CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Cobalt (II) nitrate hexahydrate with 98% purity obtained from Sigma-Aldrich Company, and ammonium molybdate tetrahydrate obtained from Sigma-Aldrich Company were used as precursors for the synthesis of SWNTs. Silica gel was obtained from Aldrich Chemical Company, Inc. It has a specific surface area of 500 m^2/g and the particle size in the range of 70-230 mesh (63-210 μm). Hydrochloric acid with 37 wt% received from Merck KGaA Company and analytical grade sodium hydroxide with 99.3% purity obtained from Labscan Asia Co., Ltd were used for pH adjustment. Sodium dodecylbenzenesulfonate (SDBS) with a purity of 88%, anionic Surfactant was purchased from Acros Company. Alcohol ethoxylate (Surfonic L24-7), a nonionic Surfactant received from Hunstsman Co.,Ltd have seven moles of ethoxylate with 12-14 carbon number in the alkyl group. Deionized water purchased from the government pharmaceutical, Thailand was used to prepare all solutions. All chemicals were used as received without any purification.

3.1.2 Gases

All gasses (air, hydrogen, helium and carbondioxide) used in this study were high purity grade and supplied by Thai Industrial Gas Public, Co., Ltd, Thailand.

3.2 Experimental Methodology

3.2.1 Synthesis procedure of Single-Walled Carbon Nanotubes

Currently, there are three techniques for the synthesis of SWNTs: laser ablation, arc discharge and catalytic decomposition. Even though, the laser ablation and arc discharge techniques give high qualities of SWNTs, they are not suitable toward a large scale production. Alternatively, the catalytic decomposition of carbon-containing molecules appears as a promising technique for a large scale the production with at a relatively low cost. In this study, SWNTs were produced by a catalytic chemical vapor deposition method of the disproportionation CO over Co:Mo/SiO$_2$ catalyst.

a) Preparation of Catalyst

In this study a CoMo catalyst was prepared by using cobalt nitrate and ammonium heptamolybdate catalyst precursors over a silica support using incipient wetness impregnation method. Silica has an average pore size of 6 nm, a BET area of 500 m^2/g, and particle sizes in the range of 70-230 mesh. The total metallic loading in the catalyst was fixed at 6 wt% with a Co:Mo molar ratio of 1:3 which exhibited the highest selectivity towards SWNTs according to the previous work (Resasco et al, 2002). Subsequent to impregnation, the catalyst was primary dried in air at room temperature for a few, then dried overnight in an oven at 110°C, and calcinated in flowing air at 500°C for 3 h.

b) Synthesis of SWNT with CoMoCAT Method

An amount of 0.3 g of fresh catalyst sample was placed in an 8 mm horizontal quartz tubular reactor. Before exposure to the CO feedstock, the catalyst was heated up to 500°C in a flow of gaseous H$_2$ for 30 min, and further heated to 850°C in flowing He. Subsequently, CO was introduced continuously at this temperature for 30 min under a flow of pure CO at 5 atm, and at a flow rate of 500 cm^3/min. Figure 3.1 shows experimental set-up of SWNTs production. After that, the system was cooled down to room temperature under natural convection. The SWNT grown by this method contained large portions of the spent catalyst, and silica support.
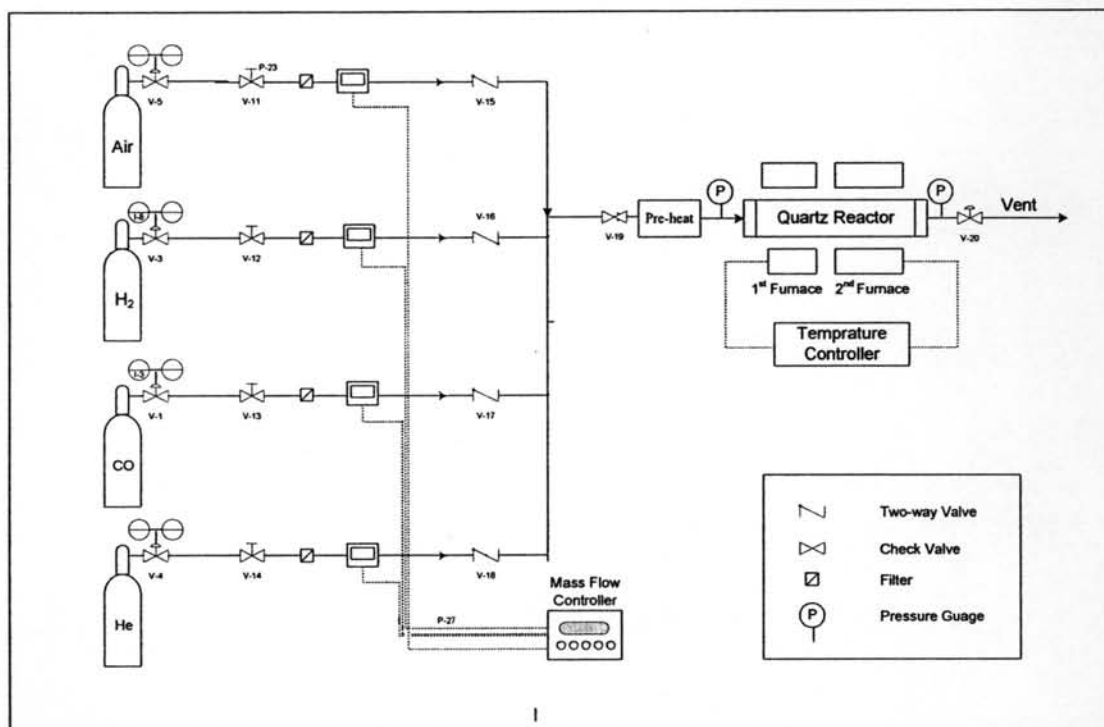
Figure 3.1 Schematic flow diagram for SWNTs production unit.

3.2.2 Oxidative Pretreatment

The oxidative pretreatment was first employed to oxidize the spent catalysts to metal oxides, leading to the enhancement of the catalyst dissolution efficiency by using HCl. It is obvious that low temperature oxidation is able to remove partially the disordered carbon. Temperature gravimetric analysis (TGA) was applied for the investigation of the transformation of the spent catalyst from metallic to metal oxides. An amount of 20 mg of the SWNT samples was first placed to the platinum pan and the sample was heated up at different temperature with a constant flow 100 ml/min of 5% O_2 in helium. From the TGA results, the optimum conditions were selected for the oxidative pretreatment step. Then, the SWNT sample treated under these optimum conditions was used for further experiment

3.2.3 Catalyst Dissolution

The impurities of both the cobalt and molybdenum have been hindering the advanced properties of the SWNTs. In order to minimize these adverse effects, HCl was used to dissolve these metals in this study. In this work, the effects of HCl concentration, sonication time, and reaction temperature were investigated. All experiment was repeated at least three times to ensure reproducibility. A specific amount of the oxidized SWNTs (0.1 g) was first added in a beaker containing 1 mL of a HCl solution with different concentrations: 0.5, 1, 5, 8 and 12 M. The beaker was placed in to the sonication bath at 70°C for 5 h. Subsequently, the treated SWNTs were separated from the acid solution by filtering with a filter paper. Finally, the solution was taken to analyze Co and Mo concentrations. From the results, an optimum condition was selected for further investigation.

A certain amount of oxidized SWNTs about 0.1 g was added in a beaker. Then, 5 ml of 10 M HCl was added. The mixed solution was then sonicated at 70°C. The sonication time was varied in 1 to 7 h. The remaining solids was separated from the acid solution by filtering. Subsequently, the concentrations of Co and Mo were analyzed by ICP. Then, an optimum sonication time was obtained and used for next experiments.

The same procedure was used to observe the effect of temperature. 0.1 g of the oxidized SWNT sample was added into 1 mL of 10 M HCl. The reaction temperature was varied from room temperature (30°C) to 40°C, 50°C and 70°C for 3 h. The same procedure was performed to investigate to the cycle number of the catalyst dissolution.

3.2.4 Silica Dissolution

Since the silica was used as a catalyst support, the as-synthesized SWNTs still contained a large fraction of silica (greater than 90%). In this study, NaOH was selected to dissolve the silica in the as-synthesized SWNTs. An amount 0.01 g of SWNTs sample treated with both oxidative and acid steps was further dissolved in1.5 ml of 5 M sodium hydroxide solution at 70°C and 12 h. These conditions were obtained from the optimal conditions of previous work (Chuaybumrung., 2006). ICP was used to determine the concentrations of silica.

3.2.5 Determination of Point of Zero Charge (PZC)

A certain amount of 0.1 g of silica, carbon black or as-synthesized SWNTs sample was placed into a vial, which contained different initial solution pHs in the range of 1-14. The initial solution pH value was adjusted by adding either concentrated hydrochloric acid or sodium hydroxide. After that, the mixture was left overnight to reach equilibrium at 30°C. The final pH (equilibrium) was then measured. The measurement of pH was done by using a pH meter (Hanna Instrument, 310).

3.2.6 Contact Angle Measurement

A desired quantity if 2 g of grinded samples (silica, carbon black, as-synthesized SWNTs) was compressed by hydraulic pressure to obtain a smooth-surface pellet. The compressed sample was measured for the contact angle after being dropped with distilled water. The measurement of contact angle was carried out by using a contact angle meter (KRUSS, DO3020/3021).

3.2.7 Surface Tension Measurement

The surface tension of aqueous solution containing different surfactant concentrations was measured by using a tensiometer with a Du-Nuay ring (Kruss, K10T). The original micelle concentration of each surfactant was obtained from the plot of surface tension and surfactant concentration where the surface tension reaches the maximum value.

3.2.8 Froth Flotation Experiments

In this study, the effects of surfactant type, surfactant concentration and solution pH were investigated. As mentioned before, the as-synthesized SWNT sample was treated by the three sequential steps of oxidation, acid leaching and silica dissolution. The treated SWNT sample was taken for the froth flotation experiments. The treated SWNT sample was first rinsed with distillated water until the solution pH became neutral and subsequently dried at 110 °C to obtain dried weight. A certain amount of the treated SWNT sample was mixed with a surfactant solution to obtain a

total solid concentration of 0.25 mg/mL. In this investigation, two types of surfactants: SDBS and Suffonic L24-7 were used. The mixed solution was transferred into a froth flotation column. A schematic diagram of the froth flotation unit used in this study is shown in Figure 3.2. A glass cylindrical column with 3 cm internal diagram and 150 cm height was used as the froth flotation column (see in Figure. 3.3). Air Zero was introduced into the column through a sintered glass disk, having pore size diameters about 16 - 40 μm. The accumulated froth at the top of the column came out into a receiver. The experiment was terminated when no foam came out. The collected foam was broken by freezing. After that, the overflow foam solution was washed with distilled water, and centrifuged 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).
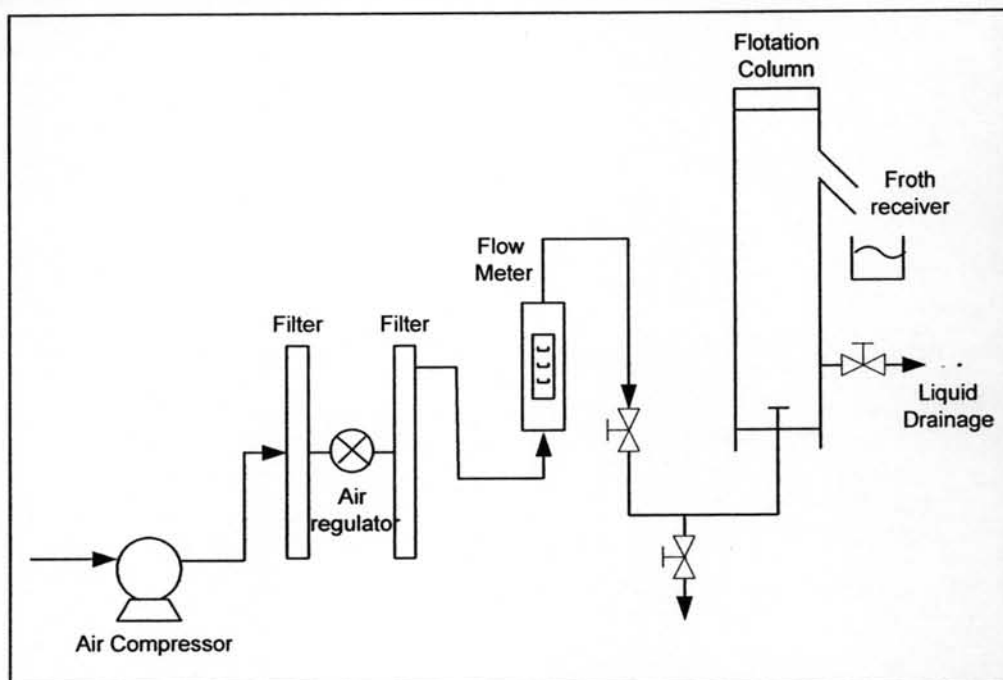

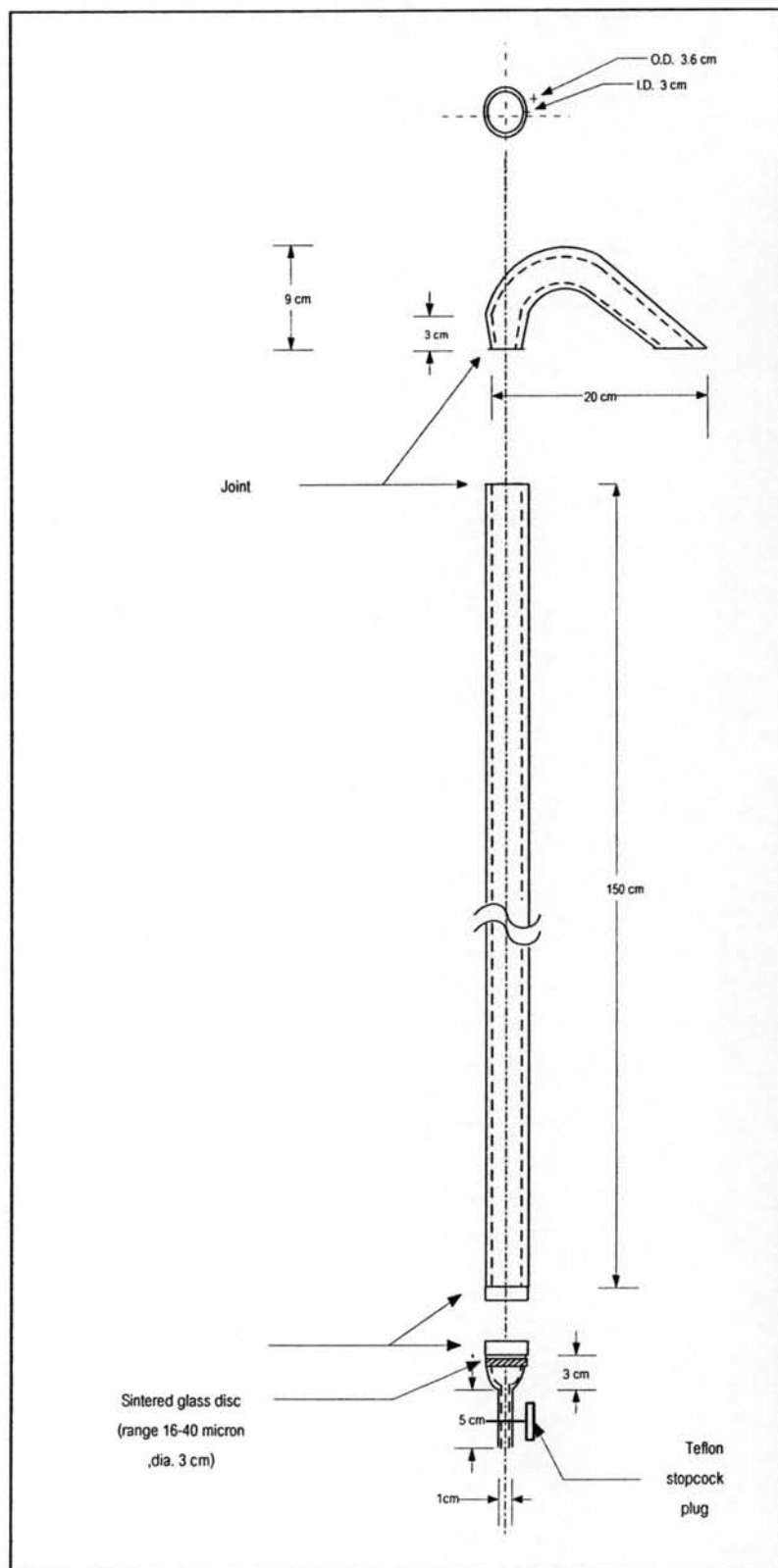**Figure 3.2** Schematic diagram of the froth flotation process.

Figure 3.3 Schematic diagram of froth flotation column.

3.3 Analytical method

3.3.1 Inductively Coupled Plasma

An Inductively Coupled Plasma (ICP) was used to determine the concentration of Co and Mo and Si

3.3.2 Laser Raman Spectroscopy

Laser raman spectroscopy is a non-destructive analysis technique and this technique can measure 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 identify the structures of materials. 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. Furthermore, it may also be used to determine the orientation of nanotubes in polymer matrices or within nanotube bundles (Richard, 2000).

The samples before and after each purification step 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 were used in the range of 3.0 to 5.0 mW.

3.3.3 Temperature Programmed Oxidation (TPO)

This TPO technique can provide quantitative properties of carbonaceous species. The TPO analysis was performed under a continuous flow of O_2/He (ratio 2:1) with a total flow rate of 40 sccm. A sample about 10-12 mg was placed in a quartz tube and it was secured with packing quartz wool. The packed sample was heated linearly with a constant rate of 10°C/min controlled by temperature programed equipment to reach a maximum tempertaure of 850°C. Each carbon fraction of the sample was reacted with oxygen (O_2) to produce oxidation products such as water (H_2O) and carbon dioxide (CO_2). The produced CO_2 was mixed with CH_4 and then these mixed gas was passed through a methanator containing Ni/Al_2O_3 catalyst to convert the carbon dioxide (CO_2) to methane (CH_4). Consequently, the produced CH_4 was detected by a flame ionizaton detector (FID)

(SRI, 110). The area under the curve of each carbon fraction 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.

3.3.4 Scanning Electron Microscopy (SEM)

The surface morphology of samples was observed by a JSM5800 Scanning Electron Microscope (SEM), which was operated at 20 kV. Prior to the analysis, samples were coated by a thin layer of gold with 15 mA for 3 minutes.

3.3.5 X-ray Photoelectron Spectroscopy (XPS)

The oxidation stage of Mo and Co were analyzed by using a X-ray photoelectron spectroscopy (XPS) (digital electronics, 8017), equipped with a dual Mg/Al anode. The sample was excited by a non-monochromatised Mg Kα source (1253.6 eV) run at 14 kV and 15 mA. The analyzer was operated at the constant energy mode (CAE). For any individual peak energy region, a pass energy of 20 eV set across the hemispheres was used. Survey spectra were measured at 50 eV pass energy. The sample powers were prepared as pellets, mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. For each sample, the binding energy regions corresponding to Si, Mo and Co are 95-115, 220-245, and 760-820 eV, respectively. The constant charging of the samples was removed by referencing all the energies to the C 1s set at 284.8 eV, arising from the adventitious carbon. The invariance of the peak shapes and widths at the beginning and at end of the analyses ensured absence of differential charging. The analysis of all peaks was performed with the software provided by VG, based on non-linear least squares fitting program using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley, *et al.*, (1972) and Sherwood, *et al.*, (1990). Constraints in the intensity ratios of the two Mo 3d and Co 2p doublet components were used in accordance with the spin-orbit coupling rules. Atomic concentrations were calculated from peak intensities using the correction factors provided with the software. The binding energy (BE) values are quoted with a precision of $\pm$ 0.15 eV. In order to check for possible radiation damage, spectra of the Mo 3d and Co 2p regions were

acquired as the first and last regions during multiplex acquisition and no differences were observed.