

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Cobalt(II) nitrate hexahydrate was obtained from Sigma-Aldrich Company, 98+%, A.C.S. reagent.
- Ammonium molybdate tetrahydrate was obtained from Sigma-Aldrich Company, ACS reagent.
- Silica gel was obtained from Aldrich Chemical Company, Inc. its surface area is 500 m²/g and the size is about 70-230 mesh (63-210 μm).
- Hydrochloric acid fuming 37 %wt obtained from Merck KGaA Company.
- Sodium hydroxide analytical grade obtained from Labscan Asia Co., Ltd. The purity about 99.3 wt%.
- Sodium dodecylbenzenesulfonate (SDBS) purchased from Acros Company. The purity about 88 wt%
- Deionized water

All chemicals were used as received without any purification.

3.1.2 Gases

All of the gases were obtained from Thai Industrial Gas Public Co., Ltd, Thailand (Air zero grade, High purity hydrogen, High purity helium, High purity carbon monoxide).

3.2 Experimental Methodology

This research consists of five parts. The first part was produced the single-walled carbon nanotube by catalytic decomposition method. The second part was investigated of the catalyst dissolution, which the effect of sonication time, hydrochloric concentration and reaction temperature were studied. The third part was

the purification experiment after dissolved catalyst particles, which is forth flotation part. In this part we were study the effect of surfactant concentration, pH solution and air flow rate. To get more carbon purity, the dissolution of silica was necessary so we was investigated in part four after that we also study froth flotation process after dissolved catalyst and silica particles in part five. The effect which we study in part four and five was same as part two and three, respectively. This study we used Scanning lectron microscopy (SEM) to observe the surface of SWNTs, Laser Raman spectroscopy and Temperature programmed oxidation (TPO) to determine the quality and quantity of SWNT, respectively.

3.2.1 Production of Single-walled Carbon Nanotubes

The procedures used thus far for SWNTs production include arc discharge, laser ablation, and catalytic decomposition of carbon containing molecules over a metal catalyst. Although the arc discharge and laser ablation method are known to produce high-quality SWNTs, the amounts of SWNTs obtained by the two technique range from milligrams to grams. However, many potential applications of SWNTs will require much larger quantities. The catalytic decomposition of carbon-containing molecules appears as a promising technique for scale-up the production process at a relatively low cost. In this study, we will produce the SWNTs from the catalytic decomposition method by using cobalt and molybdenum as a catalyst supported on silica.

3.2.1.1 *Catalysts Preparation and Pretreatment*

The catalyst supported on silica was prepared by using incipient wetness impregnation technique. The Co and Mo were prepared by using aqueous solution of cobalt nitrate and ammonium heptamolybdate, respectively. The bimetallic catalysts were prepared by coimpregnation of aqueous metal solution to obtain metal-to-Mo molar ratios of 1:3. In this section, total metal loading in the catalyst was 6 wt%. Silica has an average pore size of 6 nm, BET area of 500 m²/g, and particle size in the range of 70-230 mesh. After impregnation, the catalysts were first dried in air at room temperature for a few hours, then dried overnight in oven at 110 °C, and finally calcined in flowing of dry air at 500 °C for 3 hour.

3.2.1.2 Production of Single-walled Carbon Nanotubes

The experimental was conducted by placing 0.3 mg of calcined catalyst in 8 mm horizontal quartz tubular reactor and heated in H₂ up to 500 °C and then in He up to 850 °C. Subsequently, carbon monoxide, as a carbon-containing gas, was induced at the same temperature and at a flow rate 100 cm³/min. The system was kept under these conditions for 30 min. At the end of each run, the system was cooled down to room temperature under the flow of helium gas.

3.2.2 Dissolution of Catalyst Particles

The SWNTs concentration of 0.1 g was fixed for this experiment. At first the SWNTs were placed in an oven at 250°C for 12 hours to oxidize the Co and Mo species which remained in the sample. At that point, the heater was turn off and the oven was allowed to cool by natural convection. The parameters of sonication time, hydrochloric (HCl) concentration and reaction temperature were studied. The Atomic Adsorption Spectroscopy (AAS) was used to detect the amount of metal particle which dissolved.

3.2.2.1 Effect of Sonication Time

A certain amount of calcined SWNTs about 0.1 g were placed in a beaker. Then add HCl, which a concentrate at 10 M, about 5 ml in the beaker and placed it into the sonication bath at 70°C. The reaction time was varies in 1 hr, 3 hr, 5 hr and 7 hr. The reaction time was started when turn on the sonication bath. The SWNTs were separated from the acid solution by filtering with a filter paper and then take the solution to find the amount of metal dissolved by AAS.

3.2.2.2 Effect of Hydrochloric Acid Concentration

This part was also use 0.1 g of calcined SWNTs. The HCl concentration was varies in 1 M, 3 M, 5 M, 8 M and 10M and fixed the sonication time at 3 hr and operated at 70°C. The same procedure as mentioned before was done.

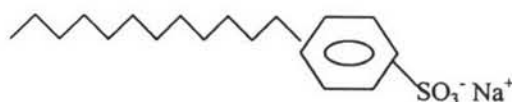
3.2.2.3 Effect of Reaction Temperature

The experiment was also carried out by adding 0.1 g of calcined SWNTs and 6 M of HCl concentration in the beaker. The temperature was

varied from room temperature (30°C), 40°C, 50°C and 70°C with a constant reaction time of 3 hr. The same procedure as mentioned before was done.

3.2.3 Froth Flotation Experiment (after dissolved catalyst particles)

The SWNTs concentration of 0.25 mg/ml were fixed for the purification experiment. The SWNTs were treated by HCl to dissolve the catalyst particles with the optimum condition which we gain from part 3.2.2. The SWNTs and silica which remain in suspended form were separated from the acid solution by filtering with a filter paper. This solid was rinse with DI-water in many times to make sure the acid does not remain in the SWNTs. After that, this sample was mixed together with the surfactant solution. In this study we select the anionic surfactant, sodium dodecylbenzenesulfonate, as a key of separation because we want to separate the SWNTs out from the silica particle so we were adjust the pH solution to make the surface charge of the SWNTs to positively charged and silica in the negatively charged. From this reason the SWNTs were separated from silica particle. In the froth flotation part, the parameter of surfactant concentration, pH solution and air flow rate were studied.



Sodium dodecylbenzenesulfonate, SDBS

A schematic diagram of the froth flotation unit used in this study is shown in Figure 3.1. A glass cylindrical column with 3 cm internal diameter and 150 cm height was used as the froth flotation column (see in Figure 3.2). Air Zero was introduced into the column through a sintered glass disk, having pore size diameters about 16 - 40 μm . The froth accumulated at the top of the column came out into a receiver. The experiment was terminates when no foam came out. The froth collected was broken by freezing. After that the over flow foam solution was washed with distilled water and centrifuge many times to remove the surfactant. The washed solid was dried at 110°C and took to characterize by Laser Raman spectroscopy and the Temperature programmed oxidation (TPO).

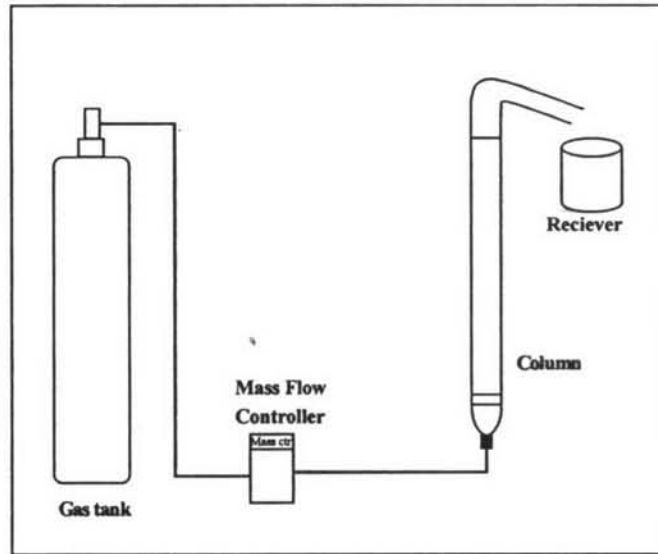


Figure 3.1 Experimental froth flotation apparatus.

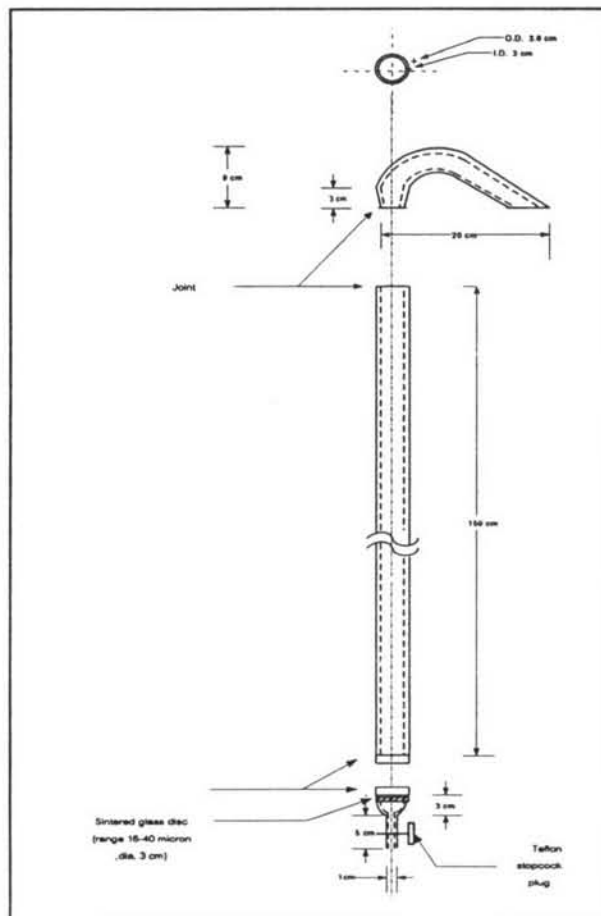


Figure 3.2 Schematic diagram of froth flotation column.

3.2.4 Dissolution of Silica Particle

As we know, SWNTs consist of silica more than 90% so the dissolving of silica particle was necessary to get more carbon purity. At first, SWNTs also treated by HCl to dissolve the catalyst particles with the optimum condition which we gain from part 3.2.2 and filtering with a filter paper. This solid was rinse with DI-water in many times to make sure the acid does not remain in the SWNT. After that, the sample was further treated by NaOH to dissolve silica by varying sonication time, NaOH concentration and reaction temperature. The Atomic Adsorption Spectroscopy (AAS) was used to detect the amount of silica particle dissolved.

3.2.4.1 *Effect of Sonication Time*

A certain amount of SWNTs, which treated by HCl, about 0.1 g were placed in a beaker. Then add the NaOH, which a concentrate at 10 M, about 30 ml in the beaker and placed it into the sonication bath at 70°C. The reaction time was varies in 1 hr, 3 hr, 5 hr and 7 hr. The reaction time was started when turn on the sonication bath. The SWNTs were separated from the basic solution by filtering with a filter paper and then take the solution to find the amount of silica dissolved by AAS.

3.2.4.2 *Effect of Hydrochloric Acid Concentration*

This part was also use 0.1 g of SWNTs, which treated by HCl. The NaOH concentration was varies in 1 M, 3 M, 5 M, 8 M and 10M and fixed the sonication time at 3 hr and operated at 70°C. The same procedure as mentioned before was done.

3.2.4.3 *Effect of Reaction Temperature*

The experiment was also carried out by adding 0.1 g of calcined SWNTs and 5 M of NaOH concentration in the beaker. The temperature was varied from room temperature (30°C), 40°C, 50°C and 70°C with a constant reaction time of 3 hr. The same procedure as mentioned before was done.

3.2.5 Froth Flotation Experiment (After dissolved catalyst and silica particles)

The SWNTs concentrate 0.25 mg/ml were fixed for the purification experiment. The SWNTs were treated by HCl to dissolve the catalyst particles and NaOH to dissolve silica with the optimum condition which we gain from part 3.2.2 and 3.2.4, respectively. After that, this sample was mixed together with the surfactant solution. In this section we also use the same surfactant as part 3.2.3 and study in pH solution, surfactant concentration and air flow rate.

A schematic diagram of froth flotation unit was same as mention before.

3.3 Analytical Method

3.3.1 Dissolution of Catalyst and Silica Particles

An Atomic Analysis spectroscopy (AAS) was used to determine the amount of catalyst and silica in the SWNTs before and after treated by HCl and NaOH, respectively.

3.3.2 Carbon Product Characterization

The collapsed froth solution, which was washed by distilled water and finally dried at 110°C, was taken to analyze for carbon content and carbon structures. The characterization of carbon products were carried out by a number of techniques including Laser Raman spectroscopy and Temperature programmed oxidation (TPO) which were used to determine quality and quantity the solid samples.

3.3.2.1 *Laser Raman Spectroscopy*

Raman spectroscopy is a non-destructive analysis technique and measurements can be made over a wide range of temperatures or pressures. It can provide unique information about vibrational and electronic properties of materials. Even though it is not a direct method, it can also be used to determine the structures of materials. Because the Raman intensity of a vibration or phonon in a crystal depends on the relative directions of the crystal axis and the electric wave polarization of the incident and scattered light, it may also be used to determine the

orientation of nanotubes in polymer matrices or within nanotube bundles (Richard, 2000).

The sample before and after purification by froth flotation were studied by comparing laser Raman spectra. The Raman spectroscopy used in this study was Yvon-Horiba LabRam 800 equipped with a CCD (charge-couple device) with laser excitation sources having a wavelength of 632 nm (He-Ne laser). The laser powers used were in the range of 3.0 to 5.0 mW.

3.3.2.2 Temperature Programmed Oxidation (TPO)

This TPO technique can investigate for quantitative properties of carbon nanotubes. The TPO analysis was performed at a continuous flow of O₂/He (ratio 2:1) with a total flow rate of 40 sccm. A carbon sample about 10-12 mg was placed in the quartz tube and it was secured with packing quartz wool the sample temperature was linearly increased with a constant rate of 13°C/min to reach a maximum temperature of 850°C. The carbon fraction of the sample was reacted with oxygen (O₂) to produce oxidation products such as water (H₂O) and carbon dioxide (CO₂). After this reaction, CO₂ and H₂ in the effluent gas were passed to a methanator containing Ni/Al₂O₃ catalyst to convert into carbon dioxide (CO₂) to methane (CH₄). Consequently, CH₄ was detected with a flame ionization detector (FID SRI Model 110). The area under the curve obtained was used to calculate carbon content in the sample. Moreover, the shape of the curve can be used to determine the type of carbon formation. In other words, carbons with different morphology or different locations are burnt at different temperatures.

3.3.2.3 Scanning Electron Microscopy (SEM)

The surface morphology of the resulting electrospun SWNTs were observed by a JSM5800 Scanning Electron Microscope (SEM), which was operated at 20 kV, at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Samples were coated by a thin layer of gold prior to the analysis.