



## A Review of CO<sub>2</sub> Capture by Absorption and Adsorption

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### ABSTRACT

Global warming resulting from the emission of greenhouse gases, especially CO<sub>2</sub>, has become a widespread concern in the recent years. Though various CO<sub>2</sub> capture technologies have been proposed, chemical absorption and adsorption are currently believed to be the most suitable ones for post-combustion power plants. The operation of the chemical absorption process is reviewed in this work, together with the use of absorbents, such as the ionic liquid, alkanolamines and their blended aqueous solutions. The major concerns for this technology, including CO<sub>2</sub> capture efficiency, absorption rate, energy required in regeneration, and volume of absorber, are addressed. For adsorption, in addition to physical adsorbents, various mesoporous solid adsorbents impregnated with polyamines and grafted with aminosilanes are reviewed in this work. The major concerns for selection of adsorbent, including cost, adsorption rate, CO<sub>2</sub> adsorption capacity, and thermal stability, are compared and discussed. More effective and less energy-consuming regeneration techniques for CO<sub>2</sub>-loaded adsorbents are also proposed. Future works for both absorption and adsorption are suggested.

**Keywords:** CO<sub>2</sub> capture; Absorption; Rotating packed bed; Adsorption; Amine-based adsorbents.

### INTRODUCTION

Global warming resulted from the emission of greenhouse gases has received widespread attention. Among the greenhouse gases, CO<sub>2</sub> contributes more than 60% to global warming because of its huge emission amount (Albo *et al.*, 2010). The CO<sub>2</sub> concentration in atmosphere now is closed to 400 ppm which is significantly higher than the pre-industrial level of about 300 ppm (Oh, 2010). To mitigate global warming, Kyoto Protocol urges 37 industrialized nations and European Union to reduce their greenhouse gas emissions to a level of 5.2% on average lower than those of 1990 during the period of 2008 to 2012. Copenhagen Accord also requests the global temperature increase be limited to 2°C above the pre-industrial level by 2100. International Energy Agency (IEA) pointed out to achieve the ± 2°C goal, CO<sub>2</sub> capture and storage (CCS) technology is required and the contribution would be 19% in 2050. It is therefore essential to develop the CCS technologies to cope with the global demand of CO<sub>2</sub> reduction.

Though various CO<sub>2</sub> capture technologies including physical absorption (Little *et al.*, 1991; Chiesa and Consolmi, 1999), chemical absorption (Bishnoi and Rochelle, 2000; Aroonwilas and Veawab, 2004; Rochelle, 2009),

adsorption (Harlick and Tezel, 2004; Chang *et al.*, 2009a), and membrane (Powell and Qiao, 2006) exist, they are not matured yet for post-combustion power plants. This is because that huge amount of flue gas is needed to treat and significant mass transfer limitations exist in the processes.

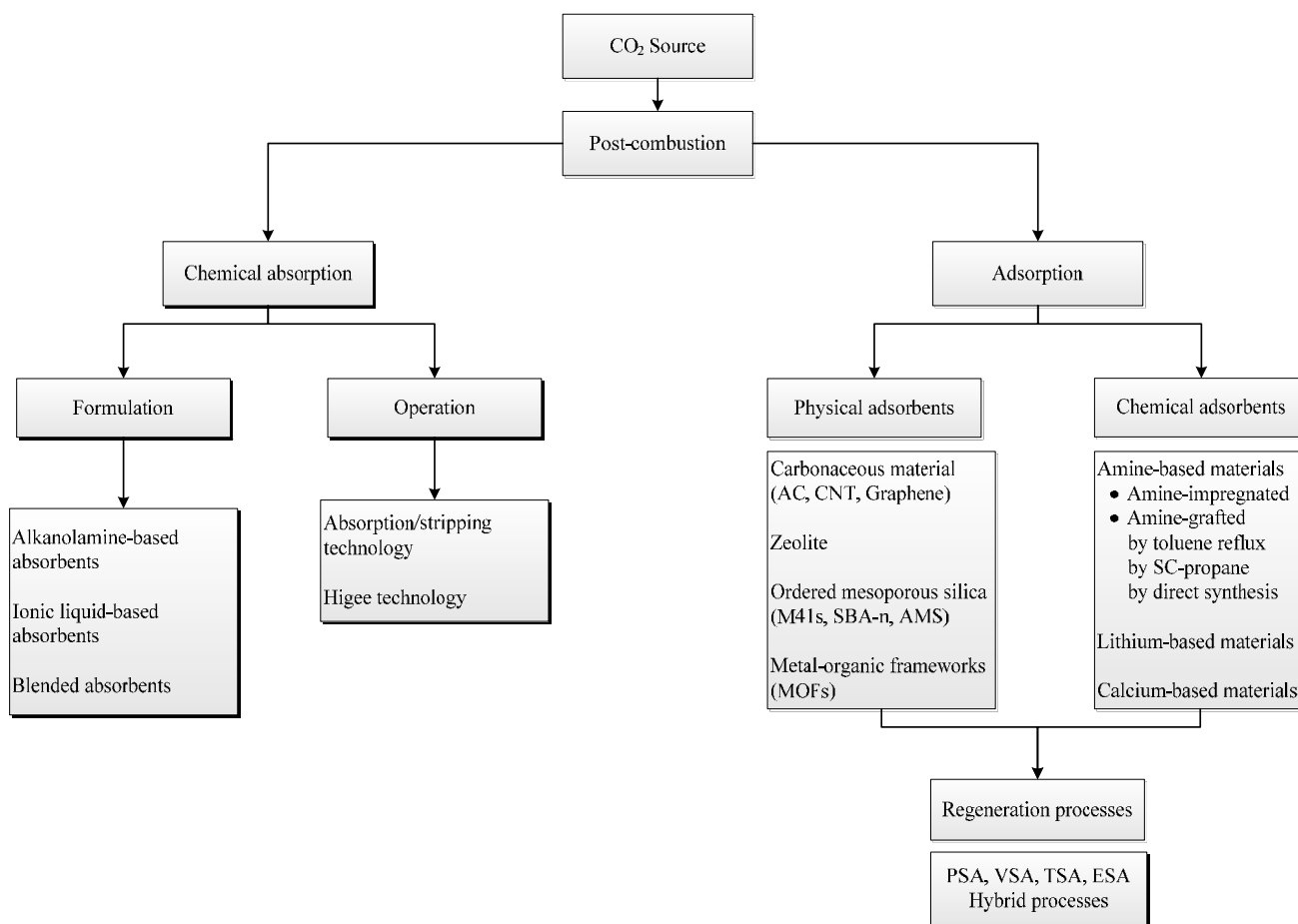
Among these technologies, chemical absorption using aqueous alkanolamine solutions is proposed to be the most applicable technology for CO<sub>2</sub> capture before 2030 (Rochelle, 2009). However, the alkanolamine aqueous solutions possess some drawbacks such as high equipment corrosion rate, high energy consumption in regeneration, and a large absorber volume required. As a result, solid adsorption processes are suggested and studied to overcome those inherent problems in chemical absorption. Impregnation or grafting of amines has been proposed to enhance the originally limited adsorption capacity and to promote the mass transfer rate of CO<sub>2</sub> into porous, or mesoporous adsorbents. The objectives of this paper is to review the technologies including chemical absorption and mesoporous adsorbents impregnated or grafted with amines for CO<sub>2</sub> capture for post-combustion power plants and regeneration processes concerning energy consumption. A schematic flow diagram (Fig. 1) is also depicted to demonstrate the CO<sub>2</sub> capture by absorption and adsorption.

### CO<sub>2</sub> CAPTURE BY ABSORPTION

#### *Physical Absorption*

The operation of physical absorption is based on Henry's Law. CO<sub>2</sub> is absorbed under a high pressure and a low

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**Fig. 1.** Flow diagram for CO<sub>2</sub> capture by absorption and adsorption.

temperature, and desorbed at reduced pressure and increased temperature. This technology has been widely applied to many industrial processes including nature gas, synthesis gas and hydrogen production with high CO<sub>2</sub> contents (Olajire, 2010). There are many existing commercial processes such as Selexol Process, Rectisol Process, Purisol Process, Morphysorb Process, and Fluor process. The absorbents are dimethylether or propylene glycol for Selexol Process, methanol for Rectisol Process, N-methylpyrrolidone for Purisol Process, morpholine for Morphysorb Process and propylene carbonate for Fluor Process. Selexol process can be applied to remove both CO<sub>2</sub> and H<sub>2</sub>S under a low temperature operation and to regenerate absorbent by decreasing pressure or stripping (Olajire, 2010). The advantages of this process are low vapor pressure, low toxicity and less corrosive solvent. Rectisol process is favored when dealing with the exhausted gas containing sulfur. The advantages include less corrosive and more stable absorbent. The advantage of Purisol process is its low energy consumption. Morphysorb process is a relatively new process. The operation cost is 30% to 40% lower than that for Selexol process (Kohl, 1997; Gielen, 2003). Fluor process is more suitable for gases containing CO<sub>2</sub> partial pressures higher than 60 psig. The solubility of CO<sub>2</sub> in the solvent is high in this process (Simmonds and Hurst, 2004).

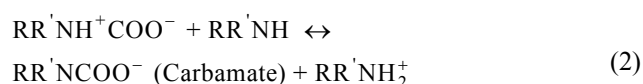
### **Chemical Absorption - Amine Absorption/Stripping Technology**

A typical chemical absorption process consists of an absorber and a stripper in which absorbent is thermally regenerated. In a chemical absorption process, the flue gas containing CO<sub>2</sub> enters a packed bed absorber from the bottom and contacts counter-currently with a CO<sub>2</sub>-lean absorbent, after absorption, the CO<sub>2</sub>-rich absorbent flows into a stripper for thermal regeneration. After regeneration, the CO<sub>2</sub>-lean absorbent is pumped back to the absorber for cyclic use. The pure CO<sub>2</sub> released from the stripper is compressed for the subsequent transportation and storage. The operation pressure is around 1.0 bar and the temperatures in the absorber and stripper are generally in the ranges of 40–60°C and 120–140°C, respectively. The theoretically minimum energy required for recovery of CO<sub>2</sub> from a flue gas and compression of CO<sub>2</sub> to 150 bar is 0.396 GJ/tonne CO<sub>2</sub>. For a practical operation, an energy of 0.72 GJ/tonne CO<sub>2</sub> is hopefully to be achieved (Rochelle, 2009). According to the US DOE CO<sub>2</sub> capture goal, a 90% CO<sub>2</sub> capture efficiency with a less than 35% increase in cost is needed to achieve for post-combustion (DOE, 2010), therefore the improvements on absorbent efficiency, absorption operation, and thermal regeneration are needed to achieve.

The advantage of a chemical absorption technology is that it is the most matured technology for CO<sub>2</sub> capture and

it has been commercialized for many decades, though not for CO<sub>2</sub> capture from power plants. Another advantage of this technology is that it is suitable for retrofitting of the existing power plants. However, this technology exists several drawbacks including (1) low CO<sub>2</sub> loading capacity; (2) high equipment corrosion rate; (3) amine degradation by SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>2</sub> in the flue gases which induces a high absorbent makeup rate; (4) high energy consumption during high temperature absorbent regeneration; (5) large equipment size (Resnik, 2004 and Haszeldine, 2009). The possible remedies to these drawbacks include the improvement of absorbents and operations as addressed below.

Alkanolamines are widely used as the absorbents for CO<sub>2</sub> capture. The structures of alkanolamines include primary, secondary, ternary amines containing at least one OH and amine group such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). The reactivity of amines to CO<sub>2</sub> follows the order primary, secondary and ternary amines, for example, the reaction constants with CO<sub>2</sub> are 7,000, 1,200 and 3.5 m<sup>3</sup>/s/kmol for MEA, DEA and MDEA at 25°C, respectively (Sada *et al.*, 1976; Hikita *et al.*, 1979; Bishnoi and Rochelle, 2002). On the contrary, the CO<sub>2</sub> loading capacity for ternary amine is 1.0 mole of CO<sub>2</sub> per mole of amine, higher than those of primary and secondary amines where the CO<sub>2</sub> loading capacity lies between 0.5–1.0 mole of CO<sub>2</sub> per mole of amine, as can be seen from the following equations,



The overall reaction is



The reaction of primary and secondary amine with CO<sub>2</sub> is to form zwitterion first and then to form carbamate. The reaction of a ternary amine with CO<sub>2</sub> is to form bicarbonate but not to form carbamate (Bishnoi and Rochelle, 2000; Xiao *et al.*, 2000; Liao and Li, 2002).



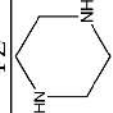
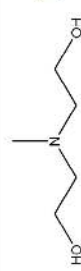


Because of various properties and advantages of various amines, mixed amines have been proposed to enhance CO<sub>2</sub> capture efficiency and to reduce regeneration cost. In addition to the primary, secondary and ternary amines, the steric hindrance amines such as 2-amino-2-methyl-1-propanol (AMP) were also proposed to use. This is because that the steric character reduces the stability of the formed carbamate, thus carbamate can undergo hydrolysis to form bicarbonate and in the meanwhile, release free amine molecules for further reaction with CO<sub>2</sub> and consequently enhance the CO<sub>2</sub> equilibrium loading capacity to 1.0 mol of CO<sub>2</sub> per mol of amine, as high as that of ternary amine. Piperazine (PZ) is a cyclic diamine which has been used as the promoter for

CO<sub>2</sub> capture because of its rapid formation of carbamate with CO<sub>2</sub> (Freeman *et al.*, 2010). As being a great CO<sub>2</sub> capture promoter, the thermodynamic properties of PZ such as CO<sub>2</sub> solubility, volatility, and heat capacity have been reported in the literature (Ermatchkov *et al.*, 2006; Dugas and Rochelle, 2009; Nguyen *et al.*, 2010) and are listed in Table 1. In a recent report by Freeman *et al.* (2010), PZ is observed to be an effective resistant to oxygen degradation and thermal degradation to a temperature up to 150°C. Therefore, a concentrated aqueous PZ solution is suggested by these authors. However, the solubility of PZ in water is limited, for example, the solubility is 14 wt% at 20°C, CO<sub>2</sub> capture by a high PZ content solution is therefore needed to carry out at high temperatures.

The degradation of alkanolamine is an important issue in chemical absorption processes because it causes economic, operational, and environmental problems. As for a commonly used absorbent, for example, MEA, the degradation would cause the replacement of ~2.2 kg MEA for capturing one tonne of CO<sub>2</sub>, leading to an increase of operation cost (Arnold *et al.*, 1982). Degradation can generally be classified into three types, thermal degradation, carbamate polymerization, and oxidative degradation (Goff and Rochelle, 2006). Thermal degradation requires the operation at high temperatures, generally above 200°C. This kind of degradation does not occur for dealing with the power plant exhausted gases because the operation temperature in thermal regeneration is not at high. Oxidative degradation is mainly resulted from the dissolved oxygen (DO) in absorbent. Hence this type of degradation often occurs in CO<sub>2</sub> capture from the flue gases containing high O<sub>2</sub> content such as 5% (Chakravarti *et al.*, 2001). Goff and Rochelle (2004) observed the degradation of MEA by DO belonged to a mass transfer control instead of the reaction control. The degradation products of MEA are mainly formate, hydroxyethyl formamide, hydroxyethyl imidazole and oxalate, glycolat and acetate are also present, however, are in low concentrations (Sexton and Rochelle, 2011). To reduce DO in absorbent, four methods including the addition of O<sub>2</sub> scavenger, reaction inhibitor, chelating agents, and strong stable salts have been proposed. Three additives, Inhibitor A (an inorganic compound), Na<sub>2</sub>SO<sub>3</sub>, and formaldehyde have been suggested (Goff and Rochelle, 2006). Carbamate polymerization requires the presence of amine at high temperatures so that it typically occurs in the stripper during the thermal regeneration. The detailed mechanism for thermal degradation of MEA by carbamate polymerization can be found elsewhere (Davis and Rochelle, 2009).

The amine absorption/stripping technology is an energy intensive process and the overall cost of a CO<sub>2</sub> capture process is 52–77 US\$/tonne CO<sub>2</sub> (Rochelle, 2009). The regeneration energy for CO<sub>2</sub> capture from a conventional coal-fired power plant lies from 3.24 to 4.2 GJ/tonne CO<sub>2</sub> (International Energy Agency, 2004). In this process, most energy consumption comes from the solvent regeneration step, occupying about 60% of the required energy. One of the means to reduce regeneration energy is to improve the operation in a stripper. Tobiesen and Svendsen (2006)

Table 1. Physical and chemical properties of the common used absorbents.

Property	MEA	AEEA	PZ	MDEA	NaOH	AMP	DETA
Molecular structure					$\text{Na}^+ \text{OH}^-$		
MW (g/mol)	61.08	104.15	86.14	119.16	40	89.14	103.17
Density (g/cm <sup>3</sup> ) (293K)	1.012	1.029	1.1	1.038	1.515	0.934	0.955
Boiling point (K)	443	513	420	243	1390	438	207
Vapor pressure (293K) (kPa)	0.0085	0.00015	0.1066	0.0013	0.4	0.1347	0.02
Vapor pressure (393K) (kPa)	15.9	0.969	41.66				
Solubility (293K)	Freely soluble	Freely soluble	14 wt%	Freely soluble	Freely soluble	Freely soluble	Freely soluble
Pseudo first order rate constant at 298 K (m <sup>3</sup> /kmol/s)	7,000 Hikita <i>et al.</i> , 1979	12,100 Mamun <i>et al.</i> , 2007	53,700 Bishnoi and Rochelle, 2000	3.5 Bishnoi and Rochelle, 2002		681 Xiao <i>et al.</i> , 2000	49,740 Hartono <i>et al.</i> , 2009
Activation energy (kJ/mol)	46.7 Mandal <i>et al.</i> , 2001	N/A	35 Cullinane and Rochelle, 2004	44.3 Pani <i>et al.</i> , 1997		41.7 Alper, 1990	
CO <sub>2</sub> Absorption capacity (mol of CO <sub>2</sub> /mol of absorbent)	0.5	1.0	1.0	1.0	0.5	1.0	1.0

found that the regeneration of MEA solution depended on reboiler temperature. Besides, a higher pressure in stripper could reduce the energy required for the subsequent compression. The effects of the operation variables such as CO<sub>2</sub> loading, alkanolamine concentration, and pressure on regeneration of the MEA solution were studied by Abu-Zahra *et al.* (2007). In their studied CO<sub>2</sub> loading range, lying from 0.25 to 0.33 mol of CO<sub>2</sub>/mol of MEA, a higher alkanolamine concentration was found to require less regeneration energy to achieve a 90% CO<sub>2</sub> capture efficiency when the temperature and pressure in a stripper were 128°C and 240 kPa, respectively. For example, the regeneration energies for 30 wt% and 40 wt% MEA aqueous solutions were 3.3 and 3.01 GJ/tonne CO<sub>2</sub>, respectively.

### Ionic Liquid

Recently, ionic liquid (IL) has attracted widespread attention owing to its unique properties such as very low vapor pressure, good thermal stability, high polarity, and non-toxicity. IL has been extensively used as the solvents for catalysis and synthesis. For CO<sub>2</sub> capture, IL can be applied to absorb CO<sub>2</sub> by either physical absorption or chemical absorption. For physical absorption, the factors influencing CO<sub>2</sub> solubility in IL include free volume and size of IL as well as cation and anion. In general, anion has more influence on CO<sub>2</sub> solubility than cation, can be seen in Table 2 in which Henry's constants of the imidazolium-based IL are given. Anthony *et al.* (2005) found that CO<sub>2</sub> solubility was little affected by the cations as ammonium and pyrrolidinium. However, the CO<sub>2</sub> solubility in bis(trifluoromethylsulfonyl)imide (Tf<sub>2</sub>N) was higher than those in tetrafluoroborate (BF<sub>4</sub>) and hexafluorophosphate (PF<sub>6</sub>), indicating the more significant effect of anion on CO<sub>2</sub> solubility. For use of IL in chemical absorption, the structure of IL containing amino-function group that can react with CO<sub>2</sub> can be selected. This kind of IL is called task-specific ionic liquid (TSIL), because IL is synthesized with the desired properties. Bates *et al.* (2002) found that the CO<sub>2</sub> absorption capacity of TSIL was three times higher than that of the IL in physical absorption. However, there exists a limitation of TSIL for CO<sub>2</sub> absorption that is high viscosity possessed by TSIL which is due to the formation of hydrogen bond between cation and anion. To enhance CO<sub>2</sub> capture capacity of IL, Zhang *et al.* (2009b)

proposed to use the supported ILs. The viscosity of an IL [aP<sub>4443</sub>][AA] was found to increase markedly with CO<sub>2</sub> absorption, leading to the highest CO<sub>2</sub> capture capacity as only 0.20 mol of CO<sub>2</sub> per mol of IL. However, the CO<sub>2</sub> capture capacity could be enhanced to 1.2 mol of CO<sub>2</sub> per mol of IL when the IL was loaded onto the support silical gel. This porous support not only provides high surface area as about 500 m<sup>2</sup>/g for loading IL but also allows the occurrence of physical absorption where CO<sub>2</sub> is absorbed on its surface.

To reduce the drawback of high viscosity of ILs, the blended solutions containing IL and alkanolamine are also proposed for CO<sub>2</sub> capture. In addition to reduce high viscosity drawback, the increases of energy efficiency, absorption rate, and CO<sub>2</sub> absorption capacity are also reported when a blended solution is used (Camper *et al.*, 2008; Zhang *et al.*, 2010).

### Higee Technology

Due to a huge amount of exhausted gas from fossil fuel power plants is needed to treat and significant mass transfer resistances exist at gas-liquid interface in a conventional absorption apparatus such as packed bed, spray column, and bubble column, the volume of absorber is generally quite large. For example, for a 600 MW LGN-fired power plant using the conventional MEA absorption process, the diameter and height of an absorber are 4.7 and 44 m, respectively, whereas the height of the stripper is about 25 m (Yokoyama, 2006). The major capital costs of the absorption/stripper process are absorber and stripper, occupying around 55% and 17% of the total capital cost, respectively (Abu-Zahra *et al.*, 2007). It is therefore expected to lower equipment cost by reducing the sizes of absorber and stripper. To enhance mass transfer rate between gas and liquid, a rotating packed bed (RPB) was initially proposed by Ramshaw and Mallinson (1981). This technology is also denoted as Higee. In a RPB, liquid contacts gas on the surface of packing under high centrifugal field. With high gravity, liquid is split into small droplets and thin film during it passes through the packing, and consequently the gas-liquid contact area and mass transfer rate are increased. RPB can be classified into 2 types, countercurrent flow and cross flow, depending on the flow directions of gas and liquid. RPB has been used to many unit operations such as

**Table 2.** Henry's constant for Imidazolium-based ILs.

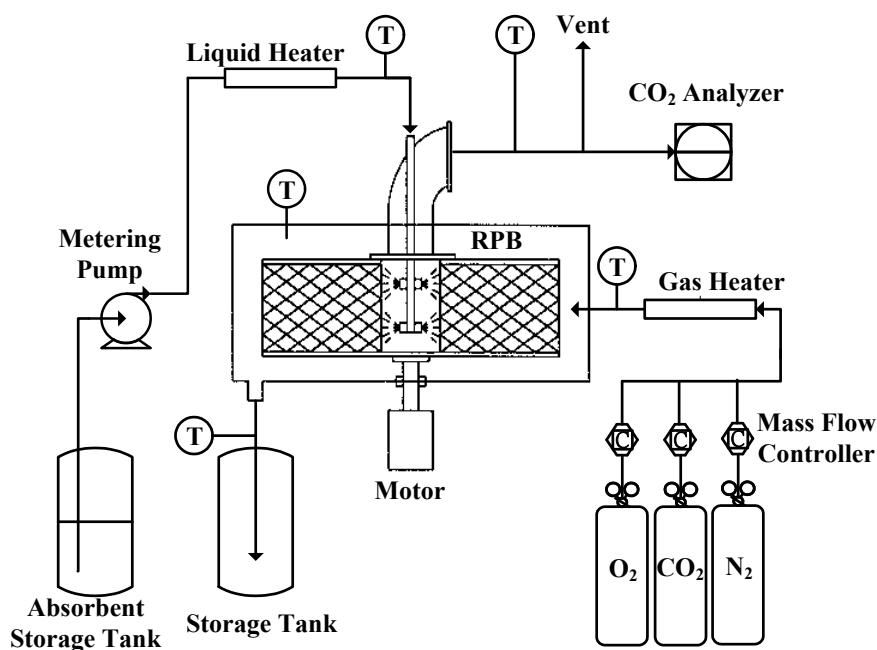
ILs	H <sub>CO2</sub> (bar)						Ref.
	10°C	20°C	25°C	30°C	40°C	50°C	
[Bmim][Tf <sub>2</sub> N]	28 ± 2	30.7 ± 0.3	34.3 ± 0.8	42 ± 2	45 ± 3	51 ± 2	Hou and Baltus, 2007
[Pmmim][Tf <sub>2</sub> N]	29.6 ± 0.6	34 ± 3	38.5 ± 0.9	40.4 ± 0.6	46 ± 3	53 ± 2	Hou and Baltus, 2007
[Bmpy][Tf <sub>2</sub> N]	26 ± 1	31.2 ± 0.1	33 ± 1	35 ± 2	41 ± 4	46 ± 1	Hou and Baltus, 2007
[Perfluoro-hmim][Tf <sub>2</sub> N]	25.5 ± 0.2	29.2 ± 0.4	31 ± 2	32 ± 2	36 ± 4	42 ± 2	Hou and Baltus, 2007
[Bmim][BF <sub>4</sub> ]	41.9 ± 0.2	52 ± 2	56 ± 2	63 ± 2	73 ± 1	84 ± 4	Hou and Baltus, 2007
[Bmim][PF <sub>6</sub> ]	38.7 ± 0.4		53.4 ± 0.3			81.3 ± 0.5	Cadena <i>et al.</i> , 2004
[Bmmim][PF <sub>6</sub> ]	47.3 ± 7.5		61.8 ± 2.1			88.5 ± 1.8	Cadena <i>et al.</i> , 2004
[Bmmim][BF <sub>4</sub> ]	45.7 ± 3.4		61.0 ± 1.6			92.2 ± 1.2	Cadena <i>et al.</i> , 2004
[Emim][Tf <sub>2</sub> N]	25.3 ± 1.3		35.6 ± 1.4			51.5 ± 1.2	Cadena <i>et al.</i> , 2004
[Emmim][Tf <sub>2</sub> N]	28.6 ± 1.2		39.6 ± 1.4			60.5 ± 1.5	Cadena <i>et al.</i> , 2004

absorption (Munjal *et al.*, 1989a, b; Lin *et al.*, 2003; Cheng and Tan, 2006; Tan and Chen, 2006; Jassim *et al.*, 2007; Cheng and Tan, 2009; Cheng and Tan, 2010, Cheng and Tan, 2011, Yu *et al.*, 2012), desorption (Keyvani and Gardner, 1989; Lin and Liu, 2006, 2007), dehydration (Flowler, 1989), volatile organic compounds (VOCs) absorption (Singh *et al.*, 1992; Hsu and Lin, 2011), seawater deaeration (Peel *et al.*, 1998), synthesis of nanoparticles (Chen *et al.*, 2000; Wang *et al.*, 2004), distillation (Lin *et al.*, 2002; Nascimento *et al.*, 2009), ozonation (Lin and Liu, 2003; Ku *et al.*, 2008; Chang *et al.*, 2009b).

Munjal *et al.* (1989a, b) showed a significant improvement of the gas-liquid mass transfer for CO<sub>2</sub> capture using an aqueous solution containing 0.5 to 1.0 N of NaOH. The gas-liquid effective interfacial area as a function of the rotating speed and liquid flow rate over the glass bead packing was evaluated by Fowler *et al.* (1989). They also examined the effects of rotating speed and liquid flow rate on mass-transfer rate of CO<sub>2</sub> into an aqueous diethanolamine (DEA) solution in a RPB packed with the reticulated material. They found that the mass-transfer rate in a RPB was an order of magnitude higher than that in a packed tower. Lin *et al.* (2003) used aqueous solutions containing 0.2 to 2 kmol/m<sup>3</sup> of MEA, AMP and NaOH to capture CO<sub>2</sub> from a gas stream containing 1–10 vol% of CO<sub>2</sub>. Their experiment apparatus is shown in Fig. 2. They found that the overall mass-transfer coefficient ( $K_{GA}$ ) depended on rotating speed, gas flow rate, and liquid flow rate. The measured  $K_{GA}$  in a RPB were significantly higher than those in a packed bed packed with the EX structure packing where it provided  $K_{GA}$  of about 10–33 times higher than a packed bed packed with random packing (Aroonwilas and Tontiwachwuthikul, 1997). Tan and Chen (2006) used the aqueous solutions containing 1.0 M MEA, AMP, MDEA,

PZ and their mixtures to capture 10 vol% CO<sub>2</sub> in a RPB. They found that the  $K_{GA}$  in a RPB were 2 to 5 times higher than those in a conventional packed bed. Furthermore, their experimental results showed that PZ was the most effective promoter. Jassim *et al.* (2007) used MEA to absorb 3.5–4.5 vol% of CO<sub>2</sub> in a RPB. Their result indicated that the height of transfer unit (HTU) of a RPB lay from 14 to 27 cm; whereas the HTU of a conventional packed bed was about 2.4 m. The  $K_{GA}$  in a RPB were found to be 10 times higher than those in a conventional packed bed. Cheng and Tan (2009) used aqueous solutions containing 30 wt% MEA, 2-(2-aminoethylamino) ethanol (AEEA), PZ, and AMP to absorb 10 vol% CO<sub>2</sub> in a RPB. The CO<sub>2</sub> capture efficiency could be higher than 90% whereas the HTU was lower than 2 cm, the HTU were significantly lower than those in a conventional packed bed for the aqueous solutions containing 15 wt% PZ + 15 wt% MEA and 15 wt% PZ + 15 wt% AEEA. Cheng *et al.* (2010) used MEA, AEEA, PZ and their mixtures to capture CO<sub>2</sub> from a hot stove gas in steel making process where the CO<sub>2</sub> concentration was about 30 vol%. Their experimental results indicated that a higher content of PZ in the solution, the higher CO<sub>2</sub> capture efficiency could be achieved. The short contact time between gas and liquid in a RPB could obviously be overcome by the high reaction rate between absorbent and CO<sub>2</sub>, and thus, CO<sub>2</sub> capture in a RPB is suggested to select the absorbents with high reaction rate with CO<sub>2</sub>. For example, at 25°C, the reaction rate of AEEA and PZ with CO<sub>2</sub> are 12,100 and 53,700 m<sup>3</sup>/s/kmol, respectively, higher than that of MEA with CO<sub>2</sub> as 7,000 m<sup>3</sup>/s/kmol (Table 1).

In addition to capture CO<sub>2</sub> by RPB from power plants and steel making process, Cheng and Tan (2006, 2011) also observed that RPB could be applied to treat gases



**Fig. 2.** Experimental apparatus for CO<sub>2</sub> absorption in a rotating packed bed (Lin *et al.*, 2003; Cheng and Tan, 2006; Tan and Chen, 2006; Cheng and Tan, 2009; Cheng *et al.*, 2010; Cheng and Tan, 2011; Yu *et al.*, 2012).

containing ppm level of CO<sub>2</sub> for improvement of zinc/air battery life and improvement of the quality of indoor air. Cheng and Tan (2006) found that the CO<sub>2</sub> concentration could be reduced from 500 ppm to a level below 20 ppm using 2.0 L of amine-based aqueous solution at a temperature range of 283–313 K. Cheng and Tan (2011) successfully reduced indoor CO<sub>2</sub> concentration from 1000 ppm to a level much less than 100 ppm over a very long period of time using an aqueous solutions containing 15 wt% diethylenetriamine (DETA) and 15 wt% PZ. Using the factorial design technology, gas flow rate was found to be the most dominant factors affecting K<sub>Ga</sub> and HTU as compared with rotating speed, temperature, and liquid flow rate. To avoid oxygen degradation, Cheng and Tan (2011) and Yu *et al.* (2012) found that the addition of an oxygen scavenger, Na<sub>2</sub>SO<sub>3</sub>, was helpful. The dissolved oxygen in solution was found to decrease with increasing temperature because of its physical absorption nature. Besides, more CO<sub>2</sub> dissolved in liquid impeded oxygen dissolution as well. Cheng and Tan (2011) and Yu *et al.* (2012) also proposed an algebraic model comprising stirred tanks in series and followed by a gas-liquid contactor to simulate CO<sub>2</sub> capture in a RPB. This proposed model could avoid complicated calculations using differential equations. The calculated results for different inlet CO<sub>2</sub> concentrations, 1000 ppm and 10 vol%, showed fairly agreement with the experimental data on the exit CO<sub>2</sub> concentrations. The molecular structure, physical and chemical properties of the adsorbents used for CO<sub>2</sub> capture in a RPB described above are shown in Table 1.

## CO<sub>2</sub> CAPTURE BY ADSORPTION

Because aqueous amine absorption processes exhibit some disadvantages such as low contact area between gas and liquid, low CO<sub>2</sub> loading, and severe absorbent corrosion, solid adsorption process may be an alternative to achieve the CO<sub>2</sub> capture purpose. Though the rate-limiting step for adsorption as the diffusion of CO<sub>2</sub> from flue gas to the inside pore of a mesoporous adsorbent is about 3 orders of magnitude higher than that for aqueous amine absorption as the CO<sub>2</sub> mass transfer across the gas-liquid interface (Khatri *et al.*, 2005), some existing problems including low CO<sub>2</sub> adsorption capacities at low pressures and influenced by water vapor and gases other than CO<sub>2</sub> still hinder the practical application of adsorption to capture CO<sub>2</sub>.

In several excellent reviews on CO<sub>2</sub> capture by adsorption (Choi *et al.*, 2009, 2010; Sayari *et al.*, 2011), it can be understood that to develop an appropriate CO<sub>2</sub> capture adsorbent should satisfy (1) low-cost raw materials, (2) low heat capacity, (3) fast kinetics, (4) high CO<sub>2</sub> adsorption capacity, (5) high CO<sub>2</sub> selectivity and (6) thermal, chemical, and mechanical stabilities under extensive cycling. A variety of solid adsorbents have been proposed to take into account of their structures and compositions, adsorption mechanisms, and regeneration. In this article, physical adsorption, mesoporous adsorbents impregnated and grated with amines, grafting using supercritical fluid (SCF), and regeneration techniques are reviewed.

## Physical Adsorbent

Though carbonaceous adsorbents such as activated carbon (Plaza *et al.*, 2010) have been widely used for CO<sub>2</sub> capture due to their wide availability, low cost, high thermal stability and low sensitivity to moisture, their application is limited to treat high pressure gases. The weak CO<sub>2</sub> adsorption of carbonaceous materials in a range of 50–120°C leads to high sensitivity in temperature and relatively low selectivity in operation. As a consequence, current research focuses on how to improve the CO<sub>2</sub> adsorption capacity and selectivity via two ways: (1) to improve surface area and pore structure of the carbonaceous adsorbents either using different precursors or fabricating different structures such as ordered mesoporous carbon (Saha and Deng, 2010), single-wall CNT (Cinke *et al.*, 2003), multi-walled CNT (Su *et al.*, 2009; Hsu *et al.*, 2010), graphene (Ghosh *et al.*, 2008), *etc.*; (2) to increase alkalinity by chemical modification on surface.

Zeolites as the physical adsorbents for CO<sub>2</sub> capture have also been reported. The adsorption efficiencies of zeolites are largely affected by their size, charge density, and chemical composition of cations in their porous structures (Wang *et al.*, 2011b). Accordingly, a number of reports focus on zeolites with highly crystalline structure, high surface area, and 3-dimensional pore structures by altering their composition as Si/Al ratio. Another research field focuses on the exchange with alkali and alkaline-earth cations in the structure of zeolites to enhance the CO<sub>2</sub> adsorption. Though CO<sub>2</sub> adsorption can be enhanced by these approaches, there exist several drawbacks. The CO<sub>2</sub> adsorption capacity and the CO<sub>2</sub>/N<sub>2</sub> selectivity are relatively low (Sayari *et al.* 2011). Besides, the CO<sub>2</sub> adsorption capacity greatly declines in the presence of moisture in gas because of their highly hydrophilic character, thus a high regeneration temperature (often above 300°C) is needed.

Ordered mesoporous silica may be a candidate because of its high surface area, high pore volume, tunable pore size and good thermal and mechanical stability. So far mesoporous silicas including the families of M41S, Santa Barbara Amorphous type material (SBA-n), anionic-surfactant-templated mesoporous silica (AMS), *etc.*, have been reported (Liu *et al.*, 2005; Sun *et al.*, 2007; Chew *et al.*, 2010). However, the CO<sub>2</sub> adsorption capacities are not high enough, especially, at atmospheric pressure, to allow their practicability.

Metal-organic frameworks (MOFs) have attracted significant interest in the recent years due to their remarkably high surface area, controllable pore structures and tunable pore surface properties, which can be easily tuned by changing either the metallic clusters or the organic ligands. Yaghi's group first reported MOFs for CO<sub>2</sub> capture at room temperature (Millward and Yaghi, 2005). Thereafter they have developed new types of MOFs for CO<sub>2</sub> capture (Banerjee *et al.*, 2008; Wang *et al.*, 2008a; Banerjee *et al.*, 2009; Britt *et al.*, 2009). Zhou's group (Kuppler *et al.*, 2009; Li *et al.*, 2009, 2011) reviewed the progress of MOFs for CO<sub>2</sub> capture from experimental to molecular simulation. In their review, MOFs exhibit exceptional CO<sub>2</sub> adsorption capacity to deal with pure CO<sub>2</sub>

at high pressures. Their adsorption capacities are dramatically reduced when they are exposed to a gas mixture. Though MOFs have been shown to be the promising adsorbents for CO<sub>2</sub> capture in laboratory, more studies are required to verify their practical applications.

CO<sub>2</sub> adsorption capacities of several commonly used materials are summarized in Table 3. It can be seen that low CO<sub>2</sub> selectivity is the major drawback for most physical adsorbents. Although carbonaceous and MOFs materials exhibiting relatively higher CO<sub>2</sub> adsorption capacity seem to be as the promising CO<sub>2</sub> adsorbents, the operations are at high pressures and low temperatures. In the other hand, silica materials have lower adsorption capacity and selectivity toward CO<sub>2</sub>, their abundant surface OH groups can facilitate chemical modification to improve their CO<sub>2</sub> adsorption capacity and selectivity and thus treat a flue gas with low CO<sub>2</sub> partial pressure.

#### Chemical Adsorbent: Amine-Based

Many studies have been devoted to improve CO<sub>2</sub> adsorption and selectivity by chemical modification on the surface of solid materials possessing high surface area. The basic organic group (amine) and inorganic metal oxide (alkali metal or alkali-earth metal) are of particular interest. The interaction between the acidic CO<sub>2</sub> molecules and modified basic active sites on the surface facilitates CO<sub>2</sub> adsorption through the formation of covalent bonding.

Amine-based adsorbents have widely been studied and exhibited the advantage as low heat of regeneration over aqueous amines due to the low heat capacity of solid supports. Their low CO<sub>2</sub> adsorption capacity and high cost, however, are the major challenges to commercialize. Recently, the improvement of amine-based adsorbents was proposed by the approaches: (1) the preparation of supports with high amine loading, (2) the use of amine with high

nitrogen content (as shown in Fig. 3), and (3) the effective methods for amine introduction (Wang *et al.*, 2011b). According to the type of the interactions between amines and supports, the amine-based adsorbents can be categorized as amine-impregnated and amine-grafted materials via weak interactions and strong covalent bonding, respectively (Sayari *et al.*, 2011). Typically, the amine-grafted adsorbents exhibit comparatively higher adsorption rate and higher stability in cyclic runs than the amine-impregnated ones. However, the grafted amount of amine depends on surface silanol groups, sometimes leading to a comparatively lower amine loading as compared with the impregnated amount. Although the higher amine loadings may be achieved by impregnation, a large diffusion resistance also occurs (Serna-Guerrero and Sayari, 2010). Besides, kinetics and heat effects are needed to evaluate the feasibility of operation under practical conditions containing 3–5% water and 10–15% CO<sub>2</sub> at 55°C in coal power plant flue gases (Fisher *et al.*, 2009).

#### Amine-Impregnated Adsorbent

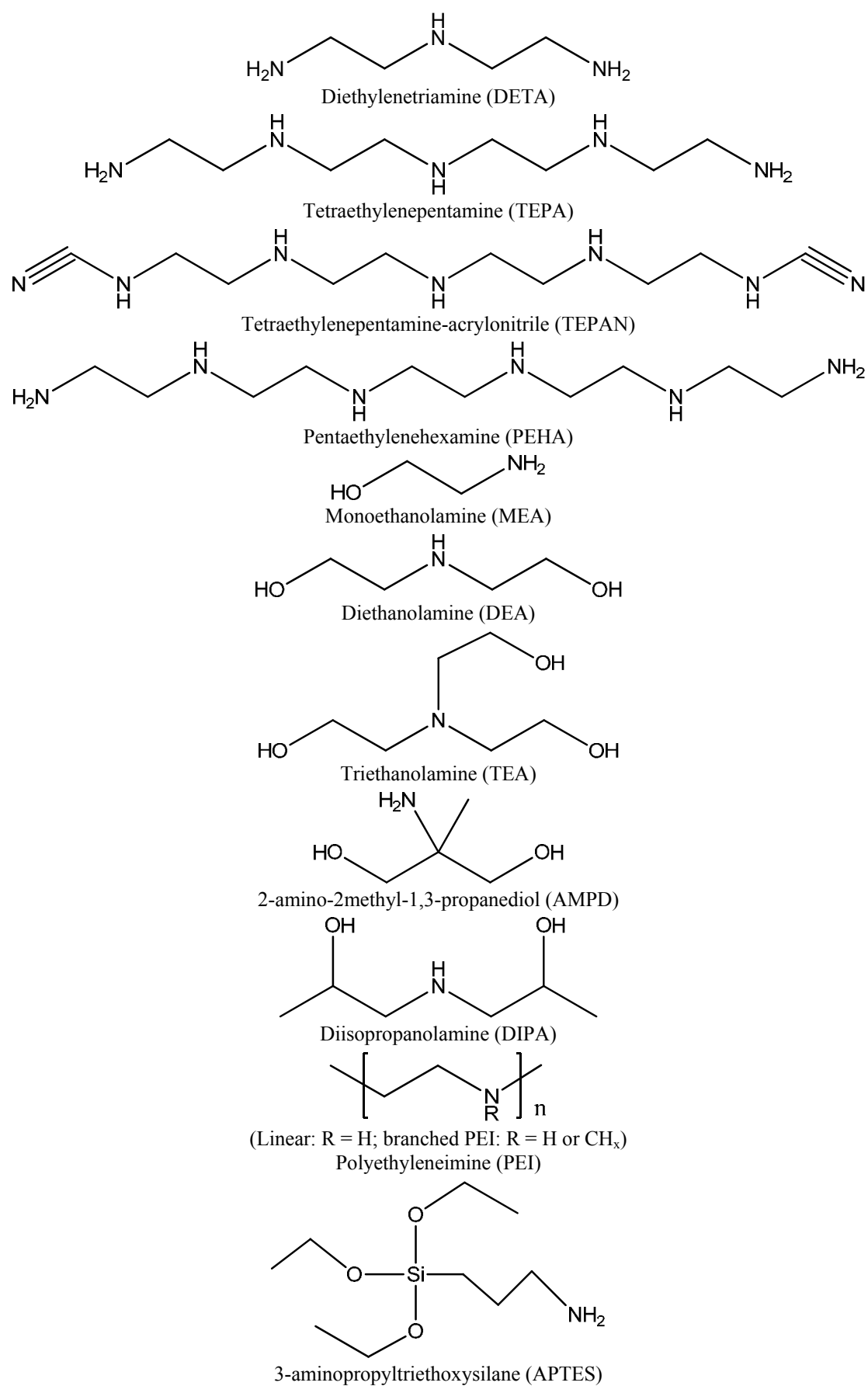
Song and his coworkers reported the effects of polyethylenimine (PEI) loading, gas conditions, temperature, moisture and supports on CO<sub>2</sub> adsorption capacity for the PEI-impregnated mesoporous silica and carbonaceous materials (Xu *et al.*, 2002, 2005; Ma *et al.*, 2009; Wang *et al.*, 2009, 2011a). A higher PEI loading significantly enhanced CO<sub>2</sub> adsorption capacity together with the decreases of surface area, pore size and pore volume of the PEI-impregnated supports. The highest CO<sub>2</sub> adsorption capacity of 3.02 mmol/g for the PEI-impregnated MCM-41 (PEI/MCM-41) with 75 wt% of PEI loading was observed under pure CO<sub>2</sub> at 75°C, while the highest amine efficiency (CO<sub>2</sub>/N molar ratio) occurred at 50 wt% PEI loading and was reduced with an increase of PEI loading. In general, the amine loading is not directly related to the amines for

**Table 3.** CO<sub>2</sub> adsorption capacities and operating conditions for supports.

Support Type	Adsorption			Operating Condition		Method	Ref.	
	$S^a$ (m <sup>2</sup> /g)	$V_p^b$ (cm <sup>3</sup> /g)	$D_p^c$ (nm)	Capacity (mmol/g)	Gas Composition			$T$ (°C)
AC	1762	-	-	1.66	-	25	TGA	Plaza <i>et al.</i> , 2007
Meso-Carbon	798	0.87	6.3	1.50	100% CO <sub>2</sub>	25	Ads. isotherm	Saha and Deng, 2010
SWCNT	1587	1.55	-	4.02	100% CO <sub>2</sub>	35	Ads. isotherm	Cinke <i>et al.</i> , 2003
MWCNT	407	0.45	23.5	1.73	50% CO <sub>2</sub>	20	Ads. isotherm	Su <i>et al.</i> , 2009
Graphene	1550	-	-	7.95	100% CO <sub>2</sub>	-78	Ads. isotherm	Ghosh <i>et al.</i> , 2008
MCM-41	1229	1.15	2.7	0.14	15% CO <sub>2</sub> (4.3% O <sub>2</sub> ) in N <sub>2</sub>	75	TGA	Xu <i>et al.</i> , 2003
MCM-41	1229	1.15	2.7	0.20	100% CO <sub>2</sub>	75	TGA	Xu <i>et al.</i> , 2003
MCM-41	1229	1.15	2.7	0.62	100% CO <sub>2</sub>	25	TGA	Xu <i>et al.</i> , 2003
MCM-41	1267	0.32	1.8	1.58	100% CO <sub>2</sub>	20	Ads. isotherm	Macario <i>et al.</i> , 2005
SBA-15	950	1.31	6.6	0.11	15% CO <sub>2</sub> (4.3% O <sub>2</sub> ) in N <sub>2</sub>	75	TGA	Ma <i>et al.</i> , 2011a
As-SBA-15	345	0.71	8.9	0.05	100% CO <sub>2</sub>	75	TPD-TPD	Yue <i>et al.</i> , 2006
SBA-15	725	1.12	9.3	0.04	100% CO <sub>2</sub>	75	TPD-TPD	Yue <i>et al.</i> , 2006
SBA-15	802	1.31	7.7	0.50	10% CO <sub>2</sub>	25	Ads. isotherm	Liu <i>et al.</i> , 2005
KIT-6	895	1.22	6.0	0.02	100% CO <sub>2</sub>	75	TGA	Son <i>et al.</i> , 2008
HMS	561	1.44	9.8	0.22	100% CO <sub>2</sub>	25	TGA	Chen <i>et al.</i> , 2010
Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	0.84	100% CO <sub>2</sub>	25	TGA	Plaza <i>et al.</i> , 2008
PMMA (Diaion)	470	1.20	14.0	3.40	100% CO <sub>2</sub>	45	TP-MS	Jiang <i>et al.</i> , 2011

<sup>a</sup> Surface area; <sup>b</sup> Pore Volume; <sup>c</sup> Pore size.





**Fig. 3.** Structures of amines, silanes, monomers, and polymers used in the synthesis of solid supported amine adsorbents.

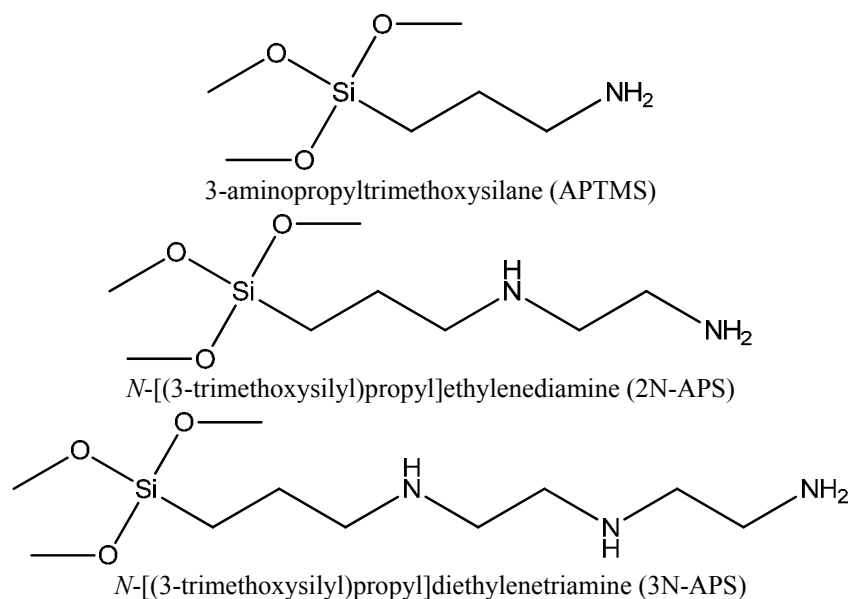


Fig. 3. (continued).

CO<sub>2</sub> adsorption because the formation of the aggregated amine on supports would reduce the amine accessible to CO<sub>2</sub>. When the PEI/MCM-41 with 50 wt% PEI loading was used to treat an anhydrous gas containing 15% CO<sub>2</sub> in N<sub>2</sub> at 75°C, the adsorption capacity was found to reduce to 2.03 mmol/g. When the temperature was decreased from 75 to 25°C, the CO<sub>2</sub> adsorption capacity was found to decrease as well. It is known that CO<sub>2</sub> adsorption is an exothermic process, the increasing temperature is unfavorable for CO<sub>2</sub> adsorption capacity. However, the formation of bulk-like PEI inside the pore at low temperature leads to CO<sub>2</sub> adsorption as a diffusion-limited process (Sayari *et al.*, 2011). At high temperature, the high CO<sub>2</sub> adsorption capacity is possibly due to the high diffusion rate of CO<sub>2</sub> into bulk-like PEI and the increasing reaction rate of CO<sub>2</sub> with PEI. The similar observation was also reported by Heydari-Gorji and Sayari (2011) and Qi *et al.* (2011).

Song's group further studied the effect of moisture on CO<sub>2</sub> capture using the PEI/MCM-41 and showed that the CO<sub>2</sub> adsorption capacity was increased from 2.03 mmol/g for an anhydrous flow containing 15% of CO<sub>2</sub> to 2.84 mmol/g for a flow containing 10% of moisture and 13% of CO<sub>2</sub>. The improvement of CO<sub>2</sub> adsorption capacity was interpreted in terms of adsorption mechanisms, i.e., the formation of carbamate and bicarbonate under anhydrous and hydrous conditions, respectively (Sayari and Belmabkhout, 2010). The positive effect of moisture was only observed for the molar concentration of moisture not higher than that of CO<sub>2</sub>. Concerned with structure of support, Song's group also prepared the PEI-impregnated SBA-15 with a PEI loading of 50 wt% and found a higher CO<sub>2</sub> adsorption capacity as 3.18 mmol/g, which was about 1.5 times higher than the PEI/MCM-41 for an anhydrous flow containing 15% CO<sub>2</sub> at 75°C. Ahn's group also reported the effect of support (Son *et al.*, 2008; Chen *et al.*, 2010) and demonstrated that CO<sub>2</sub> adsorption capacity and kinetics were mainly influenced by pore size and followed an order of hexagonal

mesoporous silica (HMS) > KIT-6 > SBA-16 ≈ SBA-15 > MCM-48 > MCM-41.

Zhu's group studied CO<sub>2</sub> capture by the tetraethylenepentamine (TEPA)-impregnated mesoporous SBA-15 and MCM-41 with and without template removal (Yue *et al.*, 2006, 2008a). The TEPA-impregnated adsorbents exhibited the CO<sub>2</sub> adsorption capacities as 3.93 mmol/g for a 70 wt% of TEPA loaded onto the as-SBA-15 and 5.39 mmol/g for a 60 wt% of TEPA loaded onto the as-MCM-41. They also demonstrated an improvement around 10% for the as-synthesized supports over the calcined supports, indicating the template removal might not be required. This was probably due to that the template in the pore could prevent TEPA from aggregating to clusters. They further investigated a mixture of TEPA and diethanolamine (DEA) impregnated into the as-synthesized SBA-15 (Yue *et al.*, 2008b). In this case, the highest CO<sub>2</sub> adsorption capacity as 4.00 mmol/g was obtained at a loading of 35% TEPA and 15% DEA, while the maximum CO<sub>2</sub>/N ratio around 0.4 was observed at a loading of 30% TEPA and 20% DEA under anhydrous pure CO<sub>2</sub>. They also demonstrated a stable cyclic performance of the TEPA-DEA/SBA-15 with the CO<sub>2</sub> adsorption capacity of from 3.77 to 3.61 mmol/g in 6 adsorption-desorption cycles under an anhydrous flow of 5% CO<sub>2</sub> in N<sub>2</sub>.

Chuang and his coworkers reported that the beta-zeolite impregnated with TEPA exhibited the higher TEPA loading and higher CO<sub>2</sub> adsorption capacity than the amorphous Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> impregnated with TEPA, most likely due to the higher pore volume and better structural properties including pore size, surface area, and pore structure possessed by beta-zeolite (Fisher *et al.*, 2009). They also pointed out that Al<sub>2</sub>O<sub>3</sub> with high acidity would adsorb significant amount of H<sub>2</sub>O, consequently result in a reduction of CO<sub>2</sub> adsorption capacity. Chuang's group further investigated the role of polyethylene glycol (PEG) as an additive for the TEPA/SiO<sub>2</sub>. The addition of PEG was found to decrease

CO<sub>2</sub> adsorption capacity, however, the cyclic stability and the adsorption half-time relative to adsorption rate were improved. Besides, the addition of PEG also increased the fraction of weakly adsorbed CO<sub>2</sub> species (Zwitterion as shown in Eq. (1)), which was related to a hydrogen-bonding species (i.e., NH<sub>2</sub>-O) (Tanthana and Chuang, 2010).

Plaza *et al.* (2007, 2008) studied CO<sub>2</sub> capture using activated carbon and alumina impregnated with various types of amines including primary and secondary alkylamines such as DETA, pentaethylenehexamine (PEHA) and PEI, alkanolamines such as diisopropanolamine (DIPA), sterically hindered 2-amino-2-methyl-1,3-propanediol (AMPD), and triethanolamine (TEA). Their results indicated that the DETA-impregnated alumina exhibited the highest CO<sub>2</sub> adsorption capacity throughout the tested temperature range. The decrease of CO<sub>2</sub> adsorption capacity for impregnation of amine-impregnated activated carbon was mainly due to reduction of microporous volume responsible for physical adsorption of CO<sub>2</sub>. They further studied the carbon-based supports derived from sewage sludge and air-oxidized olive stones impregnated with PEI and found that the increase of CO<sub>2</sub> adsorption capacity depended on the textural properties of the support and the surface modification methodology (Plaza *et al.*, 2009).

The supports other than mesoporous materials to impregnate amines have also been reported in the literature. Filburn's group impregnated a variety of amines including MEA, DETA, TEA, PEI, TEPA, ethyleneamine (E-100), TEPAN and E-100AN (AN denotes the reaction-modifies amine with acrylonitrile) into a polymeric material polymethylmethacrylate (PMMA) (Filburn *et al.*, 2005; Lee *et al.*, 2008). Among their prepared adsorbents, the TEPA-impregnated PMMA exhibited an adsorption capacity of 21.45 mmol/g at 23°C for the N<sub>2</sub> gas containing 15% CO<sub>2</sub> and 2.6% H<sub>2</sub>O. The CO<sub>2</sub> adsorption capacity was found to decrease at high temperatures. In addition, they first converted primary amines like MEA by the reaction with acrylonitrile to secondary amines, and then impregnated these secondary amines into supports. The formed secondary amines exhibited a larger increase in cyclic CO<sub>2</sub> adsorption capacities than the primary amines. The supports including PMMA, polystyrene (PS) and silicon dioxide were also performed by the DOE/NTEL's group (Gray *et al.*, 2009; Ebner *et al.*, 2011; Jiang *et al.*, 2011; Li *et al.*, 2011). The nano-layered amine-based adsorbents using layer-by-layer nanoassembly technology via alternate deposition of PEI and an oppositely-charged polymer like PMMA and polystyrene sulfonate prepared by NTEL people were also used for CO<sub>2</sub> capture. A CO<sub>2</sub> adsorption capacity as 1.70 mmol/g under an anhydrous flow of pure CO<sub>2</sub> at 40°C was observed.

The amine-impregnated adsorbents produced using various amines and supports as described above are summarized in Table 4. It seems to be more appropriate to use supports with large pore size and pore volume to impregnate amine. However, the decreases in adsorption rate, amine efficiency (CO<sub>2</sub>/N ratio) and cyclic performance were observed accompanied by high amine loading. Thus, how to overcome these drawbacks in order to promote the performance of amine-impregnated adsorbent needs further studies.

### **Amine-Grafted Adsorbent**

Though high CO<sub>2</sub> adsorption capacity was observed in amine-impregnated materials, the lack of thermal stability in desorption was also reported (D'Alessandro *et al.*, 2010). To overcome this limitation, aminosilanes were proposed to be covalently grafted onto the intrachannel surface of the mesoporous silicas through silylation. Generally, there are two preparation methods, post modification and direct synthesis (also called co-condensation). Several studies have been reported for synthesis of amine-grafted silicas for CO<sub>2</sub> capture using aminosilanes such as (3-aminopropyl)triethoxysilane (APS), *N*-[(3-trimethoxysilyl)propyl]ethylenediamine (2N-APS) and *N*-[(3-trimethoxysilyl)propyl]diethylenetriamine (3N-APS). Leal *et al.* (1995) firstly published the work on APS-grafted silica gel for CO<sub>2</sub> capture and proposed the CO<sub>2</sub> adsorption via the formation of ammonium carbamate under anhydrous condition and the formation of ammonium bicarbonate in the presence of moisture leading to one amino group reacted with one molecular CO<sub>2</sub>. This APS-grafted silica gel exhibited a CO<sub>2</sub> adsorption capacity as 0.41 and 0.89 mmol/g under an anhydrous and hydrous flow with pure CO<sub>2</sub> at 27°C, respectively. Huang *et al.* (2003) studied CO<sub>2</sub> capture by the APS-grafted mesoporous silica MCM-48 and silica xerogel. The CO<sub>2</sub> adsorption capacities at room temperature were found to be of 2.05 and 1.14 mmol/g for the APS-grafted MCM-48 under anhydrous condition with pure CO<sub>2</sub> and 5% CO<sub>2</sub> in helium, respectively, which was almost two times the APS-grafted silica xerogel at the same conditions. Chaffee's group reported APS- and 3N-APS-grafted hexagonal mesoporous silica (HMS) and amorphous silica gel for CO<sub>2</sub> capture (Knowles *et al.*, 2005, 2006). The APS-HMS exhibited higher CO<sub>2</sub> adsorption capacity as 1.59 mmol/g than that of APS-grafted amorphous silicas as 0.68 mmol/g and 3N-APS-HMS as 1.34 mmol/g under a hydrous flow with 90% CO<sub>2</sub> in Ar at 20°C. The differences were caused by the extent of surface grafting that was influenced by diffusion of amines in pores, amount of silanol groups on surface, and porosity of the support. Chuang's group synthesized the APS- and 2N-APS-grafted SBA-15 for CO<sub>2</sub> capture and reported all the CO<sub>2</sub> adsorption capacities less than 1 mmol/g, mainly due to the supports with low surface area, around 200 m<sup>2</sup>/g (Chang *et al.*, 2003; Khatri *et al.*, 2005, 2006). They also used in situ infrared spectroscopy coupled with mass spectrometry to further study the effects of amine nature, adsorbed CO<sub>2</sub> species, and SO<sub>2</sub> on CO<sub>2</sub> adsorption capacity. Their analyses demonstrated that the rate of formation of carbonate species was higher than that of bicarbonates species and the amine nature on the surface affected the regeneration temperature of adsorbents. Yogo's group synthesized a series of amine-grafted SBA-15 and investigated the effects of amine natures, pretreatment of support and moisture on CO<sub>2</sub> adsorption (Hiyoshi *et al.*, 2005). They showed that CO<sub>2</sub> adsorption capacities were comparable under both anhydrous and hydrous conditions. The use of 3N-APS for grafting on hydrolyzed SBA-15 (boiled in water) resulted in a higher amine density (N atoms per unit nm<sup>2</sup>) and a higher CO<sub>2</sub> adsorption capacity

**Table 4.** CO<sub>2</sub> adsorption capacities and operating conditions for amine-impregnated supports.

Amine (wt%)	Support			Adsorption		Operating condition		Method	Ref.
	Type	$S$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$D_p$ (nm)	Capacity (mmol/g)	Gas composition	$T$ (°C)		
PEI	MCM-41	1229	1.15	2.7	3.02	100% CO <sub>2</sub>	75	TGA	Xu et al. 2003
PEI	MCM-41	1229	1.15	2.7	2.55	100% CO <sub>2</sub>	75	TGA	Xu et al. 2003
PEI	MCM-41	1229	1.15	2.7	0.75	100% CO <sub>2</sub>	25	TGA	Xu et al. 2003
PEI	MCM-41	1229	1.15	2.7	2.03	15% CO <sub>2</sub> in N <sub>2</sub>	75	TGA	Xu et al. 2005
PEI	MCM-41	1229	1.15	2.7	2.84	13% CO <sub>2</sub> (10% H <sub>2</sub> O) in N <sub>2</sub>	75	TGA	Xu et al. 2005
PEI	SBA-15	950	1.31	6.6	3.18	15% CO <sub>2</sub> in N <sub>2</sub>	75	TGA	Ma et al., 2009
PEI	Silica gel	550	-	-	3.07	100% CO <sub>2</sub>	75	TGA	Xu et al. 2003
PEI	Carbon black	1486	2.93	-	3.07	100% CO <sub>2</sub>	75	TGA	Wang et al., 2011a
PEI	MCM-41	1042	0.85	2.8	2.52	100% CO <sub>2</sub>	75	TGA	Son et al. 2008
PEI	MCM-48	1162	1.17	3.1	2.70	100% CO <sub>2</sub>	75	TGA	Son et al. 2008
PEI	SBA-15	753	0.94	5.5	2.89	100% CO <sub>2</sub>	75	TGA	Son et al. 2008
PEI	SBA-16	736	0.75	4.1	2.93	100% CO <sub>2</sub>	75	TGA	Son et al. 2008
PEI	KIT-6	895	1.22	6.0	3.07	100% CO <sub>2</sub>	75	TGA	Son et al. 2008
PEI	HMS	561	1.44	9.8	4.18	100% CO <sub>2</sub>	75	TGA	Chen et al., 2010
TEPA	as-SBA-15	345	0.71	8.9	3.93	100% CO <sub>2</sub>	100	TPD-TCD	Yue et al. 2006
TEPA	As-MCM-41	76	0.36	10.5	5.39	100% CO <sub>2</sub>	75	TPD-TCD	Yue et al., 2008a
TEPA/DEA	SBA-15	725	1.12	9.3	4.00	100% CO <sub>2</sub>	75	TPD-TCD	Yue et al., 2008b
TEPA	Al <sub>2</sub> O <sub>3</sub>	225	-	-	0.19	10% CO <sub>2</sub> in Ar	30	TPD-MS	Fisher II et al., 2009
TEPA	SiO <sub>2</sub>	180	-	-	0.68	10% CO <sub>2</sub> in Ar	30	TPD-MS	Fisher II et al., 2009
TEPA	Beta zeolite	680	-	-	2.08	10% CO <sub>2</sub> in Ar	30	TPD-MS	Fisher II et al., 2009
TEPA/PEG	Fumed silica	-	-	-	2.09	15% CO <sub>2</sub> (4% H <sub>2</sub> O) in air	55	TPD-MS	Tanthana and Chuang, 2010
TEPA/PEG	Fumed silica	-	-	-	1.11	15% CO <sub>2</sub> (4% H <sub>2</sub> O) in air	55	TPD-MS	Tanthana and Chuang, 2010
DETA	AC	1762	-	-	1.01	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2007
PEHA	AC	1762	-	-	1.18	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2007
PEI	AC	1762	-	-	1.14	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2007
DETA	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	1.75	100% CO <sub>2</sub>	100	TGA	Plaza et al., 2008
PEI	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	1.50	100% CO <sub>2</sub>	100	TGA	Plaza et al., 2008
PEHA	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	1.03	100% CO <sub>2</sub>	97	TGA	Plaza et al., 2008
DIPA	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	0.93	100% CO <sub>2</sub>	37	TGA	Plaza et al., 2008
AMPD	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	0.57	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2008
TEA	Meso-Al <sub>2</sub> O <sub>3</sub>	271	-	-	0.39	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2008
PEI	AC	1079	0.50	-	1.98	100% CO <sub>2</sub>	25	TGA	Plaza et al., 2009
TEPA	PMMA	470	1.20	14.0	21.45	15% CO <sub>2</sub> (2.6% H <sub>2</sub> O) in N <sub>2</sub>	23	CO <sub>2</sub> analyzer	Lee et al., 2008
PEI	SiO <sub>2</sub>	300	1.30	-	2.80	100% CO <sub>2</sub>	60	TGA	Ebner et al., 2011
PEI	SiO <sub>2</sub>	300	1.30	-	3.95	10% CO <sub>2</sub> (2% H <sub>2</sub> O) in He	60	TGA	Gray et al., 2009
PEI	PMMA	470	1.20	14.0	3.60	10% CO <sub>2</sub> (2% H <sub>2</sub> O) in He	60	TGA	Gray et al., 2009
PEI/PSS	PMMA	470	1.20	14.0	1.70	100% CO <sub>2</sub>	40	TGA	Jiang et al. 2011

than other aminosilanes. Furthermore, 3N-APS-SBA-15 was reported to be stable over 50 cycles for the adsorption at 60°C and the desorption at 100°C. The effect of boiling water pretreatment on silica supports was also investigated by Wei *et al.* (2008) who observed that the surface Si-O-Si bonds were hydrolyzed after the boiling water pretreatment, as a result, more Si-OH groups were generated for aminosilanes grafting.

In our previous work, APS, 2N-APS and 3N-APS were grafted onto MCM-41, SBA-15 and pore expanded-SBA-15 (Chang *et al.*, 2009a). The experimental results showed that SBA-15 was the most appropriate support because its pore size could accommodate more amines and avoid blocking during CO<sub>2</sub> adsorption. Besides, its high pore surface area providing large amount of silanol group was more beneficial for aminosilane grafting. Among the studied amines, 3N-APS exhibited the highest CO<sub>2</sub> adsorption capacity as 2.74 and 3.06 mmol/g at 40°C under anhydrous and hydrous (78% RH) flows containing 17% CO<sub>2</sub>, respectively, followed by 2N-APS and APS.

Sayari's group carried out comprehensive study on amine-grafted MCM-41 and pore-expanded MCM-41 (PE-MCM-41) for CO<sub>2</sub> capture. They demonstrated the effects of pore size and pore volume on CO<sub>2</sub> adsorption capacity and adsorption rate, and concluded that the larger pore diameter and pore volume of PE-MCM-41 enhanced CO<sub>2</sub> adsorption. The optimum grafting condition of 3N-APS onto PE-MCM-41 in toluene, how to increase selectivity toward CO<sub>2</sub> over other gases and how to enhance cyclic stability were also suggested. Sayari's group further demonstrated the formation of urea groups, which was stable in desorption, would result in the deactivation of the amine-grafted adsorbents. They, therefore, suggested using humid streams to prevent the deactivation and to improve the stability of amine-based adsorbents (Belmabkhout *et al.*, 2009; Belmabkhout and Sayari, 2010; Belmabkhout *et al.*, 2010a, b, 2011a, b; Harlick and Sayari, 2006, 2007; Sayari and Belmabkhout, 2010; Serna-Guerrero and Sayari, 2010; Serna-Guerrero *et al.*, 2010a, b, c, d).

The other approach to synthesize amine-grafted adsorbent is the direct synthesis via the co-condensation of siloxane and aminosilane in the presence of an organic template. The direct synthesis can be carried out in acidic or basic media. Though many reports are existing for the use of APS (Che *et al.*, 2003; Chong and Zhao, 2003; Yokoi *et al.*, 2003; Yokoi *et al.*, 2004; Wang *et al.*, 2005; Yokoi *et al.*, 2006; Yokoi and Tatsumi, 2007; Kim, *et al.*, 2008; Hao *et al.*, 2011; Osei-Prempeh *et al.*, 2011), 2N-APS (Wang *et al.*, 2006; Kim *et al.*, 2008), and 3N-APS (Kim *et al.*, 2008) as the amine precursors, the synthesized amine-grafted adsorbents were not used for CO<sub>2</sub> capture. Chong and Zhao (2003) applied the direct synthesis at acidic condition (pH < 2) to synthesize SBA-15 with controllable pore size and the desired amount of amine groups in it. Wang *et al.* (2005, 2006) successfully prepared APS-SBA-15 with long-range ordered structure via the direct synthesis by hydrolysis of TEOS prior to the addition of APS in view of different hydrolysis rates for these two compounds. However, the occurred protonation of amine groups was

not beneficial for CO<sub>2</sub> adsorption. Tatsumi's group reported the direct synthesis of APS at basic condition using various templates including cationic surfactant as hexadecyltrimethylammonium bromide (CTAB) and anionic surfactants as sodium dodecyl sulfate (SDS), lauric acid sodium salt (LAS), and *N*-myristoyl-L-alanine (Yokoi *et al.*, 2003, 2004, 2006, 2007; Yokoi and Tatsumi, 2007; Yokoi *et al.*, 2010). Although large amount of aminosilane grafted on the mesostructure silicate wall was obtained, the synthesized adsorbents were designed to metal adsorption, immobilization of enzyme and catalyst not to CO<sub>2</sub> adsorption. Ahn's group reported a comparative study for the amine-grafted mesoporous silica using the anhydrous grafting and direct synthesis methods (Kim *et al.*, 2008). They used anionic surfactants such as LAS, SDS, LAS and *N*-lauroylsarcosine sodium salt (LSS) as the templates to synthesize APS-grafted AMS at basic condition. The prepared adsorbents exhibited the amine content up to 3.33 mmol/g and CO<sub>2</sub> adsorption capacity up to 1.25 mmol/g in pure CO<sub>2</sub> at 25°C. Osei-Prempeh *et al.* (2011) applied the cationic fluorinated surfactant in the direct synthesis of APS-grafted MCM-41 which exhibited a monoamine loading of 1.20 mmol/g and a CO<sub>2</sub> adsorption capacity of 0.49 mmol/g in pure CO<sub>2</sub> at 50°C.

In view of protonation of amine groups, our group is trying to apply a post-treatment including template removal and basic washing to directly synthesize amine-grafted mesoporous silica in order to turn the protonated amine (-NH<sub>3</sub><sup>+</sup>) into the basic amino (-NH<sub>2</sub>) that is believed to be helpful for CO<sub>2</sub> adsorption. We synthesized the monoamine-grafted mesoporous silicas APS-SBA-15, APS-MCM-41 and APS-AMS by the direct synthesis method at both acidic and basic conditions, and then applied the post-treatment of ethanol washing at acidic or basic condition. The synthesized adsorbents showed high amine content on internal surface, low pore blocking, and high CO<sub>2</sub> adsorption capacity as a result.

### **Supercritical Fluid Approach**

Another approach to improved amine-loaded adsorbents is to use an effective solvent to infuse more amine into mesoporous supports. Basically, amines need to diffuse into pore first and then reacts via weak interaction (impregnation) or covalent bonding (grafting) between amines and surface silanol. Organic solvents have generally been used, but they have some drawbacks including high viscosity and surface tension, low diffusivity, and high toxicity. The replacement of organic solvents by supercritical fluid (SCF) has been widespread explored and proved to be an alternative mainly due to high diffusivity and negligible surface tension possessed by a SCF. Moreover, SCF gas-like viscosity allows it rapid penetration into cavities of mesoporous materials. Because of those unique properties, supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) has been widely applied to substitute organic solvents in variety of chemical processes. But due to the formation of insoluble carbamic acid salts between CO<sub>2</sub> and amine, SC-CO<sub>2</sub> is not suitable for the present purpose. Supercritical propane (SC-propane, P<sub>c</sub> = 4.2 MPa, T<sub>c</sub> = 96.7°C), on the other hand, can be regarded

as the candidate. Despite flammability, propane possesses several advantages such as low cost, low toxicity, less reaction time, and usability under a wide range of pressures and temperatures. Besides, propane can be completely removed from solid support after pressure releasing. The use of SC-propane as the solvent for various applications is existing in the literature, for example, Hitzler *et al.* (1998) successfully carried out hydrogenation of nitrogen-containing compounds in SC-propane. De Gooijer *et al.* (1999) successfully used near critical propane as the solvent for impregnation of 1,4-diaminobutane into the maleic anhydride grafted polyethylene. Our group successfully applied SC-propane as the solvent to graft APS onto our own synthesized mesoporous silica SBA-15. The SC-propane grafting apparatus was depicted in Fig. 4. To the best of our knowledge, this preparation means has not been proposed yet. The results obtained indicated that the use of SC-propane in grafting could enhance diffusion rate of APS into mesoporous structure and reduce viscosity of the solution, consequently, a higher loading of APS onto SBA-15 in a fixed period of time was achieved and the subsequent CO<sub>2</sub> adsorption capacity could then be increased accordingly. This work has been submitted to journal and is under review.

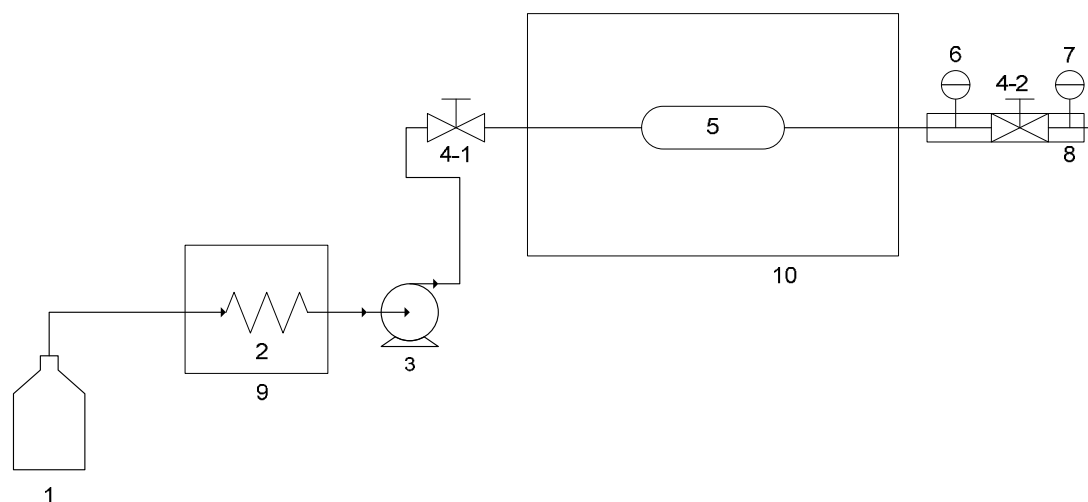
The amine-grafted adsorbents produced using various amines and mesoporous supports are summarized in Table 5. It can be seen from Table 5 that amine-grafted materials can only be produced using the supports possessing surface hydroxyl groups. It is also found that amine loading depended on surface area and availability of silanol groups on surface.

#### Other Adsorbents

Porous inorganic metal oxides such as alkali metals or alkali-earth metals providing alkalinity have also been widely used to incorporate or disperse in porous supports for CO<sub>2</sub> capture. Among various metal oxides, lithium-based materials were once considered as the effective CO<sub>2</sub>

adsorbents because of their high adsorption capacity, but the existence of serious diffusion resistance hindered their industrial application (Kato *et al.*, 2002; Xiong *et al.*, 2003; Venegas *et al.*, 2007; Iwan *et al.*, 2009). The calcium-based adsorbents possessing high adsorption capacity, long-term durability, fast adsorption/desorption kinetic, good mechanical strength, wide availability and low cost in natural minerals have been widely studied for CO<sub>2</sub> capture (Huang *et al.*, 2010). Calcium oxide (CaO) can react stoichiometrically with CO<sub>2</sub> at high temperatures to form calcium carbonate (CaCO<sub>3</sub>) which can be regenerated to CaO upon thermal decarbonation. The exothermic carbonation reaction and endothermic decarbonation form a cyclic process. The major challenge of this cycle in practical applications is the sharp decay of total reversibility with cycles (Abanades and Alvarez, 2003; Alvarez and Abanades, 2005a, b). The deactivation is due to the decrease of available surface area for carbonation, leading to an increasing thickness of CaCO<sub>3</sub> on CaO.

In recent publications, the improvement of CO<sub>2</sub> adsorption capacity and cyclic performance of the calcium-based adsorbents are proposed by (1) reactivation by steam hydration, (2) incorporation of inert materials, and (3) modification of pore structure. Manovic and Anthony (2007, 2008) demonstrated that the reactivation of CaO by steam hydration process could lead to an increased pore volume and an improvement of cyclic performance. Though the enhancement of the stability of sorbents in cyclic runs can be achieved via the incorporation of inert materials such as alkali metals, MgO, NaCl, CaTiO<sub>3</sub>, *etc.* with CaO (Aihara *et al.*, 2001; Salvador *et al.*, 2003; Roesch *et al.*, 2005), some additives were found to be destructive or disadvantageous to the stability of adsorbents (Hasler *et al.*, 2003; Lu *et al.*, 2006) and to increase equipment capacity as well as operation cost. The modification of pore structure could be achieved by incorporation of Al into CaO to form mayonite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) (Li *et al.*, 2006; Martavaltzi and



1: Propane tank; 2: Coil; 3: Syringe pump; 4: Valves; 5: Reactor; 6: Pressure gauge; 7: Thermocouple; 8: Heating tape; 9: Ice bath; 10: Oven.

**Fig. 4.** SC-propane grafting apparatus.



**Table 5.** CO<sub>2</sub> adsorption capacities and operating conditions for amine-grafted supports.

Amine	Support		S (m <sup>2</sup> /g)	Adsorption Capacity		N content (mmol/g)	CO <sub>2</sub> /N	Operating condition		Method	Ref.
	Type	S (m <sup>2</sup> /g)		Capacity (mmol/g)	Capacity (mmol/g)			Gas composition	T (°C)		
APS	Silica gel	340	0.89	1.27	0.70	100% CO <sub>2</sub> (humid)	27	TPD-GC	Leal et al., 1995		
APS	Silica gel	340	0.41	1.27	0.32	100% CO <sub>2</sub>	27	TPD-GC	Leal et al., 1995		
APS	MCM-48	1389	2.05	2.3	0.89	100% CO <sub>2</sub>	RT	TPD-MS	Huang et al., 2003		
APS	MCM-48	1389	1.14	2.3	0.50	5% CO <sub>2</sub> in He	RT	TPD-MS	Huang et al., 2003		
APS	Silica xerogel	816	1.15	1.7	0.68	100% CO <sub>2</sub>	RT	TPD-MS	Huang et al., 2003		
APS	HMS	1125	1.59	2.29	0.69	90% CO <sub>2</sub> (humid) in Ar	20	TGA	Knowles et al., 2005		
APS	SiO <sub>2</sub> gel	567	0.68	1.14	0.60	90% CO <sub>2</sub> (humid) in Ar	20	TGA	Knowles et al., 2005		
APS	SBA-15	204	0.41	-	-	4% CO <sub>2</sub> (humid) in He	25	TPD-MS	Chang et al., 2003		
APS	SBA-15	204	0.22	-	-	4% CO <sub>2</sub> in He	25	TPD-MS	Chang et al., 2003		
APS	SBA-15	204	0.73	-	-	10% CO <sub>2</sub> (4% D <sub>2</sub> O) in Ar	25	TPD-MS	Khatri et al., 2006		
APS	SBA-15	820	0.66	2.61	0.25	15% CO <sub>2</sub> (12% H <sub>2</sub> O) in He	60	GC-TCD	Hiyoshi et al., 2005		
APS	MCM-41	1188	0.83	2.35	0.35	100% CO <sub>2</sub>	25	TGA	Kim et al., 2008		
APS	MCM-41	864	0.39	2.02	0.15	5% CO <sub>2</sub> in N <sub>2</sub>	30	TGA	Chang et al., 2009		
APS	SBA-15	782	0.45	1.89	0.21	5% CO <sub>2</sub> in N <sub>2</sub>	30	TGA	Chang et al., 2009		
APS	SBA-15	782	1.02	1.89	0.60	15% CO <sub>2</sub> (78% RH) in N <sub>2</sub>	60	TGA	Chang et al., 2009		
APS	SBA-15	782	1.06	1.89	0.63	15% CO <sub>2</sub> in N <sub>2</sub>	60	TGA	Chang et al., 2009		
APS	PE-SBA-15	655	0.15	1.59	0.10	5% CO <sub>2</sub> in N <sub>2</sub>	30	TGA	Chang et al., 2009		
2N-APS	SBA-15	-	0.79	-	-	10% CO <sub>2</sub> (4% H <sub>2</sub> O) in He	25	TPD-MS	Khatri et al., 2005		
2N-APS	SBA-15	820	1.51	4.61	0.33	15% CO <sub>2</sub> (12% H <sub>2</sub> O) in He	60	GC-TCD	Hiyoshi et al., 2005		
2N-APS	SBA-15	782	2.09	3.25	0.64	15% CO <sub>2</sub> (78% RH) in N <sub>2</sub>	60	TGA	Chang et al., 2009		
2N-APS	SBA-15	782	1.73	3.25	0.53	15% CO <sub>2</sub> in N <sub>2</sub>	60	TGA	Chang et al., 2009		
2N-APS	SBA-16	479	0.73	3.06	0.24	15% CO <sub>2</sub> in N <sub>2</sub>	60	TGA	Wei et al., 2008		
3N-APS	HMS	1268	1.34	4.57	0.29	90% CO <sub>2</sub> (humid) in Ar	20	TGA	Knowles et al., 2006		
3N-APS	SiO <sub>2</sub> gel	567	1.05	2.64	0.40	90% CO <sub>2</sub> (humid) in Ar	20	TGA	Knowles et al., 2006		
3N-APS	SBA-15	820	1.80	5.80	0.31	15% CO <sub>2</sub> (12% H <sub>2</sub> O) in He	60	GC-TCD	Hiyoshi et al., 2005		
3N-APS	SBA-15	782	3.06	3.68	0.83	17% CO <sub>2</sub> (78% RH) in N <sub>2</sub>	40	TGA	Chang et al., 2009		
3N-APS	SBA-15	782	2.74	3.68	0.74	17% CO <sub>2</sub> in N <sub>2</sub>	40	TGA	Chang et al., 2009		
3N-APS	PE-MCM-41	1230	2.51	7.90	0.32	5% CO <sub>2</sub> (74% RH) in N <sub>2</sub>	25	TGA-MS	Serna-Guerrero et al., 2010d		
3N-APS	PE-MCM-41	1230	2.05	7.90	0.26	5% CO <sub>2</sub> in N <sub>2</sub>	25	TGA-MS	Serna-Guerrero et al., 2010d		

Lemonidou, 2008; Wu *et al.*, 2008). Those obtained materials exhibited high adsorption capacities over 5 mmol/g in a temperature range from 600 and 700°C and long-term stability in cyclic runs which was attributed to the presence of  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  as the binder which inhibited the sintering of CaO particles. Fan's group generated a mesoporous structured CaO from the precipitated  $\text{CaCO}_3$  which was synthesized by reacting  $\text{Ca}^{2+}$  ions with  $\text{CO}_3^{2-}$  ions in water. A high adsorption capacity of 14 mmol/g could be achieved (Gupta and Fan, 2002; Yu and Fan, 2011). Our group successfully synthesized CaO-based mesoporous adsorbents containing different amount of Ca in SBA-15 (Huang *et al.*, 2010). A limited amount of Ca ions could be well dispersed to form small CaO particles onto the surface and pore of SBA-15 which provided a stable framework inhibiting deactivation of CaO. The resultant CaO-modified SBA-15 was found to possess high adsorption capacity and long-term durability for  $\text{CO}_2$  capture.

### Regeneration Process

On account of industrial application, an effective and less energy-consumed regeneration of the  $\text{CO}_2$  captured adsorbents is definitely needed to develop. The regeneration techniques include (1) pressure swing adsorption (PSA), (2) vacuum swing adsorption (VSA), (3) temperature swing adsorption (TSA), (4) electric swing adsorption (ESA), the increase of temperature by conducting electricity through the conductive adsorbents; (5) pressure and temperature hybrid process (PTSA), and (6) washing (Olajire, 2010).

In PSA, adsorption is typically performed at pressures higher than atmospheric pressure, while desorption is performed at atmospheric pressure. In VSA, adsorption operates at atmospheric pressure and near-room temperature and desorption operates at lower pressures. Both PSA and VSA are performed by altering the pressures. Generally, the adsorbents with high adsorption capacity and high selectivity toward  $\text{CO}_2$  are preferred. Recent researches have focused on the new adsorbent development, process optimization, and equipment innovation for PSA and VSA processes (Kikkinides and Yang, 1993; Chue *et al.*, 1995; Ho *et al.*, 2008; Li *et al.*, 2008; Dasgupta *et al.*, 2009; Zhang *et al.*, 2009a; Dasgupta *et al.*, 2012; Grande *et al.*, 2012; Krishna and Long, 2012; Krishna and van Baten, 2012; Krishna, 2012; Liu *et al.*, 2012; Lopes *et al.*, 2012; Rezaei and Webley, 2012; Ribeiro *et al.*, 2012). Yang's group studied the feasibility of the PSA process for the first time to concentrate and recover  $\text{CO}_2$  from the flue gas using AC, carbon molecular sieve (CMS), and zeolite 13X as adsorbents (Kikkinides and Yang, 1993; Chue *et al.*, 1995). They compared zeolite 13X and AC by the heat of adsorption, working capacity, purge requirement, and equilibrium selectivity, and concluded that the former adsorbent was a better adsorbent for bulk separation of  $\text{CO}_2$  from the flue gas. Krishna and coworkers examined a variety of MOFs by PSA process due to the flexible framework exhibiting large pressure-dependent changes in pore volume (Krishna and Long, 2012; Krishna and van Baten, 2012; Krishna, 2012). Webley and coworkers presented an optimization methodology and results for the

structure of adsorbents at a pore level by evaluating the effect of pore geometry, size and overall adsorbent porosity on ultimate working capacity of adsorbents applied in PSA process (Rezaei and Webley, 2012). Dasgupta *et al.* (2009) studied PEI impregnated SBA-15 as an adsorbent used in a single column five-step PSA, which was found to be comparable with reported commercial zeolite adsorbents in literature. Rodrigues and coworkers investigated the integration of PSA process by altering the operation stages and steps. The performance parameters of each proposed process, such as  $\text{CO}_2$  purity,  $\text{CO}_2$  recovery, and power consumption, were evaluated and compared with those of other processes reported previously in the literature (Liu *et al.*, 2012; Lopes *et al.*, 2012; Ribeiro *et al.*, 2012). Ho *et al.* (2008) examined the economic feasibility of  $\text{CO}_2$  capture from power-plant flue gas by PSA process. Zhang *et al.* (2008) made a comparison between 6 and 9 step cyclic operations with their VSA systems. They demonstrated that the power consumption and  $\text{CO}_2$  capture cost are significantly influenced by adsorbent type, process configuration, and operating parameters such as feed gas pressure, vacuum pressure, temperature, and extents of purge.

In TSA, the regeneration is achieved by hot air or steam. The regeneration time is in general longer than PSA. Chuang and his coworker carried out the TSA process using solid amine in a dual column. One adsorbent bed column was expected to capture more than 90% of  $\text{CO}_2$  from the flue gas at 30–40°C and the other one was regenerated at 120–135°C to produce more than 99% purity of  $\text{CO}_2$ . To achieve continuous removal of the  $\text{CO}_2$  from the flue gas, a number of dual columns were necessary which depended on the time needed for  $\text{CO}_2$  adsorption, sorbent regeneration, and cooling of the regenerated column as well as specific  $\text{CO}_2$  adsorption capacity of adsorbents (Fisher *et al.*, 2009). Schladt *et al.* (2007) applied a statistical overview method called the Taguchi fractional factorial experiment to evaluate the importance of variables to a packed bed TSA system with a amine-impregnated PMMA adsorbent. Eight variables were considered, including cycle time (15–20 min), feed  $\text{CO}_2$  concentration (6–9 mmHg), adsorption temperature (25–30°C), gas residence time (1.7–3 s), desorption temperature (50–60°C), desorption pressure (26–93 mmHg), inlet dew point (0–25°C), and amine type (TEPA and E-100). They identified desorption pressure (9–93 mmHg) and desorption temperature (30–60°C) as the most significant factors affecting capture in the supported amine system. Pirngruber *et al.* (2009) simulated the breakthrough curves to evaluate the diffusion rate of  $\text{CO}_2$  and discussed the design of a potential adsorption process. They demonstrated that desorption by heating with water vapor (TSA) was not very favorable, due to the high vapor consumption needed for heating the column. Moreover, the time needed for regeneration was much longer than the adsorption step since the thermal inertia resulted in long heating and cooling times. Therefore, the total number of columns in a regeneration mode for each column would be largely increased. Clause and coworkers demonstrated the experimental and numerical parametric studies on the performance of zeolite (13X and 5A) in



indirect TSA processes by means of an internal heat exchanger. They reported that a purity above 95% could be achieved with a CO<sub>2</sub> recovery of 81%, CO<sub>2</sub> adsorption capacity of 1.31 mmol/g, and a specific energy consumption of 3.23 GJ/tonne CO<sub>2</sub>. Their results showed that this process exhibited potential as compared with other adsorption processes (Merel *et al.*, 2008; Clausse *et al.*, 2011). Kulkarni and Sholl (2012) estimated a specific TSA process and suggested the operating cost to be of the order 80–150 US\$/tonne CO<sub>2</sub>. They also demonstrated the monetary cost as a function of increasing CO<sub>2</sub> adsorption capacity of the adsorbent. The cost of CO<sub>2</sub> capture can be decreased to 50–80 US\$/tonne CO<sub>2</sub> for different sources of electricity by maintaining the CO<sub>2</sub> adsorption capacity to 2 mmol/g.

Recently, some researchers have studied the use of a hybrid pressure (or vacuum)/temperature swing adsorption (PTSA or VTSA) process to improve CO<sub>2</sub> capture. Pugsley *et al.* (1994) studied the performance of PTSA theoretically, which could achieve 90% purity with 70% recovery. Ishibashi *et al.* (1996) investigated a VTSA to capture CO<sub>2</sub> from the flue gas in a pilot plant at 1000 Nm<sup>3</sup>/h. The cycle was composed of adsorption at atmospheric pressure and desorption at 50–100 mbar and 50–100°C. Lu *et al.* (2009) use the 2N-APS grafted mesoporous spherical-silica particles (MSP) under a TSA process with a regeneration temperature of 120°C and a VSA process. They suggested that the combination of thermal and vacuum could improve desorption rate. Tlili *et al.* (2009) also studied the use of VTSA and could achieve 99% purity for both VSA and TSA processes. They concluded that the recovery depended on desorption temperature and purge flow rate.

In ESA, heat is generated by Joule effect via electric current passing through the adsorbents. The in situ heating route can effectively deliver heat to adsorbents without heating the additional media, thus ESA offers several advantages including less heat demanded, fast heating rate, better desorption kinetics and dynamics and independent control of gas and heat flow rates as compared with PSA and TSA (An *et al.*, 2011). Grande and his coworkers have reported several works on ESA for CO<sub>2</sub> capture by monolith activated carbon, carbon molecular sieves, and zeolite-based adsorbents (Grande and Rodrigues, 2008; Grande *et al.*, 2009; Ribeiro *et al.*, 2011). They proposed the process without cooling step and simulated that the recovery and purity of CO<sub>2</sub> at 80% can be reached with an energy consumption of 2.04 GJ/tonne CO<sub>2</sub>, which is equivalent to 4.08 GJ/tonne CO<sub>2</sub> of heat in a power plant with 50% efficiency. They also showed the seven steps operation and reported that a purity of 89.7%, recovery of 70%, and energy consumption of 1.9 GJ/tonne CO<sub>2</sub> was obtained by this process. However, relatively low CO<sub>2</sub> adsorption capacity and selectivity at the CO<sub>2</sub> partial pressure below 10 kPa were observed as well. Our group focused on ESA for CO<sub>2</sub> capture by activated carbon fiber cloth (ACFC). Though the modifications of ACFC by aminosilane grafting, alkanolamine impregnation, and calcination under NH<sub>3</sub> were found to improve CO<sub>2</sub> adsorption capacity and cyclic performance, the CO<sub>2</sub> adsorption capacity was not comparable with that of the mesoporous adsorbents grafted

with amines. Hence, further research is required to make ESA in practical application.

## CONCLUSIONS

Owing to huge amount of the flue gases needs to treat and low CO<sub>2</sub> partial pressure in flue gas for post-combustion power plants, chemical absorption is definitely more suitable than physical absorption to achieve CO<sub>2</sub> capture purpose. However, chemical absorption is an energy intensive process in which more than 60% of total energy consumed in stripper for thermal regeneration of CO<sub>2</sub>-rich chemical absorbents. To make chemical absorption practical application, the future research should focus on the improvements of absorbent formulation and process efficiency. To achieve the purpose, the following approaches are suggested to undergo: (1) to use absorbents with less corrosion, less viscosity, low vapor pressure, rapid reaction rate with CO<sub>2</sub>, high CO<sub>2</sub> absorption capacity, and less regeneration energy, a compromised formulation is needed because all the mentioned properties may not be satisfied in the meantime, (2) to enhance high gas-to-liquid mass and heat transfer rates in absorber and stripper, (3) to reduce equipment volume and capital cost, (4) to prevent the negative effects of SO<sub>x</sub>, NO<sub>x</sub>, and oxygen on absorbent, and (5) to develop a more suitable model for the scale up purpose. In respect to these concerns, the absorbents should not be limited to alkanolamines but ionic liquid and other alkaline absorbents as well as the mixtures are also needed to test their potential. For absorption operation, a rotating packed bed, also called Higee, has been proved to possess higher mass and heat transfer rates and smaller height of transfer unit than those of a packed bed, this kind of operation is therefore deserved to pay more attention to verify its practical applicability.

Physical adsorption is most suitable for CO<sub>2</sub> capture at high pressures and low temperatures, it is therefore not particularly applicable for the post-combustion CO<sub>2</sub> capture. On the other hand, chemically modified adsorbents have been proved to be feasible. Among the proposed adsorbents, amine-based chemical adsorbents with large surface area and high amine content have been extensively investigated due to their large CO<sub>2</sub> adsorption capacity, high adsorption and desorption rates, high tolerance to moisture, and high selectivity towards CO<sub>2</sub> over other gases. To make chemically modified adsorbents practical application, the following works are purposed to carry out: (1) to synthesize porous supports allowing to load more amines onto supports, (2) to use amines with high nitrogen content and high accessibility to CO<sub>2</sub>, (3) to develop more effective means for loading amine onto support, (4) to produce amine-based chemical adsorbents with high thermal stability, and (5) to develop one-pot synthesis technique for amine-grafted adsorbents. In view of regeneration of CO<sub>2</sub>-loaded adsorbents, though TSA is widely used currently, ESA offers several advantages over TSA such as less heat required and fast heating rate, it is therefore deserved to pay attention to. However, the development of suitable adsorbents with high CO<sub>2</sub> adsorption capacity is still demanded.

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