



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Carbon Dioxide

Containing two double bonds (O=C=O) and linear shape, carbon dioxide can be found in Earth's atmosphere and is considered as one of the greenhouse gases. The properties of carbon dioxide are summarized in Table 2.1.

Table 2.1 Properties of Carbon dioxide (lenntech.com)

Property	Value
Molecular weight	44.01 g/mol
Specific gravity	1.53 at 21 °C
Critical density	468 kg/m ³
Concentration in air	370.3 *10 ⁷ ppm
Stability	High
Liquid	Pressure < 415.8 kPa
Solid	Temperature < -78 °C
Henry constant for solubility	298.15 mol/ kg * bar
Acidity	6.35, 10.33 pK _a
Diameter of carbon dioxide	2.8 Å-3.4 Å

In December 2009, the amount of carbon dioxide at sea level was reported at 387.46 ppm. Carbon dioxide has been increased at 0.00560 ppm per day (co2uniting.com). Human activities and natural carbon cycles are two main ways of carbon dioxide emission. Thus, human activities such as burning of oil, coal and gas, and deforestation are now becoming the major sources of carbon dioxide emission

(epa.gov). About 40% of total carbon dioxide emissions come from fossil fuel-fired power plants (Carapellucci and Milazzo, 2003). Flue gas, which is produced from power plant, consists of mostly nitrogen, carbon dioxide, water, and oxygen. Table 2.2 represents the flue gas composition ranges for power plants fueled by gas, oil, and coal and flue gas temperatures from different sources are summarized in Table 2.3. Moreover, carbon dioxide can be produced as a by-product of several industrial activities such as from hydrogen production plant, fermentation of sugar and sodium phosphate manufacture etc. (en.wikipedia.org).

Table 2.2 Flue gas composition (EPRS Energy Co. Inc., 2009)

	Natural Gas	Fuel oil	Coal
Nitrogen	78-80%	78-80%	78-80%
Carbon dioxide	10-12%	12-14%	
Oxygen	2-3%	2-6%	7%
Carbon monoxide	70-110 ppm	70-160 ppm	
Nitrogen oxide	50-70 ppm	50-110 ppm	1%
Ammonia	Used in removal of NO _x		
Sulfur dioxide		180-250 ppm	>2,000 ppm
Hydrocarbon		<60 ppm	>200lb/year/plant
Mercury			
Fly ash	non	minimal	12%

Table 2.3 Fuels-exhaust temperature (enigneeringtoolbox.com)

Appliance Type	Exhaust Temperature (°C)
Chemical Oxidation	730 - 800
Fluidized-bed combustor	870 - 980
Liquefied-petroleum gas-fired heating appliance with draft hood	182
Gas-fired heating appliance, no draft hood	238
Oil-fired heating appliance, residential	293
Oil-fired heating appliance, forced draft over 400.000 Btu/h	182
Diesel exhaust	540 - 650

2.2 Carbon Dioxide Capture and Separation

Environmental problems due to emissions of pollutants from combustion of fossil fuels have become global problems, including air toxics and greenhouse gases. Carbon dioxide is the largest contributor in regard of its amount present in the atmosphere (Yang *et al.*, 2008). Several methods such as energy consumption reduction by increasing the efficiency of energy conversion, switch of less carbon intense fuels, and renewable energies have been suggested to reduce the amount of carbon dioxide emission into the atmosphere. These options, however, may not be enough to lessen all global warming in the future, so the technology of carbon dioxide capture and storage (CCS) has been recently considered as an important option for mitigating global warming (Young *et al.*, 2008).

For power plants, carbon dioxide separation and capture processes can be divided into several scenarios: post-combustion processes, pre-combustion processes, and oxy-fuel combustion.

Post-combustion process is shown in Figure 2.1. The burning of fossil fuels produces flue gases, which include carbon dioxide, water vapor, sulfur dioxide and nitrogen. Carbon dioxide is separated and captured from the flue gas. This process is also used to remove carbon dioxide from natural gas. Another advantage of this technique is it produces a relatively pure carbon dioxide stream (Young *et al.*, 2008).

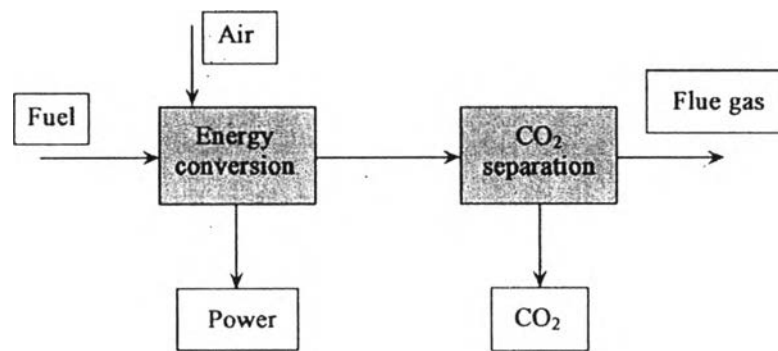


Figure 2.1 Post-combustion process (Young *et al.*, 2008).

The pre-combustion carbon dioxide capture is a process, where the carbon in the fuel is separated before the combustion process. The principle of this process is to first convert the fossil fuel into carbon dioxide and hydrogen gas (H_2). The hydrogen and carbon dioxide are then separated in the same way as in the post-combustion process, although a smaller installation can be used. This results in a hydrogen-rich gas, which can be used in power plants or as fuel in vehicles. The combustion of hydrogen does not lead to any production of carbon dioxide (Young *et al.*, 2008).

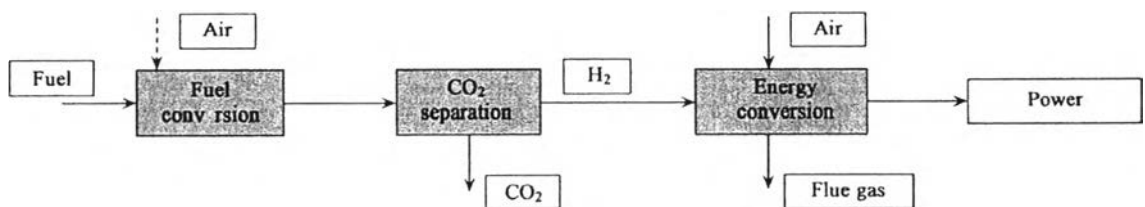


Figure 2.2 Pre-combustion process (Young *et al.*, 2008).

Burning fossil fuels with an oxygen-enriched gas mixture instead of air is the principle of the oxy-fuel combustion process. This results in a flue gas that mainly comprises carbon dioxide and water, as well as a small concentration of impurities such as argon and oxygen. In this way, the oxy-fuel combustion process provides an opportunity to capture carbon dioxide by direct physical compression and cooling techniques (such as a low-temperature separation/distillation process) (Natural Resources Canada, 2008).

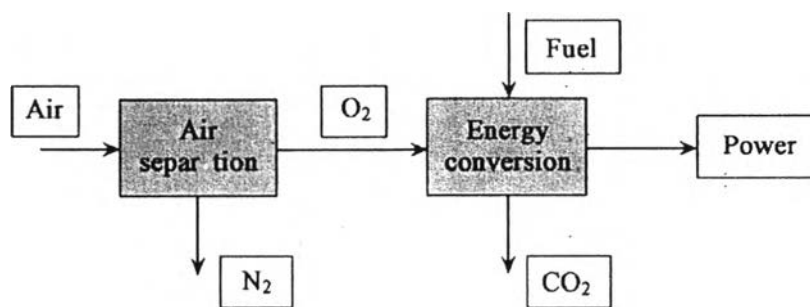


Figure 2.3 Oxy-fuel combustion process (Young *et al.*, 2008).

Several different chemical separation technologies that can be applied to pre-combustion carbon dioxide capture including solvent absorption, membrane, and adsorbent based processes (Singh *et al.*, 2009).

2.2.1 Absorption

Absorption is a process that molecules, atoms, or ions get into the bulk phases which can be gas, liquid, or solid material. This method can separate a substance from a mixture by selectively dissolving in proper solvent. Reversible solvent absorption is a mature technology using amine solutions such as monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) etc. as solvent absorbent (Young *et al.*, 2001). The commercial solvent that has been used in carbon dioxide absorption is a 30 wt% solution of monoethanolamine (MEA) (Notz *et al.*, 2010). This method allows the flue gas to be contacted with a amine solvent so carbon dioxide can be absorbed by the amine solvent. Considered as weak acid, carbon dioxide can react with a base solvent to form carbamate (Yang *et al.*, 2008). After the reaction, the carbon dioxide-rich amine solvent is sent to a regeneration process to

separate carbon dioxide from the amine solvent. The solvent can be used again in the absorption process. Xu *et al.* (2005) reported that this technique has some drawbacks such as high energy consumption, equipment corrosion, and solvent degradation in the presence of oxygen. In accordance with Xu *et al.* (2005), Scholes *et al.* (2010) mentioned that solvent absorption requires high heating utility at the regeneration process and has some environmental impacts.

2.2.2 Membrane Separation

Membrane separation is the method that can separate a substance from a mixture by using its thin barriers. Although there are several materials that can be used as membrane such as polymeric membranes, inorganic membrane, carbon membranes, alumina membranes, silica membranes, zeolite membranes, and mixed-matrix and hybrid membranes. However, polymeric membranes have been widely used. Scholes *et al.* (2010) proposed a polymeric membrane system for gas separation. The principle of this method is to separate one or more gases from a feed mixture and generate a specific gas rich permeate. Thus, this polymeric membrane provides less selectivity and cannot be used at a high temperature of flue gas (Yang *et al.*, 2008). To tackle that problem, mixed-matrix and hybrid membranes were proposed by several works (Abidi *et al.*, 2006 and Luebke *et al.*, 2006). Hybrid membranes are also called surface-modified inorganic membranes. This type of membranes is very effective for carbon dioxide separation because this porous inorganic material allows large flux while the surface-modified provides selectivity.

2.3 Adsorption

Adsorption is now considered as the promising method for carbon dioxide capture. The principle of this separating method is the preferential adsorption of certain substances from the mixture. For a gas separation process, a solid adsorbent is exposed to the gas mixture and the gas molecules that are favor to this solid will form bonds with it and become attached (Yang, 2003). An adsorbent is the material that holds an adsorbate, and the adsorbate is the molecules that bind to the surface. Desorption is the process for removing the molecules from the surface. There are two

types of adsorption depending on the interaction between an adsorbate and adsorbent. Chemisorption is a process that an adsorbate forms a strong interaction with an adsorbent, while physisorption is the process that an adsorbate is held by physical forces such as van der Waals force (Masel, 1996). The differences between these two processes are summarized in Table 2.4 (Ruthven, 1984).

Table 2.4 Differences between chemisorption and physisorption (Ruthven, 1984)

	Chemisorption	Physisorption
Temperature	High temperature	Close to the boiling point of adsorbate
Type of interaction	Strong; Covalent bond	Weak; van der Waals force
Binding energy	1-10 eV	10-100 meV
Adsorption	May be slow and irreversible	Rapid and Reversible
Types of adsorption	Monolayer	Multilayer or monolayer

In order to mitigate the amount of total carbon dioxide emission, the primary requirement for adsorption process is an adsorbent with high selectivity, capacity, and life. The selectivity may depend on a difference in either adsorption kinetics or adsorption equilibrium but most of the adsorption processes in current use depend on equilibrium selectivity. In considering such processes, it is convenient to define a separation factor:

$$\alpha_{AB} = \frac{X_A / X_B}{Y_A / Y_B}, \quad (2.1)$$

where X_A and Y_A are, respectively, the mole fractions of component A in adsorbed and fluid phases at equilibrium. The separation factor defined in this way is precisely analogous to the relative volatility, which measures the ease with which the components may be separated by distillation. The analogy is, however, purely formal and there is no quantitative relationship between the separation factor and relative

volatility. For two given components, the relative volatility is fixed whereas the separation factor varies widely depending on the adsorbent (Ruthven, 1984).

Nowadays, the adsorption separation processes can be divided into two broad classes; cyclic batch systems, in which the adsorbent bed is alternately saturated and regenerated in a cyclic manner, and continuous flow systems, generally involving continuous countercurrent contact between feed and adsorbent (Ruthven, 1984).

For cyclic batch adsorption processes, there are four basic methods to regenerate the adsorbents.

1. Thermal Swing. An adsorbent is heated to a temperature at which the adsorbed species are desorbed and removed from the bed in the fluid stream.
2. Pressure Swing. To regenerate the adsorbent, pressure is reduced at a constant temperature and then purging the bed at a low pressure. This method can be used only to gaseous systems.
3. Purge Gas Stripping. To regenerate the adsorbent, non-adsorbing inert gas is purged to the adsorber at a constant pressure and temperature. This method can be used only when the adsorbed species are weakly held.
4. Displacement Desorption. To regenerate the adsorbent, the temperature and pressure are maintained constant and a competitively adsorbed species is purged to the adsorber. This method is applicable to both gas and liquid systems (Ruthven, 1984).

Pressure swing adsorption (PSA), temperature swing adsorption (TSA) and vacuum swing adsorption (VSA) are very well known techniques for the adsorption process (Yang *et al.*, 2008). Economical and environmentally friendly system, the PSA has been considered to be one of the promising systems and UOP commercialized this process since 1966 (UOP.com). The principle of PSA process is that adsorbents are capable of selectively adsorbing carbon dioxide. Carbon dioxide are adsorbed at high pressure and desorbed at low pressure. The PSA process can be operated at high temperatures, typically the temperature of fuel gas source, to remove most of the carbon dioxide, and overcomes the need to cool the fuel gas to ambient temperature prior to the removal of carbon dioxide (Young and Rodrigues., 2008).

The advantages and disadvantages of each method are summarized in Table 2.5.

Table 2.5 Summary of factors governing choice of regeneration method (Ruthven, 1984)

Method	Advantages	Disadvantages
Thermal Swing	Good for strongly adsorbed species	Thermal aging of adsorbent
	Desorbate may be recovered at high concentration	Heat loss means inefficiency in energy usage
	Gases and Liquids	
Pressure Swing	Good where weakly adsorbed species is required in high purity	Very low P may be required
	Rapid cycling-efficient use of adsorbent	Desorbate recovered at low purity
Displacement desorption	Good for strongly held species	Product separation and recovery needed
	Avoids thermal aging of adsorbent	

2.4 Adsorbent

An adsorbent is the material that is used to hold an adsorbate in the adsorption process. Porous materials can be used as an adsorbent because of their porosities. Besides porosities, the important physical characteristics for a decent adsorbent include pore volume, pore size distribution, and surface area. Nowadays, commercial adsorbents are used in the form of spherical pellets, rods, moldings, or monoliths with a diameter between 0.5 mm to 10 mm. Moreover, an adsorbent should contain high abrasion resistance, high thermal stability, and small pore diameter. Besides those qualities, a decent adsorbent should have a distinct pore structure, which enables fast transport of the gaseous vapors. For industrial adsorbents, there are three types of adsorbent. First, oxygen-containing compounds are hydrophilic and polar

such as silica gel and zeolite. Second, carbon-base compounds are hydrophobic and non-polar such as activated carbon and graphite. Lastly, polymer-base compounds are polar and non-polar functional groups in a porous polymer matrix (en.wikipedia.org).

2.4.1 Activated Carbon

Activated carbon is made from carbonaceous matters such as wood, peat, coals, petroleum coke, and coir (Yang, 2003). There are two methods to produce activated carbon. First, physical reactivation consists of carbonization step and activation or oxidation step. In carbonization, a raw material is pyrolyzed at a temperature between 600-900 °C in the absence of air. The carbonized material is oxidized in the present of air at a temperature above 250 °C. Another method is chemical activation which is preferred because this method is operated at a lower temperature. In the carbonization step, a raw material, which is impregnated with chemicals such as phosphoric acid, potassium hydroxide, sodium hydroxide, and zinc chloride, is carbonized at 450-900 °C (en.wikipedia.org). The conditions at the pyrolysis and oxidation process are the main factor to determine the total pore volume and the pore size distribution for activated carbon (Ruthven, 1984). There are many classifications of activated carbon such as powdered activated carbon, granular activated carbon, extruded activated carbon, and polymer coated carbon. Another type of activated carbon that has been developed is carbon fiber composite molecular sieve (CFCMS). This material is composed of petroleum pitch-derived carbon fiber and a phenolic resin-derived binder. Some attractive features of this material such as high micropore volume and large BET surface area make it likely to provide a better adsorption capacity than zeolites and conventional granular activated carbons (An *et al.*, 2010). Table 2.6 represents the pore size, pore volume, and surface area of typical activated carbon. Activated carbon' surface is non-polar so this adsorbent tends to be hydrophobic and organophilic. Figure 2.4 represents activated carbon adsorbed gases and chemicals.

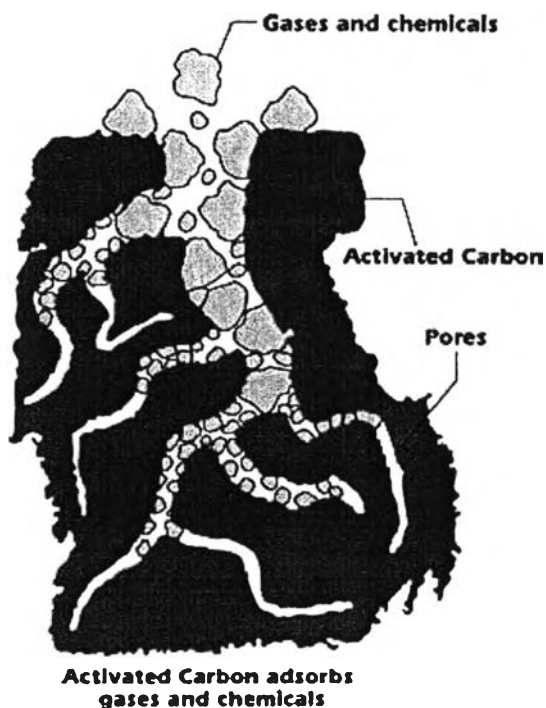


Figure 2.4 Activated carbon adsorbs gases and chemicals (methachemical.com).

Table 2.6 Pore sizes in typical activated carbon (Ruthven, 1984)

	Micropores	Mesopores	Macropores
Diameter (Å)	<20	20-500	>500
Pore volume (cm³/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m²/g)	100-1000	10-100	0.5-2

Activated carbon is useful for carbon dioxide capture because it contains a high specific area and their pore structure can be controlled by the activation conditions. Thus, the interactions between adsorbate and adsorbent should also be taken into consideration. Guo *et al.* (2006) investigated the adsorption of carbon dioxide on raw activated carbon and three modified activated carbon at temperatures ranging from 30 to 60 °C using a vacuum adsorption apparatus. Four carbon samples were used in this study. Sample A was a commercially activated carbon. Sample B was

impregnated with 4% KOH. Sample C was impregnated with a mixture of ethylenediamine and ethanol (the volume ratio of ethylenediamine and ethanol was 2:1). Sample D was impregnated with a mixture of 4% KOH, ethylenediamine, and ethanol (the volume ratio of ethylenediamine and ethanol was 2:1). They found that the volume adsorbed on the modified carbon samples B, C, and D were larger than that on the raw carbon sample. Somy *et al.* (2009) studied the effect of impregnation of activated carbon with Cr_2O and Fe_2O_3 and promotion by Zn^{2+} using the volumetric method with P-V-T measurement. The adsorption process was operated at room temperature and the samples were regenerated at 40 °C. They found that pore volume of modified samples was decreased because of the presence of metals. Thus, the modified activated carbon, especially impregnated by Cr_2O , can increase carbon dioxide adsorbed amount. Moreover, samples that were impregnated by both Cr_2O and zinc carbonate hydroxide led to 25% increase in carbon dioxide capture capacity. In accordance with Somy *et al.* (2009), Kim *et al.* (2010) investigated the effect of copper oxide loaded on porous carbons by a postoxidation method. The adsorption process was operated at 25 °C and 1.0 atm. They found that copper oxide can enhance the adsorption capacity of carbon dioxide because metal oxides serve as an electron donor and carbon dioxide molecules act as a weak acid. According to the above experiments and reasons, modified activated carbon with amine groups or metal oxides can increase the adsorption capacity of carbon dioxide and chemisorption plays a major role in these methods.

2.4.2 Silica Gel

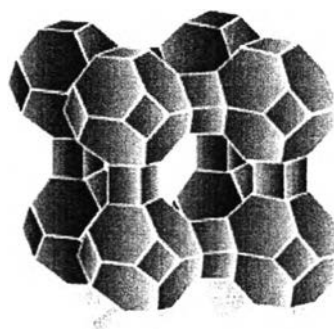
Silica gel is a solid, continuous network of spherical particles of colloidal silica. There are a number of preparation methods such as hydrolysis of soluble alkali with acid and direct removal of sodium from sodium silicate solutions by ion exchange, which result in different pore structures (Yang, 2003). The chemical composition of silica gel can be expressed as $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The presence of hydroxyl groups imparts a degree of polarity to the surface of silica gel so that molecules such as water, alcohols, phenols, amines, and unsaturated hydrocarbons are adsorbed in preference to non-polar molecules (Ruthven, 1984). Table 2.7 represents some properties of two commercial silica gels.

Table 2.7 Properties of commercial Silica Gel (Ruthven, 1984)

	High Area	Low Area
Specific pore volume (cm ³ /g)	0.43	1.15
Average pore diameter (Å)	22	140
Specific surface Area (m ² /g)	800	340
Particle density (g/cm ³)	1.09	0.62

2.4.3 Zeolites

Zeolites are microporous crystalline aluminosilicates. The zeolite framework consists of an assemblage of SiO₄ and AlO₄ tetrahedral, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the micropore structure is determined by the crystal lattice it is precisely uniform with no distribution of pore size. According to this feature, zeolites are unique from the conventional microporous adsorbents (Ruthven, 1984).

**Figure 2.5** Structure of zeolite (co2crc.com.au, 2008).

From Figure 2.5, each vertex represents the location of a Si or Al atom while the lines represent, approximately, the diameters of the oxygen atoms or ions

which are very much larger than the tetrahedral Si or Al atoms. Each aluminum atom has one negative charge on the framework which must be balanced by an exchangeable cation such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . The exchangeable cations are located at preferred sites within the framework and play a very crucial role in determining the adsorptive properties (Ruthven, 1984). The Si/Al ratio is normally never less than one. The aluminum atom can be removed and replaced by silicon in some zeolites. The inner atoms in the windows are oxygen. The ring size of the aperture controls the maximum size of the molecules or ion species that can enter the pores of zeolites (Yang, 2003). About 175 unique zeolites frameworks have been identified but some of those are important in gas separation including Type X, Y, -zeolites.

The crystallallographic unit cell of zeolites X and Y consists of an array of eight cages and the framework may be thought of as a tetrahedral lattice of sodalite units connected through six-membered oxygen bridges. The difference between the X and Y is the ratio of Si/Al. Zeolites X contain about 1-1.5 of Si/Al while zeolites Y contain about 1.5-3. There is a corresponding difference in the number of exchangeable univalent cations, which varies from about 10-12 per cage for X to as low as 6 for high silica Y (Ruthven, 1984).

Jadhav *et al.* (2007) studied the adsorption of modified zeolite 13X with monoethanolamine (MEA) by using impregnation method. MEA loadings ranged from 0.5-25 wt%. The carbon dioxide adsorption capacity of adsorbents was evaluated by using the breakthrough adsorption method and the adsorption condition were estimated in the temperature range between 30 °C to 120 °C. Jadhav *et al.* (2007) found that at 30 °C a small MEA loading (0.5 wt%) has carbon dioxide adsorption capacity almost unchanged. Thus, for the much higher loading (25 wt%), the capacity has decreased to 17.5 mL/g due to the limited access to adsorption sites for carbon dioxide at higher loading. 13X-MEA-10 (10 wt%) gave the highest capacity of 44 mL/g. compared with 28 mL/g. They also explained that at the room temperature, where adsorption is mostly physical in nature, higher surface area and pore volume are very important. Thus, in this study, both surface area and pore volume of modified zeolite were reduced significantly. At a higher temperature about 120 °C, the 50 wt% loading gave the highest adsorption capacity of 14 mL/g even though the

surface area and pore volume decreased while the unmodified zeolite gave only 4 mL/g and 6.6 mL/g for 10 wt%. Jadhav *et al.* (2007) explained that at 120 °C, the combined adsorption-absorption played roles in the sorption of carbon dioxide wherein the MEA molecules in the pore of the zeolite functions as a solvent contained in a reactor providing better contact between carbon dioxide and MEA. They also compared the carbon dioxide adsorption capacities at different temperatures and found that the adsorption capacity of the modified zeolite with MEA loading at 50 wt% increased with increasing temperature. This is because at an elevated temperature, the kinetics of the reaction significantly increased the adsorption capacity with the temperature and chemisorptions acts as an activated process.

Chatti *et al.* (2009) also studied the modified zeolite 13X with various amines including MEA, ethylenediamine (ED), and isopropanol amine (IPA). After immobilizing zeolite 13X with MEA 50 wt%, pore volume and BET surface area decreased dramatically. Thus, at 75 °C, the adsorption capacities increased from 16.01 mg/g for unmodified 13X to 19.98 mg/g. The highest adsorption capacity was 22.78 mg/g for 13X/IPA.

Xu *et al.* (2009) studied the carbon dioxide adsorption by using β -zeolite and modified it with MEA by wet impregnation method. The MEA functionalized β -zeolites were characterized by X-ray diffraction (XRD), N₂ adsorption, and thermogravimetric analysis (TGA) and the results show that the structure of zeolite was well preserved. At the 5 wt% MEA loading, the adsorption amount of carbon dioxide was 1.37 mmol/g while the adsorption amount of CH₄ and N₂ was only 0.29 and 0.07 mmol/g, respectively. When the MEA loading enhanced, the adsorption capacities of all adsorbates decreased because the pore size was reduced.

2.4.4 Mesoporous Silicates

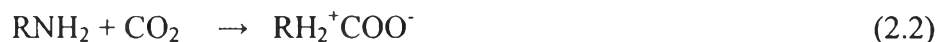
In order to improve adsorbents, considerable synthetic effort has been devoted to develop the adsorbents with pore diameters within the mesoporous range (Beck *et al.*, 1992). One of the well-developed mesoporous materials is silica because it is chemical inert, thermal stability, harmless, and inexpensive (Nandiyanto *et al.*, 2009). Porous inorganic solids have been used as catalysts and sorption media

because of their large internal surface area. In 1992, scientists at the Mobil Corporation discovered highly ordered mesoporous silica materials. These materials contain uniform cylindrical pores with a diameter in a range between 2 nm and 30 nm. The surface area of these materials is between 700 m²/g and 1500 m²/g. High chemical and thermal stability make these materials ideal for use as supports for adsorption and catalysis. MCM-41 (Mobile Crystalline of Materials), which contains micrometer-sized particles with hexagonally ordered mesopores was first reported by Mobil researchers (Trewyn *et al.*, 2006).

To enhance the carbon dioxide capacity, there are several works that focus on modified mesoporous silica with amine groups. Zelenak *et al.* (2008) studied the effect of modified SBA-12 with 3-aminopropyl (AP), 3-(methylamino)propyl (MAP), and 3-(phenylamino)propyl (PAP) using thermal gravimetric analysis to evaluate the adsorption capacity. Carbon dioxide sorption/desorption performed at 25 °C and the results showed that carbon dioxide sorption capacities were 1.04 mmol/g for the sample SBA-12/AP, 0.98 mmol/g for the sample SBA-12/MAP and 0.68 mmol/g for the sample SBA-12/PAP. Among the three amine groups, PAP is the weakest base so it gave the lowest sorption capacity of carbon dioxide. MAP is considered to be the strongest base because of the electron donating methyl group but the steric hindrance effect made the lower accessibility of lone electron pair of MAP which may result in lower sorption capacity.

Chang *et al.* (2009) investigated the effect of modified mesoporous silicas including MCM-41, SBA-15, and pore-expanded MCM-41 with pore size in a range of 2 – 17 nm by mono-, di-, and tri-aminosilanes. The result showed that the amine-grafted SBA-15 gave the highest carbon dioxide adsorption capacities ranging from 1.06 mmol/g to 2.41 mmol/g under an anhydrous gas stream with 15% carbon dioxide and ranging from 1.02 mmol/g to 2.72 mmol/g under a gas stream with 15% carbon dioxide and a RH of 78% at 60 °C. They also found that the carbon dioxide adsorption capacity was higher when water vapor was present in the feed gas. Chang *et al.* (2009) and Zelenak *et al.* (2008) mentioned that sorption capacity can increase with the presence of water because carbamate formed during the reaction of amines with carbon dioxide can further react with carbon dioxide and water to form bicarbonate or amine group can directly react with carbon dioxide and water. The overall

reaction of carbon dioxide and amines is divided into two steps: the formation of carbon dioxide-amines zwitterion and amine or H₂O deprotonation of this zwitterion:



where RNHCOOH and RNHCOO⁻RNH₃⁺ are carbamic acid and ammonium carbamate salt, respectively. Figures 2.6, 2.7, and 2.8 represent carbon dioxide reaction pathway with monoamine, di-amine, and tri-amine-grafted on mesoporous silica.

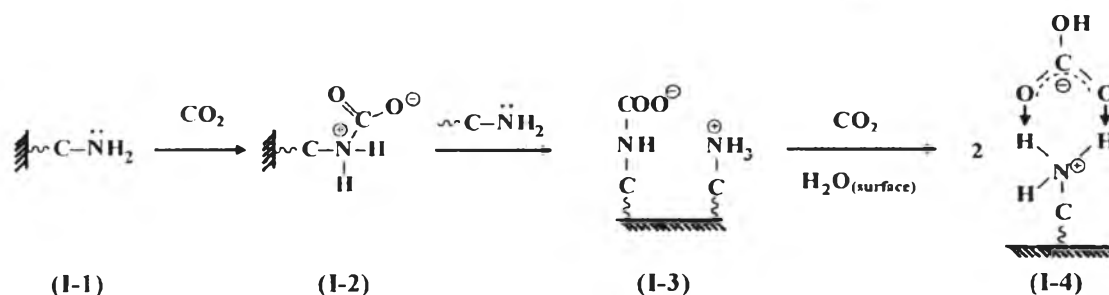


Figure 2.6 Carbon dioxide reaction pathway with monoamine-grafted on mesoporous silica (Chang *et al.*, 2009).

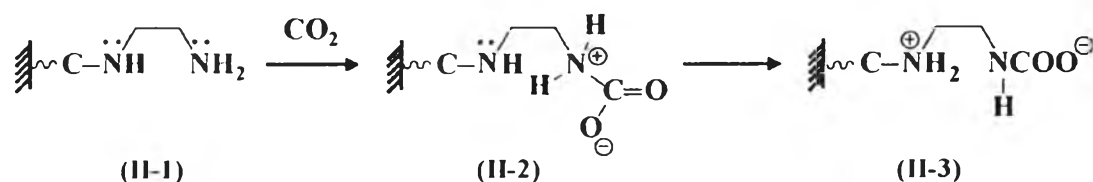


Figure 2.7 Carbon dioxide reaction pathway with di-amine-grafted on mesoporous silica (Chang *et al.*, 2009).

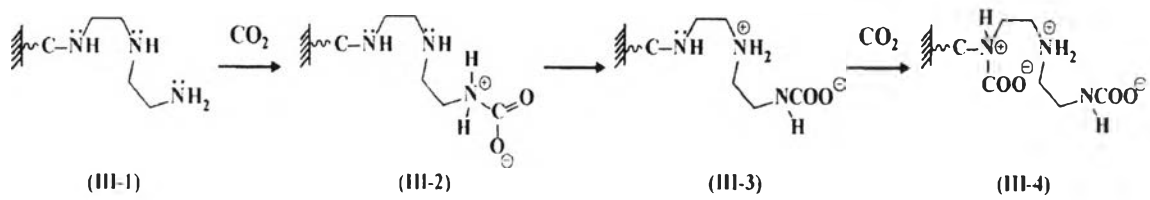


Figure 2.8 Carbon dioxide reaction pathway with tri-amine-grafted on mesoporous silica (Chang *et al.*, 2009).

Sanz *et al.* (2010) studied the effect of impregnated SBA-15 by branched polyethyleneimine (PEI) with different amounts of branched PEI (10, 30, 50, and 70 wt%) using volumetric analyzer to evaluate the adsorption capacity. The adsorption processes were operated at 25 °C, 45 °C, and 75 °C and with the pressure ranging from 0.01 to 6 bar. They found that all SBA-PEI gave higher carbon dioxide adsorption capacities than pure SBA-15. The highest amount of carbon dioxide adsorbed (88.2 mg/g) at 45 °C belongs to SBA-15-PEI(70). Chemisorption of carbon dioxide on amino sites of the impregnated SBA-15 seems to be the main adsorption mechanism. They also mentioned that branched PEI contains about 25% of tertiary amino groups and these types of amines are not active for carbon dioxide anhydrous adsorption. On the other hand, linear PEI gave the better performance of carbon dioxide adsorption but branched PEI needed less energy than linear PEI in the regeneration step. In industrial desulfurization process, the condition of outlet gas was 45 °C and atmospheric pressure. To test the regeneration runs, several adsorption-desorption processes were carried out at 45 °C. After four cycles, the carbon dioxide adsorption capacities remain constant so that a stable condition is attained.