Synthesis of Carbon Nanotubes by Chemical Vapor Deposition using Co-MCM-41 as Catalyst

UPES

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(Signature) 18|4|2015

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2011-2015

Certificate

This is to certify that the work contained in this major report titled **"Synthesis of Carbon Nanotubes by Chemical vapor Deposition using Co-MCM-41 as Catalyst"** is being carried out by Anubhav Sharma, Adit Sharma, Pankaj Sharma, R. Venkata Subramanian, Vibhav Katoch and Vikesh Singh Rawat under my supervision as an academic activity in B.Tech Material science with specialization in Nanotechnology (2011-2015).

18/4/2015

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<u>Acknowledgement</u>

It was a great experience for us to have worked under the excellent guidance of our mentor **Dr. Gopalakrishnan** (Department of Chemical Engineering) and co-members. This minor project report has not only given us an insight into the Nanotechnology, synthesis process, testing techniques, but has also instilled in us a sense of team work with full utilization of the resources available.

This training would not have been possible without the indispensable support of the activity coordinator Dr. **Garimella V. Subrahmanyam** and other faculty members who guided us through the project.

We wish to come up with an excellent working model within the time frame.
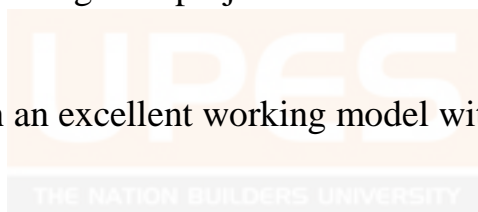
Chapter 1: Hydrogen and Its Storage

1.1 Introduction

Hydrogen is considered as a future alternative to fossil fuels. There have been many evidences involving the mishaps involved in transportation and storage of Hydrogen gas. The primary physical hazards associated with hydrogen gas are its flammability and explosive range. This is because hydrogen can form a flammable mixture with air over a wide range of concentrations, and very low energy is needed to ignite hydrogen-air mixtures. This means that, a hydrogen leak will most likely lead to an explosion

Symbol	H
Atomic Number	1
Atomic Weight	1.008
Group	1
Block	s-block
Period	Period 1
Electronic Configuration	$1s^1$
Phase	Gas
Color	Colorless
Melting Point	13.99 K
Boiling Point	20.271 K
Heat of Fusion	0.117 kJ-mol^{-1}
Heat of vaporization	0.904 kJ-mol^{-1}

Table 1: Some Basic Properties of Hydrogen

Hydrogen can be stored by using various methods which include high pressures, cryogenics, and chemical compounds that release H_2 by increasing the temperature.

Storage of hydrogen is focused on storing it as a lightweight, energy carrier so that it can be used for various applications.

Hydrogen in liquid or slush form can be used for various applications, but liquid hydrogen need cryogenic storage as liquid hydrogen boils around 20.27 $\underline{K}$ (−252.882 °C) so, liquefaction of hydrogen leads to a large loss of energy. Hence to avoid the large energy loss the storage device must be insulated properly but adding insulating layers will increases the cost. The energy density of liquid hydrogen by volume is less than conventional fuels.

Hydrogen in compressed form is stored by different process. Energy density of hydrogen gas by weight is good, but energy density of hydrogen gas by volume is low, hence large devices are needed to store hydrogen gas where as for the same amount of energy smaller and lighter hydrocarbon tank are required. The energy density by volume can be increased by increasing the pressure making the storage tanks smaller, but not lighter. Hydrogen in compressed form costs 2.1% more. So, compressing the hydrogen without recovery of energy will lead to more loss of energy to compress the gas.

1.2 Established technologies

Hydrogen can be stored by different technologies which are broadly divided into following:

1. Chemical storage
2. Physical storage

1.2.1 Chemical storage
1. Metal hydrides

Metal Halides like as $TiFeH_2$, $LaNi_5H_6$,$NaAlH_4$, $LiAlH_4$, MgH2, LiH, , and palladium hydride, with changing degrees of efficiency, can be used for storing hydrogen. Few are easy-to-fuel liquids at low pressure and temperature, whereas solids could be turned into small pellets. Such materials have better energy density by volume, but their energy density by weight is sometimes worse than few of the main hydrocarbon fuels.

Most of the metal hydrides bind strongly with hydrogen, due to which high temperatures above and around 120 °C are required to release the amount of hydrogen content absorbed in them which increases the cost. This energy cost can be bring down by using hydride alloys. These alloys consist of a strong hydride former and a weak hydride such as$LiBH_4$, $LiNH_2$, and $NaBH_4$.

These hydride alloys are able to form weaker bonds; therefore less amount of input is required to release stored hydrogen from these alloys. However if the interactions are too weak, the pressure required for re-hydriding will be high, thereby eliminating the energy savings. The target for hydrogen storage fuel devices is nearly about <100 °C for release and <700 bar for recharge.

An alternative method to bring down the dissociation temperatures is doping the hydride alloys with activators. This has been successful but its complex synthesis makes it difficult for using it for various applications as it is difficult to recharge it with hydrogen easily.

Currently there are only few hydrides are capable of achieving the 9 wt. % such as lithium, boron and aluminum based compounds.
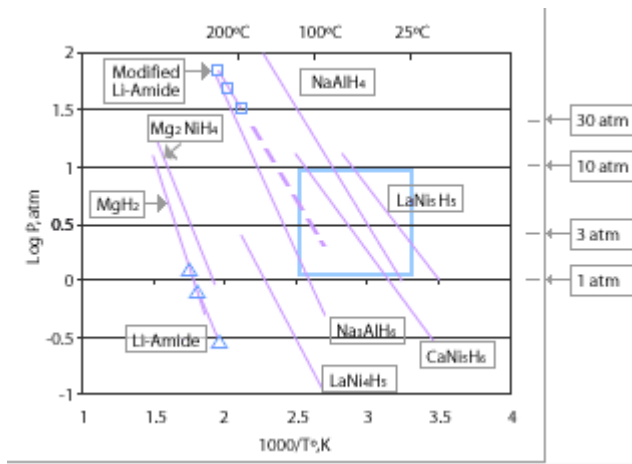
Figure 1: Graph showing the relation between Temperature and Pressure for hydrogen storage

2. Non-metal hydrides

Non-metal hydrides such as hydrazine are used as an alternative to hydrogen in fuel cells. The hydrazine fuel is liquid at room temperature so it is easy to handle and can be stored more easily than hydrogen. By storing hydrazine in a storing tank full of a double-bonded carbon-oxygen carbonyl, hydrazine reacts carbonyl and forms a safe solid product called hydrazine. By then flushing the tank with warm water giving out liquid hydrazine hydrate. The liquid hydrazine hydrate breaks down into nitrogen and hydrogen which then bonds with oxygen, releasing out water.

3. Carbohydrates

Carbohydrates (polymeric $C_6H_{10}O_5$) release H_2 in a bio reformer arbitrated by the enzyme cocktail-cell-free synthetic pathway biotransformation. Carbohydrate gives high hydrogen

storage densities when it is in liquid form with low pressurization and cryogenic constraints which can also be stored in the form of solid powder. Carbohydrates are renewable bio resource which are easily available hence using them can cut the expenses.

Complete conversion of carbohydrates at ambient reaction conditions can give high energy density hydrogen carrier with a density of 14.8 wt. %.

4. **Liquid organic hydrogen carriers (LOHC)**

Unsaturated organic compounds have the ability to store huge amounts of hydrogen. These unsaturated organic compounds such as *Liquid Organic Hydrogen Carriers* (LOHC) are hydrogenated for storing hydrogen and dehydrogenate whenever the energy or hydrogen is required. Heterocyclic aromatic compounds are most suitable for storing hydrogen.

LOHCs provide relatively high gravimetric storage densities and the overall energy efficiency is much higher than other chemical storage techniques.

5. **Ammonia**
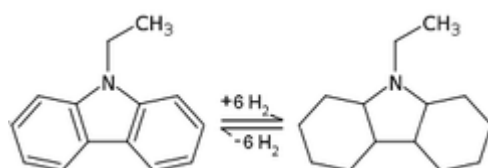
Ammonia (NH_3) in the presence of an appropriate catalytic reformer releases H_2. It provides high hydrogen storage densities in liquid form with mild pressurization and cryogenic constraints. Ammonia can also be stored in liquid form at room temperature and pressure when it is mixed with water. It is one of the most commonly produced chemical, so it is easily available. Ammonia can produce hydrogen without any harmful waste, or it can be mixed with existing hydrocarbon fuels and under the right conditions it burn efficiently. In its pure form ammonia burns poorly at the atmospheric pressures, but under some controlled constraints ammonia in compressed form in an automobile engine it is a useful fuel for slightly upgraded gasoline engines.

6. **Metal-organic frameworks**

Metal-organic frameworks (MOFs) represent a class of synthetic porous materials that can be used to store hydrogen and energy at the molecular level. They are highly crystalline in nature and their inorganic-organic hybrid structures that contain organic ligands as linkers and metal

clusters or ions as nodes. Heating MOFs under vacuum removes solvent molecules occupying the pores during solvent exchange. Without destabilizing the frame porous structure of MOFs can be achieved and by physisorption hydrogen molecules will be adsorbed onto the surface of MOFs pores. Comparing to zeolites and porous carbon materials, pores and surface area of MOFs is very high in number which allows higher hydrogen storage in a given volume. By varying several factors such as surface area, catenation, ligand structure, pore size, spill over, and sample purity can lead to varying amount of hydrogen storage in MOFs.

1.2.2 Physical storage

1. Cryo-compressed

Hydrogen storage by cryo-compressed method is the only technology that full fills all the 2015 DOE targets for gravimetric and volumetric efficiency. Results show that cryo-compressed have interesting cost benefits: ownership cost and storage system cost are the lowest when compared to any other process.

Cryo-compressed method uses cold hydrogen in order to achieve a high energy density. But due to heat transfer with the environment the hydrogen gets warmed up, the tank is let to go to high pressures. The hydrogen takes much more time before the hydrogen has to vent, and in most of the situations, to keep the pressure of the tank below the venting limit large amount of hydrogen is used by the car.

2. Clathrate hydrates

Clathrate hydrates are water-based crystalline solids consists of small polar molecules or non-polar molecules with large amount of hydrophobic moieties trapped. Clathrate hydrates are clathrate compounds in which consist of water molecule and the guest molecule i.e. a gas or liquid. Without the presence of the trapped gas or liquid molecules, the lattice structure would collapse. H_2 caged in a clathrate hydrate can be used as a fuel but to provide stability high pressures is required. But doping Hydrates with small amount of activating substances like THF reduces temperature and pressure which increases the overall efficiency. These clathrates have good hydrogen storage densities of around 5 wt. % and 40 kg/m^3.

3. Carbon nanotubes

Carbon nanotubes are promising materials for hydrogen storage, and storage of hydrogen is possible and feasible through both physisorption and chemisorption methods. While various studies have shown that the physisorption of molecular hydrogen, there is no direct proof of high storage of hydrogen at low temperature. Whereas the chemisorption mechanism gives storage capacity through the saturation of C–C π bonds with atomic hydrogen, but direct experimental

proof of the efficiency and feasibility of storage of the hydrogen through chemisorption methods has not yet been tested.
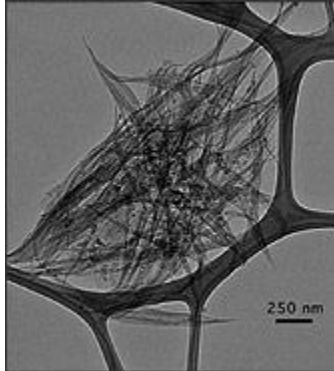
Figure 2: Carbon Nanotubes

The defect sites on Carbon nanotubes act as adsorption sites for storing hydrogen which are created by oxidation and pre-treatment by using a La catalyst after which Pd catalysts are deposited on the surface of CNT for dissociation of H2 into atomic hydrogen, which are then spilled over the defected locations or sites. The total amount of hydrogen stored in CNTs decreases with rise in annealing temperature of the process. These results are attributed to the crystallization of the defective structure of CNTs into graphitic structure.

This is of our interest and detailed description is given regarding this.
One of the method of synthesizing the CNT is by catalytic chemical vapor deposition using metal incorporated MCM-41 catalysts.

Chapter 2: Mesoporous Material and Catalyst

2.1 Introduction

Material can be categorized into many different ways depending upon the respective properties of different materials, like hard, Soft, porous, flexible etc. porous materials are those materials which tiny pores present over the surface of the materials, earthen pot is the best example of this type of material in laymen language.so depending upon the pore size, these type of material can be branched into three category and that are

a) Microporous Materials
b) Mesoporous Materials
c) Macroporous Materials

Microporous Materials

These kind of materials have their pore size less than 2 nm in diameter, for example – zeolites and metal organic frameworks. These materials are being used in laboratories, medicine applications.

Mesoporous Materials

These material contain pores with diameter between 2 to 50 nm. Typical mesoporous materials include some kinds of silica and alumina that have similarly-sized fine mesopores. Oxides of titanium, zirconium, and cerium, tin are also reported as mesoporous oxides.

Macroporous Materials

Materials having their pore diameter greater than 50 nm are called as Macroporous materials.

2.2 Mesoporous Materials

2.2.1 History

In 1992, scientists connected with Mobil Research and Development Corporation reported the union of another group of mesoporous sub-atomic strainers (M41S) with particularly substantial uniform pore structures. Move metal can be joined into the pore dividers of the mesoporous atomic sifters balancing out scattered synergist destinations furthermore display great auxiliary soundness.

Blend and utilizations of mesoporous solids have gotten concentrated consideration because of their exceedingly requested structures, bigger pore size, and high surface zone. Because of stable mesoporous structure and very much characterized surface properties, mesoporous materials appear to be perfect for the development of cnts.

Types of Mesoporous Materials

Mesoporous materials can be categorized into different types based on its composition material and that too differ in the respective pore size, which further differentiate each other regarding the properties of individual mesopores material.

Most common types of mesoporous material are

1. MCM 41
2. SBA 15
3. MGO
4. MSM 14.

.

SBA 15

SBA-15 is a mesoporous silica sifter in light of uniform hexagonal pores with a slender pore size circulation and a tunable pore measurement of somewhere around 5 and 15 nm. The thickness of the structure dividers is around 3.1 to 6.4 nm, which gives the material a higher aqueous and mechanical steadiness than, for occurrence, MCM-41. The high inside surface region of regularly 400–900 m2/g makes SBA-15 an appropriate material for different applications. It can be utilized as a part of ecological investigation for adsorption and partition, propelled optics, as a bolster material for impetuses and as a format for the creation of nanostructured carbon or platinum imitate.

MCM 41

Mobil Composition of Matter No. 41 (MCM – 41) is a mesoporous material with hexagonal pore structure from a group of silicate solids that were initially grown via analysts at Mobil Oil Corporation and that can be utilized as impetuses or impetus bolsters.

MCM-41 contains standard plan of round and hollow mesopores that structures 1D pore framework. It is portrayed by a freely flexible pore breadth, a sharp pore circulation, a huge surface and an expansive pore volume. The pores are bigger than with zeolites and the pore dispersion can without much of a stretch be balanced, and as effectively talked about mesopores have their distance across between 2 to 6.5 nm.

Characteristics of MCM-41

The M41S family containing MCM-41 and related mesoporous sub-atomic strainers are of interest due to their incredible exceptional properties, for example, vast surface zone (>1000 m2/g), pore volume (>0.8 cm3/g), tight pore size conveyance and the straightforwardness with which their surface can be functionalized. Likewise, their uniform and tunable pore distances across make them very much adjusted as great synergist bolsters. By and large, unadulterated siliceous MCM-41 has constrained synergist action, yet dynamic reactant locales can be produced in Si-MCM-41 by isomorphously substituting silicon with move metal. A few studies have been committed to the examination of move metal substituted MCM-41 in view of their extensive variety of utilizations in catalysis.

Synthesis of MCM-41

Cobalt based MCM- 41 was used for the Carbon nanotubes production.

```
┌─────────────────────────┐          ┌─────────────────────────┐
│  28.42g Na metasilicate │          │       50ml $H_2O$       │
└─────────────────────────┘          └─────────────────────────┘
                    ╲                          ╱
                     ▼                        ▼
┌──────────┐      ┌─────────────────────────────┐      ┌──────────┐
│  Metal   │      │      Stirring for 0.5 hr.   │      │  10 ml   │
│  Salt    │      └─────────────────────────────┘      │  $H_2O$  │
└──────────┘            ╲                   ╱           └──────────┘
              ┌─────────────────────────────┐
              │      Stirring for 1 hr.      │
┌──────────┐  └─────────────────────────────┘
│ 80 ml 2N │        ╲
│ $H_2SO_4$│  ┌─────────────────────────────┐
└──────────┘  │      Stirring for 2 hr.      │
              └─────────────────────────────┘
┌──────────┐        ╲                   ╱    ┌──────────┐
│ 6.728g   │  ┌─────────────────────────────┐│  20 ml   │
│  CTAB    │  │      Stirring for 2 hr.      ││  $H_2O$  │
└──────────┘  └─────────────────────────────┘└──────────┘
                         │
              ╱─────────────────────╲
             │  Autoclave at150⁰C    │
             │    For 48* hrs.       │
              ╲─────────────────────╱
                         │
              ┌─────────────────────┐
              │   M-MCM-41 M=        │
              │   Fe, Co, Fe + Co    │
              └─────────────────────┘
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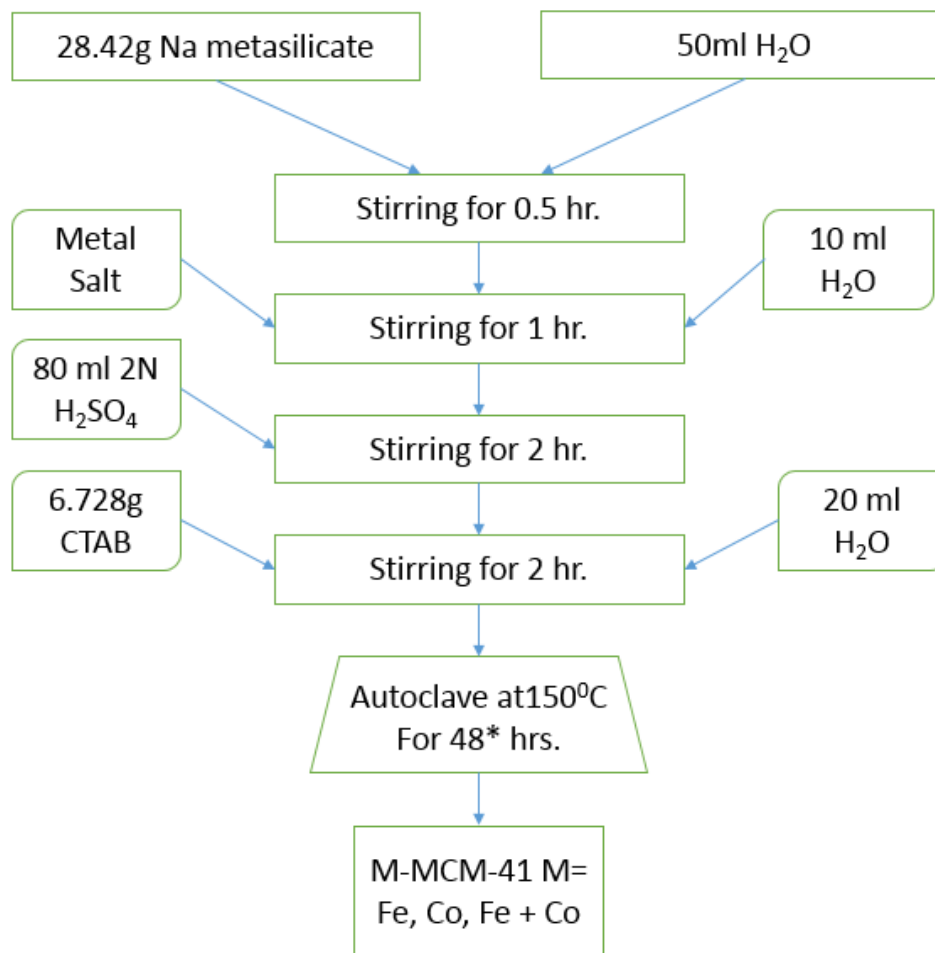Autoclave at150^{0}C For 48* hrs.

M-MCM-41 M= Fe, Co, Fe + Co

Figure 3: Flow Chart for Synthesis of Co-MCM-41

Chapter 3: Carbon Nanotubes and its synthesis

3.1 Introduction

Carbon nanotubes are the allotropes of carbon. A single walled carbon nanotube is a one atom thick sheet of graphite rolled into a seamless cylinder with diameter of the order of a nanometer. This results in a nanostructure where the length-to-diameter ration exceeds1, 000,000. On the other hand the multiwalled carbon nanotubes are basically made up of a number of concentric tubes.

3.2 Carbon Nanotubes Synthesis

Carbon Nanotubes can be synthesized by 4 major roots

1. Arc Discharge
2. Laser ablation
3. Chemical Vapor Deposition
4. Ball Milling

3.2.1 Laser Ablation

Laser ablation is the process of removing material from a solid surface by irradiating it with a laser beam. During low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. During high laser flux, the material is converted to a plasma. In general laser ablation refers to removing material with a pulsed laser, but it is possible to ablate material with a continuous wave laser beam if the laser intensity is high enough.

Advantages of lase ablation are:

1. No solvents are used, so it is environmentally friendly and operators are not exposed to chemicals.
2. The process is gentler than abrasive techniques, e.g. carbon fibers within a composite material are not damaged. It is relatively easy to use.
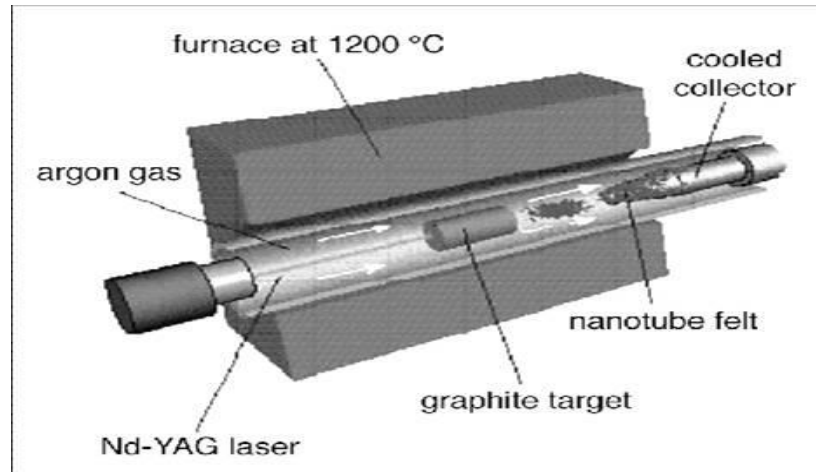
Figure 4: Laser Ablation Mechanism

3.2.2 Arc Discharge

An ionized gas system is considered as plasma. When a gas made conducting by providing a high potential difference via electrodes inside the gas systems, so that the gas yields up its electrons and thus ionizes, plasma is obtained. Plasma consists of electrons, ions as well as neutral particles. Due to high conductivity of the plasma, arc is generated. Between the two closely spaced electrodes in vacuum or in low pressure inert gas atmosphere, which results in heat. The heat produced can be utilized to vaporize and ionize the electrodes and also some other materials present inside the discharge chamber. Plasma arc method has been used in the deposition of carbon nanotube. An electric arc passes from anode to cathode due to which anode vaporizes and get deposited to the other electrode as well as on the inside of the chamber wall.

For carbon nanotube deposition carbon electrodes are used through which atomic carbon cations are produced due to arcing. These cations move to cathode to pick up electrons and get deposited to form nanotubes.

The electrodes can be made of the other materials provided that they must have electrical conductivity.
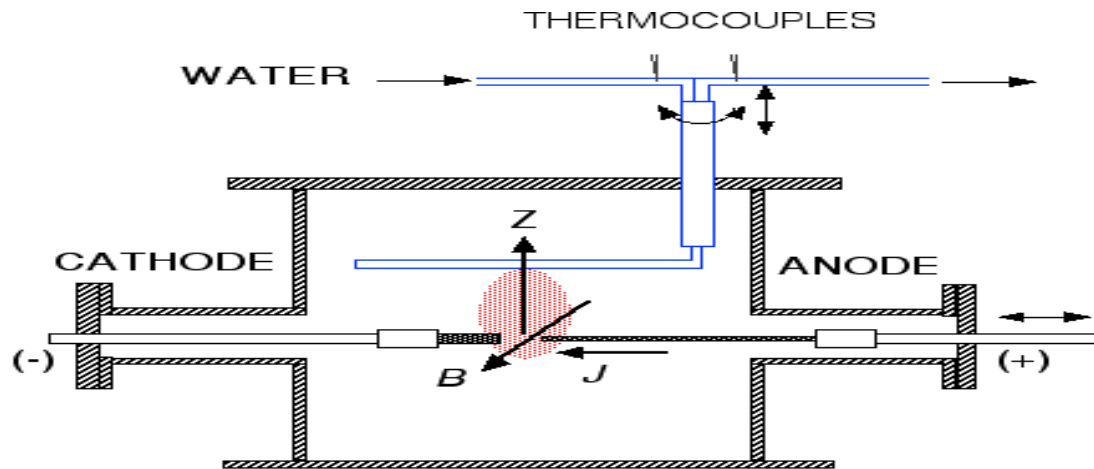
Figure 5: Arc discharge Device

Advantages of plasma arc discharge

1. Boron and silicon nitrite nanotubes can also be formed by this method.
2. Fewer defects in the synthesis of carbon nanotubes.
3. High flexibility of carbon nanostructures that are produced.
4. Does not produce any toxic byproducts.
5. Lower emission capability degradation than those produced by other techniques.

Disadvantages of plasma arc discharge

1. It is generally characterized by poor control.
2. The lower temperatures do not result in efficient synthesis, while the higher temperatures cause the destruction of carbon nanotubes and their crystallization.
3. When the deposit increases the distance between the cooled electrode and the deposit surface increases.

3.2.3 Chemical Vapor Deposition

Introduction

It is used to produce high – purity, high performance solid materials, usually in the form of a thin film on a substrate. In a typical CVD process, a wafer substrate is exposed to one or more volatile precursors, which react and decompose on the substrate surface to produce the desired deposit. Volatile byproducts are produced, which are removed by gas flow through the reaction chamber.

Type of Chemical Vapor Deposition Processes

Number of forms of CVD are in wide use and are frequently referenced in the literature. These processes differ by means of chemical reaction are initiated and process conditions.

1. Atmospheric pressure CVD
2. Low pressure CVD
3. Ultrahigh vacuum CVD
4. Aerosol assisted CVD
5. Direct liquid injection CVD
6. Plasma Enhanced CVD
7. Metalorganic CVD

Advantages and Disadvantages of CVD

1. Easy to increase scale to industrials production
2. Large length
3. Simple to perform
4. Pure product
5. Defects are common

3.3 Growth Mechanism

Now there are generally two cases of growth mechanism of carbon nanotubes.

1. Tip growth
2. Base growth

Tip Growth happens when the catalyst-substrate interactions are weak, hydrocarbon decomposes on the top of the metal surface, carbon diffuses down through the metal, and CNT precipitates out of the metal bottom, pushing the whole metal particle off the substrate. As long as the metal's top is open for fresh hydrocarbon decomposition, the concentration gradient exists in the metal allowing carbon diffusion, and CNT continues to grow longer and longer. Once the metal is fully covered with excess carbon, its catalytic activity ceases and the CNT growth is stopped. This is known as "tip-growth model".
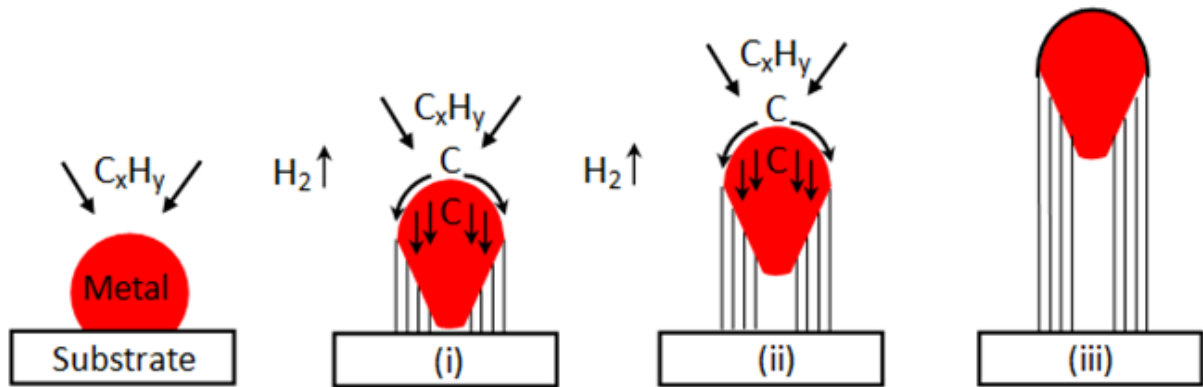
Figure 6: Tip Growth Mechanism

In the other case, when the catalyst-substrate interaction is strong, initial hydrocarbon decomposition and carbon diffusion take place similar to that in the tip-growth case, but the CNT precipitation fails to push the metal particle up; so the precipitation is compelled to emerge out from the metal's apex. At first, carbon crystallizes out as a hemispherical dome which then extends up in the form of seamless graphitic cylinder. Subsequent hydrocarbon decomposition takes place on the lower peripheral surface of the metal, and as-dissolved carbon diffuses upward. Thus CNT grows up with the catalyst particle rooted on its base; hence, this is known as "base-growth model".
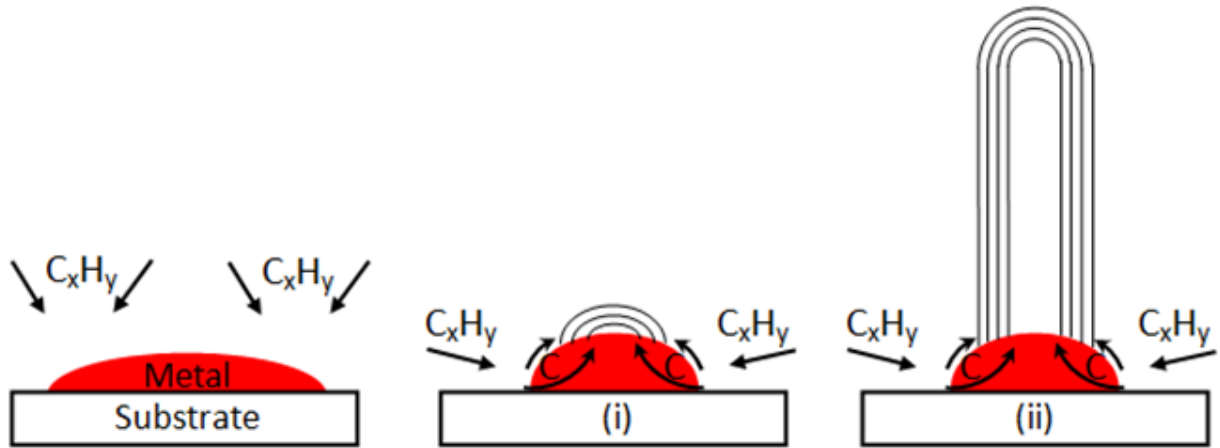
Figure 7: Base Growth Mechanism

Parameters affecting the growth in MOCVD

- Temperature of growth
- Flows rate of the precursor
- Reactor pressure

Chapter 4: Three zone Chemical Vapor Deposition

4.1 Construction

The heart of the three zone chemical vapor deposition equipment is horizontally mounted ceramic tube (Al_2O_3), which can attain upto 1800°c via resistive heating of molybdenum. Temperature is programmed by the PID located in the front side of CVD equipment. Temperature is monitored by three independent thermocouples located behind the equipment. Mass flow controller provided by Alborg, is used to measure the gas flowing into the furnace. Other auxiliary equipment's such as vacuum pump and cooler can be found at the bottom of stand.

Figure 8: three zone CVD Furnace

4.2 Risks and Caution in Operating Chemical Vapor Deposition Equipment

Chemical vapor deposition is widely used method in synthesizing different kinds of nanoparticles. In synthesis of carbon nanotubes various explosive gases such as hydrogen and acetylene are used, combining with high temperature inside the furnace, if faultily handled it is likely to have an explosion, which could cause damage to life and property.
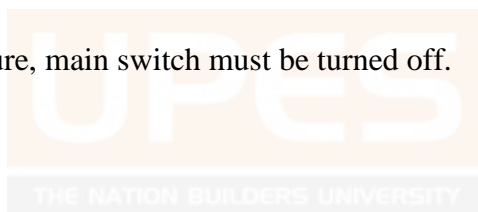
Here are some basic understanding of what could cause an explosion, hence prevent it from happening.

- Hydrogen and acetylene combines reacts with the atmospheric oxygen to explode, whereas inert gases such as argon and nitrogen has no reactivity with oxygen. Hence inert gas sources must be used whenever there is presence of air/ oxygen.
- The outlet tube from furnace must be put out in fume hood or let to bubble in a beaker containing water for the safe dispose of gases.
- The outflow of gases indicates that no excessive pressure is built inside the furnace; hence the outlet must be checked for gases to bubble out.
- On operating under vacuum, excessive care must be taken to avoid opening the outlet valve, especially when dipped in water; Outlet could suck in water, henceforth flooding the entire equipment.
- In case of power failure, main switch must be turned off.

4.3 Steps for Operation of CVD Equipment and Synthesis of Carbon Nanotubes

1
- Close all valves in cylinder and the equipment.
- Switch on the main switch

2
- Look in the PID temperature controller, generally in the start it is at ambiant temperature (20-35°C)
- Switch on the switch of mass flow controller should be ~0ml/min, indicating no gas flow

3
- Sample in inserted into the furnace through the outlet side by unclamping the steel portion.
- Boat should be positioned accurately in the three appropriate zone to have accurate temperature reading. Use linear scale to measursing and positioning inside the furnace

4
- All valves should be closed except that of vaccum pump valve. Vaccum pump is operated for 20min, to create a rough vaccum in the furnace.
- **Excessive care must be taken, to make sure that outlet valve and gas inlet valve is closed.

5
- Temperature programming is done, for the experiment.
- Mass flow controller is switched on

6
- Argon gas is flushed into the furnace at approximatly 100ml/min till the furnace attrains the reduction temperature.
- Argon gas cylinder is turned off and Hydrogen gas is passed at 100ml/min for 20-40 min at the reducation temperature
- Hydrogen gas cylinder is turned off and Carbon source gas (acvetylene) alone or along with argon as carrier gas is passed at 40ml/min for 20-40min.

7
- Furnace switch is turned off and the furnce is let to cool to room temperature in argon atmosphere, with flow at 100ml/min

4.4 Mass Flow Controller

Gas flow is important variable in the synthesis of carbon nanotube, hence it is very important for the accurate measurement of gas flow. Unit of measurement of gas flow is SCCM or ml/min.

Valve of the cylinder and mass flow controller must be open before the programming the mass flow controller. The mass flow controller is generally preconfigured for a particular gas, in case of using for different gas, the flow value is divided by the K factor and the mass flow controller is set for the calculated value.

Say the acetylene gas is to be flowed at 40ml/min in a mass flow controller, preconfigured for nitrogen. The K factor for acetylene is 0.5829. Hence 40/0.5829=68ml/min. Hence the value on mass flow controller should be set for 66ml/min.

Manual for Alborg mass flow controller 'gfc series' can be downloaded at below mentioned link.

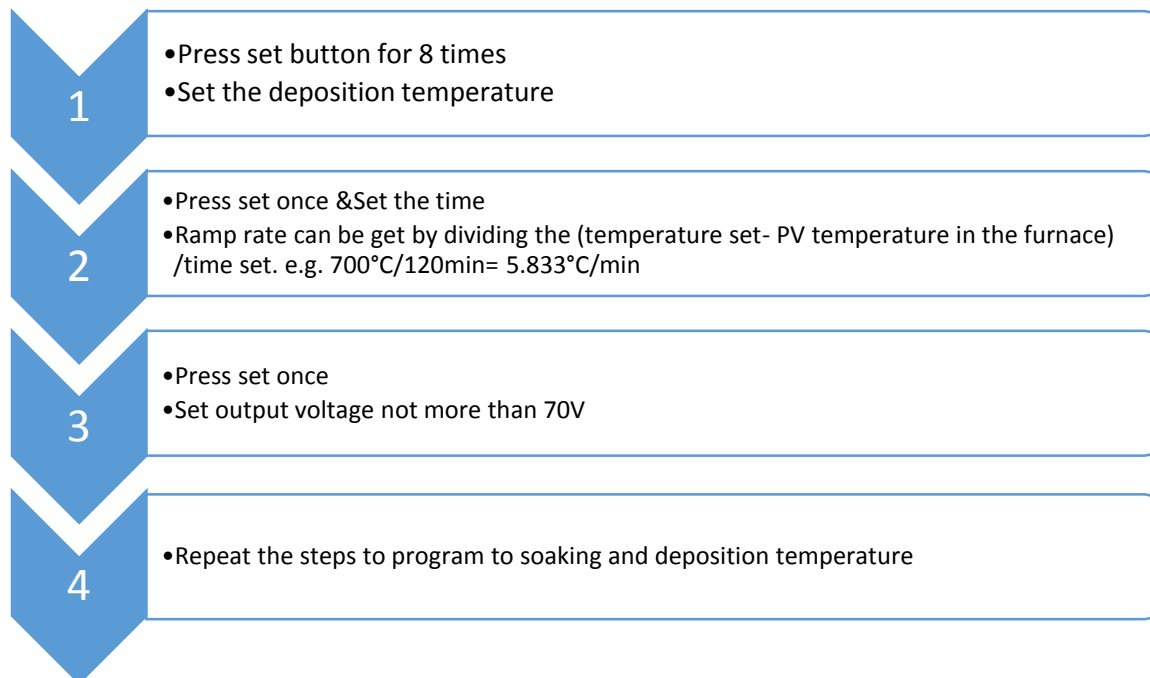## 4.5 Programming Temperature PID controller

Figure 9: Temperature PID controller

Programming the PID controller for the reaction is a necessary part of the experiment. Steps for programming the PID controller is given in the following steps.

Nomenclature:

PV	Measured Value
SV	Set Value
Set	Navigating Values
←↑↓	Side, Up, Down

Table 2: Depicting the Keys on PID

1	• Press set button for 8 times • Set the deposition temperature

2	• Press set once &Set the time • Ramp rate can be get by dividing the (temperature set- PV temperature in the furnace) /time set. e.g. 700°C/120min= 5.833°C/min

3	• Press set once • Set output voltage not more than 70V

4	• Repeat the steps to program to soaking and deposition temperature

4.6 Experiment:

CNTs were prepared via CVD method by vapor growth of acetylene over Co-MCM-41 in horizontal glass tube, with acetylene as carbon source, argon as carrier gas and hydrogen for reduction of surface. Sample was soaked at 625°c in hydrogen environment for 20min in each case and deposition temperature was 700°c,750°c,800 °**c** in which the sample was soaked for 20min. Flow of argon gas was maintained at 100ml/min, hydrogen 100ml/min, and acetylene at 40ml/min. The samples were let to cool down to room temperature in argon atmosphere.

Chapter 5: Purification

5.1 Introduction

Purification is the process of removal of the undesirable foreign impurity from the base material. Different methods are deployed for the purification such as:

1. Filtration
2. Centrifugation
3. Evaporation
4. Liquid-liquid Extraction
5. Recrystallization
6. Crystallization
7. Adsorption
8. Refining
9. Distillation
10. Electrolysis
11. Sublimation

For our case we use the filtration process

The sample derived from after the CVD process has four basis components:

1. Metal that acts as a Catalyst.
2. Silicon that acts as a template.
3. Carbon (Carbon Nanotubes) that has deposited after the process.
4. Other unwanted substances or trace impurities

Purification of Sample generally refers to separation of CNTs from other species such as residual catalyst, silicon and other species. In the purification of carbon nanotube different acids are used for removal of impurities. Table below depicts the chemicals and their quantity used.

S. No.	Chemical Used	Quantity (ml)
1	Hydrofluoric acid	10
2	Hydrochloric Acid	10
3	Nitric Acid	10
4	Distilled water	120

Table 3: List of Chemicals Used for Purification

S. No.	Apparatus Used	Quantity
1	Glass Rod	1
2	Beakers	3
3	Glass Funnel	1
4	*Polypropylene Bottle*	1
5	*Petri Dish*	3
6	*Measuring Cylinder (100ml)*	1
7	*Desiccator*	1
8	*Gloves*	1
9	*Whatman filter paper Number 1*	10
10	*Spatula*	1

Table 4: List of apparatus Used for Purification

Figure 10 & 11: Apparatus and Filter paper used.

Electronic equipment used

1. Magnetic Stirrer with a Magnetic bit

Figure 12: REMI Magnetic Stirrer with sample loaded in PP Bottle

2. Hot air Oven

Figure 13: Hot Air

5.2 Detailed Description of the Procedure

1. First purification is done with Hydrofluoric acid. HF is mixed with water in the Polypropylene beaker in the ration 1:4. HF is used for removal of silicates from carbon nanotubes. Glass beaker is not used whenever we are doing purification with HF acid, as it dissolves silica. 10ml HF acid is mixed with 40ml water in polypropylene beaker. CNTs dipped in above solution is stirred using magnetic stirrer for 6 hours at 300-600 rpm. Than using a filter paper filtration is done. Filtrate collected on filter paper is washed with ethanol and heated in oven at 75°C for 6 hours. Filtrate is collected from the filter paper.

2. The sample derived from above step is treated with Hydrochloric acid. HCl is used for removal of corresponding metal from carbon nanotubes. 10ml HCl is mixed with 40ml water in polypropylene beaker. CNTs dipped in above solution is stirred using magnetic stirrer for 6 hours at 300-700 rpm. Filtration is carried out using filter paper. Filtrate collected on filter paper is washed with ethanol and is heated using oven at 75°C for 6 hours. Filtrate is collected from filter paper using a spatula.

3. Finally the sample is treated with Nitric Acid .Nitric Acid is used for removal of other trace impurities from carbon nanotubes. Nitric acid is mixed with water in the ratio 1:4 in

a glass beaker. CNTs dipped in solution of Nitric Acid and water is stirred for 6 hours at 300-700 rpm. Filtration is carried out using filter paper. Filtrate collected on filter paper is washed with ethanol and is heated using oven at 75°C for 6 hours. Filtrate is collected from filter paper and pure carbon nanotubes are obtained.

4. Sample is weighed by an electronic weighing machine and sent for characterization and testing.
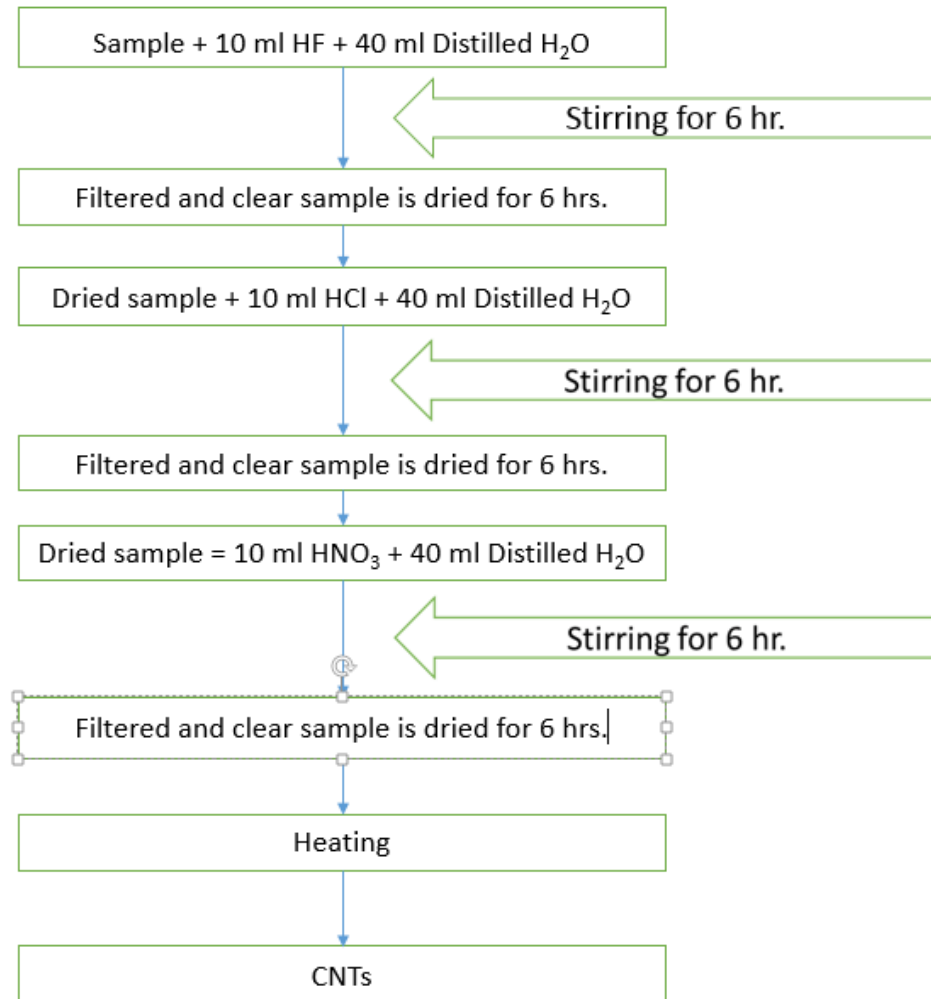
Sample + 10 ml HF + 40 ml Distilled H_2O

Stirring for 6 hr.

Filtered and clear sample is dried for 6 hrs.

Dried sample + 10 ml HCl + 40 ml Distilled H_2O

Stirring for 6 hr.

Filtered and clear sample is dried for 6 hrs.

Dried sample = 10 ml HNO_3 + 40 ml Distilled H_2O

Stirring for 6 hr.

Filtered and clear sample is dried for 6 hrs.

Heating

CNTs

Figure 14: Flowchart depicting purification of CNT's

Chapter 6: Results and Discussions

Results for Co-MCM-41

Surface Area

Single point surface area at P/Po = 0.296064339: 829.1307 m²/g

BET Surface Area: 904.5082 m²/g

Langmuir Surface Area: 1593.0271 m²/g

BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter: 923.703 m²/g

BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter: 994.5335 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 233.4968 nm diameter at P/Po = 0.991734374: 0.860170 cm³/g

T-Plot microspore volume: -0.237660 cm³/g

BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter: 0.804250 cm³/g

BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter: 0.828563 cm³/g

Pore Size

Adsorption average pore width (4V/A by BET): 3.80392 nm

BJH Adsorption average pore diameter (4V/A): 3.4827 nm

BJH Desorption average pore diameter (4V/A): 3.3325 nm

Nanoparticle Size
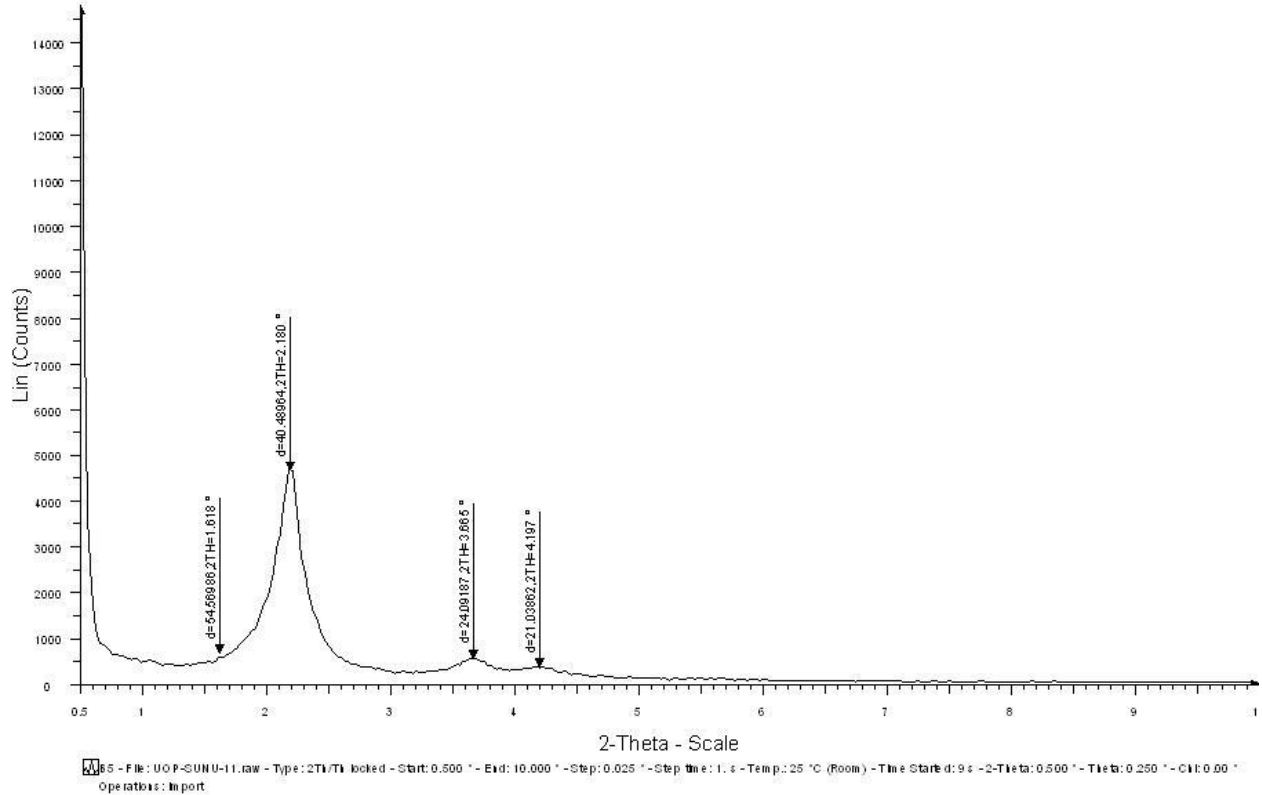
Average Particle Size 6.6334 nm

XRD Results

Figure 15: XRD Results for Co-MCM-

The reported XRD pattern of MCM-41 in the literature shows a strong peak in the 2θ range of 1.8–2.8∘ due to (1 0 0) diffraction lines and weak peaks in the 2θ range of 3.8–4.8∘ and 6.2–6.7∘ due to higher order such as (1 1 0), (2 0 0) and (2 1 0) diffractions indicating the formation of well-ordered hexagonal symmetry of MCM-41 mesoporous materials. From our result it confirms that the well-structured MCM-41 is formed is strong peak at 2.2º, weak peaks at 3.6º and 4.2º.

SEM Results for MCM-41
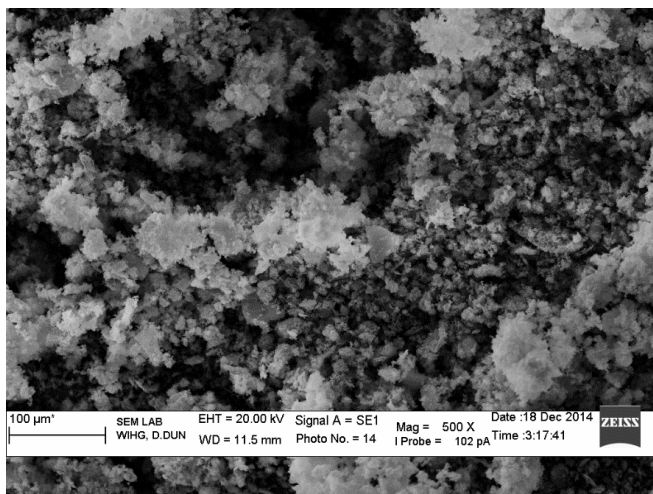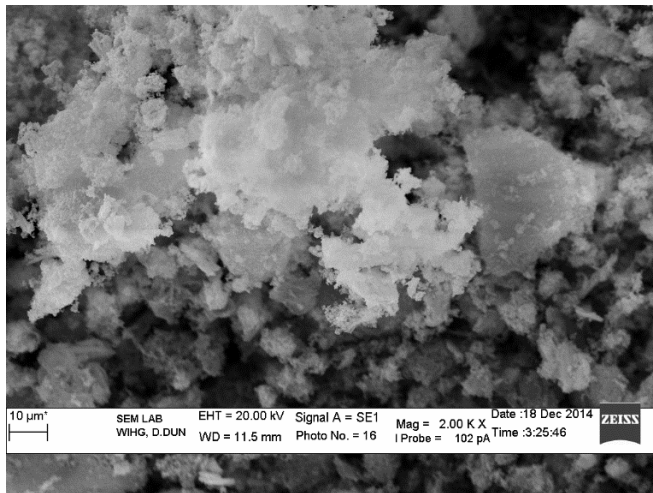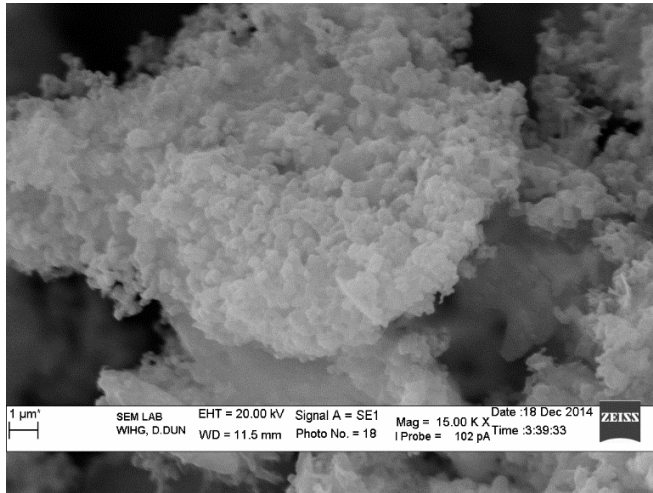
Results for Carbon Nanotubes

Batch 1 results: Experiments were performed on Co-MCM-41 Sample

- ➡ Weight of the catalyst= 0.1gm

- ➡ Weight of sample + Boat = 82.71 gm

- ➡ Weight of Sample obtained after CVD process = 83.11 gm

- ➡ Yield = 400

Batch 2: Experiment was performed at three different temperatures to see the nature of Deposition.

S70 denotes deposition temperature of sample was 700°C

S75 denotes deposition temperature of sample was 750°C

S80 denotes deposition temperature of sample was 800°C

Table below depicts the yield of sample at three different temperatures.

Sample Code	Weight of Catalyst Y_0	Weight of Boat	Boat + Catalyst	Weight After Experiment Y_1	Yield $(Y_1 - y_0 /y_0)*100$
S70	0.1	12.3671	12.4671	12.6671	200 %
S75	0.1	12.0974	12.1974	12.4274	230%
S80	0.1	10.8	10.90	11.2024	302 %

Chapter 7: Conclusion

We were able to succefully synthesis the Co-MCM-41 Materials. Results of which are coated above.

The successful commissioning and working of the CVD was performed for the synthesis of carbon Nanotubes using Co-MCM-41 as a catalyst.

Chapter 8: References

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