Study of Iron Dispersion on Carbon Nanofiber via Deposition Precipitation Method

by

Muhammad Zaid Bin Salman

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak, Malaysia

CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. Suriati Sufian)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD ZAID BIN SALMAN

ABSTRACT

This research work reports the discoveries of the iron dispersion on carbon nanofiber via deposition precipitation method. The aim of this research is to study the iron dispersion pattern and particle size distribution on CNF supported iron catalyst. The goal is achieved by functionalizing carbon nanofiber as a catalyst support and impregnating iron precursor on the fiber through deposition precipitation technique.

In this project, CNF supported iron catalysts have been prepared using iron nitrate, $Fe(NO_3)_3$ as a precursor by homogeneous deposition precipitation (HDP) method with the presence of urea as the precipitating agent. The amount of iron loading was varied from 10, 20 to 30wt% and the catalysts were prepared for 6, 8 to 10 hours. The CNF powder has been undergone surface oxidation treatment using 1M nitric acid (HNO_3) as the oxidizing agent. Characterization of the pre-treated CNF support was performed by Point Zero Charge (PZC) analysis. Meanwhile, the CNF supported iron catalyst was characterized by transmission electron microscope (TEM) and field emission scanning electron microscope (FESEM) for studying the surface morphology as well as determining the iron particle distribution and size. Thermogravimetric analysis (TGA) was used to determine the thermal properties of the CNF supported iron catalyst. The HDP method turned out to be suitable for the preparation of small uniform iron particles on CNF with high thermostability although the method was produced low yield of iron loading.

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First and foremost, the author shall express an infinite gratitude to Allah the Almighty for bestowing physical and mental strength in conducting this project until it is well finished.

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ABBREVIATIONS & NOMENCLATURES

CNF Carbon Nanofiber

CNT Carbon Nanotube

HDP Homogeneous Deposition Precipitation

PZC Point Zero Charge

TEM Transmission Electron Microscope

FESEM Field Emission Scanning Electron Microscope

EDX Energy Dispersive X-ray

XRD X-ray Diffraction

TGA Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 Project Background

The consumption of raw material and production of unwanted product can be reduced by pertaining a better supported metal catalyst to be used in chemical, as well as in energy industries. In order to improve quality of catalyst that is indicated by its activity, selectivity and stability; it is necessary to control over its preparation.[4] In catalyst preparation, there are two stages involve which primarily starts from providing metal salt component onto support and proceed with conversion of the supported metal to metal oxide.[5] The first stage is known as dispersion and it can be done by impregnation, adsorption from solution, co-precipitation or deposition precipitation technique. The second stage is known as calcination or reduction; where the supported catalyst is thermally treated in an inert or active atmosphere that content of either oxygen or hydrogen only.

In recent years, carbon based nanostructured material has been discovered to be one of the potential catalyst support materials. The carbon nanomaterials such as carbon nanotubes and carbon nanofiber give an opportunity of pertaining a better supported catalyst. It has been 10 years since the first application of carbon nanofiber as catalyst support by Rodriguez and co-workers which employing of active phase (Fe or FeCu) via incipient wetness method onto surface of carbon nanofiber; followed by calcination and reduction.[5] Carbon nanofiber or simply CNF outperforms the other carbon material due to its better control of surface properties, chemical inertness, has high accessibility, thermally stable, better mechanical strength and tunable bulk density.[6]

1.2 Problem Statement

Poor selectivity and yield in any catalytic reaction is a common setback in any heterogeneous system due to inactivity of catalyst in which the activity is often expressed by the number of active sites. Besides, the common problem, it is also negatively influenced by mass transfer limitation in stagnant liquid in the catalyst support pores. In order to minimize the impact, the activity of catalyst must be improved. This can be attained by having catalyst that is active enough and has significant number of active site. In order to have a high number of active site, catalyst support must comprise large specific surface area. Meanwhile, by maximizing porosity and decreasing tortuosity of the catalyst support, the restrain in mass transfer can be reduced.[7] Despite of employing conventional catalyst support, carbon nanofiber is highly potential to be a novel catalyst support due to good combination of structure identity which is extremely open morphology, having intense pore volume and large surface area.

1.3 Objective and Job Scope

1. To synthesize CNF as catalyst support
    - Scope: Rendering iron precursor on CNF through deposition precipitation technique
2. To study the iron particle dispersion and size on CNF surface
    - Scope: Characterization through analytical equipment such as FESEM

CHAPTER 2

LITERATURE REVIEW

2.1 Catalyst and Catalysis

2.1.1 Concept and History of Catalyst

In chemistry point of view, catalyst is a substance that speeds up the rate of reaction without undergoing a permanent chemical change. Catalyst increases reaction rate by providing an alternative route involving a different transition state and lower activation energy.[8] Historically, the term “catalysis” is derived from Greek words; *kata-*, “down,” and *lyein*, “loosen”. The term was first uttered in 1835 by Jöns Jacob Berzelius, a Swedish chemist to associate a group of observations made by other chemists in the late 18th and early 19th centuries. Amongst of the observations are the improved starch to sugar conversion by acids, observed by Gottlieb Sigismund Constantin Kirchhoff; Sir Humphry Davy’s observations that the speeding up combustion of various gases by platinum; the discovery of the stability of hydrogen peroxide in acid solution but its decomposition in the presence of alkali and such metals as manganese, silver, platinum, and gold; and the observation that the conversion of alcohol to acetic acid with the presence platinum. Those substances that promote the reaction is called catalyst.[9]

2.1.2 Catalyst and Activation Energy

To increase the rate of a reaction it is needed to increase the number of successful collisions. One possible way of doing this is to provide an alternative way for the reaction to happen which has a lower activation energy. Adding a catalyst has exactly this effect on activation energy. A catalyst provides an alternative route for the reaction as shown in the diagram below.

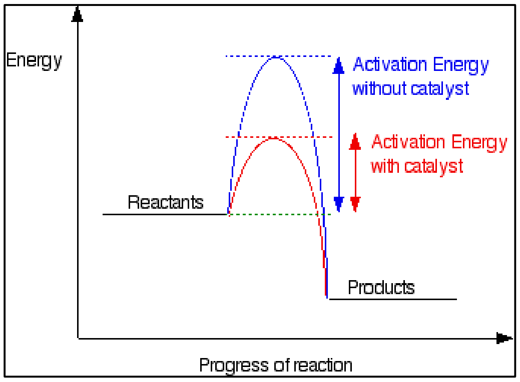


Figure 1 Activation energy pattern of a reaction [1]

There is a common phrase regarding activation energy which is; "A catalyst provides an alternative route for the reaction with a lower activation energy." Accurately, it does not "lower" the activation energy of the reaction. There is an understated difference between the two statements that is easily illustrated with a simple analogy. Suppose that there is a mountain between two valleys so that the only way for people to get from one valley to the other is over the mountain. Only the most active people will manage to get from one valley to the other. Now, suppose a tunnel is cut through the mountain and many people will now manage to get from one valley to the other by this easier route. It can be said that the tunnel route has lower activation energy than going over the mountain. However, it does not mean that the mountain is lowered. The tunnel instead, has provided an alternative route but has not lowered the original one. The original mountain is still there, and some people will still choose to climb it. [10]

In living things, enzyme is an example of catalyst which responsible for many biochemical reactions such as breaking down of lactose in milk by lactase. The term catalysis or catalytic action denotes the reaction between reactant and catalyst; subsequently forming an intermediate that is readily to react with each other or with another reactant, to form the desired product. In addition, catalyst can be classified into homogeneous and heterogeneous catalysts. The presence of homogeneous catalyst in such a way that it itself has same phase with the system while heterogeneous catalyst has different phase from the system e.g. solid iron catalyst used in ammonia synthesis where the reactant in gas phase.[11]

2.1.3 Common Catalyst in Industrial Processes

Table 1 Catalyst in industrial processes [12]

Process	Catalyst
Ammonia synthesis	Iron
Sulfuric acid manufacture	Nitrogen(II) oxide, platinum
Cracking of petroleum	Zeolites
Hydrogenation of unsaturated hydrocarbons	Nickel, platinum, or palladium
Oxidation of hydrocarbons in automobile exhausts	Copper(II) oxide, vanadium(V) oxide, platinum, palladium
Isomerization of ***n***-butane to isobutane	Aluminum chloride, hydrogen chloride

Table 1 shows the wide range of reaction with specific catalyst that is commonly used.[12] In chemical process, most of catalyst in solid are metals or the oxides, sulfides, and halides of metallic elements and of the semi-metallic elements boron, aluminum, and silicon. Gaseous and liquid catalysts are commonly used in their pure form or in combination with suitable carriers or solvents; solid catalysts are commonly dispersed in other substances known as catalyst supports. In chemical industry, employment of catalyst is a necessary in order to yield desired product faster.

2.2 Catalyst Support

2.2.1 Concept of Supported Catalyst

The term support in catalysis denotes the material which catalyst particle is affixed on. The primary purpose of introducing active phase on a support is to increase the dispersion thus increase the activity of the catalyst itself indicated by the number of active phase. This feature of supported catalysts is important; especially with regard to precious-metal catalysts, because it allows more effective utilization of the metal than can be achieved in bulk-metal systems. However, in the case of base-metal catalysts the use of the support is often primarily aimed at improving the catalyst stability. This can be achieved by suitable interaction between the active material and the support. For example: unsupported copper oxide is a very active oxidation catalyst but suffers from thermal instability at high temperatures. However, when copper oxide is supported on a high-surface-area alumina, its thermal stability is improved. A wide range of techniques has been employed for the incorporation of a catalytically active species onto a support material in order to increase dispersion of active phase, have a better control of porous structure, improve mechanical strength and avoid sintering.[4]

2.2.2 Significance of Catalyst Support

The roles of the support may include; increase the effective surface area and provide suitable pore structure to improve reactivity and selectivity. Besides, it increases the mechanical strength to withstand stresses caused by pressure, temperature, phase transformation, etc. Having catalyst support will increase the thermal stability to prevent aggregation and sintering so that the active components will stay dispersed. Furthermore, catalyst support provides acidic or basic sites needed for catalytic reactions and it will form new compound with active component (such as solid solution) and change the activity of the catalyst. Moreover, it enhances the ability to withstand poisoning by either decomposing or adsorbing poisoning species. Reduce the amount of active component and lower the cost.[13]

2.2.3 Carbon Nanofiber as Catalyst Support

There are myriad materials conventionally employed as catalyst that includes silica, alumina, zeolite, magnesia and carbon. Conventionally, there are classification of carbon as support that are commonly used such as activated charcoals, chemically activated charcoals, carbon blacks and graphite, not to mention the recently founded carbon based nanomaterials i.e. carbon nanotubes and nanofiber [14]. It is proposed that carbon nanofiber can be employed as a catalyst support in three ways; (I) Using small aggregates of entangle CNF loaded with the catalyst active phase, (II) Application of larger aggregates of entangle bodies to form a fixed bed and (III) CNF forms a layer structured materials such as foam, monoliths or felt to keep diffusion distance short.[7] It has been 10 years since the first application of carbon nanofiber as catalyst support by Rodriguez and co-worker by introducing active phase iron and copper metal precursor (Fe or FeCu) onto CNF via incipient wetness technique.[15] Despite of testing with γ-alumina and activated carbon, Rodriguez found that FeCu/CNF promotes higher activity in hydrogenation of ethene due to distinctive metal-support contact between iron-copper particle with the basal-plane of CNF. Moreover, in more extensive research of CNF as catalyst support had been done by Hoogenraad and co-worker. They were inspired by the difficulty of using activated carbon as support for liquid phase catalysis.[15] Activated carbon (AC) is difficult to control and mechanically frail; leads to filtration problem in slurry-based processes. For instance, the result for attrition resistance by ultrasonic treatment in ethanol; comparing CNF and AC shows that no shifting of particle size distribution (PSD) while severe attrition appears in AC.[15] Furthermore, Ingvar and co-workers had synthesized platinum-CNF supported catalyst via several method which are ion exchange, homogeneous deposition precipitation, impregnation, colloidal and modified polyol method. They found that, by polyol method, it yield highest platinum loading on carbon nanofiber.[16] **Table 2** summarizes the academia papers which discuss on synthesizing carbon nanofiber as catalyst support.

Table 2 Summary on past researches

Author	Year	Metal Precursor	Manipulated Variable	Chemicals	Technique	Conclusion
F.F. Prinsloo, D. Hauman, R. Slabbert	2011	Iron	NAV	Diluted urea	Homogeneous Precipitation	* Getting a narrow crystallite distribution (uniform) * Percentage metal dispersion is low * Carbon partly gasifies when calcine at high temperature (1053K)
Kvande, I., et al.,	2007	Platinum	NAV	Nitric acid, Sulfuric acid,	Iron Exchange, Deposition Precipitation, Impregnation, Colloidal & Modified Polyol	* DP method is on the 4th place in terms of Pt loading, but particle size is among the smallest (1-2nm) * Modified Polyol yield most of Pt but gives largest particle size (4-5nm)
Toebes, M.L., et al.,	2004	Platinum & Ruthenium	pH solution	Potassium Hydroxide, Nitric Acid, Urea	Deposition Precipitation (DP) & Ion Adsorption (IA)	* Metal precursors are homogeneously distributed, highly dispersed, uniform particle size (1-2nm) and thermally stable * Loading of platinum is higher via DP instead of IA * Found a linear relationship between number of acidic oxygen containing group with metal loading
van der Lee, M.K., et al	2005	Nickel	pH of solution	Nitric Acid Urea	Deposition Precipitation	* Test with different functionalized CNF; CNF-oxidized, CNF-partial reduced and CNF-thermally treated. Found that particle attachment only at oxidized CNF due to presence of carboxylic acid group. * pH 3.5 nucleation starts to occur on CNF * Metal particle size, 5nm

2.3 Carbon Nanofiber

2.3.1 Concept of Carbon Nanofiber

CNF is a newly found fibrous carbon material which is more versatile and has better properties than carbon nanotube. Its outstanding mechanical, electrical and structural properties make it usable in myriad applications. Carbon nanofiber or simply CNF is a building of layers of graphene which are well arranged at an angle of fiber axis. What is graphene? It is a novel two-dimensional material which can be seen as a monolayer of carbon atoms arranged in a hexagonal lattice and also referred as monolayer graphite.[17] Such axis can be described as herringbone, cup-stacked or stacked.[18] In actual, these axis forms accordingly to the form of catalyst particle.

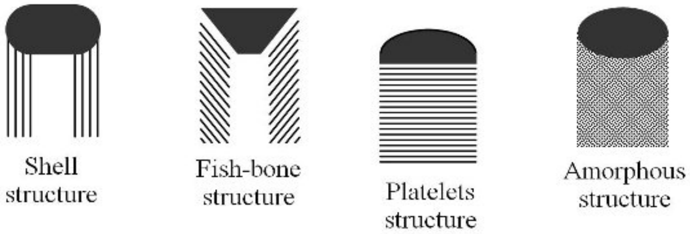


Figure 2 Schematic cross sectional illustration of CNF[2]

Production of carbon nanofiber may varies in terms of carbon source and method of synthesis. The most widely method is by carbon vapor deposition (CVD) of carbon or simply called ‘cracking’ at a very high temperature with the presence of catalyst. The diagram below shows the steps of CNF’s development which I s an endothermic reaction. The reaction needs for very high temperature in order to break the covalent bond of carbon and hydrogen. Lower ratio of carbon-hydrogen, tend to yield higher yield while reactions occurs to lower energy.

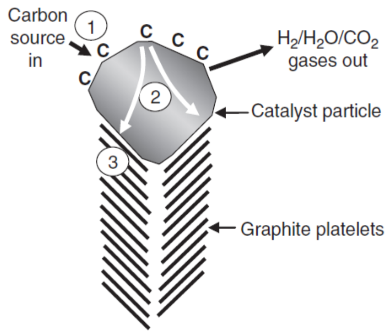


Figure 3 Growth process of CNF[3]

The first stage, is the decomposition of carbon source gas on the surface of metallic catalyst. Next, the carbon species undergoes dissolution and dispersion into nanoparticles to form metal-carbon solid state. Lastly, carbon grows continuously until it become supersaturated that lead to various configurations of carbon nanofiber.[3]

2.3.2 Properties of Carbon Nanofiber as a Catalyst Support

Amongst the prominent properties that are considered in designing catalyst are the activity, selectivity, regeneration ability and stability. The stability of catalyst is much influenced by the support that it affixed to. By having catalyst support, it promotes better properties such as mechanical strength, dispersion, stability in catalysis and selectivity of catalyst. In choosing the right catalyst support, it should pose a good interaction with metal precursor like in this case, carbon nanofiber indeed has good metal-support interaction due to exposed surface of the carbon nanofiber mainly consists of prismatic planes with high surface reactivity.[19] Besides, CNF has large specific surface area; ranging from 100-200 m^2/g that is able to host vast number of metal precursor and offers a better contact with reactant-support. The surface of CNF houses an intense pore volume ranging from 0.5-2 cm^3/g. However, it does not have so called “ink bottled” pores on surface which lessen the diffusion phenomena. Thus, it reduces mass transfer limitation of reactant to reach metal precursor in reaction.[20]

It is frequently mentioned in many academic papers that the main attribute makes CNF has good potential as a catalyst support is due to its inertness and stability from corrosive attack in acidic and basic media. Besides, it is resistant towards most organic solvent due to its hydrophobic behaviour and poor wettability. Due to these circumstances, it is a requisite for as produced CNF to undergo surface oxidation by pre-treatment with oxidizing agent such as nitric acid before it can be emplaced with active phase. By curing, it promotes the formation of polar-oxygen containing surface group which helps in introducing catalyst via wet chemical routes. Moreover, CNF can withstand against sintering at high temperature reaction especially in gas reaction. In addition, it is undisputable that due to high entanglement CNF layers, it results in better mechanical strength which is main criteria to apply as catalyst support, not to mention that it has bulk crushing strength of 1Mpa which is good for fixed bed reactor operation. On top of that, CNF possess better thermal as well as electrical conductivity. [14]

2.4 Concept of Deposition Precipitation Method

Deposition precipitation technique can be considered mainstream in industry. The process involves of precipitating metal precursor from homogenous solution of metal compound on supporting material.

1. Formation of insoluble metal precursor
2. Removal metal from its solution
3. Formation of metal crystal on the surface of support.

The common difficulty implementing this method is to allow a slow precipitation to occur into the pores of support; thus yields a well distribution of metal particle onto the support after its nucleation or growth. Nevertheless, a rapid nucleation of metal particle in the solution bulk should be avoided so that it will not agglomerate or forming a cluster of crystallite; thus the metal will only adsorbed on the surface instead of affix into the pores of support. In order to retrieve best result, it is necessary to have a slow mixing of an alkali solution so that local concentration will not rise. In an experiment, urea is found to be the best base to be added up at room temperature.[21] Urea will work when mixture temperature is risen up to 90°C; where it will slowly hydrolyze and generate ammonium hydroxide which mix homogeneously through the solution. The pH of the solution remains practically constant as the rate of precipitation is higher than that of hydrolysis. Best results in terms of homogeneous distribution are also obtained when an interaction between the support and the active precursor takes place: for instance the formation of Cu or Fe hydrosilicate, instead of hydroxides, has been pointed out on the surface of silica.

CHAPTER 3

METHODOLOGY

3.1 Research and Project Activities

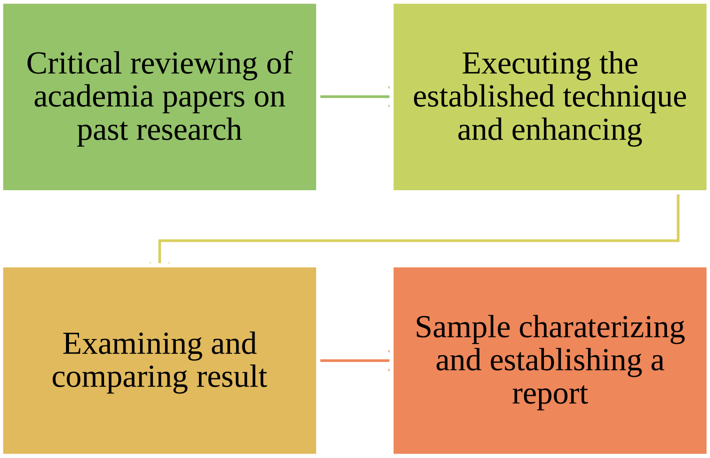


Figure 4 Research methodology

The project activities in this research are mainly experimental work. After a thorough review of past research papers is done, experimental work will be conducted to investigate the effect of the understudy variables on the result obtained. The research is primarily conducted by studying past research papers which report on the same techniques being used to synthesize supported catalyst via specifies method as stated before. There are many researches discuss on synthesizing carbon nanofiber as a catalyst support. However, there are not much research has been done on synthesizing iron on carbon nanofiber. Nevertheless, the method that were used can be applied during experimental work and the method must be tested whether it is done in an efficient way. Once the experimental work is finished and results are acquired, a report will be established.

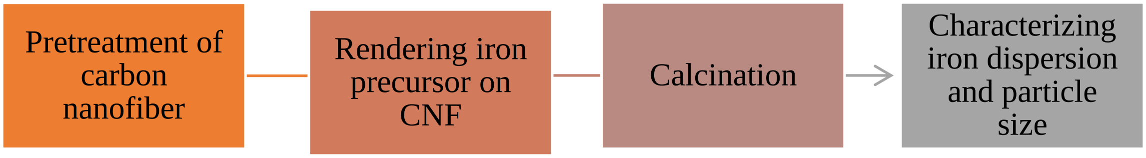


Figure 5 Experiment methodology

The objective of this research will be achieved through execution of job scopes as stated in the diagram above. The experimental work is primarily starts from pretreatment or functionalizing carbon nanofiber before it can be used as support. This process also known as surface oxidation of CNF; which is conducted by refluxing CNF in nitric acid solution. Next, it is proceed with rendering iron precursor on CNF via deposition precipitation technique and lastly, the samples will be sent out for characterization which are X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscope-Energy Dispersive X-ray (FESEM-EDX) in order to examine the dispersion of metal precursor and the particle size distribution.

3.2 Experimental Works

3.2.1 Chemicals

1. Commercial CNF (herringbone type)
2. Iron nitrate (III) nonahydrate salt, $Fe(NO_3)_3.9H_20$
3. Urea platelet
4. Nitric acid, HNO_3, 65% concentration
5. Deionized water

3.2.2 Apparatus

Reflux apparatus set up

1. 2-neck flask
2. Rubber stopper
3. Liebig glass condenser
4. Still pot
5. Hot plate with stirrer
6. Thermometer 100˚C
7. Retort stand and clamp
8. Magnetic stirrer

Sample and chemical handling apparatus

1. Erlenmeyer flask
2. Volumetric flask
3. Beaker
4. Ultrasonic bath
5. Mortar and pestle

Amount of Chemicals Consumed

Table 3 Amount of chemicals consumed

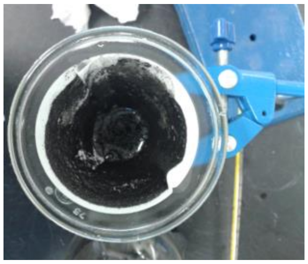
	Iron Nitrate Nonahydrate (g)	**Urea (g)**	**Oxalic Acid (g)**
Iron Loading (wt%)			
10	0.41	0.549	0.384
20	0.92	1.235	0.864
30	1.58	2.12	1.481

3.2.3 Procedures

Pre-treatment of Carbon Nanofiber

The surface oxidation of carbon nanofiber was primarily started with soaking CNF powder in nitric acid solution. Next, the mixture was placed in an ultrasonic bath for 10 minutes to wet and disperse the powder very well.

After the dispersing step had finished, the mixture was subsequently undergone the main process that is oxidation. The solution was heated up to 80°C in reflux condition. The process took an hour and the mixture was stirred at moderate pace.

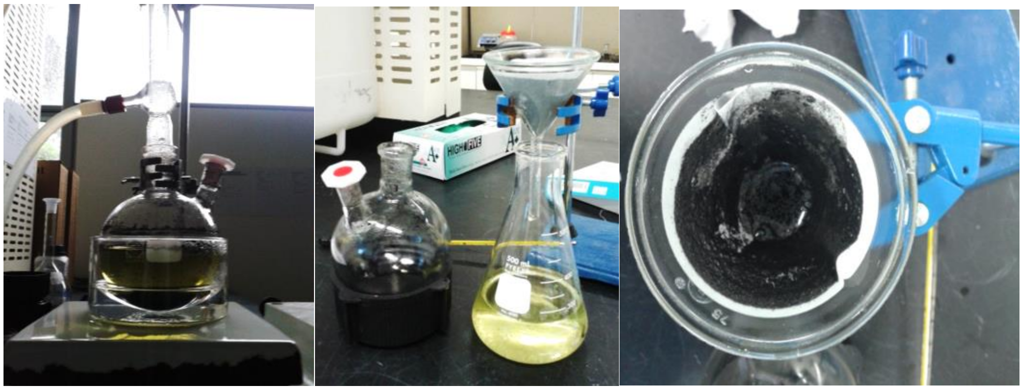


After an hour reaction took place, the mixture was filtered and the treated CNF was washed with deionized water until the filtrate pH reached 5 to 6. The CNF later was dried in carbolite oven at 70°C

Synthesizing Iron on CNF via Deposition Precipitation Method

The deposition precipitation procedure was much similar to pretreatment of CNF process. It started with immersing the dried, treated CNF powder in 250mL deionized water. Next, the mixture was placed in an ultrasonic bath for 10 minutes to wet and disperse the powder very well.

Next, the mixture was placed in the reflux up and keep stirred. Before the mixture could be heated up, oxalic acid powder is poured into the mixture. They are then heated up to 80°C. Once the solution reached 80°C, iron nitrate salt and urea are added consecutively. Time is taken once all the chemicals had finished being poured into the flask. The reaction took 6, 8, and 10 hours.



Once the reaction completed, the mixture was filtered and the iron loaded CNF was washed with deionized water until the filtrate pH reached 5 to 6. The slurry was later dried in carbolite oven at 70°C overnight. Next, the catalyst was undergone calcination at 250°C.

Sampling Method

Table 4 Sample preparation method

Iron Loading (wt%)	Impregnation Duration (hour)	Batch	FESEM (mg)	Amount CNF Needed (g)
10	6	A1	15	0.5
		A2	x	0.5
	8	B1	15	0.5
		B2	x	0.5
	10	C1	15	0.5
		C2	x	0.5
20	6	D1	15	0.5
		D2	x	0.5
	8	E1	15	0.5
		E2	x	0.5
	10	F1	15	0.5
		F2	x	0.5
30	6	G1	15	0.5
		G2	x	0.5
	8	H1	15	0.5
		H2	x	0.5
	10	I1	15	0.5
		I2	x	0.5

3.3 Characterization Method

Characterization of dispersion of iron on CNF is necessary as it can be used as a basis to compare the effectiveness compared to other research had been done.

3.3.1 Zeta Potential Analysis or Point Zero Charge (PZC)

Zeta potential is a scientific word for electrokinetic potential in colloidal systems which is commonly denoted by zeta letter, ζ. Theoretically, it is viewed as the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. In order to distinguish the high and low–charged surface, a value of 25 mV (positive or negative) can be taken as the arbitrary indicator. In this study, zeta potential was used to determine the potential of pre-treated CNF surface. The pH of the aqueous slurry and the PZC of the CNF may give a good indication about the surface oxygen complexes and the electronic charges of carbon. The surface charge comes from the interaction of CNF and the nitric acid solution which later determines the strength of the CNF-metal precursor interaction during impregnation.

3.3.2 Transmission Electron Microscope (TEM)

Transmission Electron Microscope works by utilizing a high voltage electron beam to produce an image. The source of electron is gained from an electron gun which normally equipped with tungsten filament cathode which the cathode itself emits electron. In the other side, anode works by accelerating electron which commonly at +100keV (40 to 400 keV) with respect to the cathode. The beam is then focused by electrostatic and electromagnetic lenses and later being transmitted through the specimen part which is transparent and disperse the beam out. The image is produced when the beam scattered out which carries the profile of the structure that is magnified by the microscope lenses. The different visual of the specimen structure is viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintilla or material such as zinc sulphide. Later, the image can be captured by exposing a photographic film or plate directly to the electron beam, or a high-resolution phosphor may be coupled by means of a lens optical system or a fibre optic light-guide to the sensor of a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed on a monitor or computer.

However, there is limitation in TEM resolution which mainly due to spherical aberration, but new generations of aberration correctors manage partially solving the spherical aberration problem in order to increase the resolution. Software correction of spherical aberration for the High Resolution TEM (HRTEM) allows the production of images with satisfactory resolution to show carbon atoms in diamond separately. The ability to determine the positions of atoms within materials has made the HRTEM an important tool for nano-technologies research and development. It is used partly for the sample characterization this project.

3.3.3 Field Emission Scanning Electron Microscope- Energy Dispersive X-ray (FESEM-EDX)

Field Emission Scanning Electron Microscope able to create an image by penetrating the specimen with a focused electron beam that is scanned across a rectangular area of the specimen. The energy of incident electron beam that penetrate each point gets lesser as it is transformed to another such as heat, light emission (cathodoluminescence), emission of low-energy secondary electrons or X-ray emission. The display of the FESEM maps the varying intensity of any of these signals into the image in a position corresponding to the position of the beam on the specimen when the signal was generated. Generally, the image resolution of FESEM is about an order of magnitude poorer than TEM. However, because the FESEM image relies on surface processes rather than transmission, it able to visualize bulk samples up to several centimetres in size (depending on instrument design) and has much greater depth of view, and so can produce images that are a good representation of the 3D structure of the sample.

In addition to secondary electrons imaging, backscattered electrons imaging and Energy Dispersive X-ray (EDX) Analysis are also useful tools widely used for chemical analysis. The intensity of backscattered electrons generated by electron bombardment can be correlated to the atomic number of the element within the sampling volume. Hence, qualitative elemental information can be revealed. The characteristic X-rays emitted from the sample serve as fingerprints and give elemental information of the samples including semi-quantitative analysis, quantitative analysis, line profiling and spatial distribution of elements. FESEM with X-ray analysis is efficient, inexpensive, and non-destructive to surface analysis. It has wide ranges of applications both in industry and research.

3.3.4 Thermogravimetric Analysis (TGA)

TGA is an analysis to investigate the changes of weight of specimen to temperature. The results of TGA result depend on the precision of three measurements; weight, temperature, and temperature change. Besides, TGA is able to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, and solvent residues. In this project, the catalyst purity and stability with respect to oxidation was examined by TGA. The mass change at a given temperature characterizes the beginning of the oxidation of the carbonaceous support. The appearance of more than one oxidation peak indicates the presence of impurities such as amorphous carbon.

3.4 Key Milestone

Problem Statement and Objective of the project

Identifying the purpose of this research project

Literature Review

Gathering as much information as possible from various sources such as journals and websites

Experiment Design

Identifying the subjects that need to be investigated and the experimental procedures, as well as the chemicals needed and the collection of results

Data Analysis and Interpretation

The findings obtained are analyzed and interpreted critically. Compare with other literature readings will also be done.

Documentation and Reporting

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will also be discussed.

Figure 6 Key milestones of the project

3.5 Gantt Chart

This project research is conducted accordingly to the plans that have been proposed by the coordinators in FYP I and II. In FYP I, the progress are to critically summarize the research papers that are related with project; proceed with writing up reports on the theoretical aspects of the research. Meanwhile, in FYP II, it is required to implement the experimental works and analyzing the results.

Table 5 Gantt chart of project

	WEEK												
TASK	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**13**	**14**
Selection of Project Title	🟥												
Preliminary Research Work and Literature Review		🟥	🟥	🟥	🟥	🟥							
Submission of Extended Proposal Defense						🟥							
Preparation for Oral Proposal Defense							🟥	🟥					
Oral Proposal Defence Presentation									🟥				
Detailed Literature Review									🟥	🟥	🟥	🟥	
Preparation of Interim Report				🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥		
Submission of Interim Draft Report												🟥	
Submission of Interim Final Report													🟥

Table 6 Gantt chart of experimental work

	WEEK											
TASK	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**Semester Break**	**1-9**	**10-13**
Placing Order for Chemicals & Apparatus	🟦											
Getting Laboratory Access		🟦										
Receiving Chemicals & Apparatus				🟦								
Executing Experiment					🟦	🟦	🟦	🟦	🟦		🟦	
Result Analysis											🟦	
Establishing Report												🟦

CHAPTER 4

RESULT & DISCUSSION

There were nine samples prepared with respect to the variation of iron loading weight percent and reaction duration. Those samples profile are stated in the **Table 4** in **METHODOLOGY** section. The iron weight percent ranging from 10, 20 to 30 wt% and the duration are from 6, 8 to 10 hours. Due to time constraint, there were six of them had been taken out for characterization as has been mentioned in last chapter in determining the dispersion of iron particle and its size. In this section, it will be discussed on the findings from the characterization for each analysis.

4.1 Point Zero Charge Analysis (PZC)

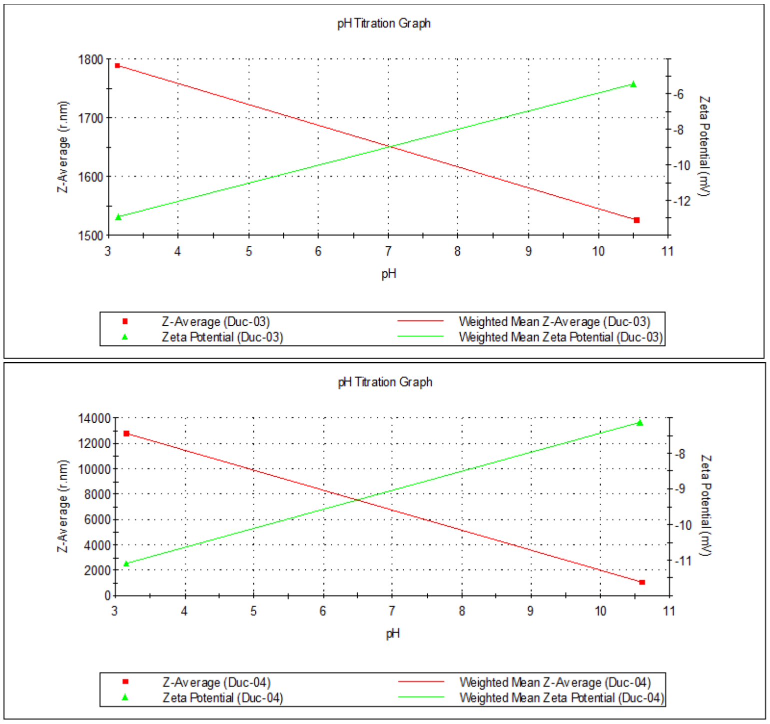


Figure 7 (Top) PZC against pH of sample Acid 03, (bottom) PZC against pH of sample Acid 04

Table 7 PZC and pH of nitric acid treated CNF

Sample	CNF	CNF-HNO_3 (03)	CNF-HNO_3 (04)
PZC	-11.9	-9.2	-9.1
pH	8.00	6.82	6.88

Table 7 shows the potential and pH of slurry of pristine and functionalized CNF which are randomly taken from batch Acid 03 and Acid 04. It is seen that the pristine CNF shows a basic property. The other functionalized CNF are neutral. Meanwhile, the PZC of pristine CNF is much lower than functionalized CNF which makes the pristine CNF has no ability to attract the cation (metal precursor). From the result, it can be deduced that the functionalized CNF were not acidic enough or having much lower PZC. It is expected that the pH ranges between 3-5 in which PZC should be approximately to zero, in order to ensure higher uptake of iron precursor during impregnation.[14] The subsequent effect of this analysis can be observed through FESEM characterization where it exhibits the distribution and uptake of iron on CNF visually. Generally, all of prepared CNF supported iron catalyst have fewer iron loading. Nevertheless, the iron particles are well dispersed and uniform in size.

It is believed that, higher pH of the functionalized CNF arises from the insufficient of nitric acid concentration during pre-treatment. Although many papers used concentrated HNO_3, they are also reported that such concentrated HNO_3 damages the CNF surface. [22] Therefore, it is suggested that the concentration of HNO_3 solution should be tested extensively in order to find the optimum one.

4.2 Transmission Electron Microscope (TEM)

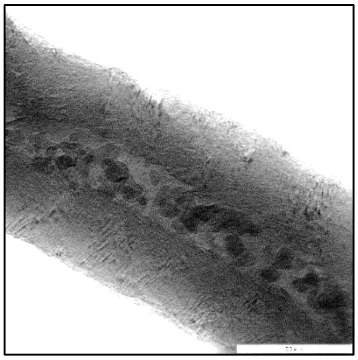


Figure 8 TEM image of sample A1

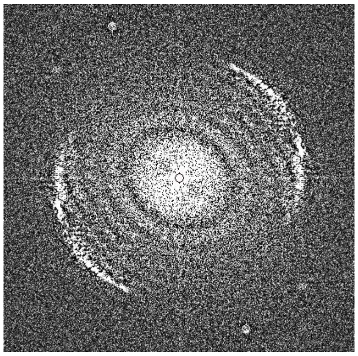


Figure 9 SAED analysis of sample

Figure 8 depicts the structure of iron loaded carbon nanofiber which was characterized through TEM analysis while **Figure 9** shows the Selected Area Electron Diffraction analysis (SAED) which was done along with TEM; implies the electron diffraction pattern of CNF herringbone type.[23] The sample that is under study here is from batch A1 which the iron loading is 10 wt% and the duration of reaction is 6 hours. The first image shows the CNF structure after pretreatment process and before iron is loaded on. It is noticed that the graphene layers are aligned in herringbone axis but there is a hollow space along the fiber. Meaning to say the fiber itself is not solid in structure, thus there is possibility of any impurity to be deposited inside the fiber. This statement is approved when it can be seen in the other two pictures show the iron particles are inside the string. The particle is denoted by the black dots which fill the hollow space. In contradiction, the experiment supposed to yield the iron particle on the surface instead.

It is hypothesized that the case happens due to the end of each fiber is cut off during acid treatment which later allows the iron particle to be inside.[24] Since the amount of iron loading for this batch is the least and the duration is the shortest, most probable the successive samples face the same issue since the CNF powder used are all similar and the treatment process is controlled. In order to avoid this case happen, there are several ways can be implemented. First, the carbon nanofiber that is used must be a solid cup stacked or herringbone type which there is no hollow inside the fiber. These two types of CNF are chosen due to their surface structure that has higher tortuosity and rougher. This allows the catalyst particle to be anchored right on the surface.

4.3 Field Emission Scanning Electron Microscope (FESEM)

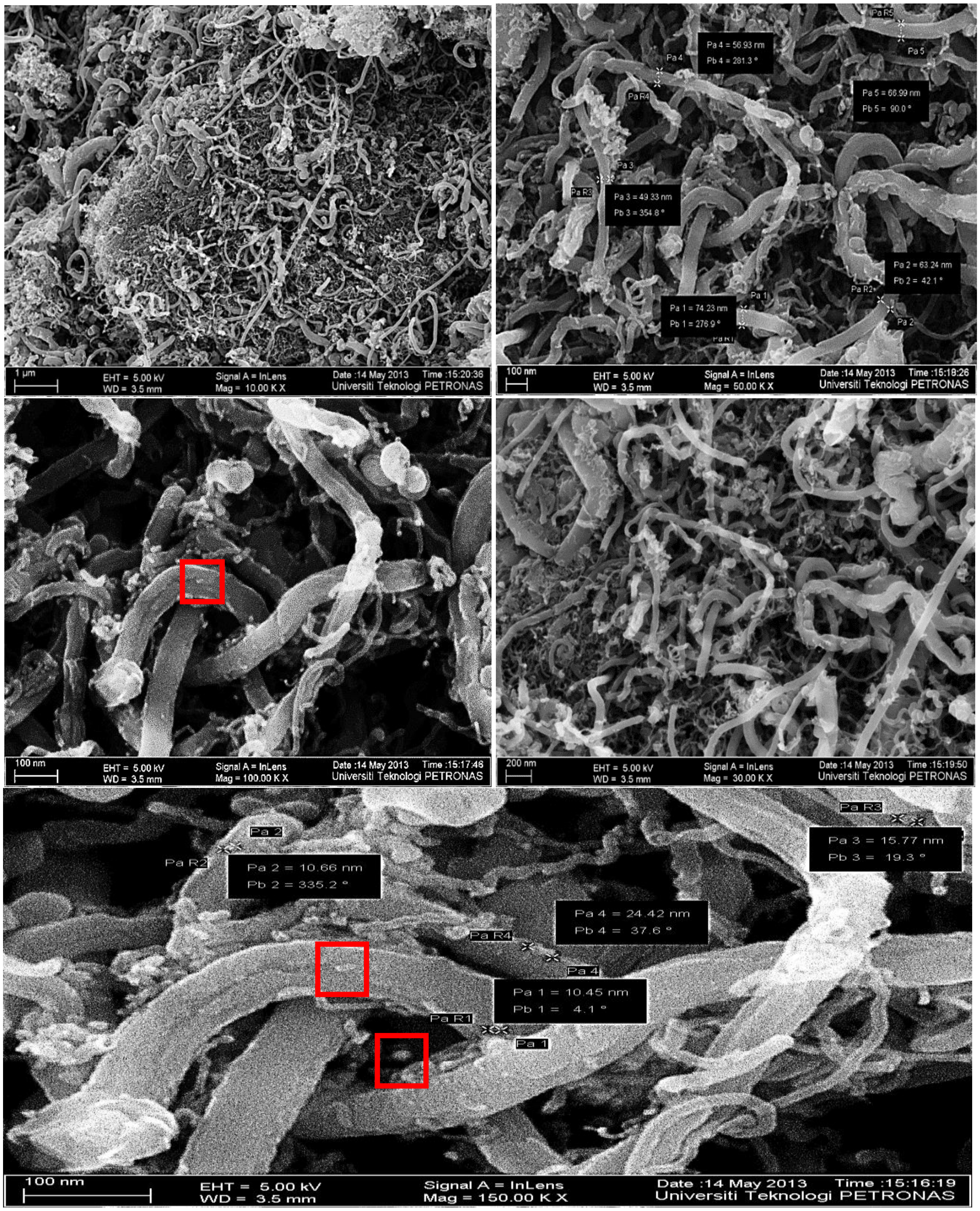


Figure 10 FESEM image of sample Batch C1

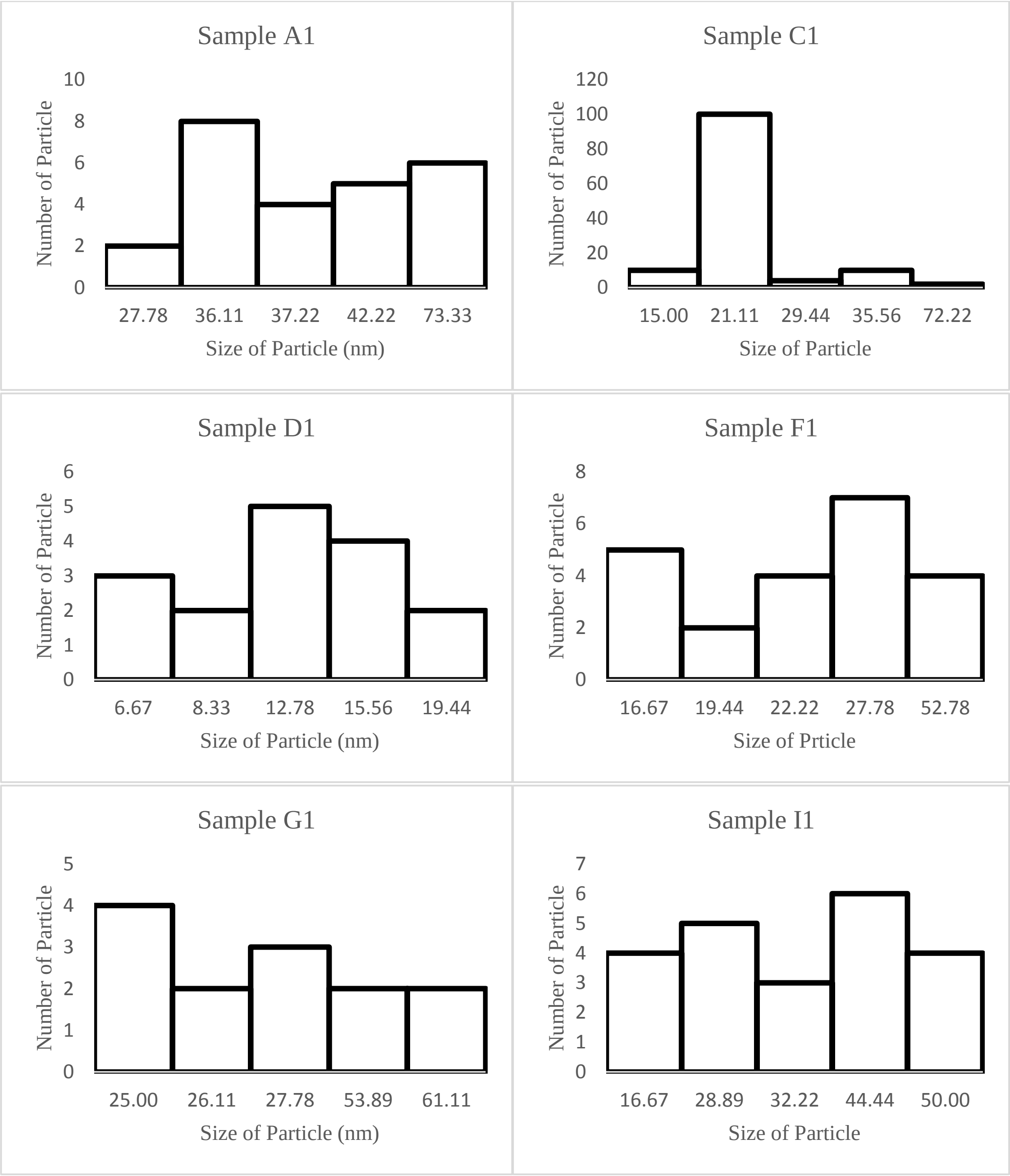


Figure 11 Number of iron particle and size distribution

FESEM images of the carbon nanofiber supported iron oxide catalysts are given in **Figure 10.** The presence of the iron oxide crystallites on the external surface of CNF surface is clearly visible from those images. The method that is used in this analysis is by randomly selecting 10 locations of sample which are visualized in 10 magnifications ranging from 10k to 150k times magnification. The reason to select 10 locations is to make a distribution pattern and to average the dispersion of iron particles along with their size on CNF. This will make the counting more accurate. From the 10k x magnification, it is noticed that the carbon nanofiber used has not high purity of CNF content which a large amount of carbon nanotube (CNT) can be seen mixed with the sample. The CNT can be identified by looking at the strand which is shorter and smaller than CNF. The important of using high purity CNF is to yield the most of iron fiber attached on CNF. The consecutive images clearly shows the iron particles attached on CNF which are denoted by the white tiny dots. In FESEM, the presentation of the compound is different than TEM, whereby any metallic material can be identified with white spots while TEM is in black spots.

The individual crystallite diameters which are visible in 100k x magnification were measured with the aid of the Adobe Photoshop CS3 software package and are also given in **Figure 11.** Based on the observation, the size of the particles can be considered uniform, and well distributed on CNF surface although there some part are not covered. The amount of particle loading is influenced by the surface morphology and the amount of oxygen containing group on CNF surface. This can be attained during pretreatment of fiber with acid or any oxidizing agent. However, the concentration of acid (in this case) must be studied since it plays role in giving the optimum oxidation of CNF surface. If the concentration is too high, it might damage the surface while if it is too low there will be no oxidation occurs.

Along with FESEM, it was done EDX analysis on the samples where it summarizes the elements present on the sample. **Table 8** presents the EDX result for all samples. The results shows that carbon element is dominant with more than 93 wt% since carbon nanofiber is the backbone of the catalysts. Besides, it is noticed that oxygen elements is the second largest with more than 3 wt%. This number exceeds the amount of iron in the samples with the weight percentage is less than 1%. For an effective deposition, it is expected that the weight percentage of iron should be nearly equivalent to oxygen. This is due to the oxygen plays role as the binding site or the functional group where it attracts the iron particle to be deposited on CNF surface. This group of oxygen presents during pre-treatment process of CNF where the oxygen containing group which carries negative charge are sourced from the nitric acid solution. However, there is also possibility that the oxygen detected by EDX comes from air which attach to CNF during the catalyst impregnation. This can be seen in **Table 8** that as the reaction time prolongs, the oxygen uptake gets higher while the number of iron decreases. In other words, as the time was prolong, more oxygen from surrounding air dissolves in the impregnation slurry thus attached to the functionalize CNF surface. It is hypothesized that the oxygen molecule from air masks the CNF surface thus it avoids the iron particle to be deposited. Therefore, as it is suggested somewhere in [14] that the importance of bubbling inert gases such as nitrogen into the slurry during impregnation in order to avoid the oxygen from dissolving in the slurry.

Table 8 EDX result

A1		
	Weight %	Atomic %
Carbon, C	93.75	95.63
Oxygen, O	5.48	4.20
Iron, Fe	0.70	0.17

C1		
	Weight %	Atomic %
Carbon, C	93.12	95.1
Oxygen, O	6.20	4.75
Iron, Fe	0.68	0.15

D1		
	Weight %	Atomic %
Carbon, C	95.12	96.7
Oxygen, O	4.11	3.14
Iron, Fe	0.77	0.17

F1		
	Weight %	Atomic %
Carbon, C	95.16	96.57
Oxygen, O	4.36	3.33
Iron, Fe	0.48	0.10

G1		
	Weight %	Atomic %
Carbon, C	96.00	97.30
Oxygen, O	3.28	2.51
Iron, Fe	0.72	0.19

I1		
	Weight %	Atomic %
Carbon, C	94.84	96.31
Oxygen, O	4.72	3.60
Iron, Fe	0.44	0.10

4.4 Thermogravimetric Analysis (TGA)

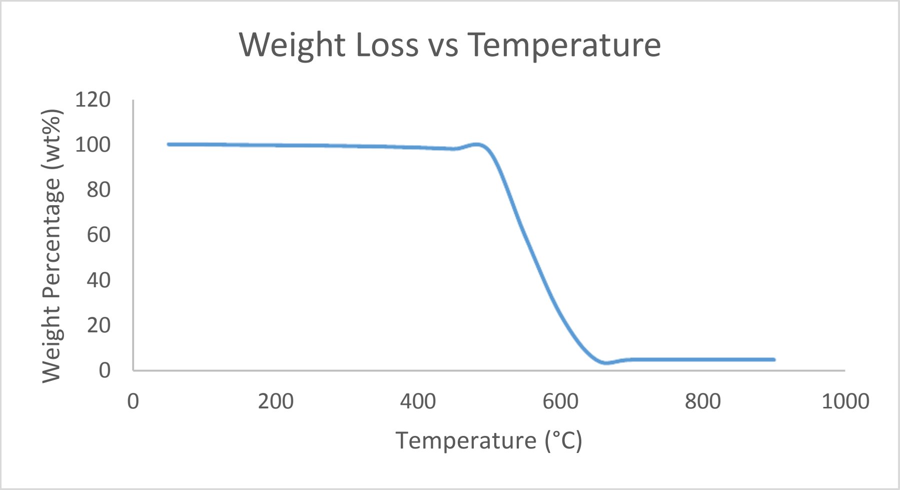


Figure 12 Weight loss against temperature

Figure 12 shows the result from TGA analysis which as stated before to see the changes of weight of sample against temperature. The sample was taken from batch G1 which was prepared with 30 wt% iron and reacted within six hours. It was tested from 50°C to 500°C which the heating rate was 20°C per minute. The reason to test until 500°C is because this sample is meant to be tested in ammonia production which the operating temperature ranging from 400°C -500°C. The graph shows that there is not much fluctuation in mass loss up to 500°C. Meaning to say this sample is resist to the operating temperature and slightly affected by sintering. Many academia papers stated that the total mass loss occurs at 600°C.[22] This mass lost was attributed to the removal of carbon. Generally, the following properties of CNF can be determined using the TGA curve;

1. The catalyst impurities mass in as produced CNF.
2. The number of functional groups per CNF carbon.
3. The mass of a reactive species absorbed by a functional group on CNF.

CHAPTER 5

CONCLUSION & FUTURE WORK

The main objective of this project that is to study the dispersion of iron particle on carbon nanofiber it is achieved by primarily started with pre-treatment of CNF followed by rendering iron via deposition precipitation method. From this research, it was found that after pretreatment process, the PZC value is -9.80 which is slightly differs it from the pristine CNF yet still able to uptake iron precursor during iron impregnation. The iron particle dispersion and size distribution was studied via FESEM and TEM analysis. It was found that the iron are well dispersed on the CNF surface which has the particle size between 20-30 nm which is quite similar finding somewhere in [24]. Suffice to say, it can be seen the dispersion is satisfactorily achieved and the distribution of particle size is quite uniform, where agglomeration is hardly be noticed. Furthermore, TGA analysis shows that the sample prepared are withstand to temperature 550°C which also exhibits the average temperature of CNF supported metal catalyst.

Study of iron dispersion on carbon nanofiber is an interesting research project. Employing CNF as catalyst support is still recent in material science, surely, there will be a lot more to discover and can be enhanced. Considering the findings attained, the author personally would like to propose some suggestion in terms of the experimental procedure and project handling generally, so that there will be improvement in the future.

Suggestions for improvement in experimental procedure

1. Carbon nanofiber selection
    - Carbon nanofiber to be used must be high purity and must be less with carbon nanotube. Besides, the type of CNF should be herringbone or

stacked type without hollow cavity inside the fiber. This is to ensure that there will be no impurities deposited inside the CNF.

2. Pre-treatment process
    - The usage of nitric acid is acceptable as it has been used over in many research. However, the concentration and the treatment procedure must be improvised. Perhaps 6-7 molar concentration will be the optimum.
3. Deposition precipitation method
    - This method actually requires for a sophisticated set up. The lack in this experiment compared to the research papers are nitrogen supply, pH meter, stirrer with controlled stirring rate and an autoclave reactor. Conducting in the reflux set up is insufficient as it gives poor result.
    - In order to avoid oxygen molecules dissolve in the slurry, nitrogen gas must be bubbled throughout the reaction period.
4. Characterization
    - Characterization can be done by analyzing the pristine CNF and functionalized at the earlier stage. This is to distinguish the surface properties of CNF and to ensure that the functionalized CNF is good enough to be employed for impregnation.

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