



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Greenhouse Gases (GHGs)

GHGs are gases in an atmosphere that absorb and emit radiation within the infrared range. This process is the cause of the greenhouse effect. The primary GHGs in the Earth's atmosphere are water vapor, carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and ozone (O<sub>3</sub>). Greenhouse gases exceedingly affect the Earth's temperature: without the gases, the Earth's surface would be on an average about 33 °C (59 °F) (Pevida *et al.*, 2008).

The main sources of GHGs (en.wikipedia.org):

- Fossil fuels and biomass burning leads to an increase in CO<sub>2</sub> atmospheric concentrations.
- Fermentation, manure, and paddy fields lead to an increase in CH<sub>4</sub> atmospheric concentrations. In addition, vented septic systems that enhance and target the fermentation process are sources of atmospheric methane.
- Use of chlorofluorocarbons (CFCs) in refrigeration systems, and CFCs and halons in fire suppression systems and manufacturing processes lead to an increase in CFCs atmospheric concentrations.
- Agricultural activities, including the use of fertilizers, lead to an increase in N<sub>2</sub>O atmospheric concentrations.

In addition to the main GHGs listed above, other greenhouse gases including sulfur hexafluoride, hydrofluorocarbons, perfluorocarbons, and nitrogen trifluoride have a high global warming potential (GWP) but is only emitted in very small quantities (en.wikipedia.org).

Since the start of the Industrial Revolution, the burning of fossil fuels has contributed to the increase in CO<sub>2</sub> in the Earth's atmosphere. CO<sub>2</sub> emissions result from completed and/or uncompleted combustion. CO<sub>2</sub> is a product of stoichiometric combustion of carbon in the open air. CO<sub>2</sub> emissions are directly proportional to

energy consumption (Arenillas *et al.*, 2005).

### 2.1.1 Carbon Dioxide (CO<sub>2</sub>)

Carbon dioxide (chemical formula CO<sub>2</sub>) is a chemical compound composed of two oxygen atoms formed covalent bonded with a single carbon atom. CO<sub>2</sub> is a gas phase at room temperature and atmospheric pressure and survives in Earth's atmosphere in this state. CO<sub>2</sub> composes of 0.039% of total gas in the atmosphere (en.wikipedia.org). Standard properties of CO<sub>2</sub> are shown in Table 2.1.

**Table 2.1** Properties of CO<sub>2</sub> (en.wikipedia.org)

Properties	
Molecular formula	CO <sub>2</sub>
Molar mass	44.01 g/mol
Exact mass	43.989829244 g/mol
Appearance	Colorless gas
Odor	Odorless
Density	1.562 g/mL (solid at 1 atm and -78.5 °C) 0.770 g/mL (liquid at 56 atm and 20 °C) 1.977 g/L (gas at 1 atm and 0 °C)
Specific gravity	1.53 at 21 °C
Melting point	-78 °C (194.7 K).
Boiling point	-57 °C (216.6 K) at 5.184 bar
Solubility in water	1.45 g/L at 25 °C, 100 kPa
Acidity (pK <sub>a</sub> )	6.35, 10.33
Refractive index (n <sub>D</sub> )	1.1120
Viscosity	0.07 cP at -78 °C

CO<sub>2</sub> is not a liquid phase at pressure below 5.1 atm (520 kPa). At 1 atm, the gas is a solid phase at a temperature below -78 °C (-108 °F; 195.1 K), and the gas will become a complete solid crystal at a temperature above -78 °C. In its

solid phase, CO<sub>2</sub> is commonly called dry ice (Xu *et al.*, 2005). CO<sub>2</sub> is an acidic oxide because an aqueous solution of CO<sub>2</sub> tested with litmus shows color from blue to pink. It is the anhydride of carbonic acid and/or an acid that is unstable in aqueous solution, from which it cannot be concentrated (en.wikipedia.org).

The two main sources of CO<sub>2</sub> emissions are from burning coal used for generating electricity and petroleum used for transportation. Since the beginning of the Industrial Revolution, the concentrations of most GHGs have increased (www.epa.gov). For example, the mole fraction of CO<sub>2</sub> has increased by about 36% to 380 ppm, or 100 ppm over industrial levels. CO<sub>2</sub> is rapidly increased in about 30 years ago (www.eia.gov/environment.html). Table 2.2 shows the seven sources of CO<sub>2</sub> from fossil fuel combustion from 2000 to 2004:

**Table 2.2** Seven sources of CO<sub>2</sub> from fossil fuel combustion in from 2000 to 2004 (www.eia.gov/environment.html)

Seven main fossil fuel combustion sources	Contribution (%)
Liquid fuels (e.g., gasoline, fuel oil)	36
Solid fuels (e.g., coal)	35
Gaseous fuels (e.g., natural gas)	20
Cement production	3
Flaring gas industrially and at wells	< 1
Non-fuel hydrocarbons	< 1
"International bunker fuels" of transport not included in national inventories	4

In 2005, the world's top-20 emitters composed of 80% of total greenhouse gas emissions. Table 2.3 shows the top-5 emitters for the year 2005 (www.eoearth.org). The second column shows the country's share of the global total of annual emissions. The third column shows the country's average annual per capita emissions, in tons of greenhouse gases per person.

**Table 2.3** Top-5 CO<sub>2</sub> emitters for the year 2005 (www.eoearth.org)

Country or region	% of global total annual emissions	Tons of GHG per capita
United States	16	24.1
Indonesia	6	12.9
European Union	11	10.6
China	17	5.8
India	5	2.1

Several methods such as reducing energy consumption by increasing the efficiency of energy conversion, feeding the lean carbon extreme fuels and rich oxygen intense air, and increasing the use of renewable energy are proposed to reduce the amount of CO<sub>2</sub> emission into the atmosphere. However, these options may not be enough to stop global warming, so technologies of CO<sub>2</sub> capture and storage (CCS) have been considered as important optional processes for retarding global warming (Young and Rodrigues, 2008).

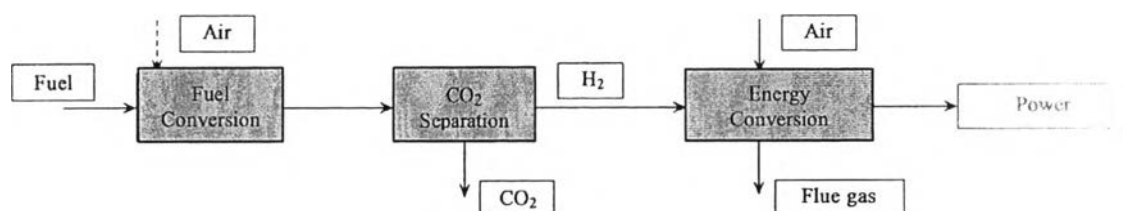
## 2.2 Technologies for CO<sub>2</sub> Capture

For power plants, there are several technologies for CO<sub>2</sub> capture and sequestration processes: pre-combustion (hydrogen) processes, pre-combustion (Oxy-fuel) processes and post-combustion capture of CO<sub>2</sub> processes.

### 2.2.1 Pre-combustion (Hydrogen) Process

The idea behind a pre-combustion (hydrogen) process is to separate carbon from the fuel before the combustion process. This technology provides a CO<sub>2</sub> emission free fuel for the future. The capture process consists of three stages. Firstly, the fossil fuel or coal is converted to CO<sub>2</sub> and H<sub>2</sub> gas. Secondly, CO<sub>2</sub> and H<sub>2</sub> are divided in the same way as a post-combustion process, although a smaller unit can be installed. CO<sub>2</sub> can then be compressed to liquid and transported to a storage site.

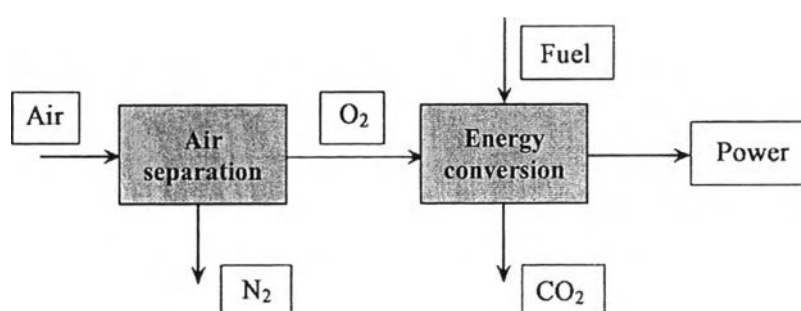
Finally, a hydrogen-rich gas can be used in power plants or as fuel in vehicles. The combustion of  $H_2$  does not lead to any production of  $CO_2$  (www.geos.ed.ac.uk.).



**Figure 2.1** Pre-combustion (hydrogen) process (Young and Rodrigues, 2008).

### 2.2.2 Pre-combustion (Oxy-fuel) Process

In a pre-combustion (Oxy-fuel) process, carbon in the fuel is burned with an oxygen-enriched gas mixture instead of air. This results in a flue gas that mainly comprises  $CO_2$  and  $H_2O$ , as well as a small concentration of impurities such as argon (Ar) and oxygen ( $O_2$ ). This process is represented in Figure 2.2. In this way, the oxy-fuel combustion process provides an opportunity to capture  $CO_2$  by direct physical compression and cooling techniques by various techniques such as low-temperature separation/distillation process (Natural Resources Canada, 2008).

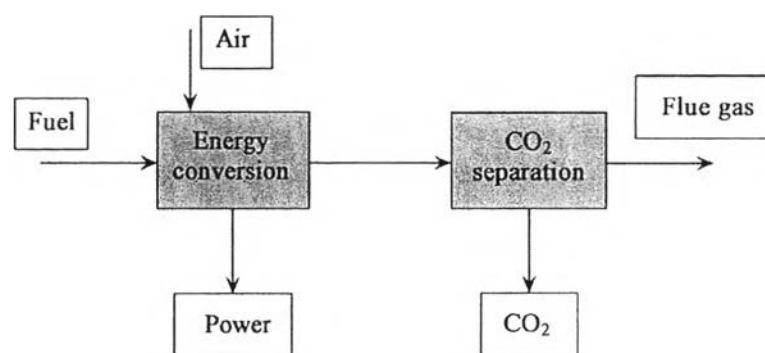


**Figure 2.2** Pre-combustion (oxy-fuel) process (Young and Rodrigues, 2008).

### 2.2.3 Post-combustion Process

For a post-combustion process, carbon in the fuel is separated after the combustion process producing flue gases, which include  $CO_2$ ,  $H_2O$ ,  $SO_2$ , and  $N_2$ .

CO<sub>2</sub> is separated and captured from the flue gas. This process removes CO<sub>2</sub> from natural gas. Post-combustion process shows in Figure 2.3. Production of a relative pure CO<sub>2</sub> stream is an advantage of this technique (Young and Rodrigues, 2008). Several CO<sub>2</sub> capture and separation technologies that can be applied to pre-combustion CO<sub>2</sub> capture including Chemical absorption/adsorption, physical absorption/adsorption, membrane separation, cryogenic fractionation, and etc. (Singh *et al.*, 2009).



**Figure 2.3** Post-combustion process (Young and Rodrigues, 2008).

## 2.3 CO<sub>2</sub> Capture and Separation Methods

There are many technologies for CO<sub>2</sub> capture, but technologies available or being considered for CO<sub>2</sub> capture are:

- Chemical absorption (liquid absorbent)
- Physical absorption/adsorption (PSA, VSA, TSA, ESA, solid absorbents)
- Chemical adsorption (modified solid adsorbents)
- Membrane separation
- Cryogenic fractionation

### 2.3.1 Chemical Absorption

Chemical absorption is one of the most suitable methods for the separation of CO<sub>2</sub> from exhausting gases, when CO<sub>2</sub> has a low concentration (5-

15 vol%) in a gaseous stream at atmospheric pressure. The separation process of CO<sub>2</sub> by chemical absorption consists of two steps:

- The absorption of CO<sub>2</sub> by chemical solvents at a low temperature (40-65 °C).
- The recovery of CO<sub>2</sub> from chemical solvents by using low-grade heat (at temperature in the range of 100-150 °C), usually extracted from power plants.

Chemical solvents associate with acid base neutralization reaction. They can be applied for low to moderate CO<sub>2</sub> partial pressure (3.5 to 21.0 kPa). Several available solvents used commercially are monoethanol amine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) (Blauwhoff *et al.*, 1984, Kohl and Nielsen, 1997; Rinker *et al.*, 2000; Silva and Svendsen, 2003). 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.

### 2.3.2 Physical Absorption/Adsorption

Physical absorption/adsorption is a suitable method for the separation of CO<sub>2</sub> from flue gas. The separation process of CO<sub>2</sub> by physical absorption/adsorption can be achieved through one of the following techniques:

- The gas stream passes through a solid absorbent (e.g. activated carbon and zeolites), and the CO<sub>2</sub> is captured on the surface of the particles by (non-chemical) surface forces. Once collected, the particles are heated, releasing (desorbing) the CO<sub>2</sub> ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).
- Pressure swing adsorption (PSA) is a technology for separating some gas species from a mixture of gases under pressure. It operates at near-ambient temperatures and so diverges from cryogenic gas separation techniques. The special adsorbent

materials (e.g. zeolites, molecular sieve, and etc.) preferentially adsorb the target gas species at high pressure. Finally, the process swings to low pressure to desorb the adsorbent materials ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).

- Vacuum swing adsorption (VSA) is a non-cryogenic gas separation technology with special solids or adsorbents. VSA process separates certain gas species from a gaseous mixture under minimum pressure. The adsorbents (e.g. zeolites and molecular sieve) adsorb the target gas species at near ambient pressure. After reaction, the process swings to a vacuum to regenerate the adsorbent materials ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).
- Temperature swing adsorption (TSA) is a technology for regenerating a bed of adsorbent that is loaded with the targeted impurity gas with raising its temperature. TSA can be cooperated with pressure swing adsorption (PSA) to change a pressure to release adsorbed gas. Finally, TSA process swings temperature to push off the gas adsorption ([www.xebecinc.com](http://www.xebecinc.com)).
- Electric swing adsorption (ESA) is an adsorption cycle with electrothermal desorption step, achieved by direct heating of the adsorbent particles passing electric current through them (Petkovska *et al.*, 2007).

Physical adsorption has not been considered for large-scale CO<sub>2</sub> capture from flue gas because the capacity and CO<sub>2</sub> selectivity of available adsorbents are low. However, these techniques should be enhanced in combination with another capture technology ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).

### 2.3.3 Chemical Adsorption

Chemical adsorption (chemisorption) is an adsorption, which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate in a monolayer on the surface (IUPAC Compendium of Chemical Terminology, 1997).



Chemical adsorption almost uses a solid adsorbent (e.g. activated carbon, zeolites, silica gel, and molecular sieve) or a modified solid adsorbent with acidic or basic passed through the gas stream (fuel gas), and the CO<sub>2</sub> is captured on the surface of the particles by chemical bonding on the surface force. Once collected, the particles are heated, releasing (desorbing) CO<sub>2</sub> by regeneration techniques ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).

Chemical adsorption is considered as one of the potential options to reduce CO<sub>2</sub> emission on an industrial scale because this technique is the development of cost-effective techniques, low energy requirement, ease of applicability over a relatively wide range of temperature and pressure for CO<sub>2</sub> separation and capture (Shafeeyan *et al.*, 2010; Arenillas *et al.*, 2005; Drage *et al.*, 2007).

#### 2.3.4 Membrane Separation

Membrane separation is used to capture CO<sub>2</sub> from both natural gas during the sweetening process and from the flue gases of fossil fuel power plants. Thus far, the technologies for removal of acidic gases from such processes have included selective membrane separation and solvent recovery. Membrane separation is a hybrid process that may lead to lower operational costs and reduced capital expenditure (Simioni *et al.*, 2010).

Porous or semi-porous structure is used in gas separation membranes, through which some chemical species permeate more easily than others, causing one component to pass through the membrane faster than another porous inorganic: palladium membranes, polymeric membranes and zeolites ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)).

Even though membrane separation can be used in various applications, this technique still has some drawback such as high-energy requirement, solvent losses by flooding, amine deactivation, and secondary CO<sub>2</sub> production associated to solvent regeneration by steam (Favre, 2007).

#### 2.3.5 Cryogenic Fractionation

Cryogenic fractionation is a compressing process of the gas stream, and cooling it to a low temperature enough to allow separation by distillation. The resulting liquid CO<sub>2</sub> may then be removed for disposal. This process can be used for

high CO<sub>2</sub> concentrations (typically >90%) but it requires high energy for refrigeration. Some components such as water have to be removed before the gas stream is cooled to avoid blockages ([www.esru.strath.ac.uk](http://www.esru.strath.ac.uk)). These technologies remove CO<sub>2</sub> at near ambient pressures thus requiring substantial amount of compression to levels needed for geo-sequestration (physical and chemical absorption). Cryogenic CO<sub>2</sub> removal methods can capture CO<sub>2</sub> in a liquid form thus making it relatively easy to pump underground for storage or send for enhanced oil recovery (Hart and Gnanendran, 2009).

Hart and Gnanendran (2009) tested the new cryogenic CO<sub>2</sub> removal method for demonstration plant and is soon to be implemented in commercial field applications. They found that the CryoCell® CO<sub>2</sub> removal technology has been successfully demonstrated in a field trial, where the laboratory concepts of cryogenic CO<sub>2</sub> removal from high CO<sub>2</sub> natural gas using solid CO<sub>2</sub> formation have been effectively scaled up into a small field application. The field test program has demonstrated the technical viability of solid phase CO<sub>2</sub> separation and cost comparison studies indicate improved economic viability for high CO<sub>2</sub> gas field developments. They found that using the tuned CryoFlash® models several field application studies have been carried out for potential customers from various part of the world with plant capacities ranging from 50 - 200 mmscf/d of plant feed.

## 2.4 Solid Adsorbents

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm ([en.wikipedia.org](http://en.wikipedia.org)). They must have high surface area, high thermal stability, and small to moderate pore diameters, which result in high surface capacity for adsorption (Guo *et al.*, 2006). The adsorbents must also have a different pore structure that is suitable for fast transport of gaseous vapors ([en.wikipedia.org](http://en.wikipedia.org)). There are many solid adsorbents for CO<sub>2</sub> capture, but adsorbents available or being considered for CO<sub>2</sub> capture are: activated carbon, zeolite molecular sieve, mesoporous silicate, and silica gel

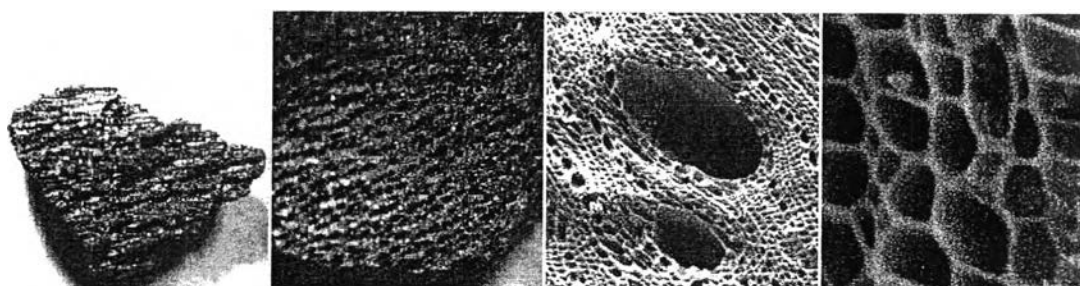
### 2.4.1 Activated Carbon (AC)

Activated carbon (AC), also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus have a very high surface area available for adsorption or chemical reaction. Surface of AC is non-polar; hence, AC shows hydrophobic and organophilic surface (Henning and Degel, 1990). Table 2.4 shows the diameter, pore volume, and surface area of typical AC.

**Table 2.4** Pore sizes in typical activated carbon (Ruthven, 1984)

	Micro-pores	Meso-pores	Macro-pores
<b>Diameter (nm)</b>	< 2	2-50	> 50
<b>Pore volume (cm<sup>3</sup>/g)</b>	0.15-0.5	0.02-0.1	0.2-0.5
<b>Surface area (m<sup>2</sup>/g)</b>	100-1000	10-100	0.5-2

A gram of AC may have a surface area in excess of 400 m<sup>2</sup>, with 1,500 m<sup>2</sup> being achievable (Abdolhosseini *et al.*, 2005). Figure 2.4 shows AC surface and pore enlargement increases from left to right by SEM.



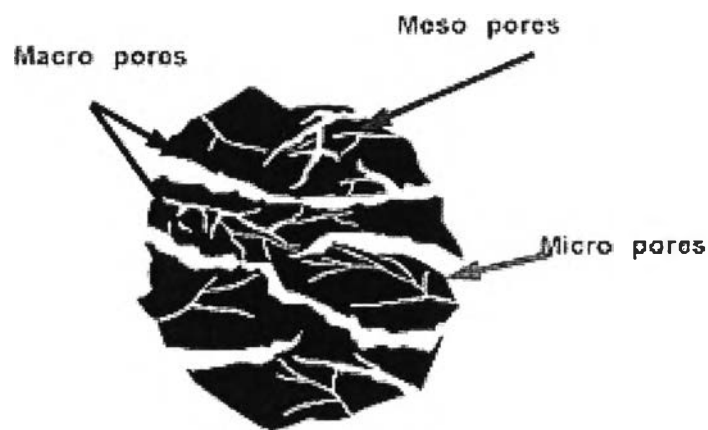
**Figure 2.4** AC surface and pores enlargement increases from left to right by SEM (Kvech and Tull, 1997).

ACs are carbon produced from carbonaceous raw materials such as nutshells, peat, wood, coir, lignite, coal, and petroleum pitch (en.wikipedia.org). ACs are complex materials that are difficult to classify on the basis of their behavior,

surface characteristics and preparation methods (Henning and Degel, 1990). However, they are classified in five classes based on their physical characteristics:

- Powdered activated carbon (PAC)
- Granular activated carbon (EAC)
- Extruded activated carbon (GAC)
- Impregnated carbon
- Polymer coated carbon

Adsorption on AC is considered as one of the potential techniques because of cost advantage, energy requirement, and wide range of temperature and pressure to operation (Arenillas *et al.*, 2005; Drage *et al.*, 2007). Adsorption on AC is also selective, favoring nonpolar over polar substances. Compared with other commercial adsorbents, AC has a broad spectrum of adsorptive activity, excellent physical and chemical stability, and ease of production from readily available materials (Leffel and Abdolhossein, 2005). The adsorption process on AC takes place in three steps: (see Figure 2.5)



**Figure 2.5** AC structure-schematic ([www.afssociety.org](http://www.afssociety.org)).

1. Macro-pore transport: The large macro-pores act as channels for molecules to transfer through the carbon to the meso and micro pores.
2. Meso-pore transport: The medium meso-pores act as channels for adsorption of carbon molecule.

3. Micro-pore transport: The small micro-pores act as channels for large adsorption of carbon molecule (Henning and Degel, 1990).

There are several works focusing on CO<sub>2</sub> adsorption by AC modified with dopants like acidic group, basic group, and neutral. Carabineiro *et al.* (2001) studied the kinetics and conversion of the reaction of CO<sub>2</sub> with AC without catalyst and impregnated with precursor salts of Mg, Ba, Pb, Cu, and Fe, and their binary mixtures in the temperature range of 300 to 900 °C. Binary mixtures of those metals with vanadium oxide were also studied. They found that the CO<sub>2</sub> adsorption amount decreased with increasing temperature. The best additive for CO<sub>2</sub> capture is Fe oxide followed by Mg, V, and Ba oxides with no synergetic effect. The Arrhenius plot for the CO<sub>2</sub> reaction confirmed that the vanadium binary mixtures showed the best oxide synergetic effects and showed high efficiency of CO<sub>2</sub> adsorption. Fe+V showed the best efficiency of CO<sub>2</sub> adsorption (Carabineiro *et al.*, 2003).

Somy *et al.* (2008) studied effects of impregnation of AC with Cr<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> and promoted by Zn<sup>2+</sup> on CO<sub>2</sub> adsorption at ambient temperature and low pressure. They found that Cr<sub>2</sub>O was an effective metal oxide species, which can increase CO<sub>2</sub> adsorption on the impregnated AC. However, the sample impregnated with both Cr<sub>2</sub>O and zinc carbonate hydroxides led to a 25 % increase in the CO<sub>2</sub> capture capacity compared to the raw sample. Fe<sub>2</sub>O<sub>3</sub> was not an effective impregnating species for AC modification because the large molecular size of Fe<sub>2</sub>O<sub>3</sub> may be improper on the AC surface. It may also cause blocking of micro-pores, which can result in the decrease in the adsorption capacity (Somy *et al.*, 2008).

Kim *et al.* (2010) studied effects of copper oxide-loaded porous carbons (Cu<sub>2</sub>O/PCs) and effects of the oxidation degree on the CO<sub>2</sub> adsorption capacity. They prepared Cu<sub>2</sub>O/PC by using a post-oxidation method at 300 °C. The CO<sub>2</sub> adsorption behaviors were evaluated by a PCT (pressure-composition-temperature). They found that the as-received sample had a specific area and micro-pores volume of 2,100 m<sup>2</sup>/g and 1.15 cm<sup>3</sup>/g, respectively, indicating that they were highly micro-pore. However, they decreased after copper electroplating with the neat Cu/PCs sample due to the pore filling or blocking behaviors by the metallic copper particles. The result clearly indicated that metallic copper did not enhance the adsorption or storage of CO<sub>2</sub> on the Cu/PCs samples at room temperature and 1.0

atm because the metal is acidic in nature (electron acceptor). This means that acidic CO<sub>2</sub> can have repulsive forces with the transition metal, resulting in the decrease in the adsorption capacity. In contrast, metal oxides such as copper oxide, calcium oxide, or magnesium oxide have base features, implying that they are electron acceptor friendly.

Furthermore, there are works to study on the use of nitrogen containing groups to modify AC (Aroua *et al.*, 2008; Shafeeyan *et al.*, 2010; Zhang *et al.*, 2010). Aroua *et al.* (2008) investigated the effects of amount of PEI impregnated on AC for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> adsorption capacities (carbon molecular basket, CMB). CMB was produced at PEI weight percentages of 0.06, 0.11, 0.13, 0.26, 0.27, and 0.28 wt%. They found that the enhanced adsorption of CO<sub>2</sub> was attributed to the increase in the nitrogen functional groups on the AC surface as introduced by the impregnation of PEI. This explanation could also be extended for that of CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> as well. The increase in the adsorption capacities of all gases corresponded to the amount of impregnated PEI from virgin AC to 0.26 wt% PEI/AC. The adsorption capacities decreased onwards for 0.27 and 0.28 wt% PEI/AC due to excess constriction of pore size in the CMB rendering reduced accessibility of gas molecules into the inner pores. The amount of PEI impregnation determined for optimum uptake of gas adsorption was 0.26 wt% PEI/AC. The maximum adsorption capacity for the gases follows the sequence: CO<sub>2</sub>  $\gg$  CH<sub>4</sub> > O<sub>2</sub> > N<sub>2</sub> for all the CMB samples.

After that, Shafeeyan *et al.* (2010) studied the development an adsorbent with high adsorption capacity at higher temperatures with added water. Two methods for producing AC with basic surface were considered: ammonia treatment without preliminary oxidation and amination of oxidized samples. In both modification techniques, they found that the presence of nitrogen functionalities on carbon surface generally increased the CO<sub>2</sub> adsorption capacity. The basic nitrogen surface groups, particularly through oxidation followed by amination significantly enhanced the adsorption ability of the carbon adsorbent towards CO<sub>2</sub>, mainly due to the increase in micropore volume and surface basicity. The results indicated that

oxidation followed by high temperature of post-oxidation ammonia treatment (800 °C) considerably enhanced the CO<sub>2</sub> uptake at higher temperature.

Zhang *et al.* (2010) investigated the enhancement of CO<sub>2</sub> adsorption on ACs with high surface area modified by using microwave irradiation under N<sub>2</sub> or H<sub>2</sub> flows and ammonia impregnation at 298 K and 328 K in the pressure range from vacuum to 30.0 bar. Results showed that after surface modification, the contents of elements C and N of the samples increased, while the element O of the samples decreased in comparison with the original AC. Correspondingly, the amounts of the surface basic groups of the modified ACs increased, while those of the surface acidic groups decreased as compared to the original AC. The use of microwave irradiation in an atmosphere of N<sub>2</sub> to modify the carbon can increase the total basic groups of the ACs surface. It was found that the more the total basic groups on the surfaces of the modified AC, the higher its adsorption capacity of CO<sub>2</sub>. In addition, the amounts of CO<sub>2</sub> adsorption on all the samples decreased with increasing temperature, and the higher the temperature, the larger the amounts of CO<sub>2</sub> adsorption. It was observed that the modified AC samples had higher CO<sub>2</sub> adsorption capacities than the original AC. And the more the surface basic groups of the AC showed the higher the adsorption capacity of the AC for CO<sub>2</sub>. The amount of CO<sub>2</sub> adsorption on the modified AC by the microwave irradiation in the atmosphere of N<sub>2</sub> was up to 3.75 mmol/g at 1 atm and 293 K, having an increase of 28 % in comparison with the original AC (Zhang *et al.*, 2010).

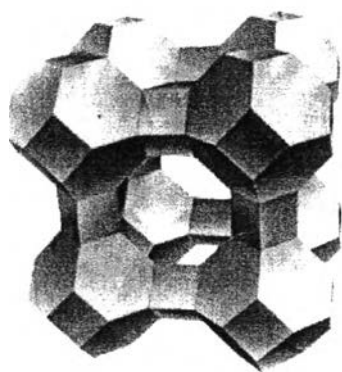
For the industrial scale, the regeneration process has to be considered. The regenerated ability is approximated to 70 % of the original carbon. The re-activated carbon is then mixed with a portion of new AC for higher efficiency and is then returned to its place in the plant process (Clark, 1989). Table 2.5 represents reactivation process of AC at different stages.

**Table 2.5** Reactivation process of AC at different stages (Clark, 1989)

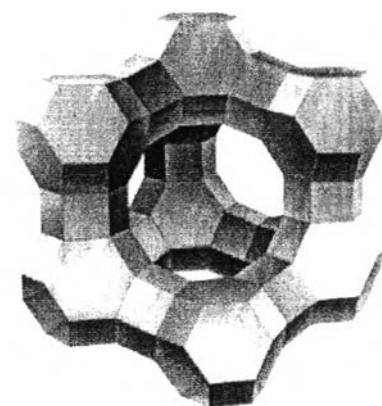
Stage	Temperature (°C)	Action
Drying	< 100	GAC dewatered to 50% of original weight
Desorption	100 - 649	Volatile materials driven off
Pyrolysis	100 - 649	Heavy organics burnt leaving residue
Gasification	>>649 and >>1038	Vapors and residues from previous stages driven out of pore

#### 2.4.2 Zeolite Molecular Sieve

A zeolite is a 3-dimensional microporous crystalline solid with structures. They generally contain silicon, aluminium, and oxygen in their framework and cations, water and/or other molecules within their pores (www.bza.org). The corresponding crystallographic structure is formed by tetrahedras of (AlO<sub>4</sub>) and (SiO<sub>4</sub>). These tetrahedras are the basic building blocks for various zeolite structures, such as zeolites A and X, the most common commercial adsorbents (www.molecularsieve.org). They are often also referred to as *zeolite molecular sieves*. Figure 2.6 shows two types of zeolite molecular sieves.



Zeolite molecular sieve type A



Zeolite molecular sieve type X

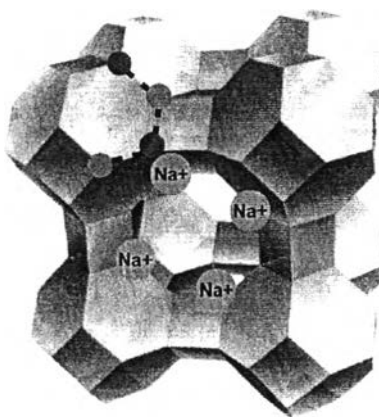
**Figure 2.6** Zeolite molecular sieve structure-schematic (www.molecularsieve.org).

Zeolite molecular sieves have a porous structure that can adjust several types of cations, such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and others. These positive ions



are active and can exchange readily with the others in a contact solution (en.wikipedia.org). Figure 2.7 shows a structure of zeolite referred to molecular sieve type A.

Zeolite molecular sieves are commonly used as commercial adsorbents in processes with a worldwide market of several million tonnes per annum. Major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry, and construction (Bell, 2001).



**Figure 2.7** Zeolite structure-schematic (www.molecularsieve.org).

Methods for regeneration of zeolite molecular sieves include pressure change (as in O<sub>2</sub> concentrators), heating and purging with a carrier gas (as when used in ethanol dehydration), or heating under high vacuum. Temperatures typically used to regenerate water-adsorbed molecular sieves range from 130 °C to 250 °C (www.desiccantpacks.net).

To enhance the CO<sub>2</sub> adsorption capacity, there are many works that focus on zeolites modified with nitrogen containing groups. Jadhav *et al.* (2007) studied the adsorption of zeolite 13X modified with monoethanolamine (MEA) by impregnation method. MEA loadings ranged from 0.5–25 wt% CO<sub>2</sub> adsorption capacity of adsorbents was evaluated by using the breakthrough adsorption method in the temperature range between 30 and 120 °C. They found that a small MEA loading (0.5 wt%) has CO<sub>2</sub> adsorption capacity almost unchanged at 30 °C. For the

much higher loading (25 wt%), the capacity decreased to 17.5 mL/g due to the limited access to adsorption sites for CO<sub>2</sub>. 13X-MEA-10 (10 wt%) gave the highest capacity of 44 mL/g compared with 28 mL/g of unmodified zeolite 13X. They also explained that at the room temperature, where adsorption is mostly physical in nature, higher surface area and pore volume are very important. 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%. They explained that at 120 °C, the combined adsorption-absorption played roles in the sorption of CO<sub>2</sub> wherein the MEA molecules in the pore of the zeolite functions as a solvent contained in a reactor providing better contact between CO<sub>2</sub> and MEA. They also compared the CO<sub>2</sub> adsorption capacities at different temperatures and found that the adsorption capacity of the modified zeolite with the 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 chemisorption acts as an activated process.

Xu *et al.* (2008) investigated a new type of composite adsorbents synthesized by incorporating MEA into  $\beta$ -zeolite. The adsorption capacity for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> on  $\beta$ -zeolite with different amine loadings was examined at 303 K. The comparison of adsorption performance of MEA- $\beta$ -zeolite with other adsorbents was also conducted. The results showed that the structure of zeolite was well preserved after MEA modification. Compared with CH<sub>4</sub> and N<sub>2</sub>, CO<sub>2</sub> was preferentially adsorbed on the investigated adsorbents. The introduction of MEA significantly improved the selectivity of both CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub>, the optimal selectivity of CO<sub>2</sub>/CH<sub>4</sub> can reach as high as 7.70 on 40 wt% of MEA-functionalized  $\beta$ -zeolite (MEA(40)- $\beta$ ) at 1 atm and 303 K. Steric effect and chemical adsorbate-adsorbent interaction were responsible for such high adsorption selectivity of CO<sub>2</sub>.

### 2.4.3 Mesoporous Silicates

Mesoporous silicates are silicates with a special morphology. They are porous inorganic solids that found great utility as catalysts and sorption media because of their large internal surface area. One of the well-developed mesoporous

materials is silica because it is chemical inert, thermal stability, harmless, and inexpensive (Nandiyanto *et al.*, 2008).

In 1992, scientists at the Mobil Corporation discovered highly ordered mesoporous silica materials. These materials contain uniform cylindrical pores with a diameter in a large pore size ( $2 \text{ nm} \leq \text{size} \leq 20 \text{ nm}$ ) and ordered arrays of cylindrical meso-pores with very regular pore morphology. The surface area of these materials is between  $700 \text{ m}^2/\text{g}$  and  $1,500 \text{ m}^2/\text{g}$ . The large surface areas of these solids increase the probability that a reactant molecule in solution will come into contact with the catalyst surface and react. The large pore size and ordered pore morphology allow one to be sure that the reactant molecules are small enough to diffuse into the pores. MCM-41 (Mobile Crystalline of Materials), which contains micrometer-sized particles with hexagonally ordered meso-pore was the first reported by Mobil researchers (Trewyn *et al.*, 2007).

To enhance the  $\text{CO}_2$  capacity, there are several works that focused on modified mesoporous silica with amine groups. Xu *et al.* (2005) investigated effects of MCM-41 modified with PEI (MCM-41/PEI or MBS-1) for  $\text{CO}_2$  adsorption from flue gas of a natural gas-fired boiler ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{N}_2$ , and  $\text{O}_2$ ). They found that the adsorbent adsorbed very little  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CO}$ . The adsorbent simultaneously adsorbed  $\text{CO}_2$  and  $\text{NO}_x$ . However,  $\text{CO}_2$  was more selectively separated from the flue gas than  $\text{NO}_x$  around 3,000 times. Furthermore, they studied effects of promoting moisture on the adsorption separation of  $\text{CO}_2$  from flue gas. They found that the moisture helps “molecular basket” enhance adsorbent more effectively adsorbed  $\text{CO}_2$ .

After that, Ma *et al.* (2009) developed a new generation of “molecular basket” sorbents (SBA-15/PEI or MBS-2) by the optimum combination of the nanoporous material and  $\text{CO}_2/\text{H}_2\text{S}$ -philic polymer sorbent to increase the  $\text{CO}_2$  and  $\text{H}_2\text{S}$  adsorption capacity from flue gas, synthesis gas, reformat, natural gas, coal/biomass gasification gas, and biogas. The sorption of  $\text{CO}_2$  on MBS-2 at  $75 \text{ }^\circ\text{C}$  was the highest, as also observed for MBS-1. They found that MBS-2 gave a sorption capacity of  $140 \text{ mg of CO}_2/\text{g}$  at  $75 \text{ }^\circ\text{C}$  under partial pressure of  $15 \text{ kPa}$ . This capacity value is about 50 % higher than that of MBS-1 at the same loading amount of PEI, more than 100 % higher than the saturation absorption capacity of the 15

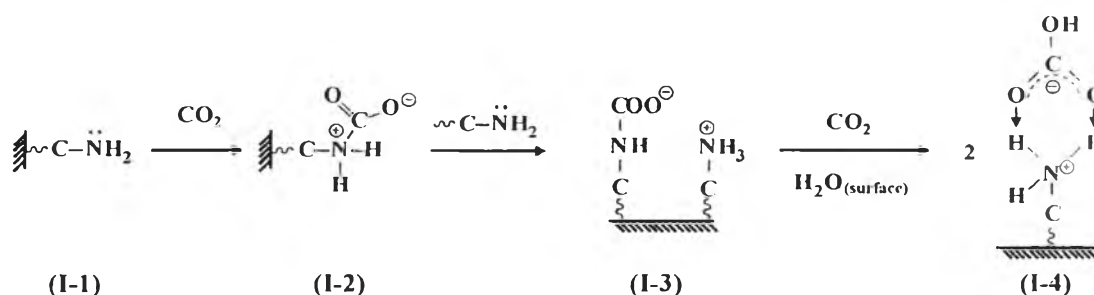
wt% MEA aqueous solution (Austgen and Rochelle, 1991) and 30 wt% DEA aqueous solution (Rebolledo-Libreros and Trejo, 2004), and more than 300 % higher than the saturation absorption capacity of the 47 wt% MDEA aqueous solution (Sidi-Boumedine *et al.*, 2004) at the same partial pressure. The capacity of MBS-2 is higher than that of the hyperbranched aminosilica sorbent (SBA-HA) (Hicks *et al.*, 2008). SBA-15 as a support improved the sorption capacity of CO<sub>2</sub> more significantly than that of H<sub>2</sub>S, indicating that the diffusion barrier of CO<sub>2</sub> in bulk of PEI held in the pores may be higher than that of H<sub>2</sub>S. This sorbent not only processes a high sorption capacity and high selectivity but also has excellent regenerability and stability in the sorption-desorption cycles. By comparing the difference in the physical properties between the two support materials, a much higher capacity of MBS-2 than MBS-1 may be ascribed to two factors of the support materials: (1) the pore diameter of SBA-15 is approximately twice that of MCM-41, and (2) the pore volume of SBA-15 (1.31 cm<sup>3</sup>/g) is higher than that of MCM-41 (1.15 cm<sup>3</sup>/g) by 14 %, which allows the MBS-2 prepared from SBA-15 to have a higher surface area than that from MCM-41 after the same PEI loading (50 wt%). Both higher surface area and larger pore diameter of SBA-15 may significantly increase the total number of the accessible sorption sites in MBS-2 and thus enhance the CO<sub>2</sub> mass transfer in the sorption process. The moisture effect on the sorption capacity of MBS-2 for CO<sub>2</sub> was examined by adding 3.0 vol% of H<sub>2</sub>O into the flue gas. The presence of moisture increased the saturation capacity of MBS-2 for CO<sub>2</sub> sorption by 35 %, which is consistent with the work on MBS-1 (Xu *et al.*, 2005).

Zelenak *et al.* (2008) studied effects of SBA-12 modified with 3-aminopropyl (AP), 3-(methylamino) propyl (MAP), and 3-(phynylamino) propyl (PAP) using thermal gravimetric analysis to evaluate the adsorption capacity. CO<sub>2</sub> sorption/desorption was performed at 25 °C. The results showed that CO<sub>2</sub> 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 CO<sub>2</sub>. 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 that may result in lower sorption capacity.

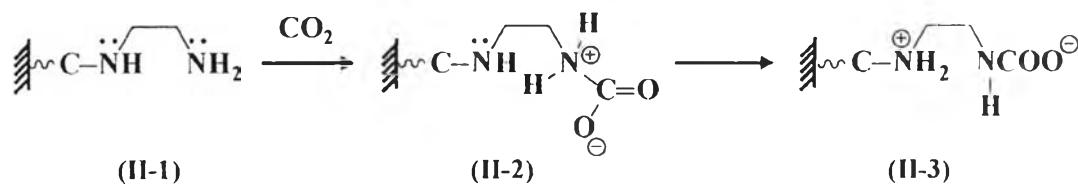
Chang *et al.* (2009) investigated effects of modified mesoporous silicates including MCM-41, SBA-15, and pore-expanded MCM-41 with pore size in a range of 2–17 nm by mono-, di-, and tri-aminosilanes. The result showed that the amine-grafted SBA-15 gave the highest CO<sub>2</sub> adsorption capacities ranging from 1.06 mmol/g to 2.41 mmol/g under an anhydrous gas stream with 15 % CO<sub>2</sub> and ranging from 1.02 mmol/g to 2.72 mmol/g under a gas stream with 15 % CO<sub>2</sub> and a RH of 78 % at 60 °C. They also found that the CO<sub>2</sub> 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 CO<sub>2</sub> can further react with CO<sub>2</sub> and water to form bicarbonate or amine group can directly react with CO<sub>2</sub> and water. The overall reaction of CO<sub>2</sub> and amines is divided into two steps: the formation of carbon dioxide-amines zwitterion and amine or H<sub>2</sub>O deprotonation of this zwitterion:



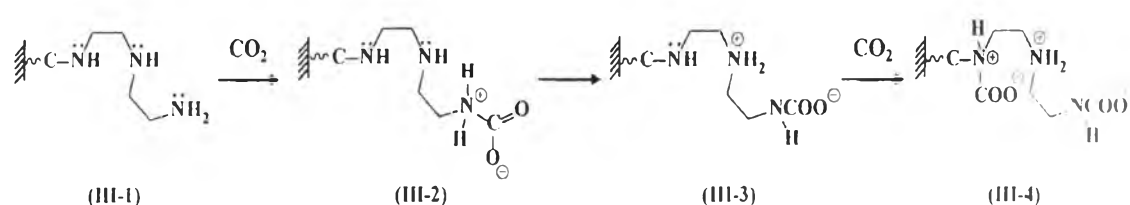
where RNHCOOH and RNHCOO<sup>-</sup>RNH<sub>3</sub><sup>+</sup> are carbamic acid and ammonium carbamate salt, respectively. Figures 2.8, 2.9, and 2.10 represent CO<sub>2</sub> reaction pathway with monoamine, di-amine, and tri-amine-grafted on mesoporous silica.



**Figure 2.8** CO<sub>2</sub> reaction pathways with monoamine-grafted on mesoporous silicates (Chang *et al.*, 2009).



**Figure 2.9** CO<sub>2</sub> reaction pathways with di-amine-grafted on mesoporous silicates (Chang *et al.*, 2009).



**Figure 2.10** CO<sub>2</sub> reaction pathways with tri-amine-grafted on mesoporous silica (Chang *et al.*, 2009).

#### 2.4.4 Silica Gel

A silica gel is a granular, vitreous, highly porous form of silica made synthetically from sodium silicate. Despite its name, silica gel is a solid. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. As a desiccant, it has an average pore size of 2.4 nm and has a strong affinity for water molecules (en.wikipedia.org). Table 2.6 shows the properties of commercial silica gel.

**Table 2.6** Properties of commercial silica gel (Ruthven, 1984)

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

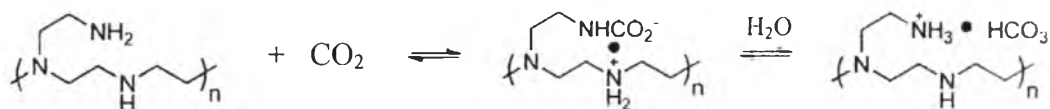
Silica gel's high surface area (around 800 m<sup>2</sup>/g) allows it to absorb water readily, making it useful as a desiccant (drying agent). Once saturated with water, the gel can be regenerated by heating it to 120 °C (250 °F) for two hrs. (en.wikipedia.org). Some types of silica gel will "pop" when exposed to enough water. Silica gel prepares from the solution of sodium silicate that is acidified to produce a gelatinous precipitation, and then dehydrated to produce colorless silica gel.

The main objective of this thesis is how activated carbon should be modified to enhance surface basicity for CO<sub>2</sub> adsorption.

## 2.5 Basic Surfaces

Primary and secondary amines in aqueous solution such as mono- and di-ethanolamine are used on a large scale to capture CO<sub>2</sub> from industrial streams due to their ability to chemisorb acidic gases like CO<sub>2</sub>. These amines are also more suitable for the capture of CO<sub>2</sub> from gas mixtures, which are practically oxygen free or contain a low concentration of oxygen since these groups of amines tend to degrade over time.

To lower the energy cost, polyamines deposited on solid supports have been proposed as an alternative to aqueous solutions. Polyethylenimines (PEIs) in particular have attracted much attention. The reaction of PEI with CO<sub>2</sub> is represented in Figure 2.11.



**Figure 2.11** Reaction of CO<sub>2</sub> with PEI.

The repeating unit of the polymer in this figure is only a simplified model representation showing the three different types of amines present in PEI. The primary and secondary amino groups in PEI react with CO<sub>2</sub> to form carbamates. In the presence of water these carbamates can react further to form a bicarbonate species (Goepfert *et al.*, 2011).