APPLICATION OF CARBON NANOMATERIALS AS SUPPORTS IN HETEROGENEOUS CATALYSIS

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CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
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by

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

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

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(Dr. Moulay Rachid Babaa)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

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.

MOHD SHARIFUDDIN BIN AHMAD FUAT

ABSTRACT

The overall objective of this project is to investigate the application of carbon nanomaterials as support in heterogeneous catalysis. In the study, carbon nanomaterials such as single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), carbon replica of zeolites and activated carbon are proposed as support in heterogeneous catalysis. The performance of carbon nanomaterials used will be studied and the comparison with activated carbon will be made to determine the effectiveness of the carbon nanomaterials as potential support in heterogeneous catalysis. The heterogeneous distribution of the nanoparticles that will be use such as nickel, iron and cobalt were evidenced by bulk and surface structural and compositional characterizations, that is, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction, Fourier Transform Infrared (FTIR) and thermo gravimetric analysis (TGA). The significant of the application of carbon nanomaterials will be observed with the improvement in the catalytic efficiency of the chemical reaction. Various applications of carbon nanomaterials as support in heterogeneous catalysis can be seen in pharmaceutical, electrical, optical and mechanical applications.

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With highest Gratitude,

……………………………….

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Abbreviations and Nomenclatures

CNT	Carbon Nanotube
SWNT	Single-walled nanotube
MWNT	Multi-walled nanotube
TEM	Transmission electron microscope
SEM	Scanning electron microscope
XRD	X-ray diffraction
FTIR	Fourier transform infrared
KBr	Potassium Bromide
TGA	Thermogravimetric Analysis

1 INTRODUCTION

1.1 Background of study

Nowadays, process development in modern materials is increasingly adapting a number of high throughput experimental strategies to efficiently study and optimize heterogeneous catalytic processes. Significant economic benefits had span many industries due to rapid development of highly active and selective catalyst. The rising of nanotechnologies also could greatly benefit from high throughput experimental methodology as the industry strive to control and harness the advantages of well-defined nanoscale materials. Some examples of useful nanostructure building blocks are tubes, rods, spheres, well-defined synthetic oligomers (i.e. molecular wires, oligonucleotides) or molecular assemblies, self-assembled biological systems, polymers, and other structures. Carbon nanotubes (CNTs) are very important example of nanoscale materials that critically depend on catalyst development.

Carbon nanotubes are an interesting new molecular form of carbon in the fullerene family due to their unique electronic and mechanical properties and also their resistance to acid/basic media. The extraordinary mechanical and electronic properties of single-walled CNTs (SWNTs) as well as multi-walled CNTs (MWNTs) have led to intensive research activities across the world investigating their various potential applications such as gas sensors and composites fabrication. However, the inert nature of the surface of nanotubes is unfavorable and need to be improved. It is necessary to modify the surface of nanotubes to improve the interaction of CNTs and foreign molecules. In this study, the oxygen containing groups which are interesting to improve the interaction of CNTs with the solvent matrix are formed on the surface of nanotubes by chemical treatment in which nitric acid is used. Although the chemical treatment by using nitric acid has a lengthy process, it is still the most used functionalization method.

The nanoparticles that are synthesized in this study are zinc oxide nanoparticles. The synthesis process follow the hydrothermal route where zinc nitrate tetra hydrate and sodium hydroxide (salt) are mix together in the solution phase and heat under certain condition. Multi-walled nanotubes will be employed as support in the new nanoparticles produce and the catalytic activity of the new material will be test by a reaction such as benzene hydrogenation.

1.2 Problem Statement

The discovery of carbon nanomaterials such as carbon nanotubes had impact a wide range of application. Carbon nanotubes (CNTs) for example have captured researcher's interest since their discovery. The support of carbon nanomaterials in heterogeneous catalysis significantly enhance the catalytic efficiency of nanoparticles like platinum, Pt; palladium, Pd; nickel, Ni; and ruthenium, Ru for many reaction. Carbon nanotubes supported nanoparticles have attracted much interest in many important research fields due to their high thermal and electronic conductivities, good resistance to acidic/basic chemicals at high temperature, controllable porosity, and tuneable surface properties [1, 2]. The main focus in this project is to investigate the application of carbon nanomaterials as support in heterogeneous catalysis particularly to improve the effectiveness of nanomaterials as support in term of increasing the life span of the catalyst, thus reduce the operation cost for catalyst. The application of combination of carbon nanomaterials and catalyst is widely used in variety of electrical, mechanical and pharmaceutical applications. Thus, this will help to accelerate the development of nanoscale science and technology.

1.3 Objectives

The objective of the research is to investigate the application of carbon nanomaterials which are single-wall nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), carbon replica of zeolites and activated carbon as support in heterogeneous catalysis. The performance of all carbon nanomaterials will be observed and they will be compared to activated carbon to determine the effectiveness of the carbon nanomaterials. The project also is done to obtain the homogeneously dispersed nanoparticles via functionalized carbon nanotubes. The performance of the carbon nanomaterials as potential support in heterogeneous catalysis will be determined from the capability of enhancing the efficiency of the chemical reaction.

1.4 Scope of study

The project is divided into three phases in order to achieve the objectives. Firstly, the backgrounds of carbon nanomaterials such as multi-walled carbon nanotubes are studied. The objectives, methodology and current technologies as well as implementation are identified and understood. Next phase is the preparation for the experimental work such as preparing the solution and research on the equipments used for characterization such as Fourier-Transform Infrared (FT-IR), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and X-ray diffraction (XRD).The samples produced from the experiment will be evaluated for performance test. The final phase is the evaluation and presentation of the result achieved from the experiment.

2 LITERATURE REVIEW AND THEORY

2.1 Nanomaterials

The applications that have morphological features smaller than a one tenth of a micrometer in at least one dimension are known as nanomaterials. Some authors restricting their size to as low as 1 to ~30 nm, a logical definition would situate the nanoscale between microscale (0.1 micrometer) and atomic/molecular scale (about 0.2 nanometers). The great increased ratio of surface area to volume present in many nanoscale materials makes possible new quantum mechanical effects, like the "quantum size effect" where the electronic properties of solids are altered with the great reductions in particle size. This can only become pronounced when the nanometer size range is reached. The physical properties also will be altered in a certain number with the change from macroscopic systems. This is really related with nanotechnology which is the synthesis and application of ideas from science and engineering towards the understanding and production of novel materials and devices. These products generally make many use of physical properties associated with small scales.

Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macro scale, thus enabling unique applications. For example, stable materials can turn into combustible (aluminum); inert materials attain catalytic properties (platinum); and insulator becomes conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as an effective chemical catalyst at nanoscales. Nanosize powder particles (a few nanometers in diameter, also called nanoparticles) are potentially important in ceramics, powder metallurgy, the achievement of uniform nanoporosity and similar applications. A serious technological problem that impedes such applications is the strong tendency of small particles to form clumps ("agglomerates"). However, a number of dispersants such as ammonium citrate (aqueous) and imidazoline or oleyl alcohol (nonaqeous) are promising solutions as possible additives for deagglomeration.

2.1.1 Fullerenes

Materials referred to as "nanomaterials" generally fall into two categories: fullerenes, and inorganic nanoparticles. The fullerenes are a class of allotropes of carbon which conceptually are graphene sheets rolled into tubes or spheres. These include the carbon nanotubes which are of interest both because of their mechanical strength and also because of their electrical properties.

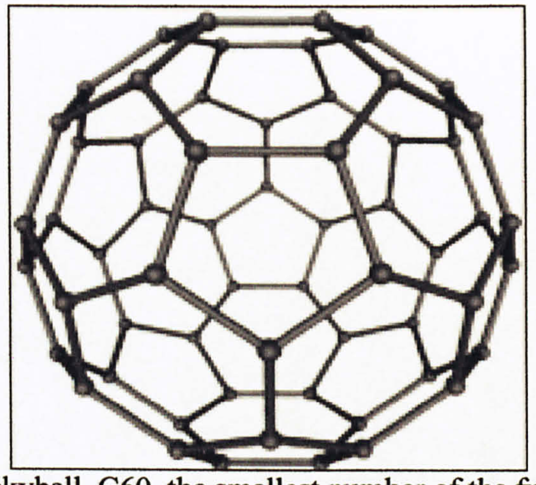


Figure 1: Buckyball, C60, the smallest number of the fullerene family

The chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely this will continue to be for a long time. Such as in April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure of resistant bacteria and even target certain types of cancer cells such as melanoma. In the field of nanotechnology, heat resistance and superconductivity are among the properties attracting intense research. [12]

2.1.2 Nanoparticles

Nanoparticles are interest due to their mechanical, electrical, magnetic, optical, chemical and other properties. Nanoparticles have been used as chemical catalysts. They have great scientific interest as they are effectively a link between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often different. Nanoparticles exhibit a number of special properties relative to bulk material. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same ductility as bulk copper. The change in properties is not always desirable. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. For example gold nanoparticles appear deep red to black in solution [13]. A very high surface area to volume ratio of nanoparticles also provides a remarkable driving force for diffusion, especially at elevated temperatures. Sintering is possible at lower temperatures and over shorter durations than for larger particles. This theoretically does not affect the density of the final product, though flow difficulties and the tendency of nanoparticles to agglomerate do complicate matters. The surface effects of nanoparticles also reduce the incipient melting temperature.

2.2 Carbon nanotubes

Carbon nanotubes, also called CNTs are tubes of pure carbon, a few nanometers in diameter and long. They can be divided into single-walled and multi-walled (tubes within tubes). The main characteristics of CNTs are electrically conducting or semiconducting; stronger than steel; tougher than Kevlar; and fireproof. Nanotubes are members of the fullerene (form of carbon having a large molecule consisting of an empty cage of 60 or more carbon atoms) structural family, which also includes the spherical buckyballs. The ends of nanotubes are capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotubes is on the order of a few nanometers (approximately 1/50,000th of the width of a human hair), while they can be up to several millimeters in length.

Applied quantum chemistry, specifically, orbital hybridization is used to describe the nature of the bonding of a carbon nanotubes. Similar to graphite, the chemical bonding of nanotubes is composed entirely of sp^2 bonds. This bonding structure is stronger than the sp^3 bonds found in diamonds, provides the molecules with very unique strength. Nanotubes, naturally support themselves into "ropes" that held together by Van der Waals forces. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving the possibility of producing strong, unlimited-length wires through high-pressure nanotubes linking.

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotubes was tested to have a tensile strength of 63 gigapascals (GPa).
All carbon nanotubes are very good thermal conductors along the tube, exhibiting a property known as 'ballistic conduction', but good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature; compared to copper which is a well-known metal for its good thermal conductivity, which transmits 385 watts per meter per K. The temperature

stability of carbon nanotubes is estimated to be up to 2800°C in vacuum and about 750°C in air. The strength and flexibility of carbon nanotubes hold the potential of use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering [9].

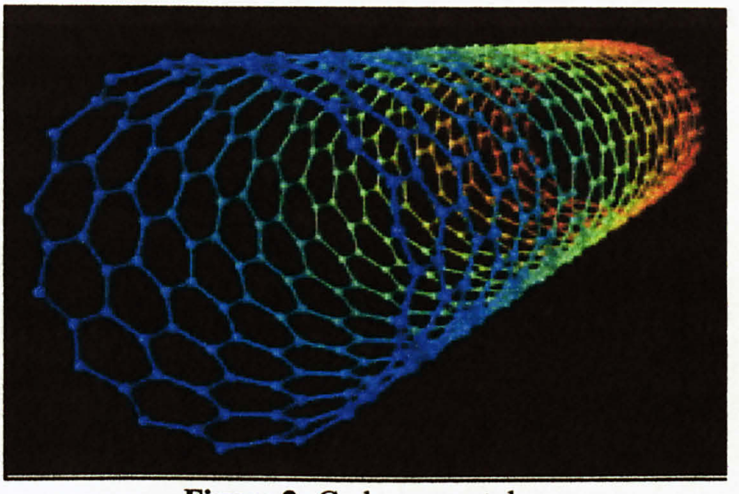


Figure 2: Carbon nanotubes

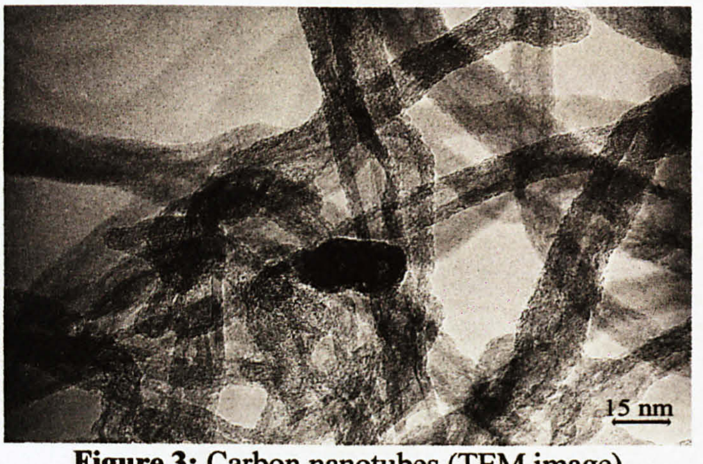


Figure 3: Carbon nanotubes (TEM image)

2.2.1 Single-walled carbon nanotubes (SWNTs)

Most single-walled nanotubes (SWNTs) have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. Single-walled nanotubes are an essential type of carbon nanotubes because they show electric properties that are not shared by the multi-walled carbon nanotubes (MWNTs) variants. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors.

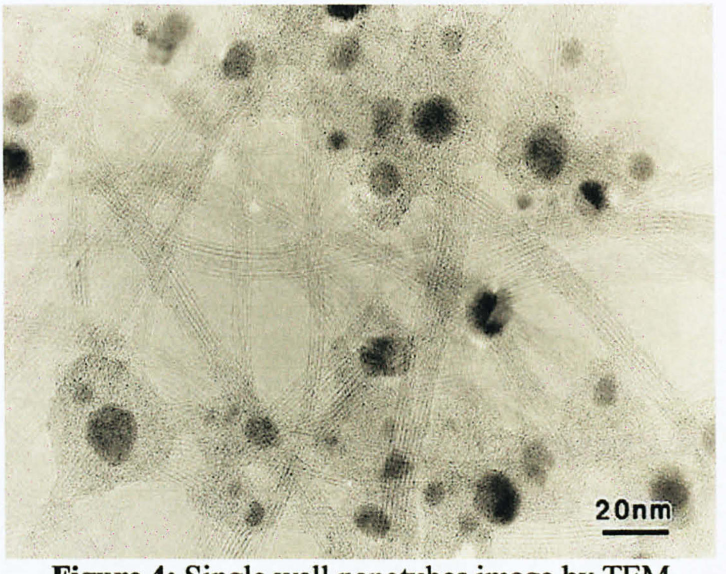


Figure 4: Single wall nanotubes image by TEM

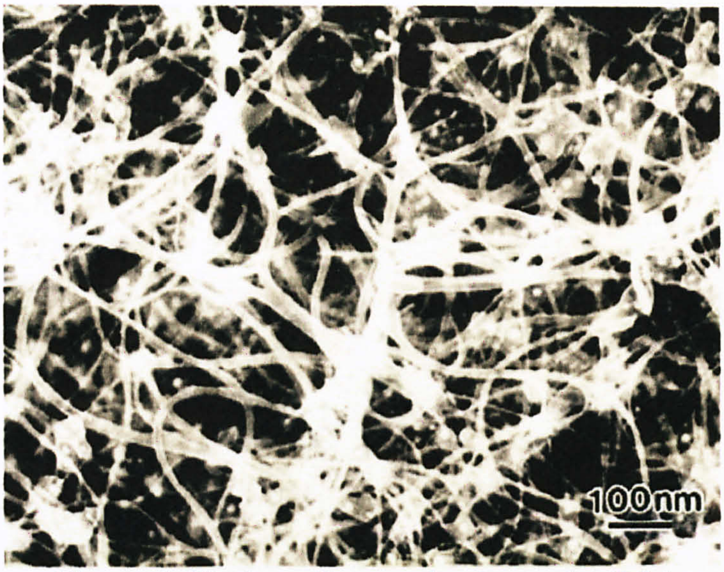


Figure 5: Single wall nanotubes image by SEM

2.2.2 Multi-walled carbon nanotubes (MWNTs)

A Multi-walled nanotubes (MWNTs) contains multiple layers of graphite rolled in on them to form a tube shape. There are two models which can be used to describe the structures of multi-walled nanotubes. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g. at (0, 8) single-walled nanotube (SWNT) within a larger (0, 10) single-walled nanotubes. In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 3.3 Å (330 pm).

The special place of double-walled carbon nanotubes (MWNTs) must be emphasized here because their morphology and properties are similar to SWNT but their resistance to chemicals is significantly improved. This is especially important when functionalization is required (grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotubes and thus modifying both its mechanical and electrical properties. In the case of MWNT, only the outer wall is modified.

2.2.3 Properties of CNTs

Strength

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of their tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain the tubes undergo before fracture by releasing strain energy. CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional or bending stress. Below is **Table 1** show the comparison of mechanical properties of single-walled nanotubes and multi-walled nanotubes.

Table 1: Comparison of Mechanical Properties of SWNT and MWNT

Material	Young's Modulus (TPa)	Tensile Strength (GPa)	Elongation at Break (%)
SWNT	~1 (from 1 to 5)	13-53^E	16
MWNT	0.8-0.9^E	150	N/A

E = Experimental observation

Simple geometrical considerations suggest that carbon nanotubes should be much softer in the radial direction rather than along the tube axis. TEM observation of radial elasticity also suggested that even the van der Waals forces can deform two adjacent nanotubes [13].

Kinetic

Multi-walled nanotubes, multiple concentric nanotubes nested within one another, exhibit a striking telescoping property whereby an inner nanotubes core may slide, almost without friction, within its outer nanotubes shell thus creating an atomically perfect linear or rotational bearing. A true example of the great molecular technology is the precise positioning of atoms to create useful machines such as the world's smallest rotational motor.

Electrical

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair ($n=m$) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting. In theory, metallic nanotubes can carry an electrical current density of 4×10^9 A/cm^2 which is more than 1,000 times greater than metals such as copper [13].

Thermal

It is expected that all nanotubes are very good thermal conductors along the tube. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per Kelvin at room temperature; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 watts per meter per K. The temperature stability of carbon nanotubes is estimated to be up to 2800°C in vacuum and about 750°C in air.

Unique

Carbon nanotubes (CNTs) provide a variety of unique performance attributes to a long list of markets and applications. The table below shows the specific CNT attributes that will be crucial to enable breakthrough performance improvements in wide range of application.

		Markets									
		Energy		Electronics		Automotive		Stuctural Composites		Others	
		Battery	Wind	Semicon and Disk Drive	ITO replacement	Electrostatic painting	Fuel systems	Aerospace	Sporting goods	Thermal Management	Flame Retardant
CNT Performance Attribute	High electrical conductivity	X		X	X	X	X	X			
	High thermal conductivity	X		X						X	X
	High tensile strength	X	X					X	X		
	High elasticity		X					X	X		
	High absorbency		X			X		X	X		
	High aspect ratio (L/D)	X	X	X	X	X	X	X	X	X	X
	Low weight		X			X	X	X	X		

Figure 6: CNTs performance attribute

2.2.4 Application of carbon nanotubes

The strength and flexibility of CNTs makes them of potential use in controlling other nanoscale structures, which suggest that they play an important role in nanotechnology engineering. It has been tested that the highest tensile strength an individual multi-walled carbon nanotube is 63 GPa.

Structure

Because of the carbon nanotube's superior mechanical properties, many structures ranging from everyday items like clothes and sports gear to combat jackets and space elevators. However, the space elevator will require further efforts in refining carbon nanotube technology, as the practical tensile strength of carbon nanotubes can still be greatly improved.

Electrical

Their unique dimensions to an unusual current conduction mechanism make them ideal components of electrical circuits. For example, they have shown to exhibit strong electron-phonon resonances, which indicate that under certain direct current (DC) bias and doping conditions their current and the average electron velocity, as well as the electron concentration on the tube oscillate at terahertz frequencies.

Reduce oxygen in fuel cells

Nitrogen-doped carbon nanotubes may replace platinum catalysts used to reduce oxygen in fuel cells. A forest of vertically-aligned nanotubes can reduce oxygen in alkaline solution more effectively than platinum, which has been used in such applications since the 1960s. The nanotubes have the added benefit of not being subject to carbon monoxide poisoning.

2.2.5 Carbon replica of Zeolites

Carbon replica of zeolites is a micro porous carbon with narrow pore size distribution and extremely large specific surfaces. The synthesis procedure for carbon replication of zeolites consists of several steps such as pore filling of the parent zeolites with the carbon precursor, carbonization by thermal treatment, and subsequent liberation of the carbon replica from the zeolites framework by dissolving in HF. During the pore filling different processes like diffusion, adsorption, desorption, and polymerization of precursor molecules occur simultaneously. Since these processes compete partially, the quality of the resulting carbon should depend on the relative rates of the individual processes. In case of incomplete pore filling the carbon framework will be less stable and the pore structure of the carbon material will be less well defined.

2.2.6 Activated carbon (for comparison)

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. [5] The word activated in the name is sometimes substituted by active. Due to its high degree of micro porosity, just one gram of activated carbon has a surface area of approximately 500 m^2 (or about 2 tennis courts), as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material. Activated carbon is usually derived from charcoal.

Under an electron microscope, the high surface-area structures of activated carbon are revealed. Individual particles are intensely convoluted and display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These microspores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behavior are usually done with nitrogen gas at 77 K under high vacuum, but in everyday terms activated carbon is perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of an atmosphere. Physically, activated carbon binds materials by Van der Waals force or London dispersion force.

Activated carbon does not bind well to certain chemicals, including alcohols, glycols, ammonia, strong acids and bases, metals and most inorganic, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does adsorb iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is used as an indication of total surface area.

Activated carbon can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulfide (H_2S), ammonia (NH_3), formaldehyde (HCOH), radioisotopes iodine-131 (^{131}I) and mercury (Hg). This property is known as chemisorptions. In this project, activated carbon will be used for the comparison among others carbon nanomaterials used.

2.3 Review of related article

The role of nanomaterials in industries is growing. There are many literatures that related to the application of carbon nanomaterials as support in heterogeneous catalysis. The potential of carbon nanomaterials as support for nanoparticles have attracted many researchers from different fields to discover the effect of carbon nanomaterials in chemical reaction. The advantages of carbon nanomaterials such as carbon nanotubes, nanofibers and diamond like carbon have been studied to clearly understand the effectiveness of the carbon nanomaterials as support in heterogeneous catalysis [3]. Four carbon nanomaterials will be tested in these projects that are single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), carbon replica of zeolites and activated carbon.

As for the nanoparticles that will be use is zinc oxide. An example from the review is the investigation of NH3 decomposition reaction over Fe-Co bimetallic nanoparticles and employed carbon nanotubes (CNTs) to support metallic phases and to provide efficient electron transfer during the reaction is made. The results show great promise of carbon nanotubes as support to the catalytic NH_3 decomposition reaction where it was found to improve the thermal stability rather than the turnover rate of nanoparticles.

Another related article, J. AM. Chem Soc. *Application of carbon nanotubes as support in heterogeneous catalysis*, 1994 (116) give explanation on how well carbon nanotubes as support in heterogeneous catalysis. Carbon nanotubes contains graphitic carbon needles, ranging from 4 to 30 nm in diameter and up to 1 pm in length, in addition to polyhedral carbon particles with onion like shell structures, 5-20 nm in diameter. The surface area of this solid was determined by N2 physisorption at 77 K and is about 27 m2 g-l. The supported Ru catalysts were prepared by adsorption of a ruthenium precursor in toluene solution. Ruthenium 2, 5-pentanedionate (3 1.85 mg, Aldrich) was dissolved in toluene (4 cm3, SDS, 99.3%) and then contacted for 72 h with carbon nanotubes material (0.8 8); it was found that this carbon material is insoluble in toluene.

Toluene was removed by evaporation, and the residue dried in a vacuum desiccator at 353 K overnight. The resulting solid was treated for 3 h under a stream of nitrogen at 523 K and then reduced for 1 h in a stream of diluted hydrogen (H2/N2 = 10/90 mol/mol) according to published procedures. The Ru/nanotubes catalyst contains 0.2 wt % Ru as determined by chemical analysis. The catalyst was characterized by hydrogen chemisorption and transmission electron microscopy. The hydrogen chemisorptions were carried out in a static volumetric apparatus. The adsorption isotherm was determined at 373 K in the 6.6-33 kPa pressure range. The hydrogen monolayer coverage was calculated by extrapolating to zero pressure. From this value and using unity H/Ru stoichiometry, the percentage of ruthenium atoms present at the surface was determined (dispersion = 30%; Ru particle size = 3.5 nm). For the purpose of TEM characterization, a Ru/nanotube suspension in ethanol was sonicated and deposited on a copper grid covered with a carbon film; the examinations were carried out with a JEOL 200 CX apparatus with an accelerating voltage of 100 kV.

3 METHODOLOGY

3.1 List of Chemicals

Due to some problem in the unavailability of the chemicals, the author starts the experiment with multi-walled carbon nanotubes as carbon nanomaterials and will repeat the experiment in the future. Below are the chemicals that will be use during the experiment.

1. Multi-walled carbon nanotubes
2. 69% of Nitric Acid
3. Silica Oil
4. Zinc Nitrate Tetra hydrate
5. Sodium Hydroxide
6. Ethanol

Possible test/probe reaction:

Ammonia decomposition

$NH_3 + H \rightarrow NH_2 + H_2$

Hydrogenation of cinnamaldehyde

$C_9H_8O + H2 \rightarrow C_9H_{10}O$

Hydrogenation of benzene

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$

3.2 Project Activities and Research Methodology

1. Bibliography study.
2. Identifying carbon nanomaterials, nanoparticles and chemical reaction that will be used for the project.
3. Preparation of tools and equipments.
4. Experimental procedures
    a. Functionalization of MWNTs

b. Synthesis of zinc oxide nanoparticles
c. Synthesis of MWNTs-supported zinc oxide nanoparticles

5. Sample characterization
    a. Fourier Transform Infrared (FTIR)
    b. Powder X-ray diffraction (XRD)
    c. Scanning Electron Microscopy (SEM)
    d. Transmission Electron Microscopy (TEM)
    e. Thermo Gravimetric Analysis (TGA)

Experimental Procedure

Characterization of pristine Multi Walled Nanotubes (MWNTs) using FTIR

1. 1 mg of MWNTs is grinded with a specially purified salt (299 mg of potassium bromide) finely (to remove scattering effects from large crystals).
2. This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.
3. Measurement is done and the result is analyzed to determine the functional groups within the peaks.

Functionalization of MWNTs using nitric acid

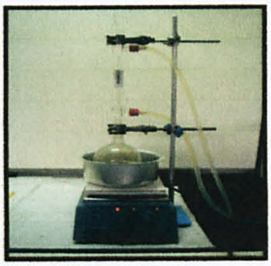
4. 40 mg of MWNTs and 100 mL of nitric acid (69%) HNO_3 was stirred with reflux at 1hour and 30 minute at 100°C temperature under ventilation in a fume hood.
5. The resulting solution was repeatedly washed with distilled water until the pH become neutral.
6. Filtration of the solution was done to get the sample that was functionalized MWNTs.
7. The sample was dried in vacuum oven at 70°C for storage.

Flow process of functionalization of multi-walled nanotubes (MWNTs) with nitric acid.

Acid Treatment (MWNTs + HNO_3)

↓

Heating at reflux condition



↓

Filtration under vacuum

↓

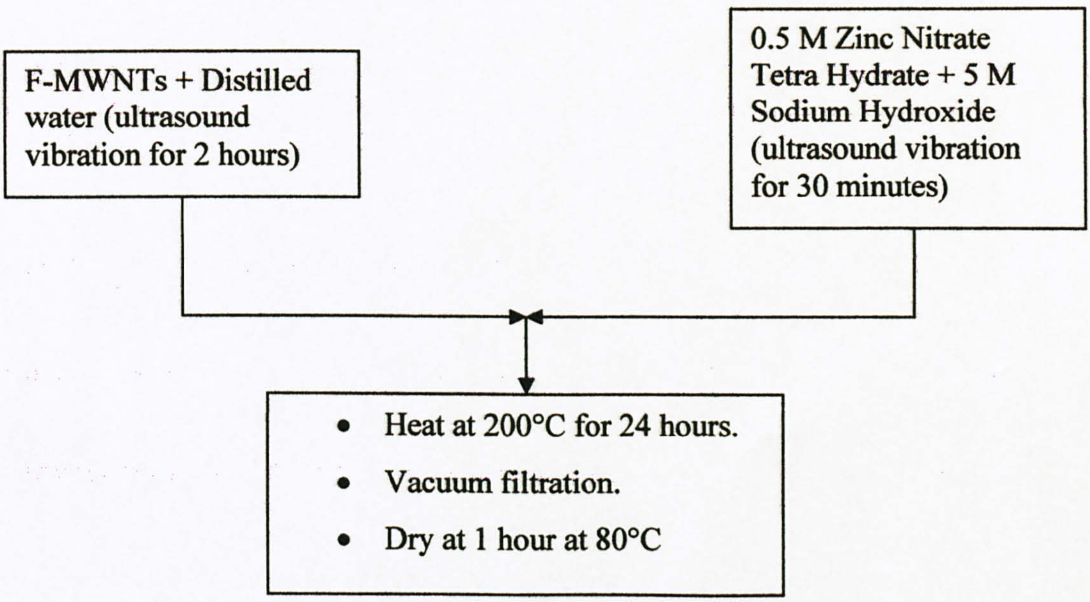
Functionalized MWNTs (F-MWNTs) was stored at high temperature

<u>Characterization of functionalized Multi Walled Nanotubes (MWNTs) using FTIR</u>

8. The same steps as characterization of pristine MWNTs were done to get the result of FTIR for functionalized MWNTs.
9. The result of FTIR for both pristine and functionalized MWNTs was compared to determine the functional groups present in the sample.

Synthesis of Zinc Oxide Nanoparticles

10. 40 mg of functionalized MWNTs were dissolved in distilled water.
11. 0.5 M of zinc nitrate tetra hydrate and 5 M of sodium hydroxide solutions were prepared in distilled water.
12. MWNTs solutions and sodium hydroxide solutions were slowly added to the zinc nitrate tetra hydrate solution under manual stirring followed by sonication for 30 min to obtain homogeneous solution.
13. 10 mL of the above solution was loaded into a 20 mL of Teflon-lined autoclave, which was subsequently filled with 2 mL of absolute ethanol.
14. The autoclave was sealed and maintained at temperature of 200 °C and then allowed to cool down to room temperature naturally.
15. The precipitates were filtered, washed with distilled water to remove the soluble nitrates and with ethanol to reduce agglomeration, and later dried for one hour at 80 °C. New material formed here will undergo characterization.



Test Reaction (Hydrogenation of Benzene to cyclohexane) for new material

Objective: To evaluate the catalytic activity of MWNTs supported Zinc Oxide nanoparticles.

16. Reaction was carried out in a reactor under atmospheric pressure.
17. H_2 gas was employed as reductant and carrier gas.
18. H_2 flow was 40 $mL.min^{-1}$.
19. 100 mg catalyst was loaded into reactor and reduced in-situ at 400°C for two hours before the reaction was performed.
20. 1 L benzene was injected into the reactor every time.
21. The product and reactant were analyzed by gas chromatograph.

3.3 Key Milestone and Gantt chart

3.3.1 Final Year Project One (FYP 1)

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■											
3	Submission of Preliminary Report				X											
5	Project Work					■	■	■								
6	Submission of Progress Report									X						
7	Seminar (compulsory)										■	■	■	■		
8	Oral Presentation														X	

Remarks;

X: Suggested milestone

■: Process

3.3.2 Final Year Project Two (FYP 2)

No	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Characterization and functionalization of pristine MWNTs															
2	Submission of Progress Report 1				X											
3	Characterization of functionalized MWNTs (project work continue)															
4	Submission of Progress Report 2									X						
5	Seminar (compulsory)															
6	Project work continue (Samples undergo test reaction), data gathering and analysis of results.															
7	Poster Exhibition												X	X		
8	Submission of Dissertation (soft bound)														X	
9	Oral Presentation															X
10	Submission of Project Dissertation (Hard Bound)															X

Remarks;

X: Suggested milestone

: Process

3.4 Tools and Equipments Required

3.4.1 Fourier Transform-Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a tool that identifies types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR is used for identifying chemicals that are either organic or inorganic. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Bonds and groups of bonds vibrate at specific frequencies.

A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are specific to that molecule. FTIR spectroscopy does not require a vacuum condition since neither oxygen nor nitrogen can absorb infrared rays. FTIR analysis can be applied to small quantities of materials, whether solid, liquid, or gaseous. FTIR shows formation of oxygen containing groups such as C=O and COOH.

3.4.2 X-Ray Diffraction (XRD)

Use to find the geometry or shape of a molecule using X-rays. It is based on the elastic scattering of X-rays from structures that have long range order. Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials. Powder diffraction is also a common method for determining strains in crystalline materials.

3.4.3 Scanning Electron Microscope (SEM)

Scanning electron microscope produces images by probing the specimen with a focused electron beam that is scanned across a rectangular area of the specimen. At each point on the specimen the incident electron beam loses some energy, and that lost energy is converted into other forms, such as heat, emission of low-energy secondary electrons, light emission (cathodoluminescence) or x-ray emission. The display of the SEM 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 an SEM is about an order of magnitude poorer than that of a TEM. However, because the SEM image relies on surface processes rather than transmission it is able to image bulk samples up to several centimeters in size (depending on instrument design) and has a much greater depth of view, and so can produce images that are a good representation of the 3D structure of the sample.

3.4.4 Transmission Electron Microscope (TEM)

Transmission electron microscope uses a high voltage electron beam to create an image. The electrons are emitted by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at +100keV (40 to 400 keV) with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the lens system of the microscope. The spatial variation in this information (the "image") is viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintilla or material such as zinc sulfide. The image can be photographically recorded 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.

Resolution of the TEM is limited primarily by spherical aberration, but new generations of aberration correctors have been able to partially overcome spherical aberration to increase resolution. Software correction of spherical aberration for the High Resolution TEM (HRTEM) has allowed the production of images with sufficient resolution to show carbon atoms in diamond separated. 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 for the characterization of the result in this project.

3.4.5 Thermo gravimetric analysis (TGA)

In this project, the author also uses TGA as a type of testing method that is performed on the samples to determine changes in weight in relation to change in temperature. The analysis of TGA result relies on the precision of three measurements; weight, temperature, and temperature change. TGA also can be use to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, and solvent residues. The catalyst purity and stability with respect to oxidation was investigated 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.

3.4.6 Nitrogen Adsorption (BET)

Brunauer, Emmett, Teller (BET) analysis revealed that functionalization causes generation of defects on the sidewalls and opening of the ends of CNTs. It is important analysis technique for measurement of the specific surface area of a material and it follows BET theory which is a rule for physical adsorption of gas molecules on a solid surface. It is important to indicate the increase in specific surface area of pristine and functionalized CNTs.

4 RESULT AND DISCUSSION

4.1 Sample analysis and characterization

All the samples from the experiment will be analyzed and the characterization will be done. Some of the samples were sent outside for characterization purposes. The related tools and equipment used for the sample analysis and characterization as mentioned in chapter 3 help in determining the effectiveness of the carbon nanomaterials used as support to the heterogeneous catalysis.

4.2 FTIR

Figure 7 below shows the result of Fourier Transform Infrared (FTIR).

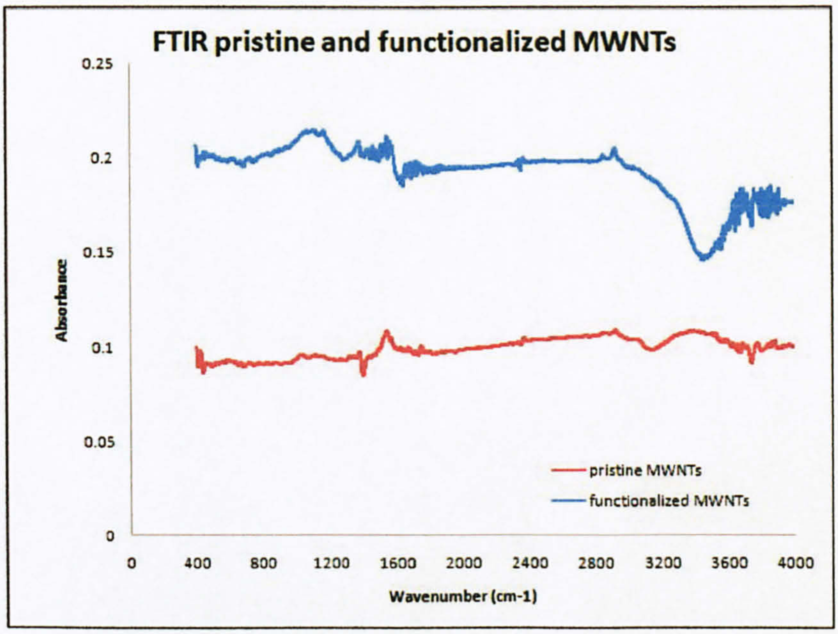


Figure 7: FTIR result for pristine and functionalized MWNTs

4.2.1 Discussion of FTIR result

Nanotubes with the presence of van der Waals attraction between tubes which are hydrophobic and due to their carbonic nature, they exhibit low dispersibility in water and organic solvents. However, after functionalization of MWNTs with nitric acid, they show hydrophilic behaviors. They show better dispersibility particularly due to the OH groups formed in the acid that make hydrogen bonding with water molecules.

Figure 7 above are FTIR spectra of pristine and functionalized MWNTs which are plotted based on Absorbance (Abs) versus Wave number (1/cm). The main concern is the FTIR spectra of functionalized MWNTs. From Figure 7, the peaks which are identified at 3274.90, 1325 and 1700 cm $^{-1}$ characterize C-O, C=O and O=H bonds in functionalized multi-walled nanotubes, MWNTs. The peaks at 1700 and 3500 cm^{-1} can be attributed to acidic group like carboxyl, phenol and lactol. Meanwhile, peak at 1581.52 characterize C=C bond in CNTs which is appeared after disappearing of bond symmetry because of connection of oxygenated functional group. The results of FTIR also proved to be the evidence of surface functionalization and peaks identified at certain wave number characterize certain functional group in functionalized MWNTs.

4.3 XRD

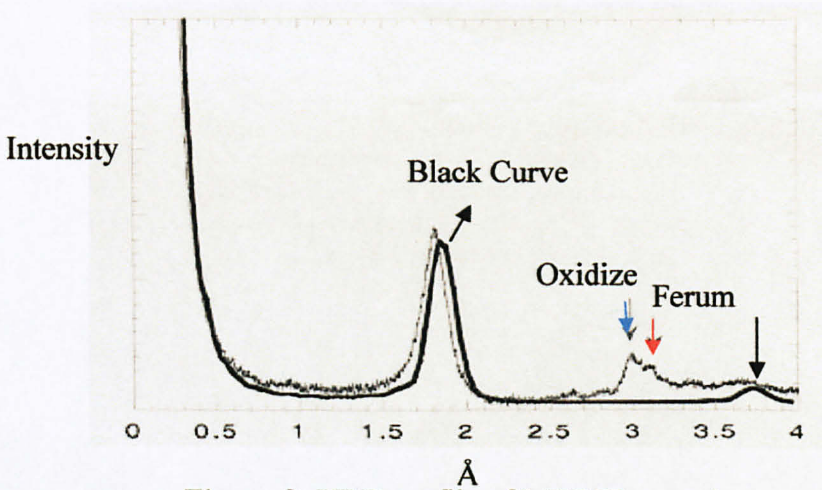


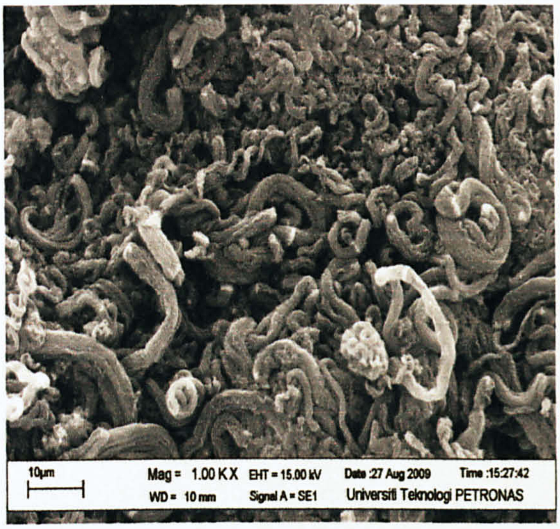
Figure 8: XRD profile of MWNTs sample

4.3.1 Discussion of XRD result

From figure 8 above, the data shows a little ray of $3Å^{-1}$ visible to the remainder of oxidize/functionalized (arrow in blue) and a little ray lied on ferum (arrow in red). The model (black curve) is the sum of the responses of tubes has 3, 4, 5... 12 layers, with same quantity of tubes of each type. It reproduced the data well (including the second order with $3.7Å^{-1}$)

4.4 SEM

Below are the results for SEM image of pristine MWNTs and functionalized MWNTs.



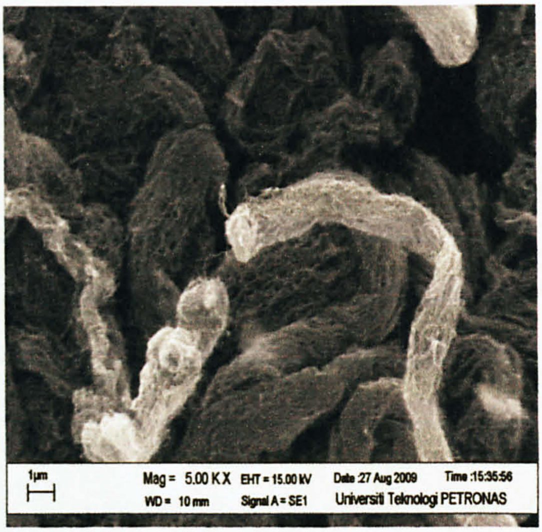


Figure 9: (a) SEM image of pristine MWNTs with 1000 times magnification and (b) with 5000 times magnification.

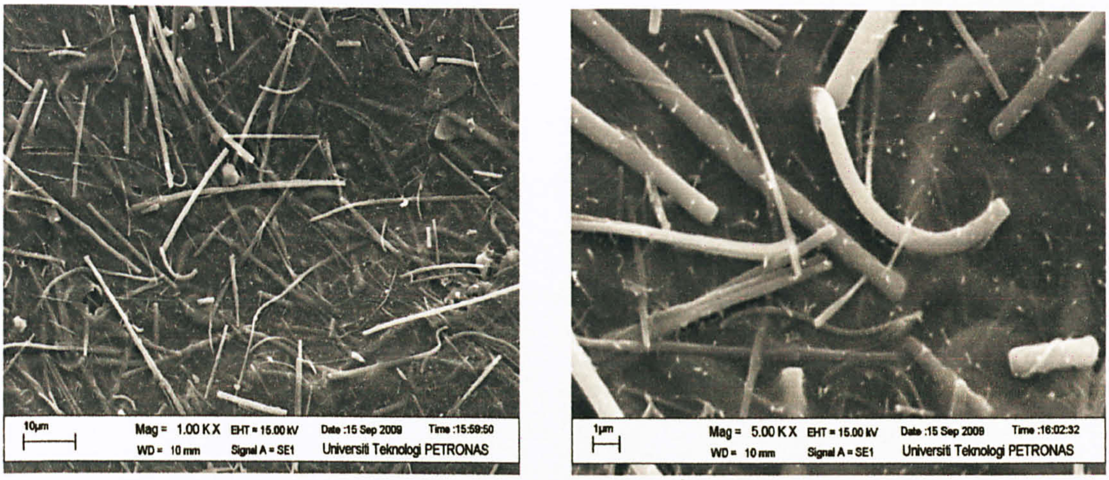


Figure 10: (a) SEM image of functionalized MWNTs with 1000 times magnification and (b) with 5000 times magnification

4.4.1 Discussion of SEM result

Figure 9 and 10 shows the SEM images of the pristine and functionalized multi-walled nanotubes samples respectively. The morphologies of pristine-MWNTs and functionalized-MWNTs with two types of magnification were observed by SEM. Pristine multi-walled nanotubes in figure 9 shows some agglomeration and large cluster of nanotubes. It also present that the end of the tube was not open as can be seen in figure 9 (b) with 1000 time magnification. In the case of functionalized-MWNTs, uniform and well dispersed particles on MWNTs surface were observed. The end of the tube was observed and it was shown that it was opened. Thus, it was prove that functionalization causes opening up the tube ends and generation of defects on the sidewall of nanotubes, therefore access into the cavity of the nanotubes can be achieved.

4.5 TEM

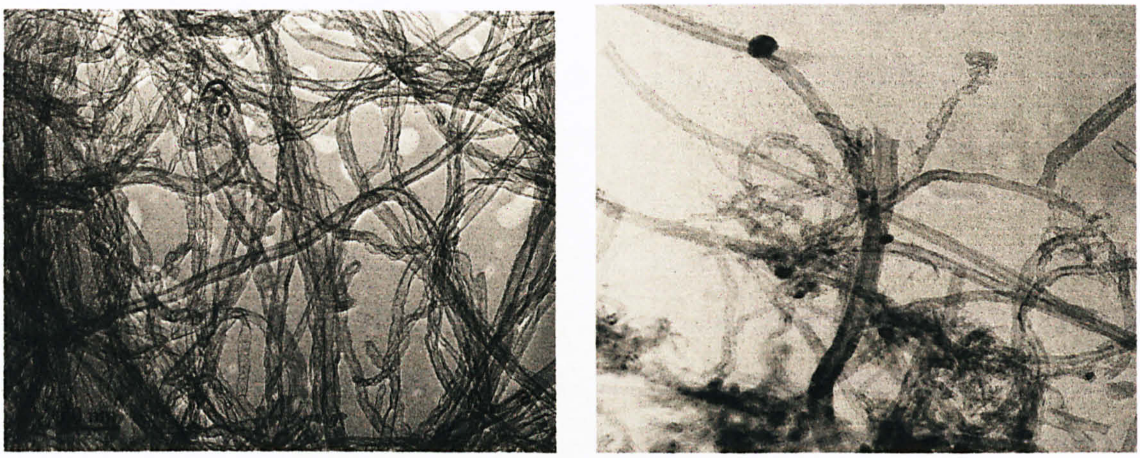


Figure 11: (a) TEM image of pristine MWNTs (b) TEM image of functionalized MWNTs

4.5.1 Discussion of TEM result

Figure 11 shows the TEM images of pristine-MWNTs and functionalized-MWNTs. As shown in the figure 11 (a) pristine-MWNTs seemed to present some agglomerates compared to functionalized-MWNTs that shows uniform dispersion of the particles on multi-walled nanotubes surface. The functionalized-MWNTs also show the opening up of the tubes end.

4.6 TGA

The author just managed to get the result for functionalized MWNTs since the results for pristine MWNTs was not received yet.

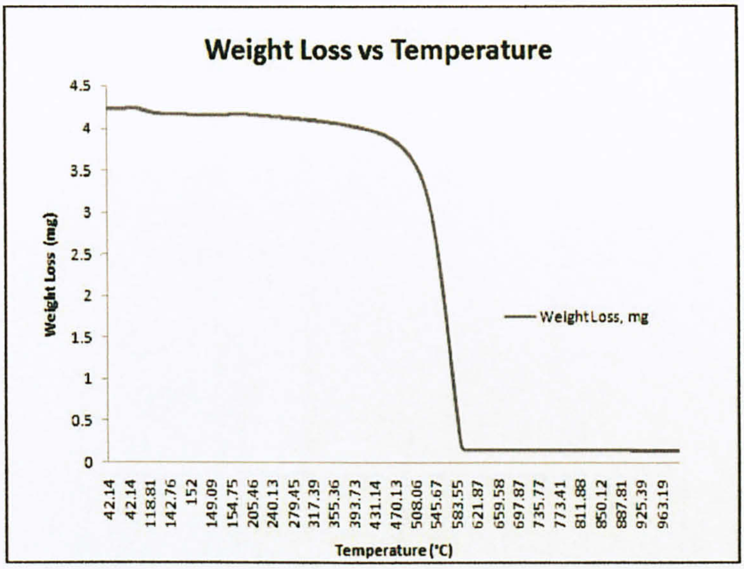


Figure 12: TGA profile of functionalized MWNTs

4.6.1 Discussion of TGA result

Figure 12 shows TGA curve of functionalized MWNTs. In this curve, it is plotted base on the weight loss in mg versus temperature in degree Celsius. Peak at about 100°C shows some weight loss due to the oxidized or functionalized of MWNTs. From this TGA curve, it seemed that almost 90% of total mass was lost at 583.5°C. This mass lost was attributed to the removal of carbon.

Generally, the following properties of MWNTs can be determined using the TGA curve;

1. The mass of catalyst impurity in as synthesized MWNTs.
2. The number of functional groups per MWNT carbon.
3. The mass of a reactive species absorbed by a functional group on MWNTs.

5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Based on the project studied, the main objective which is to show the performance of carbon nanomaterials as support in heterogeneous catalysis was achieved. Carbon nanotubes is used because of its good mechanical properties (such as flexible and can be bent without structural changes, light, high tensile strength and young modulus), thermal properties (good thermal conductor and able to transmit up to 6000 per meter per Kelvin) and high surface area (SWNT; 400-900 m^2/g, MWNT; 50-250m^2/g).

Functionalization of multi-walled nanotubes (MWNTs) by using nitric acid which so called acid treatment produce oxygenated functional groups. Due to the strong oxidation feature and its lengthy process, functionalization using nitric acid could be more destructive. Functionalization also causes opening up tube ends and generation defects on the sidewall of nanotubes, thus access into the cavity of the nanotubes can be achieved. The results of SEM and TEM also prove the uniform and well dispersed particles on functionalized multi-walled nanotubes (MWNTs) compared to some agglomerates in the pristine MWNTs.

Zinc oxide nanoparticles were synthesized by a hydrothermal route using zinc nitrate tetra hydrate salt as the starting materials. The surface morphology analysis by using SEM and XRD will help to confirm the synthesis of zinc oxide nanoparticles.

It is expected that nanoparticles supported by functionalized MWNTs catalyst show better conversion for the probe reaction tested than that of unmodified counterpart, which may be attributed to the high dispersion of nanoparticles and special frame and properties of F-MWNTs. Thus, it will open up the use of unique carbon nanostructure for CNTs related to various applications such as composite materials, micromechanical resonators, transistors and energy storage devices.

5.2 RECOMMENDATION

Based on the project findings, the author would like to propose some recommendation so that the project can be done successfully. Due to the time constraint and some problem with the chemicals and equipments availability, the experiment cannot run smoothly. For the moment, the effectiveness of carbon nanomaterials as support in heterogeneous catalysis remains unclear since the experiment was not finished. The catalytic activity test should be done to prove that the carbon nanomaterials such as multi-walled nanotubes manage to improve the conversion of a test reaction. For future works, the characterization of zinc oxide nanoparticles, functionalized MWNTs-supported zinc oxide nanoparticles and pristine MWNTs-supported zinc oxide nanoparticles that had been synthesized should be done by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) to confirm the surface morphology, uniform composition and high crystalinity of the samples.

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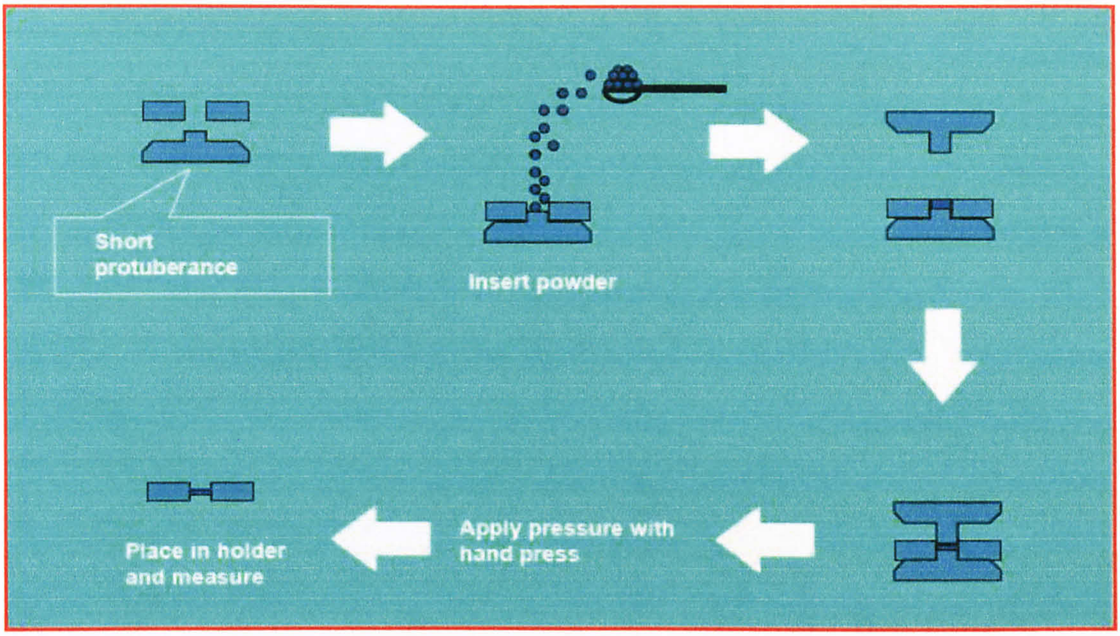
7 APPENDICES

7.1 Appendix A: KBr disk technique for FTIR analysis



7.2 Appendix B: Absorption position in FTIR