DWCNTs) with 1.0-1.5 nm i.d and multi-walled carbon nanotubes (MWCNTs) with an inner diameter (i.d.) less than 10 nm. The results obtained demonstrated that there exists an electronic interaction between metal species and the CNT surface and that the strength can vary with the type of metal and the inner diameter of the CNTs [20].

The ability to manipulate the physical and chemical properties of metal and metal oxide clusters by encapsulating them in a confined nano-space of porous materials is gaining popularity [21]. Being a carbonaceous material, CNTs are provided with a well-developed inner channel and pore structure which can help prevent metal sintering as well as achieve good metal dispersion [22].

The possibility of confining Cu-ZrO₂ catalyst particles inside CNTs provides an interesting approach to CO₂ hydrogenation reaction. This approach could be further evaluated by the

functionalization of the CNTs with various surface groups, such as carboxylic groups, oxygen-containing groups, and hydroxyl groups to elucidate the effects of copper and zirconia confinement in CO₂ conversion to methanol.

1.2 Problem Statement

Carbon dioxide is the most prevalent greenhouse gas which is able to absorb atmospheric heat and contribute to climate change. Global average atmospheric CO₂ was measured at 409.8 ppm in 2019 and 407.4 ± 0.1 ppm in 2018, according to the state of the atmosphere in NOAA's 2019 and 2018 report [23]. This was an increase of 2.4 ± 0.1 ppm from 2018 and 2.5 ± 0.1 ppm from 2017, corresponding to the growth of about 2.2 ± 0.1 ppm between 2016 and 2017, making it the highest ever record [24]. As such, a cost-effective measure is necessary to reduce the CO₂ emitted by humans.

Studies have shown that the incorporation of an active catalyst within the CNTs can be used for catalysis [20,21,25–29]. In this work, we propose the use of copper, zirconia, and both copper-zirconia (Cu-ZrO₂) bimetallic catalysts confined within CNTs for the conversion of CO₂ into methanol. The study will investigate whether placing Cu-ZrO₂ into the tubular channels could increase the selectivity, activity, and ultimately increase the yield of methanol from the catalyst used. The research questions that are posed in this study relating to the Cu-ZrO₂@CNTs catalyst are:

- Can ZrO₂ and Cu be placed inside a CNT?
- Can the Cu-ZrO₂ catalyst be placed inside a CNT?
- Do CNTs serve as appropriate catalyst supports for the hydrogenation reaction?
- To what extent does the choice of the catalyst influence the productivity of methanol?
- What influence does confinement of a catalyst play in the yield of methanol?
- Do the single catalysts influence the productivity of methanol?
- What are the advantages of confining the single and bimetallic catalyst?
- What is the difference in reactivity and productivity when nano-catalysts are placed inside the CNTs as opposed to when incorporated outside?

1.3. Purpose of the study

1.3.1. Aim of the study.

The study aims to synthesize and characterize Cu, ZrO₂, and Cu-ZrO₂ placed inside multi-walled carbon nanotubes and evaluate them as catalysts for the hydrogenation of CO₂ to methanol.

1.3.2 Objective of the study

- To synthesize and characterize multi-walled carbon nanotubes (MWCNTs) through catalytic chemical vapour deposition using acetylene as the carbon precursor.
- To prepare a series of Cu and ZrO₂ single catalysts and Cu/ZrO₂ bimetallic catalysts (varying ratios) using the incipient wetness method.
- To incorporate a series of Cu and ZrO₂ single catalysts and Cu-ZrO₂ based catalysts inside and outside the synthesized MWCNTs through the impregnation method.
- Produce methanol using a conventional fixed-bed flow reactor and study the effects of the Cu and ZrO₂ single catalysts and Cu-ZrO₂/MWCNTs bimetallic catalysts on the CO₂ hydrogenation reaction.
- To study the synthesized materials using various characterization techniques such as transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, X-ray diffraction (XRD), Thermo-gravimetric analysis (TGA), etc.

1.4 Outline of the dissertation

Chapter 1: Gives the motivation, aims, and objectives of the study.

Chapter 2: Provides a thorough review of the application of confinement in a CNTs cavity, particle distribution, and a brief historical account of CO₂ hydrogenation.

Chapter 3: Shows the experimental procedure and results for synthesizing CNTs, catalyst preparation, and hydrogenation reactions in a stainless steel fixed-bed reactor.

Chapter 4: Reports on the synthesis and confinement of copper nanoparticles in a study entitled: Study and characterization of confined copper within carbon nanotubes.

Chapter 5: Reports on the preparation of zirconia nanoparticles in a study entitled: Study and characterization of confined zirconia within carbon nanotubes.

Chapter 6: Reports on the synthesis and subsequent manipulation of the CNTs properties and

confinement of copper-zirconia within carbon nanotubes in a study entitled: Study and characterization of confined Cu-ZrO₂ within carbon nanotubes.

Chapter 7: Reports on the utilization of the new catalysts in a fixed-bed reactor for hydrogenation and the application of as-synthesized CNTs in the hydrogenation reaction to methanol.

Chapter 8: This chapter provides conclusions and recommendations for this study.

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Chapter 2

Background and Literature review

Carbon dioxide (CO₂) is abundant and its use as a primary resource for valuable products has sparked worldwide interest in both industrial and academic research facilities employing homogeneous, heterogeneous, and photo or electro-catalysts [1]. CO₂ hydrogenation has attracted the attention of many researchers in recent years because of the potential influence it might have on the economy and its effectiveness in converting CO₂ to value-added fuels and chemicals [2].

2.1 Carbon dioxide -An environmental issue

Climate change has become a global challenge impacting humanity due to the exponential rise of greenhouse gas emissions. With the expansion of the economy and population, global energy consumption has also rapidly increased [3]. The majority of energy is derived through incineration of non-renewable fossil fuels and resources, which causes the production of greenhouse gases and extensive accumulation of carbon dioxide in the atmosphere [2]. CO₂ is currently the most anthropogenic greenhouse gas with the highest emission rate. In 2018, CO₂ was accountable for about 81.3 percent of all greenhouse gases [figure 2.1].

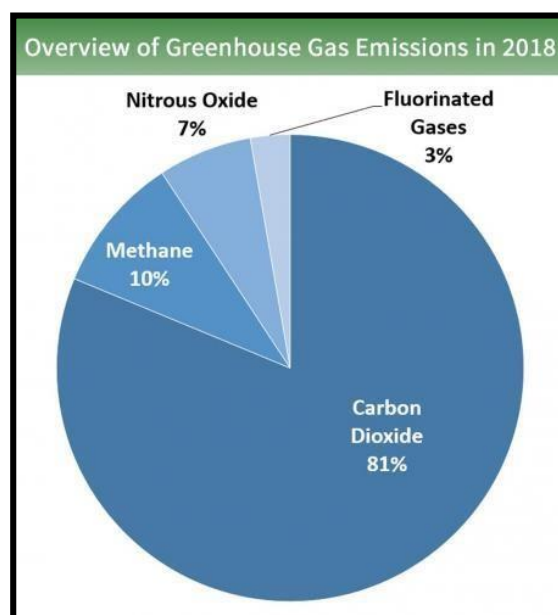


Figure 2.1: Overview of greenhouse gas emissions from all documented contributing factors as produced in 2018

The incessant and substantial increment of the CO₂ emissions has resulted in a surge of the global average temperatures [4]. The global average atmospheric CO₂ in 2019 was 409.8 parts per million (ppm) and these levels were reported to be higher than at any time in the previous 800,000 years. The last time CO₂ levels in the atmospheric were this elevated was during the pre-industrial period, more than 3 million years ago. According to the global fossil fuel committee, carbon emissions from fossil fuels have increased by about 90 percent, with emissions from fossil fuel combustion and industrial procedures accounting for approximately 78 percent of the entire increase in GHG emissions from 1970 to 2011 [figure 2.2a] [5,6]. Agriculture, disforestation, and other terrestrial-use transformations being the second-largest contributor [4].

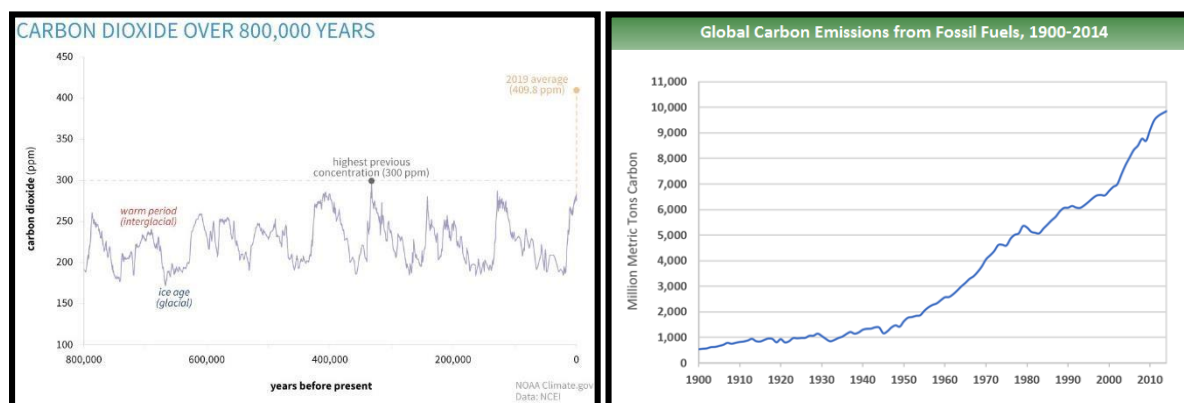


Figure 2.2: a) Global atmospheric carbon dioxide concentrations (CO₂) in ppm for the past 800,000 years. Graph by NOAA Climate.gov based via NOAA/NCIE Paleoclimatology Program and b) Global carbon emission from fossil fuels

CO₂ is not just a harmful greenhouse gas, but also an important source of carbon for making organic chemicals, materials, and carbohydrates (e.g., foods). CO₂ can be used to synthesize a variety of chemicals, ingredients, and fuels, which can be a long-term sustainable process because renewable energy sources like solar energy are used as an energy supply for chemical production. It is worth noting that the amount of CO₂ emitted in concentrated CO₂-rich flue gases from power plants and waste gases from industrial processing plants has surpassed the amount of carbon used to make most chemicals, organic products, and “liquid transportation fuel [6]. The increase in the concentration of CO₂ has revamped the quest for a massive scale of research into finding effective ways of reducing these emissions.

2.2 Reduction of CO₂

Numerous strategies have been employed to decrease the CO₂ emission build-up and examples of such techniques are: (a) carbon capture and storage [7], which intends to collect and store

significant amounts of CO₂, (b) conversion of CO₂ to chemicals [8], and (c) carbon capture and utilization that aims to convert CO₂ to fuels such as methanol (MeOH) and dimethyl ether (DME) which are key feedstocks for industrial chemicals [9].

Depending on the partial pressure, operating conditions, and gas composition, CO₂ may be captured from a variety of sources [3,7]. Carbon capture entails capturing waste CO₂, delivering it to a stowage facility, and disposing it where it is not going to be released into the stratosphere. CO₂ is predominantly captured from the air or industrial sources (such as natural gas power generation plants, synthetic fuel plants, fossil fuel-based hydrogen production plants, and biomass energy facilities) using a variety of technologies, including absorption, adsorption, chemical looping membrane gas separation or gas hydrate technologies [1,10].

Direct air capture sucks CO₂ out of the air by using fans to circulate over substances that bind specifically to CO₂. This method is advantageous because it can eliminate carbon that is already in the environment rather than capturing new emissions. However, since CO₂ in the atmosphere is less abundant, only about one out of every 2,500 molecules is CO₂, extracting CO₂ is more expensive than collecting carbon directly from fossil fuel plants or renewable sources. There are, therefore, no economic incentives (such as carbon tax) or secondary environmental benefits (enhanced soil quality) to removing CO₂ from the air. The best solution is to improve technology so that CO₂ can be captured more effectively and used for conversion [2,8].

The majority of the commercial carbon capture and storage projects that are currently in operation have found applications in natural gas processing fertilizers and hydrogen production by utilizing pre-combustion technologies [1]. CO₂ can be differentiated from natural gas and other hydrocarbons with an efficiency of 70-85% for hydrogen production. Most of the hydrogen is produced from fossil fuels by steam reforming of natural gases, partial oxidation of methane, and coal gasification. Other methods of hydrogen production include biomass gasification and water electrolysis [2,4,9].

Steam reforming from natural gases and fossil fuels is currently the cheapest source for hydrogen production and it involves heating a catalyst to high temperatures, resulting in the formation of carbon monoxide (CO), CO₂, and other GHGs as products. This is known as grey hydrogen production (of hydrogen from fossil fuels, resulting in carbon emissions). When renewable or carbon energy is used to split water, the hydrogen product is referred to as green hydrogen.

Methods to produce hydrogen without the use of fossil fuels involve the process of water splitting of water molecules into its component's oxygen and hydrogen [11]. Using emerging hydrogen technological innovations and taking the environmental aspects into account, green hydrogen is the preferred and prospective choice for the valorization of CO₂. Utilizing CO₂ that is trapped and stored in the environment, combined with green hydrogen, is reported to be a direct environmentally friendly method to methanol production without the use of fossil fuels.

2.3 Carbon dioxide hydrogenation to methanol

In this project, we aim to convert CO₂ to methanol through a hydrogenation reaction. We opted for the direct CO₂ conversion to the methanol route because it results in fewer by-products and requires less energy in product purification [1]. The use of renewable energy to convert CO₂ into methanol has been proposed as one of the most effective methods for conserving energy whilst tackling rising temperatures and the energy crisis.

The additional advantage in producing methanol from CO₂ includes, (a) its high energy density by volume and by weight, (b) it does not require high pressures for storage at room temperature, (c) it is a relatively low toxicity and safe to handle fuel and shows limited risks in its distribution and (d) it has no negative environmental effects during the production and use of methanol as a primary feedstock. Moreover, methanol is an environmentally friendly fuel, but it has roughly half the energy density of commonly used fuels. Several bulk methanol-based chemicals are found in many household products including paints, varnishes, cleaning products, and as a motor fuel or gasoline blending component [1].

Thermo-catalytic hydrogenation of CO₂ to methanol is a viable method of reducing CO₂ emissions [12–14]. Since methanol can be processed in multitudes, this method is commercially viable. Methanol as a reactant for the production of commercially essential chemicals such as methanal, ethanoic acid and unsaturated hydrocarbons, which helps to combat fossil fuel depletion [15,16]. The CO₂ hydrogenation reaction is strongly exothermic, and CO₂ activation is difficult due to its high stability. Therefore, catalysts are employed to reduce the activation energy of the hydrogenation step and break the CO₂ bonds [17]. This product is synthesized from syngas (CO and H₂) over the desired catalysts (Eq. (2.1)) [18].

Furthermore, the reverse water gas shift reaction (Eq. (2.2)) is a significant side reaction that is noticeable at high reaction temperatures. Water vapour is a by-product of CO₂ hydrogenation to methanol and the reverse water-gas shift reaction and the presence of water not only inhibits the methanol formation but also facilitates catalyst deactivation by sintering [19]. To reinforce the technological strategies for conversion of the CO₂ into methanol, an effective catalyst that has enhanced reactivity, selectivity, and stability is inherently required for using CO₂-rich feed gas conditions:



2.3.1 Catalytic systems for CO₂ hydrogenation

In order to increase methanol output while minimizing by-product formation, highly efficient catalysts are by far the most critical aspect in CO₂ molecule activation. Catalysts for CO₂ hydrogenation were primarily derived from CO hydrogenation catalysts. The heterogeneous catalytic activity of CO₂ hydrogenation to methanol is influenced by several factors, including: (a) the metal and the catalyst structure; (b) the metal's uniform particle size; (c) metal dispersity on the support; (d) the catalyst surface; (e) the active sites on a catalyst; (f) its stability and long-term operation; (g) the type of promoter and support used; (h) the growth rate of the metal [20–23].

A suitable catalyst for the hydrogenation of CO₂ to methanol is required to possess three distinct characteristics: (a) the ability to adsorb and activate CO₂ and stabilize the active intermediates for hydrogenation to methanol rather than the reverse water gas shift (RWGs) reaction, (b) the ability to dissociate the H-H bond in H₂ and facilitate its reaction with the intermediates to produce methanol and (c) the ability to prevent poisoning on the active site [9].

Multi-component catalyst systems consisting of at least two intertwined components are considered as a promising material to balance the three above-mentioned capabilities [9]. Many active metals such as copper, gold, palladium, and platinum have been employed as catalysts for the CO₂ hydrogenation to methanol [27]. From amongst these, gold and palladium possess high activities but are limited in their applications due to their high cost [29]. Hence, the two widely used active metals used are copper and zinc, due to their high efficiencies and low cost [30].

Copper-zinc (Cu-Zn) based catalysts have become well known as efficient catalysts with copper exhibiting active sites for hydrogen spill-over. On the other hand, it has been confirmed that Cu nanoparticles alone cannot be the only reactive sites [1]. Hence, Zn oxides usually plays a part in the distribution of the metallic copper particles and the synergy between copper and zinc oxide. This results in a transfer of electrons from the zinc oxide to the metallic copper (which exists as Cu^0 and Cu^+ species) [31].

Kurtz *et al.* discussed the Cu-ZnO, Cu- Al_2O_3 and the ternary Cu-ZnO- Al_2O_3 catalysts for their catalytic properties and reactivities in methanol synthesis. Activity measurements were performed in conjunction with the determination of specific Cu surface area during a rapid aging test. ZnO was selected because it was reported to be highly active but it, however, exhibited a pronounced deactivation behaviour in the aging test while the ZnO-free Cu- Al_2O_3 catalyst deactivated to a lesser extent. This deactivation behaviour was attributed to the thermal sintering of the Cu crystallites. Al_2O_3 was found to be a structural promoter of Cu/ZnO inhibiting the thermal sintering of the Cu crystallites. When examining the sintering of Cu species, researchers discovered a strong connection among the loss of catalyst activity and the reduction in specific surface area.

Deerattrakul *et al.* [17] analysed the possibilities of using the Cu-Zn bimetallic catalyst supported on reduced graphene oxide nanosheets for the conversion of CO_2 to methanol through hydrogenation. The catalyst was produced using an incipient wetness impregnation method, and its structural, surface reactivity, and adsorption properties were thoroughly examined using various characterization techniques. ZnO was reported to aid in improving the dispersion of metallic copper particles and it also contained the active sites for hydrogen spill-over. They reported an interaction between ZnO and Cu, which caused an electron transfer from Zn oxide to Cu metal, occurring as Cu^0 and Cu^+ species, which are crucial for CO_2 conversion. While Cu-Zn has been extensively researched for methanol synthesis, the activity results obtained from this study were below par because the metals had low active surface area and were prone to sintering.

Witoon *et al.* [18] focused on enhancing the activity, selectivity, and stability of the CuO- ZnO- ZrO_2 catalyst, and this was achieved by adding graphene oxide (GO) for the evaluation of CO_2 to methanol. A series of GO-supported CuO-ZnO- ZrO_2 catalysts with different GO contents were prepared via the reverse co-precipitation method. The currently accepted dual- site mechanism for CO_2 hydrogenation to methanol involves H_2 molecules dissociatively

absorbed on the copper site to form copper hydride species, while the adsorption of CO₂ as bicarbonate takes place on an interface between Cu and ZnO and the ZrO₂ sites. The atomic hydrogen then transfers from the copper site to that of ZrO₂ where it undergoes stepwise hydrogenation but because the surface areas of Cu, ZnO, and ZrO₂ are nearly identical, the presence of GO in the system created more active sites. However, adding higher contents of GO interrupted the co-precipitation with the mixed metal oxides and this led to the formation of isolated metal oxide particles as well as a considerable increase in CuO crystallite size, resulting in a lower space-time yield of methanol and thus a lower methanol production rate.

Din *et al.* [24] described the production of methanol through direct hydrogenation over Cu/ZrO₂ catalysts at varied ZrO₂ concentrations. The deposition precipitation method was used to synthesize the Cu-ZrO₂-carbon nanofiber system. The Cu-ZrO₂ system is well researched because of ZrO₂'s basic character and its ability to increase the dispersion of copper and its surface basicity. The surface area of the metallic copper was enhanced with the presentation of high ZrO₂ concentrations and the methanol turnover showed a bilinear relationship with ZrO₂. In as much as the methanol production rate progressively increased with the increase of the dispersed copper ratio, the conversion and yield of methanol were very small.

The effect of the reduction temperature of Pd-CeO₂ on the activity and selectivity for CO₂ hydrogenation was studied by Shen *et al.* [25]. They discovered that the reduction temperature had an effect on the Pd-CeO₂ catalyst's structural properties as well as its catalytic behavior. At the reduction temperature of 500°C, the overall conversion of CO₂ was reduced, and the product selectivity significantly changed. The surface of palladium drastically changed at high temperatures, owing to a decrease in ceria species (CeO₂ and Ce₂O₃) particle sizes and a rise in Pd particle sizes. The weak interaction between Pd particle growth and the sintering of ceria as support resulted in a decrease in CO₂ conversion. At high temperatures, the Ce³⁺ species acted as active sites for the dissociation of CO₂ to form CO and this consequently reduced the formation of methanol.

Numerous attempts have been made to incorporate metal/metal oxides onto CNTs for the conversion carbon dioxide. Recently, Sun *et al.* [26], utilized Cu-ZrO₂ as a catalyst supported on nitrogen-doped CNTs for carbon dioxide hydrogenation to methanol [27]. The analysis results indicated that the occurrence of pyridinic nitrogen increased the dispersion of the copper oxide nanoparticles, promoting Cu reduction and decreasing the Cu particle size whilst enhancing H₂ adsorption capabilities. These characteristics contributed to the vehement

adsorption of CO₂, therefore, activating methanol formation. The reported Cu- ZrO₂/CNT composite possessed more active sites and gave a methanol yield of 8,64 % and space-time of 102,21 mg g_{cat}⁻¹h⁻¹ as compared to the other catalysts which have pyrrolic nitrogen [26].

In a study conducted by Liang *et al.*, Pd-ZnO catalysts supported on MWCNTs were synthesized [28]. The study reported on the efficiency of different types of catalyst supports including CNTs (h & p-types), activated carbon, and γ -Al₂O₃. CNTs which substituted activated carbon or alumina as a catalyst support resulted in a rise of metallic Pd species in the form of Pd-Zn alloys in the surface of the support, despite the slight transition in apparent energy for the CO₂ hydrogenation reaction. This active Pd-species was closely linked to methanol formation. As compared to the p-type MWCNT, the h-type MWCNT had a more active sites (with more suspended bonds) and a higher capacity for H₂ adsorption. Liang *et al.* reported on the turnover frequency of CO₂ hydrogenation to have reached 1,15x10⁻² s⁻¹ over the 16% Pd_{0,1}Zn₁/AC and 20%Pd_{0,1}Zn₁/ γ -Al₂O₃ respectively [29].

There have been many reports on the effectiveness of N-doped CNTs–Cu/ZrO₂ as catalyst support for the hydrogenation of CO₂. To date, there are few reports on the efficiency of pristine CNTs for the incorporation of Cu-ZrO₂ for the hydrogenation of CO₂ to methanol. Wang *et al.* focused on the effects of carbon surface chemistry by preparing Cu-ZrO₂ catalyst support on CNTs with a variety of functional groups. A maximum production of methanol with a turnover frequency of 1,61x10⁻² s⁻¹ and space-time yield of 840 mg cat⁻¹h⁻¹ was acquired with a Cu- ZrO₂-CNTs catalyst with CNTs doped by nitrogen-containing groups and a loading of only about 10,3% under the reaction conditions of 260°C and 3,0 MPa [13].

2.3.2 Catalyst supports

The current methanol synthesis catalyst has drawbacks such as low mechanical strength, poor thermal stability, toxicity, and a short lifetime. Lately, focus has shifted to a number of features of the catalyst mechanism. In particular, supported metals perform well in the CO₂ hydrogenation of methanol. A relevant support provides a good configuration and should have the potential of controlling the reaction dynamics among the primary components of the catalyst and promoter. Metal-oxides are normally used as supports. The selection of the oxide supports is broad and examples include Al₂O₃, CeO₂, Cr₂O₃, Ga₂O₃, Nb₂O₅, MgO, SiO₂, TiO₂, ZnO, and ZrO₂ [30]. The appropriate support must be stable under reaction conditions and also

must have some function in modulating the interactions between the primary component of the catalyst and the promoter [31]. Researchers have reported the importance of supports, which not only aid in metal dispersion and the formation of support-metal interfacial sites, but in altering the reaction properties on the catalyst surface acidity or basicity, as well as oxygen vacancy concentrations, by exacerbating the interactions with other additives [31].

Currently, the copper-zinc oxide supported on alumina (Cu-ZnO/Al₂O₃) catalyst is widely applied in the hydrogenation of CO₂ to produce industrial methanol. This reaction is usually done under high pressure and at an elevated temperature [32]. However, this Cu/ZnO/Al₂O₃ catalyst is not as promising when the feed gas is changed from CO₂-containing syngas to CO₂-containing H₂ in the methanol synthesis.

Hydrogenating CO₂ to produce methanol results in loads of H₂O and CO production. The reverse water gas shift (RWGS) results in a lower selectivity towards methanol and tends to be a key problem [33]. Furthermore, alumina-based catalysts display poor activity for hydrogenating carbon dioxide to methanol due to the alumina's high-water affinity [34]. Hence, replacing Al₂O₃ with zirconia (ZrO₂) has been found to improve the catalytic performance for CO₂ hydrogenation to methanol due to the high-water tolerance of ZrO₂. ZrO₂ is of special interest to use as catalyst support due to its superior mechanical properties, good long-term stability, high specific surface area, and semiconducting properties [32].

2.5. Multi-walled carbon nanotubes as a catalyst support in CO₂ hydrogenation

Graphitic carbon materials including the likes of carbon spheres, activated carbon, carbon fibers and carbon nanotubes are good candidates for application as catalyst/catalyst support for various reactions due to their captivating physical and thermal characteristics [35]. These properties include unique structural stability over a wide range of temperature, surface areas that are resistant to basic and acidic media, and the ability to alter their surface to achieve specific applications [36]. Carbonaceous materials such as CNTs and AC have strong hydrophobicity and thus can prompt the H₂O desorption from CNTs surfaces. Therefore, carbon materials are a desirable catalyst support material as they can reduce the negative effects of the presence of H₂O in a reaction. Because of its appealing physicochemical and thermal attributes, such as high surface area (usually 180–200 m²g⁻¹), multiple-walled carbon nanotubes are commonly used as catalyst supports. Mainly because they possess evenly

distributed and straight pores, an inert carbon surface, and excellent thermal stability, as well as a superior hydrogen adsorption performance [37].

Carbon nanotubes are hollow cylindrical tubes of graphitic carbon with nano diameters and micrometer lengths [38]. Methods for the synthesis of CNTs are well documented in the literature [38–42]. CNTs are indisputably one of the most critical facets of nanotechnology, whereby catalysis is among the interesting potential application of these nanostructures. This material presents an interesting alternative to conventional supports for several reasons including high purity that eliminates self-poisoning, impressive mechanical properties, and high electrical conductivity. Moreover, the material's good thermal stability exists with high accessibility of the active phase and the absence of any microporosity. This reduces diffusion and intra-particle mass transfer in the reaction medium; tuning of the metal-support interactions could directly affect the catalytic activity and selectivity along with the confinement effects in their inner cavity [35, 36].

2.5.1 Utilization of CNTs as nano-reactors

The prospect of using the interior channels of the carbon nanotube as a nano-reactor with a few nanometers in diameter and some micrometers in length is an intriguing challenge. This possibility has only been explored in recent years after the discovery of MWCNTs. CNTs can be studied by opening, filling, capillarity, and wetting [44]. Secondly, in comparison with traditional supports, MWCNTs have high flexibility for the dispersion of the active phase through: a) modulation of their specific surface area ($50\text{--}500\text{ m}^2\text{g}^{-1}$) or their internal diameter (5–100 nm), b) chemical modification involving surface functionalization or heteroatom doping (nitrogen- or boron-doped MWCNTs) and c) deposition of the catalytic phase either on their exterior surface or in their inner channels [28].

The opportunity of catalyst confinement allows the exploitation of the CNTs as a nano-reactor, Provided the change in the characteristics of the encapsulated phase and the potential electronic participation of the interior walls of the CNTs in catalysis [43]. There are several dynamics taking place when foreign molecules are included within the CNTs. For instance, the inclusion of H_2O , and hydrocarbons inside CNTs were thoroughly researched, both practically and hypothetically, in comparison with the adsorption of the molecules on the exterior surface of MWCNTs. The above-mentioned confined species can adsorb with stronger van der Waals forces (higher binding energies) since they are enhanced by the spatial restriction and the

influence of tube curvature as opposed to the outside where the curvature binds less strongly to an adsorbate [28].

The internal functionalization of MWCNTs results in what is termed confinement effect [3,43,45]. Several factors that may contribute to this effect have been identified as [43]: (a) As metal nanoparticles were positioned within or outside MWCNTs, different electronic interactions occurred; (b) a variation in the molecule's classical arrangement due to limited space; for example, in a CNT, the H₂O molecule formed a unique cyclic conjugated system; (c) reactant enrichment on the interior walls; and (d) transport resistance along the MWCNT longitudinal axis. All these aspects are directly related to the effect of internalization and catalysis when MWCNTs can be viewed as nano-reactors [3].

There are some unique failures concerning the confinement properties of CNTs. For instance, the reactivity of Fe₃O₄ nanoparticles increased (i.e. easier reduction), whereas that of Fe nanoparticles was reduced (complex oxidation) as soon as they are driven inside MWCNTs [44]. The stability of certain metal crystal phases was affected, such as the case of face-centered cubic (fcc) γ -Fe nanoparticles, which are normally stable in the around the ranges of 1100-1600°C, but when encapsulated within the channels CNTs, they maintained their crystal structure. Moreover, despite the increased van der Waals forces, the crystal structure of the confined species underwent distortion in some cases when the CNTs were restricted in motion [46]. When water molecules and ionic liquids were encapsulated within CNTs, dimensionally restricted phase transformations were documented. CNT membranes are also promising for a various of applications due to the extremely efficiency in water transfer and gas through the hydrophobic cavity of CNTs [44].

The internal cavity of CNTs can be accessed using a variety of synthetic approaches. CNTs are usually tip-closed when they are manufactured, which means that their tips might be partially blocked from foreign molecules or chemical species. As a result, before any CNT functionalization, a tip-opening step is needed. This is normally achieved by thermal annealing or through acidic treatment (i.e. H₂SO₄/HNO₃ or HNO₃) [3]. Tsang *et al.* reported the insertion of several metal oxides by wet techniques after a tip opening by refluxing in concentrated HNO₃ [3].

Currently, there are three major methods for introducing nanoparticles (NPs) into carbon nanotubes (CNTs). Firstly, the incipient wetness impregnation techniques which rely on the filling of oxidized CNTs by capillary action with a solution containing a metal salt or

synthesized NPs. Secondly, metal may be introduced into the CNT cavity by sublimating a metal precursor. An additional washing step is usually done to remove NPs accumulated on the surface of CNTs. When these two methods are used, selectivity can be significantly improved. The third method, which involves a multi-step technique, requires the production of CNTs inside anodic aluminium oxide membranes, filling the resultant aluminium oxide-CNT composite with NPs, and then removing the alumina membrane. However, this latter approach, on the other hand, has scaling issues [44].

According to studies, CO₂ hydrogenation is among the most effective approaches to achieving CO₂ chemical fixation, improve climate conditions, and reduce fossil resource depletion [3]. CO₂ hydrogenation requires several key components: 1) a good catalyst, 2) a reaction with hydrogen, and 3) the catalyst must be able to function with low and high CO₂ concentrations. The goal of studying this topic for many has been to modify the existing industrial catalyst or develop an inexpensive catalyst to replace the currently available one with one that possesses higher activity, selectivity, and stability as a catalyst for CO₂ hydrogenation.

Several possibilities have been explored aimed at enhancing the performance of as-existing catalyst systems. One approach is to confine a catalyst such that sintering will be limited during catalytic reactions. The ongoing research includes the following [29,47–50]: -

- i. Development of an efficient strategy to place nanoparticles inside carbon nanotubes.
- ii. Studies on the effects of spatial confinement of a bimetallic catalyst.
- iii. Tuning methanol selectivity from CO₂ via a metal-support interaction.
- iv. Evaluation of the size dependence of carbon nanotube confinement in catalysis.
- v. Development of CO₂ hydrogenation of a catalyst prepared using a solvent-free route.
- vi. Study of the role of copper nanoparticle sizes in low-pressure methanol production.
- vii. Studies on the influence of calcination, reduction, and metal loading of catalysts for CO₂ hydrogenation.

2.6. Catalyst preparation

Catalyst preparation methods are reported to have a strong effect on catalytic activity and selectivity. Several techniques exist for catalyst preparation, such as [21, 22]: impregnation

methods, co-precipitation methods, sol-gel methods, chemical vapor deposition methods, deposition-precipitation methods, and solvated metal atom dispersion methods, etc. Despite the numerous techniques available for catalyst preparation, the impregnation and co-precipitation methods remain the most widely used, as opposed to the other techniques.

2.6.1 Precipitation

Precipitation is the development of a new solid phase (precipitate) from a homogeneous liquid solution (discontinuously, i.e., with phase separation). Marcilly pioneered a scientific approach for catalysts preparation via precipitation [24,47,48]. Physical transformations (change in solvent temperature, solvent evaporation) may cause the precipitate to form from a homogeneous liquid phase, but chemical processes are the most common cause (addition of bases or acids, use of complex-forming agents) [22].

Marcilly emphasized the importance of super-saturation in assessing the morphology, texture, and composition of the precipitates, as well as other aspects including the pH, temperature, the quality of the compound, the existence of impurities, and the precipitation methods. In practice, obtaining high super-saturation conditions is difficult due to the normal evolution of systems toward a reduction in super-saturation due to solid particle nucleation and reagent intake. This method, however, can result in Ostwald ripening [22,23].

2.6.2. Co-precipitation

The composition of the precipitate in a framework containing at least two metallic mixtures is dictated by the distinction in the solvency of the components as well as the chemistry involved during precipitation. Generally, under the conditions of either a slow precipitation rate or poor mixing within the reaction medium, co-precipitation is selective, and the co-precipitate is heterogeneous in composition. After the formation of the co-precipitate, a hydrothermal treatment that transforms amorphous precipitates into crystalline material under thermal means or by surface acidity variation may be carried out [23]. Hydrothermal treatment includes hydrothermal liquefaction, gasification, and carbonization [25]. This procedure is widely applied to prepare molecular sieves [25].

2.6.3. Deposition-precipitation

This technique exploits the deposition and precipitation of metal ions from a liquid medium

[26]. In conjunction with adsorption, this procedure can bring forth a thoroughly dispersed and a uniform active precursor despite the high metal content. The advantage of the deposition-precipitation method relates to particle size control and size distribution. The method also reduces the chances of forming bulk mixed compounds on the support alongside the active phase [27].

When nucleation first occurs, a reactant converts the catalyst intermediate into a non-soluble state, which is then produced gradually in solution as its concentration is expanded uniformly throughout the solution. The precipitate is deposited exclusively (adsorbed) onto the support. A second procedure uses the injection of the precipitating agent below the surface of the suspension containing the solid support and the precursor compound [23].

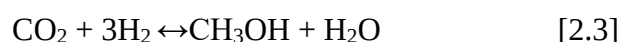
2.6.4. Impregnation

Impregnation denotes a procedure whereby a certain volume of solution containing the precursor of the catalyst is contacted with solid support. The technique is known as incipient wetness when the solution's volume is equivalent to or less than the support pore volume. The support pore volume is determined by saturating the dry support with water and measuring the precise amount of water applied. The impregnation method is the most straightforward, cost-effective, and widely used method for producing assisted metal catalysts [22,23].

The metal loading is usually achieved through contact between a liquid solution containing dissolved metal ions and the support surface. The liquid remaining is removed by drying in an oven and in the process, the metal salt (typically a metal-nitrate or metal-chloride) is crystallized onto the surface or into the walls of the pores of the support material [2,22,23,28]. The catalyst is then calcined at a desired temperature to form a metal oxide on the support and remove other unwanted species.

2.7. Carbon dioxide hydrogenation mechanism to methanol

Methanol hydrogenation mechanism has been widely studied and the reaction has been carried out to fully understand the interaction between the metals. Hydrogenation of CO₂ is widely accepted to occur on the surface of an active metal and the reaction path is presented in (Eq. (2.3)).



This conversion to methanol is kinetically limited to low temperatures and thermodynamically limited to high temperatures, leading to a low space-time yield [17]. This direct synthesis process was reported to be thermodynamically feasible under the conditions with lower temperature and higher pressure [20]. Simultaneously, the water shift reaction (given by Eq. (2.4)) occurs as a side reaction in the conventional process, consuming water [13, 14, 17].



The addition of the water shift reaction produces a powerful driving force that significantly increases synthesis gas conversion [30]. Furthermore, the reverse water-gas shift reaction (see Eq. (2.5)) is a significant side reaction that is normally seen at high reaction temperatures. Water vapour, a by-product of CO₂ hydrogenation to methanol formation also facilitates catalyst deactivation by sintering [18].

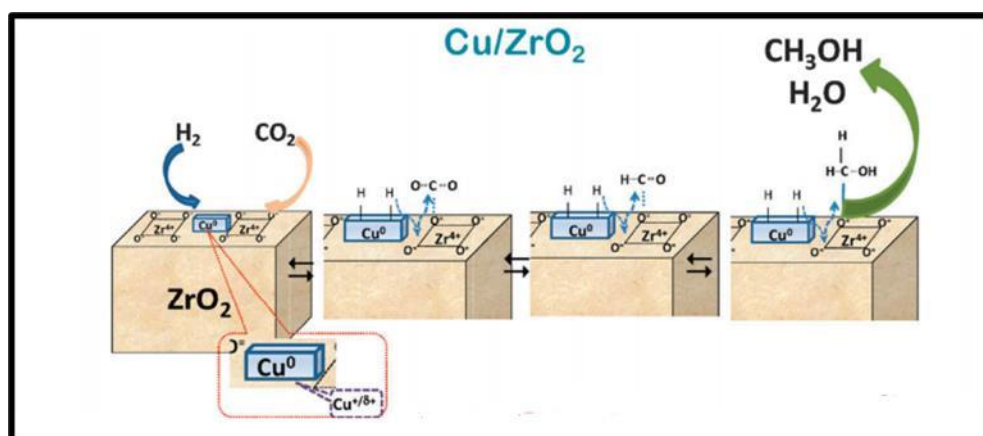
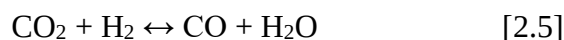


Figure 2.3: Catalyst surface and functionality of the various surface sites on Cu/ZrO₂ under CO₂ hydrogenation (Goeppert A, Czaun M, Jones JP, Surya Prakash GK, Olah GA. Recycling of carbon dioxide to methanol and derived products-closing the loop. Chem Soc Rev. 2014;43(23):7995–8048)

Herein, our work is focused on using Cu-ZrO₂ supported on/in CNTs as a catalytic system because it has two have active centers that can be beneficial for the CO₂ conversion to methanol. According to the currently accepted dual-site or bifunctional mechanism (**Figure 2.3**), the adsorption and dissociation of hydrogen occur on the Cu site, while the adsorption of CO₂ as bicarbonate takes place on the ZrO₂ site. Via hydrogen spill-over, the atomic hydrogen then transfers from the surface of Cu onto the surface of ZrO₂ and hydrogenates stepwise the adsorbed carbon-containing species to methanol, which is desorbed from the surface. However, there are two important aspects of the reaction mechanisms: (1) the nature of the active sites and (2) the reaction path [14].

The aim of this study included synthesizing catalyst materials (Cu, ZrO₂, and Cu-ZrO₂) which would be encapsulated within the channels of the as-synthesized multi-walled carbon nanotubes. This composite catalyst would then be characterized and evaluated for the conversion of CO₂ to methanol under mild conditions. We anticipate that the catalytic test would give comparable results with studies that were conducted with the same Cu-ZrO₂ catalyst but decorated outside the tubes. The success of this project could potentially lead to the testing and implementation under industrial conditions.

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Chapter 3

Synthesis and characterization of carbon nanotubes using a chemical vapour deposition technique

3.1. Introduction

This chapter presents the experimental procedure for catalyst preparation, carbon nanotube synthesis, and characterization techniques used in this research. The data relating to the properties of the synthesized CNTs is also presented and discussed.

Since the discovery of polyhedral carbon clusters (fullerenes) and graphite-like nanostructures such as carbon nanotubes, spheres, fibers, and onions, interest in carbon-based nanomaterials increased in intensity [1–3]. These carbon nanomaterials can have various morphologies, sizes, and shapes which afford them excellent properties. These properties are significant for their application as catalyst supports, promoters, sensors, hydrogen storage, etc. [4,5]. Carbon nanotubes (CNTs) come in three varieties: single-walled (SWNTs), double-walled (DWNTs), and multi-walled (MWNTs). They present several interesting properties such as high aspect-ratio, ultra-light weight, tremendous strength, high thermal conductivity, and remarkable electronic properties ranging from metallic to semiconducting [5,6].

Functionalization/doping of CNTs provides means of modifying /altering the properties of CNTs. SWCNTs have an enhanced photoluminescence capacity which can be beneficial in diagnostics, whereas MWCNTs have a large surface area that makes provision for more efficient internal encapsulation and external functionalization with active metals [7,8]. Various synthesis methods have been employed to make MWCNTs. These methods include arc discharge, laser ablation, thermal synthesis process, and chemical vapour deposition methods [9]. Amongst these synthesis methods, only catalytic chemical vapor deposition (CCVD) has been reported to allow controlled synthesis of carbon nanotubes and commercially produce a high yield. With the CCVD method, alignment, orientation, diameter, purity, and length of the nanotubes can be controlled during the reaction. The reactions are normally done in horizontal reactors [4,5,10,11]. The reactor consists of a heated quartz glass tube, with adapted connectors to allow gases to flow throughout the reactor and a thermocouple fitted to control the

temperature inside the furnace. The glass tubes have an internal diameter of 19 mm and lengths varying from 300 mm to 600 mm depending on the furnace used to provide controllable heating steadily. The furnace is equipped to resist high temperatures up to 1200°C. The heat supplied is used to “crack” the molecule into reactive atomic carbon [4,5,8,9]. In the CCVD method, catalyst support, dispersed with a small metal catalyst such as Fe, Co, Ni (transitional metals) is placed into the hotspot of the furnace under a constant flow of hydrocarbon mixture gas [4,9]. The growth process involves heating a metal catalyst (typically at 700°C).

In the CVD processes, the metal catalyst particle was found in the core of the nanotube signifying that CNTs growth starts from the catalyst particle. Thus, the nature of the support used during synthesis plays a vital role. MWCNTs have been produced by metal catalysts supported on CaCO_3 such as MgO/CaCO_3 , Ni/CaCO_3 , Co/CaCO_3 , and $\text{Fe-Co}/\text{CaCO}_3$. CaCO_3 can be easily removed during purification, CaO can be dissolved in dilute acids such as HCl and HNO_3 [5]. Studies have shown that Fe-Co catalyst is more effective when supported on CaCO_3 [4,5,7–10]. Using a 2^4 Factorial design of the experiment, Bankole *et al.* [12] examined the impact of drying time, calcination, temperature, stirring speed, and the weight of CaCO_3 support on the yield and reliability of the catalyst. According to the quantitative research results, there is a clear link and a synergetic effect between the stirring speed and the weight of the support. These parameters were noted to exert the highest impact on the product and nature of the catalyst. The results also indicate that the Fe-Co catalyst yielded the highest yield and that the CaCO_3 support favoured the growth of CNTs.

Mhlanga *et al* [5] synthesized three different methods using Fe, Co, and Fe-Co bimetallic catalyst support on CaCO_3 and prepared via wet impregnation. The synthesized CNTs demonstrated that the production is affected by temperature, gas flow, and synthesis time. The different synthesis methods generated CNTs with similar sizes and the Fe-Co bimetallic catalyst showed the best activity and near 100% selectivity to CNTs can be observed under optimal reaction conditions.

Kathyayini *et al.* [13] investigated the growth of MWCNTs using Fe, Co, and Fe-Co using Ca and Mg oxides, hydroxides, and carbonates as support. Their catalyst support mixture was prepared by wet impregnation method and revealed that Fe-Co support catalyst gave the best activity. An excellent activity was achieved by favourable metal-support interaction, which greatly influenced the CNT selectivity.

In this study, we report the growth of MWCNTs using a well-established and studied method, the catalytic decomposition of acetylene (C_2H_2) over $\text{Fe-Co}/\text{CaCO}_3$ catalyst as the carbon

source, under nitrogen atmosphere. CNT synthesis was carried out following the experimental procedure reported in [5,12]. This procedure involves both catalyst preparation and CNT production.

3.2. Materials and experimental methods

3.2.1. Chemicals and gases

Sigma-Aldrich, Ace (Associated chemicals enterprise and Mk Chemicals were the sources of chemical (solid and liquid) used in this study. African oxygen (AFROX) supplied all the gases used. Distilled water generated in the school of chemistry was used. No further purification was done before usage.

3.2.2. Preparation of Fe-Co/CaCO₃ catalyst for the synthesis of CNTs

Fe-Co/CaCO₃ metal support catalyst was prepared by the wetness technique as reported by Mhlanga *et al* [5]. The catalyst was prepared by dissolving about 3,62 g of Fe(NO₃)₃.9H₂O and 2,48 g of Co(NO₃)₂.6H₂O in water to make a 0,3 M Fe-Co (50:50w/w) solution. This solution was added to the CaCO₃ support (10 g) and this mixture was allowed to stir at 1600 rpm for 30 min. The resulting slurry was allowed to dry at room temperature and later dried in an oven at 120°C for 12 hours. The metal support mixture was then cooled at room temperature, grounded, and screened through a 150 µm sieve. The catalyst powder obtained was then calcined at 400°C for 16 hours in the air, the total loading of Fe-Co catalyst on the catalyst was 5%.

3.2.3. Production of CNTs

CNTs were synthesized using a procedure that was reported by Mhlanga *et al.* [5]. 0,5g of the as-prepared supported metal catalyst was placed in the ceramic boat, the boat was then inserted in the center of the CVD furnace. The furnace was then heated to 700°C at 10°C/min and nitrogen gas was passed over the catalyst at a flow rate of 40 ml/min. Once the set temperature was attained, the N₂ flow rate was adjusted to 240 ml/min and acetylene gas (C₂H₂) was introduced at 90 ml/min. The reaction was allowed to proceed for 60 min, after which, the flow of acetylene was stopped. After this, the nitrogen flow rate was reduced and maintained at 40 ml/min and the furnace was left to cool to room temperature. The boat was then removed from the reactor and weighed. The black CNT powder was obtained and labelled as raw CNTs.

3.2.4. Purification of the synthesized CNTs

Nitric acid treatment was used to purify the as-synthesised CNTs [14,15]. About 1g was purified using 55% HNO₃ under reflux in an oil bath at 110°C for 4hours. This is done to eliminate the CaO, Fe-Co particle residue, and the amorphous carbons that serve as impurities that occur during catalyst production. The mixture was then filtered and washed with distilled water to remove the residual HNO₃, this was done until the pH of the filtrate was 7. The mixture was filtered out to obtain the wet CNTs, which were then dried at 100°C for 12 hrs to ensure that we obtain open-end CNTs and remove the catalyst residue.

3.2.5. Carbon yield determination

The CNT's yield was calculated using the relationship provided by Yeoh *et al.* [8] as presented in the equation below:

$$\text{CNTs yield (\%)} = \frac{(M_{\text{total}} - M_{\text{catalyst}})}{M_{\text{catalyst}}} \times 100$$

Where the M_{total} is the total mass of the final catalyst and carbon production after the CVD reaction process and M_{catalyst} is the initial mass of Fe-Co/CaCO₃

3.3. Characterization techniques

To assess their chemical & physical relationships, various techniques were used to classify the synthesized materials. Techniques were used to evaluate, among others, the structural morphology, crystallization, surface area and how they would be appropriate for hydrogenation application [16].

Using powder X-ray diffraction (PXRD / XRD), the prepared materials were analysed to determine the crystallographic phases, sample composition and the results were compared with those obtained from energy-dispersive x-ray spectroscopy (EDX). To investigate their intrinsic and extrinsic structural morphology, surface composition and, confinement inside the CNT channels, Transmission Electron Microscopy (TEM) was used [17–19].

Brunauer-Emmett-Teller (BET) was used to carry out the specific surface area, pore-volume, and pore size. The thermal stability of the pristine, filtered, and confined CNTs was investigated using thermogravimetric analysis (TGA).

3.3.1. Transmission electron microscopy (TEM) analysis

TEM is a technique that uses an electron beam to image a nanoparticle sample, providing a

much higher resolution than is possible with light-based imaging techniques. TEM is the preferred method for calculating nanoparticle size, grain size, size distribution, and morphology directly.

TEM FEI Technai G2 spirit electron microscope, operating at 120KeV, was used to study the morphology of pristine, purified, and confined materials. The samples for TEM preparation were dispersed in ethanol and the mixture was sonicated to form a suspension. A drop of the suspension was dispersed onto the nickel/copper grid, dried at room temperature, and analysed.

3.3.2. Energy-dispersive X-ray spectroscopy

EDX is an x-ray technique used to identify the elementary composition and to enhance the accuracy of the morphological evolution of the components. EDX systems are attachments to scanning electron microscopy (SEM) or TEM instruments where the imaging capability of the microscope recognizes samples of interest. This is made possible through the wavelengths and energy that is characteristic of the particular element which is produced by the X-rays. In this analysis, EDX was performed to identify and confirm the presence of metals confined to the CNT channels. The study was carried out via the TEM; hence the preparation of the sample was the same [19–21].

3.3.3. Thermogravimetric analysis (TGA)

TGA studies the mass as the temperature of the sample varies over time. This analysis gives information that provides physical phenomena such as phase transitions, absorption, adsorption, and desorption, as well as on chemical phenomena such as chemisorption and thermal decomposition [12,17]. The basic theory is that at different temperatures, substances with different degradation temperatures can decompose and vaporize, but it does not provide an insight into surface coverage.

A Perkin Elmer Pyris 4000 and STA 6000 TGA were used for thermal analysis, mass composition, and thermal stability [4,22]. For any sample, an average of 7mg to 10mg was placed in a high-temperature resistant pan and inserted in the instrument furnace. The sample was heated from 35°C to 900°C at a constant heating rate of 10°C/min under air. The initial and final weight of the sample was recorded.

3.3.4. Powder X-ray diffraction (XRD)

XRD analysis is an extensively used technique for the characterization of nanoparticles and it

provides information regarding the crystalline structure, nature of the phase, lattice parameters (using the Scherrer equation) and, crystalline grain size [23,24]. The composition of the particles can be determined by comparing the position and intensity of the peaks.

In this work, the sample's composition was analyzed using a Bruker D2 phase, which uses Co-K α radiation at 30 kV over a range of $10^{\circ} \leq 2\theta \leq 90^{\circ}$. The samples were run for 20 min and EVA was used for matching and identifying the peak patterns obtained.

3.3.5. Brunauer-Emmett-Teller (BET)

BET analysis is widely used to determine the specific surface area, pore size, pore-volume, and nitrogen isotherms. It is based on the physical adsorption theory of gas on a solid surface and is preferred because it is a relatively precise, fast, and easy method for this purpose [25–27]. To determine the surface areas of the synthesized materials, 0.2 g of the sample was first degassed in nitrogen at $\sim 150^{\circ}\text{C}$ - 200°C for 4hrs. The nitrogen adsorption isotherms, specific area and, pore size distribution at the synthesized materials were taken at 77 K with a micromeritics Tristar 3000.

3.4. Results and discussions

3.4.1. Transmission electron microscopy analysis

TEM, XRD, and TGA were used to confirm that CNTs were synthesized and that purification was successful however the images showed that there were still some remnants of the initial Fe/Co-CaCO₃. The as-synthesized CNTs were spongy in texture. (figure 3.1) revealed that all CNTs were multi-walled (figure 3.1.a), arranged randomly, and had open ends. The open ends are reported to be suitable for CO₂ hydrogenation and aids in the increase of the BET surface area. They had a spaghetti-like nature with a diameter range of 7-29 nm. Some of the unpurified and purified nanotubes formed contained some residue from the catalyst (Fe-Co and CaO) which were embedded on the graphite layers (figure 3.1b). However, these remaining catalysts were completely encapsulated by a layer of carbon, which renders them inaccessible to the reactants [28]. There was some catalyst which was found in the tips of CNT suggesting that they were made via base-growth mode involving a strong interaction between Co-Fe particles and the CaO

Table 3.1: shows the structural properties of CNTs.

Sample	Size distribution	Average diameter(nm)
Unpurified CNTs	8-27	17
Purified CNTs	7-28	16

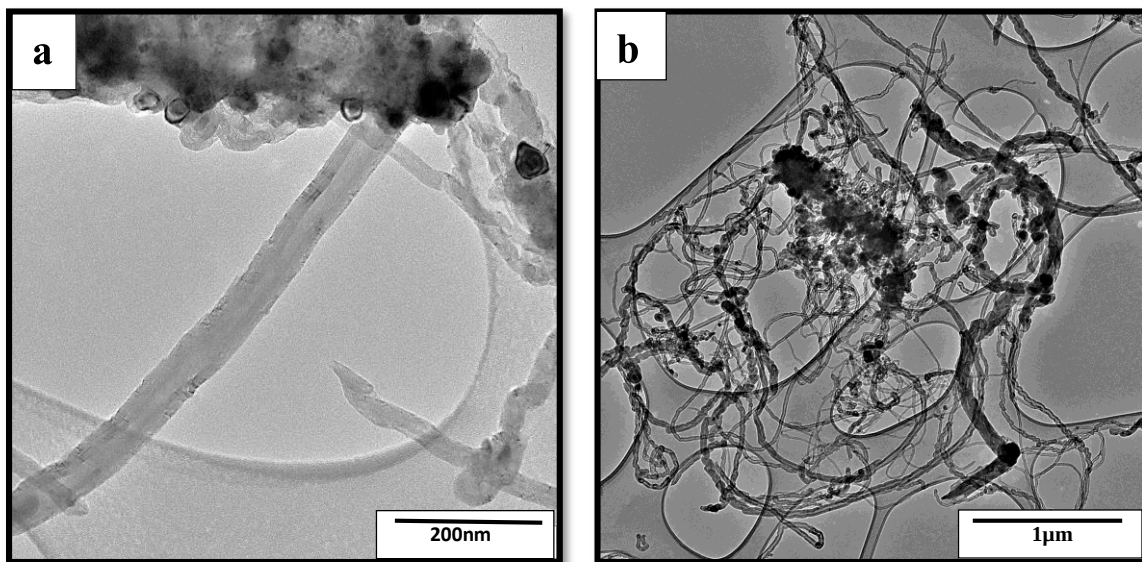


Figure 3.1: TEM micrographs for (a and b) Unpurified CNTs

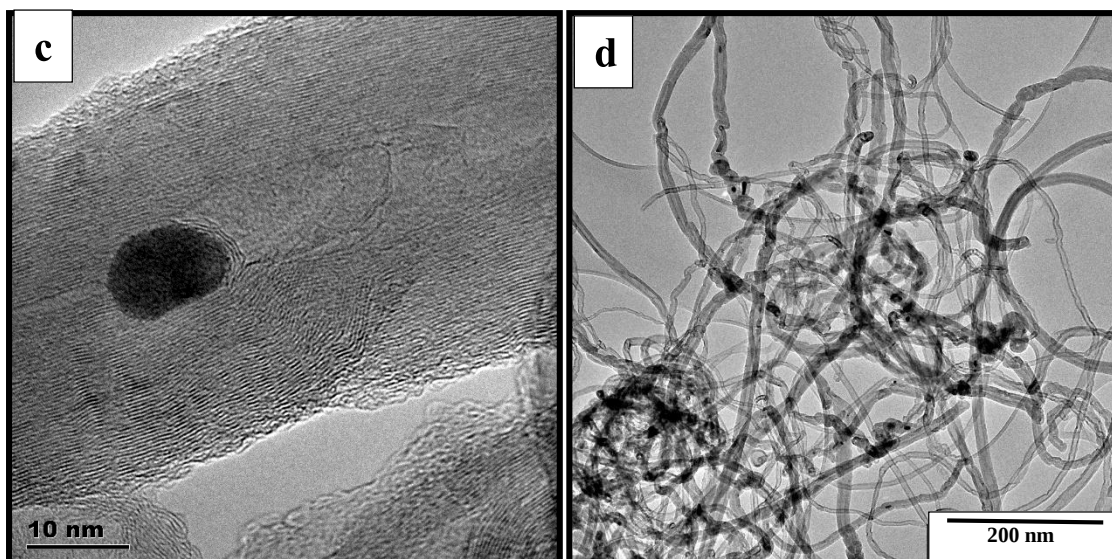


Figure 3.2: HRTEM micrographs for c) purified CNTs and d) TEM of Purified CNTs

3.4.2 Yield of CNTs

The yields were calculated by subtracting the initial mass of the Fe-Co/CaCO₃ catalyst from the total mass of the final weight, which was divided by the initial mass multiplied by 100. Yields are relatively reported as the amount of the product relative to the amount of the catalyst used and it is usually more <100%. We found that using equation 1, stated above, our yields ranged from 202.5 percent to 300 percent.

3.4.3 Bruanuer-Emmette Teller

BET measurements were conducted to investigate the changes in the specific surface area and the porosity of the materials from N₂ adsorption & desorption isotherms, the specific surface areas and pore volume of the purified CNTs are shown in Table 3.2. Figure 3.3b shows the nitrogen adsorption-desorption isotherms of the synthesized purified CNT materials. The N₂ adsorption-desorption isotherm of the CNTs samples shows a Type IV adsorption isotherms at high relative pressures. The observed increase in surface area and porosity of the materials could be attributed to 1) the formation of the HNO₃ purification carboxyl and hydroxyl groups, 2) the mean diameters, and 3) the texture and tip openings [29].

Table 3.2: Shows BET surface areas and porosity of the synthesized material

Sample	Surface Area(m ² /g)	Pore volume(cm ³ /g)	Pore size(nm)
Purified CNTs	90.9	0.34	15.35
Unpurified CNTs	83.4	0.28	14.73

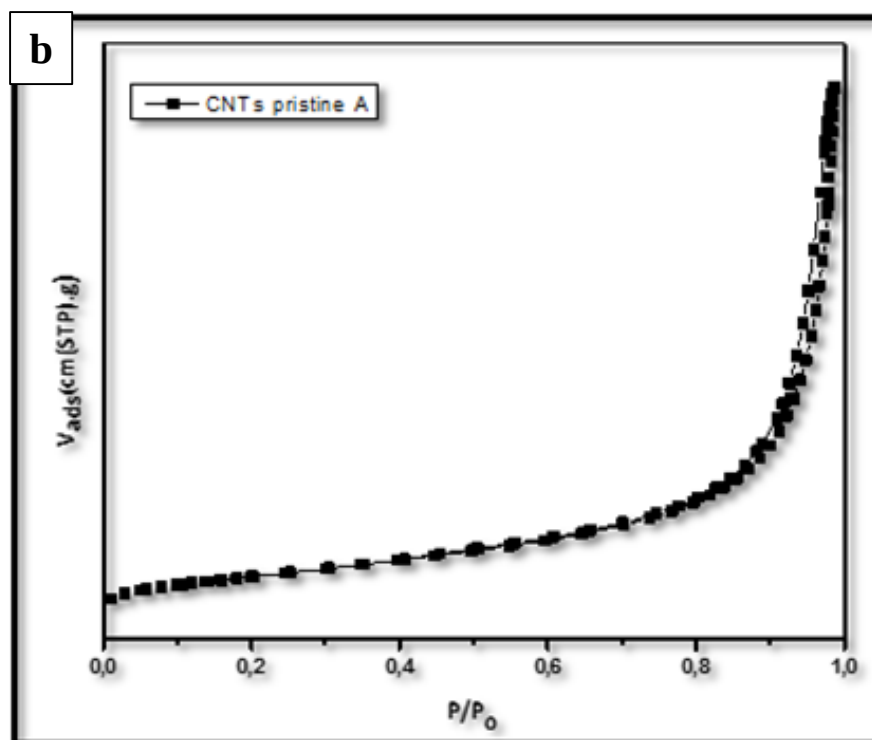
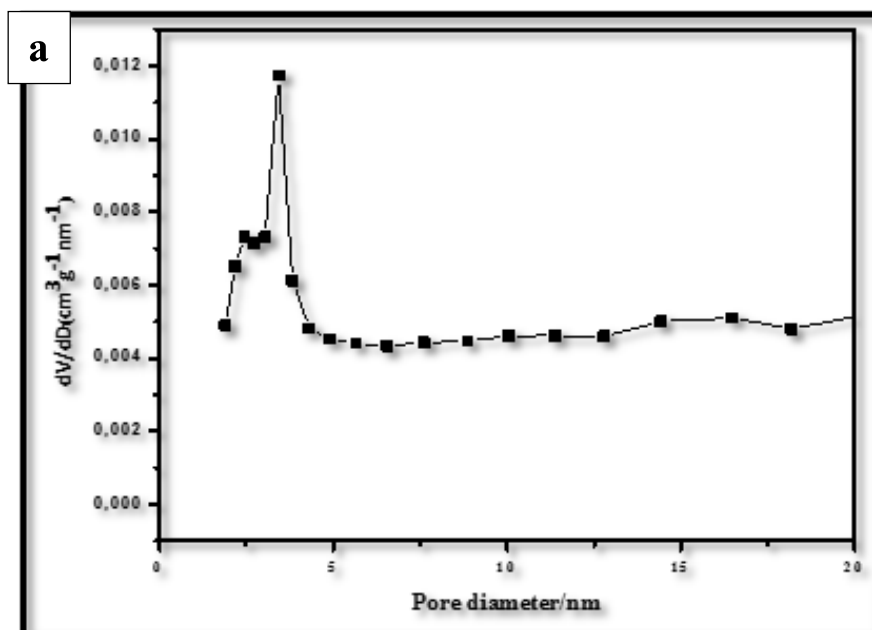


Table 3.3: shows the a) pore size distribution and b) nitrogen adsorption-desorption isotherms of the purified material

3.4.4. X-ray diffraction data

Figure 3.4 shows the XRD patterns of the unpurified CNTs and that of purified CNTs and they had two similar diffraction patterns. An intense sharp peak was observed in both supports at 2 θ at 26°, which corresponds to the crystal plane 002. Other low-intensity peaks at 2 θ were seen at 31,4° (110), 43° (111), 44,3° (100), and 54.2° (220) [5]. The most dominant peaks seen on both the supports were at 2 θ 26.5°, 43° and 44.3°, which could be connected to (002) diffractions of graphite, which confirms that we synthesized CNTs. From the purified supported, we observed the disappearance of diffraction peaks located at 2 θ 18.4°, 34°, 37°, and 54.2°. CaCO₃, Co, Fe, Co-Fe, and CaO may be related to these peaks and their absence may be their nanometer scale and the higher dispersion of the CaCO₃ metal particles [7]. Due to the detection limit of the instrument, they are inaccessible and the metal residues seen in TEM which were encapsulated could not be detected in the purified sample.

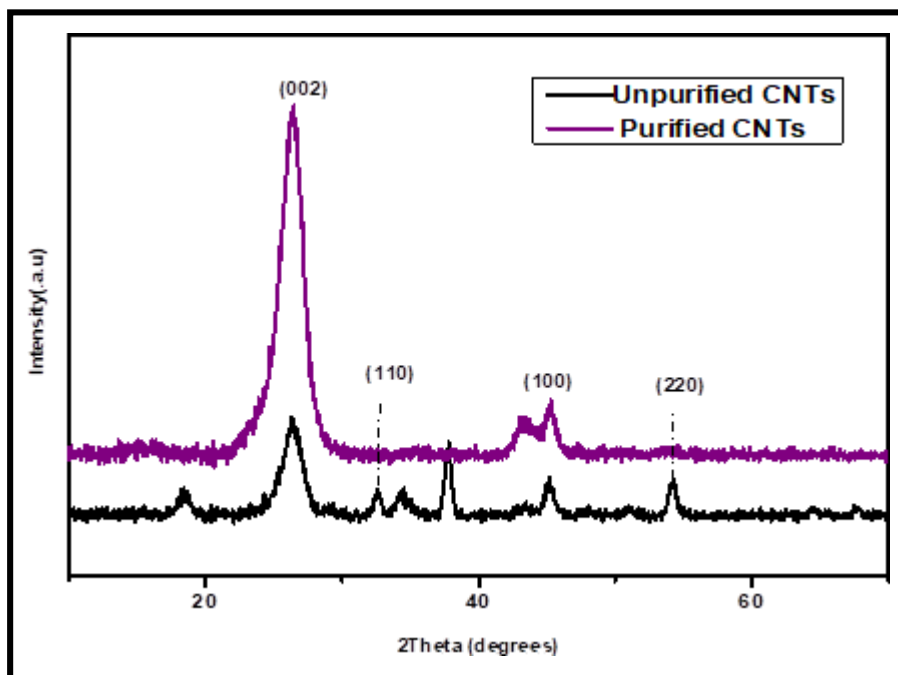


Figure 3.4: XRD patterns for the synthesized P-CNTs and raw CNTs

3.4.5 Thermogravimetric analysis

The thermal stabilities of the purified CNTs were analyzed under air. The study was also used to evaluate the purity of CNTs after the purification. The TGA profiles with the corresponding derivative curves are presented in figure 3.5. The TGA showed that there was no loss of mass below 500°C, suggesting that amorphous carbon was not present as confirmed by TEM and XRD [27]. The TGA profiles also showed that some weight gain (seen through the broad peak)

on the purified CNTs and this can be accounted for by the transition from Fe to FeOx. The weight loss derivative curve showed that no weight gain was formed from metal oxides, suggesting that HNO₃ purification was effective in removing 99% of the 20% residue which is observed on the unpurified CNTs and this was confirmed by XRD.

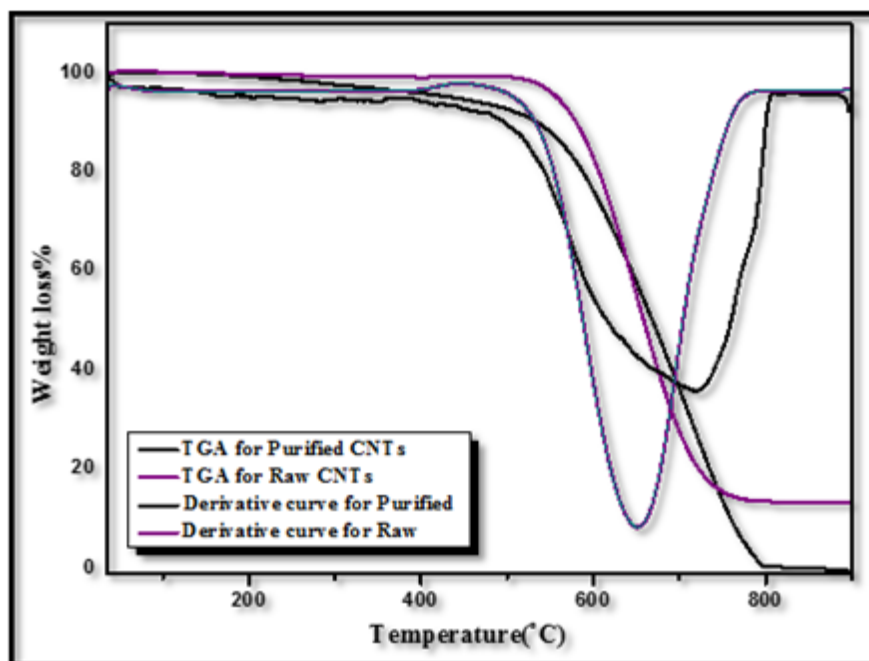


Figure 3.5: TGA profiles of p-CNTs and unpurified CNTs

3.5. CONCLUSION

Our results describe the optimized method for the synthesis of carbon nanotubes and the purification adapted to yield open-cut tips that are suitable for the application. We successfully synthesized clean CNTs (99% purity) using the chemical catalytic vapor deposition of acetylene gas over CaCO₃ supported Fe-Co catalyst. The carbon nanotubes formed were mostly open-cut tips, multi-walled, and had higher yields. The presence of the Fe-Co residues which were seen on TEM but could not be detected in XRD. The residues could not be detected because the quantities were below the XRD detection limit, and this was confirmed by TGA. These residues have been embedded inside the wall as seen in figure 3.2a. These residues have been reported to have no effect on our application in the hydrogenation reaction. The purified CNTs will be used for the rest of the reactions reported in the study.

3.6. References

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Chapter 4

Study and characterization of confined copper within carbon nanotubes

4.1 Introduction

The continued use of fossil fuels worldwide has contributed to the increased accumulation of CO₂ in the atmosphere and a significant problem has been the global warming caused by greenhouse gases [1]. Hydrogenation of CO₂ to methanol provides one approach to reduce CO₂ emissions from CO₂-producing processes at source [2,3]. In addition to offering a prospective solution to reducing CO₂ emissions, this approach is a key process in a sustainable methanol-based economy [4].

Copper can be used to convert CO₂ and H₂ to methanol [5]. CO₂ can be adsorbed on exposed copper oxide while hydrogen is reported to react with copper species (6). The active Cu species is mainly present as Cu⁰ on a Cu/support. Intimate contact of the Cu surface with other metal oxides is necessary for facilitating the hydrogen spill-over from the Cu to Cu⁺ [2]. Although a copper-based catalyst is highly active for this reaction, the support and/or promoters strongly affect the reaction activity and selectivity [7,8].

Due to their broad application in hydrogenation, copper nanoparticles have drawn tremendous attention over the years to their use in low-temperature methanol synthesis, the water gas shift reaction, click chemistry, and in electrical and construction industries [9,10]. When reviewing the recent advances in the quest for effective catalysts which were synthesized and used in methanol synthesis via hydrogenation of CO and CO₂; Liu *et al.* noted that copper metal and low Cu (Cu⁺ and Cu^{δ+}) valence species could have an impact on the catalytic activity of Cu-based oxide catalysts [11–14]. Nevertheless, some literature reports recognized the promoting influence of many metal oxides on the reactivity of Cu and showed that structural, chemical, and electronic effects on the metal oxide enhanced the exposure of the Cu surface and led to its unique reactivity [9,15].

Cu nanomaterials possess outstanding features for the advancement of nanotechnology. Cu NPs exhibit a very high catalytic activity, a property that can be associated with their large catalytic surface area. This property was directly linked to the activity of Cu-based catalysts in the

hydrogenation of CO₂, which is less resistant to sintering and agglomeration due to its low surface energy [1]. It is well known that a nanomaterial's chemical and physical properties are greatly influenced by their morphologies and physical constraints, and this is also true of Cu nanoparticles especially when confined within CNTs [15–18].

Wang *et al.* [9] filled copper nanoparticles inside the interior of carbon nanotubes with varying tube diameters using a convenient sonication-assisted impregnation approach. The CNTs were emptied under vacuum before the impregnation step. For CNTs with smaller tube diameters, a subsequent strong auto-reduction of the confined Cu nanoparticles was observed, and this led to a downward auto-reduction trend with an increase in annealing temperature. On the other hand, Cu-CNTs catalysts with larger tube diameters exhibited reduced catalyst activity after the same heat treatment. Furthermore, the Cu nanoparticles loaded outside of CNTs catalyst were prepared and compared with the Cu nanoparticles that were filled inside. Methyl acetate hydrogenation, forming methanol and ethanol, was chosen as a model reaction to further explore the influence of the CNTs confinement effect. The confined catalyst exhibited higher catalyst activity. Heat treatment, a critical parameter, was proven as a beneficial effect on the catalytic performance of a small inner CNT diameter at the optimum temperature of 973K.

Numerous physical techniques have been adopted for the synthesis and loading of Cu nanoparticles within CNTs, such as chemical vapor deposition, co-precipitation, sol-gel, and wet chemical methods [20,21]. While there are numerous reports on the introduction of Cu [9,22,23] into CNTs with smaller inner size, the literature on the deposition of Cu with variations in metal loadings and introduction of a solvent is scarce. Problems may be envisaged for Cu due to its decreasing interactions with the CNTs surface and its ability to lose stability prompted by agglomeration. When Fe₂O₃ was confined, Fe₂O₃ turned out to be reduced at lower temperatures when deposited in the interior space rather than on the outside of small CNTs [22]. We expect that the encapsulation may lead to the stabilization of copper and reduce metal clustering. This proposal is suggested by evidence on the dependence of catalytic and redox properties of catalytic components on their location.

Herein, we report on the deposition of copper particles into the interior space of CNTs with different loadings. We performed the synthesis by an adaption of techniques given in [9,22]. However, in the technique, reported by Großmann *et al.* [22], CNTs were functionalized twice through thermal stress and by acid treatment. Depending on the CNT's diameter, Cu-NPs were collected and analysed with different size ranges and locations. It has been reported that this approach requires a technique that can readily control the fixed position of the Cu-NPs and can

control the loading to enable an increase in catalytic efficiency [9,24]. The effort in our study was driven by the interest to create a model catalyst for the investigation of Cu-ZrO₂ interaction in industrial methanol synthesis.

4.2. Experimental procedure

In this research, the synthesis of Cu nanoparticles encapsulated inside CNTs (Cu-NPs@CNTs) was achieved following the experimental procedure cited in [9,22], with some alterations. The procedure includes both the catalyst preparation and the loading of the obtained catalyst into the CNTs. This adjusted procedure is expected to produce dispersed Cu-NPs filled within different diameter CNTs.

4.2.1. Starting materials

The copper nanoparticle catalyst was prepared from copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%) and tetrahydrofuran (THF, 99%) purchased from Sigma-Aldrich and Associated Chemical Enterprises (ace) respectively and used without any further purification. African oxygen (AFROX) supplied the nitrogen (N₂, 99%), which was used in the thermal treatment experiments. Distilled water generated in the School of Chemistry was used.

4.2.2. Catalyst preparation

As synthesized and purified open-end CNTs (reported in chapter 3) with different diameters were used as the catalyst support. We conducted a three-step synthesis to prepare the Cu nanoparticles confined inside CNTs as shown in Table 4.1. In summary, 0.25 g P-CNTs (purified CNTs treated with acid) were impregnated with 4 ml of x% Cu(NO₃)₂·3H₂O (x = 3, 5, 7, 12) aqueous solution containing THF and water as solvent (ratio of THF to water was 3:1). This aqueous solution was vigorously stirred for 10 mins before the impregnation step. Impregnation was then followed by continuous stirring for 30 mins, and sonication for 45 mins. Another 0.5 ml of distilled water was added dropwise, sonication continued for 1 h, and a dry sample was obtained. The obtained sample was slowly dried at 373K for 12 h. The final catalyst was heated at 723K under a N₂ atmosphere for 3.5 h, at a rate of 5°C/min. The Cu content was varied (3 % to 12 %) and the samples labelled as 3%Cu@CNTs, 5%Cu@CNTs, 7%Cu @CNTs, and 12%Cu@CNTs.

Table 4.1: Summary of the experimental procedure

Description	Stirring Time (h)	Sonication time(h)	THF (v/v ratio)	H ₂ O (mL)	THF (mL)	heat treatment conditions
X% Cu@CNTs	0.67	0.75	3:1	1	3	T= 450°C
						r = 5°C/min
						T _{total} = 5 h

4.2.1. Characterization techniques

TEM, XRD, BET, and TGA were used as characterization techniques to evaluate the synthesized materials. The morphologies of samples were characterized by high-resolution TEM. The crystal structure of the materials was characterized using XRD, and BET was used to determine the surface area, pore size, and pore volumes of the catalyst. The thermal stability, quantity, and the differential thermogravimetric analysis of the x%Cu@CNTs were monitored using a Perkin Elmer TGA (6000).

4.3. Results and discussion

4.3.1. High-resolution transmission electron microscopy (HRTEM)

During purification (i.e. acid treatment), oxygen-containing functional groups such as the carboxyl group and hydroxyl group are introduced to the inside and outside of the CNTs. As such, due to the electrostatic force experienced by Cu(NO₃)₂ during the confinement, the Cu²⁺ ions are adsorbed onto these functional groups. The functional groups could readily be removed by heat treatment [9,24].

Figures 4.1-4.4 show the HR/TEM images of 3%Cu@CNTs, 5%Cu@CNTs, 7%Cu @CNTs, and 12%Cu@CNTs and the corresponding particle size distributions respectively. The HRTEM images (Figures 4.1a,b-4.4a,b) show that the Cu particle has mainly a spherical morphology and that it is loaded inside the hollow cavity of the CNTs. Due to the assistance of sonication and the relatively low surface tension of THF and water, the solvents were able to wet and penetrate the channels of the CNTs, driven by capillary forces [9,19,25,26]. In the second step, the water addition helped remove Cu particles from the outside of the CNTs through washing. The low magnification TEM images of all samples (Figures 4.1c,d-4.4c,d) show that majority of the particles were successfully encapsulated into the CNTs (red arrows) with only a few Cu NPs (shown by yellow arrows, particularly in the 12%Cu@CNTs sample) deposited outside the CNTs.

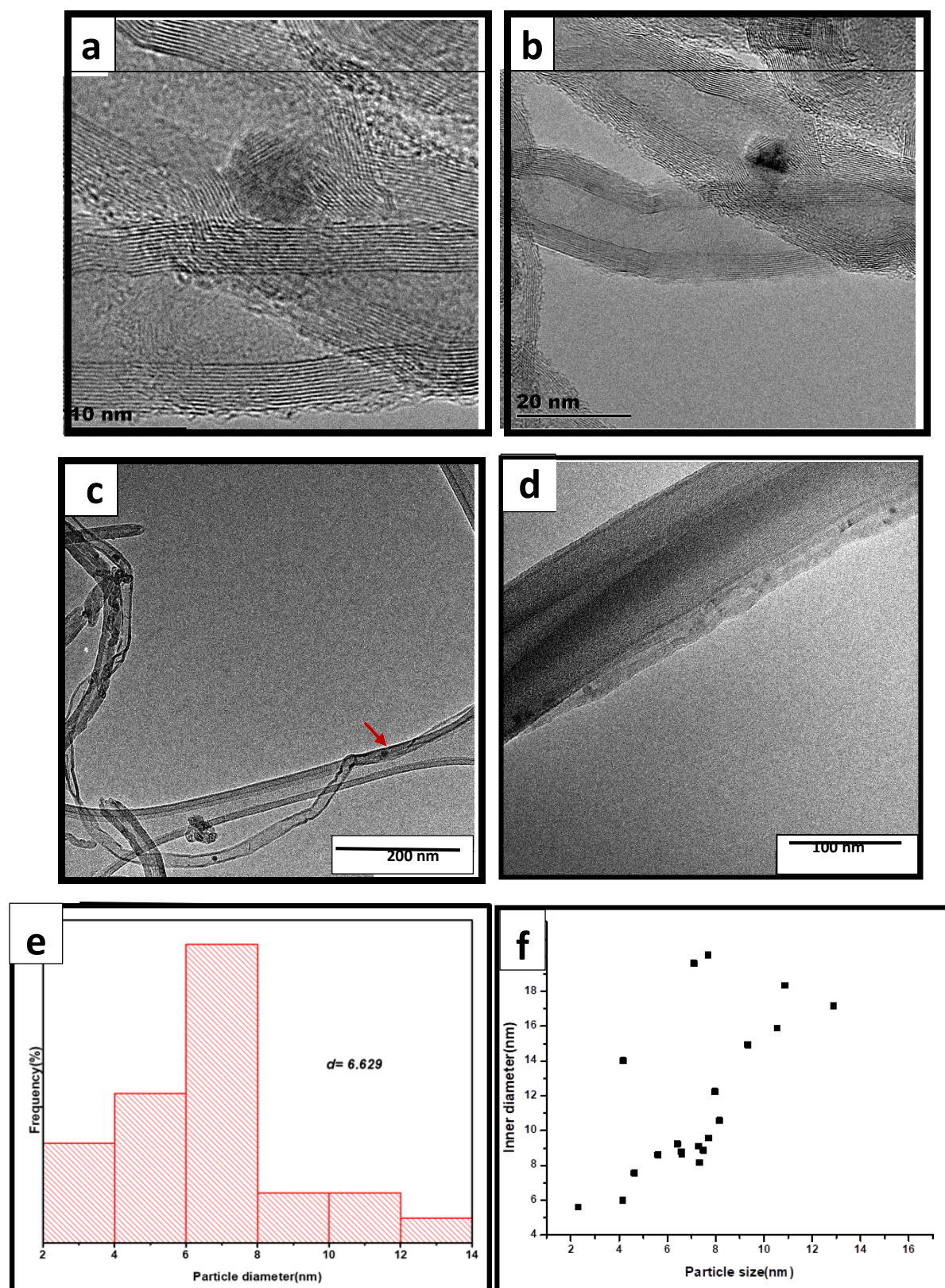


Figure 4.1: (a-d) HRTEM/TEM images, (e) the corresponding Cu particle size distributions and (f) a plot of particle size versus inner diameter for 3%Cu@CNT

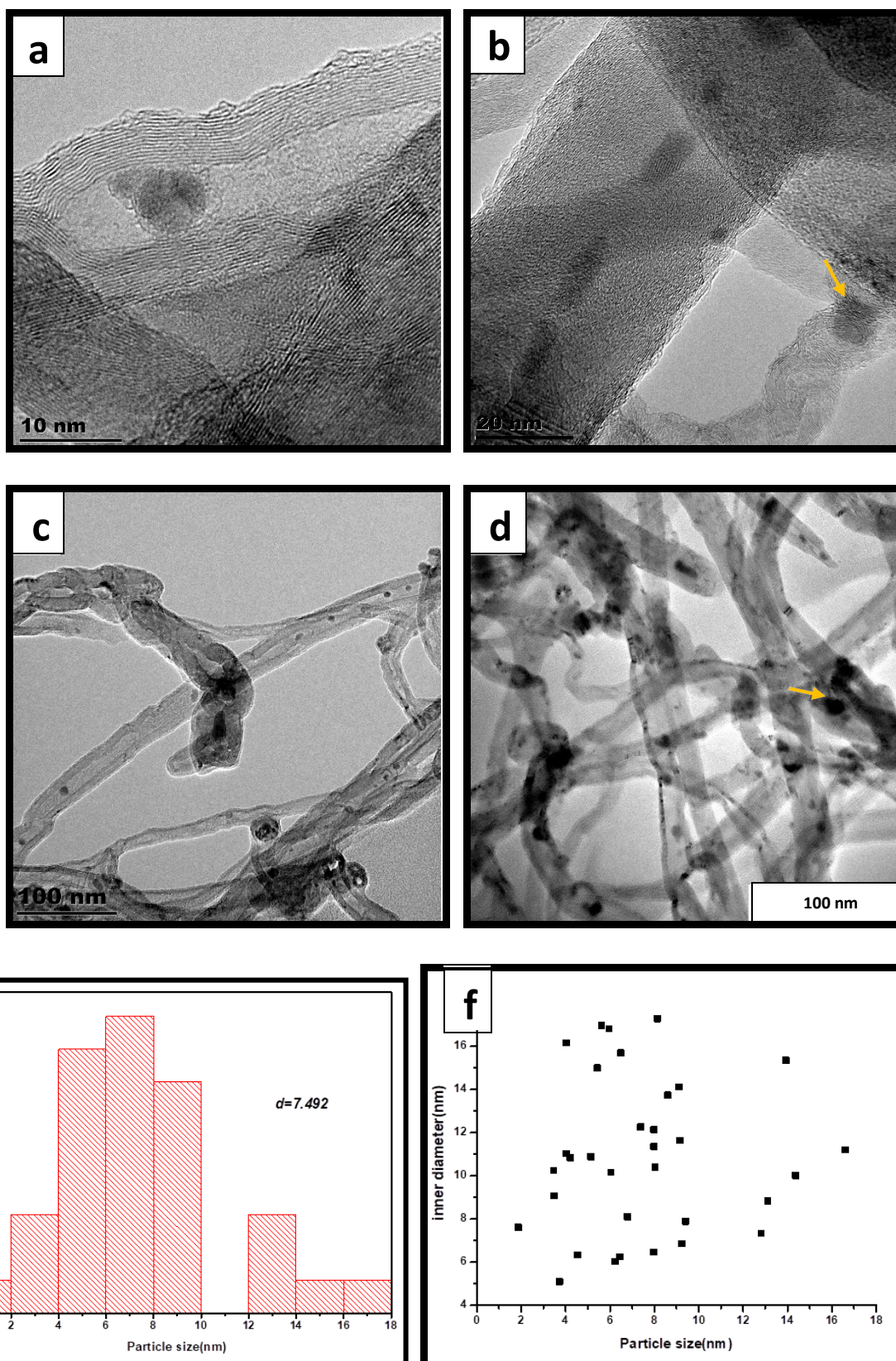


Figure 4.2: a-d) HRTEM/TEM images, (e) the corresponding Cu particle size distributions, and (f) a plot of particle size versus inner diameter for 5%Cu@CNTs

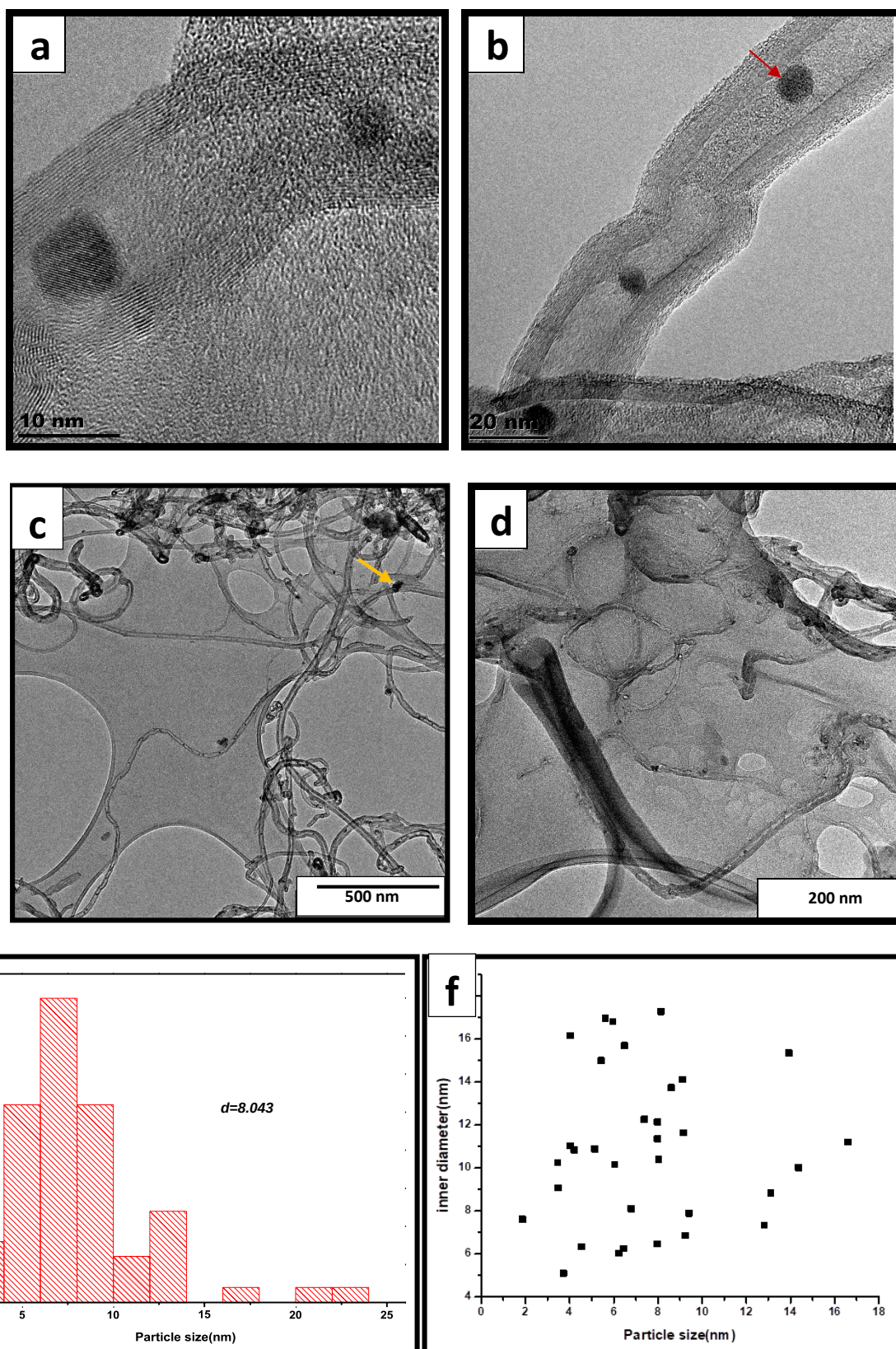


Figure 4.3: TEM images, the corresponding Cu particle size distributions (e), and a plot of particle size versus inner diameter (f) for 7%Cu@CNTs

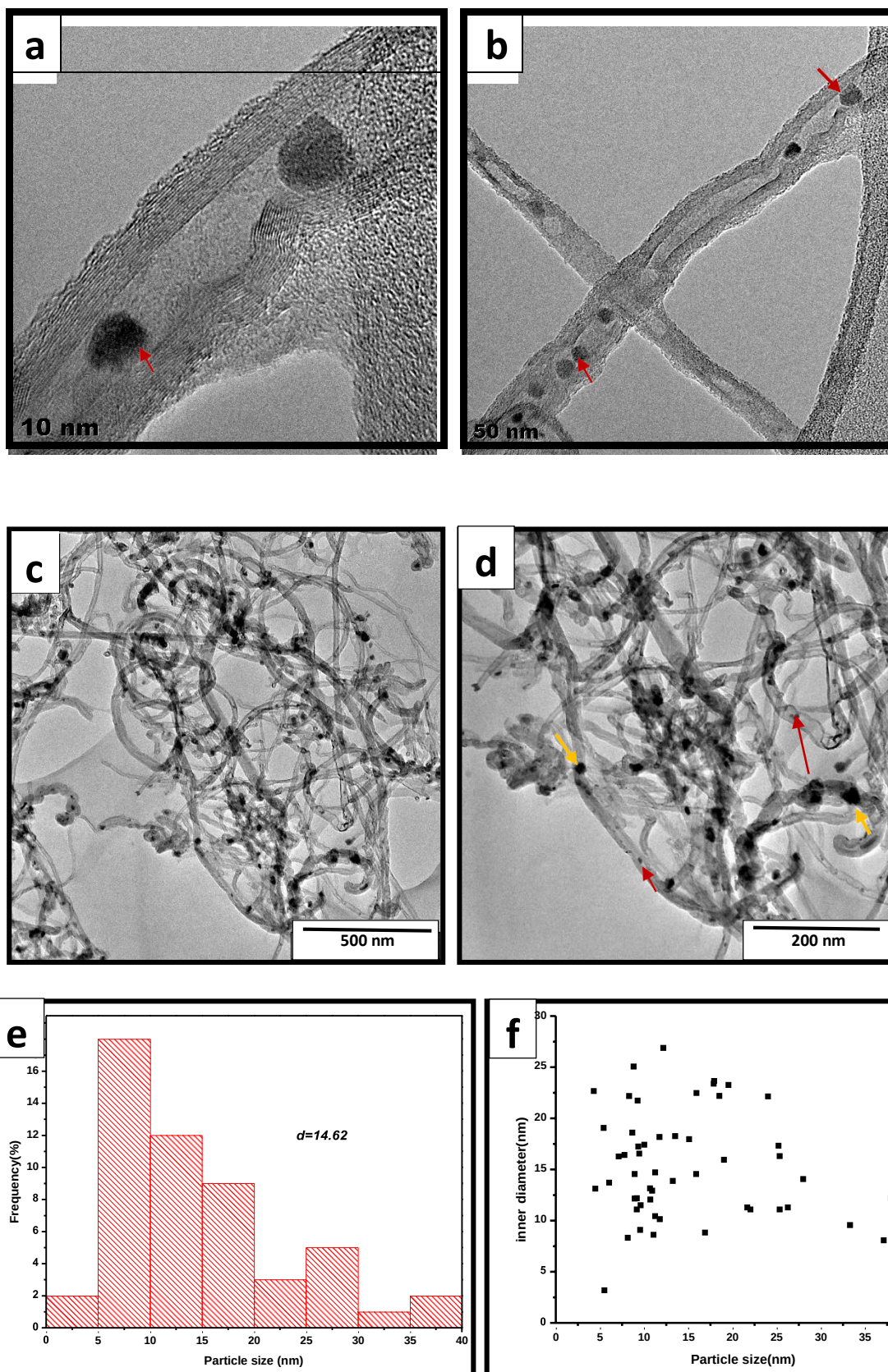


Figure 4.4: HRTEM images (a, b) and TEM images (c, b), (e) the corresponding Cu particle sizedistributions, and (f) a plot of particle size versus inner diameter of 12%Cu@CNTs

Table 4.2: shows particle sizes as analyzed using ImageJ.

Sample	Diameter (nm)	Inner Particles size(nm)	Outer Particle sizes (nm)
3%Cu-CNTs	3 - 27	2.7 – 14.0	3.9- 16.5
5%Cu-CNTs		1.3 – 18.3	5.2-24.8
7%Cu-CNTs		4.9- 22.0	5.7- 26.2
12%Cu-CNTs		2.0- 25.2	9.6- 68.4

The average diameter distribution of all the synthesized X%Cu@CNTs was determined from TEM images, using the ImageJ computer program and this was done by measuring the diameter of 100-120 particles from each sample. The histograms in figure 4.1e-4.4e showed average diameters of 6.6 nm ($\sim 14.0 \pm 2.67$) for 3%Cu@CNTs, 7.5 nm ($\sim 18.3 \pm 1.3$) for 5%Cu@CNTs, 8.0 nm ($\sim 22.0 \pm 4.9$) for 7%Cu@CNTs and 14.6 nm ($\sim 25.2 \pm 2.0$) for 12%Cu@CNTs respectively. For 3-7% loading, there was no significant change in the sizes of the Cu NPs. On the other hand, an increased average diameter in the 12%Cu@CNTs sample could be attributed to the number of few particles that were observed outside the tubes, as these particles are not hindered by the walls of the tubes. In addition, the higher loading could result in some agglomeration of small particles to form bigger particles.

Figures 4.1-4.4 (f) shows the relationship between the particle size of the Cu NPs versus the inner diameter of the CNTs. The distribution plots obtained revealed that there was a relationship between the metal loadings and the particle distribution and dispersion such that, an increase in metal loading led to a decrease in distribution and dispersion of nanoparticles. The plots also showed that the metal loadings had an influence on particle growth and limitation. The inner diameters of CNTs had an influence on the size of metals that could be deposited such that the 3-7% Cu-NPs had most of the particle growth limited around 4-12 nm with most particles confined in CNT diameter range from 5-20 nm while about 6-25 nm particle sizes were observed for 12% with more particles observed from 10-25 nm. These results indicate that metal loading together with confinement, has an influence on particle growth,

particle sizes which can be confined (based on the inner diameters), dispersion, and particle distribution.

Table 4.2 shows the summary of the range of the particle sizes (inner and outer) as analyzed using Image J from the TEM images obtained. The table consists of comparable results for the inner particle sizes and outer particle sizes. The results showed that the particles located on the outside had much bigger particle size as opposed to those confined within the tubes. We noted ranges of about 9.6 nm - 68.4 nm for the particles located outside for 12wt%, which is approximately two times those located within the tubes for the same sample. This trend was observed for all the samples. Regardless of the metal loading used, the results demonstrated that encapsulation has an adverse impact on the particle size and shape when comparing those located on the outside and those on the inside (the same trend observed for all the catalysts).

The nanoparticles were observed to be well dispersed with no apparent sintering except for the 12%Cu. Figure 4.5 (c,d) shows the TEM images of 12%Cu loaded CNTs, this sample shows an increase in particle size with the particles located outside, and this increase led to the blockage of the tubes and agglomeration. It was seen from the images and particle size distribution, that inside coverage increased with loading but when loading was higher than 10%, there appeared to be higher coverage on the outside with bigger particles. Loading did not affect the average particle size on the inside, but it affected the number of particles confined. As metal loading increased, the number of particles confined increased but changes in the shape and the size were insignificant. However, this was different for the particles located on the outside, such that the size and shape significantly changed with loading.

4.3.2. Bruanuer-Emmette Teller (BET) analysis

BET measurements were conducted to investigate the changes in the specific surface area and the porosity of the materials from N₂ adsorption & desorption isotherms. The specific surface areas and the pore volumes of the purified CNTs and x%Cu-CNTs are shown in Table 4.3. The surface areas of the x%Cu-CNTs increased as the Cu metal loading increased. This phenomenon is similar to that reported in the literature and it is attributed to the presence of CuO and Cu [22,27]. Pore volumes increase from 0.34 cm³/g in purified CNTs (without any Cu loading) to 0.6 cm³/g in 12%Cu@CNTs. The purified CNTs had the lowest surface area and pore volume as compared to the Cu-loaded CNTs.

Table 4.3: Shows BET Surface Areas and Porosity of the synthesized materials.

Sample	Surface Area (m²/g)	Pore volume (cm³/g)	Pore size (nm)
Purified CNTs	91	0.34	15.4
3%Cu@CNTs	102	0.43	16.8
5%Cu@CNTs	102	0.48	19.1
7%Cu@CNTs	111	0.46	16.5
12%Cu@CNTs	164	0.67	16.3

Figure 4.5a shows the nitrogen adsorption-desorption isotherms of the synthesized Cu-CNTs and purified CNT materials. The N₂ adsorption-desorption isotherms of all the CNTs samples showed Type IV adsorption isotherms with a hysteresis loop at high relative pressures. Type IV is usually associated with monolayer-multilayer adsorption and capillary condensation, with complete pore filling or pore blockage [9,24,28]. This phenomenon could be confirmed by the presence of the H3 Hysteresis loop, which is usually observed in plate-like particles (slit-shaped pores) [29]. Mesoporosity was centered around 3 nm with the presence of micropores also observed in samples as presented in figure 4.6a.

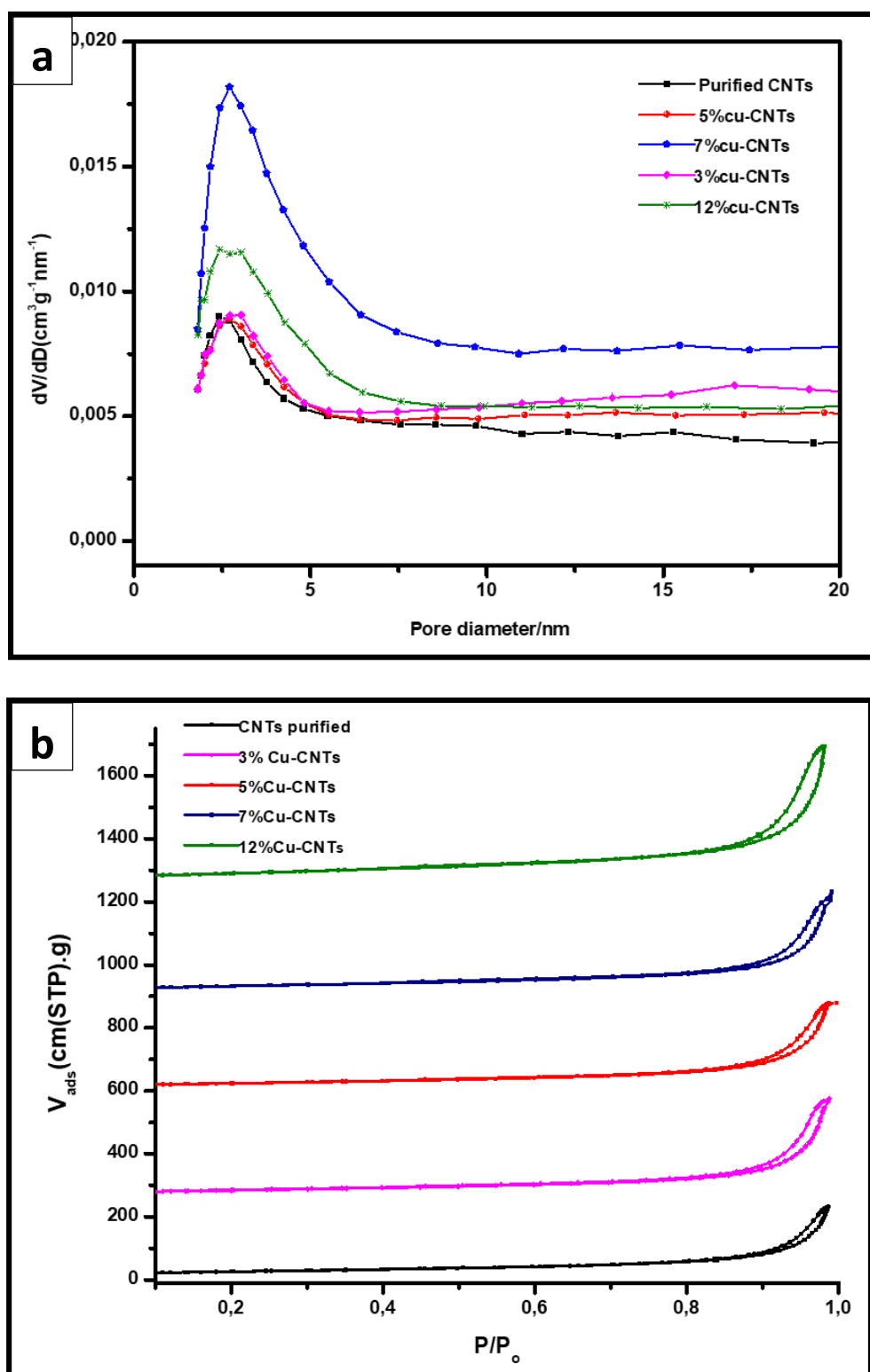


Figure 4.5: The a) pore size distribution and b) nitrogen adsorption-desorption isotherms of the synthesized materials.

4.3.4. X-ray diffraction (XRD) data

Figure 4.6 shows the XRD patterns of the prepared catalysts and that of the purified CNTs. The peaks observed in all profiles at 26.2° could be connected to (002) diffractions of graphite, which confirms the presence of CNTs [31]. Impregnating copper resulted in the XRD pattern of the material with diffraction peaks for CuO at $2\theta = \sim 39.1^\circ$ (111) and 53.6° (020). The crystal facet of metallic copper occurred at $2\theta = \sim 43.8^\circ$ while the peaks at $\sim 36.5^\circ$ and 61.3° were attributed to the (111) and (220) crystal facets of Cu_2O , respectively [23]. The crystal phase of copper inside the CNTs changed from metallic Cu to CuO when the functional groups were removed by heat treatment [9]. The diffraction peaks of the CNTs and Cu are superimposed at 44° , which is indicated by the broadness of the peaks. As seen in Figure 4.6, the characteristic diffraction peaks of CuO were observed (with a weak intensity) for all the catalysts except for Cu/CNT (12%). We noted an absence of the CuO peak on the 3% which could be attributed to the lower metal loading. At higher loadings it is possible that the Cu particles are larger and it is likely that only the Cu surface is oxidized. Thus Cu and not CuO will dominate the XRD pattern. The peak intensity of CuO is associated with the inner diameter of CNTs [23].

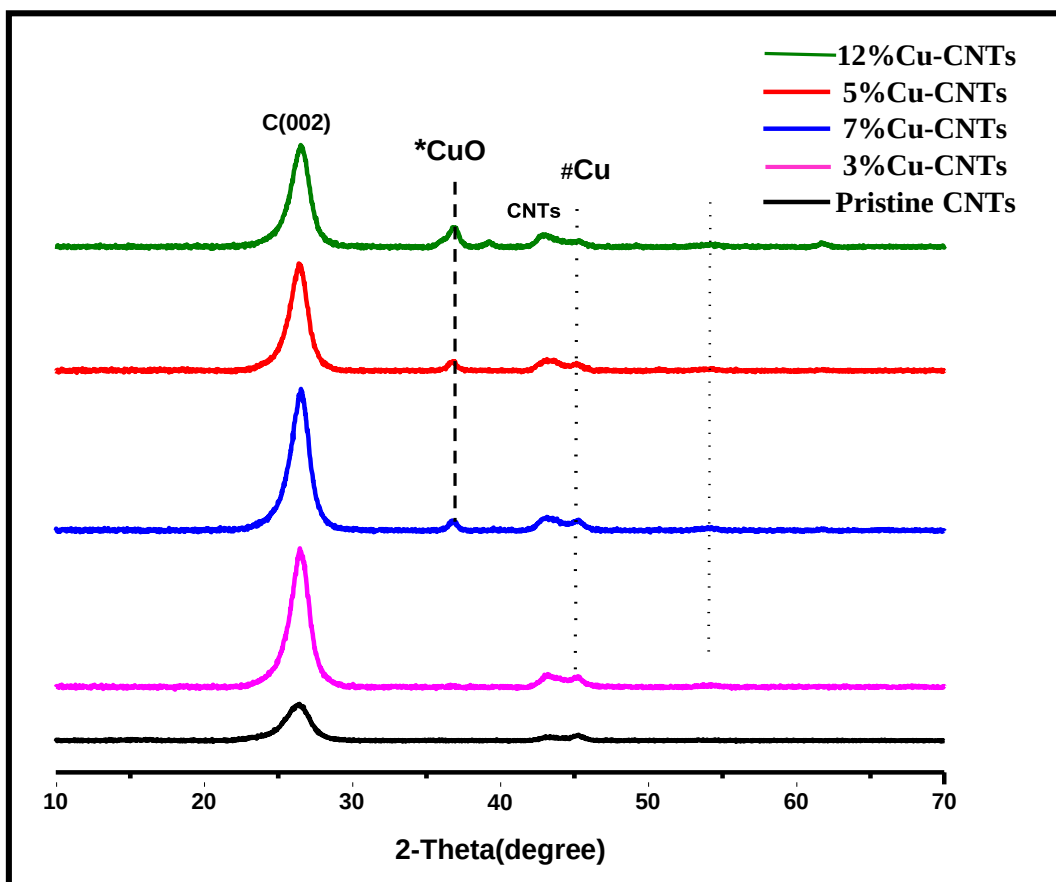


Figure 4.6: XRD patterns for the synthesized P-CNTs and X%Cu-CNTs.

To obtain the particle size, the Scherrer equation was used [24,28]

$$D = \kappa \lambda / \beta \cos \theta \dots\dots\dots 1$$

where D_{hkl} - crystallite size, β - full width half maximum in radians, λ - X-ray wavelength, θ - peak position in radians and K is the Scherrer equation given as of 0.9 [30] and λ the X-ray wavelength is given by $\lambda = 0.15406$.

The crystallite sizes obtained using the Scherrer equation are presented in Table 4.4. From the table, the metal loading of x%Cu-CNTs was analyzed and compared with the size of the nanoparticles obtained from the Scherrer equation. From the crystalline sizes obtained and ImageJ computational studies, we observed that the average particle sizes increased with an increase in metal loading and this was also confirmed by TEM images. The crystalline sizes obtained from the Scherrer for the 3% and 5% loadings corresponded to those observed with TEM analysis. The trend that the higher the loading, the higher the average particle size was observed.

Table 4.4: NP size from Scherrer equation

Sample	Crystallite size(nm)
3%Cu-CNTs	6.44
5%Cu-CNTs	7.72
7%Cu-CNTs	9.25
12%Cu-CNTs	9.32

4.3.5. Temperature programmed reduction (TPR)

TPR analysis is useful for studying the reduction behaviour of a metal oxide. A highly dispersed metal oxide is generally more easily reduced than the bulk material [23]. The reduction of the Cu could be attributed to the interaction of Cu species with the interior surface of CNTs. The shift of π electron density from the inner surface to the outer surface of the CNTs causes the interior surface of CNTs to be in an electron-deficient state [27]. Therefore, the copper inside the CNTs could, in principle, be reduced easily due to the lowered activation energy. This could occur through its interaction with the CNTs' support in an inert atmosphere. Here the oxygen atoms of copper oxide would react with carbon atoms to induce an auto-reduction reaction [23,27]. The reduction of X%Cu-CNTs and P-CNTs are presented in figure 4.8. As shown in figure 4.7, all the catalysts exhibited one partly overlapping peak at temperatures lower than 200 °C, which corresponds to the reduction of Cu_xO to Cu. It was postulated that the low-reduction-temperature peak could be attributed to the reduction of highly dispersed Cu_xO and that the high-reduction-temperature peak originated from the reduction of bulk Cu_xO [9,23,27]. It can be also observed that the temperature of the reduction peaks, either for the highly dispersed or the bulk Cu_xO species, increased with increasing Cu metal loading with 12%Cu-CNTs as the exception.

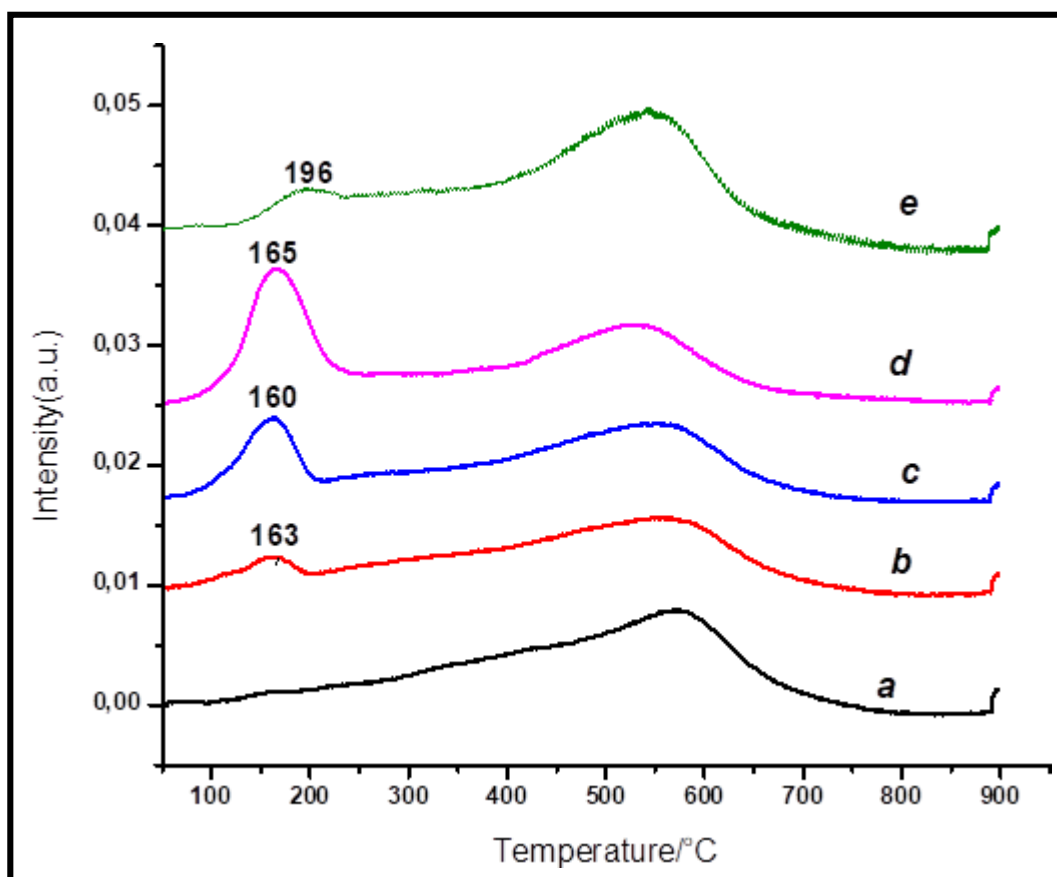


Figure 4.7: TPR profiles of a) purified CNTs, b)3%Cu/CNTs, c)5%Cu@CNTs, d)7%Cu-CNTs and e)12%Cu-CNTs

4.3.6. Thermogravimetric analysis (TGA)

The thermal stabilities of the purified CNTs and the prepared catalyst were analyzed under air by TGA. The study was also used to evaluate the purity of CNTs, and the Cu content loaded on the CNTs. The TGA profiles with the corresponding derivative curves are presented in figure 4.8. The TGA showed that there was no loss of mass below 500 °C, suggesting that there was no amorphous carbon present in the materials [31]. The curves showed one main event connected to the decomposition of carbon and a decrease in the thermal stability of CNT due to the addition of Cu, which is known to catalyze the thermal reaction of carbons in air [3,5,9]. The curve with the highest loading at 12% showed the lowest temperature for the conversion of carbon to CO₂, and this was related to the highest metal loading and/or the location of the Cu on the outside of the CNTs. The TGA curve of purified CNTs shows no residue, which indicates the successful purification of the materials. This is in agreement with

the XRD data. The estimated x%Cu loading calculated from the TGA curves were found to be 3.14 %, 5.01 %, 6.66 %, 12.08 for 3, 5, 7, and 12%Cu@CNTs respectively. The initial calculations are in agreement with the TGA data obtained, with insignificant differences which are expected.

The DTG plot shows the maximum decomposition temperature of the prepared Cu catalysts. Purified CNTs decomposed at 722 °C, and this decreased to 567, 565, 557, and 529 °C for 3, 5, 7, and 12%Cu@CNTs, respectively. The TGA results clearly show that the addition of Cu had an effect on the thermal stability of the materials and that the stability of each catalyst decreased based on the metal loading.

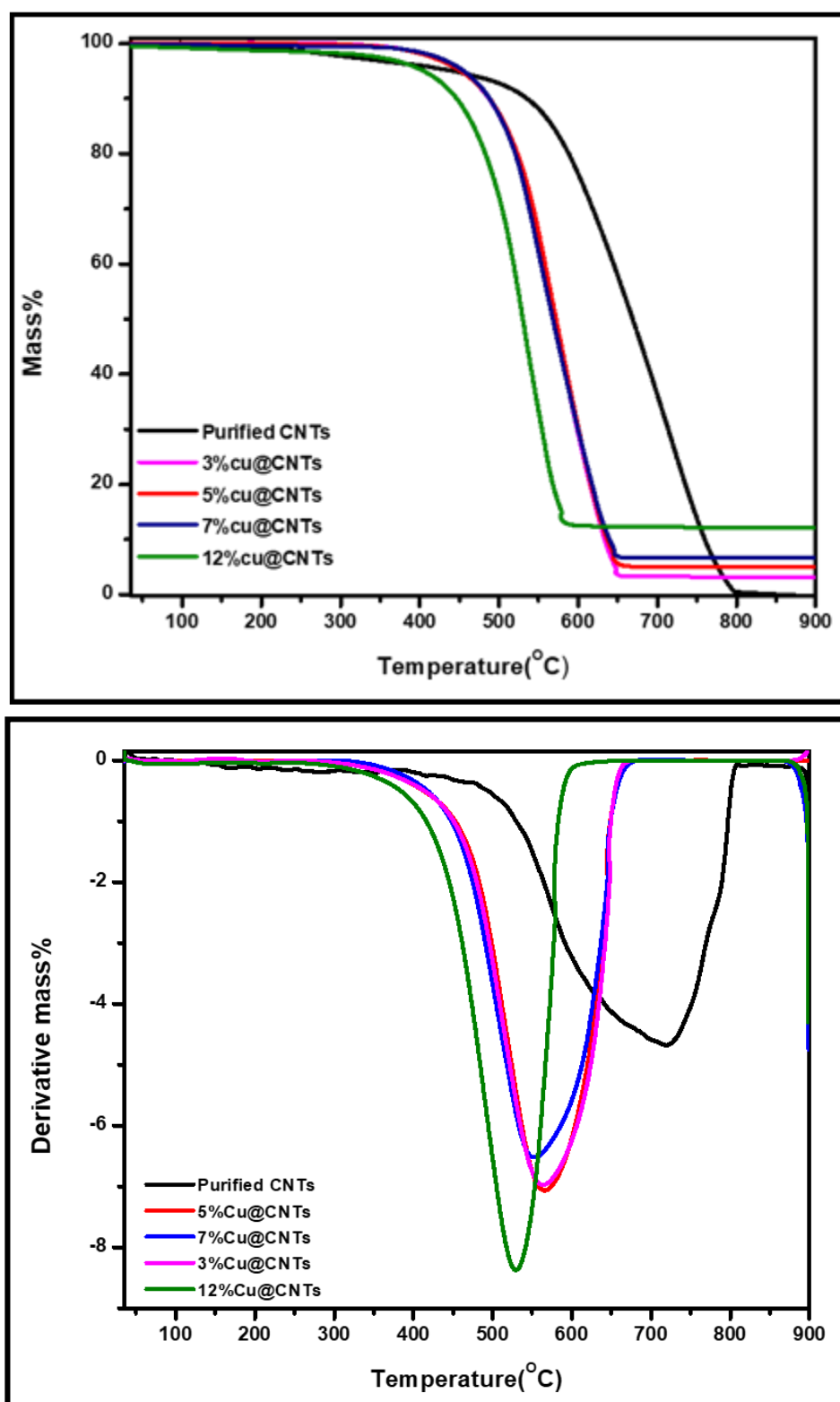


Figure 4.8: TGA and DTG profiles of P-CNTs and loaded CNTs

4.4. Discussion

To study the influence of Cu in the catalytic hydrogenation reactions and to obtain the method that would serve as a guide for the synthesis of a bimetallic confinement Cu catalyst (with varying amounts of Cu) a series of Cu-CNT catalysts were made. The results showed that the addition of copper within the CNTs channel increased the CNT's surface areas and this increased as the quantity of the Cu metal loading increased. This property could be beneficial for activity studies since it is related to particle size, particle morphology, surface texture, and porosity. TEM images indicated that the confined nanoparticles were within the CNTs. However, the 12% loaded catalyst showed Cu particles on the outside of the CNTs. The data showed that higher loadings affected the number of particles that can be confined inside the CNTs. TEM images further confirmed the influence of metal loading on the particle sizes and shapes and the Cu particle sizes were corroborated by XRD studies.

A comparison of the incorporation of metals inside CNTs with this study was made and the data from the various studies are shown in Table 4.5. Surface areas and pore volume of the analyzed materials in this study increased with loading while most studies reported, surface areas decreased after the addition of metal to the initial CNT material. This suggested that there are two competing effects – pore blockage [31,32] versus enhanced surface area due to the metal particles attached to the CNTs [21,26,33]. During acid treatment, defects are created, and CNTs are also opened at the tips and possibly in the walls.

Confinement limited the growth of the copper particles to the internal diameter of the CNTs. Thus on increased loading with Cu, the Cu particle numbers increased but their size only increased marginally. The particles that were located within the channels showed no agglomeration and their shape and size did not change much with increased loading. However, at the 12% loading, many Cu particles were found to be located outside the CNTs. Furthermore, these Cu particles had sizes larger than those found inside the CNTs. Thus at a loading of ca. 10 %, there is no further space in the CNTs for more Cu particles to form. Thus, the 7%Cu loaded catalyst showed the best results in terms of Cu dispersion, particle size, particle spacing, confinement. This was also reflected by the TGA (thermal) data.

Table 4.5: Comparison of different studies with our work.

Metals Confined (wt%)	Metal Loading (wt%)	Metal Catalyst Used	Inner CNTs Diameter (nm)	Particle Size (nm)	Inner Particle size trend	Outer particle Size trend	Surface area trend	Pore volume trend	References
~78 ~80 ~90 ~60	~ 3.13 ~5.03 ~6.89 ~12.08	Cu	5.7-24.9	14.0±2.7 18.3±1.3 23.0±4.9 38.0±2.0	Remained near the same -no significant change	Increased with loading Shape changed	Increased with Loading compared With purified CNTs and Lower loading.		This work
~65	~1.0-2.3 ~2.7-3.2 ~1.1-3.2	Ru Co Pd	5.49	2.21±1.02 3.25±2.72 4.15±1.15	Sizes varied based on the metal used. Pd and Co had bigger particle sizes while Ru had smaller sizes	Co and Ru had a similar trend in particle sizes in/out. Pd had bigger particles with sintering.	Decreased With higher loading		[32]
>30	4.4	Pd	50	6 ±4	Size increased based on the support used	No significant difference	Decreased With metal Loading		[33]
~75	10	Cu	4-10 20-30	9.7±7.0 19.0±15.1	Size increased with an increase in heating temperature	Bigger particles irrespective of the heat treatment used	Decreased With metal loading		[9]
~80	1.2	Rh-Mn- Li-Fe	4-8	0.9± 10	Size increased with reaction time used	Bigger particles as compared to those confined	N/A		[10]
50-80	5 – 23	Pt-Ru	40	22±0.7	No noticeable increase with higher loading	Bigger particles on the outer walls	N/A		[25]
~90	1	Ni	20-50	7±3	Size not affected using different solvent	The slight difference with sizes ranging between 4-9nm	N/A		[1]

~30	4.9 & 9.0 Cu	6-7	14±11	Size increased with decreased loading Size increased with the addition of Zn	Bigger particles observed outside	Decreased compared With that of purified CNTs [2] Decreased compared To purified that of CNTs And Cu-CNTs
	5.2 Cu-Zn		>100			
~50	14.3 - 15.9 Cu	20-30	16.8	N/A	Bigger particles observed compared to that inside	Increased with Loading and heating Time [3] Pore size followed the same pattern with one as an exception
~75	8 Cu	2-5 5-10 20-50	3±1 5±2 10±2	Sizes increased with increased diameter	Bigger particles observed	Decreased with Loading Compared with Purified CNTs [4]

4.5. Conclusion

X%Cu@CNTs were prepared using the simple convenient wetness impregnation technique with the assistance of sonication. We have successfully synthesized x%Cu@CNTs catalyst using tetrahydrofuran at four different loadings. From PXRD and TEM studies, it was observed that Cu particles filled within the channels of the CNTs were average and well dispersed on the inside. No agglomeration was exhibited by the catalysts with lower than 10%, whereas the 12wt% exhibited some sintering. PXRD also revealed that we have both the metallic Cu and the Cu oxide on 5wt% to 12wt%. TGA showed that the introduction of Cu had an influence on the stability of the material, with 12wt% noted as the least stable. The 12wt% had more particles on the outside due to the smaller nanotubes' sizes and the higher metal loading, this catalyst was the least stable and more agglomerated and this is mainly because approximately 40% of the particles were loaded on the outside. Furthermore, the results indicated that the introduction of the catalyst within the tubes had an influence on the particle size, shape, and dispersion of the nanoparticles. Moreover, it was observed that particles which were located outside had different shapes, size, and dispersion. The synergistic effect between the nanotube walls and Cu is estimated to involve a separate confinement effect, and this research will open up new avenues in catalyst synthesis for various hydrogenation activity studies.

4.6. References

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Chapter 5

Study and characterization of confined zirconia within carbon nanotubes

5.1. Introduction

Human beings have been transferring carbon dioxide from the lithosphere to the atmosphere in great amounts for two millennia. With the global output of goods and services growing at 3% per year over the past 30 years, carbon dioxide emissions have also risen about half as rapidly. As a result, the ambient CO₂ concentration in 2019 was about 409.2 ppm, with a 3.3 percent decline in 2020, with the implication of the covid-19 pandemic driving this decrease. The pandemic and subsequent economic crises disrupted every industry, including energy production, reducing the use of fossil fuels and pollution from the transportation sector, resulting in a reduction in emissions. As a result, the decrease in CO₂ emissions must be maintained. The recovery and direct or indirect use of CO₂ from flue gas and manufacturing industries may be one method to assist in reducing the CO₂ accumulation in the atmosphere [1,2].

The hydrogenation reaction for converting carbon dioxide to methanol offers one prospective approach to reducing CO₂ emissions [3]. The use of CO₂ as a feedstock is appealing not only because it can contribute to reducing greenhouse gas (GHG) emissions, but also because developing new ideas and new approaches for catalysis and industrial chemistry is an important way of controlling environmental pollution [4,5]. Zirconia (ZrO₂), a strong and thermally resistant material, is a promising catalyst/support for use in hydrogen reactions under reducing or oxidizing atmospheres [6]. ZrO₂ is an important technological material with broad applications such as oxygen sensors, high-temperature fuel cells, as a refractory material in metallurgy, as a thermal barrier in engines, and as catalyst support in catalysis [7].

Zirconia is a fluorite-type oxide with a face-centered-cubic (fcc) crystal structure in which each tetravalent metal ion is surrounded by eight equal nearest O²⁻ ions, which form the vertex of a cube. Oxygen vacancies that serve as active sites for certain reactions are formed when the fluorite oxide is doped by a divalent or trivalent impurity ion [6]. ZrO₂, as shown in figure 5.1,

has three low-pressure structural forms that have distinct physical and thermochemical properties. ZrO_2 has a monoclinic (m) structure at low temperatures. The tetragonal (t) phase typically occurs during the transition phase between the cubic (c) and the monoclinic phases. Geometrically, the atomic structure of the phase can be derived from that of the c phase by the displacement of oxygen ions along the c axis, followed by a shift in the lattice parameter [7].

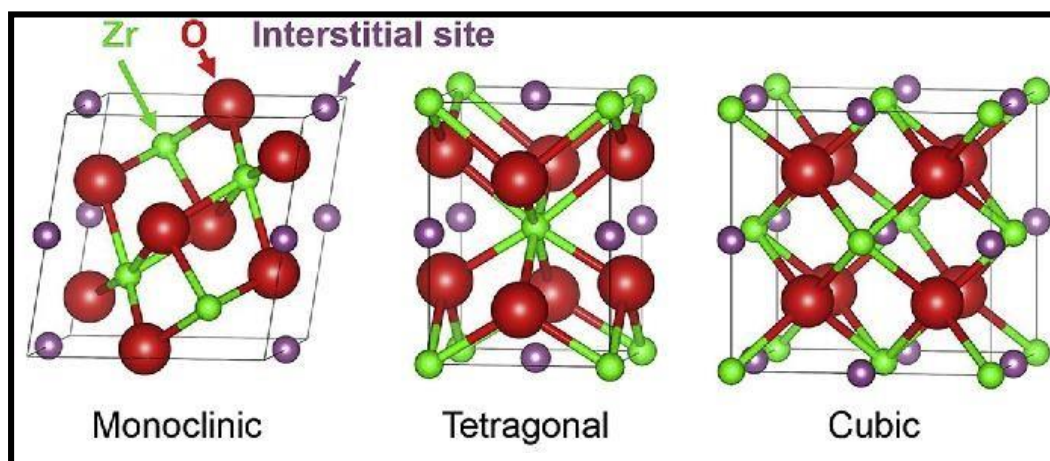


Figure 5.1: Crystal structures of monoclinic, tetragonal, and cubic ZrO_2 . The unit cell contains 4 Zr and 8 O for monoclinic and cubic ZrO_2 , and 2 Zr and 4 O for tetragonal ZrO_2 . Symbols: Zr in green, O in red and interstitial sites in purple [8]

Recent studies have shown that the ZrO_2 polymorphs (m- ZrO_2 , t- ZrO_2 & c- ZrO_2 , where m, t, and c are monoclinic, tetragonal, and cubic) have dramatically different adsorption capacities for CO and CO_2 [9]. It was reported that there is a strong dependence between the polymorphs of ZrO_2 , the strength of adsorption, and their acid-base surface properties [10]. For example, the adsorption capacity of CO_2 is more than an order of magnitude higher on m- ZrO_2 than t- ZrO_2 and this difference has been attributed to the higher Lewis concentration of basic O^{2-} site and coordinatively unsaturated (cus) Zr^{4+} Lewis acid sites present on the surface of m- ZrO_2 . Samson *et al.* [8] however showed that the highest methanol formation rate from CO_2 is obtained with t- ZrO_2 , and this can be ascribed to the different preparation procedures of the catalyst rather than to the specific crystallographic phases. The surface of ZrO_2 offers a variety of active sites, amongst them, acidic and basic hydroxyl groups (Bronsted sites) and coordinatively unsaturated Lewis acidic Zr^{4+} cations can be distinguished [8]. It was reported that these sites can contribute to the rate of catalysed reactions involving CO and CO_2 . The concentration of the structural defects in ZrO_2 are catalytically active and generally depend on the kind of polymorph.

The application of zirconia in chemical sensors, automotive catalysts, as a protective layer or as an oxide in the semiconducting industries and its use as a catalyst is currently under

investigation for several systems. Recently, attention was focused on the catalytic relevance of ZrO₂-based cermet materials and Zr-containing alloys/intermetallic compounds for C1 surface reforming reactions such as methanol stream reforming (MSR) and in natural gas-operated solid oxide fuel cells [11]. The latter cell was constructed using yttrium-stabilized zirconia as an electrolyte material and shown to have enhanced thermal compatibility with catalytically active Zr-based electrodes to avoid thermal damage by different expansion coefficients [12].

Gutierrez *et al.* [13] have shown that ZrO₂ can be introduced into a pure ordered siliceous SBA material. The results indicated that the incorporation of zirconia in the SBA's surface led to a high specific area, but this addition also produced a decrease in the specific textural characteristic, which was more pronounced at higher ZrO₂ loadings. In addition, the ZrO₂ species was located inside the mesopore and this resulted in the mesopore diameter decreasing due to a large amount of zirconia. It was also found that some large ZrO₂ agglomerates were formed on the external surface of the SBA particles and an increase in the ZrO₂ loading resulted in an increase in the size of external zirconia particles (m-ZrO₂ and t-ZrO₂) as detected by XRD. This incorporation was also reported to aid in an increase in the density of the material. The above studies showed that the introduction of Zr into the mesopore of SBA resulted in an improvement in specific surface area and material density, suggesting that the incorporation modified the material's textural properties.

It is known that the well-defined channels of CNTs can be used to introduce metal oxides into the CNTs cavity and their effects on the catalyst performance have been investigated. Recent results have shown that encapsulated nanoparticles into a CNT channel can give better catalytic performance compared to those on conventional catalysts. In these cases, the confinement in a CNTs channel has been used to interpret the catalytic behaviour of nanoparticles inside CNTs, because it can mainly modify electronic properties of the active phase, promote redox properties of metal oxides, and improve the gas-phase reactants inside the CNTs during catalytic reactions. Nevertheless, due to synthetic difficulties, the confinement effect in the CNTs channel for these materials is limited to catalytic reactions such as syngas conversion, hydrogenation, and oxidation [14].

Despite the wide uses of alumina-based catalysts, unsatisfactory CO₂ hydrogenation performance has been attributed to the presence of water combined with the strong hydrophilic character of alumina [15]. CNTs have been introduced as a better alternative as compared to the alumina-based catalyst due to their physical and chemical features (details on this issue were described in chapter 2). Chemical manipulation of CNTs is critical for the hierarchical building-up of nanomaterials into nanocomposites, nano-circuits, and in our study, nano-

reactors with unique structural properties. It has been observed that the catalytic activity using ZrO_2 -CNTs as the support is better than using Al_2O_3 , SiO_2 , and other materials [6]. These phenomena could be attributed to its high covalence nature and the degree of stability and the electrical conductivity in ZrO_2 [7].

The study on the confinement of ZrO_2 within silica shells was first reported by Qin *et al* [12]. The work investigated the encapsulation transformation of UiO-66 nanocrystal to Yttria-stabilized zirconia. The resulting catalyst had a hierarchical pore structure and was used as a reactor-like catalyst for a one-pot cascade reaction [12]. In this study, we report on the encapsulation of zirconia within the CNTs using a wetness impregnation method assisted by the use of sonication. To the best of our knowledge, studies entailing the encapsulation of zirconia within the cavity of CNT have not been documented.

5.2. Experimental procedure

The synthesis of ZrO_2 -NPs@CNTs was achieved following various experimental procedures previously used for the confinement of other metals in CNTs [16–20], with some modifications. This adjusted procedure is expected to produce dispersed ZrO_2 -NPs filled within CNTs.

5.2.1. Starting materials

The zirconia nanoparticle catalyst was prepared from zirconyl nitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), ethanol, and tetrahydrofuran (THF, 99%) purchased from Sigma-Aldrich and Associated chemical enterprises (ACE), respectively, and used without any further purification. African Oxygen (AFROX) supplied the nitrogen (N_2 , purity:99.999%), which was used in the thermal treatment experiments. Distilled water was generated in the School of Chemistry.

5.2.2. Catalyst preparation

The as-synthesized open-ended multi-walled CNTs with a range of diameters (as reported in chapter 3 section 3.2) were used. A three-step synthesis was used to prepare the ZrO_2 nanoparticles confined inside the CNTs. The metal loadings were varied to investigate the influence of loading. About 0.5 g of CNTs were impregnated with 5 ml x/y% $\text{ZrO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (x = 10,10 and y = 46,46) aqueous solution containing THF/ethanol and water as solvent (ratio of THF/ethanol to water was 3:1). This aqueous solution was vigorously stirred for 40 mins before the impregnation step. Impregnation was then followed by continuous stirring for 40 mins and sonication for 1 h. Another 1 ml of distilled water was added dropwise to the

x/y%ZrO₂-CNTs mixture, sonicated for 1 h, and the required product was obtained. The obtained sample was slowly dried at 373K for 12 h. The final catalyst was heated at 723 K under N₂ atmosphere for 3.5 h, at a rate of 5°C/min to remove the functional groups leading to the growth of the nanoparticles. The ZrO₂ content was varied from 10% to 46% with CNTs. This mass was verified using TGA analysis. The filled CNTs were defined by their loadings and solvent used: 46%ZrO₂@CNTsEtOH (EtOH for ethanol) and 46%%ZrO₂@CNTsTHF (THF for tetrahydrofuran) and 10%ZrO₂-CNTs(EtOH) and 10%ZrO₂-CNTs(THF). Loadings of 10% and 50% were targeted in the preparation.

Table 5.1: Summary of the experimental procedure

Description	Stirring Time (h)	Sonication time(h)	THF/Ethanol (v/v ratio)	H ₂ O (mL)	Solvent (mL)	heat treatment conditions
x/y%ZrO ₂ @CNTs	1h 20min	2h	3:1	1	4	T= 450°C r = 5°C/min
						T _{total} = 5 h

5.2.3. Characterization techniques

TEM, XRD, BET, and TGA were used as characterization techniques to evaluate the synthesized materials. The morphologies of the samples were characterized by TEM. The crystal structure of the materials was characterized using XRD, and BET was used to determine the surface area, pore size, and pore volumes of the catalyst. The thermal stability, quantity, and the differential thermogravimetric analysis of the x/y%ZrO₂@CNTs were performed to give information on the thermal properties (see chapter 3 for characterization techniques details).

5.3 Results and discussion

Different physical techniques have been adopted for the synthesis and loading of Cu, Ru, Fe, CeO₂, and Pd nanoparticles within CNTs, such as chemical vapor deposition, co-precipitation, sol-gel, and wet chemical methods [15–20]. The diameter of the CNTs, the solvent used, the support used, and, most importantly, the ability to easily monitor the location and loading of the synthesized NPs were all key determining factors in method selection. The confinement effect in CNTs was studied by comparing the catalysts prepared with higher loadings (46%ZrO₂@CNTs) and lower loadings (10%ZrO₂@CNTs). These catalysts were prepared using two different organic solvents namely tetrahydrofuran (THF) and ethanol (EtOH). These solvents have different surface tensions i.e. 26.40 mN/m for THF and 22.10 mN/m for EtOH

[21–23], and this has been reported to be a vital property in confinement. The catalyst was prepared using wet chemical methods and the same batch of CNTs, which had varying inner diameters and under the same conditions (Table 5.1).

5.3.1. Transmission electron microscopy

TEM characterization was performed to gain further insight into the location and the dispersion of the zirconia species using EtOH and THF solvents. Figure 5.2 shows the morphology of the CNTs filled with x/y%ZrO₂ (10%/46%ZrO₂@CNTs (EtOH and THF)). The average inner diameter and particle size distribution of all the synthesized x/y%ZrO₂@CNTs were done by measuring the individual diameter of about 100-120 particles for each sample and were processed using Image J. The TEM images of 10%ZrO₂@CNT (EtOH and THF) catalysts revealed that the catalyst particles were well dispersed inside the tubes and on the perimeter of the tube walls (see arrows in Fig. 5.2-5.3a-d). With the assistance of sonication and the relatively low surface tension of THF, ethanol, and water, the solvents were able to wet and penetrate the channels of CNTs [16]. Almost all the particles were located inside the CNTs and a few outside (about 10-15% of particles) with no apparent sintering (Figure 5.2a). It was observed that the location and dispersion of the particles varied with the metal loading and the choice of solvent used. The images show that the particles were smaller than the inner diameters of the CNTs.

Histograms representing particle size distribution and a scatter plot showing the relationship between the inner CNT diameter and the particle size and location are plotted in figures 5.2e,f, and 5.3e,f (for the 10% loading in ethanol and THF respectively). A summary of the relationship between particle sizes for the synthesized catalysts is given in Table 5.2. As seen in Table 5.2, the catalyst synthesized at lower loadings had an average of 5.1 nm and 6.2 nm (for EtOH and THF) while that prepared at higher loadings had averages of about 10 nm and 11 nm (for EtOH and THF respectively). The catalysts prepared using ethanol had smaller particle sizes as compared to those synthesized using THF. Based on THF's cyclic structure, THF is a polar aprotic (lack of polarity) solvent, whereas ethanol is a polar molar molecule with the ability to induce crystallization. This polar property of ethanol may be the primary factor influencing both the nucleation and growth of nanoparticles [24]. On the other hand, the 10%ZrO₂@CNT (EtOH) catalysts had slightly smaller particle sizes than found for the 10%ZrO₂@CNT (THF) catalysts, however, when THF was used, the particles were highly dispersed within the channels and less centered on one region (Figure 5.2e). Since the viscosities of the two solvents vary (i.e. THF (0.55 cP) and EtOH (1.1 cP)), the higher viscosity of ethanol (as compared to THF) causes nanoparticles to lose energy, forcing them to

cluster.

The TEM images of 46%ZrO₂@CNT catalysts in both solvents (EtOH and THF) revealed that the surface of the CNTs was mostly coated by zirconia particles with some presence of particles inside (approximately 10%) (Figures 5.4 and 5.5). Those located inside had chainlike structures, while the particles observed outside were shaped like strands threaded together (see arrows in figure 5.4a and Fig 5.5c). The images show that the particles inside were smaller than the diameters of the CNTs, but those on the outside were bigger than the hollow inside the CNT (Fig 5.5a and d). The histograms showed that the average particle size had an insignificant increase with the use of different solvents on each loading for the ZrO₂ catalyst (10 and 11 nm in EtOH and THF, respectively). However, these particles were still smaller than those on the outside and the quantity decreased (the number of particles confined decreased with loading). It was evident that the location and dispersion of the particles varied with the metal loading and solvent used and that confinement had an effect on the particle sizes and dispersion of the zirconia nanoparticles. The solvent played a minor role in determining the size and the deposition process inside the CNTs.

Table 5.2: Particle size analysis using ImageJ

Sample	CNTs Diameter (nm)	PXRD Crystallite size	Particle size (nm)
10%ZrO ₂ @CNTsEtOH	3-24	5.2	5.1
10%ZrO ₂ @CNTsTHF	3-24	8.0	6.2
46% ZrO ₂ @CNTsTHF	3-24	18	11
46% ZrO ₂ @CNTsEtOH	3-24	16	10

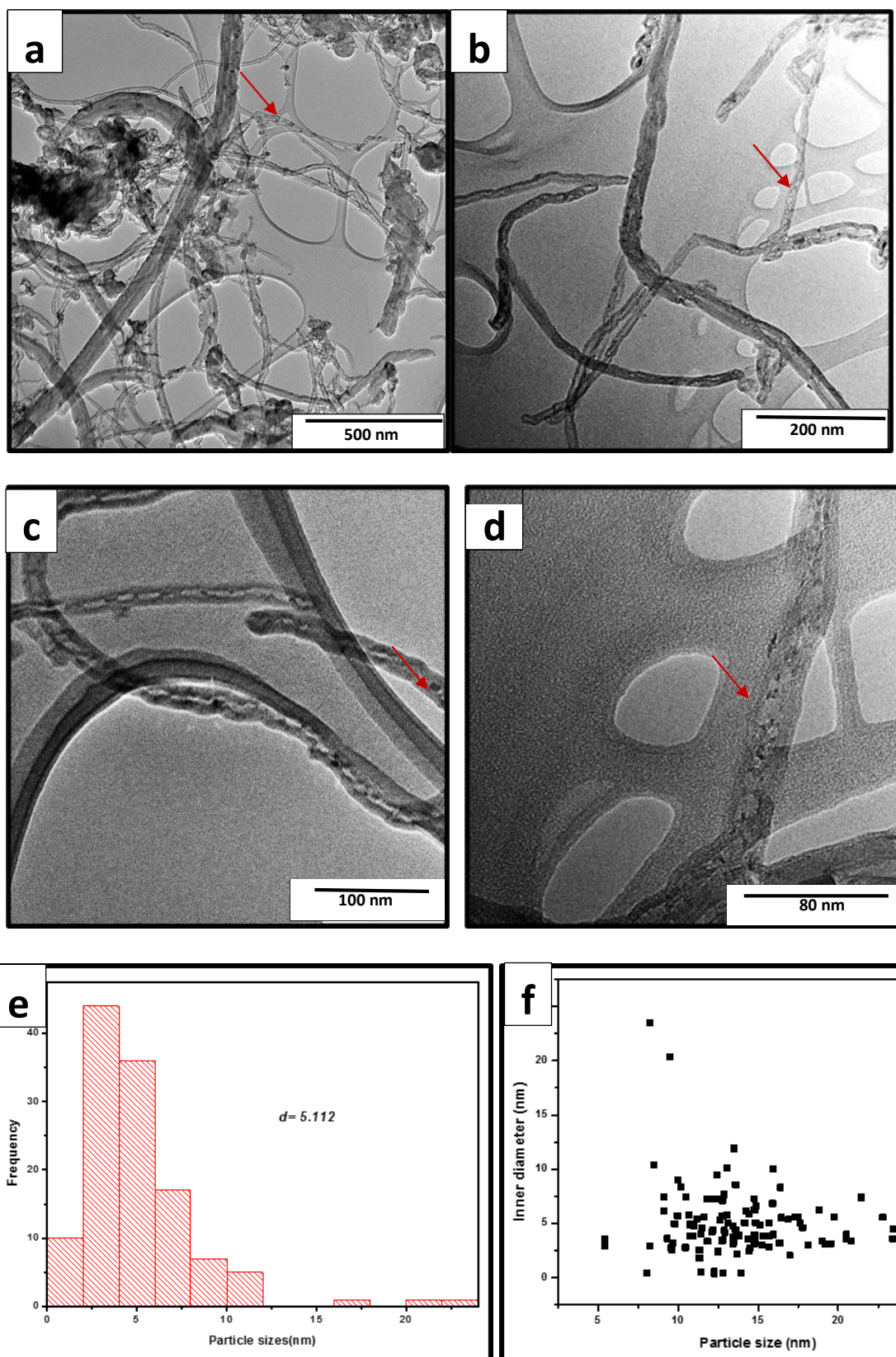


Figure 5.2: (a-d) TEM images, (e) the corresponding ZrO₂ particle size distributions (f), and a plot of particle size versus inner diameter width for 10%ZrO₂@CNTs(EtOH)

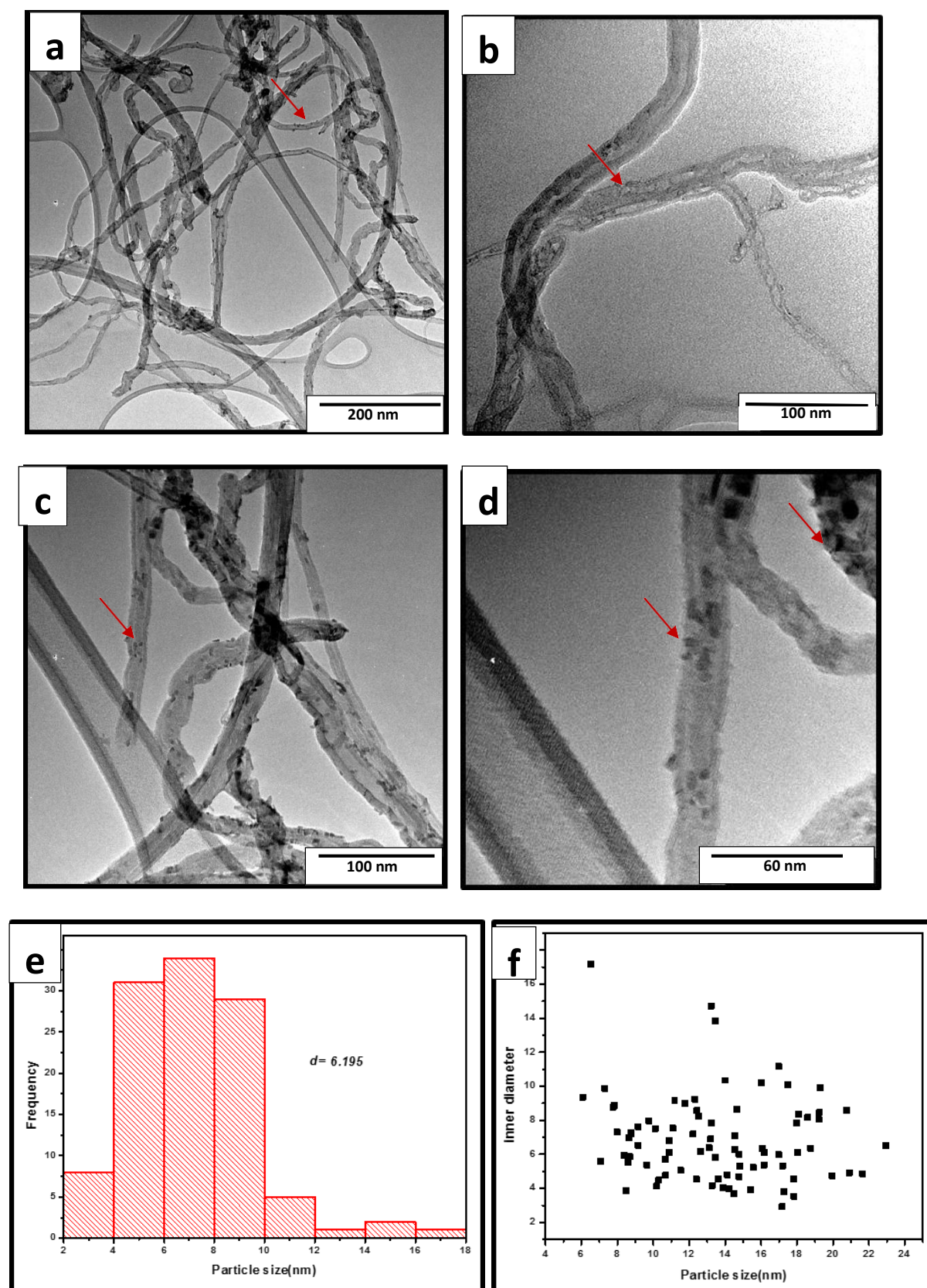


Figure 5.3: (a-d) TEM images, the corresponding ZrO₂ particle size distributions (e), and a plot of particle size versus inner diameter length (f) for 10% ZrO₂@CNTs(THF)

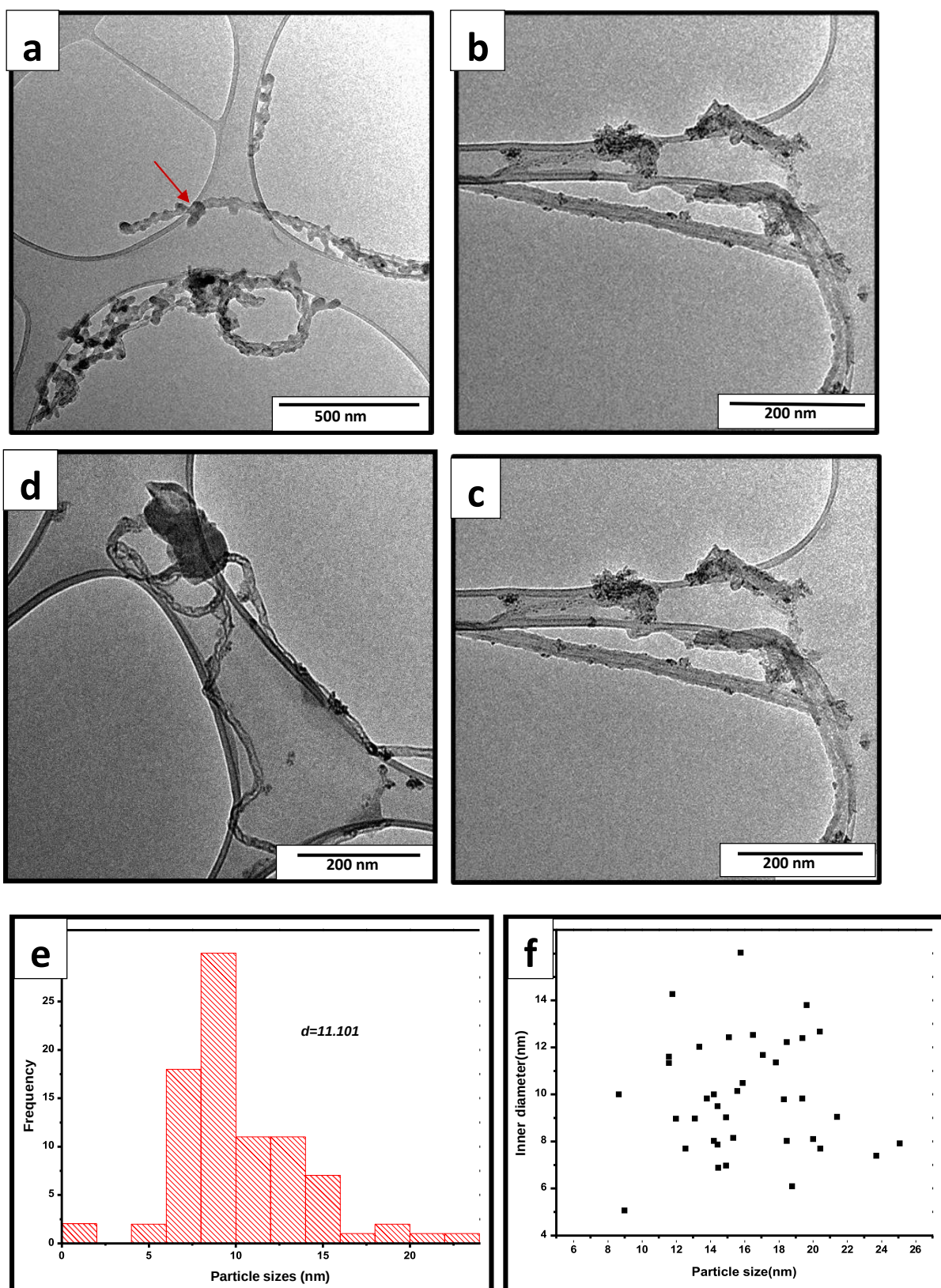


Figure 5.4: (a-d) TEM images, the corresponding ZrO₂ particle size distributions (E), and a plot of particle size versus inner diameter length(F) for 46%ZrO₂-CNTs(THF).

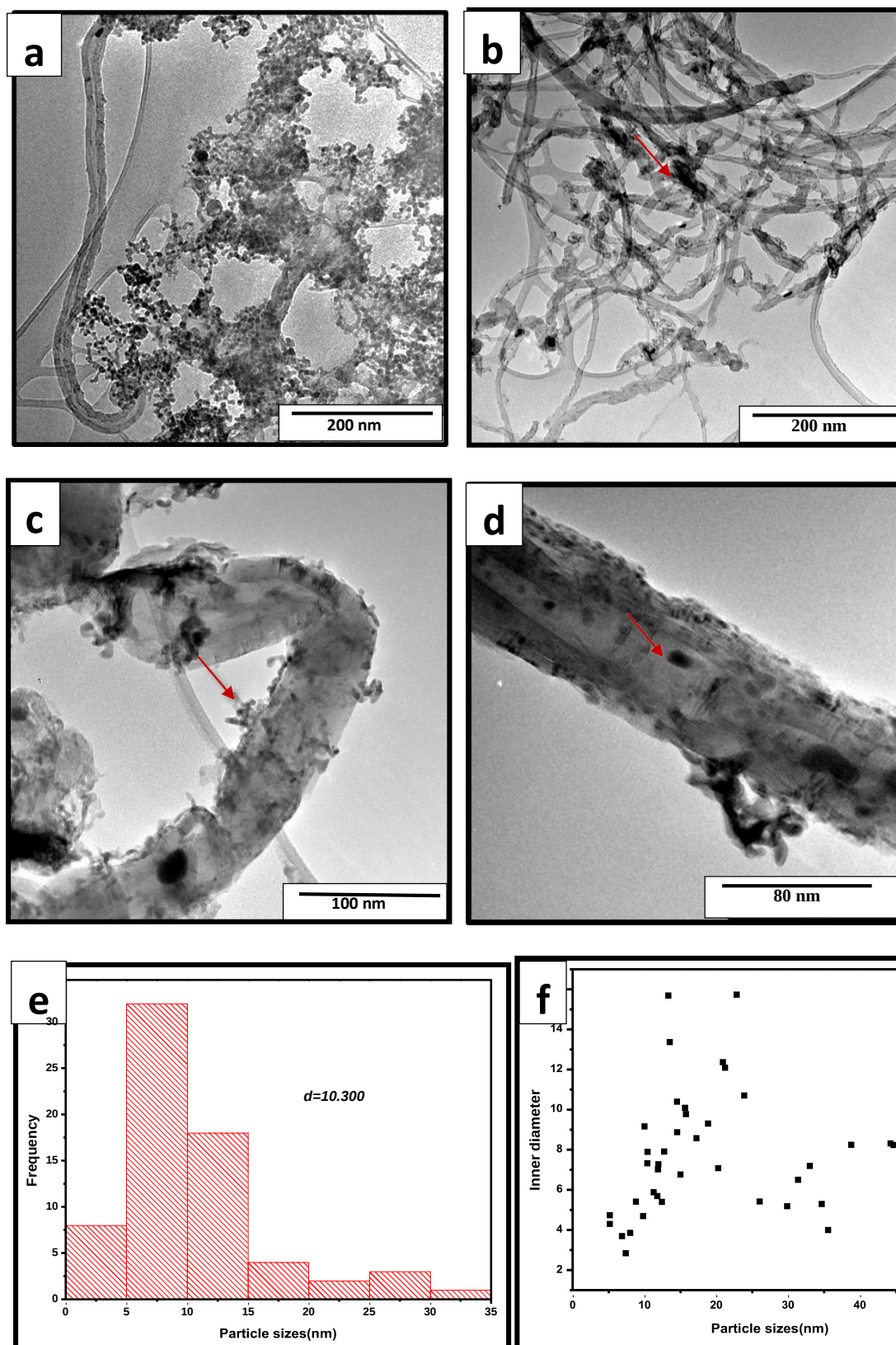


Figure 5.5: (a-d) TEM images, the corresponding ZrO₂ particle size distributions (e), and a plot of particle size versus inner diameter length (f) for 46%ZrO₂-CNTs(EtOH)

5.3.2. Brunauer-Emmett Teller (BET) analysis

The specific surface area, pore size distribution, and pore structure of the support and the corresponding catalyst were measured by nitrogen adsorption-desorption isotherms experiments (Table 5.3). The BET surface areas showed that the 46%ZrO₂@CNTsEtOH had the lowest surface area (69.1 m²/g) with a decrease in both pore volume, pore size, and surface areas as compared to the Purified-CNTs (90.9 m²/g). In contrast, the surface area of 46%ZrO₂@CNTsTHF increased (109.4 m²/g). As seen in the table, the 46%ZrO₂@CNTsEtOH had better results in terms of the surface and pore volume as compared to the 46%ZrO₂@CNTsTHF. The data showed a decrease in pore volume and pore sizes that could be attributed to pore blockage upon adding the ZrO₂ [17,19,20].

Table 5.3: BET Surface areas and porosity of the synthesized materials

Sample	Surface Area(m ² /g)	Pore volume(cm ³ /g)	Pore size(nm)
Purified CNTs (P-CNTs)	90.9	0.34	15.4
10%ZrO ₂ @CNTsEtOH	87.3	0.32	14.8
10%ZrO ₂ @CNTsTHF	70.5	0.29	16.5
46% ZrO ₂ @CNTsTHF	109.4	0.16	5.8
46%ZrO ₂ @CNTsEtOH	69.1	0.18	10.2

Figure 5.6a and b) show the nitrogen adsorption-desorption isotherms of the synthesized ZrO₂@CNTs and the pristine CNT materials. The N₂ adsorption-desorption isotherms of all the CNTs samples show Type IV adsorption isotherms with a hysteresis loop at high relative pressures. Type IV is usually associated with monolayer-multilayer adsorption and capillary condensation, with complete pore filling. This phenomenon could be confirmed by the presence of the H3 (lower loading) and H4 (higher loading) hysteresis loop. The H3 hysteresis loop is usually observed in plate-like particles (slit-shaped pores), while H4 represents the presence of narrow slit pores including pores in the micropore region [20,25]. Determination of the pore distribution showed that all the studied catalysts were mesoporous with mesoporosity centered around 3 nm. The presence of micropores was also observed in a few

samples as presented in Figures 5.5a and b. Figure 5.6c and d showed different isotherms, indicating that the pore structure for the higher loaded CNTs was changed after the introduction of zirconia while that of the lower loaded ZrO_2 was mostly retained.

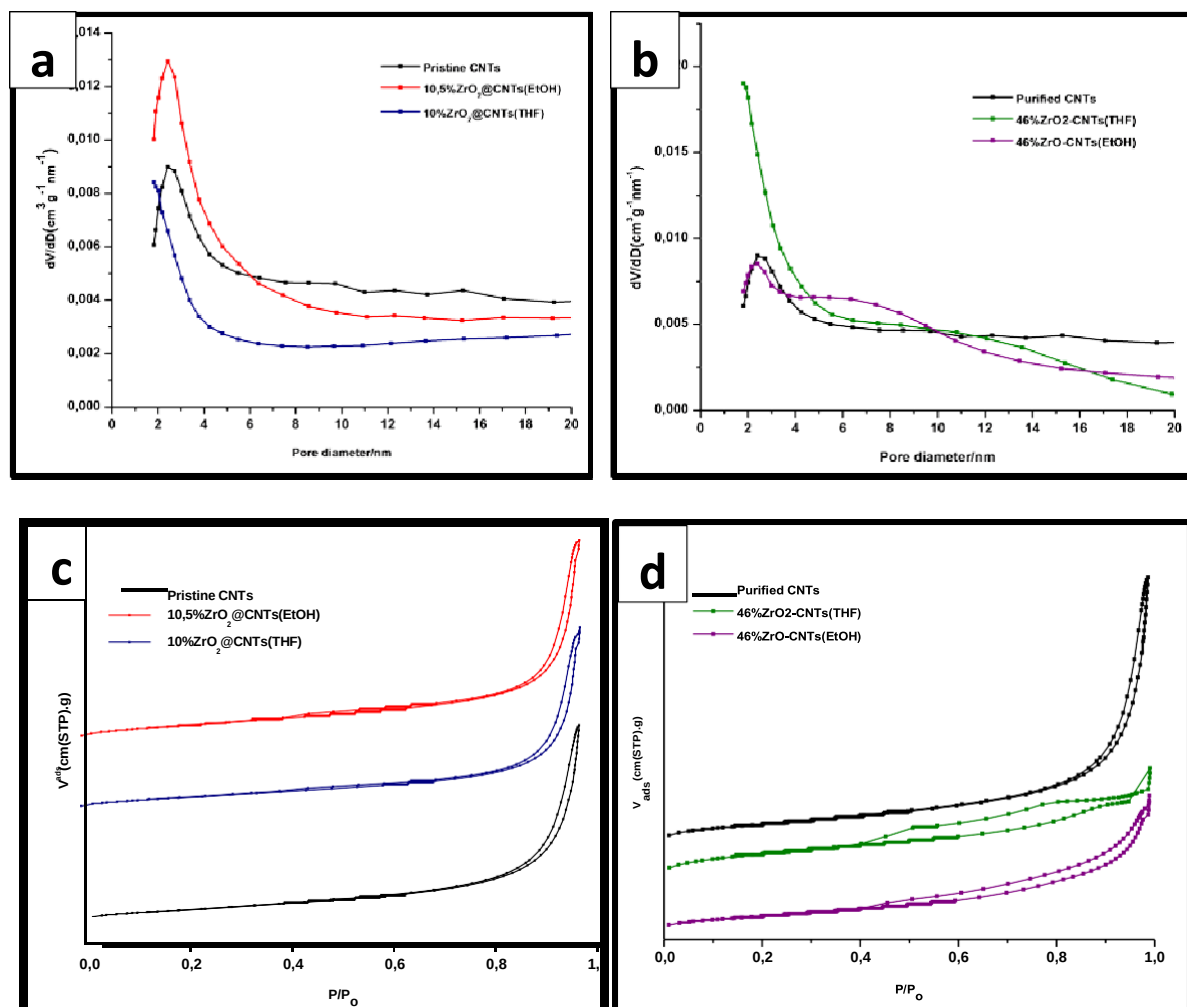


Fig 5.6 showing a) Nitrogen adsorption-desorption isotherms of 10% ZrO_2 -CNTs (EtOH) and 10% ZrO_2 -CNTs (THF); b) Nitrogen adsorption-desorption isotherms of 46% ZrO_2 -CNTs (EtOH) and 46% ZrO_2 -CNTs (THF). Figure c) showing the Pore size distribution of the CNTs as a reference with the Pore size distribution of the 10% ZrO_2 -CNTs (EtOH) and 10% ZrO_2 -CNTs (THF) and d) Pore size distribution of the 46% ZrO_2 -CNTs (EtOH) and 46% ZrO_2 -CNTs (THF).

5.3.3. X-ray diffraction (XRD) data

Figure 5.7a) shows the XRD patterns of 10% ZrO_2 -CNTs(EtOH) and 10% ZrO_2 -CNTs(THF). and that of the purified CNTs. The peaks observed in all profiles at $2\theta = 26.2^\circ$ and $2\theta = 43.9^\circ$ are the (002) and (100) diffractions of graphite and confirm the presence of CNTs. The

CNT/ZrO₂ resulted in the XRD pattern of the material with a diffraction peak corresponding to both m-ZrO₂ and t-ZrO₂ between 2theta = ~30.2° and 2theta = ~ 31,5° representing (111) diffraction peaks, which was observed in both catalysts. The m-ZrO₂ occurred at 2theta = ~54.8° and was attributed to the (112) (pdf 01-072-2743) [8,15,26]. As seen in TEM images (figure 5.5b), higher loadings of zirconia resulted in CNTs being coated with ZrO₂ on the outside of the CNTs. The peaks representing both phases of t-ZrO₂ and m-ZrO₂ occurred at 2theta = 50.1° (022/112) and 60,1° (211/122) as noted in pdf 01-072-2743 [24–26]. From figure 5.6b, we observed an increase in the m-phase in the 46%ZrO₂-CNTs (THF) which usually occurs when more zirconia is added. The m-phase occurred at 2theta = ~ 24.1, ~ 28.2°, ~ 31.5°, ~ 54.8° and 62.2°, with the appearance of t-ZrO₂ at 2theta = ~ 35,2°.

It was reported that calcination temperature had an influence on the zirconia phases, such that, when zirconium hydroxide is calcined at > 400°C, it is transformed from an amorphous ZrO₂ and t-ZrO₂ to m-ZrO₂ because the m-ZrO₂ phase is stable below 1170°C. This was confirmed in our data (figures 5.7a and b), which had the m-ZrO₂ phase dominating. The halo peak seen in figure 5.6a at 2Theta = 30° was said to be an overlap between the amorphous zirconia, m and, t phases of zirconia.

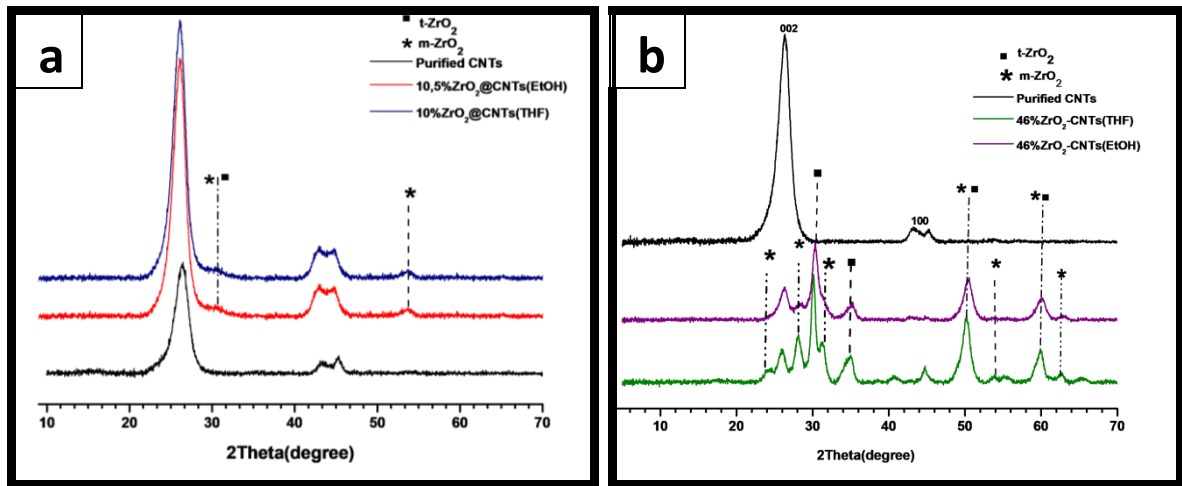


Figure 5.7: a) XRD patterns for the synthesized P-CNTs and 10%ZrO₂@CNTs and b) 46%ZrO₂-CNTs with CNT

To obtain the particle size, the Scherrer equation was used [27,28]

$$D = \kappa \lambda / \beta \cos \theta \dots\dots\dots 1$$

where D_{hkl} - crystallite size, β- full width half maximum in radians, λ- X-ray wavelength, θ- peak position in radians and K is the Scherrer equation given as of 0.9[29] and λ the X-ray wavelength is given by λ=0.15406.

The crystallite sizes obtained using the Scherrer equation are presented in table 5.3. From the table, the metal loading of x/y%ZrO₂@CNTs was analyzed and compared with the size of the nanoparticles obtained from the Scherrer equation. It was found that the choice of solvents had an influence on the particle sizes. Catalysts with THF had larger particles as compared to those with ethanol and this was noted even using lower loadings. The crystalline particle sizes obtained showed that 10% prepared catalyst of either THF or EtOH had a similar trend i.e. increase in particle sizes when THF was used, as compared to EtOH. It was observed that the average particle sizes were different from those obtained from TEM and this could be due to the fact that the Scherrer equation is mostly applied with a high degree of certainty with the size range of up to 100nm to 200nm [30]. The application of the Scherrer equation, however, gave consistent results with those of TEM images with some insignificant differences.

5.3.4. Thermogravimetric analysis (TGA)

The thermal stabilities of the purified CNTs and the prepared catalysts were analysed under air. The study was also used to evaluate the purity of CNTs, and the zirconia content loaded on the CNTs. The TGA profiles with the corresponding derivative curves are presented in figure 5.8 (a, b). A summary of the TGA profile showing the metal loadings Vs temperature peak positions are given in table 4 below. The TGA of all samples showed that there was some weight loss of mass below 100°C which could be due to moisture (Fig 5.8 a, b). All four samples showed one main event connected to the decomposition of the CNTs. A decrease in stability is noted with the addition of zirconia as seen from the TGA profiles, at the higher loading of ZrO₂ (figure 5.8b). The ethanol sample maintained higher stability even with the highest loading of 46%. The derivative curve for all catalysts had one endothermic peak at 75°C and this phenomenon was due to the disappearance of trapped moisture and the surface hydroxyl groups attached during purification [31,32]. The decrease in stability is due to the addition/presence of zirconiananoparticles, which catalyzes the reaction. The curve in figure 5.8a with THF was the least stable with the appearance of a new endothermic peak at 220°C. There could be several reasons for this peak such that there may be a secondary reaction taking place, in a way that ZrO₂ could interact with the CNT surface forming coordination complexes, or that CNTs could encourage THF to functionalize its surface and thus breaking the THF ring [33]. Therefore, ethanol seems to better solvent confinement of zirconia, and this can be due to the surface tension of ethanol being lower than that of tetrahydrofuran.

Table 5.4: metal loadings vs Temperature peak positions

Sample	Metal loading%	Temperature positions (°C)
Purified CNTs	-	720
10%ZrO₂@CNTs (EtOH)	10.5	69, 210, 300, 614
10%ZrO₂@CNTs (THF)	9.2	69, 614
46%ZrO₂@CNTs (THF)	46.4	58, 520
46%ZrO₂@CNTs (EtOH)	46.1	51, 511

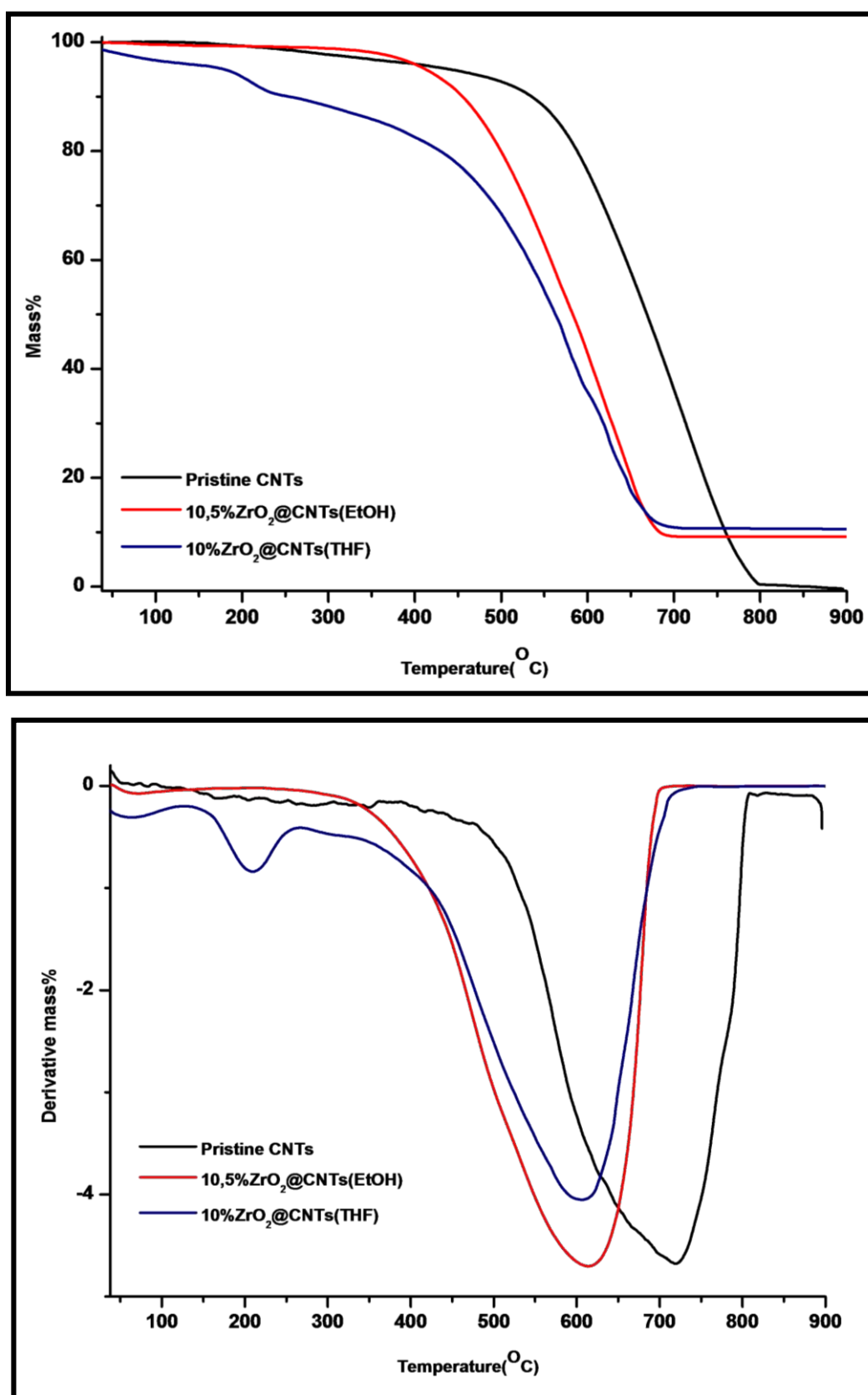


Figure 5.8: TGA profiles of P-CNTs and loaded CNT

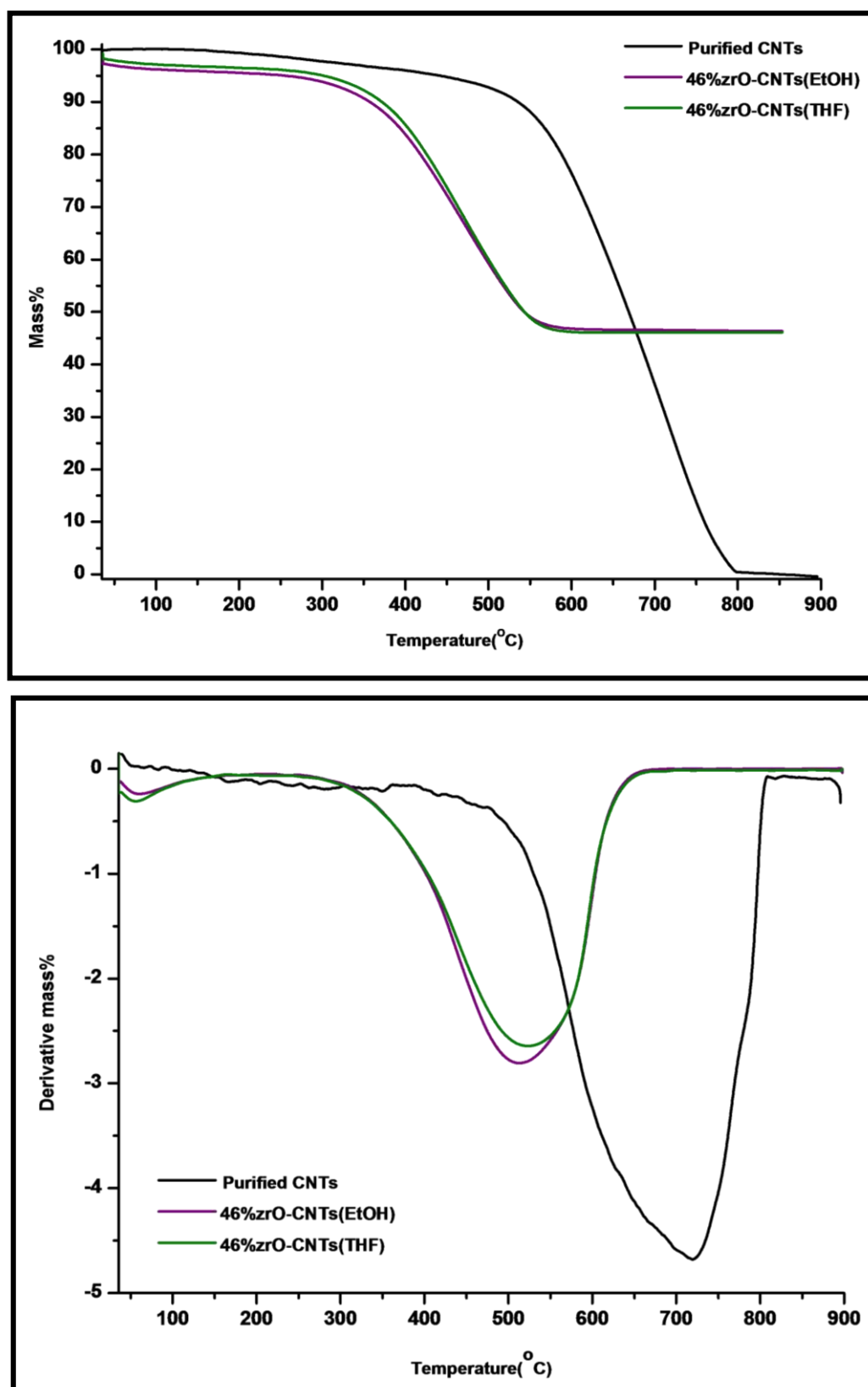


Figure 5.8: TGA profiles of P-CNTs and loaded CNT

5.3.1. Temperature programmed reduction (TPR)

Temperature-programmed reduction experiments were performed to evaluate the reducibility of ZrO_2 supported on the CNTs. Figure 5.9 shows the TPR profiles of $x/y\%\text{ZrO}_2@\text{CNTs}$ samples. For comparison, the TPR of CNTs was added and the summary of the relationship between the position of the peak and the catalyst metal loading is given in table 5.5. The profiles showed two reduction peaks centered at about 100°C - 300°C and 500°C , respectively. The 100°C temperature peak was likely due to the reduction of Zr^{4+} species. The high-temperature peak might be assigned to the reduction of the carbon species on the surface of CNTs. It can be noted from figure 5.6, that the catalyst with lower loading had lower reduction peaks than those with higher loadings. These samples had more particles on the outside than on the inside of the CNTs as confirmed by TEM. This implies that the confinement of zirconia inside the pore of CNTs resulted in easier reduction due to the shifting of the Π electron density from inner to outer supposedly caused by deviation of the graphene layers from the planarity.

Table 5.5: metal loadings vs Temperature peak positions

Sample	Metal loading (wt%)	Temperature position
Purified CNTs	-	720
10% $\text{ZrO}_2@\text{CNTs}$ (EtOH)	10	68,282,510
10% $\text{ZrO}_2@\text{CNTs}$ (THF)	10	112,208,496
46% $\text{ZrO}_2@\text{CNTs}$ (THF)	46	100,350,550
46% $\text{ZrO}_2@\text{CNTs}$ (EtOH)	46	114, 230, 500

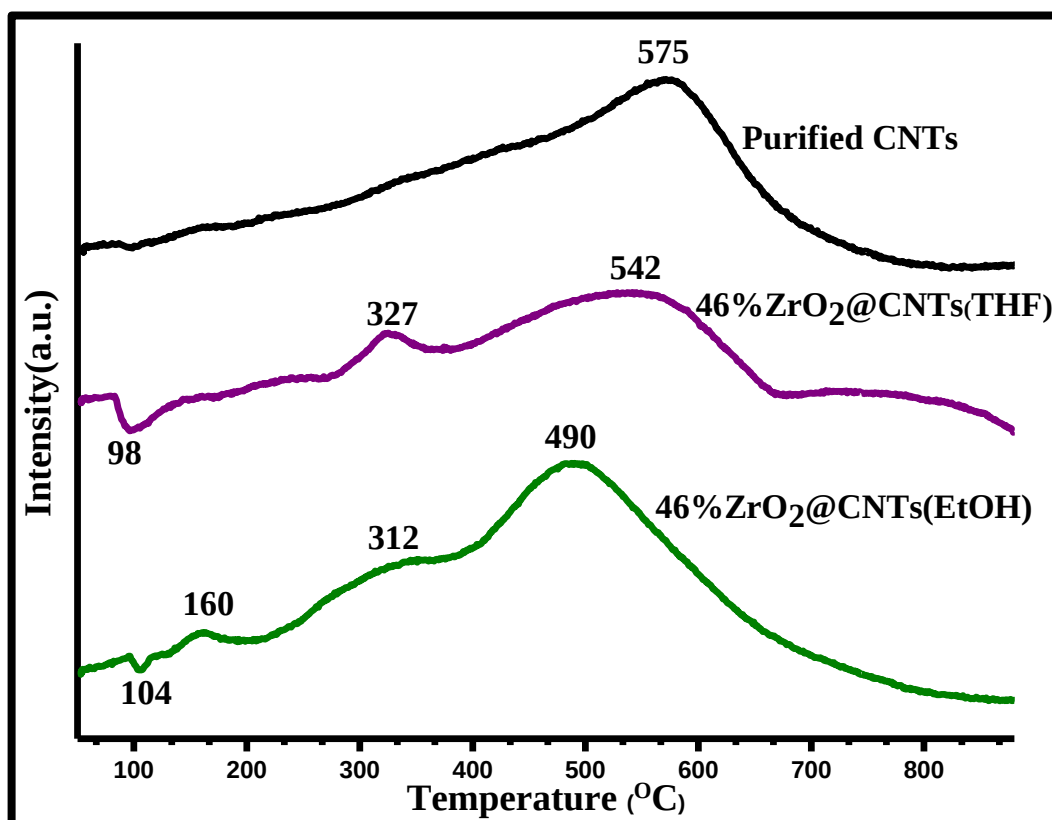
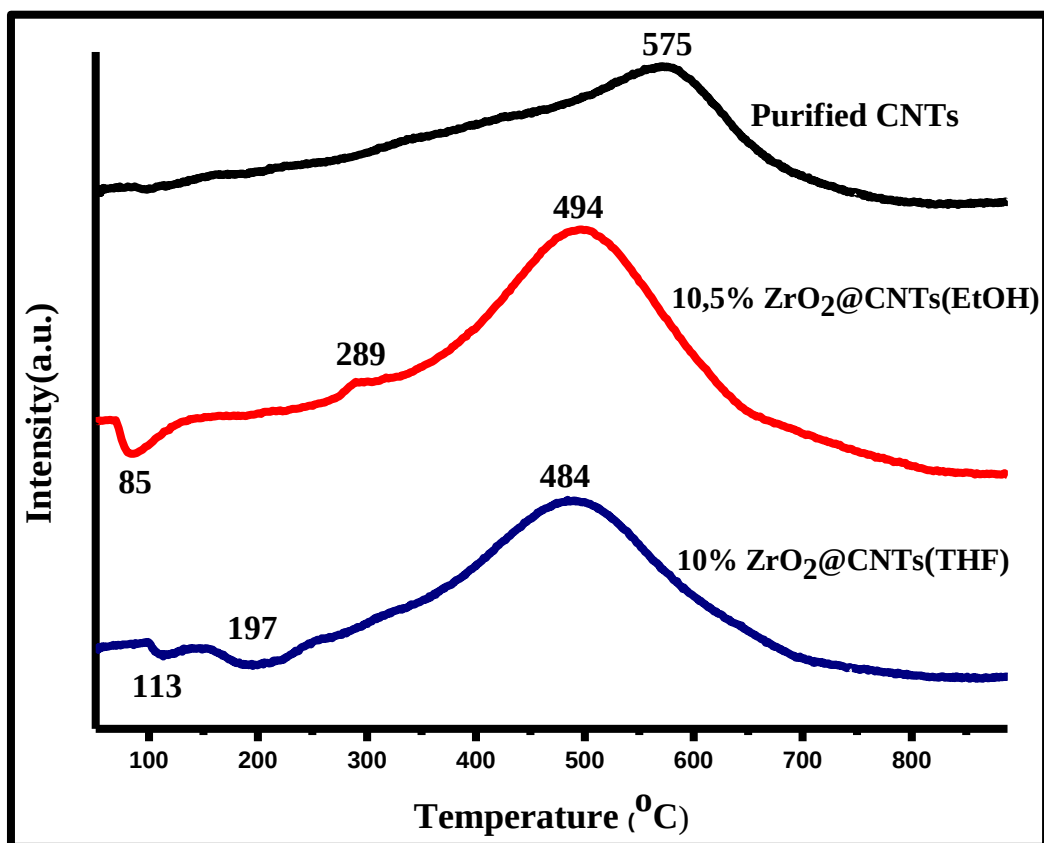


Figure 5.9: TPR profiles of P-CNTs and loaded x/y%ZrO₂@CNTs

5.4. Discussion

Numerous methods have been used successfully for confining metals within carbon nanotubes. Table 5.6 presents some of the results obtained in different studies with regards to CNT confinement using different synthetic methods and different metals including Cu [16,34], Ru, Co & Pd [22], Pd [35], Rh-Mn-Li-Fe [36], Pt-Ru [37] and Ni [38] amongst others. The encapsulation of metals relies greatly on the synthetic process, the purification method used for CNTs, the thermal treatment, and the type of solvent used.

Wang *et al* [16] filled Cu nanoparticles inside CNTs via a convenient wet chemical approach. The work focused on assessing the effect of CNTs with different diameters (small and large) on annealing temperature in copper confinement while maintaining the same loading. The resultant catalyst was used as a probe to study the catalytic effect in MeOAc hydrogenation. The results showed that CNTs with smaller inner diameters exhibited a stronger auto-reduction effect on Cu confined within CNTs. For larger inner diameters, negative effects of annealing were observed. This catalyst showed higher catalytic activity than the Cu nanoparticles loaded on the outside. Pan *et al.* [36] studied the confinement of a bicomponent Rh-Mn catalyst inside the CNTs channels, and the results showed an enhancement in the catalytic activity of syngas conversion to C₂ oxygenation concerning the outside catalyst.

However, confinement can also have a negative impact on the catalytic activity as it was observed for ammonia synthesis over Ru catalyst. The turnover frequency of the confined catalyst was much lower than the catalyst decorated on the outside. This was reported to be because of the electron density such that the Ru-out facilitated an electrophilic process of N₂ dissociation adsorption by donating less electrons to the relatively electron-enriched on the exterior surface. With the Ru encapsulated on the inside, the reaction had a weaker adsorption site for the catalyst reaction [39]. On the other hand, Zhang *et al.* [40] reported that ammonia decomposition benefitted from the confinement of the bimetallic CoFe₅ inside with approximately 96 wt.% particles were located on the inside. However, no reports have been documented on the confinement of ZrO₂ with or without the use of a solvent. Our goal with this study has been to synthesize MWCNTs and load the ZrO₂ within the channels.

ZrO₂ catalyst prepared were via the wet impregnation technique with two different solvents and two different loadings. Impact of solvation was examined, taking into consideration their surface tensions and loading. These two variables could potentially clarify the sintering effect of zirconia in catalytic reactions. There was an insignificant difference in the distribution of

particle size when either EtOH or THF was used from the data collected, and that may be since both had lower surface tensions. As loading increased (46%), the larger the particle size also increased, leading to agglomeration on the outside, but to our surprise, the particles on the inside were smaller and less agglomerated than those found on the outside. The spatial constraint that comes with confinement could account for this behaviour. The physical properties of a solvent do not appear to have a substantial effect on the final material. It should be noted that, during the synthesis, parameters like the polarity of the solvent did not seem to play a crucial role. The similar dispersion and size distribution of ZrO_2 particles may imply that the organic solvents were not chemically modified particles or interact with the zirconia.

Surprisingly, the mass loss from CNTs in the presence of ZrO_2 especially with the 46% became higher. Figure 5.7 (TGA) suggests that the MWCNTs had a good affinity to the ZrO_2 in the 10% loaded. The mass loss greatly increased as the loading increased, meaning that Zr particles helped in the degradation of CNTs and as such the catalyst was less dispersed and coagulated as seen on TEM. This phenomenon may be due to the CNTs being filled more on the outside than inside, and Pal *et al.* [41] also observed this degradation behaviour where, with the addition of 3 percent ZrO_2 , the thermal stability of the CNTs decreased.

Table 5.6: Comparison of different studies with this study.

Metals	Metal	Metal	Inner CNTs	Particle	Inner particle	Outer particle	Surface area	Pore volume	References
Confined (wt%)	Loading	Catalyst	Diameter	Size	size trend	Size trend	trend	trend	
(wt. %)	(wt. %)	Used	(nm)	(nm)					
	~9,79(THF) ~10,5(EtOH) ~46(EtOH) ~46(THF)	ZrO ₂	0.92 - 16.98	6.195 5.112 11.101 10.300	Particles were smaller regardless of the solvent used or amount of loading. Ethanol gave smaller particle sizes and THF had better dispersion	Remained the same as the inside Sintered on the outside	No apparent pattern followed		this work
	~ 3.13 ~5.03 ~6.89 ~12.08	Cu	5.7-24.9	8.01±7.27 9.32±3.27 10.2±4.89 16.03±1.98			Increased with Loading compared With purified CNTs and Lower loading.		our work
~65	~1.0-2.3 ~2.7-3.2 ~1.1-3.2	Ru Co Pd	5.49	2.21±1.02 3.25±2.72 4.15±1.15	Sizes varied based on the metal used. Pd and Co had bigger particle sizes while Ru had smaller sizes	Co and Ru had a similar trend in particle sizes in/out. Pd had bigger particles with sintering.	Decreased With higher loading		[42]

>30	4.4 Pd	50	6 ±4	Size increased based on the support used	No significant difference	Decreased [35] With metal Loading
~75	10 Cu	4-10 20-30	9.7±7.0 19.0±15.1	Size increased with an increase in heating temperature	Bigger particles irrespective of the heat treatment used	Decreased [16] With metal loading
~80	1.2 Rh-Mn- Li-Fe	4-8	0.9± 10	Size increased with reaction time used	Bigger particles as compared to those confined	N/A [36]
50-80	5 – 23 Pt-Ru	40	22±0.7	No noticeable increase with higher loading	Bigger particles on the outer walls	N/A [37]
~90	1 Ni	20-50	7±3	Size not affected using different solvent	The slight difference with sizes ranging between 4-9nm	N/A (38)
~30	4.9 & 9.0 Cu	6-7	14±11	Size increased with decreased loading	Bigger particles observed outside	Decreased compared [43] With that of purified CNTs
	5.2 Cu-Zn		>100	Size increased with the addition of Zn		
						Decreased compared To purified that of CNTs And Cu-CNTs

~50	14.3 - 15.9 Cu	20-30	16.8	N/A	Bigger particles observed compared to that inside	Increased with Loading and heating Time [44] Pore size followed the same pattern with one as an exception
~75	8 Cu	2-5 5-10 20-50	3±1 5±2 10±2	Sizes increased with increased diameter	Bigger particles observed	Decreased with Loading Compared with Purified CNTs [20]

5.4 Conclusion

In essence, our studies describe a simple method of confining Zirconia inside the CNT channels. We have successfully synthesized $\text{ZrO}_2@\text{CNTs}$ catalyst using two different solvents i.e. ethanol and tetrahydrofuran and at different loadings. From PXRD and TEM studies, it was observed that ZrO_2 particles filled within the channels of the CNTs were small and well dispersed on the inside. No agglomeration was exhibited by the lower loaded ZrO_2 , whereas the higher loaded ones were mainly coated and not confined. This was due to the sintering and the CNTs' internal diameters. PXRD also revealed that we have the monoclinic and tetragonal phases of zirconia. TGA showed that with lower loading, the ethanol catalyst was more stable than with higher loading. In addition, we found that the thermal decomposition of the CNTs was facilitated by ZrO_2 . Furthermore, the findings showed that the samples synthesized with ethanol had smaller particle sizes, but those synthesized with THF also had smaller particle sizes, albeit larger than those with ethanol, and better dispersion. Therefore, despite differences in surface tensions, THF is the best solvent preference for zirconia confinement.

This research has shown that zirconia can be filled inside the CNT channels and that the confined particles always seem to be smaller even at higher loads without apparent sintering. This suggests that this technique could be used to limit other metal oxides, but studies should be sought out on the encapsulation of metal oxides with metal loadings higher than 50%, which could potentially be used in ceramics, semiconductors, electronics, etc.

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Chapter 6

Study and characterization of confined Cu-ZrO₂ within carbon nanotubes

6.1. Introduction

The urgency of climate policy depends on how potential greenhouse gas (GHG) concentrations and global climate change are likely to develop in the absence of GHG emission control and how the world's environment and the resources they provide can be impacted by global climate change [1]. With population growth and industrialization, despite the limited quantity of fossil fuels, global energy demand is growing substantially. This imbalanced consumption has caused significant environmental problems and increased emissions of CO₂ into the atmosphere, which is the main cause of global warming and climate change [2].

CO₂ can be converted into valuable products as it is a sustainable, non-toxic, accessible, and readily available carbon resource. The influence of global warming caused by excessive CO₂ emissions can be further alleviated to some degree by this transition. More recently, studies have focused predominantly on the conversion of CO₂ to carbon monoxide, methane, DME, and long alkane chains, although a few studies have been conducted on direct conversion to methanol for the processing of chemicals and fuels i.e. CO₂ refineries [3]. There are several different routes to produce hydrocarbons from CO₂ with renewable H₂ (as discussed in the literature review).

Previous studies have investigated this reaction over copper-based catalyst on different supports and have shown that the type of support used influences the product selectivity [4]. A linear relationship was found to increase the Cu surface area and the conversion of CO₂. The selectivity to methanol in this system is related to the distribution of basic sites on the active site of the catalyst's surface [5]. The higher surface area of Cu aids in appropriate adsorption, both in strength and amount of CO₂ adsorbed, and the effective interaction between the active parts of the catalyst are of prime importance for the hydrogenation reaction, providing a guideline for the preparation of a highly effective catalyst [5].

Modifications by various additives to improve one or several aspects of the catalytic steps are one of the possible pathways to influence the above-mentioned parameters [5]. ZrO₂-containing catalysts have evoked recent interest both as additives to catalytic systems, as

isolated entities (reported in chapter 5) as well as for their ability to improve the structural integrity of various catalysts and to induce beneficial steering of reaction pathways to increase the respective selectivity [6]. ZrO_2 , as compared to the other metal oxides such as CeO_2 and Al_2O_3 , was found to be a superior support for copper in hydrogenation reactions due to its better synergy with zirconia [5].

In the field of methanol synthesis, the use of zirconia other than ZnO or alumina as an attractive support material for the activation and stabilization of copper is well known, primarily due to its unique amphoteric and redox character. It is recognized that the behaviour of these catalysts is critically dependent on many variables, including the preparatory course, structure, and catalyst constitution [7]. The phase of ZrO_2 was also found to be of importance in the Cu-ZrO_2 catalyst. Whereas the surface area and the Cu dispersion were essentially identical for both phases, Cu-ZrO_2 with $m\text{-ZrO}_2$ was 4.5 times more active for CO_2 conversion than a catalyst prepared with $t\text{-ZrO}_2$ [5].

Several methods which include oxalate-gel-co-precipitation, conventional aqueous co-precipitation, and impregnation have been comparatively examined for the preparation of binary Cu-ZrO_2 catalyst systems [7]. The results showed that the method of preparation significantly affected the dispersion of the materials, microstructural properties, and the resulting catalytic efficiency of methanol conversion, selectivity, and operation [7]. There is a competitive mechanism between the reverse water gas reaction (RWGS) and the methanol synthesis reaction in the CO_2 hydrogenation reaction. The RWGS reaction reaches thermodynamic equilibrium rapidly, while the synthesis reaction of the methanol reaction is much slower [8].

When methanol is produced from CO_2 hydrogenation, an equivalent amount of H_2O is generated. Large amounts of H_2O can both reduce the production of methanol and ramp up the crystallization of Cu and ZrO_2 , which typically leads to a rapid decrease in catalytic activities [3]. Recently, increasing attention has been drawn towards the use of multi-walled carbon nanotubes (MWCNTs), as a novel nano-carbon support and promoter. MWCNTs have many unique specific characteristics, such as a graphitized tube wall, a nanometer-sized channel made from $\text{sp}^2\text{-C}$, high electron and thermal conductivity, and a large surface area. MWCNTs can be used as a catalyst support where metal particles with catalytic activity can decorate along the external walls or be filled within the MWCNTs [9].

The inner surface of CNTs as a catalysts support has been little explored less explored [10–15]. It is anticipated that the CNT channels will provide an intriguing confinement environment

for metal catalysts and for catalytic reactions. Furthermore, confinement has been shown to alter the structure and properties of confined materials (16–18). However, studying confinement effects in catalysis requires techniques to disperse metal nanoparticles uniformly inside the CNT channels. This has remained a challenge, in particular inside small nanotubes [14].

Concerning the interesting properties of MWCNTs, in this study, MWCNTs were selected and used as a support for a Cu-ZrO₂ catalyst for the CO₂ conversion to methanol. This allowed for the study of a catalyst system that could possibly exhibit improved long-term stability, lower water affinity, and high activity.

6.2. Experimental procedure

In this study, for all the catalysts, the preparation method, conditions, and calcination temperature were noted to play a major role. The synthesis of Cu-ZrO₂@CNTs was achieved following various experimental procedures previously used for the confinement of metals in CNTs [14–16,19,20] as recorded in chapters 4 and 5, with some modifications. This adjusted procedure was expected to produce dispersed Cu-ZrO₂ filled within different diameter CNTs.

6.2.1. Starting materials

The zirconia-copper nanoparticles catalysts were prepared from zirconyl nitrate hydrate (ZrO(NO₃)₂·6H₂O, 99%) and copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%), respectively. Tetrahydrofuran (THF, 99%) was purchased from Sigma-Aldrich and Associated Chemical Enterprises (ACE) and was used without any further purification. African oxygen (AFROX) supplied the nitrogen (N₂, 99%), which was used in the thermal treatment experiments. Distilled water generated in the School of Chemistry was used in the study.

6.2.2. Catalyst preparation

In the efforts to fill CNT channels, the method used was based on the study reported by Tessonier *et al.* [18,21]. For the preparation of Cu-ZrO₂@CNTs, the following parameters were considered: 1) the affinity of the organic solvents relative to CNTs; 2) the surface tension of the solvent employed must be lower than that of CNTs, so that the CNTs could be wetted and infiltrated; and 3) the reaction behaviour of copper as compared to that of zirconia with regards to confinement.

As a result, a three-step synthesis (similar to chapters 4 and 5) was used (Table 6.1). The purified CNTs (0.5 g) (opened by acid treatment) were impregnated with about 6 ml of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in THF and 2 ml water as solvent (ratio of THF to water was 3:1). This aqueous solution was vigorously stirred for ± 12 h before the impregnation step. A light blue solution was obtained. Impregnation was then followed by continuous stirring for 1 h and sonication for 4 h. Another 1 ml of distilled water was added dropwise to the x%Cu-ZrO₂@CNTs mixture, sonicated for 3 h, and the sample was left to stir overnight. The obtained sample was slowly dried at 373K for 48 h. The final catalyst was heated at 723K under a N₂ atmosphere for 3.5 h, at a rate of 5 °C/min. The Cu-ZrO₂ content was varied (13% to 21%). The filled CNTs, were called X%Cu-ZrO₂@CNTs and the targeted loadings in the preparation were 10% to 30%. The Cu/Zr ratio was calculated to be 35/65 (wt%) for each metal loading.

Table 6.1: Summary of the experimental procedure

Description	Stirring Time (h)	Sonication time(h)	THF (v/v ratio)	H ₂ O (mL)	THF (mL)	heat treatment conditions
X% Cu-ZrO ₂ @CNTs	0.4	1.5	3:1	2	6	T= 450°C r = 5°C/min
						T _{total} = 5 h

6.3. Characterization techniques

TEM, XRD, BET, TPR, and TGA were used as characterization techniques to evaluate the synthesized materials. The morphologies of samples were characterized by TEM. The crystal structure of the materials was characterized using XRD and BET was used to determine the surface area, pore size, and volumes of the catalyst. The thermal stability, quantity, and the differential thermogravimetric analysis of the x%Cu-ZrO₂@CNTs were performed to give information on the thermal properties. TPR was used to evaluate the temperature reducibility of Cu-ZrO₂@CNTs.

6.4. Results and Discussion

6.4.1. Transmission electron microscopy

TEM characterization was performed to investigate the encapsulation and dispersion of copper and zirconia species using tetrahydrofuran and water as a solvent. The catalysts were prepared using different loadings of Cu/Zr. TEM images and EDX spectrum (using a nickel grid), of Cu-ZrO₂@CNTs catalyst are presented in (figure 6.1.). The average carbon nanotube's inner

diameter, Cu-ZrO₂ particle size (inner and outer) distribution of all the synthesized Cu-ZrO₂@CNTs was done by measuring the individual diameter of about 100-120 particles for each sample and were processed using Image J.

Table 6.2 shows the particle size distribution of all the synthesized catalysts. The particle sizes of all the catalysts found inside the CNTs were much smaller than the particles found on the outside of the nanotubes, as shown in table 6.2. The particle size distribution histograms were plotted and are shown in figures 6.1-6.5. The data showed average particle sizes of about 7.4 ± 2.5 nm and 6.1 ± 2.6 nm for particles inside (P_{in}) and outside (P_{out}) the CNTs respectively at the 13wt% loading. This is to be compared with the data for P_{in} (9.3 ± 2.4 nm and 16.5 ± 2.42 nm) and P_{out} (26.1 ± 6.0 nm and 30.2 ± 5.1 nm) at the 18wt% and 20wt% loading and the P_{in} (20.1 ± 2.18 nm and 20.4 ± 4.2 nm) and P_{out} (26.3 ± 0.7 nm and 24.8 ± 2.3 nm) at the 21wt% and 27wt% loading. It was observed that the average particle sizes increased with loading both inside and outside. The findings showed that confinement had an effect on nanoparticle growth as all particles showed an increase in the outer particle sizes as seen in table 6.2.

TEM images of X%Cu-ZrO₂@CNTs are shown in figure 6.1- 6.5 (a-c). The catalyst filled CNT (figure 6.1 (c)) and its corresponding EDX spectrum (figure 6.1 (d)) showed that the particles have two different shapes, spherical and cylindrical. The EDX spectrum showed the presence of Ni (from the grid used), Fe, Zr, C, and Cu. The presence of Fe was due to the catalyst residue remaining after the CNT synthesis. Some Fe was encapsulated and trapped by the CNTs walls (circled in figure 6.2 (b)), rendering them inaccessible. In an attempt to differentiate Cu from Zr particles, we used the HRTEM image (figure 6.4 (c)) to measure the d-spacing from the lattice fringes. Figure 6.4 (c), the HRTEM images clearly displayed lattice fringes with a spacing of 0.292 nm, which are consistent with the (101) plane of tetragonal zirconia. The image also showed the lattice fringes with a spacing of 0.208 nm, which are consistent with Cu. The HRTEM image (figure 6.4 (c)), clearly displayed (circled: red (zirconia) and yellow (copper)) additional particles with lattice fringes of 0.234 nm and 0.37 nm, which were compatible with the (111) and (-111) planes of CuO and monoclinic zirconia, respectively. On the basis of this data, in comparison with our results in chapters 4 and 5 (see figures 4.3 (b) and 5.3 (d)), we identified the dark particles with spherical shapes as copper (yellow arrow), whereas the cylindrical light particles were identified as zirconia (red arrow). Similar deduction were reported by Din *et al.* [22].

TEM analysis showed that both Cu and ZrO₂ particles were well-dispersed. In addition, all of the catalysts had a uniform particle distribution, with the exception of the 21wt% and 27wt%, which showed some sintering and overpopulation when the metal was on the outside of the CNT. Both the dispersion and particle sizes were adversely affected by the amount of catalyst loaded (20wt%, 21wt% and 27wt%) and this was noted by the densely populated and poorly dispersed catalyst in some regions (figure 6.2 (c) and 6.3 (b)). Figure 6.3 (a) had more particles on the outside than seen in Figures 6.1 and 6.2 and also displayed larger particles due to the excessive copper loading. The uniformity, confinement, and dispersion of the catalyst components all showed about 65-85% of the catalyst located inside the tubes, an optimum dispersion was observed in the case of 13wt%Cu-ZrO₂@CNTs.

Table 6.2: Particle size analysis using ImageJ.

Sample	CNTs Diameter (nm)	Average Particle size (nm)	Average Outer Particle size (nm)
13%Cu-ZrO₂@CNTs	26 ± 3	4.3	6.1
18%Cu-ZrO₂@CNTs	26 ± 3	4.0	12.1
20%Cu-ZrO₂@CNTs	26 ± 3	5.3	12.1
21%Cu-ZrO₂@CNTs	26 ± 3	11.3	15.7
26%Cu-ZrO₂@CNTs	26 ± 3	11.5	17.2

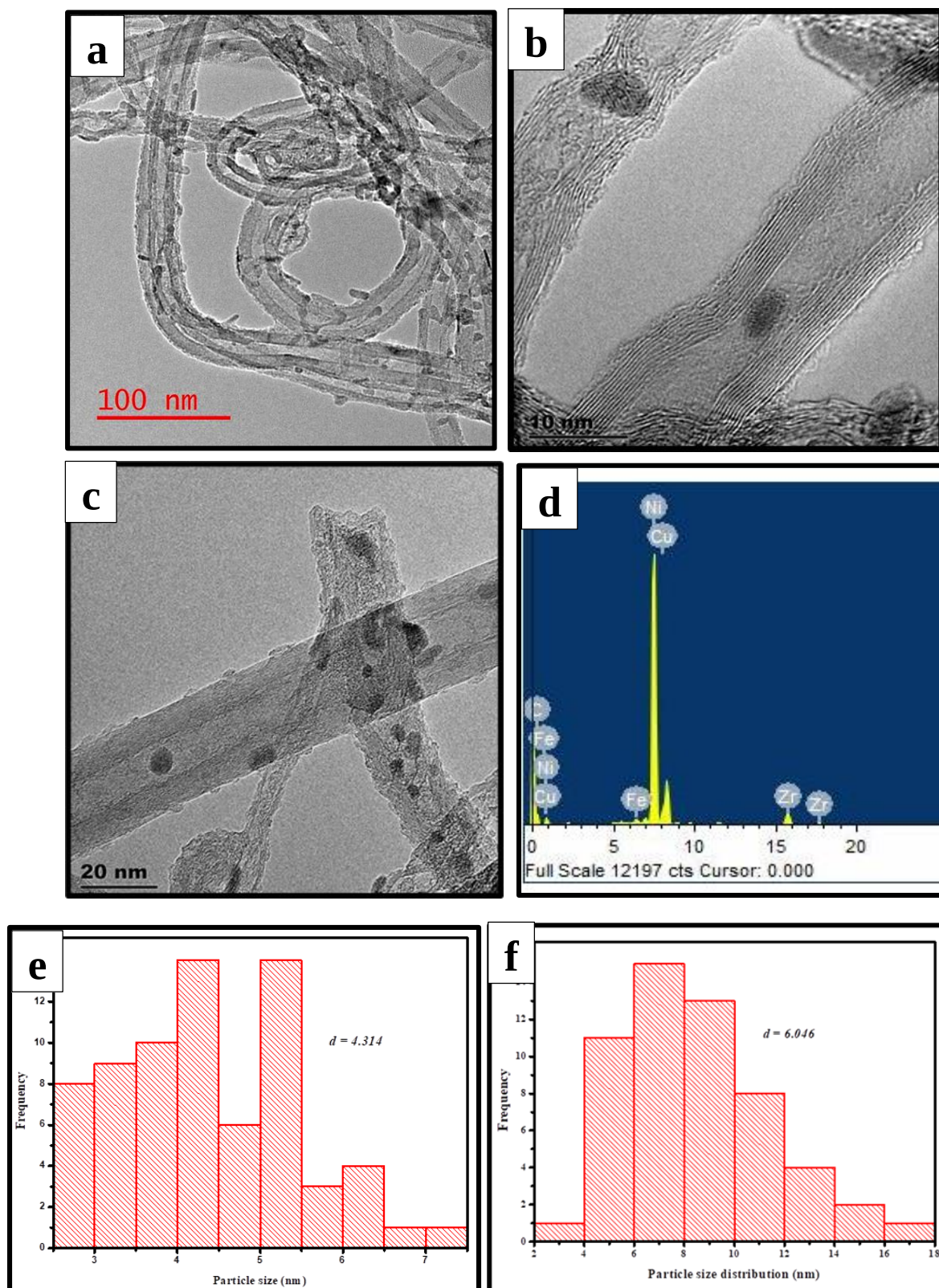


Figure 6.1: (a-c) HRTEM images, (d) the corresponding EDX spectrum taken from image (c), and the corresponding (e) inner and (f) Cu-ZrO₂ particle size distributions for 13%Cu-ZrO₂@CNTs

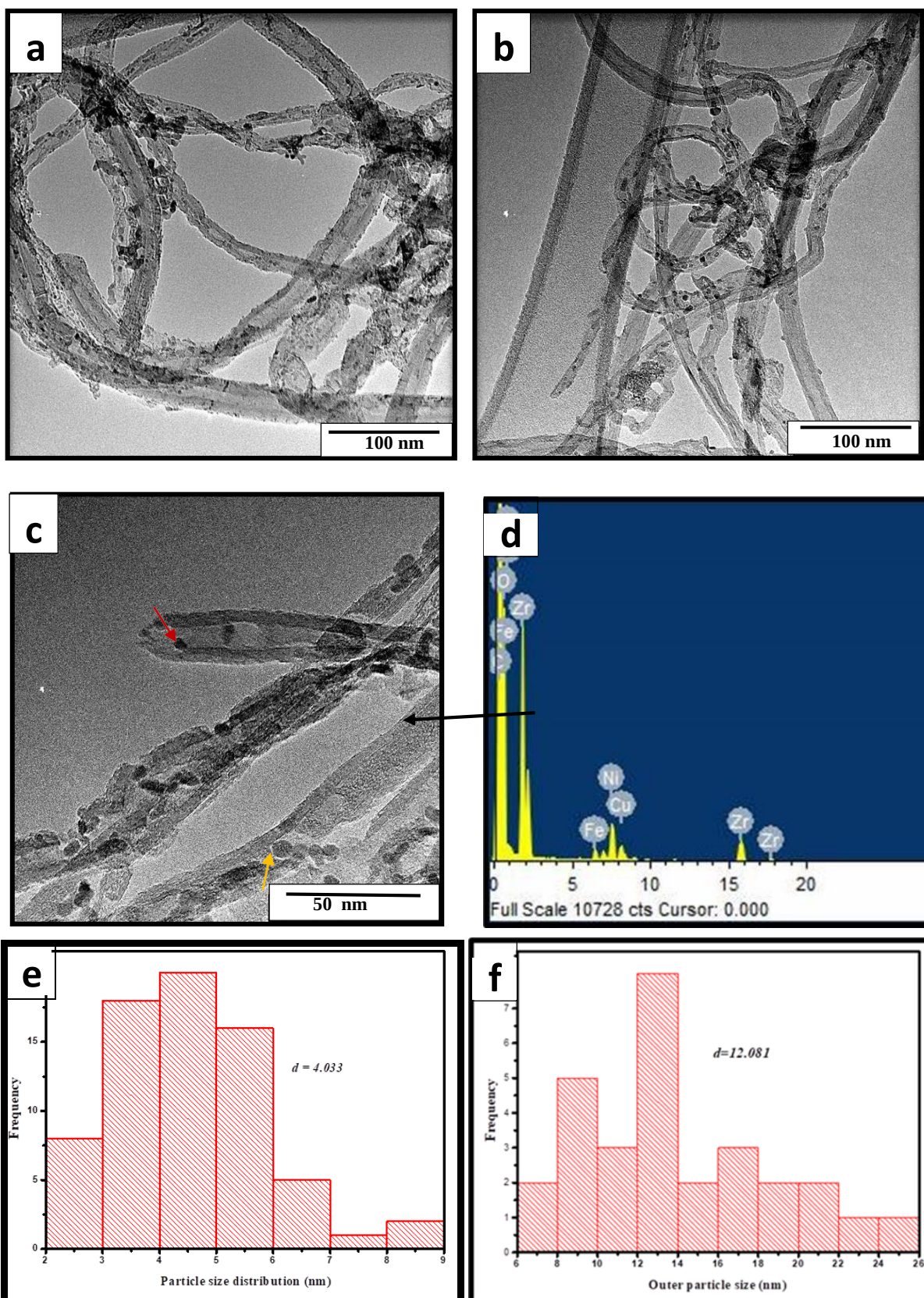


Figure 6.2: (a-c) HRTEM images, (d) the corresponding EDX spectrum taken from image (c), and the corresponding (e) inner and (f) Cu-ZrO₂ particle size distributions for 18%Cu- ZrO₂@CNTs

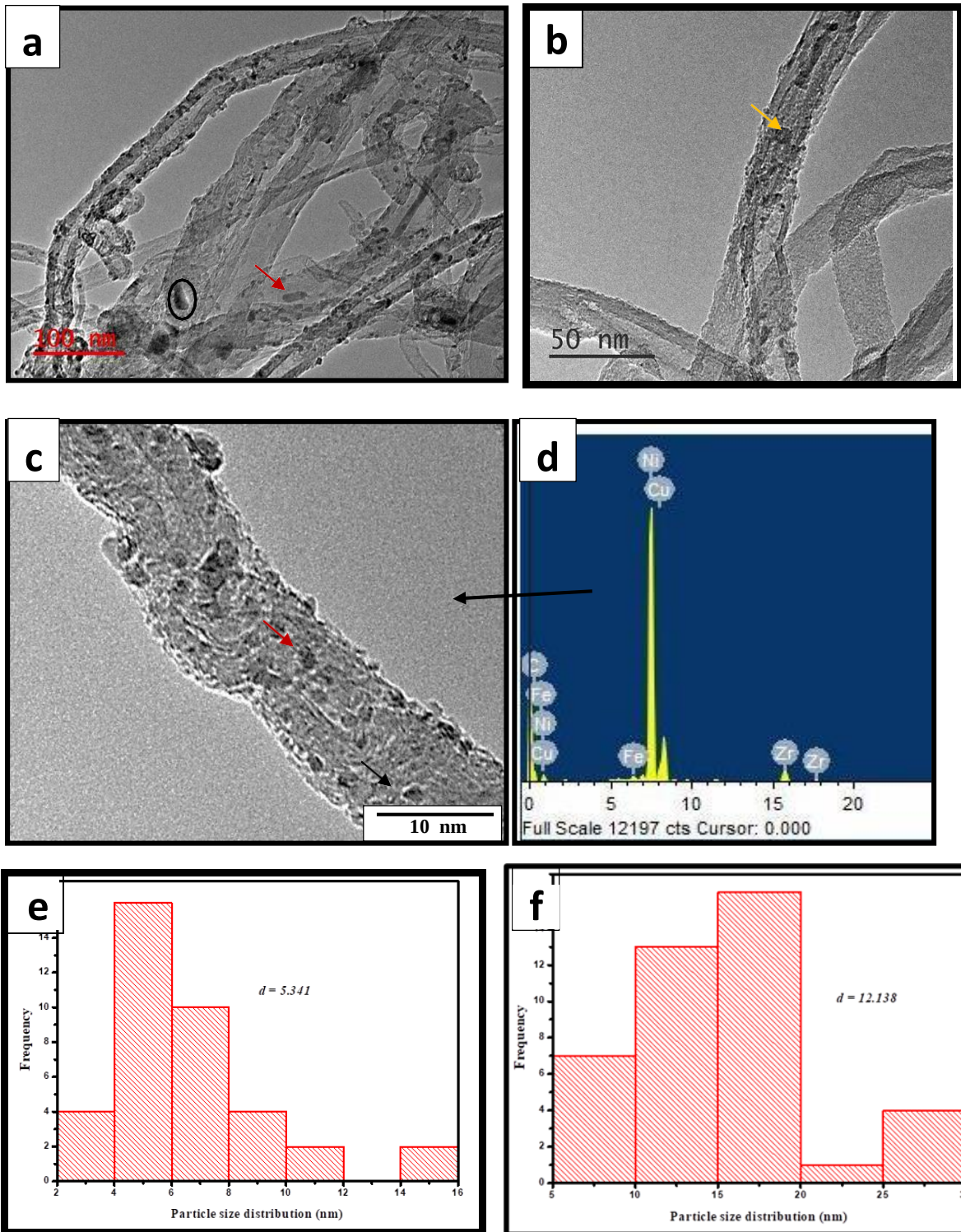


Figure 6.3: (a-c) TEM images, (d) the corresponding EDX spectrum taken from image (c), and the corresponding (e) inner and (f) outer Cu-ZrO₂ particle size distributions for 20%Cu-ZrO₂@CNTs

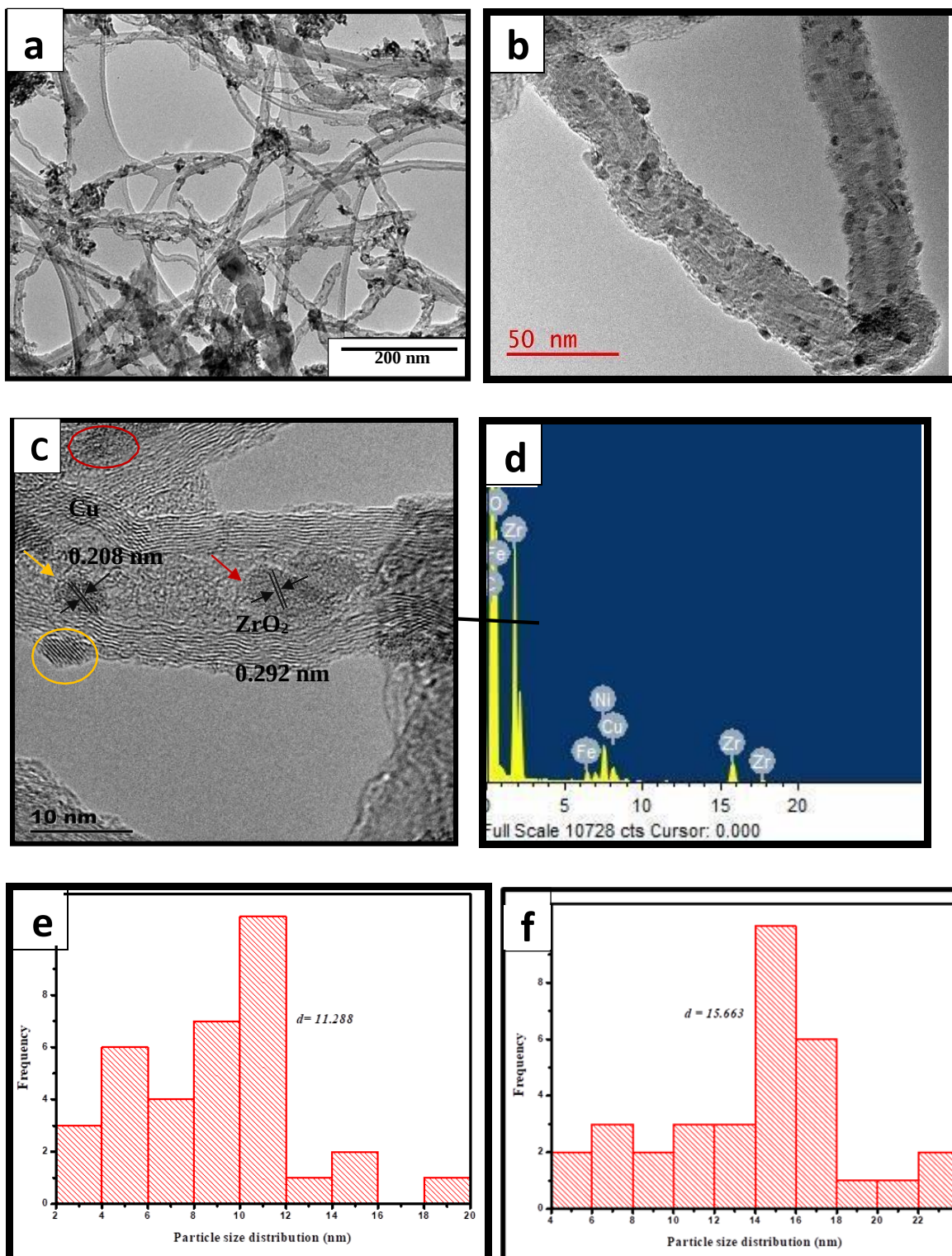


Figure 6.4: (a-c) TEM images, (d) the corresponding EDX spectrum taken from image (c), and the corresponding (e) inner and (f) Cu-ZrO₂ particle size distributions for 21%Cu-ZrO₂@CNTs

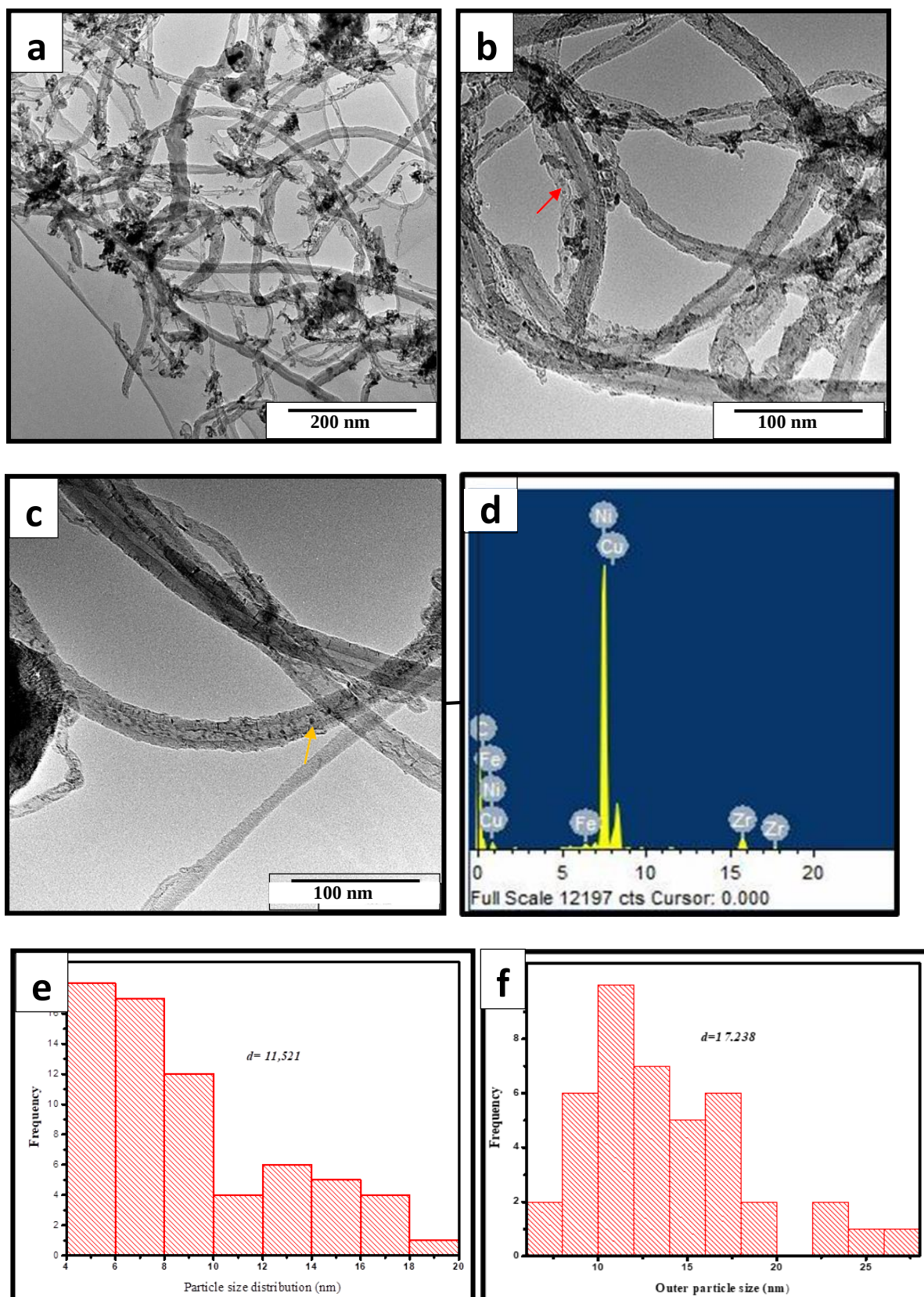


Figure 6.5: (a-c) TEM images, (d) the corresponding EDX spectrum taken from image (c), and the corresponding (e) inner and (f) Cu-ZrO₂ particle size distributions for 27%Cu-ZrO₂@CNT

6.4.2. Brunauer-Emmett Teller (BET) analysis

The physical properties including BET surface area and pore volume of Cu-ZrO₂ catalyst are summarized in table 6.3. The BET surface area of CNTs was 90.9 m²/g, while the total pore volume was 0.34 cm³/g. After loading Cu-ZrO₂, an increase in the BET surface area of all the materials was observed. This observation originates from the addition of the Cu metal and the ZrO₂ support during the impregnation process. The 13wt%Cu-ZrO₂@CNTs exhibited the highest surface area and pore volume, which might be related to the low content of copper on the support. The decline in the surface area of the 18wt% (86.7m²/g) and the 20wt% (96.48m²/g) from the 13wt% (166.7 m²/g) could indicate a partial blockage of the CNT support at higher loadings. The trend of surface area and pore volume as a function of increasing Cu/ZrO₂ content could be due to the agglomeration observed in figure 6.4 and 6.5 (a) and this is mostly when the catalyst loading is >15wt%.

Table 6.3: BET surface areas and porosity of the synthesized materials.

Sample	Surface Area(m ² /g)	Pore volume(cm ³ /g)	Pore size(nm)
Purified CNTs	91	0.34	15.4
13%Cu-ZrO ₂ @CNTs	167	0.64	15.5
18%Cu-ZrO ₂ @CNTs	87	0.36	14.6
20%Cu-ZrO ₂ @CNTs	97	0.34	15.9
21%Cu-ZrO ₂ @CNTs	102	0.28	10.9
27%Cu-ZrO ₂ @CNTs	102	0.32	12.8

Figure 6.6., shows the nitrogen physisorption isotherm and pore size distribution for X%Cu-ZrO₂@CNTs. The isotherms are IV type with a smooth step due to capillary condensation in the 0.9-1.0 relative pressure region and with H3 hysteresis. According to the IUPAC classification, these features are typical of a mesoporous material with an almost non-rigid aggregate on plate-like particles. The isotherms did not change their shape after the addition of different quantities of Cu-ZrO₂, which showed that the CNT structure did not change. The pore size distribution also revealed that the support and the loaded materials are mesoporous in nature and that the pore sizes were faintly affected by the catalyst loading. Overall, the addition of the Cu and ZrO₂ promoted a surface area increase from the initial purified CNTs used. However, the addition of more Cu and ZrO₂ content resulted in a decrease in pore volume. This

behaviour was also noted by others when Cu-ZrO₂ was decorated outside the CNTs walls [23,24].

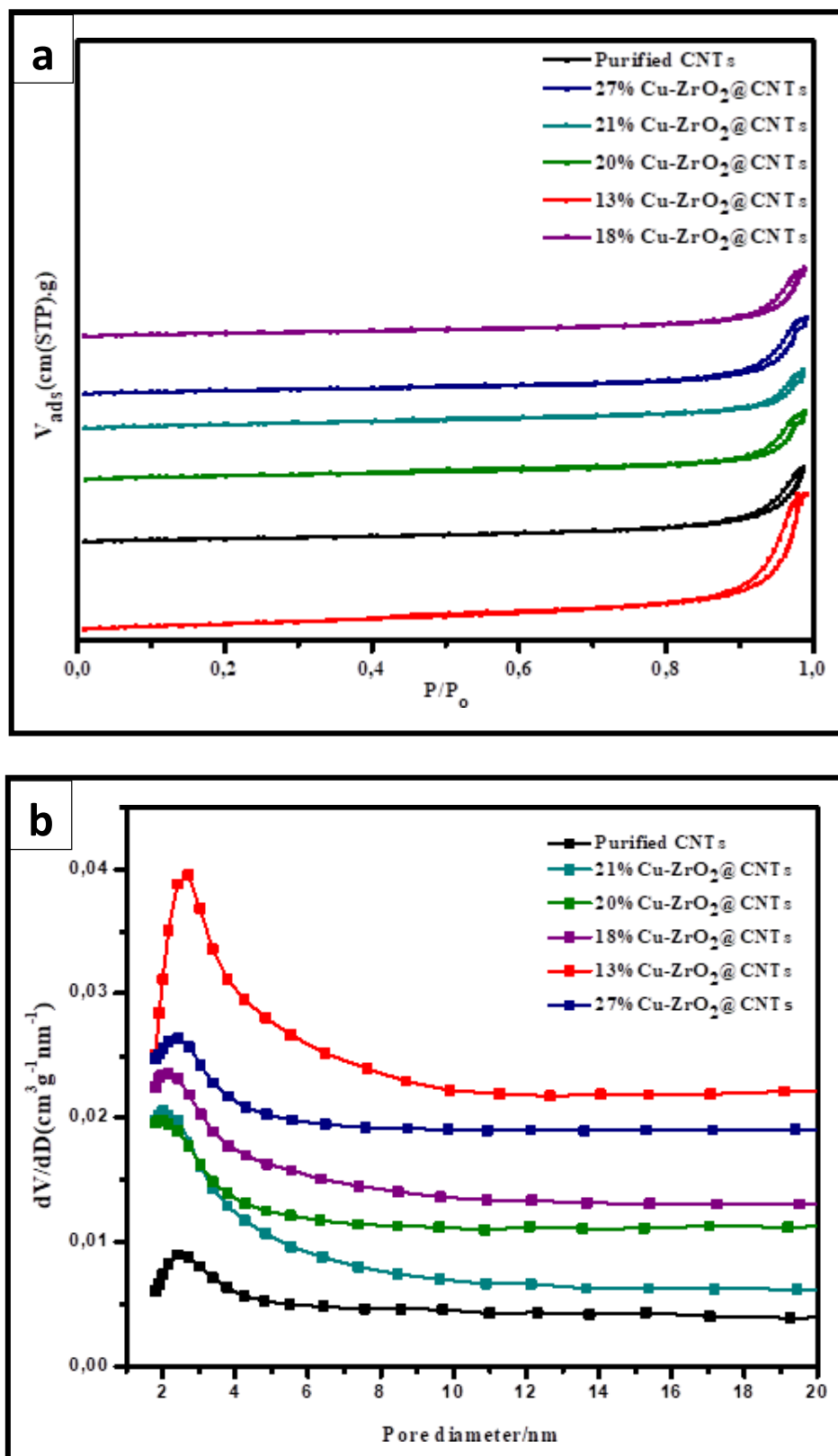


Figure 6.6: The a) nitrogen adsorption-desorption isotherms and b) pore size distribution of the synthesized materials

6.4.3. Powder X-ray diffraction (PXRD)

Phase and crystallinity of the synthesized CNTs materials and the CNTs catalyst-loaded samples were examined by the PXRD technique and the XRD patterns of the %xCu-ZrO₂@CNTs catalyst sample are presented in figure 6.7. For comparison, the diffraction pattern of the purified CNTs is also shown. The two major peaks were detected in all the samples at 2theta scale 26° and 44°, indicating the diffractions of (002) and (100) planes of graphitic carbon nanotubes [25]. A small diffraction peak visualized at 2theta of 28.3° and ~54.3° were consistent with the characteristic of tetragonal ZrO₂ (t-ZrO₂) corresponding to the lattice planes (101) and (112) respectively (PDF 01-072-2743). Another weak diffraction peak indexed at 2theta = 50.3° is due to the monoclinic ZrO₂ (m-ZrO₂) phase, corresponding to the lattice plane (110) [26]. It was also noted that the diffraction peaks at 2theta = 31.6° (111) and 43.5° (200) were indexed to Cu [15,22]. There was also an appearance of high intensity peaks corresponding to t-ZrO₂ and CuO for 21wt% and 27wt% observed at 24.2° (-111) for t-ZrO₂ and 38.7° for CuO. For 21wt% and 27wt% Cu-ZrO₂, peaks attributed to crystalline CuO can be distinguished from the characteristic ZrO₂ peaks near these diffraction angles, confirming the presence of CuO, as clusters at a higher loading of Cu. This is in accordance with the results obtained from the TPR measurements described below. We observed that the catalyst 21wt% and 27wt% experienced a shift in the position of the peaks and this shift could be due to the changes in the stoichiometric composition which results in the appearance of more ZrO₂ phase. The peak intensities of the catalysts increased in the following order: 18wt%Cu-ZrO₂@CNTs < 13wt%Cu-ZrO₂@CNTs ≤ 20wt%Cu-ZrO₂@CNTs < 21wt%Cu-ZrO₂@CNTs < 27wt%Cu-ZrO₂@CNTs. Apart from the intensities, it is apparent that the 13wt% - 20wt% catalysts exhibited similar diffraction features with an appearance of new peaks for 21wt% and 27wt%.

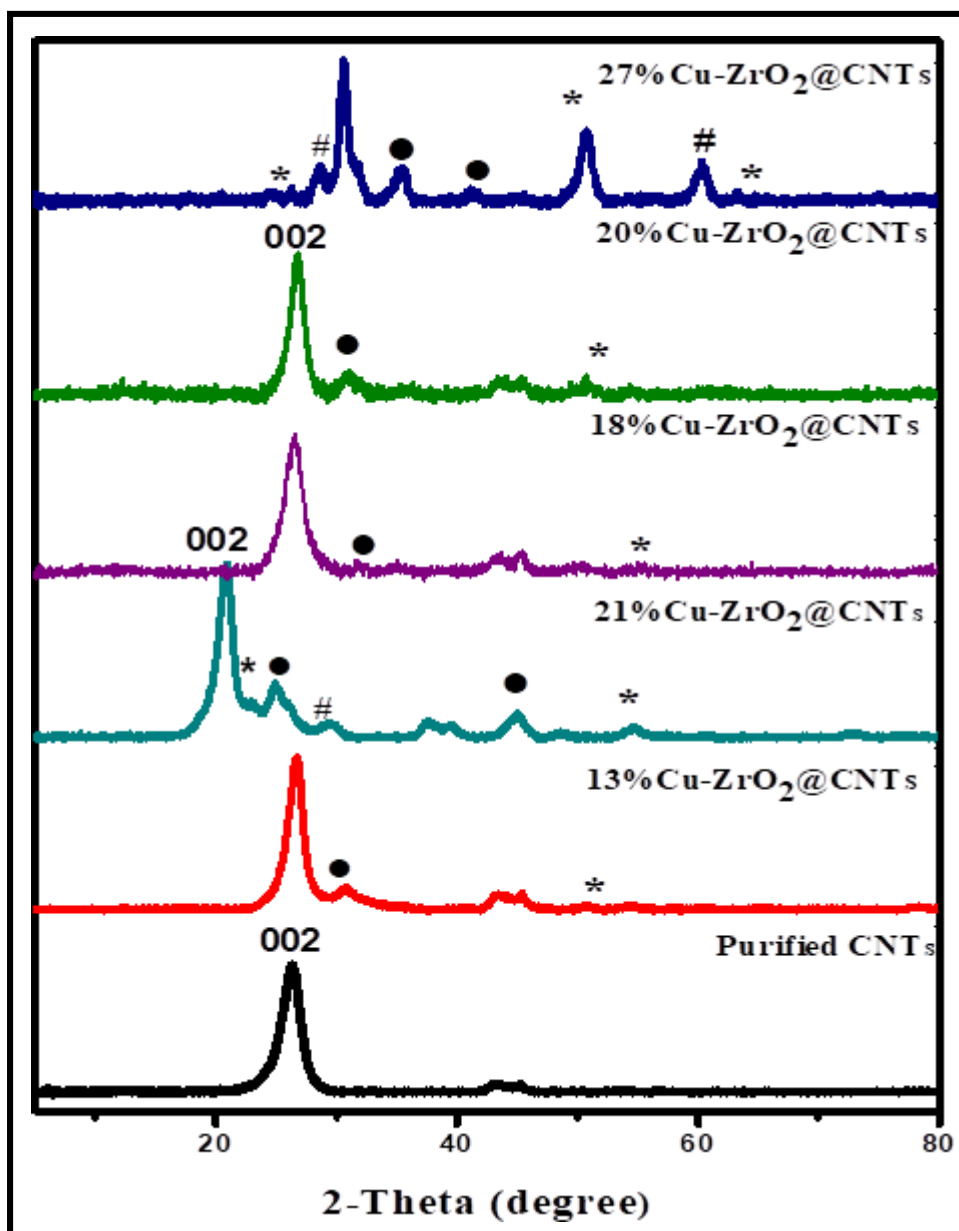


Figure 6.7: PXRD patterns for the synthesized Purified-CNTs and X%Cu-ZrO₂@CNTs. The peaks were indexed as (●) Cu , (*) m-ZrO₂ and (#) t-ZrO₂.

To obtain the particle size, the Scherrer equation was used (27,28)

$$D = \kappa\lambda/\beta\cos\theta \dots\dots\dots 1$$

where D_{hkl} - crystallite size, β - full width half maximum in radians, λ - X-ray wavelength, θ - peak position in radians and K is the Scherrer equation given as of 0.9 [29] and λ the X-ray wavelength is given by $\lambda=0.15406$.

Table 6.4: metal loadings vs crystallite sizes.

Sample	Crystallite sizes (nm)	
	Cu	ZrO ₂
13%Cu-ZrO ₂ @CNTs	6.4	5.2
18%Cu-ZrO ₂ @CNTs	8.1	7.4
20%Cu-ZrO ₂ @CNTs	11.3	9.3
21%Cu-ZrO ₂ @CNTs	12.3	11.2
27%Cu-ZrO ₂ @CNTs	15.8	13.4

The crystallite sizes obtained using the Scherrer equation are presented in table 6.4. This implied that the Cu crystalline sizes were larger than that of ZrO₂ for all the catalyst. The crystalline particle sizes pattern obtained corresponded with those obtained from TEM except for the 20wt%Cu-ZrO₂@CNTs. The crystal sizes of the bimetallic samples were much smaller, indicating that the presence of copper and zirconia together within the channels enhanced the oxide distribution and dispersion during the synthesis process.

6.4.4. Thermogravimetric analysis (TGA)

Thermal stability is a key issue for CO₂ hydrogenation reaction. Weight loss of the catalyst ranged from 13.5% to 26.7.4% (figure 6.8 and table 6.5). All catalysts had two weight loss events (minor and major) related to CNT decomposition, as shown by the decrease in stability following the addition of Cu-ZrO₂. The TGA curve for the all the synthesized catalysts had no weight loss below 450°C, suggesting that there was no amorphous carbon present. However, the derivative curve for all catalysts had one endothermic peak at 65° and this phenomenon

could be due to the disappearance of trapped moisture and the surface hydroxyl groups [30] or the desorption of the physically adsorbed water on the surface of the catalyst and desorption of the structural water [9]. The TGA curve of purified CNTs shows no residue, which indicates the successful purification of the materials. Fe residues could not be detected, which was in accordance with the XRD data, but were detected in EDX, which is likely due to the detection limit in XRD and their location as seen in TEM. The estimated x%Cu-ZrO₂ loading calculated from the TGA curves were found to be 13.4 %, 18.2 %, 19.7 %, 21.4% and 26.7 for 13, 18, 20, 21 and 27%Cu-ZrO₂@CNTs, respectively. The initial calculations are in agreement with the TGA data obtained, with insignificant differences which are expected.

The DTG plot shows the maximum decomposition temperature of the prepared Cu-ZrO₂ catalysts. Purified CNTs decomposed at 722 °C, and this decreased to 594, 584, 580, 569 and 564°C for 13, 18, 20, 21 and 27%Cu-ZrO₂@CNTs, respectively. The TGA results clearly show that the addition of Cu-ZrO₂ had an effect on the thermal stability of the materials and that the stability of each catalyst decreased based on the metal loading. The active catalyst components maintained good thermal stability, with the 13wt%Cu-ZrO₂ being the most stable material. The decrease in stability is due to the addition/presence of copper and zirconia. This behaviour was also noted for the Cu@CNTs and ZrO₂@CNTs catalyst reported in the previous chapters.

Table 6.5: metal loadings vs Temperature peak positions

Sample	Metal loading%	Temperature positions (°C)
Purified CNTs	-	720
13,5%Cu-ZrO₂@CNTs	13.4	65, 594
18%Cu-ZrO₂@CNTs	18.2	65, 584
20%Cu-ZrO₂@CNTs	19.7	65, 580
21%Cu-ZrO₂@CNTs	21.4	65, 569
27%Cu-ZrO₂@CNTs	26.7	65, 564

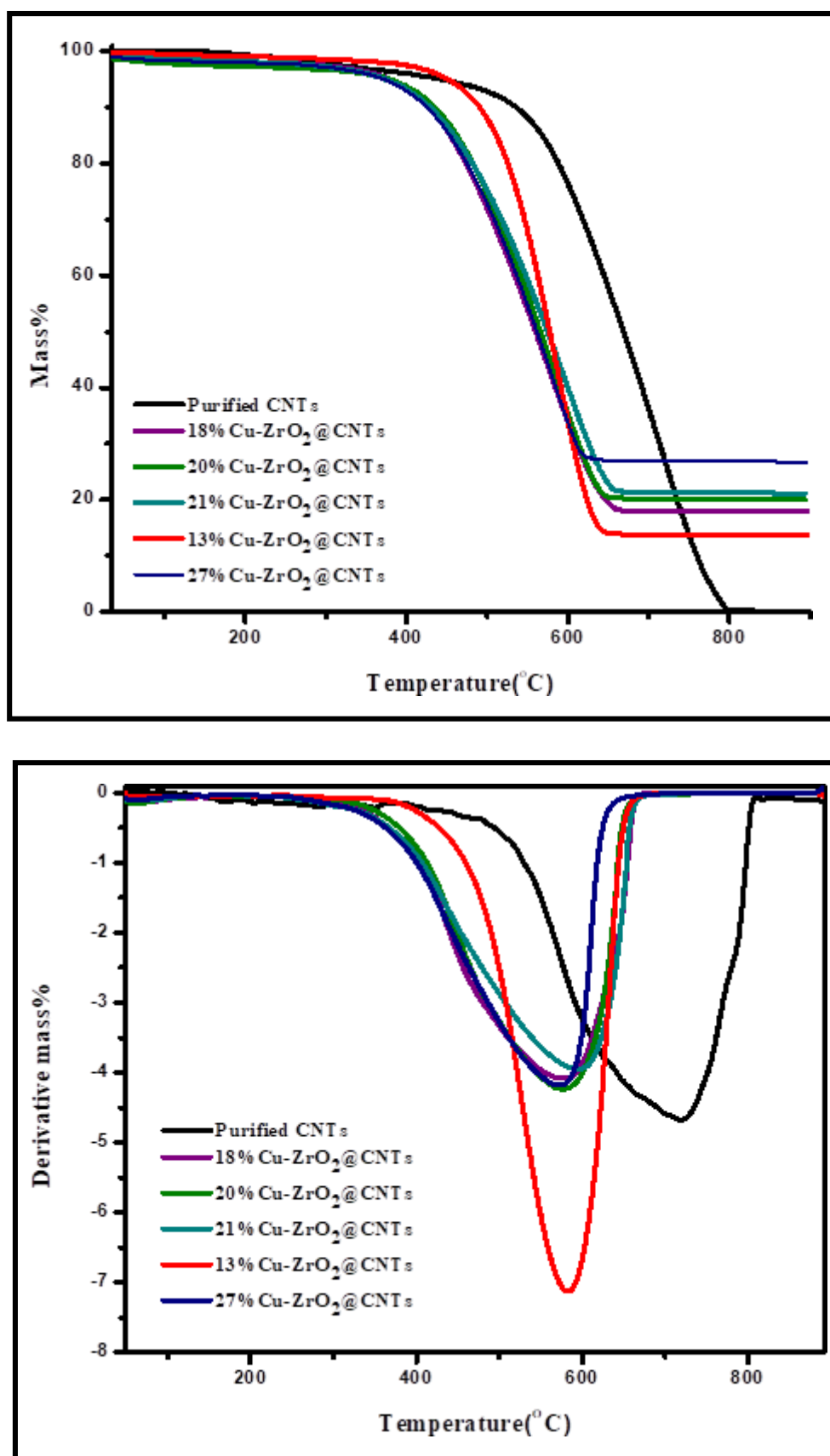


Figure 6.8: TGA profiles (TGA and DTA) of Purified-CNTs and loaded CNTs

6.4.5. Temperature programmed reduction (TPR)

TPR analysis was used to investigate the behavior of Cu and ZrO₂ in terms of reducibility. The TPR profile provides information on the dispersion of the metal species over the support, and gives details of the interaction between the metal ions and the support [31] and is essential in determining the catalyst's catalytic reduction activity. The TPR profiles of the 13wt%Cu-ZrO₂@CNTs (a), 18wt%Cu-ZrO₂@CNTs (b), 20wt%Cu-ZrO₂@CNTs (c), 21wt%Cu-ZrO₂@CNTs (d), 27wt%Cu-ZrO₂@CNTs (e), and the purified CNTs are depicted in figure 6.9. As can be seen, purified CNTs displayed one reduction peaks which is attributed to the reduction of carbon, while most the catalysts (apart from 27wt%) exhibited four reduction peaks at ~80°C, ~160°C, ~334°C and ~ 500 °C (figure 6.9 and table 6.6). Shimokawabe *et al.* [32] and Dow *et al.* [33] studied the reduction behaviour of Cu–ZrO₂ and CuO–YSZ catalysts, respectively. They illustrated that the lower temperature peaks are because of highly dispersed CuO, Cu and/or Cu²⁺ ions with an octahedral environment [34]. Based on the literature data and the XRD results, it can be concluded that the first peak is attributed to highly dispersed Cu/CuO species, while the second peaks can be assigned to the small CuO/Cu clusters with different particle sizes [15,20,34,35]. The intensities of the third peak are quite low (slightly undetectable in some samples) and may be due to the reduction of Zr⁺⁴ species [4,36,37]. A lower reduction temperature of surface Cu generally means a stronger interaction between Cu and ZrO₂ [38]. For 27wt% Cu–ZrO₂, it can be seen that there are four peaks. The first peak at low reduction temperatures (97 °C) can be ascribed to well dispersed CuO, whereas the large peaks (second and third) at high reduction temperatures (236 and 266 °C) are attributed to bulk CuO. A shift was observed for the high temperature peaks at a high Cu loading, likely due to the weakening of the metal–support interaction. This may be because some of the Cu clusters were located on the outer surface of the support and were easily accessible, while at the lower metal loading Cu species were highly disperse and were located in the pores of the support, leading to a low accessibility towards the higher reduction temperature.

Table 6.6: metal loadings vs Temperature peaks positions

Sample	Metal loading%	Temperature positions (°C)
Purified CNTs	-	573
13,5% Cu-ZrO ₂ @CNTs	13	75, 162, 534
18% Cu-ZrO ₂ @CNTs	18	81, 129, 504
20% Cu-ZrO ₂ @CNTs	20	81, 141, 498
21% Cu-ZrO ₂ @CNTs	21	80 ,139 ,486
27% Cu-ZrO ₂ @CNTs	27	97, 236, 266,475

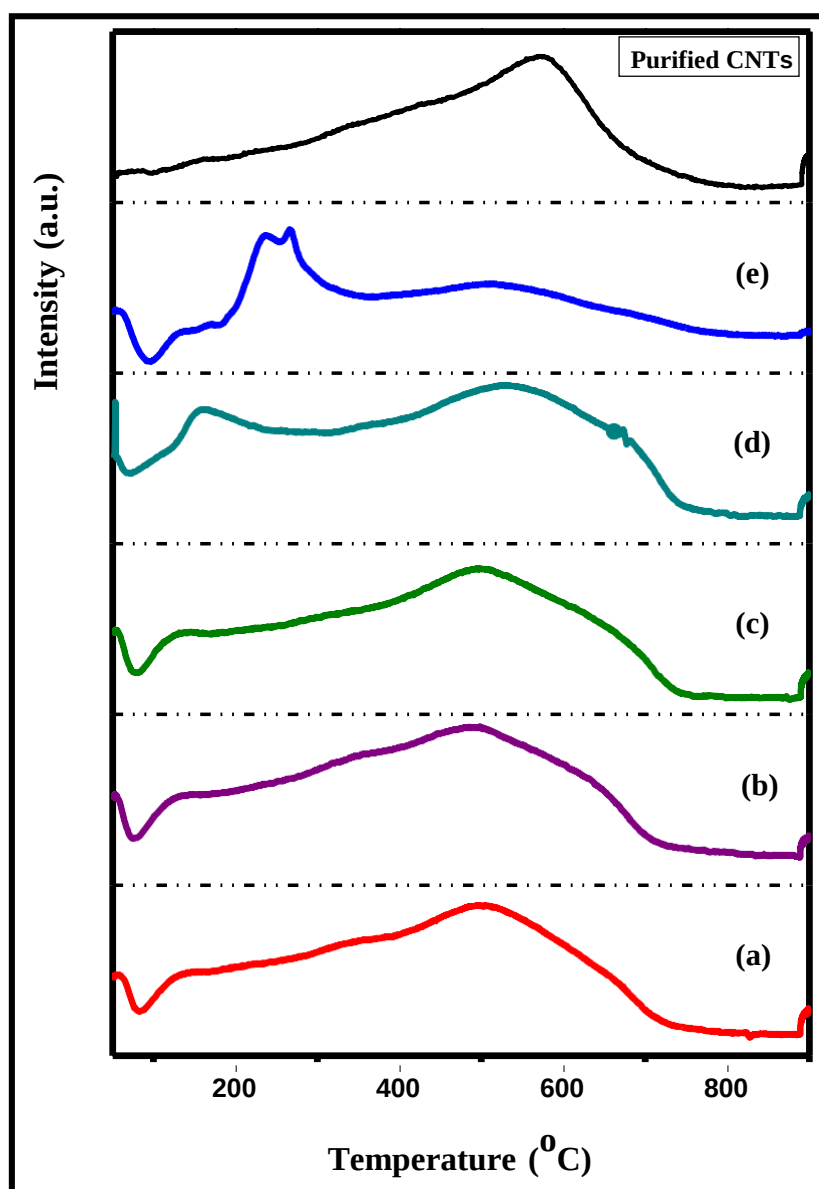


Figure 6.9: TPR profiles of Purified-CNTs and loaded CNTs.

6.5. Discussion

Metals or metal oxides have been successfully encapsulated inside carbon nanotubes using a variety of methods [11,14,17,39]. This encapsulation opportunity was pursued in this study in order to make novel Cu-ZrO₂ catalysts supported in CNTs. Table 6.7 summarizes some of the research on CNT confinement that has been conducted using varying preparation methods. The catalysts developed as a result of these studies were primarily used in catalysis (hydrogenation and Fisher Tropsch reactions). Metals used include Pd [21,40], Pt-Ru [39], Fe [41] and Co [42]. The key components for achieving confinement were stated to be the type of solvent, preparation process, and thermal treatment.

The significance and feasibility of encapsulating both copper and zirconia were investigated in this study. A wet impregnation technique was used to synthesize bimetallic Cu-ZrO₂ catalyst at three loadings while keeping the copper to zirconia mass ratios consistent (35% Cu and 65% Zr). The TEM analysis demonstrated that the MWCNTs were successfully synthesized; however, the CNTs contained some Fe residue embedded in the channels. Furthermore, TEM images revealed that both the copper and zirconia nanoparticles were effectively encapsulated inside the CNTs, with some particles located outside the tubes (15-35%). The data also showed that adding copper and zirconia (13%) to the CNTs increased the surface area of the CNTs, but that increasing the metal loading further caused the surface area to decrease due to the copper content.

According to studies, adding more than 15% copper content to the CNTs support increases the chances of agglomeration by about 90% [22,43]. Our research has shown that when confinement was used approximately 35% (ratio to ZrO₂) of the copper during the synthesis and resulted in uniform dispersion. Because of the catalyst content with respect to that of the CNTs, the 21wt% and 27wt% catalyst exhibited some pore blockage, agglomeration, and less dispersion on the outside. Our findings also confirmed that Cu and ZrO₂ had two distinct nanoparticle shapes and sizes, which PXRD confirmed.

Metals	Metal	Metal	Inner CNTs	Particle	Inner Particle	Outer	Surface	Pore	References			
Confined (wt%)	Loading	Catalyst	Diameter	Size	size trend	particle	area	volume				
	(wt. %)	Used	(nm)	(nm)		Size trend	trend	trend				
~85	13	Cu-ZrO ₂	3 -26	4.0	Particles were smaller and had different shapes.	Less dispersed and overpopulated	Initially increase, but decreased as the metal loading decreased		This work.			
~76	18			4.0								
~72	20			5.3								
~65	21			11.3								
~58	27			11.5								
	9,79(THF) ZrO ₂ ~10,5(EtOH) ~46(EtOH) ~46(THF)		0.92 - 16.98	6.195 5.112 11.101 10.300	Particles were smaller regardless of the solvent used or amount of loading. Ethanol gave smaller particle sizes and THF had better dispersion	Remained the same as the inside. Sintered on the outside	No apparent pattern followed		our work			
~78	~ 3.13	Cu	5.7-24.9	8.01±7.27	Remained near the same -no significant change	Increased with loading.						
~80	~5.03			9.32±3.27								
~90	~6.89			10.2±4.89								
~60	~12.08			16.03±1.98		Shape changed.						

~65	~1.0-2.3 Ru ~2.7-3.2 Co ~1.1-3.2 Pd	5.49	2.21±1.02 3.25±2.72 4.15±1.15	Sizes varied based on the metal used. Pd and Co had bigger particle sizes while Ru had smaller sizes	Co and Ru had a similar trend in particle sizes in/out. Pd had bigger particles with sintering.	Decreased With higher loading [40]
>30	4.4 Pd	50	6 ±4	Size increased based on the support used	No significant difference	Decreased [21] With metal Loading
~75	10 Cu	4-10 20-30	9.7±7.0 19.0±15.1	Size increased with an increase in heating temperature	Bigger particles irrespective of the heat treatment used	Decreased With Metal loading [15]
~80	1.2 Rh-Mn- Li-Fe	4-8	0.9± 10	Size increased with reaction time used	Bigger particles as compared to those confined	N/A [44]
50-80	5 – 23 Pt-Ru	40	22±0.7	No noticeable increase with higher loading	Bigger particles on the outer walls	N/A [11]
~90	1 Ni	20-50	7±3	Size not affected using different solvent	The slight difference	N/A [18]

					with sizes ranging between 4-9nm	
~30	4.9 & 9.0 Cu 5.2 Cu-Zn	6-7	14±11 >100	Size increased with decreased loading. Size increased with the addition of Zn	Bigger particles observed outside	Decreased compared [45] With that of purified CNTs Decreased compared To purified that of CNTs And Cu-CNTs
~50	14.3 - 15.9 Cu	20-30	16.8	N/A	Bigger particles observed compared to that inside	Increased with Loading and heating Time [35] Pore size followed the same pattern with one as an exception
~75	8 Cu	2-5 5-10 20-50	3±1 5±2 10±2	Sizes increased with increased diameter	Bigger particles observed	Decrease with [20] Loading Compared with Purified CNTs

6.6. Conclusion

In conclusion, we exploited encapsulation to illustrate the fabrication physicochemical properties of copper and zirconia. Cu-ZrO₂ was incorporated into CNTs channels with inner diameters of about 26 ± 3 nm using a wetness impregnation technique aided by sonication and a 450°C heat treatment. We were effective in filling both the copper and zirconia within the tubes, according to HRTEM analysis. The particle size distribution showed that the catalyst had a wide variety of particle sizes, ranging from 4 nm to 11.5 nm and that they were uniformly distributed in the channels. Cu nanoparticles were dark black and spherically shaped, while ZrO₂ was a lighter shade and cylindrical, according to HRTEM. Because of the loading, about 15-35% of the particles were detected outside the tubes. The incorporation of Cu and ZrO₂ increased surface area, which is an important factor in our probe reaction (CO₂ hydrogenation). We were able to successfully restrict the growth of Cu-ZrO₂ nanoparticles, increase surface area, and archive highly scattered nanoparticles with less sintering. These altered properties, as well as the interaction between the nanoparticles and the CNT walls, may be a solution for large-scale chemical processing. The materials obtained will be used to convert CO₂ into methanol

6.7. References

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Chapter 7

Effects of catalyst confinement within the CNTs for CO₂ hydrogenation to methanol

7.1. Introduction

The use of fossil fuels has enabled an unprecedented era of affluence and well-being for human society. However, the elevated CO₂ emissions that come with it could have a detrimental impact on global temperatures and ocean acidity. Moreover, fossil fuels are a limited commodity, and their exhaustion would compel the exploration of alternative carbon sources to preserve a sustainable economy. With the decline of non-renewable energy sources, methanol is also an alternative key component for the chemical industry and production of gasoline [1]. Olah's concept of the "methanol economy" predicted that methanol could play an unquestionable role in the foreseeable future, and CO₂ hydrogenation is one of the most promising and regenerative routes of methanol development [2].

CO₂ hydrogenation to hydrocarbons, among the other CO₂ hydrogenation pathways, is a promising way to convert CO₂ into fuels, given the depletion of fossil fuels [2]. Metals, metal oxides, and intermetallic compounds have all made significant advances in the production of catalysts. Furthermore, efforts are being made to define the possible catalyst structure at the nanoscale by using nano-structural materials, which allows for the tuning of catalyst composition and modulation of surface structures, potentially resulting in more promising catalytic performance than bulk materials prepared using conventional methods [1].

Despite these accomplishments, producing durable catalysts with good catalytic efficiency and long-term stability remains a major challenge [3]. Intermetallic compounds are a viable alternative to bimetallic catalysts, particularly in terms of regulating the formation of favorable active sites with a uniform bimetallic ratio and structural stability [4].

This chapter describes the application of Cu-ZrO₂ incorporated within the channels of carbon nanotubes in CO₂ hydrogenation to methanol as a catalyst. Cu-ZrO₂/CNTs have been used as a catalyst for converting CO₂ to methanol with CO and CH₄ as by-products [3,5–9]. Several authors have studied the hydrogenation of CO₂ with the particular emphasis on the use of a Cu-

ZrO₂ based catalyst as a composite with the CNTs as catalyst support [3,5,9,10]. In their work, Sun *et al.* focused on the role of nitrogen species on the nitrogen-doped carbon nanotubes on the dispersion of Cu oxide [11] and their results indicated that the presence of nitrogen increased the Cu nanoparticles dispersion, promoted Cu reduction, decreased the Cu particle size, and enhanced N₂ adsorption capabilities.

Deerattrakul *et al.* [12] investigated the effects of Cu-Zn metal content and reaction temperature towards methanol synthesis using graphene oxide nanosheets as support. It was observed that the supported graphene oxide nano-sheet could enhance the catalytic performance and help with the dispersion of Cu-Zn particles with the best space-time yield of 424 mg_{MeOH}g_{cat}⁻¹h⁻¹.

Dong *et al.* [13] applied a Cu/ZnO/ZrO₂ (6:3:1) catalyst made by a precipitation-reduction method and reduced by different NaBH₄, for CO₂ hydrogenation to methanol and the report stated that methanol and CO were the only carbon-containing products formed under the reaction conditions. The catalyst prepared by the precipitation reduction method had shown an advantage in methanol selectivity over the conventional Cu/ZnO/ZrO₂ catalyst, especially at 230°C. The catalytic activities for conversion for CO₂ increased with an increase in temperature while CH₃OH decreased with increasing temperature of the reaction from 230°C to 270°C. The CH₃OH selectivity was 66.8% over Cu/ZnO/ZrO₂-5 (5 mol ratio NaBH₄/Cu) sample at 230°C which is 12.7% higher than Cu/ZnO/ZrO₂-0 (0 mol ratio NaBH₄/Cu) sample. A maximum STY of CH₃OH of 0.21 gml⁻¹h⁻¹ with CO₂ conversion of 23% and methanol selectivity of 56.8% was obtained over Cu/ZnO/ZrO₂-5 at 270°C. This study demonstrated that an increase in temperature promoted conversion and activation of CO₂, however, the CO production was more prominent than that of CH₃OH because of the endothermic character of the reaction.

Most studies on the use of Cu-ZrO₂ nanoparticles to decorate the surface of carbon nanotubes as a CO₂ hydrogenation catalyst have been centred on this technique. It appears that to date, no study on the use of a Cu-ZrO₂ catalyst confined inside CNT channels has been published. As discussed in previous chapters, this confinement of the catalyst in the CNT channels has the potential to influence the particle size and prevent agglomeration of the catalyst particles through spatial restriction.

7.2 Experimental methods

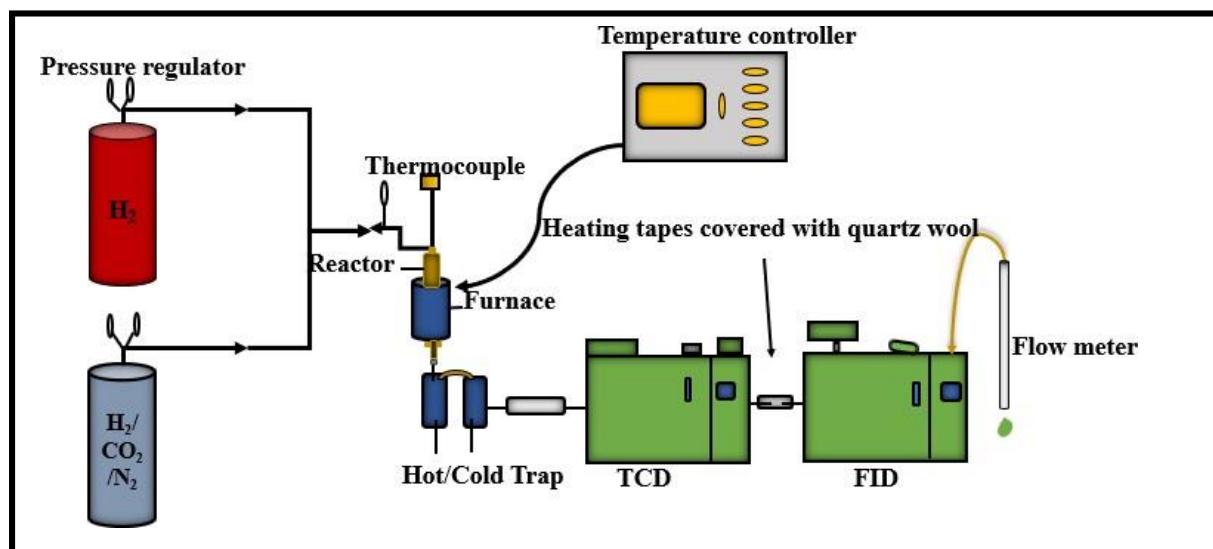
7.2.1. Materials

All the gases used in this study were supplied by AFROX (African Oxygen) Ltd. The gases used for catalyst characterization and catalyst reduction were ultra-high purity grade. The

reaction gas mixture comprised of $\text{H}_2/\text{CO}_2/\text{N}_2$ (65/25.6/9.5 vol%). Argon was used as the carrier gas flow for the thermal conductivity detector (TCD) and air, nitrogen, and hydrogen were used as carrier gases for the flame ionization detector (FID). Nitrogen was used as an internal standard to ensure accurate mass balance.

7.2.4. Hydrogenation reactor setup

The physical setup for the equipment for the hydrogenation synthesis experiment is shown in Figure 7.1. The setup consists of a stainless-steel fixed bed reactor, the reactor temperature and line temperature were controlled by using an electronic temperature controller. All lines after the reaction were kept at 150 °C with the assistance of a thermocouple and a hot trap was placed immediately after the reaction to collect the product. Pressure regulators were used to monitoring the gas pressure out of the reactor. The reactor was connected to two knockout pots i.e., the hot trap and the cold trap. The hot trap was connected at 150 °C and employed as a wax trap, while the cold trap was kept and maintained at room temperature and was used to trap water and high molecular weight hydrocarbons (e.g., methanol). All the flow lines were connected from the knockout pot to the GCs. Wax and liquid hydrocarbons were connected inside the two traps (Figure 7.1) and were analyzed using an offline gas chromatograph equipped with the FID and the TCD.



Scheme 7.1: Schematic diagram of the setup used for the CO_2 hydrogenation reaction.

7.2.1. Activity measurements

The catalyst (0.5 g) was loaded in a fixed bed reactor and a thermocouple was inserted in the

catalyst bed to monitor the temperature. Quartz wool and silica were used to suspend the catalyst bed inside the reactor. Activation of the catalyst was done using hydrogen gas. The catalyst was reduced at 250 °C, with a heating rate of 1 °C/min and a flow rate of 50 ml/min. The catalyst was reduced at a pressure of 0.2 MPa for 4 hours and allowed to cool to ambient temperature. Upon completion, the CO₂/H₂ gas mixture was introduced at a flow rate of 20 ml/min and the reactor pressure was raised to 1.5 MPa. A soap bubble flow meter was used to monitor the gas flowrate (to vent).

7.2.3. Product Analysis

Analysis of the product spectrum was done using two GCs (TCD and FID) as shown in Figure 7.2. The GCs were connected in series online with the gaseous products directed through the GCs for analysis. The characteristics of the detectors used in the GCs are shown in Table 7.1. The signals generated from both the TCD and FID were made readable with the Clarity® software. The TCD was used to analyse H₂, N₂, CO, CO₂, and FID was used to analyse and monitor the hydrocarbons expected. The conversions and selectivity were calculated from the peak areas and products obtained (Figure 7.3 b).



Figure 7.1: Digital images of the FID (left) and TCD (right).

Table 7.1: Specifications of the gas chromatographs employed.

	Online gas chromatograph 1	Online gas chromatograph 2
Detector	Thermal conductivity detector (TCD)	Flame ionization detector (FID)
Column type	Packed, stainless steel, 2m x 2.2mm, O.D = 1/8"	Packed, stainless steel, 1.5 m x 2.2 mm, O.D = 1/8"
Model type	PYE Unicam (Series 204)	Hewlett Packard 5890
Stationary phase	Carboxen-1000, 60-80 mesh	Porapack q, 80/100 mesh

Before the CO₂ hydrogenation was performed, control reactions were carried out. Calibration of the detectors was done using a six-gas mixture consisting of CO₂, CO, Ar, H₂, CH₄, and N₂. This was achieved by allowing the reaction gases to flow through the -reactor without any catalyst using similar conditions. This was done to give H₂, CO₂, and CO signals that were not influenced by the catalyst. The peaks detected were used to calculate the amount of reactant that was fed to the reactor throughout the duration of the reaction. GC traces recorded during calibration and CO₂ hydrogenation are displayed in Figure 7.3. There were no signals on the FID detector during the blank run (absence of the catalyst).

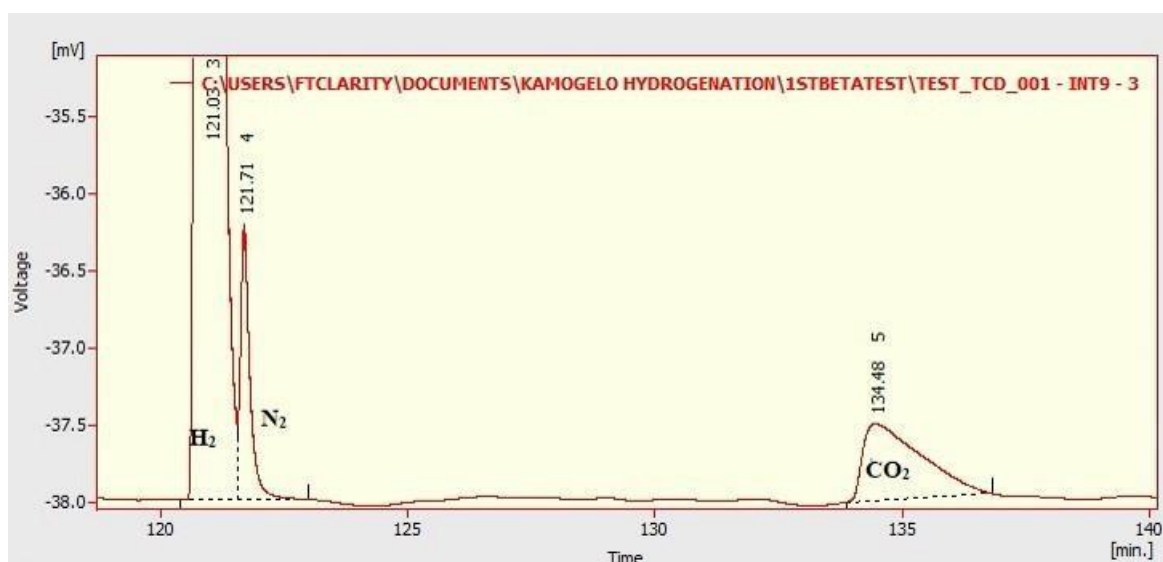


Figure 7.2: a) TCD chromatograph of CO₂ hydrogenation gases (25,6 % CO₂, 9,5% N₂, 64,9% H₂, purity: 99.999%)

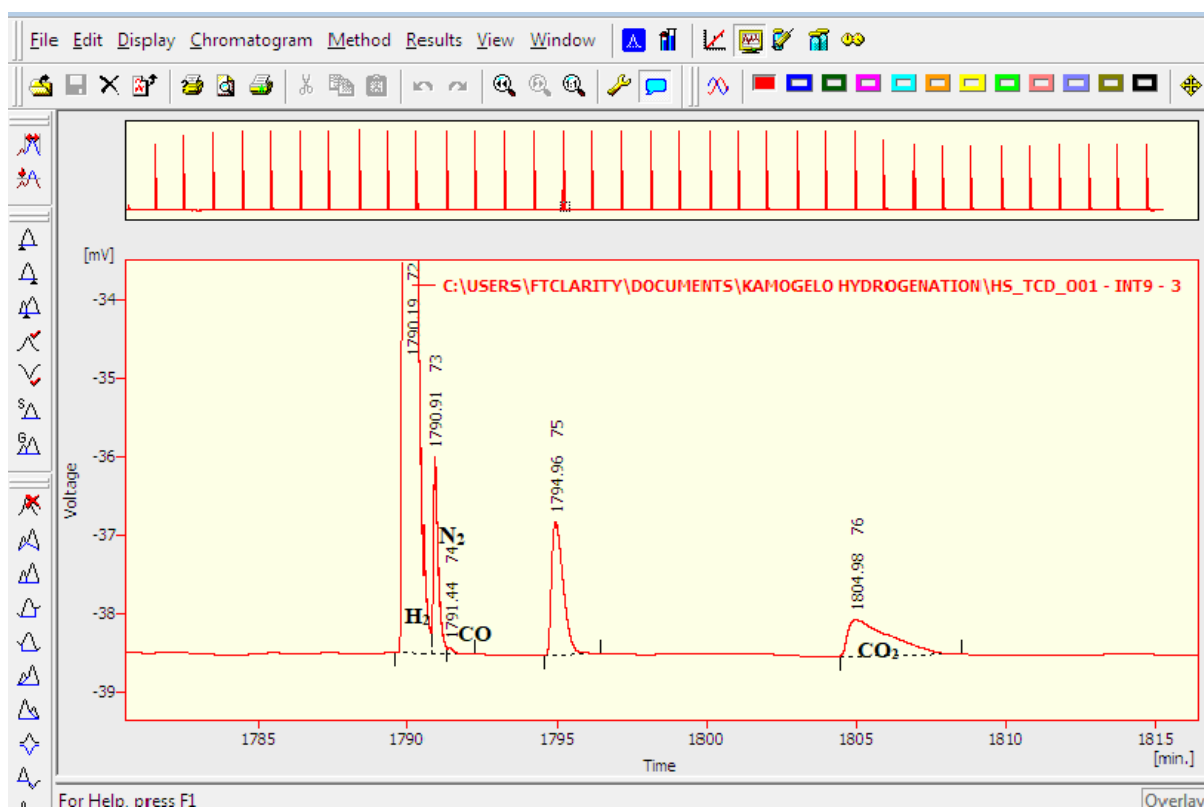


Figure 7.2: b) TCD chromatograph of CO₂ hydrogenation gaseous product mix in the presence of a catalyst.

7.2.5. Data analysis calculations

The data analysis calculations adopted in this study were previously used in studies by Witoon *et al.* [14,15], Gaikwad [16], Guil-López *et al.* [17], and Peng Gao *et al.* [18]. The calculations were performed on the carbon content under steady-state conditions for about 60 hours. The reaction reached steady-state activity after about 20 hours.

CO₂ conversion was calculated on a carbon atom basis according to the following equation:

$$CO_2 \text{ conversion} = \frac{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}}{CO_{2 \text{ outlet}}} \times 100\%$$

where CO₂ inlet and CO₂ outlet represent moles of CO₂ at the inlet and outlet, respectively.

CO was formed by the reverse water gas shift reaction and CO selectivity was calculated according to:

$$CO \text{ selectivity} = \frac{CO_{\text{outlet}}}{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}} \times 100\%$$

where CO₂ outlet denotes moles of CO₂ at the outlet.

The selectivity of individual hydrocarbon product C_nH_m based on CO-free was obtained according to:

$$C_nH_m \text{ selectivity} = \frac{nC_nH_m \text{ outlet}}{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}} - CO_{\text{outlet}}} \times 100\%$$

where C_nH_m outlet represents moles carbon of individual hydrocarbon by-product at the outlet.

7.3. Results and discussion

7.3.1. CO₂ Conversion

The catalysts Cu@CNTs (7 and 12 wt% Cu), ZrO₂@CNTs (10 and 46 wt%ZrO₂ respectively), and Cu-ZrO₂@CNTs were tested for catalytic CO₂ hydrogenation to methanol using H₂/CO₂ (3:1) and the performances of the catalysts with respect to activities, CO₂ conversion, and selectivity to methanol was determined. The catalysts were chosen based on their metal dispersion, metal loading, metal particle sizes, stability, surface area, and amount of metal/metal oxides confined within the tubes, as described in chapters 4, 5, and 6.

The catalytic hydrogenation over promoted catalysts under pressurized conditions (1.5 MPa) produced mainly CH₃OH, CO, and H₂O and a small amount of CH₄. Table 7.2 summarizes the

total average CO₂ conversion of all the catalysts at temperatures between 250 °C and 300 °C. As seen on the table, the Cu@CNT catalysts had the lowest insignificant CO₂ conversions while 10wt% ZrO₂@CNT and 46%wt ZrO₂@CNT had approximately 1.1% and 0.9% conversion, respectively. The 13wt% Cu-ZrO₂@CNTs had the highest CO₂ conversion at 39.8% followed by the 21wt% Cu-ZrO₂@CNT and 20wt% Cu-ZrO₂@CNT at 11% and 5.5% respectively. These results could indicate that the CO₂ conversion is linked to the catalyst's surface area and the effects of confinement. With the exception of the Cu@CNT (7 and 12wt%) catalysts, CO₂ conversion improved as the surface area of the catalyst increased.

Table 7.2: Average CO₂ conversion for all the catalyst

Catalyst	CO ₂ Conversion(%)	Surface area (m ² /g)
12%Cu@CNTs	0.002	164.2
7%Cu@CNTs	0.05	110.98
10%ZrO ₂ @CNTs	1,12	87.3
46%ZrO ₂ @CNTs	0,95	69.1
13%Cu-ZrO ₂ @CNTs	39,76	166.7
20%Cu-ZrO ₂ @CNTs	5,51	86.8
21%Cu-ZrO ₂ @CNTs	10,96	102.4

Figure 7.4a shows the changes in CO₂ conversion as a function of time on stream for the four catalyst systems of Cu@CNTs and ZrO₂@CNTs. The catalyst's stability was evaluated on stream for up to 60 hours, and it exhibited fluctuating activity at various reaction temperatures during the reaction time. The reaction activity of the 12wt% Cu@CNT catalyst initially showed no conversion but the activity steadily increased with a decrease per point temperature over time (Figure 7.4b). The 7wt% Cu@CNTs, on the other hand, had a positive CO₂ conversion at first, but as the temperature increased, the conversion decreased, this decrease could be due to deactivation as a result of particle agglomeration due to the weak interactions between Cu and CNTs. Surprisingly, 10wt% ZrO₂ had the highest overall (single loaded catalyst) average conversion, but it gradually decreased with temperature as shown in Figure 7.4.

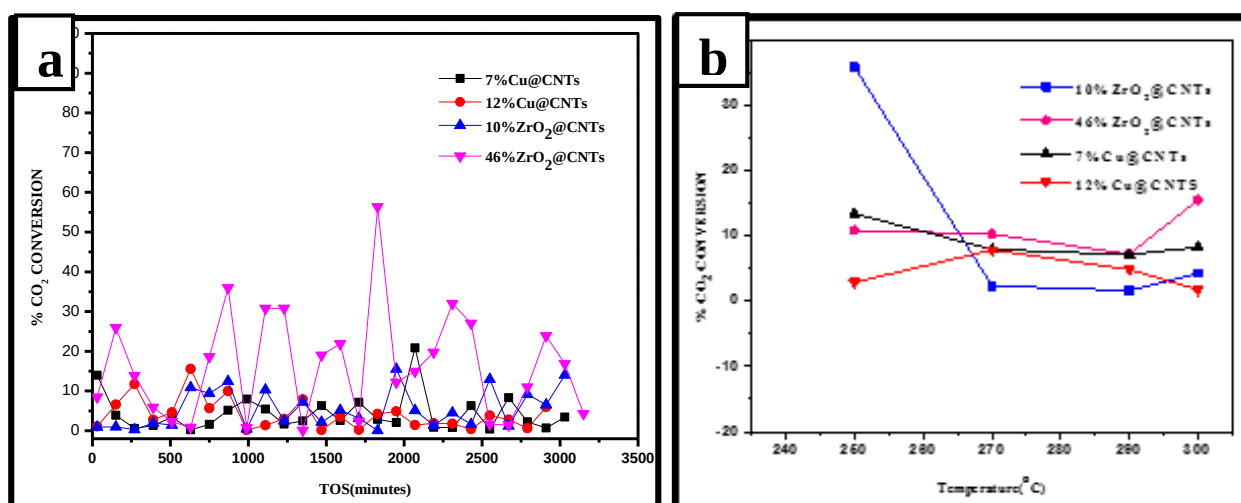


Figure 7.3: CO₂ conversion as a function of (a) time on stream and (b) reaction temperature.

The changes in the CO₂ conversion for xCu-ZrO₂@CNTs are shown in Figure 7.5a) as a function of time on stream and figure 7.5b) as a function of temperature per point (conversions were selected in the same temperature time frame and using the same catalyst). The stabilities and activities were monitored for 60 hours on stream and the catalyst displayed stable activities for the reaction period with fluctuating CO₂ conversions over time. The stability of the catalyst based on the activity (no catalyst deactivation) demonstrated that the catalyst maintained its structural stability throughout the reaction. Notably, the CO₂ conversion activity of the 13wt% Cu-ZrO₂@CNTs was the highest, while the CO₂ conversion of the 21%Cu-ZrO₂@CNT decreased with temperature and time, with some increases at certain temperatures points, and the same pattern was observed for the 20wt%Cu-ZrO₂@CNTs, except the conversion increased with temperature. The CO₂ conversion per point at different temperatures showed an increase for all catalysts with the highest conversion noted at 300 °C.

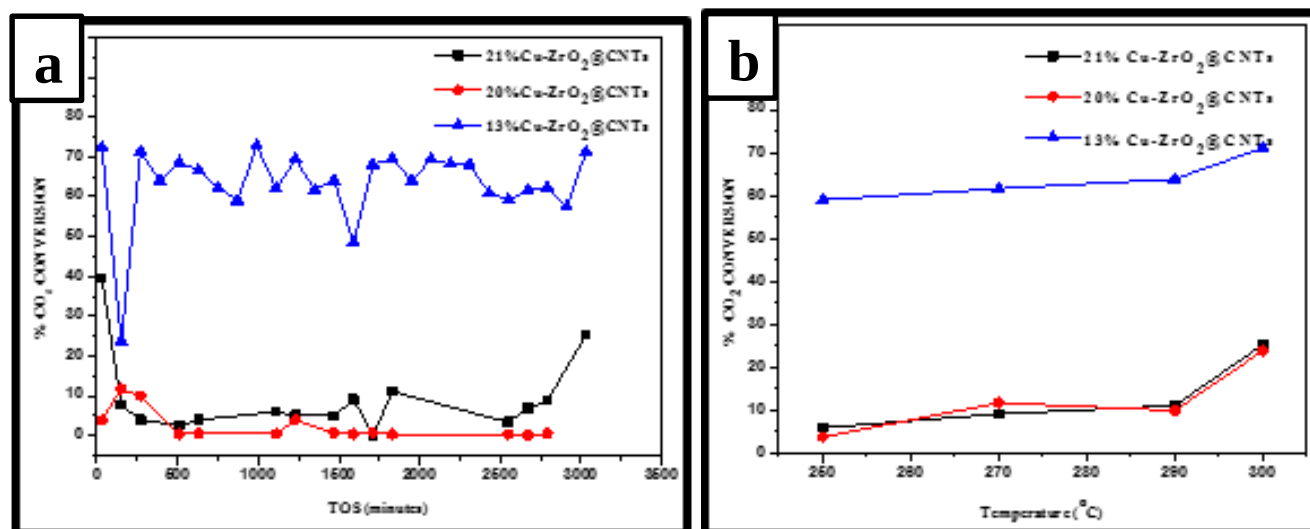


Figure 7.4: CO₂ conversion as a function of (a) time on stream and (b) reaction temperature.

7.2.1. CO₂ selectivity

As observed in Table 7.3, Cu@CNT had no significant CO₂ conversion with all of the conversions mainly accounted for by CH₃OH while 10wt% ZrO₂@CNT and 46wt% ZrO₂@CNT had approximately 1.12% and 0.85% conversion, respectively. The 10wt% ZrO₂@CNT was 100% selective towards CH₃OH while the 46wt% ZrO₂@CNT showed 3.32% selectivity towards CO and 0.85% selectivity towards CH₄ suggesting that it followed the RWGS pathway. The 13wt% Cu-ZrO₂@CNTs had the highest CO₂ conversion at 39.76 followed by the 21%Cu-ZrO₂@CNT and 20%Cu-ZrO₂@CNTs at 7.96% and 4.51 respectively. Notably, 20%Cu-ZrO₂@CNTs had the highest selectivity for the Cu-ZrO₂@CNT catalyst towards CH₃OH at 99.54% and 0.4% traces of CO and 0.06% traces of CH₄, followed by 13%Cu-ZrO₂@CNTs with 95% selectivity towards CH₃OH and 5% towards CO and 21%Cu-ZrO₂@CNTs selectivity 83.11% towards CH₃OH and 14.89% selectivity towards CH₄ and 2.04 towards CO. The difference in selectivity is shown in figure 6 below.

Essential components for successful catalysts preparation for CH₃OH synthesis are both Cu and ZrO₂. It is widely accepted that coordination, chemisorption, and activation of CO₂ occurs on the surface of Cu, hence Cu is reported as the main active component for hydrogenation.

Table 7.3: Average CO₂ conversion and product selectivity for all the catalysts

Catalyst	CO ₂ Conversion(%)	Product selectivity(%)		
		CO	CH ₄	CH ₃ OH
12%Cu@CNTs	0.05	0.7	0	99.3
7%Cu@CNTs	0.75	0.02	0	99.98
10%ZrO ₂ @CNTs	1.12	0	0	100
46%ZrO ₂ @CNTs	0.85	3.32	0.85	95.83
13%Cu-ZrO ₂ @CNTs	39.76	5	0	95
20%Cu-ZrO ₂ @CNTs	5.51	0.4	0,06	99.54
21%Cu-ZrO ₂ @CNTs	10.96	2.04	14.89	83.11

Pan *et al.* [19] found that the activity of the catalyst is directly proportional to the surface of Cu. However, Cu cannot be used as the sole catalyst. ZrO₂ acts as a promoter or support due to its oxygen vacancies which also serve as an active component and assist in hydrogen spillover. The observed increase in CO₂ conversion in the Cu-ZrO₂@CNTs catalyst is due to the synergic interaction which exists between Cu and ZrO₂ resulting in a geometric effect.

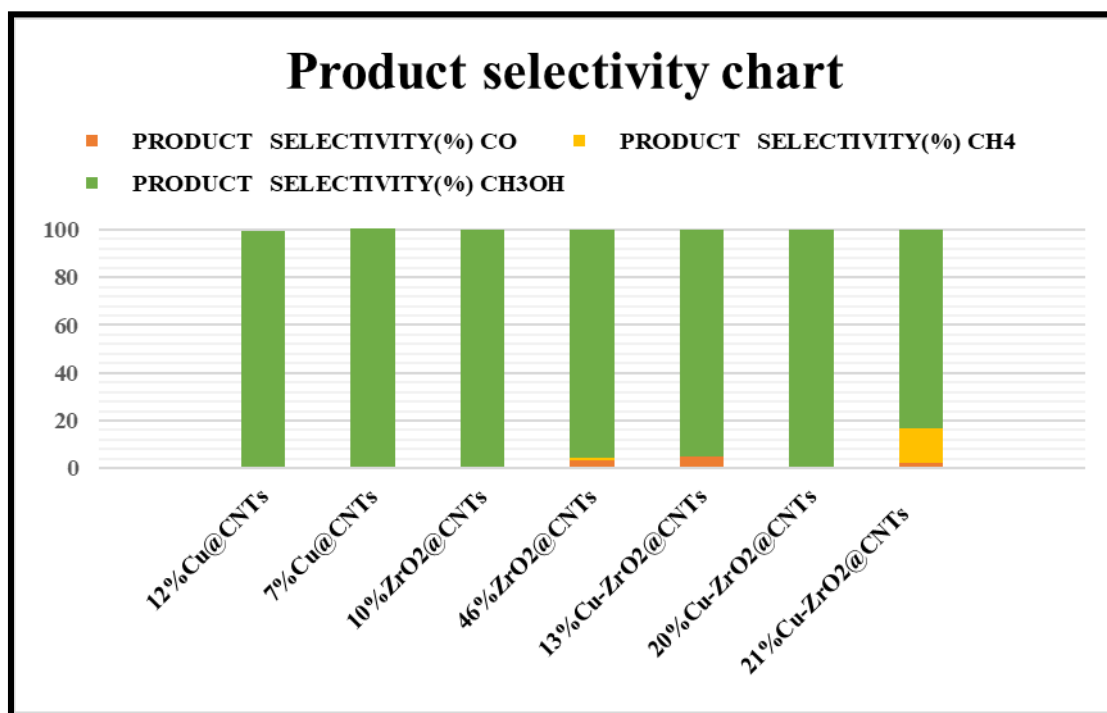


Figure 7.5: Chart showing the methanol selectivities for the various catalysts studied.

7.3. Discussion

To verify the catalytic performance of the catalyst synthesized in relation to the chemical composition, oxide structure, and confinement effect, CO₂ hydrogenation to methanol was used as the test reaction. The reaction was carried out at atmospheric pressure by feeding the tubular reactor with H₂/CO₂ = 3/1 mixture. Methanol and carbon monoxide were the main carbon-containing products, whereas traces of methane were also detected.

The stability of the catalysts was tested at 250°C to 300°C for 60 h. The deactivation was noted for the Cu@CNTs and ZrO₂@CNTs (as seen with the decrease in conversion with temperature and low CO₂ conversion). The obtained results for Cu@CNTs, ZrO₂@CNTs, and Cu-ZrO₂@CNTs demonstrated that the changes in morphology (through encapsulation) played an important role in CO₂ hydrogenation. The results indicated that Cu or ZrO₂ as the sole catalysts even with the influence of confinement resulted in much lower CO₂ conversions and weaker activity. On the other hand, Cu-ZrO₂@CNT showed an increase in CO₂ conversion and had better activities, this increase might be due to the synergy effect that exists between Cu and ZrO₂. Surprisingly, all the catalysts subsequently showed higher than expected selectivities towards methanol. This behavior can be accounted for by the high dispersity of the

nanoparticles within the channels, the particle sizes obtained, and the introduction of encapsulation through spatial restriction on the reaction [20].

Table 7.3 compares CO₂ conversion and product selectivity. Cu-ZrO₂@CNTs catalysts exhibited higher CO₂ conversion probably because of the stronger Cu-ZrO₂ support and more concentration of oxygen vacancies. These results strongly revealed that the interface between the active Cu and ZrO₂ support was essential in methanol formation. Stronger metal-support interaction in the Cu-ZrO₂@CNT catalyst guaranteed the efficient activation of CO₂ over the catalyst surface and accelerated the hydrogen spillover through ZrO₂ thereby enhancing the hydrogenation rate of the intermediates to form methanol. This result was in agreement with the previous literature about CO₂ hydrogenation [21].

In summary, this study depicted the remarkable effect of ZrO₂ morphology assisted by confinement on CO₂ hydrogenation on the Cu-based catalyst. The characterization results revealed that the physicochemical features of the prepared catalyst were markedly affected by the catalyst encapsulation. Tsang *et al.* [22] reported that 002 facets with more polarity could accelerate the excitation of thermal electrons from the O vacancies of the support to the Cu surface. This was in agreement with our results such that the generated defects assisted with the activation and conversion of CO₂, and the active Cu sites favored the rearrangement and hydrogenation of intermediates to achieve methanol.

7.4. Conclusion

In summary, the catalysts were first activated using hydrogen and were tested for activity and selectivity towards methanol in the hydrogenation of CO₂. It was observed that the surface area of the catalysts played an important role in the CO₂ conversion obtained. The degree of confinement of the active catalyst species in the channels of the CNTs had an effect on the selectivities and reaction path followed. Furthermore, it appears that all the catalysts had better stability with no indication of catalyst deactivation throughout the reaction period. This could indicate that there was a negligible amount of water produced. This work demonstrated that Cu-ZrO₂ and ZrO₂@CNTs confined within the CNTs could successfully convert CO₂ to methanol, with the highest selectivity to methanol. It was also observed that amount of conversion was mainly high at lower temperatures (below 250 °C). Moreover, to obtain better conversion rates, we suggest evaluating the activity of the catalyst we synthesized at pressures greater than 50 bars and temperatures lower than 250 °C.

7.5. References

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Chapter 8

General conclusions and recommendations

8.1. Introduction

This last chapter of the dissertation contains some concluding general remarks about the study coupled with recommendations for future studies.

8.2. Conclusions

The aim of the study was to synthesize and characterize Cu, ZrO₂, and Cu-ZrO₂ placed inside multi-walled carbon nanotubes and use the metal/metal oxide confined carbon nanotubes as catalysts for the hydrogenation of CO₂ to methanol. The multi-walled carbon nanotubes were successfully synthesized using the CCVD method and the metals were successfully loaded using the impregnation method through the assistance of a sonication technique. These catalysts were characterized using BET, TEM, PXRD, TPR, and TGA. This study successfully produced the required materials with different structural morphologies and the following conclusions were drawn from results obtained in this research project.

8.2.1. Synthesis of CNTs using CCVD and their characteristics.

Multi-walled carbon nanotubes were successfully synthesized by passing the acetylene gas over a Fe-Co/CaCO₃ catalyst using the CCVD technique. The obtained CNTs were then purified using acid treatment to remove the Fe-Co/CaCO₃ residues and to yield CNTs with open-cut tips. TEM micrographs revealed that open-cut tips on the CNTs were produced with 99% purity, with the purity confirmed through TGA and XRD data. The CNTs internal diameter measured were recorded to be about 26 ± 3 nm. However, when randomly scanning across the samples, we observed some smaller tubes. The CNTs were made in high yields of 200% to 300% from the original weight and the open-cut tips were essential in allowing for encapsulation of metals and metal oxide particles.

8.2.2. Synthesis of Cu@CNTs and their properties.

Cu@CNTs were prepared using the simple convenient wetness impregnation technique with the assistance of sonication. The Cu@CNTs catalyst was successfully synthesized using tetrahydrofuran as a solvent at four different loadings (i.e. 3, 5, 7 and 12%). TEM images

revealed that the Cu nanoparticles were confined within the channels of the CNTs and the particle sizes obtained were less than 30 nm (i.e. $\sim 25.2 \pm 1.3$ nm) for those confined inside and $\sim 68.4 \pm 3.9$ for those found outside the tubes. The TEM results also indicated that approximately 60-90 % of the particles were encapsulated within the channels and that there were differences in particle shape between those found inside and outside the CNTs. The catalyst obtained had a higher surface area and pore volume as compared with the purified CNTs. TGA data revealed that the presence of Cu had good dispersion and displayed less agglomeration but decreased the material's oxidative stability as loading increased.

8.2.3. Synthesis of ZrO₂@CNTs and their properties.

ZrO₂@CNTs were successfully prepared using a simple wetness impregnation method with two different solvents, ethanol and tetrahydrofuran, and at two different loadings per solvent. The particles confined within the channels had average particle sizes (11.1 ± 5.1) for all the prepared catalysts. TEM revealed that the ethanol-prepared samples had small particle sizes but were overpopulated, whereas the THF-prepared samples had larger particles but with a better dispersion. THF proved to be the best solvent for the preparation, with little agglomeration visible at lower loadings. The catalysts had a larger surface area and an apparent reduction ability.

8.2.4. Synthesis of Cu-ZrO₂@CNTs and their properties.

Cu-ZrO₂ with five different loadings was incorporated within the channels of the CNTs with inner diameters of about 26 ± 3 nm using a modified wetness impregnation technique assisted by sonication. TEM data revealed that the CNTs were successfully filled with bimetallic Cu-ZrO₂ inside the tubes with varying particle sizes inside and showed that Cu and ZrO₂ had distinguishable particle shapes. The encapsulation led to an increase in surface area and pore volume and a mesoporous pore structure. The Cu-ZrO₂ had smaller particle sizes, better dispersion, and stability as opposed to the Cu@CNTs and ZrO₂@CNTs particles as determined by comparative TEM and TGA studies. The particle sizes were much smaller than the inner diameter of the CNTs, which allowed sufficient space for transport of reactants and products in catalytic reactions using the metals.

8.2.5. Application of the catalysts in CO₂ hydrogenation.

In this study, the main objective was to place Cu, ZrO₂ and Cu-ZrO₂ nanoparticles within the CNTs channel and to test these as catalytic materials for converting CO₂ to methanol. To our knowledge, the use of Cu, ZrO₂, and Cu-ZrO₂ confined within CNTs was reported for the first time. The results showed that all of the catalysts tested were able to convert CO₂ to methanol.

The Cu@CNTs and ZrO₂@CNTs catalyst gave much lower conversions than the Cu-ZrO₂@CNTs catalyst.

8.3. Recommendations

The synthesis results from the catalysts obtained all showed a similar trend in terms of agglomeration at higher loadings, implying that lower metal loadings of copper (< 10%) and Cu-ZrO₂ (< 20%) are preferred. A strategy to assist the dispersion would be to introduce nitrogen doping to the CNTs. Sun *et al.* [1] found that the presence of nitrogen species, primarily pyridine N, enhanced Cu dispersion on carbon, promoted nanoparticle reduction, and resulted in smaller Cu crystalline sizes with high H₂ dissociation and adsorption capabilities.

To better understand the effect of loading and solvent choice on ZrO₂ confinement, more ZrO₂@CNTs catalysts could be made using varying loadings, calcining temperatures, and solvents and this could open up new possibilities for industrial applications, particularly in semiconductors, fuel cells, and ceramics.

The Cu-ZrO₂@CNTs that have been synthesized and applied in the CO₂ hydrogenation requires a better understanding of the conditions and pre-treatment processes needed in making the catalyst. In the above study it was noted that lower temperatures resulted in better conversions, so it is recommended that the synthesized catalyst be used at higher pressures and temperatures below 250°C.

8.4. Reference

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