CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Gas Adsorption

Adsorption is a process where molecules from the gas phase or from solid solution bind in a condensed layer on a solid or liquid phase. The molecules that bind to the surface are called the adsorbate while the substance that holds the adsorbate is called adsorbent. The process when the molecule bind is called adsorption. Removal of the molecules from the surface is called desorption (Masel, 1996)

Adsorption at the solid-gas interface can be divided into two broad classes: chemisorption and physical adsorption. Physical adsorption is reversible adsorption by weak interactions only; no covalent bonds occur between the adsorbent and the adsorbate and heats of physical adsorption are less than 15-20 kilocalories/mole. Chemisorption is adsorption involving stronger interaction between adsorbate and adsorbent usually accompanied by rearrangement of atoms within or between adsorbates, so, reaction occurs between the surface of the adsorbent and adsorbate. Heats of chemisorption are usually in excess of 20-30 kilocalories/mole.

2.1.1 Isothermal Gas Adsorption

An adsorption isotherm is the relationship at constant temperature between the partial pressure of the adsorbate and the amount adsorbed at equilibrium. This varies from zero at $P/P_0 = 0$ to infinity as P/P_0 reaches 1.

The most common adsorption experiment is the measurement of the relation between the amount of gas adsorbed and the pressure of the gas. For a given gas-solid pair, the amount of adsorbed gas at equilibrium is a function of pressure and temperature as the following,

$$v = f(P,T) \qquad (2.1)$$

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where v may be expressed in cc STP/g. At a fixed temperature v is only a function of P, which is called an adsorption isotherm (Yang, 1987).
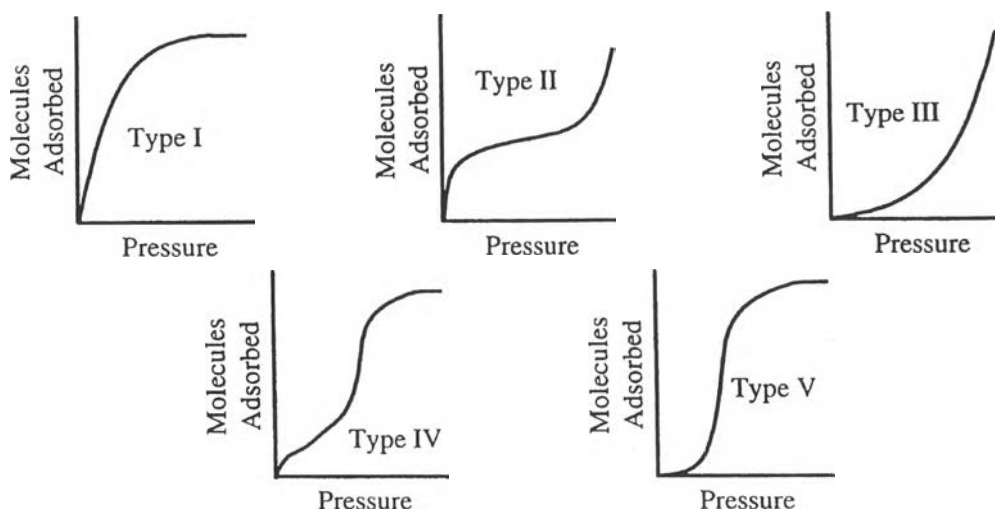

Figure 2.1. The five types of adsorption isotherms (Masel, 1996)

Adsorption isotherm may be grouped into five types indicated in Figure 2.1. Type I isotherm is an isotherm where the amount of gas increases with increasing pressure and then saturates at about a monolayer coverage. Type I isotherm is characteristic of monolayer adsorption. Type II isotherm is an isotherm where the amount adsorbed increases with increasing pressure starts to level off, and then starts at higher pressures. Type II isotherm is characteristic of multilayers adsorption. Type III is an adsorption isotherm where initially there is very little adsorption. However, once a small droplet or island of adsorbate nucleates on the surface, additional adsorption occurs more easily because of strong adsorbate-adsorbate interactions. Type IV and Type V isotherms usually occurs when multi-layers of gas adsorb onto the surface of the pore in a porous solid. Initially, the adsorption looks like a type II or type III adsorption, but eventually the adsorbed layers get so thick that they fill up the pores. As a result, no more gas can adsorb and the isotherm saturates (Masel, 1996).

The measurement of pure-gas isotherms is rather straightforward. The amount adsorbed at equilibrium can be determined by two commonly used methods. One is the constant volumetric method, where the pressure drop before and after adsorption in a closed system is measured. Another is the gravimetric method, in which the amount adsorbed is directly determined by the weight gain in a flow system (Yang, 1987).

2.1.2 Constant-Volume Method

The amount of gas is measured before and after the adsorption takes place. The amount of adsorbed phase is, then, calculated by the difference. The pressure and volume, using an appropriate P-V-T relationship can be used to determine the total gas amount. The experimental apparatus contains two compartments: a reservoir and a sample, the latter containing a dead space. Volume of both compartments can be predetermined by helium displacement. The gas in the reservoir is admitted to the sample compartment, and equilibrium is indicated by the constancy of the pressure (Yang, 1987).

2.2 Types of Adsorbent

The most common commercial adsorbents that provide their uses in gas storage and separation include activated carbon, zeolite, and molecular sieves. Some of the properties that make an adsorbent commercially attractive include high porosity, surface area, and total pore volume. The most exploited adsorbent with respect to these properties is activated carbon. Carbon, by itself, can be regarded in its graphitic form, which its density is equal to 2.25 g/cc although in its disordered crystal state it probably is closer to 2.1 g/cc (Patel, 2000). In order to explore new adsorbents, the focus has now turned to carbon nanostructures. During recent years, nanomaterials like fullerenes and carbon nanotubes have been studied for their gas storage ability. Due to their high theoretical surface area, they can become potential adsorbents and competitors to activated carbon.

2.2.1 Activated Carbon

Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature. The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stack together in random orientation and it is the spaces between the crystals, which form the micropores. The molecular structure of activated carbon is shown in Figure 2.2. The graphite platelet structure gives the activated carbon its very large surface and porosity which allows it to adsorb a wide range of compounds.
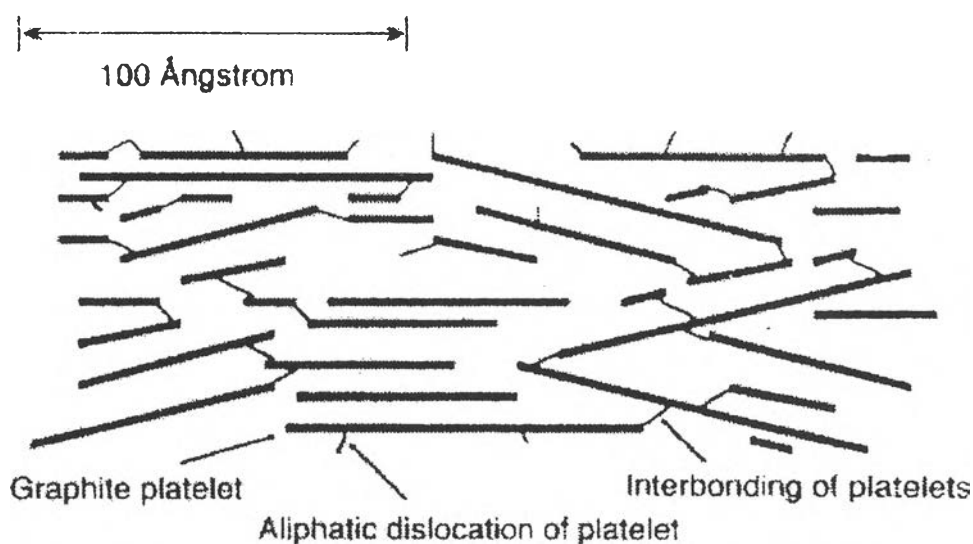

Figure 2.2. Structure of Activated Carbon

(http://www.calgoncarbon.com/bulletins/Activated_Carbon_Principles.htm)

2.2.2 Carbon Nanotubes

Carbon nanotubes are long, thin, hollow cylinders formed by rolling up a single layer of graphite. Carbon nanotubes come in a variety of diameters and lengths. Depending on the growth process, the length of the tubes can be from approximately 100 nanometers to several microns. Diameters vary from 1 to 20 nanometers. A carbon nanotube can have either one wall, for single-walled carbon nanotubes (SWNT), or as many as 20 to 30 walls, for multi-walled carbon nanotubes

(MWNT) as shown in Figure 2.3. The strand-like fibers in this image are "ropes" of individual parallel single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT). A typical rope diameter is ~20 nm and a typical SWNT diameter is ~1.4 nm. The other features of carbon nanotubes are their chemical inertness and thermal stability. They are thermally stable up to over 1000°C in vacuum.
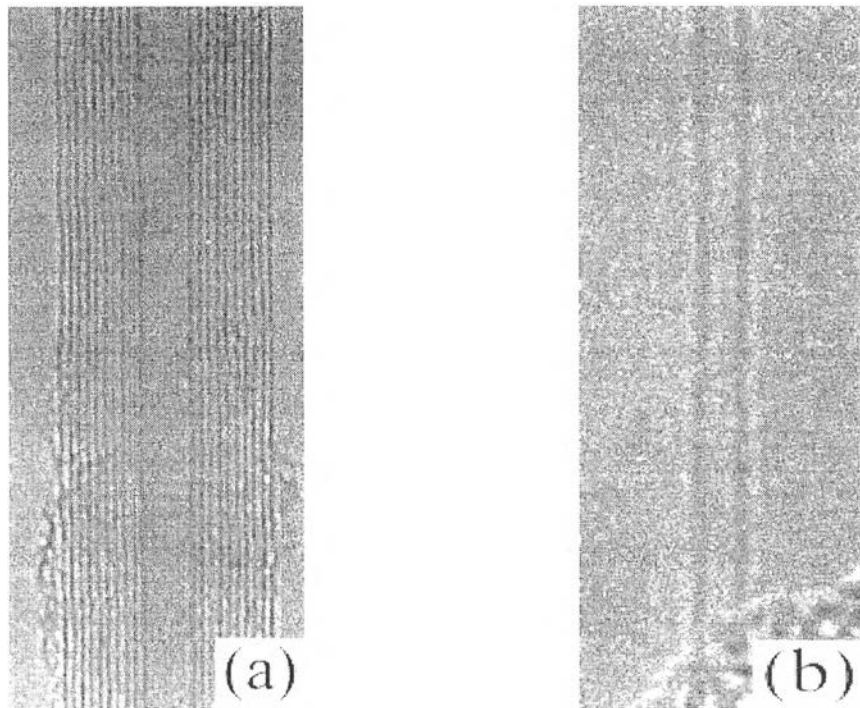

Figure 2.3. TEM images of carbon nanotubes (a) multi-walled carbon nanotubes, (b) single-walled carbon nanotubes

(http://www.physics.berkeley.edu/research/zettl/projects/imaging.html)

2.3 Hydrogen Storage in Carbon Nanotubes and Related Materials

Since carbon nanotubes were first synthesized by Iijima in 1991, their physical and chemical characteristics have been a subject of intensive research for many years. Carbon nanotubes, which have diameters of typically a few nanometers, should be able to draw up liquids by capillarity (Pederson, 1992). Within the

micropores (less than 2 nm) of a porous substance, gases can be adsorbed onto the solid surface. Due to the force of attraction between the solid and the gas, an adsorbed hydrogen phase will be much denser than the bulk gas phase. At high pressure, capillary condensation can lead to condensation of hydrogen at temperatures well above the standard condensation temperature, leading to enhanced storage density (Baumert, 1993).

Dillion *et al.* (1997) were the first to publish experimental data on hydrogen adsorption in single-walled carbon nanotubes (SWNT). Their experimental procedure, which they named Temperature Programmed Desorption, consists in measuring with a mass spectrometer the hydrogen desorbed by the carbon sample, 1 mg, during a heating run. They showed that gas could condense to high density inside narrow SWNTs. They found that unpurified soot containing only 0.1-0.2 wt% of SWNTs could also absorb about 5 to 10 weight % of H_2 at 133 K and 300 Torr. The rest of unpurified soot were consisted of a mixture of unidentified carbonaceous materials as well as a large fraction of cobalt catalyst particle (~20 wt%). With same conditions, hydrogen does not induce adsorption within a standard mesoporous activated carbon. They also suggested that the high purity SWNTs samples that have been recently produce, at that time, should be interesting candidates for evaluation.

Later, Ye and co-workers (1999) obtained 8.25 wt % of H_2 adsorption on high purity SWNTs at 80 K and 100 atm. Liu *et al.* (1999) using constant volumetric method with 500 mg of sample found that 4.2 wt%H_2 was obtained on SWNTs with a large mean diameter of about 1.85 nanometers at room temperature under modestly high-pressure (about 10 megapascal). Moreover, 78.3 % of the adsorbed hydrogen could be released under ambient pressure at room temperature, while the release of the residual stored hydrogen required some heating of the sample.

Wu *et al.* (2000) synthesized multi-walled carbon nanotubes from the catalytic decomposition of CO and CH_4. With TGA technique, the carbon nanotubes produced from CO were found to be able to uptake a certain amount of hydrogen under ambient conditions, whereas graphite powders were unable. They suggested the carbon nanotubes might be a promising material that could be used for hydrogen storage under ambient conditions.

Recently, Lee and his research group (2000) performed density-functional calculations to search for hydrogen adsorption sites and predict maximum storage capacity in SWNTs. They found two chemisorption sites at top site of the exterior and interior of the tube wall. They further observed that a form of H_2 molecule could exist in an empty space inside nanotubes. The storage capacity of hydrogen in an empty space increased linearly with tube diameter. The repulsive energies between H_2 molecules inside nanotubes limit the maximum storage capacity between H_2 molecules and the tube wall. They predicted that hydrogen storage capacity in (10,10) nanotube can exceed 14 wt%.

Zhu *et al.* (2001) showed that the bundles of aligned carbon nanotubes had a narrow pore distribution mainly in micro- and meso-pores, which were favorable for hydrogen uptake. The well-aligned carbon nanotube bundles had a hydrogen storage capacity over 3 wt% higher than randomly-ordered carbon nanotubes at room temperature and moderate pressure (3-10 MPa) determined by constant volumetric method. They also suggested that multi-walled carbon nanotubes were promising materials for hydrogen storage.

In addition, Chen *et al.* (1999) focused on alkali-doped carbon nanotubes and they found that lithium- or potassium-doped carbon nanotubes can absorb about 20 and 10 weight percent of hydrogen at moderate (200 to 400°C) and room temperatures, respectively, under ambient pressure. The CNTs used in the study were made from catalytic decomposition of CH_4. After purification, almost all of the catalyst particles were removed. More than 90% of the product was in the form of multiwalled CNTs, and 70% was in the diameter range of 25 to 35 nm. Hydrogen uptake was measured by thermogravimetry analysis (TGA).

In contrast, some months later, Yang (2000) revisited these data. He prepared the doped nanotubes following the same procedure and also measured the adsorption-desorption using a thermogravimetric analyzer. His conclusion was that special caution needed to be taken to remove any moisture contamination of the hydrogen in measuring the adsorption. Moisture, which drastically increased the weight gain, picked up and then put the results in error. So, for dry hydrogen, the adsorption is of 2.5 wt% for lithium-doped carbon nanotubes and of 1.8 wt% for

potassium-doped carbon nanotubes. Results have recently been more confirmed by Pinkerton *et al.* (2000).

More recently, Tibbetts *et al.* (2001) have studied the sorption of hydrogen by nine different carbon materials at pressure up to 11 MPa (1600 psi) and temperatures from −80 to +500 degree Celsius. Their results were remarkably similar: very little hydrogen sorption. In fact, the sorption was so little. Careful attention must be paid to calibration to get reliable answers. Furthermore, their efforts to activate the materials by reduction at high temperatures and pressures were also futile. These results cast serious doubts on any claims so far for room temperature hydrogen sorption in carbon materials higher than 1 wt.%.

Furthermore, there were some studies of hydrogen sorption in other types of carbon materials. Activated carbon nanofibers and graphite were ones of candidate materials for hydrogen uptake. Carbon nanofibers consist of graphite platelets stacked together with respect to the fiber axis, giving rise to the assorted conformations. The nanofibers vary from 5 to 100 nm in diameter. Carbon nanofibers were discovered in 1970s, but it was not until recently that they were reported in having the potential to store up hydrogen.

Chambers and colleagues (1998) did the high-pressure sorption studies of various types of graphite nanofibers (GNF). Approximately 0.2 g of different types of graphite nanofibers were used to measure the hydrogen adsorption capacity by constant volumetric method. The structures of graphite nanofibers were designated as tubular, platelet, and herringbone shape. They observed that at 120 atm and room temperature, graphite nanofibers with herringbone structure could store 67 wt % of H_2, which was the maximum hydrogen storage compared to those of the rest structures. Furthermore, this amount was about ten times the maximum value that has been reported for hydrogen storage media.

Later, the same team, Park and colleagues (1999) confirmed their results with more detailed explanations of such an important hydrogen molecule intercalation between the graphene sheets of the nanofibers. Unfortunately, up to date, this hydrogen adsorption amount-capable of solving the hydrogen storage problem-has not been confirmed, neither experimentally nor theoretically.