

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), with 98% purity, was obtained from Sigma-Aldrich Co. Ltd.

- Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), with a purity above 98%, was obtained from Sigma-Aldrich Co. Ltd.

- Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in crystalline form was obtained from Sigma-Aldrich Co. Ltd.

- Ammonium molybdate(VI) tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), with 81.0-83.0% as MoO_3 , was obtained from Sigma-Aldrich Co. Ltd.

- Ammonium perrhenate (NH_4ReO_4), with 99% purity, was obtained from Sigma-Aldrich Co. Ltd.

- Silica gel was obtained from Sigma-Aldrich Co. Ltd. it has particle sizes in the range of 70-230 mesh (62-210 μm), average pore diameter of 6 nm, a BET surface area of 480 m^2/g , and a pore volume of 0.75 cm^3/g .

- Magnesium oxide (MgO) was obtained from Sigma-Aldrich Co. Ltd. It is a fused type and has a particle size of -40 mesh (minus 40 mesh refers to material that has been sized by passing through a screen with 40 holes per inch) with a BET surface area of 4.1 m^2/g .

- γ -Alumina ($\gamma\text{-Al}_2\text{O}_3$) was obtained from Sigma-Aldrich Co. Ltd. It is a weakly acidic type and has an average particle size of 150 mesh (104 μm), pore size of 5.8 nm, and a BET surface area of 155 m^2/g .

- Carbon black, type 400R, was supplied by Cabot Company, USA. It has an average particle size of 0.24 μm and a density of 0.3 g/cm^3 .

- Nonionic surfactant, Surfonic L24-7, with a high purity of 100%, composed of linear alcohol polyethoxylate, with an average degree of polymerization of 7 and a linear alkyl chain of 12-14 carbons number, was obtained from Huntsman Company, USA.

- Hydrochloric acid (HCl), with a concentration of 37 %wt, was obtained from Merck KGaA Company.

- Sodium hydroxide (NaOH), with a purity above 97%, was obtained from Carlo Erba Company

- Sodium chloride (NaCl), with a purity of 99%, was obtained from Labscan Asia Company, Thailand.

- Deionized water

All chemicals were used as received without any further purification.

3.1.2 Gases

- Air zero was supplied by Thai Industrial Gas Co. Ltd.

- 2% of oxygen in helium balance was supplied by Thai Industrial Gas Co. Ltd.

- 5% of hydrogen in nitrogen balance was supplied by Thai Industrial Gas Co. Ltd.

- Helium, with a purity of 99.99%, was supplied by Thai Industrial Gas Co. Ltd.

- Nitrogen, with a purity of 99.99 %, was supplied by Thai Industrial Gas Co. Ltd.

- Hydrogen, with a purity of 99.99 %, was supplied by Thai Industrial Gas Co. Ltd.

- Carbon monoxide, with a purity of 95%, was obtained from Airgas Inc.

- Methane, with a purity of 99.99%, was supplied by Thai Industrial Gas Co. Ltd.

3.2 Methodology

3.2.1 Catalyst Preparation and Pretreatment

A series of supported catalysts including monometallic catalysts (Fe, Co, Ni, Mo, and Re) and bimetallic catalysts (Fe-Mo, Co-Mo, Ni-Mo, and Co-Re) was prepared by incipient wetness impregnation technique on various oxide supports

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(SiO₂, MgO, and Al₂O₃). Each catalyst was prepared to obtain a specified total metal loading and molar ratio of metals. After impregnation, the catalyst samples were first dried in air at room temperature for 2 h, then dried overnight in oven at 120°C, and finally calcined in the flow of dry-air at 500°C for 3 h.

3.2.2 Single-Walled Carbon Nanotube Synthesis

An amount of calcined catalyst (0.3-0.5 g) was placed in an 8-mm horizontal quartz tubular reactor, heated in a H₂ flow to 500°C (100 cm³/min), held on this temperature for 30 min, and then heated in a flow of He to 750-850°C (100 cm³/min). Subsequently, CO or CH₄ was introduced at a flow rate of 100-850 cm³/min at 1-5 atm and the reactor was kept under these conditions for 30 min. At the end of the reaction, the system was cooled down to room temperature under the flow of He.

3.2.3 Characterization of Fresh Catalysts and Single-Walled Carbon Nanotubes

The temperature-programmed reduction (TPR) experiments on the calcined catalysts were conducted in a Thermo Finnigan TPDRO 1100 equipped with a thermal conductivity detector (TCD). The system was operated by passing a continuous flow of 5% H₂ in N₂ balance over approximately 50 mg of the calcined catalysts, while the temperature was linearly increased at a rate of 10°C/min. The intensities of thermal conductivity, which corresponds to the amount of hydrogen consumption by the samples, were plotted with the temperature.

The temperature-programmed oxidation (TPO) experiments on an SWNT-containing sample were conducted in a TPO apparatus equipped with a flame ionization detector (FID). The system was operated by passing a continuous flow of 2% O₂ in He balance over approximately 10 mg of the sample, while the temperature was linearly increased at a rate of 10°C/min. The intensities of the FID, which corresponds to the amount of oxygen consumption by the samples, were plotted with the temperature.

The Raman spectra of nanotubes were recorded using a Jobin Yvon Horiba LabRam 800 equipped with a CCD detector and with the laser excitation

source having a wavelength of 632 nm. The Raman spectra were obtained by using 3.0-5.0 mW laser power; 15 s integration time for each spectrum; and ten Raman spectra were averaged for each sample.

The SEM, JOEL model JSM-5200-2AE, was used at the magnification of 10,000 times and an acceleration voltage of 15 kV.

Transmission electron microscopy was performed on a JEOL JEM-2000FX at an acceleration voltage of 200 kV. The sample was prepared by sonicating the spent catalyst in an isopropanol solutions, putting a few drops of the suspension onto a lacey carbon grid, and then allowing it to dry.

3.2.4 Measurement of Point of Zero Charge (PZC) and Contact Angle

To measure the PZC of a solid, 10 mL of aqueous solutions having different pH values ranging from 1 to 11 were prepared in vials by adding hydrochloric acid or sodium hydroxide to deionized water. The ionic strength of the solutions was kept constant to 0.1M by using sodium chloride to more quickly attain a state of equilibrium without affecting the final pH. After that, 0.5 g of solid was added to each vial, stirred and then left overnight to equilibrate at $25\pm 1^\circ\text{C}$. The equilibrium pH was then measured and plotted against the initial pH for each substrate. The PZC can be readily obtained from the point at which the initial pH equals the equilibrium pH.

The contact angle of the solid was determined by grinding and then pressing the powder of the solid particles with a hydraulic press under a pressure of 15 N/m^2 to obtain flat surface pellets. The pellets were then used to measure the contact angle by a KRUSS drop shape analysis system (DSA10-Mk2) with the sessile drop method using a drop of 5 μL of deionized water.

3.2.5 Surfactant Adsorption Experiment and CMC Determination

The surfactant adsorption onto solid surface was studied at $25\pm 1^\circ\text{C}$. An amount of a solid (0.1 g) was mixed with 20 mL of a surfactant solution having different initial concentrations. The mixture was well shaken and allowed to equilibrate for three days, which has been shown to be sufficient for equilibrium to be attained. After that, it was centrifuged at 15,000 rpm for 30 min. The supernatant

was decanted and the equilibrium surfactant concentration in the supernatant was analyzed by a total organic carbon analyzer (Shimadzu, TOC - VCSH). The specific surface area of a solid was measured by using a surface area analyzer (Sorptomatic, Thermo Finnigan, 1990).

To measure the critical micelle concentration (CMC) of the surfactant, the surface tensions of aqueous solutions containing various surfactant concentrations were measured by using a DuNouy-Ring Tensiometer (Krüss, K10ST). The CMC of surfactant was determined from the concentration at which the surface tension reaches a plateau.

3.2.6 Silica Dissolution Experiments

A different quantity of the as-prepared SWNT sample in the range of 0.2-1.4 g was mixed with 30 ml of a 10 M NaOH solution in a vial. This mixture was sonicated in a 440W ultrasonic bath (Crest, 575DAE) at different sonication times. To minimize the loss of carbons from the sample, the mixture was added, after the sonication was completed, to a nonionic surfactant solution without removing the remaining NaOH in the silica dissolution step for further SWNT sample purification and concentration by froth flotation. In order to determine the total amount of carbons in the NaOH-treated SWNT sample, the basic sonicated mixture was neutralized by HCl solution to obtain a pH value of 7 ± 1 and was centrifuged at 15,000 rpm for 20 min. The solid was then dried at 110°C to determine the total dried weight.

3.2.7 Froth Flotation Experiments

A schematic of the froth flotation apparatus used in this work is shown in Figure 3.1. The flotation column was a glass column with an internal diameter of 4.1 cm and a height of 75 cm. Filtered air was introduced at the bottom of the column through a sintered glass disk having pore size diameters of 40-60 μm . In order to determine the effects of foam height, surfactant concentration, and solid loading, a quantity of 300-700 ml of solutions containing different concentrations of the NaOH-pretreated SWNTs and surfactant was poured into the froth flotation column. To investigate the effect of air flow rate on the SWNT separation efficiency,

the air flow rate was varied from 40 to 120 ml/min by using a mass flow controller. The froth flotation experiments were operated in batch mode at room temperature ($25\pm 1^\circ\text{C}$) and the operation was terminated when, due to surfactant depletion, no foam came out from the top of the column. The generated foam was collected at the top of the column and was then allowed to collapse. The collapsed foam was then washed to remove the surfactant by rinsing with deionized water and centrifuging at 15,000 rpm for 20 min. This surfactant-washing step was carefully repeated several times until there was no visible foam in the sample solution. The sample solution was then dried overnight in an oven at 110°C to determine the total dried weight.

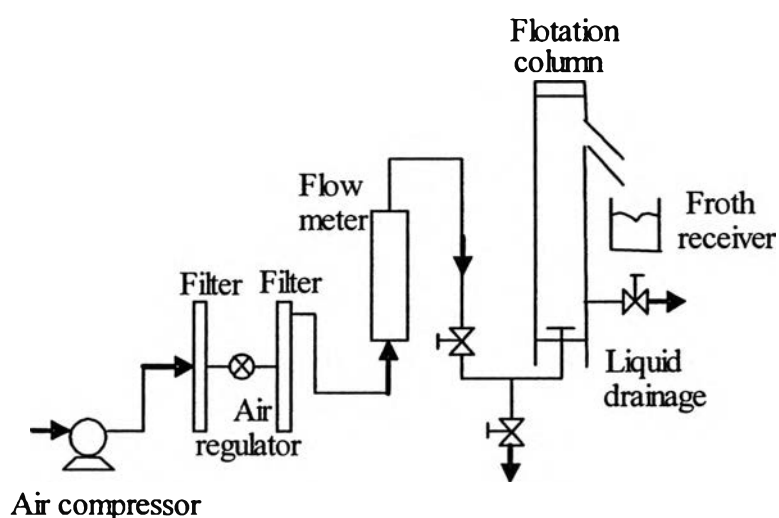


Figure 3.1 Schematic of the froth flotation apparatus.

3.2.8 Foam Characteristic Experiments

Foam characteristic experiments were also conducted independently in an extended flotation column having the same internal diameter and porosity of the sintered glass disk. After a solution having different concentrations of the NaOH-treated SWNT sample and the surfactant was transferred to the column and well mixed, filtered air was introduced at the bottom of the column at a desired flow rate. The maximum foam height divided by the initial solution height in the column is defined as foamability. After the maximum foam height was attained, the flow of air to the column was then stopped and the time required for the foam volume to collapse to one half of the maximum height was used to quantify foam stability ($t_{1/2}$).