IMPREGNATION OF IRON CATALYST ONTO CARBON NANOFIBERS

By

AHMAD FIRDAUS BIN MOHAMAD

SUPERVISOR: DR SURIATI SUFIAN

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

MAY 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

IMPREGNATION OF IRON CATALYST ONTO CARBON NANOFIBERS

By

Ahmad Firdaus bin Mohamad

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

DR SURIATI SUFIAN
UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

May 2012

CERTIFICATE 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 acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMAD FIRDAUS BIN MOHAMAD

ABSTRACT

This report outlines the background of the project "Impregnation of Iron Catalyst onto Carbon Nanofibers". Application of carbon nanofilaments which are carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in catalyst field has attracted great interest from scientist due to their excellent properties. In this experimental work, CNFs was used as catalyst support for iron catalyst due to its outstanding property that enabled it to be great catalyst support. The CNFs was synthesized by Chemical Vapor Deposition (CVD) technique and the iron oxide was deposited by incipient wetness impregnation. The composite were analysed by scanning electron microscopy (SEM) for surface morphology, X-ray Diffractometer (XRD) for the crystalline structure and Brunauer Emmet Taylor (BET) analysis to determine it surface area and pore volume. Iron catalyst been impregnated by incipent wetness impregnation using a ferric solution of nickel nitrate. Then, the solution been filtered, washed and dried to get the iron supported CNF in powder form. After purification, the powder been analysed by XRD and field emission scanning electron microscopy (Fe-SEM) together with Energy Dispersive X-Ray (EDX) analysis. A number of samples were prepared by manipulating the concentration of ferric solution of nickel nitrate and the residence time during impregnation.

ACKNOWLEDGEMENT

First of all, all praises to Allah for His guidance and blessings for giving an opportunity for the author to accomplish this Final Year Project as part of the requirements for Bachelor of Engineering (Hons.) in Chemical Engineering at Universiti Teknologi PETRONAS.

My outmost appreciation goes to the assigned supervisor for this project, Dr Suriati Sufian for the continuous guidance and support provided throughout the progression of this project. My gratitude is extended to Thien Duc Nguyen as the co-supervisor for all the continuous advice during this project.

This acknowledgement would not be complete without giving credit to UTP, especially Chemical Engineering Department laboratory technicians for giving the author an opportunity to utilize the laboratory and assisting the author in completing the experiment works.

Finally, countless appreciation goes to my family back home and my friends for their assist and help in completing this project.

Table of Contents

LIST OF TABLES AND FIGURES

ABBREVIATIONS AND NOMENCLATURES

CNFs	Carbon Nanofibers
CNTs	Carbon Nanotubes
T-CVD	Thermal Chemical Vapor Deposition
$Fe(NO_3)_3.9H_2O$	Ferric nitrate solution
Fe-SEM	Field emission scanning electron microscopy
EDX	Energy Dispersion X-ray
Fe	Ferrum

CHAPTER 1: INTRODUCTION

1.1 PROJECT BACKGROUND

In chemical engineering, chemical reactors are the vessel design to contain chemical reaction. The design of chemical reactors deals with multiple aspects of chemical engineering. Chemical engineers design reactors to maximize net present value for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product while requiring the least amount of money to purchase and operate. Normal operating expenses include energy input, energy removal, raw material costs, labour, etc. Nowadays, catalytic reactors are more preferable than the conventional reactors without catalytic reactions. For example, in ammonia production scientist has put huge effort in altering the catalyst to increase the output yield compare to modifying the catalyst.

The interest of application of carbon nanostructures in catalyst field started after carbon nanotubes and their related material are discovered as the by-product of the arc process by Ijima in 1992. Since then carbon nanostructures especially carbon nanotubes and carbon nanofiber has received significant interest. Carbon nanofibers (CNFs), vapour grown carbon fibers (VGCFs), or vapour grown carbon nanofibers (VGCNFs) are cylindric nanostructures with graphene layers arranged as stacked cones, cups or plates. Carbon nanofibers with graphene layers wrapped into perfect cylinders are called carbon nanotubes.

Among the different potential of these materials, catalysis either within the gas or the liquid phase seems to be the most promising according to the result reported in literature. Metals supported on CNF or nanotubes exhibit unusual catalytic activity and selectivity patterns when compared to those encountered with traditional catalyst support such as alumina, silica or activated carbon. The extremely high external surface area displayed by these nanomaterial significantly reduces the mass transfer limitations, especially on liquid phase reactions (Pham- Huu et al, 2001) and the low interaction between impregnated metallic phase and the exposed planes of the support which leads to the formation of active metallic phases (Rodriguez et al, 1995) were advanced to explain these catalytic behaviour.

1.2 PROBLEM STATEMENT

Rate of reaction can be increased either by modifying the reactor or the catalyst involved. However, altering the catalyst is more preferable and economical way to improve process efficiency, lower cost and less energy. Catalyst support is the material which the catalyst is affixed. Throughout the history, many types of catalyst support have been used such as activated carbon, alumina and silica. The catalyst support will act as carrier without affecting the function of catalyst.

Today it is important to consider all the criteria and aspects when seeking ways to increase the process efficiency by selecting the catalyst support. The macroscopic structures should not change the physical properties of the carbon nanostructures deposited on it. For example high mechanical strength in order to avoid breaking and catalytic bed plugging, high specific volume in order to afford a high space velocity of gaseous reactants, high thermal conductivity which is essential for catalyst operating in highly exothermic or endothermic reactions and finally high chemical resistance in order to be used in aggressive environments. Because of the excellent and advantageous properties, CNF is believed to be the solution over other existing material.

1.3 RESEARCH OBJECTIVE

This research is done solely to prepare a new catalyst who gives high loading, purity, catalytic activity, strength, but low cost. Based on background study, combining carbon nanofiber supported iron oxide seems to be the ideal solution. The research objective includes:

i) To impregnate iron catalyst onto CNFs
ii) To characterize the supported catalyst produced

With the percentage of iron loading onto CNF is as parameters, concentration of ferric solution of nickel nitrate and the residence time is used as the manipulated variables. With the result obtained, the variable can be analysed together with parameters to find the best condition for highest catalysts loading.

1.4 SCOPE OF STUDY

This experimental work covers the preparation and analysing the catalyst. These are the scope of study related to the work:

i) To prepare the iron supported CNF catalyst based on variables of:

- Concentration of ferric solution of nickel nitrate
- Residence time during impregnation

ii) To characterize and analyse the iron supported CNF produced using:

- X-ray dispersion (XRD)
- Field Emission Scanning Electron Microscopy(Fe-SEM)
- Energy Dispersive X-Ray (EDX

CHAPTER 2: LITERATURE REVIEW

2.1 CARBON NANOFIBERS

The existence of carbon nanofilaments has been observed during the natural gas reforming several decades ago, when this material were considered as undesirable by-products which led to catalyst disintegration and plugging. Later, several research groups have been involved in the identification and characterization of this new form of carbon with the aim to reduce its formation (Nelize Maria et al, 2000) .However, the interest of this new material in the field of catalyst only started after carbon nanotubes and their related materials also discovered as the by- product of the arc process by Iijima, in 1991(Ricardo Viera et al, 2002). Since then carbon nanostructures such as carbon nanotubes (CNT) and carbon nanofibers (CNF) has received tremendous interest. This is due to their exceptional mechanical, chemical, electrical, physical and chemical characteristics which make them attractive for various kinds of applications (Ping Li et al, 2006). Application of CNT and CNF include emitters for field emission display (FED) (S.S Fan et al, 1999), composites reinforcing materials (E.Hammel et al, 2004), hydrogen storage (A.C Dillon et al, 1997), bio and chemicals sensors (J.Kong et al, 2000), nano and microelectric devices (A.M Fennimore et al, 2003), and as a catalytic support electrodes for fuel cells (Wenzhen et al, 2002).

Nevertheless, the two main drawbacks had limited the application of these new materials in catalyst field; low yield of carbon nanotubes and high amount of impurities (by- product) by the synthesis routes (electric arc and laser ablation). These restrictions have been fixed by Ebbesen and Ajayan. According to the technique, the synthesis basically consists of a catalytic decomposition of carbon monoxide (CO) or certain gaseous hydrocarbons on the surface of some transition metals (Fe, Ni and Co) at temperatures between 400 and 800^{0}C. Either CNF or CNT both can be synthesized using this technique (Ebbesen TW et al, 11992). CNT are constituted by graphite layers rolled in it and parallel to the tube's axis, displaying a topmost surface constituted by the less reactive basal planes of graphite. Meanwhile, CNF are formed by piling up of graphite layers along the axis of the fibers as cone form, displaying prismatic planes with high reactivity for the adsorption of the deposited active phase.

Besides that, due to interest in CNF in catalyst field, many authors has suggested that the application of CNF as catalyst support is due to: i) their good metal/support interaction caused by the presence of the prismatic planes on nanofibers surface, ii) their high specific surface area that offers a better contact reactants/active sites and iii) absence of the ink-bottled pores that reduces the diffusion phenomena, mainly in liquid phase reaction or high mass and heat transfers reactions. However the direct use of these 1D carbon materials in conventional catalytic reactors, especially in fixed-bed configurations, is significantly hampered by their nanoscopic size. Reactor loading problems and pressure drop can occurred due to this size which means it will rendered the their use in a large scale reactor configurations.

There are many methods for preparing metal onto catalyst support surface such as sol-gel synthesis, post-modification of support material, impregnation (pore filling followed by evaporation of solvent, ion-exchange, precipitation or co-precipitation, and adsorption from solution, as well as mixing or grinding. In most catalyst, the active phase (e.g. metal, metal oxide) is deposited on a support to keep the active phase stable and highly dispersed during catalysis. Moreover the synthesis technique of carbon nanofiber supported iron catalyst is impregnation including wet impregnation and incipient wetness impregnation as well as ion adsorption based on electrostatic interaction, deposition precipitation (M.Campanati et al, 2003) (Anna-Claire Dupuis et al, 2005) Furthermore, incipient wetness impregnation and ion adsorption were used for the synthesis of highly dispersed catalysts at low loading, while high density plasma (HDP) and impregnation were used for preparation of highly loaded catalysts with intermediate dispersion.

In the research work, it focuses on the impregnation process of iron catalyst onto CNFs. The variables involved are the concentration of ferric solution of nickel nitrate and the residence time. Through the modification in the variable the percent of iron loading onto CNFs was observed. In this report also briefly include the work involve in preparation and characterization of CNFs supported iron oxide catalyst. A few summarizations from the journal are attached in appendixes for further reading.

2.2 SUMMARY FROM JOURNALS

Table 1: Few types of CNFs synthesis

Methods	Catalyst	Carbon sources	Reference
F-CVD	Ferrocence	C2H6/H2/thiophene	Ci.et al.2000
	Ferrocence	Xylene/sulphur/H2	Martin-Gullon et.al. 2006
	Cobaltence	C2H6/H2/thiophene	Singh et al.2002
Electric arc discharge	Ni-Y	He/CH4	Pacheco-Sotelo et al. 2007
C-CVD	Iron	CO/H2	Carneiro et al.2004
	Ni-Silica Ni nanoparticles	CO+CH4/H2 C2H4/H2	Toebes et al.
	Fe-Cu	C2H4/H2	2002Krishmankutty et al.
	Pt-LDO	C2H2	1997Q.Chen Jia Wang et al.
	K-Ni/Al2O3	H2/CO2	2011C.S Chen et al. 2009
	Ferrocence	Isopropyl alcohol/H2	Lu & Ting 2004

Table 2: Few types of preparation of supported catalyst

Method/ solvent	Precursors	Support	Metal wt%	Co/C (at/at) XPS	Particle size (nm)	Reference
IWI/ ethanol	Co(NO3)2.6H2O	CNF	7,5	1,023	5,9	Bezemer et al.2006
IWI, water	Co(NO3)2.6H2O	CNF	22	0,047	16	
TA, water	CoCO3	CNF	0.8	0,0034	3	J.H bitter et al. 2003
IWI, water	Ni(NO3)2.6H2O	CNF	30	-	8-60	
IWI, water	Fe(NO3)3	CNF		-	141.4	Duan Qian at al. 2011
	Fe-CNF	Mica		-	84.5	
IWI, water	H2PtCl6	CNF	5-50	-	2-20	Endo et al.2003
IWI, water	Ni(NO3)2.6H2O	CNF	12,5	-	13-14	Ochoa-Fernandez et al. 2005

Author / year	Title	Types of support/ catalyst	Methods of preparation and impregnation	Remarks
Xuezhi Duan, Gang Qian, Xinggui Zhou, Zhijun Shui, De Chen, Weikang Yuan 22 May 2010	Tuning the size and shape of Fe nanoparticles on carbon nanofibers for catalytic ammonia decomposition	CNF / Fe - the use of mica to control the shape of Fe and their distribution on CNF	**A) Fe-/mica catalyst** - prepared through the incipient wetness impregnation of Fe onto mica. **B) Fe-CNF/mica catalyst** - Synthesized by growing CNF over Fe/mica catalyst - Firstly, the Fe/mica catalyst was dried at ambient temperature for 12 hr and further dried in oven for 12 hr at 120°C. - Then it been activated at 600°C for 3 hr in flowing Ar/H_2 mixture (600/200 ml/min). - Next CO disproportion was performed at 600°C for 1.5 hr in a mixture of CO/H_2 (800/200 ml/min). **C) Fe-CNF catalyst** - produced by the CO disproportion on Fe nanoparticles from reduced Fe_3O_4 without support at the same condition for 8 hr.	- This research was done in order to compare the performance of residual Fe particles on CNFs with different microstructures. - The use of mica is to tune the shape of Fe and their interphase properties. - CO disproportion is performed to growth the CNF.

Author / year	Title	Types of support/ catalyst	Methods of preparation and impregnation	Remarks
Fangli Yuan, Hyung Kyun Yu, Hojin Ryu 7 Aug 2004	Preparation and characterization of carbon nanofibers as catalyst support material for PEMFC	CNF / Platinum (Pt)	**(CNF)-synthesis** - By Thermal-CVD in quartz tube electric furnace with C_2H_2 as carbon source. - Bulk Ni(OH)2 and Mg(OH)2 mixture of 50 mg which is has been put in alumina boat is loaded into the quartz tube with an inner diameter of 45mm and a length of 1000mm. - Then it is placed at the centre of the furnace, in which a uniform heating zone is maintained. - Argon gas been introduced into the furnace and temperature is raised from room temperature to pyrolytic temperature of 500–600 °C, with a heating rate of 5 °C/min. - Once the temperature is achieved, H_2 or mixture gas of H_2/N_2 (5% H2) of 100 sccm was flowed for 30 min. - then C_2H_2 gas at 10 sccm and H_2 gas at 100 sccm are simultaneously flowed for 30 min to prepare CNFs. - Finally, the sample is cooled down to room temperature under argon stream.. CNF is purified with HNO3 and HCl to remove Ni and MgO and stirred in 3M HNO_3 solution and refluxed for 24 h at 60 °C, and then they are stirred in 5M HCl and refluxed for 6 h at 120 °C. - Finally, the purified CNFs were washed using distilled water and isopropyl alcohol. **(Catalyst-platinum)-(impregnation)** - CNF is impregnated with 1% H2PtCl6 in distilled water. - Solution of 1% NaBH4 reducing agent is added with stirring. - Then the mixture was dried, cooled and washed repeatedly with distilled water and Pt catalyst powder is heated overnight at 80°C in an air oven.	- This research was done in order to compare the performance of two sample of CNF used as electrode catalyst support. - Two sample of CNF is synthesized using two different methods (ground and unground catalyst). - CNFs with bundle and twisted conformation synthesized using catalyst ground with the MC process used as electrode catalyst support gave better fuel cell performance compared to that prepared with CNFs synthesized using unground catalyst.

Author / year	Title	Types of support/ catalyst	Methods of preparation and impregnation	Remarks
Atsushi Tanaka, Seong-Ho Yoon, Isao Mochida 28 Dec 2003	Formation of fine Fe-Ni particles for non-supported catalytic synthesis of uniform carbon nanofibers	CNF / Ferrum	**A) Iron – nickel alloy catalyst (Fe-Ni (6/4 wt/wt %))** - Prepared by the precipitation of ferric and nickel carbonate from ferric nitrate and nickel nitrate solution using ammonium bicarbonate. - Then, the Fe-Ni carbonate was calcined at 400°C for 4 hr into Fe-Ni oxide. - Next, the oxide is reduced at 500°C for 20 hr under hydrogen and helium atmosphere (H_2/He = 1/9 vol/vol), total gas flowrate = 200 ml/min (sccm) (*first reduction) - The first reduced Fe-Ni catalyst was ground into several ten micrometers. - The ground Fe-Ni catalyst was reduced for 2 hr at H_2/He atmosphere. - Finally, the flow of CO/H_2 (1/4 vol/vol) total flowrate 200sccm was introduced for CNF growth at 580°C. (*second reduction)	- This research was done in order to investigate the steps in catalyst preparation and CNF synthesis in order to achieve uniform CNFs through the catalytic growth. - From result obtained, the temperature at second reduction is considered as an important factor to determine the size and structure of resultant CNFs.

Author / year	Title	Types of support/ catalyst	Methods of preparation and impregnation	Remarks
J.H Zhou, M.G.Zhang, L.Zhao, P.Li, X.G.Zhou, W.K.Yuan. 3 Aug 2009	Carbon fiber/graphite-felt composite supported Ru catalysts for hydrogenolysis of sorbitol.	CNF / GF support and supported Ru catalyst.	**Graphite felt –GF** - GF is cut into predefined shapes -then it is being calcinated in oven at 500°C for 6hr. -3 wt% of Ni is deposited by incipent wetness impregnation of an ethanol solution of nickel nitrate. **(CNF)-synthesis** -CNF is grown on GF by using C_2H_6 as carbon source. - two sample is prepared: i) CNF/GF1 (ratio 0.7) ii) CNF/GF2 (ratio 1.0) - All composite samples are purified with 4 mol/L HCL for several times and washed with water to remove Ni. - CNF/GF2 is treated with 30% with H_2O_2 = CNF/GF2- H_2O_2 - As synthesized composite CNF/GF2-UNT also used as reference. **(CNF-GF support and supported Ru catalysts)** - Ru is deposited by incipent wetness impregnation with $RuCl_3$ aquoes as precursor.	- This research is carried out to compare the powder Ru/CNF catalyst and structured Ru catalyst for sorbitol hydrogenolysis. - By the result obtained, the research concluded that the structured Ru catalyst had a lower activity but much higher selectivity from 57% to 79.1% to ethylene glycol, propylene glycol and glycerol.

Author / year	Title	Types of support/ catalyst	Methods of preparation and impregnation	Remarks
Wenzhen Li, Changhai Liang, Jieshan Qiu, Weijiang Zhou, Hongmei Han, Zhaobin Wei. Gongquan Sun, Qin Xin. 18 Jan 2012	Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell.	CNT / Platinum nanoparticles	**(CNT)-synthesis** - CNT is produced from high purity graphite by a classical arch discharge evaporation method. - diameter= 4-50nm - surface area = 42 m^2/g (N_2 ads) - Purification of CNT by ultrasonic treatment for 10 min - refluxed in 70% HNO_3 at 120°C for 4hr. - Surface oxidation of CNT achieved with 4.0 H_2SO_4-HNO_3 mixtures for 4hr under reflux condition. **(Catalyst-platinum)-(Reflux condition)** - 6hr reflux with chloroplatinic acid in ethylene glycol (250mg CNT/70ml solvent) at 140°C. - Then, the solid is washed and dried in air at 70°C. - Finally, Pt-CNT catalyst with metal loading 10% is obtained.	- This research is carried out due to problem for polymer electrolyte fuels cells which is the slow reaction rate of the cathode oxygen reduction reaction (ORR). - Based the preliminary experimental results, it is concluded that using CNT as supports for cathode catalyst in a direct methanol single cell produces better performance compared to XC-72 carbon (the commercial carbon support for comparison.

CHAPTER 3: METHODOLOGY

3.1 INTRODUCTION

The method of impregnation is adapted from two research works which are Asushi Tanaka et al, 2003 and Xuezhi Duan et al, 2010.

From BET measurement:

Density of CNF = 2.95398 g/cm^3 =2.95398 g/ml

Pore volume of CNF = 0.231 cm^3/g = 0.231 ml/g

3.1.1 – Sample Preparation

1) Theoretical pore volume

1- 1gram of CNF was put in a beaker.

2- Distilled water was filled in burette and added to the CNF by drop wise from the burette.

3- The addition was completed until of the last drop of distilled water formed a thick slurry solution indicating all the pore volume of CNF was filled.

4- The amount of distilled water that has been used was recorded. (V_{H_2O})

2) Drying the CNF

1) The thick slurry solution of CNF from step 1 was placed into oven.

2) The drying process was completed until the mass of CNF return to its original mass. *all water has been evaporated

3) Calculation mass of Ferrum (%Fe)

1) Molecular weight of Fe = 56 g/mol and for $Fe(NO_3)_3.9H_2O$ = 404 g/mol

Fe (ferrum)	$Fe(NO_3)_3.9H_2O$
56 g/mol	404 g/mol
(56 x Xgram) / 404 g/mol	X gram

2) Calculation for CNF:

   Each sample will use 0.1 g of CNF

   Total sample = 9

   Total mass = 0.9 g of CNF

3) For 5 % of Fe

   = (56 x Xgram) / 404 g/mol = total mass of CNF x (5/100)

   = (56 x Xgram) / 404 g/mol = 0.9 g x 0.05

X_5 = 0.32 g

4) The calculation for 10% and 20% of Fe was repeated.

Table 3 : Experimental variables

Factor (residence time)	**% Fe**	**V_{H_2O}**
1 hour	**X_5 (0.32 g)**	**0.5 ml**
	X_{10} (0.65 g)	
	X_{20} (1.30 g)	
6 hour	**X_5 (0.32 g)**	
	X_{10} (0.65 g)	
	X_{20} (1.30 g)	
24 hour	**X5 (0.32 g)**	
	X_{10} (0.65 g)	
	X_{20} (1.30 g)	

4) Impregnation of iron onto CNF

1) From step 3, the mass of iron (X_5) for 5% Fe and was mixed together with an amount of distilled water from step 1 (V_{H2O}).
2) 0.1 g of CNF was placed into a beaker.
3) The solution of ferric nitrate was slowly dropped onto the CNF.
4) The sample was left for a period of time (residence time) for 1 hour, 6 hour and 24 hour.
5) The step was repeated for 10% and 20% of Fe.

3.1.2 Sample analysis

1) Characterizations of catalyst produced

The microstructure and morphology of CNF supported catalysts were characterized using;

1- Field Emission Microscopy (Fe-SEM)
2- Energy Dispersive X-Ray (EDX)
3- X-ray Diffraction (XRD)

2) Results and analysis from completed test

1- The result obtained was observed for the iron loading onto CNF.
2- The variables which are the different concentration of iron and residence time was compared together to find the best condition that give the highest loading of iron onto CNF.

3.2 LIST OF CHEMICALS AND EQUIPMENTS

Table 4: List of equipments

ID	Equipments	Purpose
2	BET	To determine surface area, pore volume
3	Fe-SEM	To study surface morphology
4	Energy Dispersion X-Ray	To determine chemical characterization

Table 5: List of chemicals

No	Description
1	Carbon nanofibers (powder from)
3	Acetone (purity)
9	Iron nitrate nanohydrate, Merck 103883

3.3 PROJECT MILESTONE – Gantt chart

Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Timeline for 1^{st} Semester (January 2012) (COMPLETED)															
Topic Selection / Proposal	■	■					**MID SEMESTER BREAK**								
Preliminary Research Work		■	■	■	■										
Submission of Proposal Defense (Preliminary) Report															
Proposal Defense (Oral Presentation)								■	■						
Input Data Acquisition & Lab Experiments Familiarization and										■	■	■			
Submission of Interim Draft Report															
Submission of Interim Report															
Timeline for 2^{nd} Semester (May 2012)															
Lab Experiments and Data Acquisition	■	■	■	■	■	■	**MID SEMESTER BREAK**								
Submission of Progress Report															
Lab Experiments, Data Acquisition and Analysis								■	■	■	■	■			
Pre-EDX											■				
Submission of Draft Report															
Submission of Dissertation (Soft Bound)															
Submission of Technical Paper															
Oral Presentation														■	
Submission of Dissertation (Hard Bound)															

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Results

4.1.1 Field Emission Scanning Electron Microscopy (FeSEM)

The morphology of CNF as an iron catalyst supported is analysed by using FeSEM. From the result of FeSEM, the surface morphology can be observed and compared with the raw CNFs (without iron catalyst). Below are the results of samples from the experiment. From figure 1, it can be clearly seen that the CNF are entangled together and have an enormous void volume which indicate large pore volume.

Figure 1: Image of CNF at 10000x magnification

Figure 2 and 3 shows the Fe-CNFs catalyst produced in one hour residence time at different concentration of Fe. It can be seen that Fe and CNFs are easily distinguished with Fe particles had smaller particles size and CNFs have an entangled tube shape. However, figure 3 showed that there are more Fe particles attached to the CNFs.

Figure 2: image at 1 hour and 5 % concentration

Figure 3: image at 1 hour and 10 % concentration

Figure 4 to figure 6 shows the Fe-CNFs produced at 6 hour residence time with different concentration of Fe. For figure 4 and figure 5 it shows Fe particle are properly dispersed with more promising amount of Fe particles attached to CNFs. Meanwhile in figure 6 there are no distinguishes shape between Fe and CNFs indicating that the sample cannot be used due to some errors occurred.

Figure 4: image at 6 hour and 5 % concentration

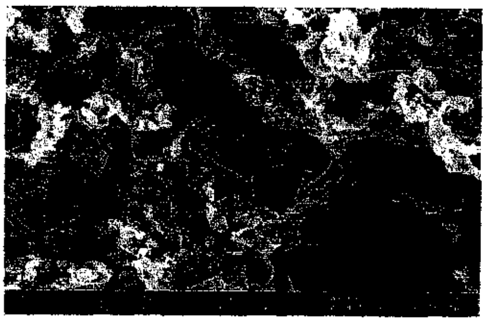

Figure 5: image at 6 hour and 10% concentration

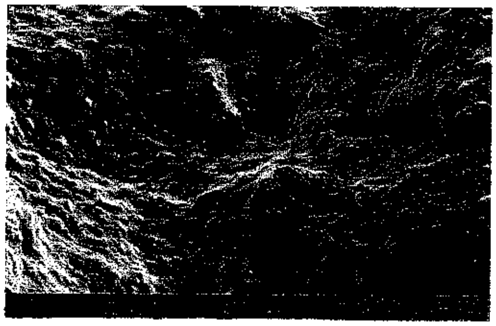

Figure 6: image at 6 hour and 20 % concentration

Figure 7 to figure 9 shows Fe-CNFs catalyst produce at 24 hour residence time with different concentration. Figure 8 show the most properly dispersed and attached of Fe particles onto the CNFs compare to the other images. For figure 9 the images shows that the Fe particles seems to be coagulate and sintering forming a bulk of Fe on the CNFs.

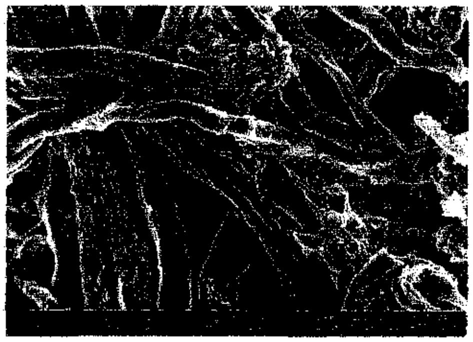

Figure 7: image at 24 hour and 5 % concentration

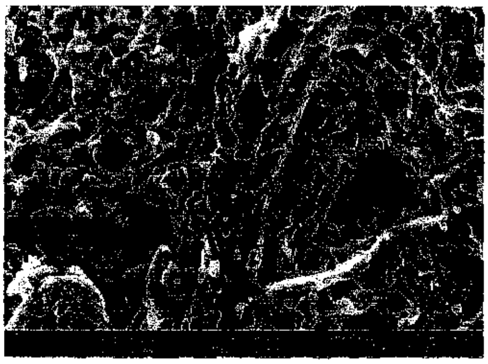

Figure 8: image at 24 hour and 10 % concentration

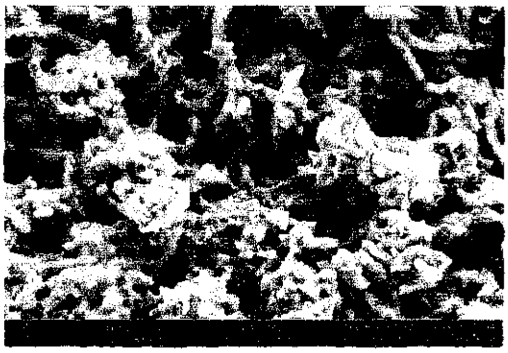

Figure 9: image at 24 hour and 20 % concentration

4.1.2 Energy Dispersion X-ray (EDX)

The chemical characterization of CNF supported iron catalyst is determined by using the EDX analysis. Below are the summarizations of the result.

The calibration standards are:

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM

Table 6: Result from EDX analysis

Variables		Elements	Weight %	Atomic %
Residence time	Concentration			
1 hour	5 %	Fe	28.01	8.62
	10 %	Fe	33.61	10.78
6 Hour	5%	Fe	20.34	4.60
	10%	Fe	23.65	6.88
	20%	Fe	17.49	2.13
24 hour	5%	Fe	33.61	10.98
	10%	Fe	38.71	14.03
	20%	Fe	36.16	13.01

4.2 DISCUSSION

4.2.1 Field Emission Scanning Electron Microscopy (Fe-SEM)

The morphologies of CNFs supported iron catalyst of each sample with different variables were analysed and examined using the Fe-SEM. For each residence time, the best concentration of ferric nitrate solution was chosen.

Table 7: Result from Fe-SEM

Residence time	Concentration of ferric nitrate solution	Figure
1 hour	10 %	3
6 hour	10 %	5
24 hour	10 %	8

From figures 3, it shows that there is an entangled network of CNF with cluster of iron attached to the surface of CNFs. This indicates that irons catalysts are successfully impregnated on the surface of the CNF. As for figure 6 and figure 9, it shows that the iron catalysts are also successfully attached to the CNFs respectively. However, figure 9 show that there is more iron catalyst on the CNFs compared to the others.

4.2.2 Energy Dispersion X-ray (EDX)

From table 6, it shows the weight and atomic percent of iron on the CNFs for each sample with different variables. For each residence time with the 10 % concentration of ferric nitrate solution, it is observed that the highest iron loading is resulted from the highest weight percent onto the CNFs.

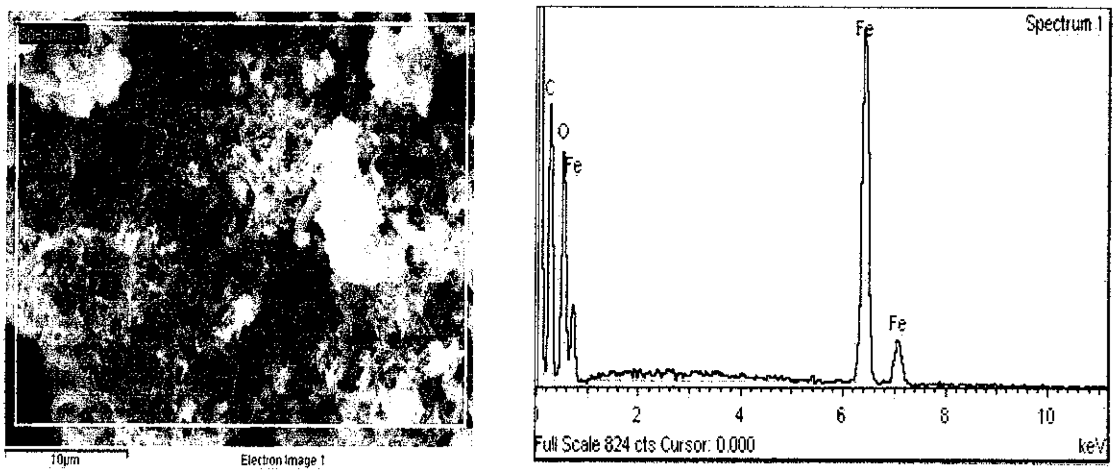

Figure 10: XRD result for 1 hour and 10 % concentration

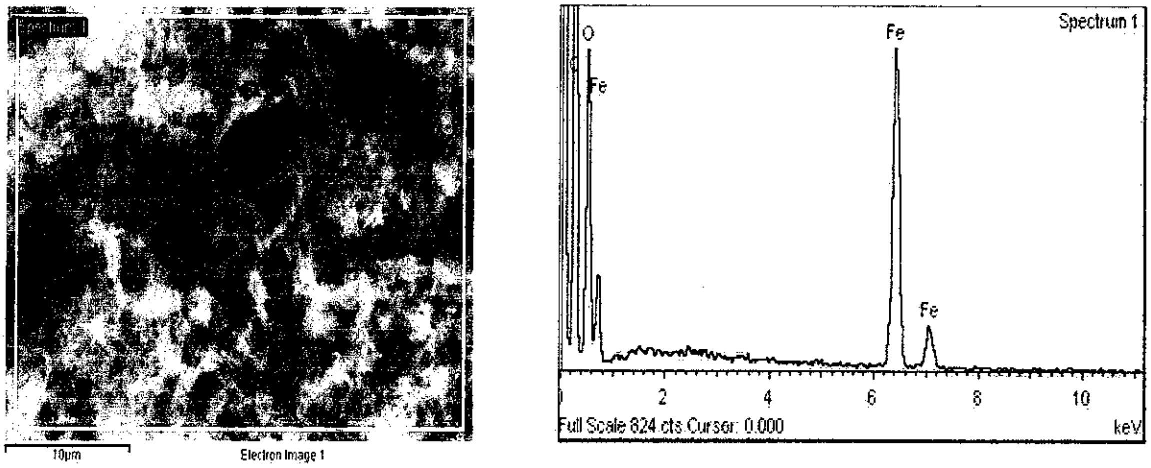

Figure 11: EDX result for 6 hour and 10 % concentration

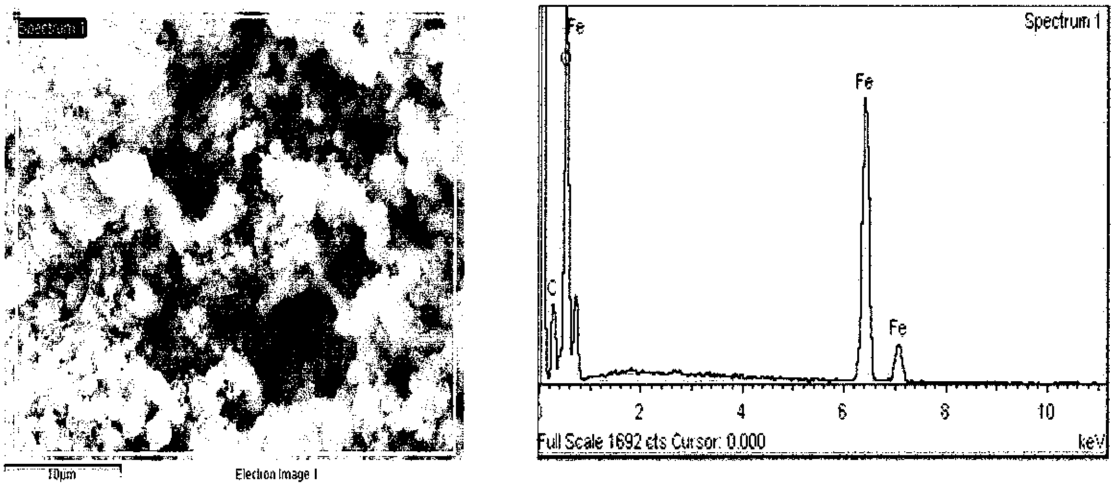

Figure 12: EDX result for 24 hour and 10% concentration

From figure 10, 11 and 12, the graph clearly shows the presence of elements in the samples. For each graph, the iron elements have the highest peak, thus the highest in terms of weight and atomic percent. This has been summarized in table 6. The residence time of 24 hour with 10% concentration of ferric nitrate solution seem to give the highest percent of iron loading onto the CNFs with 38.71 weight% and 14.03 atomic %.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The study on carbon nanofibers (CNFs) has attracted great interest due to its outstanding property as catalyst support. Based on these criteria, CNFs is selected among other studied catalyst support as material for impregnation process using the iron catalyst. The CNFs also chosen due to the problem in catalyst field that required the alteration of the catalyst compared to the modifying the reactor to increase the yield of product. In this research work, the percent of iron loading onto the CNFs is observed through some experiment. Among the parameters carried out in the experiment are residence times during the impregnation and the concentration of ferric nitrate solution. The end results are evaluated comparatively to each other. Based on the result obtained, it is found that the longer residence time during impregnation together with the suitable amount of concentration of ferric nitrate solution gives higher percent of iron loading. The iron catalyst itself is clearly attached to the CNFs without forming any coagulation due to excessive iron catalyst.

The research work of altering the catalyst is important to increase process efficiency and reducing the energy cost. The use of CNFs as catalyst support seems to be the solution over the problems rise in the catalyst field due to its outstanding mechanical, electrical and chemical properties. The study of alteration of catalyst has been conducted throughout series of experiments using different type of variables. By determining the best condition from the variables used, it will improve the catalyst loading and give higher efficiency of the supported catalyst produced.

Through the experiment, the effect of residence time and the concentration of catalyst solution are observed. Based on current work and past studies, it can be concluded that the percentage of catalyst loading onto catalyst support is higher when the residence time is longer and the concentration of catalyst is not too high. The result from 24 hour residence time with 10% concentration of Fe gives more promising result and the highest of metal loading onto the CNFs. In addition, the using various instruments such as Fe-SEM to provide the surface morphology and EDX to provide the chemical characterization.

For recommendation, the impregnation process of iron catalyst onto CNFs should be carried out numerous times at different residence time and different concentration of catalyst solution. This is to observe the effect of both variables toward the catalyst loading. In addition, other variables such as the temperature and pressure can be included in this research work. Testing on a large scale can be done if an agreement with related industry or refinery could be conducted to achieve more accurate result compared to the existing test.

REFERENCES

1) Nelize Maria de Almeida Coelho[a] ; Jomar Livramento Barros Furtado [a] ; Cuong Pham-Huu[b] ; Ricardo Viera [a*]. *"Carbon Nanofibers : a Versatile Catalytic Support",2002.*
2) Ricardo Viera, National Institute for Space Research Brazil. *'Carbon Nanofibers as Macro-structured Catalytic support';*
3) Ebbesen TW; AjayanPM ; *'Large scale synthesis of carbon nanotubes' ; Nature 1992; 358(6383):220-222.*
4) Jong KP; Geus JW *; "Carbon nanofibers- Catalytic synthesis and application. Catalytic Review Science and Engineering 2000";* 42(4): 481-510.
5) J.H Zhou ; M.G. Zhang ; L.Zhao ; P.Li ; X.G. Zhou[*] ; W.K. Yuan. *" Carbon nanofiber/graphite –felt composite supported Ru catalysts for hydrogenolysis of sorbitol"*
6) Cuong Pham-Huu,[a] ; Nicolas Keller, Vladimir V. Roddatis,[b] Gerhard Mestl,[b] Robert Schlo¨ gl[b] and Marc J. Ledoux[a] *" Large scale synthesis of carbon nanofibers by catalytic decomposition of ethane on nickel nanoclusters decoratingcarbon nanotubes"* ;
7) Ping Li[a]; Ting Li[a] ; Jing- Hou Zhou[a] ; Zhi-Jun Sui[a] ; Ying Chun Dai[a] ; Wei Kang Yuan[a,*] ; De Chen[b] *" Synthesis of carbon nanofiber/graphite-felt somposite as catalyst" ;2006.*
8) D.B.Thakur[a] ; R.M.Tiggelaar[b] ; J.G.E. Gardeniers[b] ; L.Lefferts[a] ; K.Seshan[a]. *"Carbon nanofiber based catalyst supports to be used in microreactor:Synthesis and Charachterization."*
9) Kunchan Lee ; Jiujun Zhang; Haijian Wang ; David P. Wilkinson. *"Progress in the synthesis of carbon nanotube- and Nanofiber supported Pt electrocatalysts for PEM fuel cell catalyst " ;*
10) Pham- Huu C; Viera R; Charbonierre L; Ziesel R; Ledoux MJ; *"Composites based on carbon nanotubes deposited on activated support for application in catalyst " ; French pat. 0115178;2001*
11) J. O. Pacheco-Sotelo et al., *"Carbon Nanofibers Synthesized by Glow-Arc High Frequency Discharge,"* Plasma Science, IEEE Transactions on, vol. 35, no. 2, pp. 460-466, 2007.
12) C. Singh et al., *"Synthesis and Characterization of Carbon Nanofibers Produced by the Floating Catalyst Method," J. Phys. Chem. B,* vol. 106, no. 42, pp. 10915-10922, 2002.
13) N. M. Rodriguez, A. Chambers, and R. T. K. Baker, *"Catalytic Engineering of Carbon Nanostructures,"* Langmuir, vol. 11, no. 10, pp. 3862-3866, 1995.

14) S.S Fan; M.G. Chapline; N.R Franklin; T.W. Tombler; A.M. Cassel H.J Dai; *"Self oriented regular arrays of carbon nanotubes and their field emission properties"; Science 283(1999/), 512-514*

15) E.Hammel; X.Tang; M.Trampert; T.Schmit; K.Mauthner; A.Eder; P.Potshke; *" Carbon nanofibers for composite applications"; carbon 42 (2004),1153-1158*

16) A.C Dillon; K.M Jones; T.A. Bekkedahl; C.H Kiang; D.S. Bethune; M.J Hebben; *"Storage of hydrogen in single walled carbon nanotubes "; Nature 386 (1997),377-379*

17) J.Kong; N.R.Franklin; C.W.Zhou; M.G Chapline; S.Peng; K.J.Cho; H.J. Dai; *"Nanotube molecular wores as chemical sensors"; Science 287 (2000), 622-625*

18) A.M Fennimore; T.D Yuzvinsky; W.Q Han; M.S. Fuhre; J.Cummings; A.Zettl; *"Rotational Actuators based on carbon nanotubes"; Nature 424,(2003),408-410.*

19) Wenzhen Li[a] ; Changhai Liang[a] ; Jieshan Qiu[b] ; Weijiang Zhou[a] ; Hongmei Han[b] ; Zhaobin Wei[a] ; Gongquan Sun[a] ; Qin Xin[a,*] *"Carbon nanotubes as support for cathode catalyst of direct methanol fuel cell";2002.*

20) A.V Melechko; V.I Merkulov; T.E Mcknight; M.A Guillorn; K.L Klein; D.H Lowndes; M.L Simpsons; *"Vertically aligned carbon nanofiber and related structure: controlled synthesisi and direct assembly"; J.Apl. Phys. 97 (2005)-04301.*

21) M. Campanati, G. Fornasari, and A. Vaccari, *"Fundamentals in the preparation of heterogeneous catalysts,"* Catalysis Today, vol. 77, no. 4, pp. 299-314, Jan. 2003.

22) Anne-Claire Dupuis; *"The catalyst in the CCVD of carbon nanotubes—a review";* Progress in Materials Science 50 (2005) 929–961

23) Atsushi Tanaka; Seong-Ho Yoon; Isao Mochida; "*Formation of fine Fe-Ni particles for non-supported catalytic synthesis of uniform carbon nanofiber*"; 28 Dec 2003.

24) Xuezhi Duan; Gang Qian; Xinggui Zhou; Zhijun Sui; De Chen; Weikang Yuan; " *Tuning the size and shape of Fe nanoparticles on carbon nanofibers for catalytic ammonia decomposition*'; 22 May 2010.