

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Global Warming

The climate change is caused by natural processes and human activities. Global warming is one form of the climate change. Global warming is the rise in the temperature in the atmosphere near the earth's surface. It is related to the increase in the emission of greenhouse gases from human activities. Examples of greenhouse gases (GHGs) are water vapor, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), ozone (O₃), and halogenated compounds. Some of GHGs are ozone depleting substances. Some of GHGs do not deplete ozone but are potent greenhouse gases (epa.gov).

GHGs can cause greenhouse effect directly and indirectly. Direct effect is absorption of radiation by itself. Indirect effect is chemical transformation of GHGs that produces other GHGs or altering the radiative balance of the earth. The Intergovernmental Panel of Climate Change (IPCC) developed the Global Warming Potential (GWP) to compare the ability to trap heat or potential of GHGs that affects the greenhouse effect.

Table 2.1 1995 IPCC global warming potential (GWP) values based on the effects of greenhouse gases over a 100-year time horizon (unfccc.int)

Greenhouse gas	Chemical formula	GWP
Carbon dioxide	CO ₂	1
Methane	CH ₄	21
Nitrous oxide	N ₂ O	310
HFC-23	CHF ₃	11700
HFC-32	CH ₂ F ₂	650
HFC-41	CH ₃ F	150
Perfluoromethane	CF ₄	6500
Perfluoroethane	C ₂ F ₆	9200
Perfluoropropane	C ₃ F ₈	7000
Sulphur hexafluoride	SF ₆	23900

Carbon dioxide is a major cause of global warming. Although the global warming potential (GWP) of CO₂ is low but a large amount of CO₂ emission is the big problem. Figure 2.1 shows the comparison of GHG emission in United States in 2008.

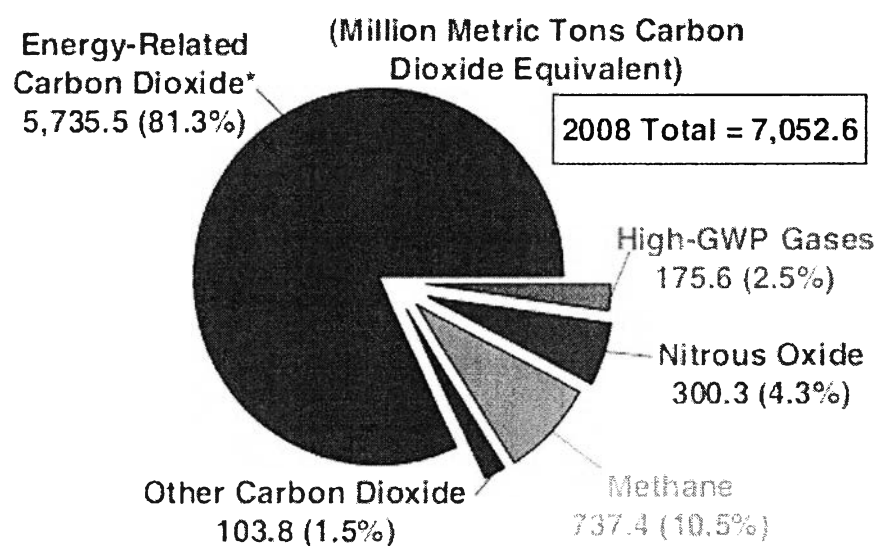


Figure 2.1 U.S. greenhouse gas emission by gas, 2008 (www.eia.gov).

In nature, CO₂ is absorbed by the earth, weathering of rock, and photosynthesis of plant or plankton. These sink phenomena of CO₂ have balanced the CO₂ emission into the atmosphere. But in the industrial era, the excessive CO₂ emission has made sink phenomena became not sufficient to maintain or balanced the CO₂ in the atmosphere. Every 3-5 gigatonnes of CO₂ mean raising 1 ppm of CO₂ in the atmosphere (Thiruvengkatahari *et al.*, 2009; Moriarty and Honnery, 2010; Lee *et al.*, 2012). Figure 2.2 shows increasing trend of CO₂ concentration in the atmosphere. IPCC predicted a temperature increase by 2-3°C from now is dangerous. Hansen *et al.* investigated that 1°C rise of temperature is maximum tolerance to prevent melting of ice and species extinction. Climate model was investigated to prevent global warming and the result showed CO₂ should not exceed 450 ppm. But scientists predicted the safe value for CO₂ concentration is 350 ppm, while it is 393.87 ppm on March, 2012 (www.esrl.noaa.gov/gmd/ccgg/trends/global.html). The CO₂ emission must be controlled.

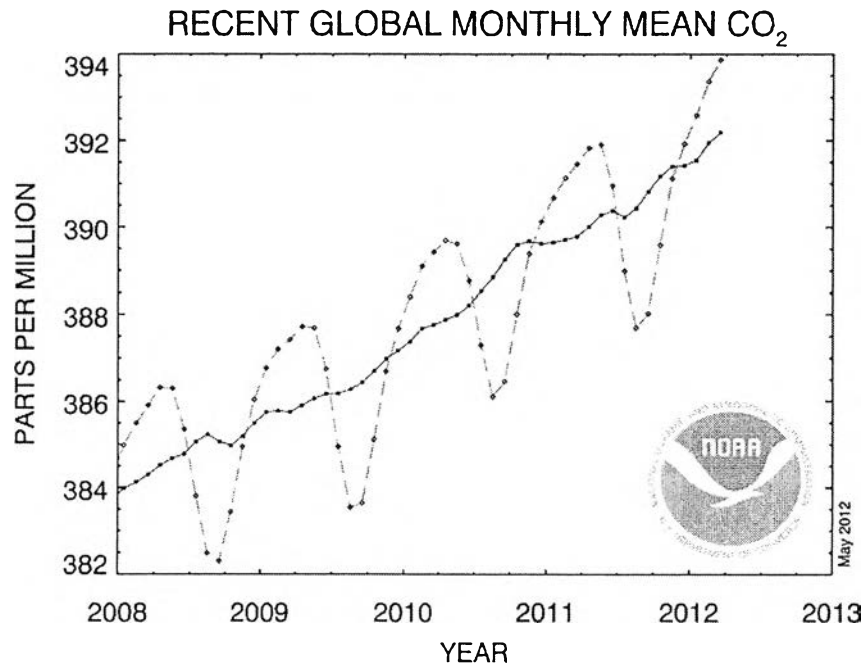


Figure 2.2 Mean carbon dioxide globally averaged over marine surface sites (www.esrl.noaa.gov).

2.2 Carbon Dioxide (CO₂)

Carbon dioxide (CO₂) is present in the atmosphere and is an important part in carbon cycle. Because of rising in CO₂ emission, CO₂ is considered to be a GHG influencing the global warming. The fossil fuel combustion is a major source of CO₂ emission as seen in Figure 2.3. Figure 2.4 shows that the highest CO₂ emission source is from electricity generation especially from coal-fired power plants (www.epa.gov). In order to reduce CO₂ emission, several ways have been suggested. There are increasing the efficiency of energy conversion, switching to use less carbon content fuel, and using renewable energy or alternative. In addition, mid-term solution called “CO₂ capture, storage and utilization (CCSU)” technology has been developed to alleviate the problems.

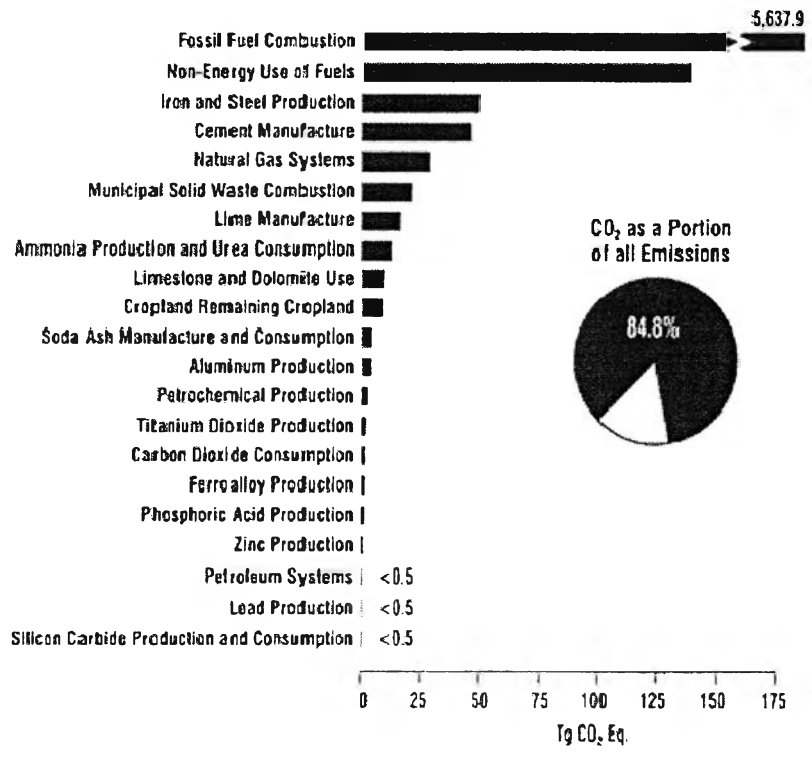


Figure 2.3 Breakdown of sources of CO₂ emissions in the U.S. in 2006 (www.epa.gov).

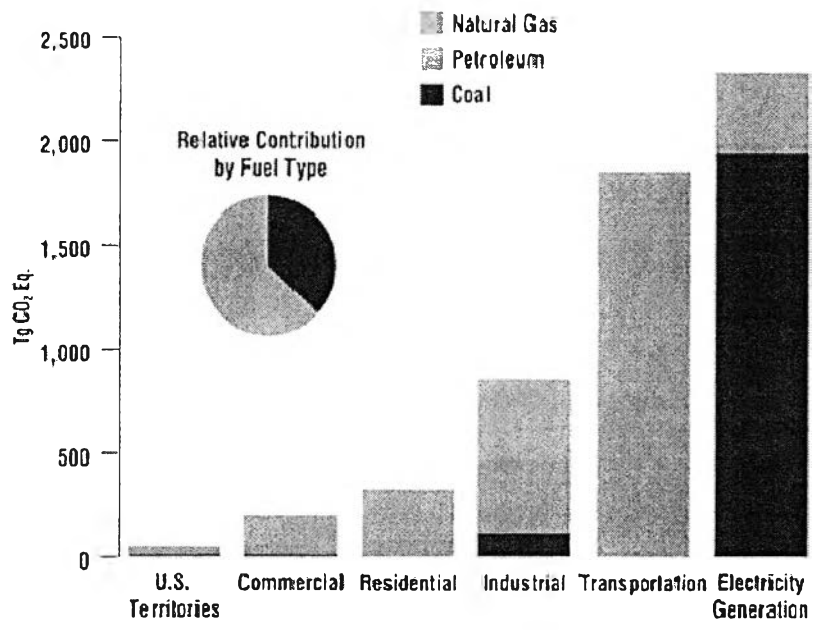


Figure 2.4 CO₂ emission from fossil fuel combustion by sector and fuel type in 2006 (www.epa.gov).

2.3 Carbon Capture and Storage (CCS)

Carbon capture and storage strategy has been invented to reduce CO₂ emission. This strategy is an effective way to remove CO₂ from large emission source such as power plant, industries. CCS needs new effective technologies with low operation costs. Nowadays, CCS can be divided into three routes:

2.3.1 Pre-combustion Capture

First, the fossil fuel is used to produce syngas (CO+H₂). Then, syn-gas passes the reactor to produce CO₂ via water-gas shift reaction. H₂ is separated from CO₂ before feeding into a combustion chamber. This concept is to decarbonize fuel before combustion as shown in Figure 2.5 (Lee *et al.*, 2012).

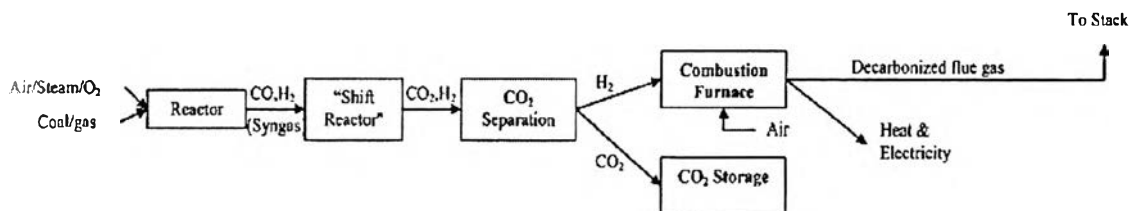


Figure 2.5 Pre-combustion CO₂ removal (Lee *et al.*, 2012).

2.3.2 Oxy-fuel Combustion Capture

As the scheme in Figure 2.6 shows, fuel combusts with high purity oxygen, which comes from an air separation unit instead of normal air. This induces complete combustion that gives flue gas containing mainly CO₂, which can be separated later (Lee *et al.*, 2012).

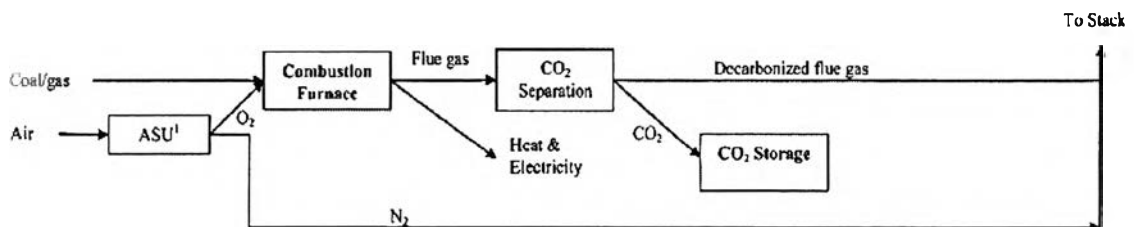


Figure 2.6 Oxy-fuel combustion CO₂ removal (Lee *et al.*, 2012).

2.3.3 Post-combustion Capture

CO₂ is removed from flue gas after combustion. This process is the most popular because the process does not involve any modification. The process captures CO₂ through absorption, adsorption, membrane and cryogenic separation (Lee *et al.*, 2012).

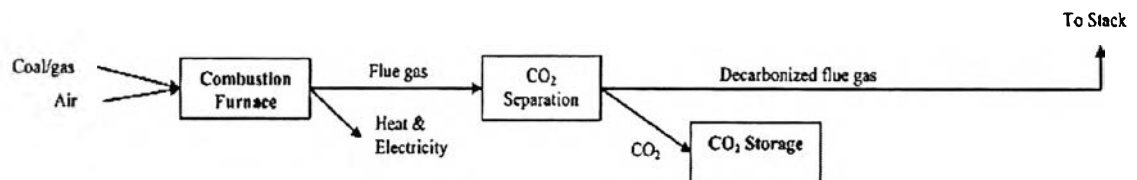


Figure 2.7 Post-combustion CO₂ removal (Lee *et al.*, 2012).

2.4 CO₂ Separation and Capture Technologies

CO₂ capture technologies can be classified into :

- Absorption
- Adsorption
- Membrane separation
- Cryogenic separation

2.4.1 Absorption

Absorption process is generally used in petroleum industries. Absorption can be classified into physical and chemical absorption. Physical absorption is based on Henry's law. CO₂ is absorbed by a solvent following the CO₂ absorption capacity equilibrium of physical absorbent. The physical solvent can absorb CO₂ effectively at high CO₂ partial pressure or high concentration of CO₂ in flue gas. Regeneration of used solvent can be done by using heat or pressure reduction (normally use pressure reduction for economical). Physical absorption is not economical when CO₂ concentration is lower than 15%vol. The common physical solvent are cold methanol (Rectisol process), dimethyleter of polyethylene glycol (Selexol process, propylene carbonate (Fluor process) and n-methyl-2-pyrrolidone (NMP-purisol). The good solvents for physical absorption are solvents

with high boiling point and low vapor pressure (Gupta *et al.*, 2003; Wang *et al.*, 2011).

The chemical absorption is commonly used for low CO₂ concentration. This process was adapted from amine-based process from gas processing industry, which is used to remove acid gas from gas streams. Chemical solvent is used to react with CO₂ to form a weakly bonded intermediate compound. Regeneration can be done by heating the compound. The capacity of CO₂ adsorption is high at low concentration of CO₂ in gas stream. The selectivity of this separation is relatively high. For drawbacks, this process has problems about the scale, efficiency, stability, and high energy consumption that lead to high operating cost. In some cases, the solvent can be degraded and oxidized under condition and corrosive that is hard to handle (Gupta *et al.*, 2003; GCEP, 2005; Wang *et al.*, 2011). Alkanolamines are generally used for CO₂ capture. Amines have different equilibrium absorption and have different selectivity (GCEP, 2005). Alkanolamines can be classified into three groups: primary amines such as monoethanol amine (MEA) and diglycolamine (DGA), secondary amines such as diethanol amine (DEA) and diisopropyl amine (DIPA), and tertiary amines such as triethanol amine (TEA) and methyldiethanol amine (MDEA).

MEA is popular for CO₂ capture in natural gas industry. The commercial process MEA absorption uses MEA solution to contact with CO₂ in a gas stream to form MEA carbamate. The MEA carbamate is regenerated by passing a stripper. In addition, DEA and MDEA are also often used as absorbents (Yang *et al.*, 2008). The reactions between amines and CO₂ are shown in Figure 2.8. From this mechanism, CO₂ reacts with 2 amines to form a stable bicarbonate compound.

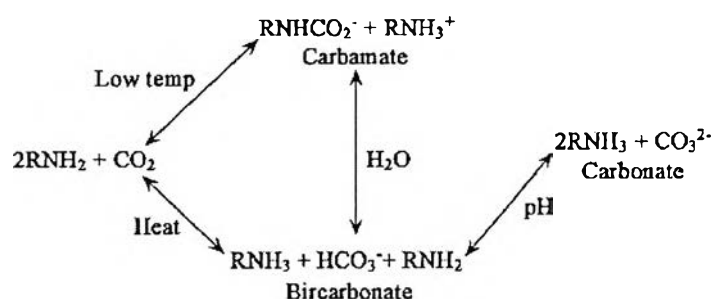


Figure 2.8 Proposed reaction sequence for the capture of carbon dioxide by liquid amine-based systems (Gray *et al.*, 2005).

2.4.2 Adsorption

Adsorption is the accumulation of substances (adsorbate) on the surface of adsorbent without diffusion into bulk. Mostly, concentration gradient is a driving force for this phenomena. Adsorption can be divided into physical adsorption or physisorption, and chemical adsorption or chemisorption.

Physical adsorption involves interaction or affinity of substance to the surface of adsorbent without forming a chemical bond. Adsorbents can separate CO₂ by weak interaction such as van der Waals force. On the other hand, chemical adsorption involves chemical bond between substance and active surface of adsorbent. Chemical adsorbents generally consist of active surface on inert support (GCEP, 2005).

The CO₂ adsorption process operates on a cycle with two steps, which are adsorption and regeneration. In the adsorption step, gas is fed through the adsorbent bed, which is selective for CO₂ and lets the other gases pass through. After the adsorbent bed saturated with CO₂, the regeneration is needed to remove CO₂ from adsorbent. There are several technology for CO₂ regeneration. In pressure swing adsorption (PSA), the pressure is reduced to regenerate the bed. In temperature swing adsorption (TSA), the temperature of the bed is raised to regenerate. The vacuum swing adsorption (VSA) is special PSA, which requires a vacuum or below atmospheric pressure to regenerate the adsorbent bed. In electric swing adsorption (ESA), the bed is heated by passing electric current through the adsorbent followed Joule effect. The PSA and TSA are commercially available technology (Gupta *et al.*, 2003; GCEP, 2005; Plaza *et al.*, 2010; Plaza *et al.*, 2011). Due to the low energy consumption, the adsorption process is very interesting technology. In addition, other advantages of adsorption are cost-effective, non-corrosive problems, and degradation of sorbents under operating condition (Gupta *et al.*, 2003; GCEP, 2005). But adsorption process may not be suitable for large-scale flue gas treatment because of low adsorption capacity and low selectivity of commercial adsorbents. In addition, adsorption of commercial adsorbent needs high CO₂ concentration. For example, zeolite has low CO₂ selectivity with wet flue gas because zeolite can adsorb water strongly (Wang *et al.*, 2011). A suitable adsorbent is required to approach the goal.

2.4.3 Membrane Separation

A membrane is a thin barrier that allows selective permeation of favorable components (permeate) or allows permeate in a mixture to pass through faster than other components. The membrane system is considered as a combination of adsorption and absorption. Polymeric membranes, inorganic microporous membranes, and palladium membranes are commonly used in CO₂ separation. But a membrane has problems with selectivity of CO₂ and problems based on type of membranes. In many cases, membrane systems have drawbacks of high energy consumption (GCEP, 2005). The efficiency of membrane depends on CO₂ concentration. High CO₂ concentration is favorable (Wang *et al.*, 2011). Supported membranes were also investigated because of their advantages such as low operating cost, low maintenance cost, high selectivity of CO₂ and high capacity (Figueroa *et al.*, 2008).

2.4.4 Cryogenic Separation

Cryogenic separation removes CO₂ from a gas stream by condensation of CO₂ (Wang *et al.*, 2011). The process is used to separate gases into very pure streams. CO₂ can be condensed at -56.6°C and atmospheric pressure. It is typically used with an oxy-fuel process (GCEP, 2005). The advantage of cryogenic process is that it enables direct production of CO₂ that is economic for transportation. But the drawback is high energy cost (Gupta *et al.*, 2003).

2.5 **Solid Adsorbents**

Suitable adsorbents for CO₂ adsorption should have several parameters, including:

- High CO₂ adsorption capacity. This property is mainly used to screen new adsorbents. Common flue gas has CO₂ partial pressure less than 0.4 bar with a total pressure of 1-2 bar and temperature less than 70-80°C. As a rule of thumb, an optimum adsorbent should have capacity around 2-4 mmol/g. The CO₂ adsorption isotherm with a high slope means the adsorbent is favorable to adsorb CO₂ (Ho *et al.*, 2008; Sayari *et al.*, 2011)

- Fast kinetics. Adsorption kinetics is important in a dynamic process. The high rate of adsorption gives working capacity approach to equilibrium capacity with less time (Sayari *et al.*, 2011).
- High CO₂ selectivity. This parameter results in purity of product. In ideal, an adsorbent should adsorb only CO₂ (Sayari *et al.*, 2011).
- Mild conditions for regeneration. The regeneration of adsorbent depends on structural and chemical properties of an adsorbent and can be done via PSA, TSA, VSA, ESA that are described before. In CO₂ adsorption, an optimum interaction is required. Weak interaction results in low capacity but easy to regenerate. On the other hand, strong interaction results in high capacity but desorption of adsorbent is difficult or needs severity condition (Sayari *et al.*, 2011).
- Stability. It means life time of an adsorbent. It has direct impact on economic for commercial scale (Sayari *et al.*, 2011).
- Tolerance to the presence of moisture and other impurities in the feed. If flue gas contains N₂, CO₂, water vapor, and impurities, this can affect an adsorbent performance. Some impurities have high affinity with adsorbent than CO₂, which may affect the CO₂ capacity of the adsorbent (Sayari *et al.*, 2011).
- Low cost. This is a very important parameter for economic of commercial scale (Sayari *et al.*, 2011).

Depending on chemical composition, structural characteristic and adsorption mechanism, adsorbents can be classified in many kinds such as activated carbon, carbon nanotube, carbon gel, silica, alumino-silicas such as zeolite, alumino-phosphates (AlPOs), alumino-silico-phosphates (SAPOs), metal organic frameworks (MOFs), hydrotalcites etc. (Sayari *et al.*, 2011; Wang *et al.*, 2011). Figure 2.9 shows available adsorbents for CO₂ adsorption in relationship between capacity and temperature.

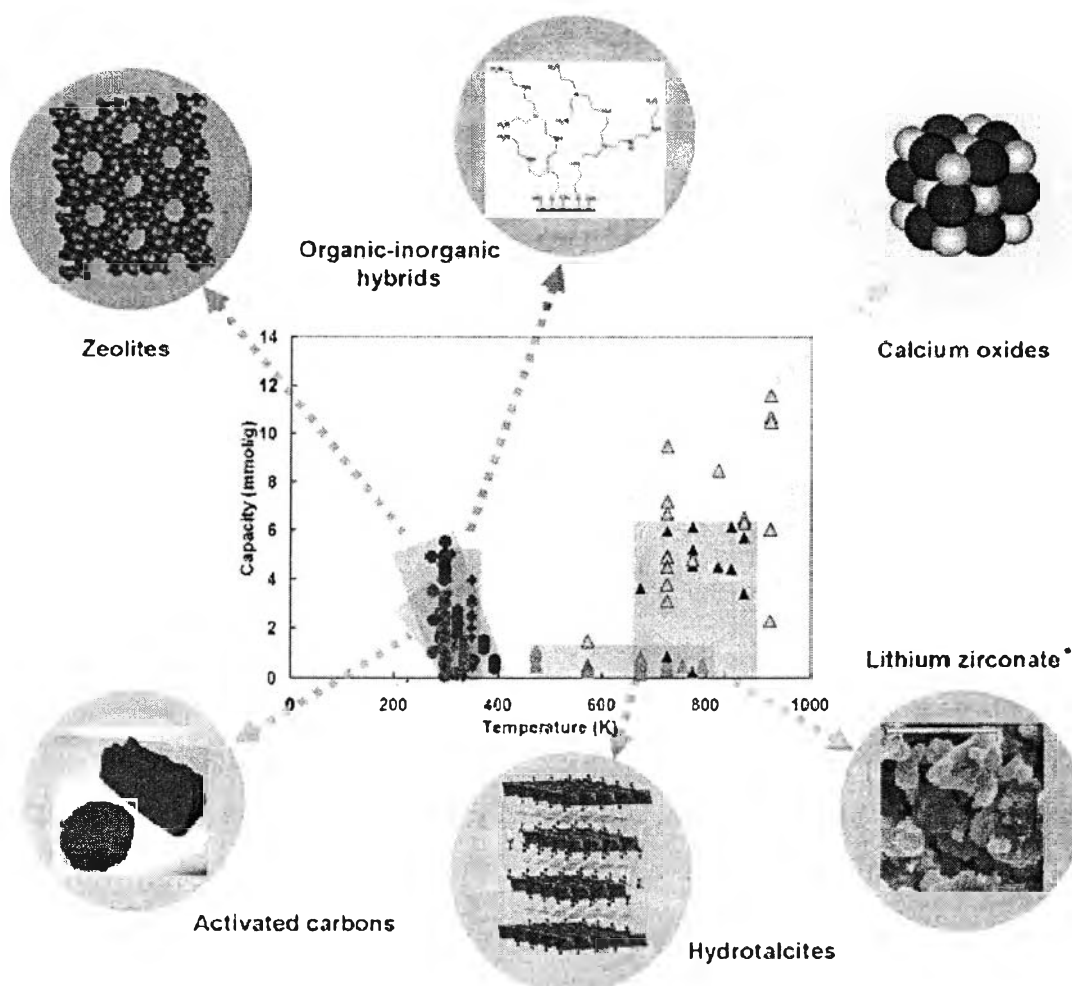


Figure 2.9 Capacity of adsorbent material for CO₂ capture in range of temperature (Choi *et al.*, 2009).

2.5.1 Activated Carbons

Among the carbon based adsorbents, activated carbons (ACs) are the most investigated material. ACs have a wide range of pore structure. The structure of ACs is shown in Figure 2.10. The different raw material leads to variations of pore size distribution, pore structure, surface structure, etc. (Choi *et al.*, 2009). ACs are produced via two steps, which are carbonization and activation. Carbonization is pyrolysis to form carbonaceous material by releasing non-carbon elements. The rigid carbon skeleton (charcoal) has been formed but it shows poor surface properties. In the activation step, the charcoal is modified for better surface properties. Both physical and chemical activation can produce higher surface area. ACs can have high porosity and high surface area that is suitable for adsorption process (Choi *et al.*,

2009; Sayari *et al.*, 2011). Compared to zeolites, ACs have lower capacity and selectivity. But the hydrophobic surface of ACs can overcome zeolites. Zeolites have high affinity to water and are critically hydrophilic to water that is hard to desorb. Adsorption ability of ACs is not affected by the presence of water (Choi *et al.*, 2009; Shafeeyan *et al.*, 2010; Dong *et al.*, 2011; Sayari *et al.*, 2011). In addition, ACs have low price and need low energy consumption (Plaza *et al.*, 2010). Properties of ACs can be adjusted by functionalization, modification, impregnation, etc. That makes ACs of interest adsorbent material for CO₂ adsorption.

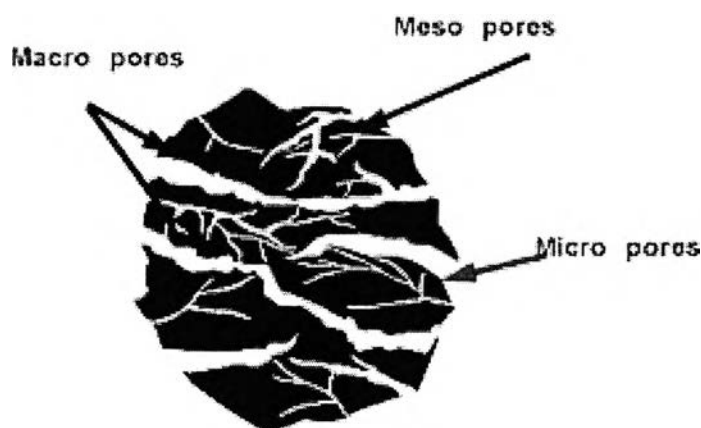


Figure 2.10 AC structure (www.afssociety.org).

Because CO₂ is weak Lewis acid, introduction of Lewis bases onto AC surface may increase CO₂ capture performance (Shafeeyan *et al.*, 2010). There are many work on modification of ACs for CO₂ capture. Pevida *et al.* (2008) studied on surface modification of commercial ACs. ACs were modified with ammonia, resulting in carboxylic group. At a high temperature, ammonia decomposes to radicals of N species and react with carbon surface to form functional group such as -NH₂, -CN, pyridinic, pyrrolic and quaternary nitrogen. Hence, the CO₂ adsorption capacity of modified ACs increased. After that, high surface area ACs were investigated by Zhang *et al.* (2010). The ACs were modified with impregnation of ammonia and microwave irradiation in N₂ or H₂ atmosphere. After modification, the composition of C and N of ACs increased but the composition of O decreased. The results showed that the basic group of ACs increased, while the acidic group of ACs decreased compared to original ACs. Using microwave irradiation in atmosphere of

N₂ resulted in the highest basic group on the AC surface and showed the highest adsorption capacity of CO₂. Effects of pre-oxidation for ammonia modification were studied by Shafeeyan *et al.* (2011). The surface oxidation has a role to introduce the oxygenated sites to the surface before introducing nitrogen functional groups to the carbon surface. It was found that decomposition of oxygenated groups on the surface increased reactivity of ammonia and radicals to form nitrogen functional group. The result showed increase in the CO₂ adsorption capacity with ammonia treatment.

2.5.2 Zeolites

Zeolite is a highly ordered microporous crystalline aluminosilicate material. Zeolite structure is built of tetrahedras of SiO₄ and AlO₄. The Al atoms in the silicate structure make the frameworks negatively charge and needs a positive charge such as cations to balance the charges. The structure of zeolites can be varied by Si/Al ratio and cations. Due to this, zeolites can have different adsorption performances. Especially, the Si/Al ratio plays a major role in the architecture of zeolite, resulting in controlling the CO₂ adsorption properties (Choi *et al.*, 2009; Sayari *et al.*, 2011). The number and nature of cations can also affect the adsorption performance. The alkali cations such as lithium or sodium can generate strong electrostatic interactions with CO₂. This results in high affinity between CO₂ and zeolites. But zeolites are hydrophilic materials that have higher affinity with water than CO₂. Zeolites are suitable for dry feed. The most common zeolites for CO₂ adsorption are X and Y zeolites (generally NaX or 13X and NaY, respectively) (Sayari *et al.*, 2011). The structure of aluminosilicate framework is the same for X and Y zeolites. Both are isostructural with the natural zeolite, faujasite. The difference of X and Y zeolites are location of cations and Si/Al ratio (www.aussiezeolite.com.au). The structure of X/Y zeolite is shown in Figure 2.11.

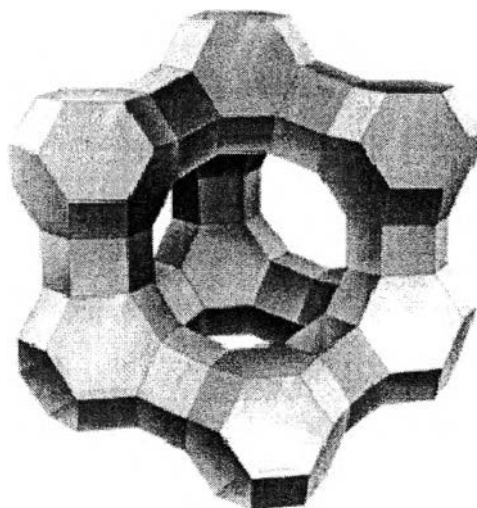


Figure 2.11 X/Y zeolites (www.molecularsieve.org)

2.5.3 Metal-based Adsorbents

Due to acidic role of CO_2 , it can be adsorbed on the basic sites of metal oxides. Metals with low charge/radius ratio are strong basic sites. Among alkaline metal oxides (Na_2O , K_2O) and alkaline earth metal oxides (CaO , MgO), CaO is generally used for CO_2 capture. CaO reacts with CO_2 and forms CaCO_3 . Then, it can be regenerated by calcination to get rid of CO_2 (Choi *et al.*, 2009). Other important adsorbents are MgO , lithium zirconates, and lithium silicates. The materials have high CO_2 adsorption capacity at high temperatures (Lee *et al.*, 2012).

Recently, the basicity of mixed oxides of cerium and gallium was investigated by using CO_2 chemisorption. Addition of gallia to ceria makes the surface become more acidic due to the decrease in the concentration of carbonate group on surface. The carbonate species were identified by infrared spectroscopy (Finos *et al.*, 2012).

2.5.4 Metal Organic Frameworks

Metal organic frameworks (MOFs) are porous crystalline materials, containing metal ions and organic linkers or ligands. The structure and geometry of MOFs can be tuned by metal ions and ligands. Due to tunable structure of MOFs, they are useful in sorption area. Adsorption performance of MOFs depends on their structure. MOFs show unfavorable CO_2 adsorption at low pressure, and CO_2 capacity

is reduced at high temperature. The selectivity is still low compared to zeolites. MOFs seem to be suitable for CO₂ storage than separation. The interesting in MOFs is adjustable properties (Lincke *et al.*, 2011; Sayari *et al.*, 2011; Natarajan *et al.*, 2012). An example of MOF structure is shown in Figure 2.12.

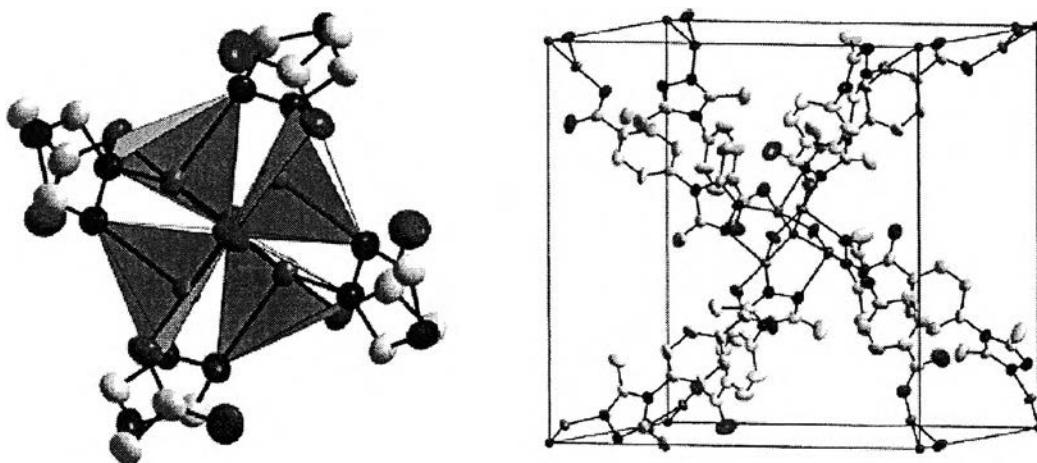


Figure 2.12 Copper-based MOF (Lincke *et al.*, 2011)

2.5.5 Mesoporous Silicas

Mesoporous silica is one form of silicas or silicates. This material is popular for using as support and molecular sieves because of its large surface area. The most used mesoporous silicas are MCM-41 and SBA-15 (en.wikipedia.org). The untreated mesoporous silicas show very low CO₂ adsorption capacity (Lee *et al.*, 2012).

2.5.6 Hydrotalcites

Hydrotalcites (HTCs) can be called layered double hydroxides or Feitknecht compounds as shown in Figure 2.13. When HTC is calcined, water in the structure loses at a temperature about 200 °C. In the range 200 – 500 °C, dehydroxylation occurs and increases the surface area. The strong basic site is active, and CO₂ can be adsorbed according to Lewis acid-base theory (Choi *et al.*, 2009).

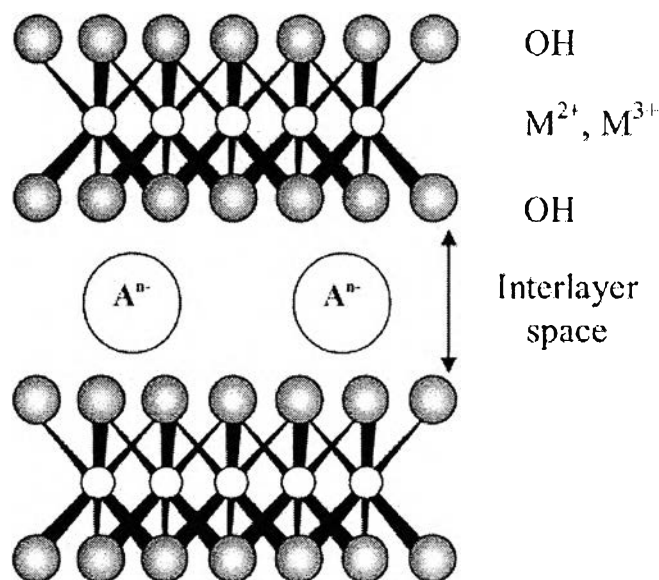


Figure 2.13 Structure of hydrotalcites (Cantrell *et al.*, 2005).

2.5.7 Carbon Gels

Carbon gels are produced from organic gels such as resorcinol-formaldehyde (RF) gels. The texture of gels could be controlled by synthesis. The preparation mainly contains three steps: gel synthesis (formation of polymer gel), gel drying (removal solvent) and pyrolysis to form carbon gels. Different drying methods result in different gels. Supercritical drying gives gel called aerogel. Cryogel is obtained by freeze-drying. Evaporative drying leads to xerogel. Among the three gels, the aerogel has the highest surface area because no shrinkage and collapse occurs (Al-Muhtaseb and Ritter, 2003; Job *et al.*, 2005; Contreras *et al.*, 2010). CO_2 adsorption in carbon aerogel was investigated by Reichenauer (2007). There are two steps of adsorption, which are a function of relative pressure. The slower step corresponds to restricted diffusion at the mouth of micropore. The faster step corresponds to different macropore size.

2.6 Amine-functionalized Adsorbents

The technology used in industry for CO_2 capture is absorption with amine solution. The removal CO_2 by amines occurs via zwitterion formation (carbamate

generation) and acid-base neutralization. Primary and secondary amines can undergo both zwitterion formation and acid-base neutralization. Tertiary amines do not form carbamates due to the amino-hydrogen atoms. So, the tertiary amines can only undergo acid-base neutralization. Yang *et al.* (2009) studied the CO₂ adsorption in amine solution with carbon-13 NMR. They suggested the reaction mechanism, which is shown in Figure 2.14.

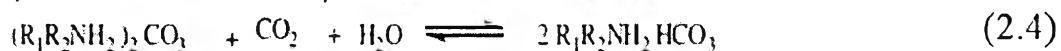
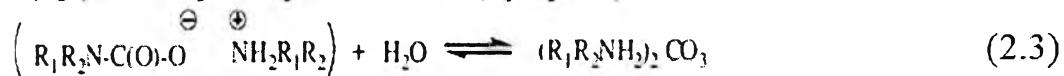
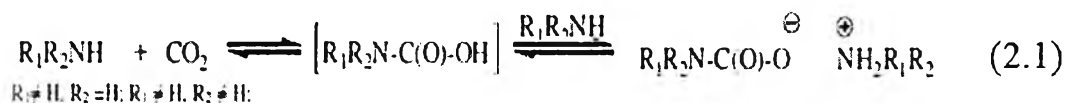


Figure 2.14 Proposed mechanism for CO₂ removal with amines (Yang *et al.*, 2009).

The zwitterion formation Eq. (2.1) was much faster than acid-base neutralization Eq. (2.2). After carbamate formed, the reaction can undergo hydrolysis and generated carbonate/bicarbonate Eq. (2.3) - (2.4). The formation of bicarbonate consumed more CO₂ than the formation of carbamates. Additionally, carbamates had high thermal stability than bicarbonate and consumed high energy in CO₂ desorption. Tertiary amines had higher potential in CO₂ adsorption because they could not form carbamate.

The liquid amine absorption process inspired to use amine-modified solid materials as adsorbents for CO₂ capture. The supported amines maintained a high selectivity of CO₂ without uptake of the other components (Sayari *et al.*, 2011). The amine-functionalized adsorbents could be classified according to type of interaction between amines and support.

2.6.1 Amine-grafted Materials

The idea of these materials is to graft amine groups on the supports. A popular way to synthesize grafted materials is using aminosilane. Leal *et al.* (1995) modified silica gel by 3-aminopropyltriethoxysilane. The grafting reaction between silica gel and 3-aminopropyltriethoxysilane occurred on the surface. The

condensation of hydroxyl groups resulting in bonding between aminosilane and surface. The amines on surface acted as the active sites for CO₂ adsorption at room temperature and desorption was achieved at about 100 °C. The adsorbent adsorbed about 10 STP cm³ of dry CO₂ per gram. After that, there were many works on grafting aminosilane on mesoporous silicas for CO₂ adsorption enhancement (Hiyoshi *et al.*, 2005; Linfang *et al.*, 2007; Zelenak *et al.*, 2008; Chang *et al.*, 2009; Ko *et al.*, 2011).

Hiyoshi *et al.* (2005) prepared aminosilane-modified SBA-15 by grafting various aminosilanes on SBA-15. The aminosilanes were 3-aminopropyltriethoxysilane (APS), N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS) and 3-trimethoxysilylpropyl)diethylenetriamine (TA). The result showed that grafting aminosilanes on SBA-15 enhanced CO₂ adsorption performance under moist and dry conditions. The efficiency of adsorption could be improved by increasing the surface density of amines. It was suggested that CO₂ was adsorbed through carbamate formation that needed densely amine groups, as shown in Figure 2.15. The capacities of adsorbents were not proportional to the amine contents but they were a function of the surface density of amine. The higher surface density of amine could introduce this mechanism to undergo easily. Comparison between amine efficiencies at the same surface density, they found that efficiency follows the order: APS > AEAPS > TA. They explained that primary amine was more effective than secondary amine and the steric hindrance might cause different efficiencies. Linfang *et al.* (2007) also studied SBA-15 modified by aminosilane. They used 3-aminopropyltriethoxysilane (APTES) functionalized on SBA-15. At a suitable prepared condition, the adsorbent could get the highest load of amine, and had a high adsorption capacity of 34.2 mg/g at room temperature and a partial pressure of CO₂ was 0.005 MPa. This adsorbent was less sensitive to temperature and CO₂ partial pressure compared with commercial ACs, and it also had excellent regeneration and stability.

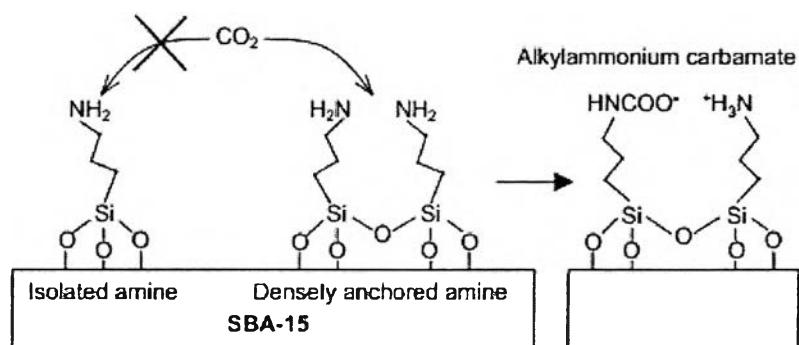


Figure 2.15 Adsorption of CO_2 on aminosilane-modified SBA-15 (Hiyoshi *et al.*, 2005).

Amine-modified SBA-12 was investigated by Zelenak *et al.* (2008). SBA-12 was modified by 3-aminopropyl (AP), 3-(methylamino)propyl (MAP) and 3-(phenylamino)propyl (PAP) ligands. The electronic effect of ligands gave the different basicity of the modified silica materials. At 25 °C, the result showed that CO_2 adsorption capacities were 1.04 mmol/g for SBA-12/AP, 0.98 mmol/g for SBA-12/MAP and 0.68 mmol/g for SBA-12/PAP. In the PAP molecule, an aromatic ring connected to nitrogen, made PAP less basic than AP or MAP. Because of the electron donating group in MAP, MAP was stronger base than AP. However, steric hindrance effect made the secondary amine (MAP) is not a stronger base than the primary amine (AP) but they were approximately equal in the basicity. In CO_2 adsorption, steric hindrance led to lower accessibility of CO_2 . That was a cause of lower CO_2 uptake of MAP than AP.

Then, Chang *et al.* (2009) studied adsorption of CO_2 on amine-grafted mesoporous silicas. The mesoporous silicas including MCM-41, SBA-15 and pore-expanded MCM-41 were modified by mono-, di- and tri-aminosilanes. The CO_2 capture under dry condition could be occurred via zwitterion mechanism. Figures 2.16-2.18 represented the CO_2 adsorption on mono-, di-, tri-amine grafted on mesoporous silicas. For monoamine, two surface primary amine sites were required for formation of carbamate. In the presence of water, carbamates could react with another CO_2 to produce bicarbonate species. In case of diamine, the adsorption of CO_2 might proceed at primary amine. The carbamate could be stabilized by intermolecular acid-base balance with secondary amine on the same site without

requiring in two amine site to catch CO₂. Tri-amine could react with CO₂ like di-amine. But there was one amine left and could interact with CO₂ to form more zwitterion. The result showed that SBA-15 was the great support for amine-grafting and gave high capacity of CO₂ adsorption. Tri-amine was given the highest capacity. Capacities increased in order mono-< di-< tri-. The TA/SBA-15 give the best CO₂ adsorption capacity of 2.41 mmol/g for dry feed and 2.72 mmol/g for wet feed. Due to formation of bicarbonate, the existence of water could improve CO₂ adsorption performance via acid-base neutralization mechanism.

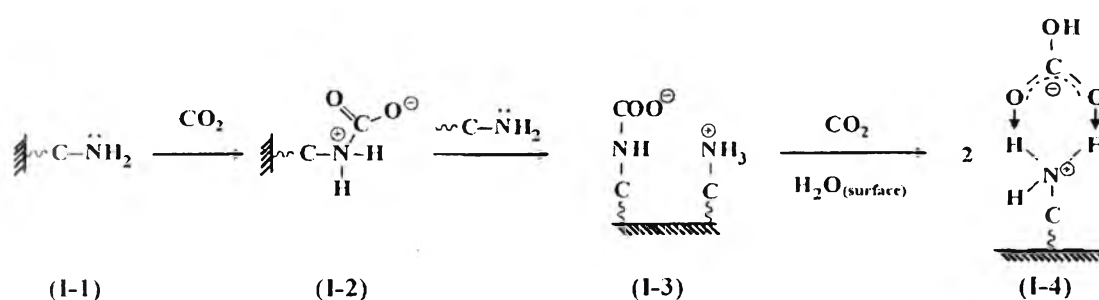


Figure 2.16 CO₂ reaction pathways with monoamine-grafted on mesoporous silicates (Chang *et al.*, 2009).

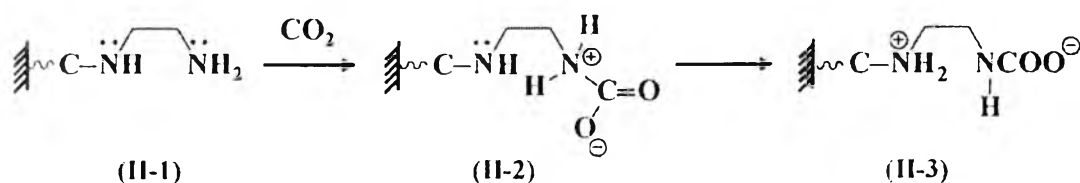


Figure 2.17 CO₂ reaction pathways with di-amine-grafted on mesoporous silicates (Chang *et al.*, 2009).

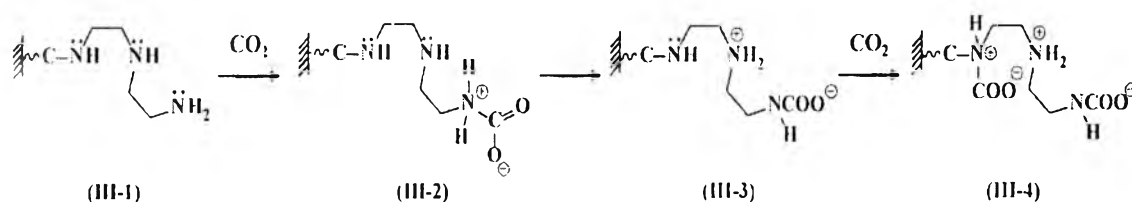


Figure 2.18 CO₂ reaction pathways with tri-amine-grafted on mesoporous silica (Chang *et al.*, 2009).

Ko *et al.* (2011) investigated effects of amine types on CO₂ capture. They used (3-aminopropyl) trimethoxysilane (APTMS), [3-(methylamino)propyl]

trimethoxy silane (MAPTMS), and [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS) as primary, secondary and tertiary amine, respectively. These amines were grafted to the surface of SBA-15. The maximum capacities of SBA-15-NH₂, SBA-15-NH-CH₃ and SBA-15-N(CH₂CH₃)₂ were 0.95, 0.75, and 0.17 mmol/g, respectively. Adsorbed CO₂ could be easily desorbed from the adsorbent with low energy consumption in the order of tertiary, secondary and primary amine. On the other hand, trends for adsorption capacities and CO₂ affinity increased in the reverse order. The proposed mechanisms for CO₂ adsorption with primary, secondary and tertiary amines were represented in Figure 2.19. Primary and secondary amines could react with CO₂ and form carbamate via zwitterion mechanism. They described the scheme. For primary and secondary amines reacted with CO₂, the first step proceeded with the lone pair electrons on amine attacking the carbon atom in CO₂ to form zwitterion. Then, deprotonation occurred to form the carbamate. Tertiary amines reacted with CO₂ via different mechanism. Tertiary amines catalyzed the formation of bicarbonate. This mechanism induced the base-catalyzed hydration of CO₂ for reaction of CO₂ and tertiary amines. This reaction could not occur with the absence of water. The amine efficiencies of adsorbents were lower than the theoretical efficiencies. That was two amines were needed to capture CO₂ for primary and secondary amines. There were some isolated amines which could not function to CO₂ capture. And the steric hindrance of amines could inhibit adsorption performance. These led to lower CO₂ capacities than theoretical value. In dry condition, electrostatic and van der Waals forces might be caused of CO₂ adsorption on tertiary amines.

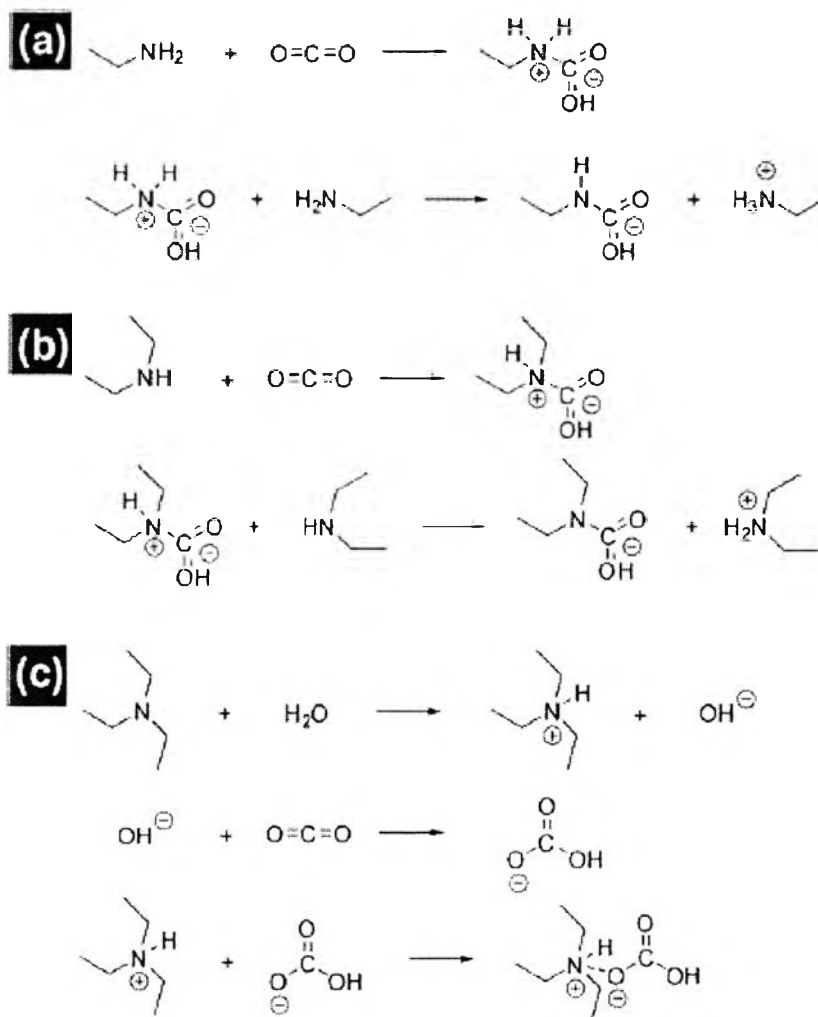


Figure 2.19 Mechanisms for the reaction of CO₂ with (a) primary (under dry condition), (b) secondary (under dry condition), and (c) tertiary amines (under humid condition) (Ko *et al.*, 2011).

The research about amine grafting on ACs was also investigated (Jang and Park, 2011). The surfaces of AC were treated by 3-chloropropyltrimethoxysilane. Then, tris-(2-aminoethyl)amine (TREN) and tri-ethylenetetramine (TETA) were grafted on the functionalized carbon surfaces as seen in Figure 2.20. The branched amine TREN grafted ACs showed CO₂ adsorption of 43.8 cm³/g at 298 K. The straight chain amine TETA grafted ACs showed CO₂ adsorption of 42.4 cm³/g at same temperature. TREN-ACs showed higher CO₂ adsorption capacities because they had two free primary amines while TETA-ACs had only one free primary amine. TREN had the three-dimension stabilization property that stabilize adsorbed CO₂ and

improve CO₂ adsorption performance, while TETA could not stabilize in three-dimension. Due to these, TREN-ACs showed high adsorption performance compared to TETA-ACs.

Many works mentioned that the presence of water can improve CO₂ adsorption capacities by formation of bicarbonate groups (Leal *et al.*, 1995; Hiyoshi *et al.*, 2005; Zelenak *et al.*, 2008; Chang *et al.*, 2009).

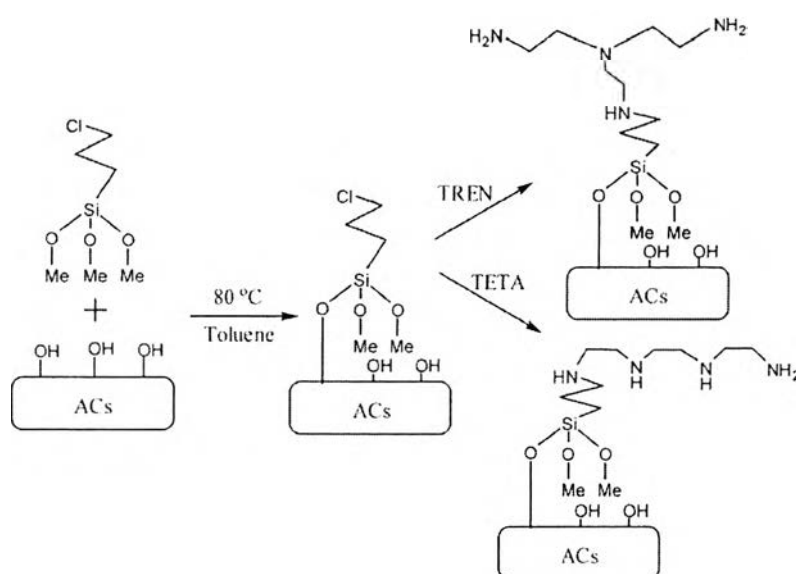


Figure 2.20 Schematic of TREN and TETA grafting on chloro-functionalized ACs (Jang and Park, 2011).

2.6.2 Amine-impregnated Adsorbents

For impregnation of amines on adsorbents, it was reported that high loading of amines could be obtained but still has problem about diffusion limitation (Sayari *et al.*, 2011).

13X zeolite is one of suitable adsorbents for CO₂ adsorption. Jadhav *et al.* (2007) studied modification of 13X zeolite by monoethanol amine (MEA). 13X zeolite showed high CO₂ adsorption capacities at low temperature and the adsorption capacities decreased at high temperature. In contrast, 13X-MEA-50 zeolite had lower capacities at low temperature and higher adsorption capacities at high temperature. At low temperature, physisorption was dominant and adsorption capacity depended on surface area of adsorbent. As the temperature increased, chemisorption was more dominant than physisorption.

After that, the MEA modified β -zeolite was analyzed (Xu *et al.*, 2009). The zeolite structure did not change after MEA modification. The result showed no increase in the CO₂ capacity of modified β -zeolite at any MEA loading. At the optimal loading, the selectivity was obtained by 7.70 of CO₂/CH₄ and 25.67 of CO₂/N₂.

ACs were also modified by amines. Khalil *et al.* (2012) modified ACs by impregnation with amines. MEA and 2-amino-2-methyl-1-propanol (AMP) were impregnated on the carbon surface resulting in reduced surface area of ACs. The result showed that AMP, MEA-impregnated ACs had higher CO₂ adsorption capacities compared to original ACs. The selectivity was improved by impregnation of MEA and AMP. MEA had better distribution than AMP due to size and shape of molecules.

Polyethyleneimine (PEI) is a very attractive polymer in CO₂ adsorption fields due to high affinity with CO₂. PEI is a polymer, which has many amine sites and contain of primary, secondary and tertiary amine. Amines functional group in backbone could help each other to stabilize CO₂. Because of different amines and large amount of amines, PEI can adsorb CO₂ via different mechanisms and can synergize to enhance CO₂ adsorption performance.

Xu *et al.* (2003) developed the CO₂ molecular basket adsorbent. The molecular basket was prepared by impregnation of PEI on MCM-41. When PEI loading was more than 30%, the molecular basket showed the synergistic effect on CO₂ adsorption. The optimum of PEI loading was 50%, and it showed the highest adsorption capacity of 246 mg/g-PEI. Higher loading of PEI showed better adsorption performance. In case of too high loading of PEI, most of PEI was coated on the external surface. The capacity was slightly greater than bulk-PEI. This work suggested that the presence of OH groups in additive might help to stabilize the formation of carbamate. One amine group could react with one molecule of CO₂ and showed improvement of adsorption performance. The effect of PEI impregnation on MCM-41 resulted in the enhancement of CO₂ selectivity and adsorption performance (Xu *et al.*, 2005).

Son *et al.* (2008) studied on PEI-loading on mesoporous silicas. The CO₂ adsorption capacities of PEI-impregnated mesoporous silicas were in the order

of KIT-6 > SBA-16 \approx SBA-15 > MCM-48 > MCM-41 due to pore size of materials. KIT-6 had the large pore volume and pore size. This led to high loading of PEI in internal surface. Increasing in the temperature, the adsorption capacities increased. At high temperature, PEI became more flexible, and more affinity or active sites appeared to CO₂. According to thermodynamics, too high temperature shifted the equilibrium to reverse direction and decreased adsorption capacity because adsorption was an exothermic process. Effect of CO₂ concentration in the feed was also investigated. Low concentration of CO₂ in the feed showed low adsorption capacities. The presence of water in the feed could enhance the CO₂ adsorption capacities (Xu *et al.*, 2005; Son *et al.*, 2008; Ma *et al.*, 2009).

Ma *et al.* (2009) developed the molecular basket sorbents (MBS) for CO₂ capture and for CO₂ and H₂S separation from flue gas. PEI(50)/SBA-15 or MBS-2 could reach adsorption capacity of 140 mg/g, which was much higher than PEI(50)/MCM-41 or MBS-1, as adsorption capacity of 89.2 mg/g. The SBA-15 impregnated with PEI was studied by Sanz *et al.* (2010). They mentioned that a theoretical calculation of amount of PEI filling in SBA-15 pores is 53.6% PEI. For small PEI loading, the PEI was dispersed on the support surface, and it allowed the accessibility of CO₂ molecules to inner adsorption sites. High loading of PEI produced pore filling effect and high packing factor effect that reduced the accessibility of CO₂ molecules to inner adsorption sites. PEI had tertiary amine groups around 25% and these group could not adsorb CO₂ in the dry feed condition. Linear PEI could achieve better performance in dry feed condition. But using branched PEI required low energy consumption for regeneration step. Raising the temperature promoted higher mobility and accessibility of CO₂. Other explanation was the increase of temperature induced PEI to expand and occupy all available space in pores. PEI modified MCM-41 and MCM-48 were also studied by Sharma *et al.* (2012). The 50 %wt PEI-MCM-48 showed the highest adsorption of 248 mg/g-PEI at 80°C. The synergistic effect was obtained in range of 30-50 %wt PEI loading. The adsorption capacity was enhanced with temperature increases.

Heydari-Gorji and Sayari (2011) investigated PEI-impregnated pore-expanded MCM-41. The optimum loading of PEI was 55% resulted in the highest CO₂ adsorption capacity of 206 mg/g. They suggested the most PEI-impregnated

materials showed the optimum temperature at about 75°C. The high loading of PEI sample showed low CO₂ adsorption capacity at low temperature due to diffusion limitation. Regeneration of adsorbent was complete at 90 to 100°C. At high temperature the kinetics of adsorption became faster and capacity can reach high by less time.

Goeppert *et al.* (2011) simplified the model of reaction between CO₂ and PEI, as seen in Figure 2.21. They used PEI with high molecular weight ($M_w=25000$) to modify fume silica due to its low volatility. In case of dry condition, the capacity of FS-PEI-30 was 52 mg/g and 75 mg/g of FS-PEI-50. In the presence of water, the capacities were 78 mg/g of FS-PEI-30 and 62 mg/g of FS-PEI-50. With a lower loading in PEI, the PEI was better dispersed than high loading and better accessible of CO₂ to amino groups. In case of high PEI loading, water might block the way to reach amino groups. Due to these, low PEI loading had higher capacity than high loading at dry condition.

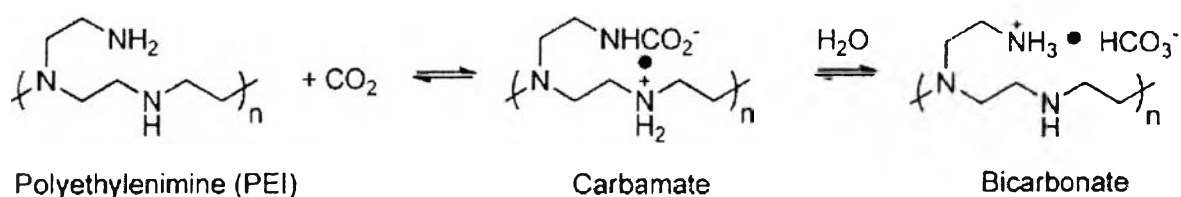


Figure 2.21 Reaction of CO₂ with PEI (Goeppert *et al.*, 2011).

The MCM-41, MCM-48 and SBA-15 modified with PEI was investigated by Sharma *et al.* (2012). The adsorption was an exothermic process, the amount of CO₂ adsorbed on the adsorbent should decrease with the temperature increased. In fact, capacities of the modified adsorbent increased as temperature increased. Most CO₂ adsorption was chemisorption on PEI and physisorption was negligible. In the same year, Gargiulo *et al.* (2012) investigated another mesoporous adsorbent, TUD-1. Capacity increased when temperature increased due to more flexibility of PEI.

Aroua *et al.* (2008) prepared molecular basket with PEI. PEI was a polymer that has good affinity with CO₂. Carbon molecular sieves (CMS) worked by physical mechanism but carbon molecular basket (CMB) worked by chemical

interaction. The capacities of CO₂, O₂, N₂, CH₄ increased with increasing of PEI loading from original ACs to 0.26 wt% PEI/AC. The synergistic effect of PEI impregnated on ACs enhanced the CO₂ adsorption capacity by increasing nitrogen functional group on the surface of ACs. Beyond 0.26 wt% PEI/AC, the capacities decreased because of pore filling effect. Yin *et al.* (2008) investigated impregnation of PEI on ACs. They suggested that PEI that had high molecular weight could diffuse into the micropores of ACs difficult. Figure 2.22 represented impregnation of PEI. For 423-PEI could fill in the micropores resulting in blockage of pores, as seen in Figure 2.22(b). In Figure 2.22(c), 600-, 1200-PEI restrict the macropores resulting in creation of mesopores.

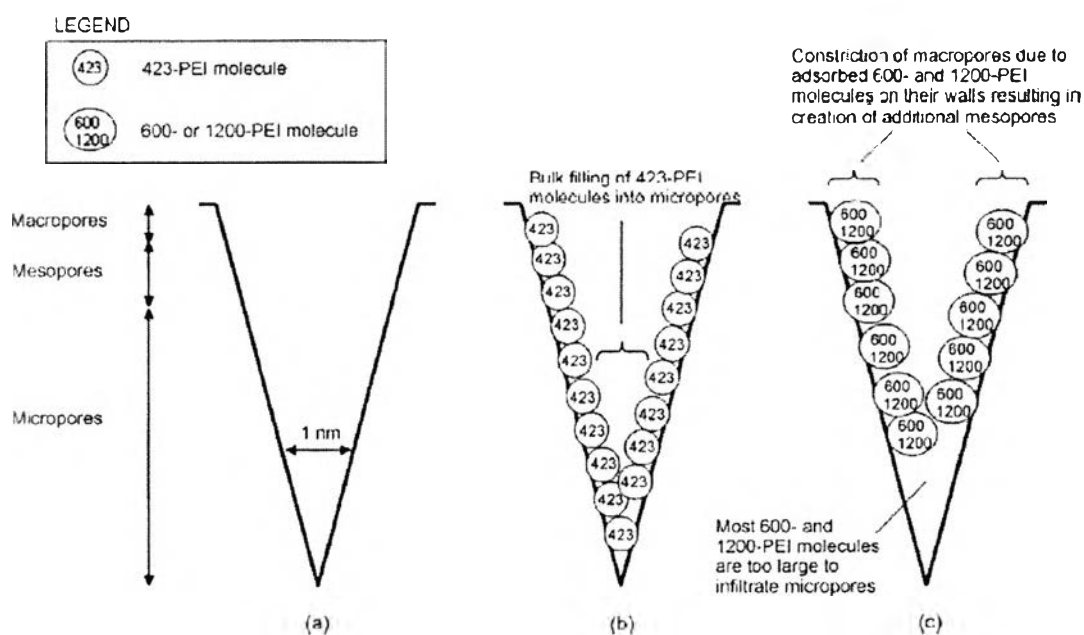


Figure 2.22 Generalized interactions between PEI molecules and textural surface (pores) of ACs (Yin *et al.*, 2008).