CHAPTER II
LITERATURE SURVEY

2.1 Introduction to Silica

Silica is the second most abundant element found on earth. Silica, like its sister element carbon, has four covalent bonding sites and can, therefore, form a very large number of potential molecules. It is frequently compared to carbon but its behavior differs from carbon. For instance, carbon rarely achieves pentacoordination in an intermediate or thermodynamically stable product while pentacoordinate silicon plays a role in the solubility of silica in water and in the hydrolysis of alkoxysilanes, such as tetraethoxysilcane (TEOS). Because the silica nucleus is larger than the carbon nucleus, silica does not easily form double or triple bonds, and silica does not readily form chains more than 6 silica atoms long. The amorphous silica and solid silica deposits typically contain a ratio of two moles of oxygen per mole of silicon. We use the formula "SiO_2" because it is convenient. However, the primary problem with SiO_2 is its Si-O-Si chemical bond strength (128 kcal/mole or 535 kJ/mole) which makes it a stable material that is difficult to manipulate chemically (www.resintech.com).
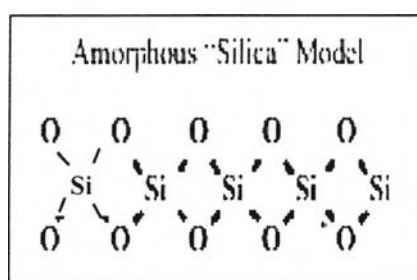

Figure 2.1 Amorphous "Silica" Model (www.resintech.com).

According to Akhmoter, silicon dioxide (SiO_2, silica) has several forms. It occurs mainly as quartz (hexagonal structure), as well as cristobalite (cubic structure) and tridymite (hexagonal structure). Silica melts at a high temperature ($1731^{\circ}C$). It

is very hard and chemically stable. Only fluorine, liquid and gaseous hydrofluoric acid, phosphoric acid and alkaline solutions react with it under normal conditions. It is insoluble in water at 150°C, but its solubility improves to 0.25 weight percent at 500°C (Iler, 1979).

2.2 Introduction to Carbon Nanotubes

Carbon nanotubes can be visualized as a graphite layer rolled up into a cylinder, which each end either open or capped with the half a fullerene as shown in Figure 2.2. Carbon nanotubes can be divided in to two types, which are multi walled carbon nanotubes (MWNTs) and single walled carbon nanotubes (SWNTs).

MWNTs are composed of two or more cylindrical layers of graphitic sheets. Iijima (1991) discovered this type of carbon nanotubes by using cathode deposit from carbon arc discharge experiment. Subsequently, in 1993 Iijima discovered SWNTs containing only one concentric layer by using in the same technique. In general, the diameter of SWNTs is around 1-2 nm and length about 5-10 micron, while the diameter of MWNTs typically ranges around 2.5-30 nm and length from a few tens of nanometers to several micrometers.
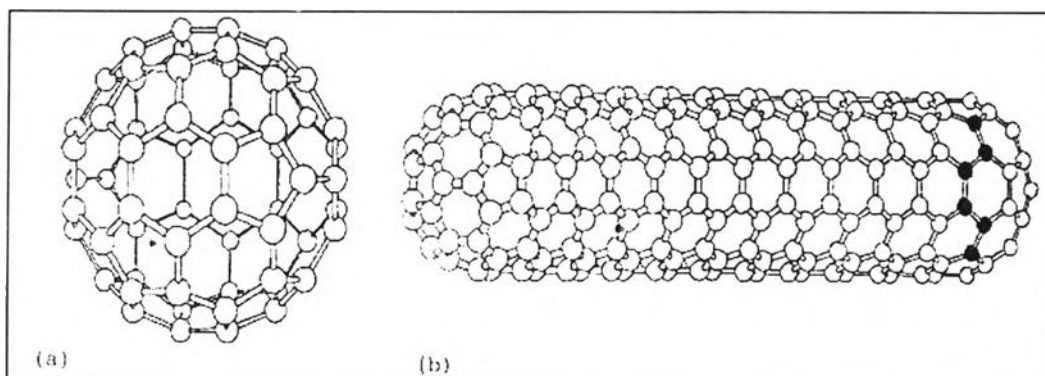

Figure 2.2 Carbon nanostructures (a) a spherical molecule, fullerene (b) a hollow cylindrical tube, carbon nanotube (Tang, 2001).

2.3 Properties and Applications of Carbon Nanotubes

Carbon nanotubes have demonstrated their potentially useful mechanical and electrical properties. According to mechanical properties, carbon nanotubes are predicted to have very high Young's modulus (Treacy *et al.*, 1996), which can be over 1 Tpa., and a maximum tensile strength close to 50 Gpa., about 50 times higher than steel. Moreover, they have shown a combination of lightweight (density = 1.3 g/cm^3) with high elastic modulus. From these properties, carbon nanotubes probably can be used as reinforcing nanofibers for composite materials. Furthermore, SWNTs also have outstanding electronic properties that they can be either a metal or semi-conductor depending on their helicity. For example, the armchair nanotubes are metallic, while, zig-zag nanotubes are semiconductor. According to SWNTs having a very small diameter, they may be used as nanoelctronic devices. Furthermore, carbon nanotubes are believed to have others practical applications such as field emission, biosensor, advanced scanning probes for scanning probe microscope, and energy storage. (Cassel *et al.*, 1999).

2.4 Production of Carbon Nanotubes

Currently, there are three techniques to synthesize carbon nanotubes, the arc discharge of carbon electrodes, the laser ablation of carbon graphite and the catalytic reaction of hydrocarbon compounds.

2.4.1 Arc Discharge of Carbon Electrodes Technique

In 1991, the first production of carbon nanotubes has been operated by arc discharge technique. This technique introduced inert gas through the reactor, which consists of anode and cathode graphite electrodes inside the chamber. After carbon anode is drilled and filled with the transition metal, the electrical current is applying through the opposite carbon electrodes, positive and negative, with the result that arc plasma is generated between both electrodes. Consequently, the carbon atoms in carbon anode are vaporized and formed carbon products, depositing

on the carbon cathode or inside the reactor chamber, as shown in Figure 2.3. The carbons produced have several forms such as SWNTs, MWNTs, carbon nanoparticles, carbon amorphous, and graphitic carbon. There are many researchers to produce the carbon nanotubes with this method. For example, Iijima *et al.* (1993) and Bethune *et al.* (1993) reported that an arc discharge with a cathode containing metal catalysts (Co, Fe, Ni) mixed to graphite powder resulted in a deposit containing SWNTs. SWNTs is usually assembled in ropes or bundle, but some single tube can also be found in the deposits. Work by Richard Smalley and his colleagues has shown that the SWNTs can also be synthesized using a purely catalytic method. The catalyst employed contained particles of molybdenum a few nanometers in diameter, supported on alumina. This was placed inside a tube furnace through which carbon monoxide was passed at a temperature of 1200°C. All the SWNTs appeared to be capped and there was no evidence that catalytic metal particles were present at the ends of the tubes. This method remains by far the best technique for the synthesis of high-quality nanotubes, but it suffers from a number of disadvantages. Firstly, it is labor intensive and requires some skill to achieve a satisfactory level of reproducibility. Secondly, the yield is rather low. Thirdly, it is a 'batch' rather than a continuous process, and it does not easily lend itself to scale-up. The methods for producing SWNTs discussed so far have involved arc-evaporation using modified electrodes.
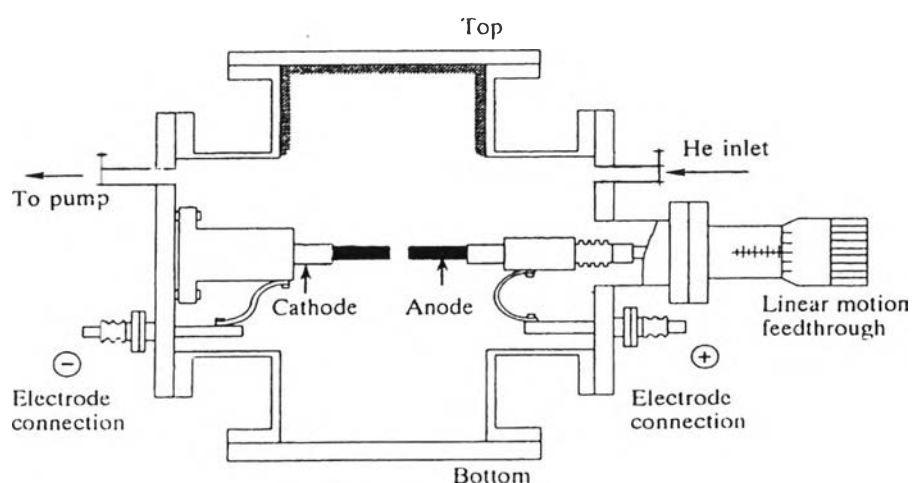

Figure 2.3 A carbon arc discharge apparatus (Harris, 1999).

2.4.2 Laser Vaporization of Carbon Graphite Technique

An advantage of the laser-vaporization method is a high yield of SWNTs with unusually uniform diameters. These highly uniform tubes have a greater tendency to form aligned bundles than those prepared using the arc-evaporation method. This technique appears to give the highest yield and the best quality material, but the high-powered lasers required for this method will obviously not be available in every laboratory. The laser vaporization method utilized intense laser pulses to ablate a carbon target containing 0.5 atomic percent age of nickel and cobalt. As illustrated in Figure 2.4, the target gas was placed in a tube-furnace heated to 1200°C. During laser ablation, a flow of inert gas is introduced to the growth chamber to carry the grown nanotubes downstream to be collected at a collecting zone. The produced SWNTs is mostly in the form of ropes consisting of tens of individual nanotubes packed into hexagonal crystals via van der Waals interactions. The growth of high quality SWNTs was demonstrated by Gou *et al.* (1995) and the optimization of SWNTs growth was achieved by Journet *et al.* (1997) using a carbon anode containing 1.0 atomic percentage of yttrium and 4.2 % of nickel as catalyst.
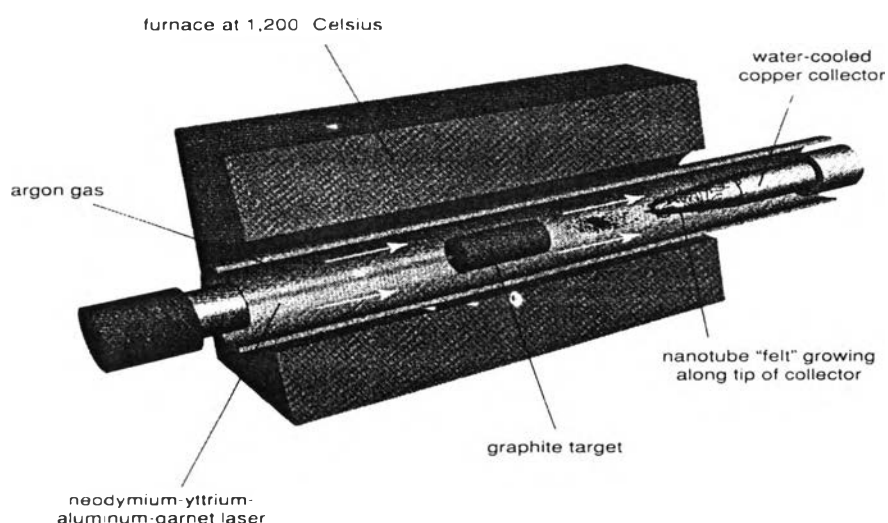

Figure 2.4 Laser vaporization apparatus (Yakobson and Smalley, 1997).

2.4.3 Catalytic Reaction of Hydrocarbon Compounds Technique

The arc discharge and laser ablation techniques are the traditional methods for obtaining the high quality nanotube materials. Nevertheless, both of them are not suitable for mass production of SWNTs because of the limitation to scale up the processes.

The catalytic decomposition of a carbon–containing molecule on a solid catalyst or CVD (Chemical Vapor Deposition) has been the best alternative to the large-scale production of SWNTs. Normally, carbon–containing gases (mostly methane and carbon monoxides) are passed over transition catalysts at elevated temperature for a period of time. At sufficiently high temperatures, these gases are catalytically decomposed, and as a result, carbon products are generated on the catalyst surfaces, as depicted in Figure 2.5. The carbon products may be formed in several types, such as carbon nanotube, carbon filament, and amorphous carbon, depending on catalysts and reaction conditions. To obtain the high quality and quantity of carbon nanotubes, the variation of catalyst composition, supporting materials, hydrocarbon gases and synthesis conditions are the crucial parameters (Xuto, 2002).
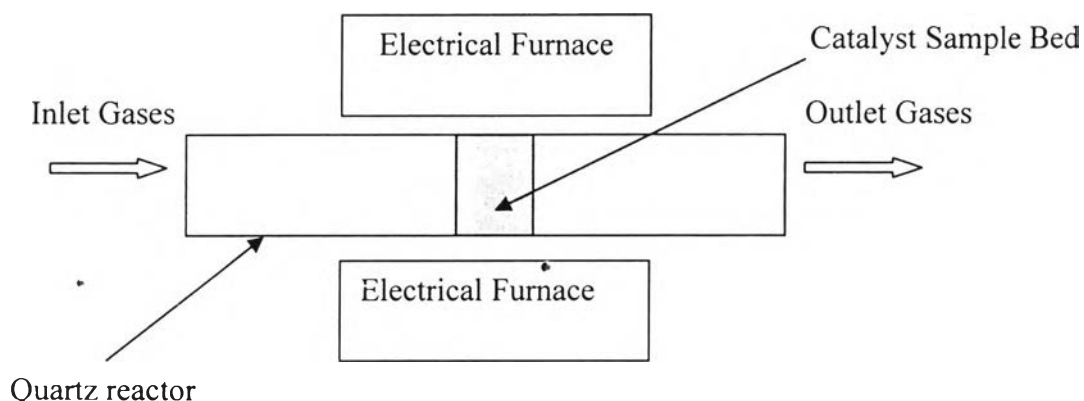
Figure 2.5 Reactor setup for catalytically growing carbon nanotubes (Kitiyanan, 2000).

2.5 Single Walled Carbon Nanotubes (SWNTs)

In 1993, Iijima and Toshinari Ichihashi of NEC, and Donald Bethune and colleagues of the IBM Almaden Research Center in California independently reported the synthesis of SWNTs. This proved to be an extremely important development, since of the SWNTs fascinating electronic and mechanical properties. In early 1993, several groups reported that foreign materials could be encapsulated inside carbon nanoparticles or nanotubes by carrying out arc-evaporation using modified electrodes. After that, in 1996 Smalley's group described an alternative method for preparing SWNTs. This method is the laser-vaporization of graphite, giving a high yield of SWNTs with unusually uniform diameters.

The catalytically produced SWNTs have a number of interesting features. In 2000, Kitiyanan and his group reported that SWNTs were first produced by the catalytic decomposition of carbon-containing molecules. To begin with, the catalytic tubes generally had small metal particles attached to one end. There was also a relatively wide range of particle diameters (approximately 1-5 nm), and it appeared that the catalytic particle determined the diameter of each tube. Finally, the catalytically formed SWNTs were generally isolated rather than grouped into bundles as is frequently the case with the tubes synthesized by arc-evaporation. This technique is suitable for scaling up and for achieving a 'controlled production' of the SWNTs.

2.6 Surfactants

The term of "surfactant" is an abbreviation of surface active agents; examples of surfactant include soaps and detergents. Surfactants are among the most versatile products of the chemical industry. Surfactants are molecules that consist of hydrophilic (water-loving) and hydrophobic (water-hating) moieties: referred to as heads and tails, respectively (as shown in Figure 2.6). The hydrophilic portion of the surfactant is made of a water soluble species while the hydrophobic portion of the surfactant is made of organic derivative groups, usually with the carbon numbers greater than eight. Most surfactants have the tail portion consisting of a long

nonpolar chain, which can be classified into three major groups: hydrocarbons, fluorocarbons, and silicone based polymers. This structure is known as amphiphiles. According to the nature of the hydrophilic head group, surfactants can be classified into four basic classes: cationic, anionic, nonionic, zwitterionic (Rosen, 1989).
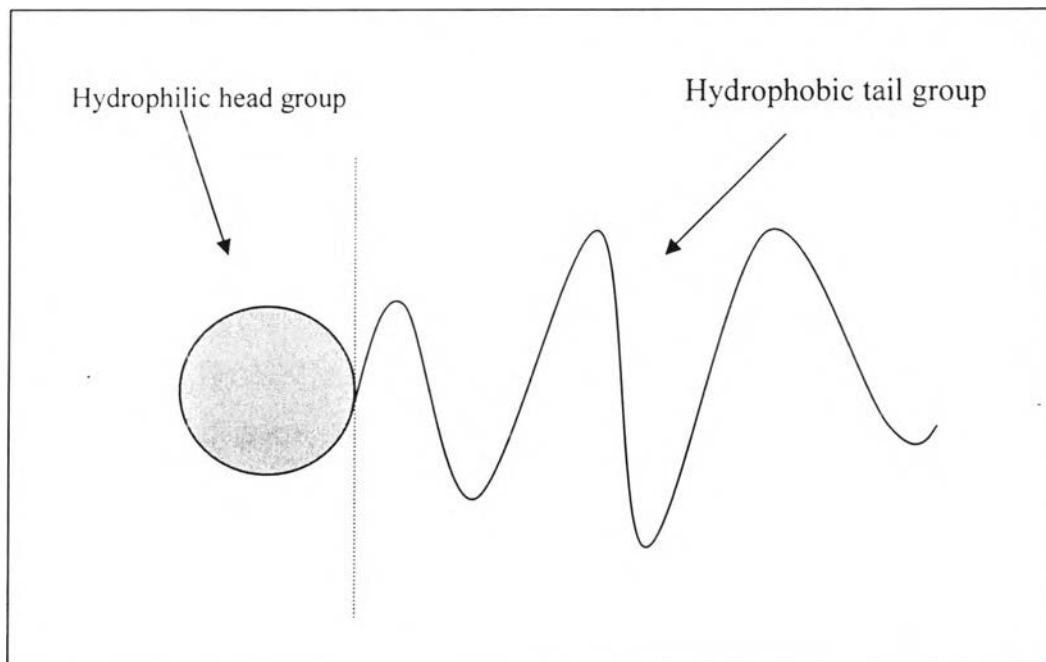

Figure 2.6 Schematic of surfactant molecule monomer (Rosen, 1989).

Surfactants do exactly what their name implies; they accumulate at surfaces, thereby altering the properties of solutions and interfaces which they contact. In fact, the surfactant monomers adsorb at the gas-liquid interface so that the hydrophilic portion of the molecules extend into the liquid phase and the hydrophobic tails extend into the gaseous phase. As expected, the adsorption of surfactants at the gas-liquid interface significantly affects the physical properties of the aqueous interface. Surfactants are capable of decreasing the surface energy of a liquid at relatively low concentration (Adamson, 1990).

Another significant phenomenon related to surfactant molecules (in this case in aqueous solution) is the formation of micelles. The hydrophobic portion of the surfactant is repelled by water while the hydrophilic portion attracts to water. As a result, singular surfactant molecules align together in globular, quite often form

spherical, colloids with the hydrophilic portion on the exterior and the hydrophobic portion on the interior. The resulting formation is called a micelle. The center core of the micelle has properties of a pseudo-oil phase; micelles are thus referred to as dispersed oil drops. Figure 2.7 shows schematically a surfactant solution containing dissolved monomeric surfactant molecule, a surfactant micelle, and the surfactants adsorbed at the air-water interface. Figure 2.8 illustrates the formation of various association structures with increasing surfactant concentration. It is likely that surfactant molecules may form spherical, cylindrical, hexagonal, lamellar and reversed micelle structures in solution by adjusting the proper physicochemical conditions such as pH, temperature and the presence of various electrolytes.
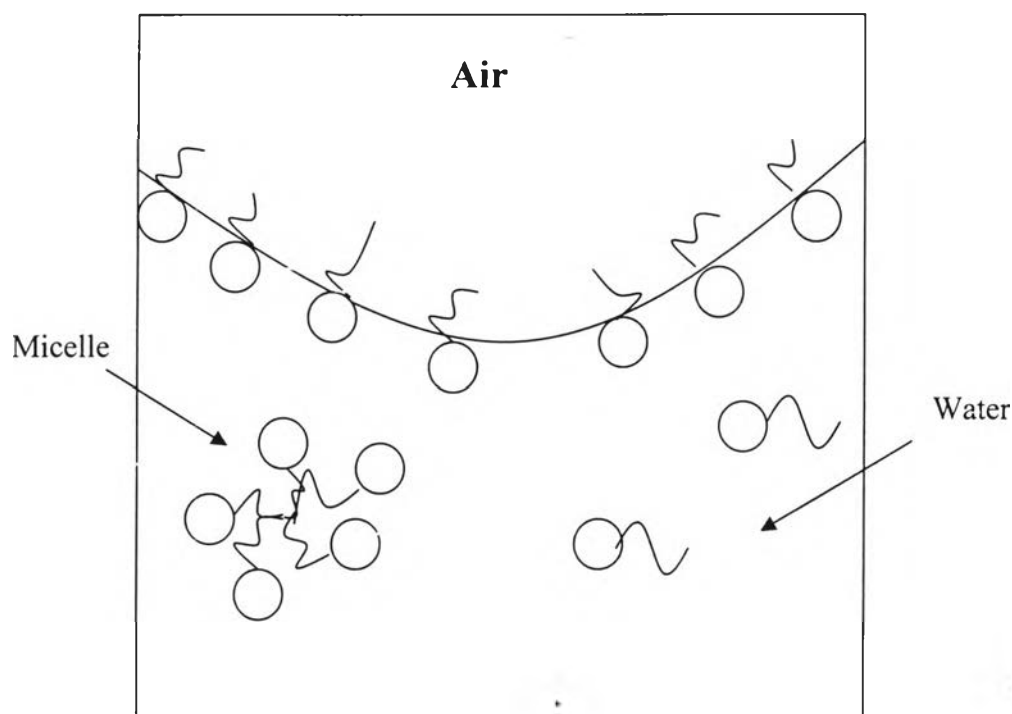

Figure 2.7 Schematic diagram of an ionic surfactant solution showing monomeric surfactant in solution and adsorbed at the air/solution interface and a micellar aggregate (Prud'homme and Khan, 1996).
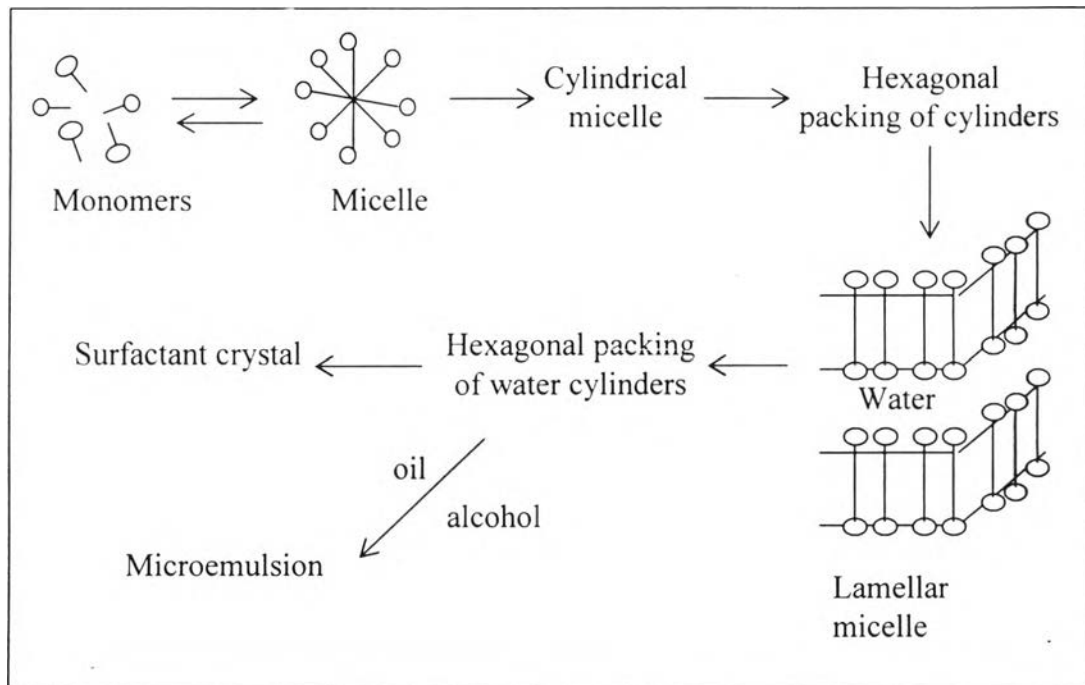
Figure 2.8 Schematic illustration of surfactant association structures (Sharma *et al.*, 1991).

Surfactants play an important role in separation processed including flotation. Flotation involves bubbling an insoluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the solution and the bubbles are accumulated as the surface as froth or foam which is skimmed off overhead. Surfactants are useful to both facilitate adhesion of target materials to the buble surface and to act as a froth prompter/stabilizer. Since reduction in interfacial tension at both air/water and oil/water interfaces is probably one of the causes of the surfactant's synergism (Scamehorn, 2000).

2.7 Purification Methods

In order to study and understand SWNTs's properties, experiments must be performed on highly purified samples. But after synthesis, SWNTs coexist with various forms of carbon and metallic particles which often obstacle characterization of the SWNTs. Then, the purification of SWNTs is of interest. Many methods have

also been developed for the purification of SWNTs, such as treatment of mixed acids or burn the raw-soot in air under a relatively high temperature.

Single walled carbon nanotubes, which used in this study, were synthesized by the catalytic decomposition of carbonmonoxide over supported Co/silica and Fe/silica. In order to obtain a high purity of carbon nanotubes, a separation step should be taken after a synthesis step. This means that this purification step is to separate carbon nanotubes from Co/silica or Fe/silica catalysts. Since carbon nanotubes stick to the catalyst surface very strongly, sonication for a long time or with higher power leads to breaking of the nanotubes from the silica support. (Hernadi *et al.*, 1996). Hernadi *et al.* (1996) conducted a SWNTs purification. In the first step, HNO_3 was used to dissolve catalyst particles from the sample. Then, it was filtered, washed with distilled water and finally with acetone. The resultant solids were sonicated in organic solvents, which are a mixture of n-hexane, acetone and iso-propanol in the ratio of 1:1:1 and then decauted by sedimentation. This sedimentation technique was found to be sufficient for the separation of the nanotubes and the remaining catalyst support particles. According to the observations, carbon nanotubes were completely removed from the catalyst surface. This residual material changed in color and lost the original rubbery texture which also showed the absence of carbon nanotubes but it was only carbon being trapped inside the pores of silica support.

After that, Li *et al.* (2000) reported a new method to purify SWNTs, which were synthesized by the catalytic decomposition of benzene and methane. This SWNTs sample with high impurities was chosen in order to test the efficiency of the procedure. This purification method used included three sequential steps: acid washing, and ultrasonic and freezing treatment. Based on the results, this procedure could remove the amorphous carbon, catalyst particles, vapor-grown carbon nanofibers and multi walled carbon nanotubes from the ropes of SWNTs without damaging the SWNTs bundles. The purified SWNTs had a very purity of about 95% with 40% yield.

Thien-Nga *et al.* (2002) demonstrated an efficient purification method using sonication. A mixture of the SWNTs suspension with inorganic nanoparticles, mainly ZrO_2 or $CaCO_3$ was treated in an ultrasonic bath. Then, the ferromagnetic

particles were mechanically removed from their graphitic shells. The magnetic particles are trapped with permanent magnetic poles and with a subsequent chemical treatment. This work used the energy of elastic impact between encapsulated catalyst and small hard inorganic particles to eject the metal kernels and trap them by a strong magnet. The SWNTs were first suspended either in soap solution or in toluene and then were dispersed in various solvents such as toluene, N, N-dimethyl formamide or 30% nitric acid. A power of nanoparticles, that are not soluble in the given medium, was then added to the suspension. This slurry was sonicated typically for 24 h. A high purity SWNTs material is obtained. However, the magnetic filed can extract only the particles from their grapheme layer (~1 nm.) not from the first carbon layer (~5 nm.).

Chattopadhyay *et al.,* (2002) reported a procedure to completely eliminate the metal catalysts, namely Co and Ni, from SWNTs soot. These magnetic impurities are entrapped inside the individual nanotubes or incorporated as carbide like material along graphitic walls. Residual catalyst has also been reported to nest in between tubes of bundles. The complete removal of entrapped metallic impurities incorporated within SWNTs was done by sonication-mediated treatment. Unpurified SWNTs soot was sonicated in acid mixture, a 1:1 mixture of aqueous HF and HNO₃, in the presence of a surfactant. The resulting dispersion was filtered and rinsed twice with deionized water at pH12. The use of HF enhances the wetting of SWNTs. The presence of the HNO₃ and surfactant were found to enhance removal of the catalyst due to SWNTs etching of end-caps/ defects and providing better dispersion, respectively. The HF/HNO₃-treated SWNTs was further vacuum annealed up to 1100°C. During this high temperature annealing process, there was a further 30% weight loss. The structural purity of the SWNTs was not compromised by HF/ HNO₃ purification treatment.

In 2003, Matarredona *et al.,* investigated the effect of chemical modifications of the surface on the extent of nanotube-surfactant interaction. This method was investigated to separate SWNTs from silica support. They used chemical treatment, which are concentrated HF or concentrated NaOH. After that, they used sodium dodeecylbenzenesulfonate (NaDDBS), which is anionic surfactant, to solubilize carbon nanotubes prepared by CoMoCAT synthesis method.

Unfortunately, the method could not open the graphitic shell without attacking the nanotubes and have some negative aspect such as toxicity, high operating cost, leave some metal particles, and structural change of purified SWNTs.

2.8 Froth Flotation

The accumulation of surfactants at the air/water interface, resulting in lowering excess Gibbs free energy of the interface is the principle phenomenon in the formation of stable foams. When a system contains solid particles, a surfactant having opposite charge can coadsorb both the surface of the solid and the air/liquid interface leading to accumulate the particulates at the forms. The adhesion of a particulate material to bubbles rising through a liquid is the basis of the froth flotation process (Scamehorn, 2000).

Flotation or froth flotation is a physicochemical property-based separation process. Forth flotation has been used in minerals processing industry since the mid-1800's with many of its broad-based applications to mineral recovery extensively developed between 1900 and 1925. Today, at least 100 different minerals are processed using froth flotation. Another major usage of froth flotation is by the coal industry for desulferization and the recovery of fine coal, once discarded as waste. Since the 1950's, flotation has been applied in many non-mineral industries including sewage treatment; water purification; paper de-inking; and chemical, plastics, and food processing (Kroschwitz and Howe-Grant, 1992).

Flotation is one of adsorptive bubble separation which is a process where a species is adsorbed at an interfacial between a dispersed phase (bubbles) and a continuous phase. Flotation involves the removal of particulate by frothing, whereas foam fractionation involves the separation of soluble species by foams (Scamehorn and Harwell, 1989). Flotation involves bubble and soluble gas (usually air) into an aqueous stream. Materials to be removed adhere to the bubbles as they rise through the process unit and are concentrated in the foam (called a froth in this case), which is skimmed off overhead. Surfactant is useful to both facilitate adhesion of target material to the bubble surface and to acts as a froth prompter/stabilizer (Feng and Aldrich, 2000).

The froth flotation process is based on the exploitation of wettability differences of particles to be separated. Differences of wettability among solid particles can be natural, or can be induced by the use of chemical adsorbates. Forth flotation is often used to separate solids of similar densities and sizes, which prevent other types of separations based upon gravity that might otherwise be employed. It may be difficult to take advantage of surface-property differences to induce selective hydrophobicity for the small particle sizes. On the other hand, particles greater than 65 mesh tend to be readily sheared from the bubble surfaces by collision with other particles or vessel walls. However, relatively low-density materials, such as coal, may be successfully separated up to 10 mesh in some systems (Kroschwitz and Howe-Grant, 1992).

There are several different types of froth flotation systems in use today including the mechanical type, of which they are many subtypes, and the flotation column. The type of froth flotation apparatus in Figure 2.9 is the batch, sub-aerated mechanical type. Frothers are also used to generate a mineral-laden froth layer and enhance particle-bubble adhesion. The products from the flotation cell are a concentrate and a tailings stream. The concentrate proceeds to the next step for further cleaning or treatment by hydro- or pyrometallurgical methods for the extraction of metals and other valuable compounds, while the tailings, which are ore components stripped of their valuable material content, are collected in lagoons known as tailings ponds.
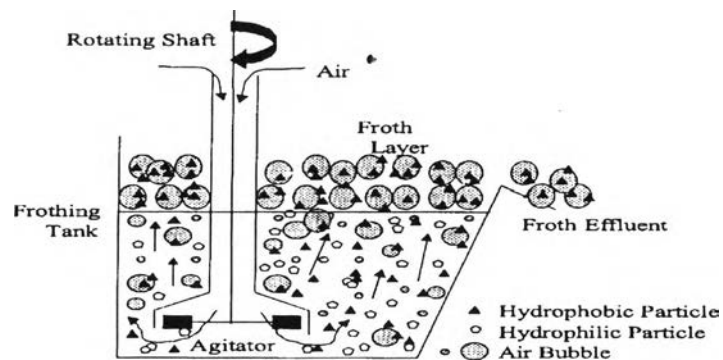

Figure 2.9 Sub-Aerated Mechanical Froth Flotation Apparatus (www.engr.pitt.edu).

2.8.1 Wettability

      Froth flotation involves three phases – solid, liquid, and gas – and the corresponding potential phase interfaces – solid-liquid, solid-gas, and solid-liquid-gas. The hydrophobic (aerophilic) or hydrophilic nature of the solids at the solid-liquid-gas interfacial region is determined by the wettability of the solid. An interfacial phenomenon of flotation is a surface chemical-base process, where numerous phenomena that simultaneously occur at the solid-liquid-air interfacial region determine it's out come. In this context, the variable known as contact angle θ illustrated in Figure 2.10, is an important correlative parameter. At θ = 0°, the liquid spreads on the solid; in aqueous media in contact with air such a solid is said to a hydrophilic and is wetted by water. Air bubbles do not adhere to hydrophilic solids in water. Conversely, hydrophobic solids are not wetted by water; air bubbles do adhere to them and the value of the contact angle is larger than zero degrees, i.e., θ > 0°(Kroschwitz and Howe-Grant, 1992).
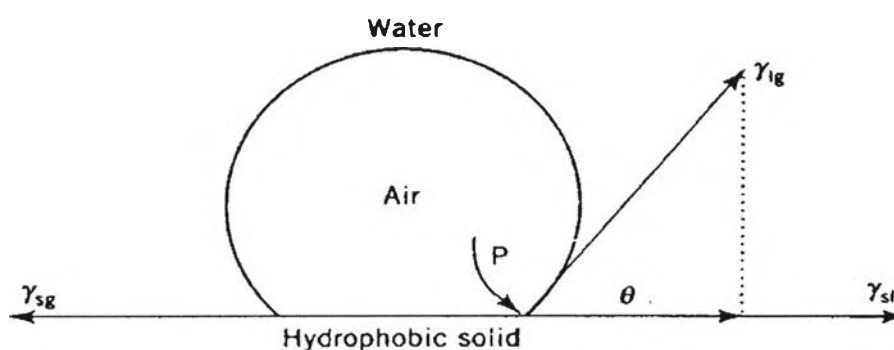

Figure 2.10 The concept of contact angle with a captive bubble in an aqueous medium, adhering to a hydrophobic solid: P is the three-phase contact point. Here, the vector γ_{lg} passes through P and forms a tangent to the curved surface of the air bubble. The contact angle θ is drawn into the liquid. (Kroschwitz and Howe-Grant, 1992).