

# UNITED KINGDOM · CHINA · MALAYSIA

# DEPARTMENT OF CHEMICAL & ENVIRONMENTAL ENGINEERING

# DEVELOPMENT, CHARACTERISATION AND EVALUATION OF NOVEL APPROACHES TO IMPROVE THE LIFETIME PERFORMANCE OF AMINE-BASED MATERIALS FOR CARBON CAPTURE IN POWER PLANTS

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## Abstract

Carbon capture and storage (CCS) is considered to be one of the strategically important carbon abatement technologies that can be used to effectively reduce the carbon emissions from fossil fuel power plants and other large scale industrial processes, which are the major stationary sources of greenhouse carbon emissions. Compared to other capture technologies, solid adsorbents looping technology (SALT) based postcombustion carbon capture, an alternative to the state-of-the-art energy intensive amine scrubbing process, is widely viewed as being the most viable technology that can be used as either as a retrofit to existing power plants or new build capacity. The potential success of SALT technology is largely determined by the development of novel CO<sub>2</sub> adsorbents. Amine immobilized solid adsorbents are highlighted to be used in SALT technology due to their high  $CO_2$  selectivity ( $CO_2/N_2 > 1000$ ), suitable adsorption temperature and tolerance of moisture. Although they have so much advantages on carbon capture, the oxidation and degradation of solid amines are still a significant problem to be overcome. The degradation of the amine adsorbent can lead to a reduction in  $CO_2$  capture performance and selectivity, an increase in the process cost and corrosion problems. The aim of this project is to 1) develop new solid adsorbent materials with higher CO<sub>2</sub> capture ability and superior adsorptiondesorption lifetime performance; 2) to investigate effective measures to minimise or effectively prevent the thermal and oxidative degradation of the sorbent materials; 3) to explore approaches that can rejuvenate the degraded sorbents for re-use or convert them into other value-added products.

Firstly, a series of PEI-the porous siliceous cellular foams (SCF) adsorbents have been developed and characterised. The results show a relationship between the textural properties of SCF and CO<sub>2</sub> adsorption ability of adsorbents. A highly effective hydrothermal methodology was developed to produce extremely mesoporous silica materials with well-defined mesoporous structures and greatly increased pore volumes of up to  $3.2 \text{ cm}^3/\text{g}$ . The PEI adsorbents prepared using SCF-3-120-24 (1.6 cm<sup>3</sup>/g) was found to have CO<sub>2</sub> capture capacities of nearly 180.8 mg/g, which represents the highest adsorption capacity ever reported for supported PEI adsorbents.

Secondly, lifetime performance testing and strategies to mitigate the thermal-oxidative degradation of PEI adsorbents and rejuvenation of the degraded PEI was investigated. The presence of moisture and additives was seen to enhance the thermal-oxidative stability of PEI. Furthermore, the doping of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> hydrates can increase the cyclic adsorption-desorption lifetime performance of PEI adsorbent. Meanwhile, the CO<sub>2</sub> adsorption capacity of one heavily degraded PEI adsorbent was increased from 2.8 wt% to 6.2 wt% after rejuvenation test.

Finally, hydrous pyrolysis and a continuous flow reactor system was used in catalytic hydrotreatments and hydrothermal treatments of six model MEA degradation compounds and two degraded MEA solvents. Most of the model compounds and degraded MEA was converted to piperazine derivatives in a H<sub>2</sub> reaction atmosphere and pyrazine derivatives in NH<sub>3</sub> reaction atmosphere. Piperazines and pyrazines are a type of important pharmaceutical intermediates.

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### CHAPTER 1 GENERAL INTRODUCTION

Fossil fuels have long been the bedrock of our global energy system and will continue to dominate our energy supply for the foreseeable future (Fig. 1.1). However, over the past century, human activities have produced vast amounts of greenhouse gas emissions, and the majority of these emissions, typically  $CO_2$ , arise from the burning fossil fuels for heat and power generation. Since the industrial revolution,  $CO_2$ emissions released into the atmosphere have reached over 2000 Gt in total and continued to increase at an annual rate of ca. 30 Gt (Fu and Gundersen, 2012), with the concentration of  $CO_2$  in the atmosphere already increased to well over 400 ppm nowadays. Consequently, there is pressing need to reduce the greenhouse carbon emissions if the catastrophic irreversible climate change is to be avoided (Bert Metz, 2005).



Fig. 1.1 The trend of world energy consumption by different sources (BP, 2017).

The UN Intergovernmental Panel on Climate Change (IPCC) predict in its reports that in a business as usual scenario, the atmospheric CO<sub>2</sub> concentration would increase to 1200 ppm, and consequently, the Earth's global temperature would rise by 6 °C, an increase that would lead to severe consequences to the Earth's whole climate system (IPCC, 2007). IEA reports highlight that should the rise in global surface temperature be stabilised below 2 °C, an agreed climate change target by 2100, the atmospheric CO<sub>2</sub> concentration must be limited to below about 450 ppm by 2100. To achieve this target, the CO<sub>2</sub> concentration should be halved from the level in 2005 and no more than one third of fossil fuel reserves should be consumed by 2050 (IEA, 2010, IEA, 2007).

Carbon abatement technologies are a group of approaches that can allow for the continual use of fossil energy with substantially reduced greenhouse carbon emissions. They include fuel switching to less carbon intensive fuels (e.g. natural gas and biomass), higher energy efficiency, and in particular, carbon capture and storage (CCS). CCS is widely regarded as a critically important technology that can dramatically cut CO<sub>2</sub> emissions without compromising energy security. L'Orange Seigo et al. (2014) estimates that by 2050, more than 3000 CCS projects is be required around the world in order to achieve the target of 50% of reduction in CO<sub>2</sub> emissions (L'Orange Seigo et al., 2014). CCS involves three technical stages, including CO<sub>2</sub> capture from power plants and other large industrial processes, CO<sub>2</sub> compression for transportation and then the injection of CO<sub>2</sub> into deep geological formations for permanent storage. Of these three CCS stages, carbon capture represents over 70% of the total CCS cost. Therefore, the successful development of effective capture technologies plays a key role in the eventual deployment of CCS technologies. Fig. 1.2 shows the chain of CCS process for fossil fuel fired power stations (Haszeldine, 2009).



Fig. 1.2 Diagrammatic representation of the CCS technology at power plants and storage of CO2 in porous rocks (Haszeldine, 2009).

The  $CO_2$  should be compressed to reduce the volume in order to reduce the cost of transportation (Bert Metz, 2005). The main approaches of  $CO_2$  transportation are pipelines system for short distances and shipping for long distances, due to the high cost of long pipelines. The pipeline network for CO<sub>2</sub> transportation represents a major investment in the whole CCS infrastructure. The geological formations for safe and permanent CO<sub>2</sub> storage include depleted oil and gas fields, saline aquifers, unmineable coal seams, and saline-filled basalt formations (Institute, 2010). There are four main methods to sequestrate CO<sub>2</sub>: geological storage, ocean storage, mineral carbonation and industrial utilization. Of these CO<sub>2</sub> storage options, geological and ocean storage are considered to be the most feasible approaches. Ocean storage can transfer CO<sub>2</sub> to the deep ocean at depths of below 3000 m due to the liquid CO<sub>2</sub> being denser than the sea water at such depths. Compared with the fossil fuel resources, ocean storage obviously has enough capacity for CO<sub>2</sub>, but it has a negative impact on the marine ecosystem as a result of the potentially significant increase in the acidity of ocean water (IPCC, 2005). The basic idea of geological storage is to inject CO<sub>2</sub> into the underground geological formations. The geological storage sites can be categorised as either non-value added and value-added sites. The difference between these two is: the usefulness of non-value-added sites is just to store CO<sub>2</sub>, such as deep saline formations. Moreover, the non-value-added sites are a good chance of long-term CO<sub>2</sub> storage. Value added CO<sub>2</sub> geo-storage approaches include enhanced oil recovery and enhanced gas recovery. In EOR technology, the CO<sub>2</sub> is injected into the oil field as a means to reduce the viscosity of the oil, and pushes the oil and gas to the producing well so as to improve the oil recovery rate (Muggeridge et al., 2014). The major concern of EOR and EGR is that the reaction between CO<sub>2</sub> and minerals and/or rocks can potentially release heavy metal ions into the underground aquatic systems.

Therefore, the United States Environmental Protection Agency (EPA) regulates EOR wells as Class II wells which need to be injected with fluids associated with oil and natural gas production to protect drinking water resources (EPA, 2010).

For the whole CCS chain, carbon capture represents the most costly element as it accounts for over 70% of total CCS cost and as a result (Leung et al., 2014), the successful development and deployment of effective capture technologies essentially determines the overall economics and hence the affordability of CCS. At present, aqueous amine scrubbing, which was originally developed for natural gas sweetening and has been used in oil and gas industry for over 60 years (Rochelle, 2009), is the state-of-the-art capture technology, but it suffers from a range of technical and operational issues should it be used for carbon capture from power plant and industrial flue gases due to the hostile flue gas conditions, such as its energy penalty, low process efficiency, solvent corrosion and degradation and the hazardous emissions of both amines and degradation products (Dumée et al., 2012). Consequently, more energyefficient and cost-effective capture technologies have to be developed. Reflecting on the major challenges of CCS, this research has been aimed to develop an alternative capture technology based on using solid CO<sub>2</sub> adsorbents rather than aqueous amine solvents, with the particular focus being the development of novel CO<sub>2</sub> adsorbents with high reversible adsorption capacity and fast adsorption kinetics. This has been followed by the development of effective strategies to mitigate the degradation of CO<sub>2</sub> sorbents and novel approaches to rejuvenate the degraded amine sorbents or convert them to other value-added products. A variety of advanced characterisation tools have been used to characterise the properties of different CO<sub>2</sub> sorbents or the products from

sorbent rejuvenation strategies to unveil the relationship or factors that govern the  $CO_2$ adsorptive properties and life-time performance of different  $CO_2$  adsorbents.

## **CHAPTER 2. Literature Review**

CCS technologies are considered to be technically feasible at commercial scale to reduce  $CO_2$  emission and the greenhouse effect. Chapter 2 will give a detailed literature review relevant to CCS. More specifically, Sections 2.1 will provide an introduction of carbon capture technologies, including oxy-fuel combustion, precombustion and post-combustion capture technology, with the  $CO_2$  separation technologies described in Section 2.2. Importantly, Section 2.3 will then demonstrate the development of solid adsorbents, which include the recent progress and the state of the art solid adsorbents that are applied for  $CO_2$  capture technologies.

### 2.1 Carbon capture and storage technologies

Fig. 2.1 presents the three major carbon capture technologies, namely oxy-fuel combustion, pre-combustion and post-combustion capture. The characteristics of each, and the associated major issues are discussed below.



Fig. 2.1 Main separation processes for post-combustion, pre-combustion and oxycombustion.(Vaseghi, 2012).

#### 2.1.1 Oxy-fuel combustion capture technology

Oxy-fuel combustion, as illustrated in Fig. 2.2 is the process of fuel combustion in a mixture of  $O_2$  and  $CO_2$ . There are three sections in the oxy-fuel combustion technology, including 1) air separation, 2) combustion and 3) cleaning and  $CO_2$  capture. In the air separation phase, the pure  $O_2$  is separated from the air through the air separation unit (ASU), which can divide air to liquid oxygen, gaseous nitrogen and other trace components. The oxygen concentration in the oxygen stream can reach 95 to 99% after ASU (Spigarelli and Kawatra, 2013). After air separation, the oxygen stream is transferred to the boiler with recycled  $CO_2$  that is the flue gas after particulate matter removal for the energy conversion. The aim of adding recycled  $CO_2$  to the oxygen stream is to reduce the temperature of combustion, because the flame temperature for pure  $O_2$  can be as high as 3500 °C, which exceeds the bearing capacity of traditional furnace materials.

According to the study from Bert Metz, a gas mixture with 30-35% of  $O_2$  and 65-70% of recycled  $CO_2$  can be used to simulate the flame temperature regarding to combustion in an air atmosphere (Bert Metz, 2005). The flue gas after combustion contains  $CO_2$  (75-80%), H<sub>2</sub>O, other trace gases and particulate matter. In the stage of the cleaning and  $CO_2$  capture, the electrostatic precipitator (ESP), desulphurization (FGD) and cooler is used to remove particulate matter, SO<sub>2</sub> and H<sub>2</sub>O. After cleaning, the level of  $CO_2$  concentration in the flue gas can reach 80-90% (Wall et al., 2013, Buhre et al., 2005, Bert Metz, 2005).

The main advantages of oxy-fuel combustion is its capability to produce a flue gas stream highly enriched in  $CO_2$  almost ready for storage and the potential saving of de-SOx and de-NOx systems due to the drastically reduced flue gas volumes because of the use of oxygen ( $O_2$ ) as opposed to air for combustion. (Jia et al., 2010). However, the production of oxygen from air separation is cost-prohibitive at present and major cost reductions in air separation are required. In addition, due to the change of combustion environment, the characteristics of oxy-fuel combustion and their impact on heat transfer, mineral transformation and ash formation behaviour of coals and resultant operational issues still need to be better understood, despite a considerable number of demonstrations at various scales (Figueroa et al., 2008, Bolland and

Undrum, 2003). Oxy-fuel combustion can be used in both new build power plants and as a retrofit to existing power plants (Figueroa et al., 2008).



Fig. 2.2 The basic process flow diagram for oxy-fuel combustion capture (Markewitz et al., 2012).

### 2.1.2 **Pre-combustion capture**

Pre-combustion provides an approach to capture CO<sub>2</sub> from a synthesis gas (syngas) stream before combustion, which is usually applied to integrated gasification combined cycle (IGCC) power plants. Fig. 2.3 displays the flow diagram of a typical pre-combustion capture process. In IGCC power plants, the syngas of high temperature (typically over 1000 °C) and high pressure (ranging from 15 to 150 atm) is generated through gasification of the primary fuel, as seen in Equations (2.1) and (2.2). The syngas which contains H<sub>2</sub> (25-45%), CO (40-50%) and CO<sub>2</sub> (10-35%) flows into a shift reactor where CO is converted to CO<sub>2</sub>, seen in Equation (2.3) (Bert Metz, 2005).

$$C_{x}H_{y} + x H_{2}O = x CO + \left(x + \frac{y}{2}\right) H_{2}$$
 (2.1)

$$C_xH_y + \frac{x}{2}O_2 = x CO + \frac{y}{2}H_2$$
 (2.2)

$$CO + H_2 O = CO_2 + H_2 \tag{2.3}$$

After that, the stream enters a sulphur removal section, aiming at protecting the CO<sub>2</sub> separation equipment and pipeline from the corrosion of sulphur compounds. The CO<sub>2</sub>

is separated from the gas stream and  $H_2$  is then combusted in combined cycle gas turbine for power generation (Scholes et al., 2010).

Compared to conventional power plants, IGCC power plant represents a higher plant efficiency and greater flexibility since the synthesis gas can be applied in the chemicals manufacture (e.g. Methanlon) while  $H_2$  can be used in e.g. fuel cells (Markewitz et al., 2012). Moreover, the high CO<sub>2</sub> partial pressure generated in IGCC can result in a driving force for separation via efficient pressure swing processes, as well as other relevant technologies available for separation. Pre-combustion capture is not as mature as post-combustion or even oxy-fuel combustion capture due to the complexity of this process, although the CO<sub>2</sub> separation and subsequent compression in themselves appear to be easier to achieve thanks to the pressure involved in the process. The major challenges of pre-combustion capture include:

- 1. The nature of the integrated design of gasification restricts that Precombustion is most applicable for new builds instead of the existing plants where post-combustion capture is preferred.
- Due to the complication of process design, Pre-combustion technologies such as IGCC are not as mature as other capture technologies like postcombustion.
- 3. The gas turbine operator has merely been successful in the application of hydrogen fuel. Further research is required to extend its potential applications.



Fig. 2.3 Process flow diagram for pre-combustion capture (Scholes et al., 2010).

#### 2.1.3 Post-combustion capture

Post-combustion capture is defined as the removal of  $CO_2$  from the flue gas after fuel combustion. Fig. 2.4 shows the flow diagram of post-combustion capture process using aqueous solvent as the absorbent. After combustion, a cleaning stage is necessary to eliminate  $SO_x$ ,  $NO_x$  and particulate matter to prevent the sorbent degradation from reaction with  $SO_x$  or  $NO_x$ , and also the foaming phenomenon resulted from the particulate matter (Davidson, 2007). Then, the cleaned flue gas flows into the  $CO_2$  separation section which includes the  $CO_2$  absorption in the absorber and the regeneration of the absorbent in the regenerator (stripper). At last, the released  $CO_2$  is compressed, transferred and stored (Wang et al., 2011a).

Post-combustion capture is an "end-of-pipe" technology that can be applied in the majority of existing coal-fired power plants at ambient pressure (Chalmers and Gibbins, 2007), which is a significant advantage. However, due to the usage of air in the combustion stage, the main disadvantage of this technology lies in the low concentration of  $CO_2$  (typically less than 15%) (Pires et al., 2011, Figueroa et al., 2008).

Therefore, the success of this technology relies on the performance of efficient absorbents for carbon separation.



Fig. 2.4 Process flow diagram for post-combustion capture (Markewitz et al., 2012).
# 2.2 Carbon separation technologies for post-combustion capture

Carbon capture is essentially a  $CO_2$  separation process, Fig. 2.5 summarizes main approaches of  $CO_2$  separation, which can be divided into four different categories according to their separation mechanisms and/or chemistries involved: absorption, cryogenic separation, membrane separation and solid adsorption.



Fig. 2.5 Different carbon dioxide separation options.

Cryogenic, membrane and solid adsorption can be applied in all carbon capture methods; however, chemical absorption is mostly suitable for post-combustion capture due to the relatively low CO<sub>2</sub> partial pressures (Olajire, 2010, Yang et al., 2008, Mondal et al., 2012). Physical absorption however is particularly applicable to pre-combustion capture due to the pressures involved the gasification process.

#### 2.2.1 Absorption

As shown in Fig. 2.6, absorption technologies can be divided into two different categories: chemical absorption and physical absorption. Chemical absorption is the process to remove  $CO_2$  through the chemical reactions between  $CO_2$  and a solvent, such as monoethanolamine (Bonenfant et al., 2008) or other amine solvents, and it is the most commonly-applied technology for carbon separation in existing plants (Yang

et al., 2008). Taking MEA for an example, the main reactions between CO<sub>2</sub> and amine are as follows (Hongyi Dang, 2003):

$$2H_2O + CO_2 \rightleftarrows H_3O^+ + HCO^{3-}$$

$$(2.4)$$

 $H_2O + HCO^{3-} \rightleftharpoons H_3O^+ + CO_3^{2-}$  (2.5)

$$H_2O + MEAH \rightleftharpoons H_3O^+ + MEA$$
 (2.6)

 $MEA + H_2O + CO_3^{2-} \rightleftharpoons H_3O^+ + MEACOO^-$ (2.7)

Due to the reversibility of the above reactions, the captured  $CO_2$  can be released at higher temperatures and the regenerated aqueous amine absorbents are then recirculated back into the absorber, which forms the loop of absorption and desorption process (Sam Wong, 2002). Fig. 2.6 shows the flow diagram of a typical chemical absorption process.

MEA has been utilized as an absorbent for more than 70 years in the natural gas industry. The novel advantages of aqueous amine  $CO_2$  absorption include its high selectivity, the low viscosity of MEA absorbent, its high theoretical absorption capacity and low capital cost. However, the amine scrubbing process suffers from a range of drawbacks, such as its low  $CO_2$  loading capacity, potentially severe corrosion, thermal/oxidative degradation and in particular its high energy penalty (Fauth et al., 2005).

Apart from the amine absorbents, inorganic chemical solvents, such as the solution of sodium carbonate, can also be used. Inorganic solvent based  $CO_2$  capture approaches need lower energy because of the lower  $CO_2$  desorption temperature required. However, the reaction rates of inorganic solvents with  $CO_2$  are often considerably lower than those of amine absorbents (Institute, 2010).

Compared to the chemical absorption, the physical absorption of  $CO_2$  is based on Henry's law. Dimethyl-ethers of polyethylene glycol and retisol are typical physical absorbents, for which the  $CO_2$  capture process is often based on pressure swing (Wang et al., 2011a). Fig. 2.6 illustrates a typical physical absorption process. Generally, physical absorption process is a preferred capture technology for pre-combustion carbon capture, rather than post-combustion capture from coal fired power plants, which attributes to the low partial pressure of  $CO_2$  (less than 15% v/v) in the flue gas and the intensive energy consumption required for flue gas compression.



Fig. 2.6 The process of physical absorption (Institute, 2010).

# 2.2.2 Cryogenic separation

Cryogenic separation is a physical process for CO<sub>2</sub> separation by cooling down gas streams to very low temperatures (-73.3 °C) to condense out CO<sub>2</sub>, based on the different boiling temperatures of the involved gas species (Olajire, 2010). At atmosphere pressure, CO<sub>2</sub> has a boiling point of -56.6°C, compared to -10 °C for SO<sub>2</sub> and -253 °C for H<sub>2</sub>, respectively. Therefore, by cooling the flue gas down to temperatures below their boiling points, different gas species including CO<sub>2</sub> can be condensed sequentially. The benefit of cryogenic separation is that the product of this technology is liquid CO<sub>2</sub>, which is ready for pipeline transportation and storage. However, due to the high cost of refrigeration, cryogenic separation is not considered to be viable for pre and post combustion capture applications, although it is the only state-of-the-art air separation technology to produce the O<sub>2</sub> required for oxy-fuel combustion (Wang et al., 2011a).

#### 2.2.3 Membrane separation

Selective gas membrane separation and gas absorption membranes are two typical membrane separation technologies. The selective gas membrane is polymeric or/and ceramic membranes. The efficiency of this membrane depends on the size of molecules and the membrane material.  $CO_2$  passes through the membrane when the flue gas goes along the membrane and the pressure of  $CO_2$  is lower than the pressure of flue gas (IEA, 2004). Multistage separation is often required in order to get high purity  $CO_2$ , which leads to high capital investment and operational cost. Fig. 2.7 demonstrates the principle of the selective gas membrane separation (McKee, 2002).

Compared with the selective gas membrane separation, gas absorption membranes technology must contain chemical absorbents in its structure. Fig. 2.8 shows the principles of gas absorption membranes (McKee, 2002). The absorbents solution flows opposite direction of the flue gas and enters from other side of the membrane. The membrane is micro-porous material, which make  $CO_2$  easier pass through the membrane. Then, the absorbent is transferred to a stripper where the material is regenerated and  $CO_2$  is recovered. The gas absorption membrane technology can protect the devices from flooding, entertainment, channelling or foaming due to the compact structure of the tank (Favre, 2007). The efficiency of gas absorption membranes technology is suitable for pre-combustion capture and air separation in oxy-fuel combustion capture systems.



Fig. 2.7 Principle of selective gas separation membrane (McKee, 2002).



Fig. 2.8 Principle of gas absorption membrane (McKee, 2002).

## 2.2.4 Solid adsorption

Solid adsorption can be a physical process, or a combination of physical and chemical processes where CO<sub>2</sub> is adsorbed onto the surface of an adsorbent material which has high affinity to CO<sub>2</sub>. Therefore, the solid adsorbents must have a high surface area with an extremely porous structure. Activated carbon, metal-organic frameworks (MOFs) and metallic oxides can be used as candidate adsorbent materials. Based on the adsorption characteristics of different adsorbents and flue gas conditions, different solid adsorbent based carbon capture process can be used, such as pressure swing adsorption (PSA), temperature swing adsorption (TSA) and electric swing adsorption (Hesas, 2013, Institute, 2010). The criteria for selecting adsorbent materials and detailed description of different solid adsorption will be further discussed in Section 2.4.

# 2.3 Amine absorption

Amine based absorbents are widely deployed for post-combustion capture, based on the reaction between  $CO_2$  and amines, with amines classified into primary, secondary and tertiary amines (Choi, 2009). Primary amine are the most studied, with MEA is the benchmark molecule in these studies (Davis and Rochelle, 2009). Meanwhile, other amines studied include diethanolamine (Demessence, 2009), methyldiethanolamine (MDEA) (Gouedard et al., 2012), et al. In this Section, the reaction mechanisms and limits of amine absorption are discussed.

## 2.3.1 Reaction mechanisms

The reaction mechanism between  $CO_2$  and primary and secondary amines is described by the carbamate mechanism, while the reaction of  $CO_2$  with tertiary amines is illustrated by the base-catalyzed hydration of  $CO_2$  (Vaidya and Kenig, 2007).

## Carbamate mechanism

Caplow and Danckwerts proposed the mechanism in two steps in blow (Danckwerts, 1979, Caplow, 1968):

Step 1: Carbamate formation (R<sub>1</sub> and R<sub>2</sub> is alkanes or H)

$$CO_2 + R_1 R_2 NH \leftrightarrow R_1 R_2 NCOO^- + H^+$$
(2.8)

Step 2: Protonated alkanolamine formation

$$H^{+} + R_1 R_2 N H \leftrightarrow R_1 R_2 N H^{+}$$
(2.9)

The sum of reactions represented by Equation 2.8 and 2.9

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH^+$$
(2.10)

Base-catalyzed hydration of CO2

In the aqueous solutions, the tertiary alkanolamines  $(R_3N)$  cannot react with CO<sub>2</sub> directly, rather such amines have a base-catalyzed hydration of CO<sub>2</sub>, which is represented as (Vaidya and Kenig, 2007)

$$R_3N + H_2O + CO_2 \leftrightarrow R_3N^+H + HCO3^-$$
(2.11)

Primary and secondary alkanolamines can react directly and rapidly with  $CO_2$  via a so-called carbamate mechanism. However, the reaction heat of the carbamate formation is high, leading to high solvent regeneration temperatures. Moreover, the maximum  $CO_2$  loading capacity of primary and secondary alkanolamines is 0.5 mol of  $CO_2$  per mol of amine. In the base-catalyzed hydration of  $CO_2$ , the tertiary amines react with  $CO_2$  to form bicarbonates in the aqueous solutions. Meanwhile, the heat of absorption associated with the bicarbonates formation is lower than the carbamate formation, which results in relatively smaller regeneration costs. Further, the  $CO_2$  loading capacity of tertiary amines is 1 mol of  $CO_2$  per mol of amine, which is stoichiometrically advantageous than the carbamate mechanism by primary and secondary amines. It was reported that the tertiary amine absorption rates can be improved by the addition of primary or secondary amines (Vaidya and Kenig, 2007).

## 2.3.2 Limitation of amine absorbent

The main limitation of amine absorbents is the degradation of the adsorption/desorption process. There are two kinds of amine degradation: thermal degradation and oxidative degradation. Degradation of amine absorbents can reduce the carbon capture capacity,  $CO_2$  selectivity and regeneration and recycling stability and so increase the cost of the process.

#### 2.3.2.1 Thermal degradation

The thermal degradation of amine absorbents is caused by a range of side reactions occurring during the absorption and desorption process and the involved mechanisms are normally quite complex. Random scission or cross-linking is often involved during the thermal molecular restructuring and transformation (Amancio-Filho et al., 2008). The mechanisms of the thermal degradation to form open-chain urea and cyclic urea are different, as shown in Fig. 2.9. For the formation of open-chain urea, there are two

ways to generate urea from carbamic acid. In route 1, carbamic acid produces isocyanate by dehydration reaction firstly. Next, the isocyamate reacts with R<sub>1</sub>R<sub>2</sub>NH (R<sub>1</sub> and R<sub>2</sub> is alkanes or H) to form urea, which leads to the loss of amine reactivity with CO<sub>2</sub>. Compared with route 1 reaction, the carbamic acid reacts with another amine (R<sub>1</sub>R<sub>2</sub>NH) to ammonium carbamate in route 2. In the formation of cyclic urea, the carbamic acid can generate different cyclic urea by reacting with different olefin. Both open-chain urea and cyclic urea can be generated in the thermal degradation process of MEA. Table 2.1 shows the main products of MEA thermal degradation. The N.N'-bis-(2-hydroxyethyl) urea is one of the typical products of MEA thermal degradation via the reaction pathway A while N-(2-hydroxyethyl)imidazolidin-2-one (HEIA) is the product of thermal degradation pathway B. Furthermore, Lepaumier et al. (Lepaumier, 2009) reported that thermal degradation without  $CO_2$  in high temperature could cause dealkylation, dimerisation and cyclisation. M-(2hydroxyethyl)ethylenediamine (HEEDA) is the product of MEA thermal degradation by this mechanism. Meanwhile, HEEDA reacts with CO<sub>2</sub> to inidazolidi-2-one by intramolecular cyclisation. HEEDA reacts with OZD to trimer, which can react with CO<sub>2</sub> to form AEHEIA through dehydration. The further degradation products derived from HEEDA are shown in Table 2.2.



Fig. 2.9 The mechanisms of thermal degradation in the adsorption/desorption process (Sayari et al., 2012).



Table 2.1 The main MEA thermal degradation products (Gouedard et al., 2012).





#### 2.3.2.2 Oxidative degradation

Oxidative degradation is caused by the reaction between amine and the  $O_2$  present in the flue gas with or without the participation of other flue gas components, such as NO<sub>x</sub> and SO<sub>x</sub>. Fig. 2.10 shows the mechanisms of the MEA oxidative degradation. Lepaumier proposed that ethylene oxide react with water into ethylene glycol after the formation of ethylene oxide and ammonia from MEA oxidation (Lepaumier, 2009). Ethylene glycol is then oxidised into aldehydes, and the latter rapidly react with O<sub>2</sub> to yield carboxylic acids. These acids can react irreversibly with amines to generate salts, which can increase the degradation ratio. A variety of products can be formed from the oxidative degradation of aqueous amine sorbents, such as oxalic acid and glycine acid, glyoxal acid, formic acid and CO<sub>2</sub>. Table 2.3 shows the main products formed from MEA Oxidative degradation (Gouedard et al., 2012). The main oxidative degradation products are usually characterised by the presence of oxygen-containing functionalities, such as hydroxyl, carbonyl, carboxyl and ester.



Fig. 2.10 Two general mechanisms of MEA oxidative degradation (Gouedard et al., 2012).

Chemical structure	Name (abbreviation)	M <sub>w</sub> (g/mol)
NH <sub>3</sub>	Ammonia	17
н	Formaldehyde	30
H <sub>3</sub> C-NH <sub>2</sub>	Methylamine	31
H	Acetaldehyde	44
H NH2	Formamide	45
н Он	Formic acid	46
H H	Glyoxal	58
ОН	Acetic acid	60
HO NH <sub>2</sub>	Glycine	75
но ОН	Glycolic acid	76

# Table 2.3 The MEA oxidative degradation products (Gouedard et al., 2012).

## 2.4 Solid adsorbents looping technology

Solid adsorbents looping technologies (SALTs) are recognised as having the potential to be a viable post-combustion capture (IPCC) technology. Some adsorbents are currently under intensive investigations and some have been demonstrated at various scales. The solid adsorbents include supported and immobilised amines, functionalised carbon materials and zeolites (Choi, 2009). Sjostrom and Krutka (2010) and Gray et al. (2008) have reported that, compared to the aqueous amine scrubbing, significant reductions in the regeneration energy consumption can be achieved for a number of solid adsorbents, particularly for supported-amine adsorbents which have received the greatest attention to date (Sjostrom and Krutka, 2010, Gray et al., 2008).

The continuous operation of a 0.5 MW<sub>e</sub> pilot plant at Hadong coal power plant, South Korea has confirmed the viability of supported-K<sub>2</sub>CO<sub>3</sub> adsorbents for SALT (Park et al., 2011). The Nottingham Group, together with their partners has been engaged in developing SALT through research into a number of solid adsorbents, including supported amines and various nitrogen-enriched carbons, which have been successfully tested at various scales up to 50 Nm<sup>3</sup>/day with simulated flue gases (Drage et al., 2008, Drage et al., 2007, Arenillas et al., 2005). A commercial silica-supported polyethyleneimine (PEI) adsorbent prepared in Nottingham was assessed independently by ADA Environmental Solutions (ADA-ES) in the USA, where the performance was amongst the best of nearly 100 adsorbents tested (Sjostrom and Krutka, 2010). Indeed, many investigations have proved that SALT is capable of capturing CO<sub>2</sub> from different flue gas streams from both natural gas and coal fired power plants.

It is widely recognised that the successful development of effective  $CO_2$  adsorbents is the key to secure the success of SALT as an alternative capture technology to the energy-intensive aqueous amine scrubbing technology. The solid adsorbents suitable for SALT must possess a high adsorption capacity, high  $CO_2$  selectivity, fast adsorption and desorption kinetics and superior resistance to thermal and/or oxidative degradation. This following Section describes the criteria and the classification of these adsorbents.

#### **2.4.1** Criteria for selecting adsorbent materials

The adsorbent materials can be evaluated from five criteria items: carbon capture capacity, adsorption/desorption kinetics,  $CO_2$  selectivity, regeneration and recycling stability, anti-interference to impurities and the cost.

#### 2.4.1.1 Adsorption capture capacity

Solid adsorbents used in SALT must have the high adsorption capacity, an essential parameter to achieve a high CO<sub>2</sub> capture rate at reduced adsorbent cycling rates (Yu, 2012). Higher adsorption capacity can effectively reduce the regeneration cycles of adsorption/desorption process or fewer quantities of adsorbent materials are required for a given flue gas flow rate, giving rise to significantly improved energy performance and process efficiency (Sayari et al., 2011, Yang, 2003, Yong, 2002).

#### 2.4.1.2 Adsorption/desorption kinetics

Adsorption/desorption kinetics show the relation between adsorption time and adsorption capture capacity. Therefore, the adsorption and desorption efficiency can be described by the kinetics-related parameters. The shorter of the residence time, the higher efficiency of adsorption and desorption. Adsorption/desorption kinetics are dependent on the inner structure and the chemical characteristics of the adsorbents (Sayari et al., 2011, Yang, 2003, Yong, 2002). Owing to the porous structures which enables diffusional transport mechanisms in micro-pores and macro-pores, the physical adsorbent materials normally represent faster kinetics than that of the chemical adsorption is used as an important factor to evaluate the performance of solid adsorbents. Fig. 2.11 shows the CO<sub>2</sub> adsorption and desorption kinetics of PEI loaded on solid adsorbents.



Fig. 2.11 The CO<sub>2</sub> adsorption and deception kinetics of the PEI solid adsorbents (Qi et al., 2012).

## 2.4.1.3 CO<sub>2</sub> selectivity

As typical flue gases consist of  $N_2$ ,  $O_2$ , and  $H_2O$ , as well as  $CO_2$ , the  $CO_2$  selectivity of the adsorbents can influence the purity of  $CO_2$  captured (Yu, 2012). Moreover,  $CO_2$ adsorption processes have a vital influence on the  $CO_2$  transportation and sequestration. Solid adsorbents use amine and other alkaline substances such as carbonate, as chemical solid adsorbents, which can enhance the  $CO_2$  selectivity. Furthermore, amines-based adsorbents can react with  $CO_2$  at low temperatures and only release  $CO_2$ at the relatively higher temperatures (desorption temperature). Meanwhile, the amine cannot react with  $N_2$ . Thus, solid amine adsorbents have high  $CO_2$  selectivity.

## 2.4.1.4 Regeneration and recycling stability

The regeneration and recycling stability can affect the lifetime of the adsorbents. There are two parameters that are required to take into account when the regeneration

stability of one adsorbent is evaluated: the heat of adsorption and the stable recycling performance. The range of chemical adsorption heat is 60-90 kJ/mol and the range of physical adsorption heat is 25-50 kJ/mol (Samanta et al., 2011). The recycling stability means the microstructure and morphology cannot change significantly after multiprocess of adsorption and desorption.

#### 2.4.1.5 Chemical stability

Flue gas contains many acidic gases and oxidative species, such SO<sub>2</sub>, NO<sub>x</sub>, and O<sub>2</sub>. The SO<sub>2</sub> and NO<sub>x</sub> can react with H<sub>2</sub>O to form sulphate and nitrate acid. Although the flue gas prior to CO<sub>2</sub> capture should have already been treated with flue gas desulfurization (FGD) and selective catalytic reduction (SCR) processes, trace quantities of SO<sub>2</sub> and NO<sub>x</sub> surviving these gas clean-up treatments can still pose significant negative impact on the performance of adsorbents, which can dramatically reduce the efficacy of the adsorbents. Therefore, solid adsorbent materials for CO<sub>2</sub> capture must possess novel performance against thermal oxidative degradation.

#### 2.4.1.6 Adsorbent costs

One of the aims of the above five factors is to reduce the amount and cost of solid adsorbents. Tarka suggested that less than 15/kg would be a reasonable price for solid adsorbents (Tarka Jr, 2006). Furthermore, the cost per kg of CO<sub>2</sub> removed is the evaluation criteria for the CO<sub>2</sub> capture technology using adsorbents. The cost of solid based adsorption is just 0.0311/kg CO<sub>2</sub> captured, which is lower than that of amine absorption (0.0552) and membrane separation (0.1127) (Nimmanterdwong et al., 2017).

#### 2.4.2 Adsorbents classification

There are two kinds of CO<sub>2</sub> solid adsorbents, physical adsorbents and chemical adsorbents. Physical adsorbents include zeolite-based adsorbent, metal-organic frameworks (MOFs), activated-carbon (ACs) materials etc. The alkali-metal carbonate-based adsorbents and amine-based solid adsorbents are chemical adsorbents. Fig. 2.12 displays the classification of different adsorbents. Sorbents can also be classified according to their adsorption and desorption temperature, adsorbents can be

classified as low temperature (<200 °C), intermediate temperature (200-400 °C) and high temperature(>400 °C) as shown in Fig. 2.13 (Wang et al., 2014a).



Fig. 2.12 The classification of CO<sub>2</sub> solid adsorbents based on the types of adsorbents



Fig. 2.13 The classification of CO<sub>2</sub> solid adsorbents based on adsorption temperature.

# 2.4.3 Zeolites

Zeolites are porous crystalline aluminosilicates, which is used as adsorbent to separate  $CO_2$  as early as in 1961 (Li et al., 2013b). In the framework of zeolites, SiO<sub>4</sub> and AlO<sub>4</sub> joined together through shared oxygen atoms in various regular arrangements to form interlocking tetrahedrons. Furthermore, due to the presence of aluminum atoms, there are free pore spaces in the original negative-charges

contained framework, which is balanced by exchangeable cations (e.g.,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ). The CO<sub>2</sub> capture capability of zeolites largely depends on the size, charge density, and distribution of these cations in the porous structure (Zhao, 1998).

There are two styles of  $CO_2$  adsorption mechanisms of zeolites: 1) typical physical adsorption whose reaction (an ion–dipole interaction) is shown in Reaction 2.12; 2) the formation of carbonate species associated with bi-coordination, as shown in Fig. 2.14 (Montanari and Busca, 2008, Jacobs, 1973, Wang et al., 2011b). Therefore, in addition to the performance of zeolites, the  $CO_2$  capture ability is sensitive to working temperature, pressure and flue gas compositions. The highest uptake at 10%  $CO_2/N_2$  and an adsorption temperature of 25 °C was obtained at 205 mg/g (Lozinska et al., 2012).

(Metal ion) 
$$x^+ \cdots \delta^- O = C = O^{\delta^+}$$
 (2.12)



Fig. 2.14 Carbonate species associated with bi-coordination in  $CO_2$  adsorption mechanisms of zeolites. (Montanari and Busca, 2008, Jacobs, 1973, Wang et al., 2011b).

In terms of practical applications, the presence of water vapor is the strongest challenge, because the water molecules can be preferentially adsorbed onto the pore surface than  $CO_2$  molecules. Thus, the  $CO_2$  capture capacity of zeolites decreases dramatically in the presence of moisture. The acidic conditions of flue gas streams are another challenge to the application of zeolites. The acidic gas species usually present in a flue gas stream can cause destruction to the zeolitic framework by de-alumination of the zeolite structures (Ertan, 2005).

#### 2.4.4 Metal-organic frameworks (MOFs)

The metal-organic frameworks (MOFs) are a category of porous materials, which are coordinated by metal cations or clusters (Venna and Carreon, 2015). Fig. 2.15 illustrates a typical MOF structure composed of a metal-based cluster and an organic linker.



Fig. 2.15 A typical MOF structure formed by a metal based cluster and an organic linker (Venna and Carreon, 2015).

MOFs can be used as CO<sub>2</sub> solid adsorbents due to their open porous framework constructed with high pore volumes, high surface areas, chemical stability and apposite pore apertures (Venna et al., 2013). Zeolitic imidazolate frameworks (ZIFs) are a typical MOF that can be used as solid adsorbents. In ZIFs, Zn, Co and Cu are linked by ditopic imidazolate to generate neutral frameworks and provide tuneable nano-sized pores, which finally formed 4 and 6-ring ZnN<sub>4</sub>, CoN<sub>4</sub>, and CuN<sub>4</sub> clusters (Hayashi et al., 2007). Important strategies for increasing the CO<sub>2</sub> capture capacity and selectivity is modifying the MOFs structures and/or organic linker in the MOFs, which can be achieved by co-ordinating unsaturated metal centres by removing the terminal bound solvent molecules. Due to the ion induced dipole interactions, these co-ordinately unsaturated metal centres used act as physical-sorption sites for CO<sub>2</sub> molecules (Wu et al., 2010). Thus, the CO<sub>2</sub> capture capacity and selectivity of MOFs is improved. Furthermore, an appropriate organic linker can also enhance the CO<sub>2</sub> capture performance of MOFs by increasing the porosity and the specific surface area or serving as extra adsorbing sites (Wang et al., 2014a).

However, there are some issues of MOFs as  $CO_2$  adsorbents. One of the problems is that MOFs are not suitable to be utilized at low  $CO_2$  concentrations, particularly below 15% (Wang et al., 2014a), which can limit their application in post-combustion capture. The  $CO_2$  adsorption ability of MOFs just was 7.5 mg/g in 15%  $CO_2$  in N<sub>2</sub> and at 30 °C (Demessence, 2009). However, modification of MOFs with amines is one solution to this problem. The  $CO_2$  uptake of MOFs have been improved to 185 mg/g in 15%  $CO_2$ in N<sub>2</sub> and at 30 °C by loading PEI into MOFs (Lin et al., 2013). Another problem is that their  $CO_2$  capture performance can be dramatically influenced by the presence of flue gas moisture. It was reported that the  $CO_2$  adsorption ability and selectivity decreased in the presence of water due to that water molecules link to the adsorption site instead of  $CO_2$  molecules (Yu and Balbuena, 2013).

## 2.4.5 Activated carbons (ACs)

ACs has been widely used as adsorbents in numerous applications due to the low cost, porous structure, high surface area and relative ease of regeneration (Davini, 2002). Fig. 2.16 shows a micrograph of ACs under scanning electron microscope (SEM). Because the CO<sub>2</sub> adsorption of ACs is physical adsorption, the adsorbents are sensitive to temperature and have poor CO<sub>2</sub> selectivity. most commercial ACs usually have very low CO<sub>2</sub> adsorption capacities in the typical flue gas temperature range of  $50\sim120^{\circ}$ C (Arenillas et al., 2005) and therefore, they often need to be surface-modified to increase their surface affinity to CO<sub>2</sub> molecules. The most important strategy for increasing CO<sub>2</sub> capture performance of carbon materials is to increase the surface area and/or modify the pore structure and increase the surface alkalinity by surface modifications. Lee and Jimenez reported that the CO<sub>2</sub> capture capacity of ACs could be improved by the design of carbon adsorbents with a large volume of small micropores (Lee and Park, 2013, Jimenez et al., 2012).



Fig. 2.16 The SEM images: a.) Pulp, b.) Peel, c.) Pulp-based AC, and d.) peel-based AC (Hesas, 2013).

Another way to enhance the  $CO_2$  capture capacity and selectivity of ACs is surface modification, such as adding amino-functionalities into the carbon structures or increasing the nitrogen content of carbons. There are two main methods for this, namely amine impregnation (Wang et al., 2011c) and surface amine grafting (Hiyoshi et al., 2005). These amines are dispersed in the pores of carbon and react with  $CO_2$  to improve the  $CO_2$  capture performance. Apart from the amine modification, there are other treatments in surface modification, such as oxidation or modification with metal oxides (Plaza et al., 2013, Bai et al., 2011). These treatments increase the amount of oxygen functional groups on the surface of ACs, which can enhance the  $CO_2$ adsorption capacity and selectivity by the electrostatic interactions between oxygen atoms and  $CO_2$  (Plaza et al., 2013).

#### 2.4.6 Alkali carbonate-based adsorbents

Alkali carbonate-based adsorbents such as  $K_2CO_3$  and  $Na_2CO_3$  have been investigated as potential  $CO_2$  adsorbent in the last few years due to the high  $CO_2$  adsorption capacity and low cost.  $CO_2$  adsorption of alkali carbonate based adsorbents was based on the carbonate-bicarbonate cycle, and the presence of moisture is critical to the adsorption reaction as shown in below. Without moisture in the flue gas, the adsorption will terminate.

Carbonation (adsorption): 
$$M_2CO_3 + H_2O + CO_2 = 2 MHCO_3$$
 (2.13)

Decarbonation (desorption): 
$$2 MHCO_3 = M_2CO_3 + H_2O + CO_2$$
 (2.14)

In carbonation,  $M_2CO_3$  reacts with  $CO_2$  in humid conditions (M means alkali metal). Fig. 2.17 demonstrates the relation between  $CO_2$  uptake and the temperature for  $K_2CO_3$  and  $Na_2CO_3$  adsorbents (Hayashi, 1998). Typically, the  $CO_2$  adsorption occurs in the temperature range of 50-100 °C, while regeneration takes place within the range of 120-200 °C. Therefore, alkali-metal carbonate-based adsorbents are suitable for the post-combustion technologies, since the temperature of flue gas is blow 200 °C and additionally the presence of water can act as the reactant.



Fig. 2.17 The relation between CO<sub>2</sub> uptake and the temperature by K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> (Hayashi, 1998).

For different alkali carbonate-based adsorbents, the adsorption capacity of  $K_2CO_3$  is higher than those of Na<sub>2</sub>CO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> when the temperature is between 40 °C and 160 °C, as shown in Fig. 2.17 (Hayashi, 1998). Supported alkali carbonate adsorbents do not have oxidative degradation issues as with other organic-based adsorbents and, in theory, they should also have high adsorption capacity as can be revealed in the above reaction equation. Thus,  $K_2CO_3$  is often supported onto different porous support materials, such as ACs, TiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, by impregnation methods, which can enhance the adsorption rate and provide the required attrition resistance of these support materials (Lee et al., 2006). The carbon capture capacity of  $K_2CO_3/Al_2O_3$  was found to remain hardly changed after ten adsorption/desorption cycles when the regeneration temperature is 130 °C (Zhao et al., 2010). A novel adsorbent ( $K_2CO_3$ /MgO/Al<sub>2</sub>O<sub>3</sub>) was tested in a fluidized-bed reactor, and the carbon adsorption capacity of  $K_2CO_3$  /MgO/Al<sub>2</sub>O<sub>3</sub> was found to reach 2.49 mmol/g at a desirable adsorption temperature of 60 °C (Li et al., 2011).

#### 2.4.7 Amine-based solid adsorbents

Amine-based solid adsorbents are the amines that are supported or grafted onto a porous solid material, such as polyethylenimine (PEI) – silica. Compared with aqueous amines, amine-based solid adsorbents have advantages in capital cost, regeneration energy requirement and corrosion resistance (Khatri, 2006). There are two ways to prepare amine-silica adsorbents: grafting and impregnation. Many groups tried to improve the  $CO_2$  capture capability of amine-based solid adsorbent through the improvement of porous materials, selection of appropriate amines and reduction of  $CO_2$  diffusion resistance.

## 2.4.7.1 Grafting method

In the grafting method, PEI is covalently bonded to the hydroxy group on the silica surface. The grafted PEI adsorbents have advantages in the thermal stability due to the strong chemical bond between amine and group on the silica surface (Ünveren et al., 2017). Burwell and Leal first reported the use of amine-grafted silica to remove SO<sub>2</sub> (Burwell, 1974). Since then, amine-grafted adsorbents for CO<sub>2</sub> capture have been investigated. There are three preparation methods for grafted PEI adsorbent: direct synthesis, anionic template synthesis and chemical grafting (Chew et al., 2010, Chen et al., 2017). Direct co-condensation synthesis is simpler than other two methods. In the direct synthesis, the aminosilanes, surfactant and porous silica was mixed and been produced to amine-based adsorbent via the hydrolysis and co-condensation. Fig. 2.18 shows the schematic of amine-grafted silica by direct co-condensation synthesis (Chew et al., 2010). Gunathilake et al. prepared mesoporous silica with amidoxime

groups, which have 79 mg/g  $CO_2$  adsorption capacity in pure  $CO_2$  adsorption gas condition (Gunathilake and Jaroniec, 2014). PEI also has been used to prepare aminegrafted silica and get highest  $CO_2$  adsorption capacity (124 mg/g) in 15%  $CO_2$  in  $N_2$  adsorption gas condition in all amine-grafted adsorbent though direct co-condensation synthesis (Klinthong et al., 2016).



Fig. 2.18 Schematic of amine-grafted silica by direct co-condensation synthesis (Chew et al., 2010).

In anionic template synthesis route, the anionic surfactants, such as aminosilane and tetraethyl orthosilicate (TEOS), are mixed and kept at selected constant temperature. Then the resulting mixture is calcined to remove the surfactant and template used. Fig. 2.19 shows a schematic of the anionic-surfactant-template method to functionalize silica with amine groups (Toshiyuki Yokoi, 2007). Tetraethylenpentamine (TEPA) and 3-aminopropyl triethoxysilane is used as the amine in preparation of amine-grafted silica via anionic template synthesis (Wen et al., 2010, Li et al., 2013a, Cui et al., 2011, Kim et al., 2008, Araki et al., 2009, Hu et al., 2011). The CO<sub>2</sub> adsorption ability of TEPA-grafted silica can reach 171mg/g and 175mg/g in pure CO<sub>2</sub> adsorption gas at 75 °C (Wen et al., 2010, Li et al., 2013a). Meanwhile, the CO<sub>2</sub> capture capability of all the amine-grafted silica with and 3-aminopropyl triethoxysilane were lower than 100mg/g (Wen et al., 2010, Li et al., 2013a, Cui et al., 2011, Kim et al., 2009, Hu et al., 2013a, Cui et al., 2008, Araki et al., 2010, Li et al., 2013a, Cui et al., 2011, Kim et al., 2008, Araki et al., 2013a). Meanwhile, the CO<sub>2</sub> capture capability of all the amine-grafted silica with and 3-aminopropyl triethoxysilane were lower than 100mg/g (Wen et al., 2010, Li et al., 2013a, Cui et al., 2011, Kim et al., 2008, Araki et al., 2013a, Cui et al., 2011, Kim et al., 2008, Araki



Fig. 2.19 Schematic of amine-grafted silica via anionic template synthesis (Toshiyuki Yokoi, 2007).

In chemical grafting, the amine-grafted adsorbent is prepared through the reaction between hydroxyl groups on the silica surface and aminosilane or amine groups with linker. Fig. 2.20 shows the schematic of chemical grafting to functionalize silica surface with amine groups. The mixture of silica and aminosilance is heated under reflux, and the unreacted aminosianes are removed by washing the materials. Sayari et al. prepared a high amine content (6.11 mmol N/g) material which has high CO<sub>2</sub> capture capability of 117 mg/g in 5% CO<sub>2</sub> in N<sub>2</sub> (Harlick, 2007). Furthermore, the bridges can link some aminosilanes to hydroxyl group, such as PEI. Du et al. used polyacrylic acid (PAA) as the linker between the PEI and silica, which is shown in Fig. 2.21 (Du et al., 2013). The CO<sub>2</sub> adsorption ability of PEI-grafted silica reached 167mg/g in pure CO<sub>2</sub> adsorption gas.



Fig. 2.20 Schematic of amine-grafted silica via post-synthesis grafting (Chew et al., 2010)



Fig. 2.21 Schematic of PEI-grafted silica by using polyacrylic acid (PAA) as the agent (Du et al., 2013).

## 2.4.7.2 Impregnation method

Impregnation is an effective way to load a large amount of amine onto mesoporous materials. Compared with the grafting method, the advantages of impregnation lie in its relatively easier preparation, higher amine loading and lower corrosion. Among the various amines, PEI has recently received intensive attention as a potential sorbent for CO<sub>2</sub> capture owing to its high carbon capture capacity, high CO<sub>2</sub> selectivity, low

energy consumption, favourable adsorption temperature, higher regeneration and recycling stability. (Qi et al., 2012, Heydari-Gorji et al., 2011a, Heydari-Gorji et al., 2011b).

In 2002, Xu reported the first PEI-impregnated CO<sub>2</sub> adsorbent and the CO<sub>2</sub> capacity of this adsorbent was obtained at 3.0 mmol/g at 75 °C in a dry 100% CO<sub>2</sub> gas atmosphere (Xu, 2002). Furthermore, the CO<sub>2</sub> adsorption ability of PEI-impregnated silica and cycling stability was found to be affected by the property of PEI, PEI loading and the porosity of silica. PEI can be classed into branched PEIs and linear PEIs. Fig. 2.22 shows the fragment of linear PEIs and branched PEIs. Because branched PEI have higher mobility and higher primary amine contents, branched PEI-silica sorbents usually have higher CO<sub>2</sub> sorption capacity and adsorption rate than supported linear PEIs at the same PEI loading levels (Li et al., 2014). Therefore, branched PEI is commonly applied to prepare PEI-silica adsorbents (Sanz et al., 2010, Vilarrasa-García, 2015, Subagyono et al., 2011, Li et al., 2015, Goeppert et al., 2011, Niu et al., 2016, Liu et al., 2015).



Fig. 2.22 The fragment of linear PEI (1) and branched PEI (2).

The reaction between PEI and  $CO_2$  is described in Fig. 2.23. In addition, the  $CO_2$  sorption capacity of PEI-impregnated silica decreases while the thermal stability increases with increasing PEI molecular weight at the same PEI loading levels, due to the lower mobility but higher thermal stability of higher molecule weight PEIs (Li et al., 2014). Additionally, the  $CO_2$  sorption capacity of adsorbents increases with the amount of PEI impregnated as a result of the increase of the active sites for  $CO_2$  molecules (Li et al., 2015). However, the increase of PEI would also increase the possibility of pore blockage that in return reduces the accessibility of the amines to  $CO_2$ . Therefore, the optimal PEI loading means the maximum uptake of  $CO_2$  by achieving the balance point between the negative effect and positive effect (Li et al., 2015).



Fig. 2.23 The reaction of PEI with CO<sub>2</sub> (Goeppert et al., 2011).

Fig. 2.24 shows the schematic of PEI-MCF-41 with different PEI loading. Although PEI loading increase can incline the adsorption site, the sticky PEI in PEI adsorbent with extreme high PEI loading fill in the pore and coat the outer surface of pore will, which increase the diffusion resistance of CO<sub>2</sub>. Therefore, PEI adsorbent with extreme high PEI loading have relatively lower CO<sub>2</sub> adsorption ability and rate (Sun et al., 2015). On the other hand, higher temperature can improve the mobility of PEI molecules to reduce the CO<sub>2</sub> diffusion resistance (Li et al., 2015, Xu et al., 2003). Thus, increasing adsorption temperature appropriately can be used to improve the CO<sub>2</sub> sorption capacity of PEI-silica with higher PEI loading.



Fig. 2.24 Schematic of PEI-MCF-41 with different PEI loading:(A) MCM-41 support;(B) low PEI loading; (C) high PEI loading; (D) extremely high PEI loading (Sun et al., 2015).

In impregnated adsorbent systems, the supports with larger pore volumes and pore diameters can facilitate better CO<sub>2</sub> adsorption performance. The large pore volumes and open structural character of the supports can ensure high amine loading and effective amine distribution and as a result, fast CO<sub>2</sub> adsorption kinetics and high CO<sub>2</sub> adsorption capacities (Wang et al., 2014a). Mesoporous silica materials have been found to be one of the most favourable supports for PEI impregnation and/or grafting, due to their high surface areas, large pore volumes, narrow pore size distributions and excellent regeneration stability (Han, 2006).

MCM-41 (Mobil composition of matter No.41), SBA-15 (Santa Barbara Amorphous) and KIT-6 as the supports were widely investigated, due to the advantage of textural and preparation. Table 2.4 shows the surface area, pore volumes and pore diameters of these three mesoporous silica by Son et al. (Son et al., 2008). Fig. 2.25 shows the

SEM image of MCM-41, SBA-15 and KIT-6, with KIT-6 showing the largest pore volume and size of these three mesoporous silicas. As one of the best-performing mesoporous silica for amine-impregnation, 50% PEI-KIT-6 can achieve a CO<sub>2</sub> uptake of about 135 mg/g in pure CO<sub>2</sub> atmosphere and have a maximum adsorption rate of 263 mg/g (Son et al., 2008). PEI adsorbent with MCM and 75% PEI loading can obtain 112 mg/g in 75 °C and 99.8% CO<sub>2</sub> adsorption condition (Xu, 2002). Klinthong et al. report that the CO<sub>2</sub> adsorption capability of 50% PEI–SBA 15 can reach 118 mg/g (Klinthong et al., 2016). However, PEI adsorbents with the highest CO<sub>2</sub> adsorption capability (208 mg/g) is mesoporous multi-lamellar silica vesicle (MMSV)-based adsorbent with 60% PEI loading in 90 °C and pure CO<sub>2</sub> adsorption condition (Zhang et al., 2016a).

Table 2.4 General structural properties of three mesoporous silica (Son et al., 2008).

mesoporous silica	BET surface area	Pore volume	Pore diameter
	( <b>m</b> <sup>2</sup> / <b>g</b> )	( cm <sup>3</sup> /g )	( <b>nm</b> )
<b>MCM-41</b>	1042	0.85	2.8
SBA-15	753	0.94	5.5
KIT-6	895	1.22	6.0



Fig. 2.25 Schematic of SEM image of three mesoporous silica: (A) MCM-41; (B) SBA-15; (C) KIT-6.

Surfactant addition can also enhance the CO<sub>2</sub> adsorption ability by creating extra CO<sub>2</sub> diffusion pathways to reduce diffusion resistance (Wang et al., 2012). CO<sub>2</sub> adsorption processes of PEI-hierarchical porous silica (HPS) with and without neutral surfactant are shown in Fig. 2.26. Wang et al. reported nine surfactants, which include cetyltrimethylammonium bromide (CTAB), dodecyltrimethyl ammonium bromide (DTAB), octadecyltrimethyl ammonium bromide (STAB), Pluronic P123 (P123),

Pluronic F127 (F127), sodium dodecylbenzenesulfonate (SDBS), sodium dodecyl sulfate (SDS), sorbitan monooleate (Span80,) and phosphatidylcholine (IPCC) (Wang et al., 2012). Span80 was found to be the best-performing surfactant among all the surfactants examined and increased the adsorption capacity of the PEI-HPS from 173 mg/g to 218 mg/g with 7 wt% SPAN addition.



Fig. 2.26 Schematic of CO<sub>2</sub> adsorption process of PEI-hierarchical porous silica (HPS) with and without surfactant (Wang et al., 2012).

## 2.4.7.3 Degradation of PEI-silica adsorbents

As with aqueous amine solvents, PEI-based solid adsorbents are also liable to different forms of degradation, including thermal degradation and oxidative degradation. Thermal degradation of PEI mainly occurs during the desorption process. PEI can react with  $CO_2$  to form urea under high temperatures and dry  $CO_2$  conditions via dehydration of carbamic acid or ammonium carbamate (Sayari et al., 2012). In addition, the PEI can also be oxidized by flue gas contained  $O_2$  and consequently lose the function for  $CO_2$  adsorption. The oxidative degradation mechanisms of branched PEI are similar to the mechanisms of MEA, due to the existence of mono-amine groups in PEI. Therefore, the main PEI oxidative degradation products contain oxygen functional groups, such as hydroxyl, carbonyl, aldehyde, carbonate ester, carboxyl, ester, et al. (Ahmadalinezhad and Sayari, 2014, Bali et al., 2013, Heydari-Gorji and Sayari, 2012, Lepaumier, 2009). Moreover, the oxidative stability of PEI adsorbent increases in the presence of  $CO_2$ , because the rate of reaction amine groups with  $CO_2$  is faster than the oxidative reaction with  $O_2$  (Heydari-Gorji and Sayari, 2012).

Many attempts have been made to reduce thermal/oxidative degradation and so prolonging the lifetime of PEI adsorbents. There are three approaches to improve the performance of PEI adsorbent:

- 1) Selection of appropriate amine
- 2) Adding moisture in flue gas
- 3) Changing the functional group

Appropriate amine should be evaluated in two aspects: thermal stability and  $CO_2$  adsorption ability. The property of PEI include molecule weight and PEI type. PEI adsorbent with higher molecule weight shows a higher thermal stability and lower  $CO_2$  adsorption ability. (Li et al., 2014), Meanwhile, linear PEI inhibits lower  $CO_2$  adsorption ability and higher thermal stability than branched (Li et al., 2014). Furthermore, as water vaper can protect the PEI molecule form thermal degradation, adding moisture to flue gas can improve the cycling stability of PEI adsorbents (Sayari et al., 2012). Fig. 2.27 shows the  $CO_2$  uptake of PEI- mesoporous silica adsorbents in both dry and humid conditions in 66 cycles (Heydari-Gorji and Sayari, 2012).



Fig. 2.27 CO<sub>2</sub> uptake during 66 CO<sub>2</sub> adsorption/desorption cycles in dry and humid conditions (Heydari-Gorji and Sayari, 2012).

For the method of modifying the active functional group, 1,2-epoxybutane was used as crosslinker to reduce the content of primary or secondary amines, and it was found that the percentage of primary amine in the EB-PEI-silica can be reduced to just 2% (Choi et al., 2016).. EB-PEI-silica was found to exhibit very high thermal stability (Choi et al., 2016). Meanwhile, (±)- epichlorohydrin (ECH) and 1,3-butadiene diepoxide (BDDE) was used as crosslinker of PEI-silica adsorbent(Jung et al., 2017). Fig. 2.28 shows the structures of (A) EB-PEI, (B) BDDE-PEI and (C) ECH-PEI (Jung et al., 2017, Choi et al., 2016).



Fig. 2.28 Structures of (A) EB-PEI, (B) BDDE-PEI and (C) ECH-PEI (Jung et al., 2017, Choi et al., 2016).

# 2.5 Concluding Remarks

Carbon capture and storage is clearly a major option that can drastically reduce global  $CO_2$  emissions without compromising energy security as we can continuously use fossil energy but without the produced CO<sub>2</sub> emissions being released into and accumulated in the atmosphere to cause climate change. However, the successful development, demonstration and deployment of efficient and affordable carbon capture technologies holds the key to the success of CCS technology as it accounts for over 70% of whole CCS cost. The high energy penalty and a range of prohibitive operational and environmental issues associated with the state-of-art aqueous amine scrubbing technology has necessitated the development of advanced or alternative capture technologies. Among all these technologies currently under development, the development of dry solid adsorbents looping technologies for CO<sub>2</sub> capture has received most attention, due to its great potentials in reducing the energy penalty and greatly improved operational and environmental performance in comparison with amine scrubbing technologies. However, despite the research efforts over recent years, it still remains to be a major challenge to increase the CO<sub>2</sub> capture capacity and improve the lifetime performance of the dry adsorbents, which directly determines the overall techno-economics of adsorption-based capture technologies.

Even with regard to the existing amine scrubbing technology, which has been used in natural gas industry for over 70 years and is being set to be the 1<sup>st</sup> generation capture technology to be deployed, also still faces many other major issues to be dealt with in addition to its high energy penalty, such as its low efficiency, corrosion and erosion, costly solvent degradation and associated toxic environmental emissions.

For all amine-based sorbent systems, which appear to be the most effective category of  $CO_2$  sorbents for low partial pressure applications, how to effectively prevent degradation or rejuvenate the degraded amine sorbents for re-use or value-added products is an important area that has not been examined, and this could lead to significantly improved techno-economic and environmental performance of  $CO_2$ capture with these technologies.
# **CHAPTER 3** Aims and Objectives

Based on the major issues identified in the literature review, the overall aim of the research is to develop new solid adsorbent materials which can facilitate higher  $CO_2$  capture capacity capacities with fast adsorption kinetics and superior adsorption-desorption lifetime performance; to explore effective measures to minimise or effectively prevent the thermal and oxidative degradation of the sorbent materials; and to investigate approaches that can potential rejuvenate the degraded sorbents for reuse or convert them into other value-added products. Highlights of the major objectives or research activities that have been carried out in this study include

- To develop new adsorbent materials with improved performance for CO<sub>2</sub> capture, including high uptake capacities, fast adsorption kinetics and superior cyclic adsorption-desorption performance. Particular focus will be given to the development of porous siliceous cellular foam (SCF) materials with large pore volumes, ranging from mseo, hybrid meso/macro and macro-structured SCFs.
- To investigate the precursor chemistries and preparation conditions on the structural and morphological properties of SCFs and hence their impact on the CO<sub>2</sub> uptake performance of the amine-impregnated SCF adsorbents prepared with amine impregnation.
- 3. To test and examine the life-time performance of the supported PEI adsorbents via programmed adsorption-desorption cycles to investigate their degradation profiles and mechanisms.
- 4. To characterise the SCF materials with a range of advanced characterisation tools to establish the relations between the CO<sub>2</sub>-capturing performance of the SCF-PEI adsorbents and the properties of the SCF substrate synthesised.
- 5. To investigate the capability and capacity of the SCF substrates for impregnation of high molecular mass PEIs in order to further improve the thermal stability of the supported PEIs. Lower molecular weight PEIs (typically ≤1800) have been mostly used in preparing supported PEI adsorbents via impregnation. However, the PEI adsorbents prepared with

lower molecular mass PEIs suffers from their relatively poor thermal stability due to the evaporation loss of the impregnated PEIs. The use of higher molecular weight PEIs has been a desire but are often restricted by the pore volumes and pore sizes of the porous support materials used. The siliceous cellular foam materials highly characterised by their novel 3D inter-connected porous structures with ultra-large pore size and pore window sizes make it possible to achieve high levels impregnation of higher molecular weight PEIs.

- 6. To develop and evaluate novel approaches to rejuvenate degraded silicasupported solid PEI adsorbents. The effectiveness of different approaches will be examined, including the use of reductive approaches e.g. hydrogenation and/or hydropyrolysis and the addition of external additives.
- 7. To explore effective approaches to rejuvenate heavily degraded amine solvents derived from amine-scrubbing CO<sub>2</sub> capture operations or convert them into value-added products. The efficacy of different approaches will be evaluated, including hydrogenation, hydrolysis and aqueous reforming under reductive and non-reductive conditions. The products from different rejuvenation trials will be characterised using advanced characterisation tools.

To achieve the objectives as highlighted above, a new category of support materials for PEI impregnation, namely three-dimensional (3-D) interconnected meso, hybrid meso-macro and macro-porous siliceous foam support materials, were firstly developed to maximise the PEI loading levels as a means to boost the  $CO_2$  capture capacity of supported-PEI adsorbents. The results are presented in Chapter 5.

Following the successful development of high capacity capture materials, the lifetime performance and degradation profiles of supported PEI adsorbents prepared with different porous silica materials, including both conventional and the newly developed 3-D interconnected siliceous foam materials, were examined comprehensively under a variety of operational conditions. Based on the performance testing results, different approaches or strategies to mitigate or avoid the degradation of the polyamine CO<sub>2</sub> sorbent materials were investigated, with all the results presented in Chapter 6.

In Chapter 7, different reductive approaches, including both catalytic hydrogenation and aqueous reforming, were comprehensively investigated as a means to rejuvenate heavily degraded amine-based  $CO_2$  sorbent materials or convert the degraded sorbents to highly value-added chemicals. The degraded sorbent samples examined included both the heavily degraded solid PEI adsorbents prepared in our laboratories and the degraded aqueous MEA solvents obtained from industrial  $CO_2$  capture plants.

# **CHAPTER 4 Methodologies**

In this Chapter, the experimental methodologies used in this PhD project are described in detail. It contained three parts: preparation of solid adsorbents, rejuvenation tests, and sample characterisation. More specifically, the preparation of solid adsorbents included the synthesis of porous siliceous cellular foams (SCF) by using templating method and preparation of PEI-silica adsorbent by wet impregnation method. Rejuvenation tests were divided into two sections: the rejuvenation of degraded polyethyleneimine (PEI) and the degraded monoethanolamine (Bonenfant et al., 2008), respectively. Furthermore, sample characterisation clarified the techniques of measurements on  $CO_2$  adsorption capability, thermos-oxidative stability, textural properties, etc and analysis of products obtained from rejuvenation tests.

# 4.1 Solid adsorbent preparation

# 4.1.1 Synthesis of siliceous cellular foams (SCF)

The siliceous cellular foams (SCF) was synthesized according to the method reported by Schmidt-Winkel and co-workers (Schmidt-Winkel, 2000) and the schematic diagram of synthesis procedure was shown in Fig. 4.1. Briefly, structure-directing agent P123 (poly(ethylene oxide)-block–poly(propylene oxide)-block–poly(ethylene oxide), EO20–PO70–EO20) and mesitylene were dissolved in hydrochloric acid solution at 40 °C to form the microemulsion template (Schmidt-Winkel, 1999). PEO-PPO-PEO micelles was the core of the microemulsion template and TMB was used as organic swelling agent. After that, tetraethyl orthosilicate (TEOS) as the silica source was added into the mixture. The hydrolysis of TEOS occurred and lasted for 20 hours at 40 °C. Then, NH<sub>4</sub>F as inorganic mineralizing agent dissolved in deionized water was added to the mixture following by second stage of aging carried out at 100 °C under a static condition. After 24 hours, the white precipitate was isolated by vacuum filtration and washed with deionized water. The wet precipitate was dried in the atmosphere and calcined at 550 °C in air for 8 hours to remove the template.



Mesitylene

Fig. 4.1 Schematic of synthesis of siliceous cellular foams with template.

#### 4.1.2 Synthesis of PEI-silica adsorbent

In this investigation, a wet impregnation method was used to prepare PEI-silica adsorbents. In a typical preparation, a calculated amount of PEI was dissolved in 10 mL water with vigorous stirring. After 15mins, the corresponding amount of calcined silica was gradually poured into the solution and the mixture was stirred overnight at room temperature. Then the mixture was dried at 40 °C in a vacuum oven for 24 hours. After that, the impregnated adsorbents were collected for further testing. The adsorbents named as X%PEI-Y-silica (X% is the PEI loading percentage and Y is the molecular weight of PEI). PEI loading percentage can be calculated by Equation 4.1. PEI with Molecular weight 600, 1800 and 10000 were used.

PEI Loading Percentage (wt%) = 
$$\frac{W_{PEI}}{W_{PEI} + W_{silica}} \times 100\%$$
 (4.1)

PEI-silica adsorbent with additives were also prepared by impregnation method. Typically, a calculated amount of additive and 0.4g PEI (Mw = 600) was dissolved in 10 mL water with vigorous stirring. After 15 mins stirring, the selected support material (typically PQ silica) was gradually poured into the solution and the mixture was then held overnight with stirring at room temperature. The samples were then dried at 40 °C in a vacuum oven for 24 hours before they were collected for further testing. Table 4.1 listed all the adsorbents with additives prepared. The additives used in the experiments included calcium borate, sodium borate, magnesium phosphate, calcium sulphate.

Additive	Additive wt. (g)	PQ silica wt. (g)	Total wt. (g)
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	0.01	0.59	1
$Na_2B_4O_7$	0.05	0.55	1
$Na_2B_4O_7$	0.1	0.5	1
$Na_2B_4O_7$	0.15	0.45	1
$Na_2B_4O_7$	0.2	0.4	1
$Na_2B_4O_7$	0.25	0.35	1
$Na_2B_4O_7$	0.3	0.3	1
CaSO <sub>4</sub>	0.1	0.5	1
CaB <sub>2</sub> O <sub>6</sub>	0.1	0.5	1
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.1	0.5	1

Table 4.1 Summary of PEI-PQ silica with additives.

# 4.2 **Rejuvenation Methodologies**

# 4.2.1 Hydropyrolysis (HyPy)

Hydropyrolysis (HyPy) was originally developed in the mid-20th century as a new method to directly convert coal into methane and light aromatic feedstocks (benzene) under high temperatures and pressures (Will Meredith, 2015). Snape et al (1989) found that the addition of catalyst like MoS<sub>2</sub> to the sample can achieve higher conversion rate at pressure only 150 kPa (Snape, 1989). Thereafter, this method was effectively used for the hydrotreatment of primary oil vapours to remove the heteroatoms (e.g. oxygen and nitrogen) from the curde oil so to obtain deoxygenated and/or denitrogenated hydrocarbons. All of those efforts have led to the development of HyPy as an preparative or analytical pyrolysis technique for many advanced applications including catalytic hydrogenation and organic geochemical studies (Sephton et al., 2005a).

The hydrogenation experiments were carried out by using a commercial HyPy apparatus patented by the University of Nottingham and manufactured by STRATA Technology Ltd. The schematic diagram and photograph of HyPy was illustrated in Fig. 4.2. The HyPy apparatus is made up of a reactor unit with the connection to a dry ice cooled silica trap. In general, the sample was placed on the top of pre-cleaned quartz wool plug in the reactor unit. The reactor works under hydrogen with a pressure of 15MPa and 5 L/min, which ensure that the product of pyrolysis can leave the heating zone quickly and is trapped on the dry ice cooled silica. Electrical connectors is employed to heat up the samples.

Hydropyrolysis method was used in the rejuvenation test of degraded PEI. In a typical procedure, a calculated amount of degraded PEI-catalyst mixture was placed into a length of borosilicate pipette, which was plugged at each end with pre-cleaned quartz wool. The samples were pyrolysed with resistive heating from 50 to 150 °C at 100 °C min–1, and then from 150 °C to the final temperature at 10 °C min–1, then held for 30 min, under a hydrogen pressure of 15 MPa. A hydrogen sweeping gas flow of 5 L min<sup>-1</sup>, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor for subsequent trapping on dry ice cooled silica.



Fig. 4.2 Schematic diagram of the hydropyrolysis equipment (Ascough et al., 2009) and the photograph of HyPy.

#### 4.2.2 High pressure pyrolysis

In addition to HyPy, high pressure hydrogenation experiments were also carried out using the high-pressure reactor shown in Fig. 4.3. There are two parts of high pressure pyrolysis: the reactor and sand bath. Parr 4740 series stainless steel (25 ml and 75 ml cylindrical) pressure vessels were used for hydrogenation experiments. The temperature of the reactor was controlled by the sand bath equipped with a K-type thermocouple, which is connected to the computer to monitor the temperature of the required temperature. When the experiments, the sand bath needs to be pre-heated to the required temperature. When the experiment finished, compressed air is used to cool the reactor to room temperature in order to prevent secondary reactions before product recovery.



Fig. 4.3 Autoclave pressure vessels for the hydrothermal treatment of model compounds, together with the sand bath heating system.

The rejuvenation tests of degraded solid PEI adsorbents and aqueous MEA solvents were performed in a carefully designed autoclave reactor. In a typical test, the calculated amount of a degraded PEI or MEA sorbent sample was first mixed with a pre-defined amount of catalyst, and the formed mixture was then transferred into a glass vessel inserted in the reactor. The autoclave was then sealed and purged with a flow of hydrogen to completely displace the air in the reactor. After the autoclave reactor pressured with hydrogen to 3 MPa, the reactor containing the sample mixture was heated up to a pre-set temperature in a sand bath and the reactor was held at the temperature for a pre-set duration of time, which was typically around 30 mins. After

cooling process, the product was collected for characterization. In addition to hydrogen, ammonia was also used as the reducing agent. To introduce ammonia into the reactor, a glass vessel containing 2ml ammonia hydroxide was placed in the reactor next to the vial with sample. Then, 0.5 MPa nitrogen was filled into the reactor after purging process. Other procedure was similar to the aforementioned hydrogen experiments.



#### 4.2.3 Continuous flow reactor system

Fig. 4.4 Image of PID Effi Microactivity system.

Based on the results from HyPy and high-pressure hydrogenation experiments with autoclave, the best performing catalysts were selected to test their activity and selectivity by using PID Effi Microactivity reactor, which is an advanced continuous flow reactor system that has been widely used in hydrocracking, hydrotreating, hydrogenation, oxidation, hydrodenitrogenation (HDN), reforming (aromatization), GTL (Fischer-Tropsch), steam reforming and so on and the schematic diagram was shown in Fig. 4.4. The PID system is composed of a fixed bed reactor with the catalyst bed placed inside. Generally, the sample flow is fed into the reactor from the upper part of the reactor at a specific flow rate that is controlled by a system of mass flow controller and the products are collected from the lower part of the reactor. As for

liquid reactant, a HPLC alternative positive displacement pump is used to pump the sample into the reactor through a low dead volume check-valve with a flow rate ranging from 0.01 and 5 ml/min at pressures up to 60 MPa. The electric forced convection heater is used to keep the gas and liquid flows at temperature about 160-180 °C in order to avoid the condensation in the system before they go into the hot box system. The liquid pre-heater is under the heater's forced flow while gas pre-heater is under the heater's direct flow, both of which temperature is higher than that of the hot box system. The liquid evaporation (evaporator) and gas preheat (pre-heater) happen in the heater, which is under the heater's force flow and direct flow, respectively. Then the vaporized liquid and preheated gas merge and flow to a 6-port valve with two options: towards the reactor and bypassing the reactor. When "towards the reactor " option is selected, the mixture reactant firstly passes through 10 µm sintered filters made of 316 stainless steel at the inlet of the reactor in order to avoid the damage of valves by fine catalyst particles. Before passing out of the system, the product is filtered by 10 µm sintered filters similar to that at inlet and goes into the liquid-gas separator to separate liquid and gaseous components from the product, and the liquid components is condensed out in the condenser and is collected manually for further analysis. As for gaseous components, they go straight to the outlet for subsequent measurement and/or analysis by chromatography.

The experiments were carried out as follows: 200 ml degraded MEA solution (5 wt% degraded MEA) was added to liquid sample reservoir. 1g 5% Pt/PQ silica catalyst was placed into the sample bed and a flow of hydrogen (3 MPa) at a flow rate of 50ml/min was introduced into the reactor. Then the reactor was heated up from ambient temperature to 200 °C using a rapid heating rate of 100 °C/min, then to final set temperature at 10 °C /min and held for 45 min in hydrogen atmosphere. Once the temperature became stable, the degraded MEA solution was introduced into the reactor at a flow rate of 5ml/min for 30min. The product was collected from the liquid outlet for further analysis.

# 4.3 Sample characterisation

# 4.3.1 Textural properties

Gas adsorption method has been widely used to characterize the textural properties of porous materials especially nitrogen adsorption at 77 K. Based on the reversible physisorption of gas molecules like nitrogen on solid surface, the adsorption capacity of selected gas as a function of pressure was obtained. Then, with the assistance of different models, the textural properties like surface area, pore volume and so can be calculated.

# 4.3.1.1 General information

In this project, Micromeritics ASAP 2420 analyser was employed to characterize the samples prepared as shown in Fig. 4.5. Prior to measurement, the sample was first degassed at 120 °C for 12 hours before analysis. Surface area values were determined by the Brunauer Emmett Teller equation. The mesopore volume and macropore volume of the silica were determined by using the Barrett-Joyner-Halenda (BJH) method and t-plot equation, respectively. Density functional theory (DFT) was applied to calculate the pore size distribution (PSD) of different samples.



Fig. 4.5 The images of Micromeritics ASAP 2420.

# 4.3.1.2 Algorithms for porosity calculation

The corresponding nitrogen isotherms of materials with different porous structure show different shapes. According to IUPAC (International Union of Pure and Applied Chemistry) classification (Sing, 1985), thousands of adsorption isotherms obtained from different materials can be classified into six major types, which are shown in Fig. 4.6 Type I is commonly observed in porous materials with microspore domain structure, the nitrogen uptake sharply increases in the low pressure region followed by virtually horizontal plateaus at high relative pressure (Sing, 1985). Type II indicates multilayers N<sub>2</sub> adsorption on non-porous or macroporous material. Point B shown in type II isotherm indicates the completion of monolayer adsorption and the start of multilayer adsorption (Weidenthaler, 2011). Type III can only occur when the interaction between adsorbent and adsorbate is weaker than adsorbate-adsorbate

interaction (Weidenthaler, 2011). Porous materials with mesoporous or macroporous structure exhibit Type IV isotherm. At the initial stage, it has similar features as type II isotherms. When the relative pressure reaches about 0.4, hysteresis loop emerged, which attributes to the gas condensation in the mesopores. Due to the different shape of hysteresis loops, the type IV isotherms can be classified into four types (Alhamami, 2014): open-at-both-ends cylindrical pores (type H1), slit pores (type H2), open-at-both-ends wedge-shaped pores (type H3) and ink bottle-like pores (type H4). Type V isotherms also show hysteresis loop at high relative pressure, which means the existence of mesopores in materials. However, the concave isotherm at low relative pressure indicates that the interaction between adsorbent and adsorbate is weaker than intermolecular interaction of adsorbate. Type VI isotherms showed multiple plateaus with increasing relative pressure, which is associated with layer-by-layer adsorption occur on a uniform surface (Weidenthaler, 2011).



Fig. 4.6 Six types of N<sub>2</sub> adsorption isotherms (Weidenthaler, 2011).

**Surface area** Brunauer-Emmett- Teller method has been widely used to calculate the specific surface area. BET theory was proposed in 1938, which extends to the analysis of multilayer adsorption isotherms compared to Langmuir model which can only deal

with type I isotherm. The calculation of surface area by using BET method is based on the following assumptions (Weidenthaler, 2011):

- 1. All adsorption sites are equivalent in homogeneous flat.
- 2. The dynamic equilibrium with vapour just occur in the uppermost molecules.
- 3. Heat of condensation is equal to the heats of adsorption in all layers except the first layer.
- 4. The layer number is infinite when  $p/p_0$  is 1
- 5. Adsorbate molecule do not evaporate when another adsorbate molecule cover it.
- 6. No lateral interaction are involved between adsorbate molecules.
- 7. The rate of evaporation and condensation is equivalent in each layer.

Thus, the BET equation can be expressed as Equation 4.2

$$\frac{p}{n_{ads}(p_o - p)} = \frac{1}{cn_m} + \frac{(c - 1)}{cn_m} \times \frac{p}{p_o}$$
(4.2)

Where, p and  $p_o$  are the equilibrium and saturation pressure, respectively,  $n_{ads}$  is the amount of gas adsorbed by unit mass of adsorbent, c is an empirical constant and  $n_m$  is the monolayer capacity. The (c-1)cn<sub>m</sub> and 1/cn<sub>m</sub> can be obtained from the plot of p/p<sub>0</sub> versus p/n<sub>ads</sub> [(p<sub>0</sub>-p)] (Fig. 4.7) and the value of c and n<sub>m</sub> can be calculated. Finally The specific surface area, S<sub>BET</sub>, can be calculated by using Equation 4.3:

$$S_{BET} = \frac{n_m}{M} N_A \sigma \tag{4.3}$$

Where M is the molecular weight of the adsorbate,  $N_A$  is the Avogadro constant and  $\sigma$  is the surface area covered by one molecule.

Total pore volume can be calculated with the amount of adsorbed gas at relative pressure of 1, where all the gas adsorbed in pores was in the form of liquid. When the liquid  $N_2$  is used as adsorbate, the total pore volume can be calculated by Equation 4.4.

$$Pore Volume (PV) = \frac{P_a V_{ads} V_m}{RT}$$
(4.4)

Where  $P_{\alpha}$  is the ambient pressure,  $V_{ads}$  is the volume of adsorbed  $N_2$  gas,  $V_m$  is the molar volume of the liquid nitrogen (34.7 cm<sup>3</sup>/mol), R is the ideal gas constant and T is the ambient temperature.



Fig. 4.7 The plot of p/p0 versus p/n<sub>ads</sub> [(p0-p)] (Weidenthaler, 2011).

**Pore size calculation** According to IUPAC, pores are classified into 3 types: microspore (< 2 nm), mesoporous (2-50 nm) and macrospore (>50nm). As for mesoporous materials, the nitrogen isotherms belong to type IV isotherm, which has a hysteresis loop at relative high pressure due to the capillary condensation of gas adsorbate in mesopores. Fig. 4.8 shows the mesoporous structure of MCF. Barrett–Joyner–Halenda (BJH) method based on the Kelvin model of pore filling can be used to calculate the mesopore size. Kelvin equation describes the relationship between the pressure when adsorbate will condense or evaporate in a cylindrical pore of a given size and size of the pores. The equation was shown in Equation 4.5 (Barrett, 1951):

$$r_k = \frac{2\Upsilon V_m}{RT} \ln \frac{p_o}{p} \tag{4.5}$$

Where,  $r_k$  is the kelvin radius,  $\Upsilon$  is the surface tension,  $V_m$  is the molar volume of the liquid nitrogen (34.7 cm<sup>3</sup>/mol), R is the ideal gas constant and T is the ambient temperature. In other words, it provides the quantity analysis of the pore size when capillary condensation occurs to the relative pressure. The adsorption branch presenting the progressive filling of mesopores provides a complete pore size distribution, whereas the desorption branch showing the rapid emptying of the mesopores gives the size distribution of necks or window size distribution. Both of them were used to characterize the prepared SCF samples. But it should be noted that this method can be only be applied to evaluate the mesopore and small macropore size range.



Fig. 4.8 Schematic cross section of siliceous mesostructured cellular foams (MCFs) (Schmidt-Winkel, 2000).

**Pore size distribution** Macroscopic treatments of adsorption isotherms like Dubinin– Radushkevich (DR) and Horvath-Kawazoe (HK) and BJH models show limited suitability for the analysis of pore size distribution. For instance, Dubinin– Radushkevich (DR) and Horvath-Kawazoe (HK) models were designed for pore size distributions of micropores, while BJH model can be only applied to the mesopores. In comparison, from the microscopic treatment on a molecular level based on statistical mechanics, density functional theory (DFT) gives more realistic description of the thermodynamic properties of the pore fluid and so provides an accurate approach to describe the pores in the range from micropores to macropores. Because the synthesized SCF samples possessed heterarchical pore size distribution from micropores to macropores, the DFT method was used to calculate the pore size distribution of SCF samples. Based on Generalised Adsorption Isotherm (GAI) equation, the experimental isotherms can be correlated with simulated isotherms generated from DFT method as shown in Equation 4.6 (Ryu, 1999)

$$N(\frac{P}{P_0}) = \int_{R_{min}}^{R_{max}} N\left(\frac{P}{P_0}, R\right) f(R) dR$$
(4.6)

Where,  $N(P/P_0)$  is the data from experimental isotherm at pressure  $P/P_0$ ,  $R_{max}$  and  $R_{min}$  are maximum pore widths and minimum pore widths, N(P/P0, R) is the isotherm data at a specific pore width R and f(R) is the pore size distribution function. Based on this, the pore size distribution can be calculated.

#### 4.3.2 Thermogravimetric analysis (TGA)

#### 4.3.2.1 TGA General information

Thermalgravimetric analysis is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes in a specific atmosphere. It has been widely used for the analysis of phase transitions, thermal decompositions, and adsorption/desorption behaviour and so on. In this research, a thermogravimetric analyser (Q500 TGA), as shown in Fig. 4.9, was applied to examine the CO<sub>2</sub> adsorption performance of prepared samples. The highest temperature for Q500 TGA was 1000 °C and the heating rate varies from 0.1 to 100 °C/min.



Fig. 4.9 Photograph of the thermogravimetric analyser (Q500 TGA).

#### 4.3.3.2 CO<sub>2</sub> adsorption experiment

The CO<sub>2</sub> adsorption capacity of the adsorbents was examined by Thermogravimetric Analyser (TGA) Q500. The experimental procedure is shown in Fig. 4.10: the sample (15-20 mg) was first heated up to 115 °C in nitrogen for 20 min in order to remove any moisture in samples. Then it was cooled down to the adsorption temperature (75 °C) and the gas flow was switched from nitrogen to simulated flue gas from coal power plant (15% CO<sub>2</sub> in N<sub>2</sub>) or NGCC powder plant (5% CO<sub>2</sub> in N<sub>2</sub>). Each adsorption process required approximate 60 mins to achieve adsorption equilibrium at 75 °C. The CO<sub>2</sub> adsorption capacity was determined by Equation 4.7.



$$CO_2 \text{ Uptake (wt\%)} = \frac{W_{final} - W_{initial}}{W_{initial}} \times 100\%$$
(4.7)

Fig. 4.10 TGA curve for CO<sub>2</sub> adsorption capability of PEI adsorbent.

# 4.3.2.3 Cyclic CO<sub>2</sub> adsorption and desorption tests

Cyclic stability testing of the prepared adsorbents was also carried out by using TGA 500. The samples were dried in pure N2 for 30 mins at 115 °C before it cooled down to adsorption temperature 75 °C. Then the gas was switched to the simulated flue gas and kept for 10 mins. Once the adsorption reached equilibrium, the sample was then heated up to 130 °C and held at this temperature for 5 mins. Up to 50 adsorption-

desorption cycles was done to verify the stability and regenerability of the samples. Fig. 4.11 illustrates the diagram of the cyclic test of the selected PEI adsorbent obtained from TGA.



Fig. 4.11 TGA curve for CO<sub>2</sub> adsorption-desorption cyclic test of PEI adsorbent.

#### 4.3.2.4 Experimental error analysis

In order to ensure the accuracy and reliability of TGA testing results, all TGA measurements was repeated three times and the standard deviation of the results were evaluated using the following Equation 4.8.

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}$$
(4.8)

Where, *s* is the standard deviation, *n* is the number of measurements for a given sample,  $x_i$  is the result for a specific measurement and  $\overline{x}$  is the mean of the results from different tests for a sample. When all results from different TGA tests for a given sample is within 95% of confidence interval, the mean of the experiment data was used as the testing result for the sample tested. However, if the result from a specific measurement was below the confidence level, the test would be repeated and the new data would be would be used for the error analysis.



#### 4.3.3 Gas chromatography-mass spectrometry (GC-MS)

Fig. 4.12 The schematic diagram of GC-MS (Kim et al., 2016).

Gas chromatography-mass spectrometry (GC-MS) is an analytical method that combines the features of gas-chromatography and mass spectrometry to identify different substances within a test sample. GC-MS can be divided into two parts: gas chromatograph and mass spectrometer. As shown in Fig. 4.12, GC-MS starts form the gas chromatograph. The sample is first vaporized and propelled gas through a capillary column packed with solid materials by an inert carrier. Due to the difference in the relative affinity for the solid phase of the column, different compounds will elute from the column at different times, which allows the mass spectrometer to capture, ionize, deflect and detect the ionized molecules separately. The mass spectrometer detects these ionized fragments based on their mass-to-charge ratios (Horning, 1973). There are three fragmentation patterns:  $\sigma$  fragmentation,  $\alpha$  fragmentation and inductive fragmentation (Demarque et al., 2016). Using computer libraries of mass spectra for different compounds, the unknown compounds can be identified and quantitated. The GC-MS composed of Varian CP-3800 gas chromatograph (GC) equipped with a Zebron ZB-1701 fused silica capillary column (60 m x 0.25 mm (i.e.), 0.25  $\mu$ m thickness) and Varian 1200 mass spectrometer (MS) was used in this project to characterise the liquid products from the hydrogenation and hydrothermal treatments.

# CHAPTER 5 Synthesis and Functionalisation of Spherical Meso-, Hybrid Meso/Macro- and Macro-porous Cellular Silica Foam Materials with Regulated Pore Sizes for CO<sub>2</sub> Capture

# 5.1 Introduction

Carbon capture and storage (CCS) has widely been recognised as being a crucial part of worldwide low carbon energy portfolios required to meet the target of global climate change without compromising energy security, given the projected soaring energy demand and the continual dominance of fossil energy in worldwide energy landscape (EIA, 2008, EIA, 2016, IEA, 2014, Schwartz, 2008). However, the successful development and deployment of enabling capture technologies holds the key to the overall success of CCS as carbon capture represents the most costly single element of the whole CCS chain, which goes from CO<sub>2</sub> capture through compression and transport to geological storage. At present, aqueous amine scrubbing at its various forms is the state-of-art capture technology for use, but the high energy penalty together with a range of environmental and operational issues (e.g. solvent degradation, equipment corrosion and toxic and corrosive emissions) has become the major challenge for the large deployment of this technology for CCS (Hamilton et al., 2009). It has been estimated that post-combustion capture (IPCC) with aqueous amine scrubbing could increase the cost of power generation by 32% and 65% for gas and coal-fired power plants, respectively. Consequently, the development of alternative cost-effective PCC technologies has received tremendous attention over recent years, with the adsorption-based solid adsorbents looping technology having become the persistent focus of many investigations due to the potentially significantly reduced energy penalty and the choice of a wide range of candidate adsorbent materials, including but not limited to zeolites (Akhtar et al., 2012, Bonenfant et al., 2008), immobilized amines (Pirngruber et al., 2009, Yu and Chuang, 2016), activated carbons (Ello et al., 2013, Romanos et al., 2012), metal-organic frameworks (MOFs) (Bao et al., 2011, Lv et al., 2014), covalent-organic frameworks (COFs) (Zeng et al., 2016, Furukawa, 2009) and zeolitic imidazolate frameworks (Hillman et al., 2018, Amro Mohamed, 2018). Among the candidate sorbent materials, immobilized amines possess many desirable CO<sub>2</sub> adsorptive properties that may not be easily obtained with other sorbent materials, such as their extremely high CO<sub>2</sub> selectivity, fast adsorption

kinetics and high adsorption capacity especially at very low CO<sub>2</sub> partial pressures, great moisture tolerance and favourable operating temperature windows of 50-80 °C that minimizes or essentially eliminate the cooling need of typical flue gas streams from power plants (Qi et al., 2011, Cheng et al., 2015, Bollini et al., 2011b, Loganathan et al., 2016, Loganathan and Ghoshal, 2017, Zhao et al., 2013).

The CO<sub>2</sub> adsorption of immobilised amine adsorbents follows the similar reaction mechanisms to those in aqueous amine absorption process, which involves the reversible formation of ammonium carbamate in anhydrous flue gas conditions and ammonium bicarbonate in wet conditions. Two typical preparation methodologies are used, namely surface grafting and direct impregnation. In general, amine-grafted silica sorbents benefit from improved amine efficiency and thermal stability but usually suffer from low amine loadings due to the limited density of accessible surface silanol groups, giving rise to CO<sub>2</sub> adsorption capacities being generally well below 3 mmol CO<sub>2</sub>/g sorbent (hereinafter abbreviated to mmol/g) or 132 mg/g. The highest adsorption capacity of ca. 4 mmol/g (176 mg/g) was obtained by Drese et al. for a hyperbranched aminosilica with a grafted amine loading of 9.78 mmol/g SBA-15. In comparison, impregnation as a more convenient and less corrosive preparation methodology can achieve much larger amine loading capacity but the produced sorbents may suffer from the potential evaporation loss of the impregnated amines, an issue that can be improved by using higher boiling amines (Goeppert et al., 2010). Builes and Vega (Builes, 2012) compared the performance of the immobilised amines prepared from different methodologies and found that compared to grafting, impregnation persistently gives rise to significantly higher adsorption capacities particularly at low CO<sub>2</sub> partial pressures, due to the mobility of the functionalised amine chains that leads to the formation of microporosity-alike networks inside the mesoporous silica support. In contrast, similar structures cannot be formed within the densely-grafted amine groups and this can limit the potentials of achieving higher adsorption capacities by increasing the grafting density.

Numerous investigations have shown that for both impregnation and grafting, the performance of supported amine sorbent is not only determined by the chemical nature

of the amines but also by the type of porous solid support dictated, with mesoporous silica materials such as MCM-41, MCM-48, SBA-15, SBA-16 and hexagonal mesoporous silica (HMS) being the most widely used solid supports because of their tuneable structures and re-addressable surface chemistry. Son et al. (Son et al., 2008) studied the CO<sub>2</sub> adsorptive properties of different mesoporous silica materials at the same maximum PEI loading of 50 wt% and found that dictated by the average pore diameter of the solid support, the CO<sub>2</sub> uptake of PEI-modified silica sorbent follows the order of KIT-6 > SBA-16  $\approx$  SBA-15 > MCM-48 > MCM-41, with the capacities varying from 3.1 mmol/g for KIT-6 with a 3-dimensional (3-D) pore diameter of 6.5 nm to 2.5 mmol/g for MCM-41 with a 1-D pore diameter of 2.8 nm. Over recent years, many efforts have been made to expand the pore diameter or increase the pore volume of mesostructured silica supports to increase the amine loading and hence  $CO_2$  uptake capacity. It has been found that regardless the preparation techniques employed, the immobilised amine sorbents prepared from using pore-expanded MCM-41, MCM-48, SBA-15 and HMS all showed considerably higher CO<sub>2</sub> adsorption capacities than their pore-unexpanded counterparts (Sanz-Pérez et al., 2018, Hori et al., 2017, Wang et al., 2015, Coasne, 2006, Chen et al., 2010). In addition to the pore size and volume of the support, the length of pore channels also play a vital role in determining the CO<sub>2</sub> adsorption capacity and kinetics of amine-modified silica adsorbents due to the mass transfer limitations within prolonged meso-channel networks. Studies found that poreexpanded mesoporous silica supports with shorter meso-channels can outperform those with longer channels by a factor of 2.7 and 1.45 for PEI-impregnated MCM-41 and SBA-15 at 50 °C in pure CO<sub>2</sub> (Heydari-Gorji, 2011) and a factor of 2.2 for aminegrafted SBA-15 at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub> (Zhou et al., 2014), respectively. However, despite the efforts in recent years, very few of the reported amine-modified silica adsorbents have CO<sub>2</sub> capture capacities greater than 3 mmol/g or 132 mg/g in 15%  $CO_2/N_2$  at the desirable adsorption temperature range of 50 ~ 75 °C, due to the amine loading limitations with conventional mesoporous silica materials. Previous studies have demonstrated that for post-combustion capture, solid amine adsorbents with a CO<sub>2</sub> capture capacity of ca. 3mmol/g for 50 wt% PEI loading is equivalent to 20 wt% aqueous MEA solvent when 90% of the CO<sub>2</sub> in typical flue gas streams was captured (Wang et al., 2013b, Yu, 2012). This suggests that more effective solid supports need to be explored to further improve the adsorption performance of immobilised amine adsorbents.

Clearly, a desirable solid support should best have large pore volume coupled with superior interconnectivity among the pores to maximise amine loading whilst reduce the mass transfer limitations of adsorption. Spherical mesocellular siliceous foam (MCF) represents a relatively new class of mesoporous silica materials with a continuous network comprised of uniform micro-spherical cells interconnected by large window pore channels, giving rise to a rigid macro-spherical geometry with 3dimmentional porous framework with large pore size, pore volume and surface area. Compared with other mesoporous materials which usually consist of non-intersecting tubular pores, the unique geometrical configuration of MCF make it a desirable category of support materials for preparing immobilised amine CO<sub>2</sub> sorbents. Early investigations have demonstrated that mesocellular silica foam-supported PEI sorbents can significantly outperform other mesoporous silica materials by up to 30% for CO<sub>2</sub> adsorption, with capacities reaching up to 3.5 mmol CO<sub>2</sub>/g at 75 °C and 15 kPa CO<sub>2</sub> (Yan et al., 2011, Subagyono et al., 2011, Subagyono et al., 2014), compared to virtually all other mesoporous silica-supported PEIs with capacities being generally below 2.5 mmol CO<sub>2</sub>/g under similar conditions (Son et al., 2008, Zhou et al., 2014). To date, however, the impact of preparation and precursor chemistries on CO<sub>2</sub> adsorption of the resulting sorbents has not been examined in details. In this study, a variety of siliceous cellular foam materials with varying cellular networks from mesostructured to macro-structured were prepared with different precursor and preparation chemistries, and their corresponding performance as the candidates for preparing high capacity CO<sub>2</sub> adsorbents was evaluated.

# 5.2 Experimental

#### 5.2.1 Chemicals

Non-ionic tri-block copolymer surfactant Pluronic P123 (EO20-PO70-EO20, MWav =5800), HCl (37%), 1,3,5,-Trimethylbenzene(TMB), tetraethyl orthosilicate (TEOS, 99.999), ammonium fluoride (NH<sub>4</sub>F, 99.99%), different branched polyethyleneimines with average molecular weight (MW) varying from 600 to 60000 were obtained from Sigma-Aldrich. PQ silica was supplied by PQ Corporation.

# 5.2.2 Preparation of siliceous cellular foams and polyamine-impregnated CO<sub>2</sub> adsorbents

The porous siliceous cellular foams (SCF) with variable pore and window sizes were synthesised from using a modified version of the micro-emulsion method reported earlier by Schmidt-Winkel and co-workers (Schmidt-Winkel, 2000), with the amphipathic surfactant P123 as being the template and TMB as the pore-expanding agent. Briefly, in a typical preparation with TEOS as the silicon source and TMB/P123 mass ratio of 1:1, 8g of P123 was firstly dissolved in 150 ml of 1.5M HCl at 40 °C and then 8g of TMB was added. Following 40 min of further stirring, 18.4 ml of TEOS and 10 ml of 2.5 M NH<sub>4</sub>F solution (F/Si molar ratio 0.03) was added into the mixture under vigorous stirring and the resultant solution was kept at 40 °C for variable duration times with continuous stirring. During this process, the hydrolysis of the TEOS at the surface of P123-coated TMB droplets leads to the formation of a composite shell material with interconnected cells and windows at the areas of contact of adjacent droplets. The formed milky reaction mixture was then transferred into an autoclave and kept at 100 or 120 °C for variable duration times under static conditions. The asprepared white precipitate was separated by filtration and dried at ambient temperature. The dried precipitate was then calcined in air at 550 °C for 8 hours to obtain the porous silica support. The effect of different preparation parameters on the surface textual properties of silica supports and hence the CO<sub>2</sub> adsorptive properties of their supported polyamine sorbents were investigated, including TMB/P123 ratio, aging time and aging temperature. For clarity and easy comparisons, the SCF materials synthesised under different conditions are denoted as SCF-x-y-z where x, y and z represents the TMB/P123 ratio, aging temperature and time, respectively. Table 5.1 summarises the preparation parameters examined.

Sample	Initial P123 concentration, wt%	TMB/P123 mass ratio	Aging Temperature (°C)	Aging Time (hours)
SCF-0-100-24	5.0	0	100	24
SCF-0.4-100-24	5.0	0.4	100	24
SCF-0.6-100-24	5.0	0.6	100	24
SF-1-100-24	5.0	1	100	24
SCF-1d-100-24	10.0	1	100	24
SCF-1-70-24	5.0	1	70	24
SCF-1-80-24	5.0	1	80	24
SCF-1-90-24	5.0	1	90	24
SCF-1-100-12	5.0	1	100	12
SCF-1-100-42	5.0	1	100	42
SCF-1-100-60	5.0	1	100	60
SCF-1-120-24	5.0	1	120	24
SCF-2-100-24	5.0	2	100	24
SCF-2-100-42	5.0	2	100	42
SCF-3-100-24	5.0	3	100	24
SCF-3-100-42	5.0	3	100	42
SCF-3-120-24	5.0	3	120	24

Table 5.1 Summary of preparation conditions for different SCF materials.

Amine functionalisation of the SCF materials was achieved using a modified wet impregnation method. In this modified methodology, water rather than alkanols (Heydari-Gorji, 2011, Xu et al., 2003, Yan et al., 2011) was used for the first time as the more cost-effective solvent. In a typical preparation, a calculated amount of selected polyamines was first dissolved 10 ml of water under continuous stirring for 20 min, and then the corresponding amount of SCF support was gradually added into the solution. After overnight stirring, the mixture was subjected to vacuum drying at 50 °C to yield the PEI-functionalised SCF adsorbents. A branched polyethylenimine with an average molecular weight (MW) of 600, designated as PEI-600, was used in

most preparations but for selected SCF samples, other amines were also examined, including tetraethylenepentamine (TEPA) and other PEIs with variable MW from 1800 to 60,000. All the polyamines were obtained from Sigma-Aldrich. The PEI content of SCF CO<sub>2</sub> adsorbent was determined by TGA as the weight loss of the prepared SCF adsorbents when they were heated up and burned in air (100 cm<sup>3</sup>/min) at 700 °C to a constant weight. It was found that the weight loss obtained as the PEI contents agreed well with the pre-defined contents used in the impregnation, confirming the validity of the methodology.

# 5.2.3 Characterisation of SCF materials

The textual properties of the synthesised SCF materials were determined by nitrogen sorption isotherms with a Micromeritics ASAP 2420 apparatus at 77K. In a typical measurement, the silica was first degassed at 120 °C for 12 hours before analysis. Specific surface areas were determined using the Brunauer Emmett Teller (BET) equation. In addition, the pore volume, pore size distribution, cell pore size and window size of the mesostructured silica were determined by using the Barrett-Joyner-Halenda (BJH) method.

A FEI Quanta 600 Scanning Electron Microscope (SEM) was used to illustrate the morphology and microstructure of the MCF samples.

#### 5.2.4 Characterisation of PEI-modified SCF adsorbents

The CO<sub>2</sub> adsorption and desorption performance of PEI-modified SCF adsorbents was evaluated with a TGA500 thermogravimetric analyser (TA Instruments), using a simulated flue gas stream containing 15% CO<sub>2</sub> in N<sub>2</sub>. Prior to any measurement, each individual sample was first subjected to a pre-treatment at 120 °C in N<sub>2</sub> for 20 mins to remove any remaining moisture and/or pre-adsorbed gases, and the sample was then allowed to cool down to the selected temperature for adsorption tests. Three different types of CO<sub>2</sub> adsorption measurements were performed, including 1) temperature-programmed CO<sub>2</sub> adsorption; 2) CO<sub>2</sub> adsorption isotherms at selected temperatures; and 3) the cyclic lifetime performance testing of the sorbents.

For temperature-programmed adsorption, the sample was cooled down to 30 °C when the gas supply was switched from N<sub>2</sub> to 15% CO<sub>2</sub> in N<sub>2</sub>. The sample was first held at this temperature for 30 min to reach equilibrium CO<sub>2</sub> adsorption before the temperature was allowed to ramp to 130 °C at an extremely slow heating rate of 0.1 °C /min. The optimal adsorption temperature determined from the temperatureprogrammed adsorption test protocol was then selected to evaluate the CO<sub>2</sub>-capturing performance of individual sorbent samples prepared. CO<sub>2</sub> adsorption capacity was taken as the weight gain after the sample was exposed to the CO<sub>2</sub>-containg gas flows and reached equilibrium adsorption. The adsorption measurement was repeated typically three times for each sample or set of conditions and the average value was used.

Cyclic adsorption and desorption tests were also carried out. In each cyclic test, the sample was first allowed to reach equilibrium adsorption at 75 °C in the simulated flue gas test and with the gas supply switched to  $N_2$ , the sample was then heated up at flow rate of 15 °C /min to 130 °C and held at this temperature for 20 min. The same procedure was repeated for 50 cycles.

# 5.3 **Results and Discussion**



#### 5.3.1 Surface textural and morphological characterisations of SCF materials

Fig. 5.1  $N_2$  adsorption isotherms and pore size distributions of the SCF samples prepared with different precursor chemistries under different conditions.

Fig. 5.1 presents the nitrogen adsorption-desorption isotherms and pore size distributions of the porous SCF samples, which were synthesized under different conditions to reveal the effect of the precursor and preparation chemistries on the textural and morphological characteristics of the siliceous foams and hence their corresponding performance as candidate supports for preparing high capacity  $CO_2$  adsorbents. As shown in Fig. 5.1, all synthesised cellular forms were found to have type IV isotherms with steep but variable types of hysteresis loop in the high relative pressure region, which is characteristic for typical meso-modulated materials that exhibit ink-bottle or thermodynamic effects associated with the condensation and evaporation of adsorbate in the adjoining mesopores with smaller connecting channels or bottle necks. With increasing TMB/P123 ratio as shown in Fig. 5.1 (a, b), the sorption hysteresis loops shifted dramatically toward higher relative pressures with increasing amount of N<sub>2</sub> adsorbed, which led to narrower pore size distributions (PSD)

that also shifted toward larger pore diameters. This confirms the pore expansion behaviour of TMB. Meanwhile, with increasing amount of TMB used, the pore hysteresis loop of the cellular materials also transformed from the wide H2 type hysteresis loops, which indicate the network nature of relatively uniform ink-bottle or channel-like pores, to the narrower H1 type hysteresis that is associated with the porous frameworks of higher pore size uniformity and facile pore connectivity. Clearly, the shift took place as a result of reduced curvatures or increased sizes of more uniform spherical composite micelles with increasing TMB concentration, due to the greater hydrophobic cores formed by the central hydrophobic polypropylene oxide chains of P123 dissolved into the non-polar TMB.

In general, the effect of aging time and aging temperature on pore hysteresis, as shown in Fig. 5.1(c, d), follows somehow the same trend as that of TMB. In general, the results demonstrate that an aging temperature of 100 °C and a TMB/P123 ratio of 1.0 gives better control over the pore size distributions particularly in the mesoporous region, while the cellular materials synthesised at 120 °C or with higher TMB/P123 ratios ( $\geq$  2), such as SCF-1-120-24, SCF-3-120-42 and SCF-2-100-42 appear to be almost entirely macro-structured with reduced volumes of nitrogen adsorbed and wider pore size distributions centred between 60 and 90 nm (Fig. 5.1(b, d)).

Table 5.2 summarises the surface textural properties of the cellular foam samples derived from the sorption isotherms, while Fig. 5.2 presents the variation of pore volume, pore diameter and window size with the synthesis parameters. The cell diameter or the sizes of cell cavities of the cellular foams were calculated using the adsorption branches of the N<sub>2</sub> isotherms, assuming that the pores are spherical, while the window size or the diameter of the channels connecting the pores were derived from the desorption branch of the isotherms (assuming cylindrical windows), using a modified BdB-FHH model proposed by Lukens et al.(Lukens, 1999). It is evident that both the cell diameters and the window sizes increase significantly with increasing TMB concentration, aging time and aging temperature. Compared with the effect of aging time, however, the effect of TMB concentration and aging temperature appears to be more significant. At an aging temperature of 100 °C and aging time of 24 hours, increasing the TMB/P123 ratio from 1 to 3 dramatically expanded the cell cavity size from 8.1 to 21.2 nm and the window size from 4.4 nm to 11.2 nm, respectively,

highlighting the novel pore expanding effects of TMB (Fig. 5.1a). Regarding the effect of aging temperature, although it appears to be quite modest at temperatures below 100 °C, a sharp increase in both the pore diameters and window sizes was observed when the aging temperature was increased slightly from 100 to 120 °C, as shown in Fig. 5.1(b). Closer examinations of the results shown in Table 5.2 and Fig. 5.2 also interestingly reveal that compared to the window sizes, the cell diameters increased more significantly with increasing TMB concentration, aging time and aging temperature. This suggests that the condensation of silica, which was responsible for the formation of the shells of TMB-cored micelles or micro-emulsion droplets, was significantly enhanced due to the accelerated hydrolysis of TEOS and aggregation of smaller micelles at higher aging temperatures, TMB concentrations and longer aging time, leading to the formation of larger cells with denser and thicker shells or walls.

Sample	BET Surface	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>meso</sub> (cm <sup>3</sup> /g)	V <sub>macro</sub> (cm <sup>3</sup> /g)	Pore Size (nm)	Window
	Area					Diameter
	(m <sup>2</sup> /g)					(nm)
SCF-0-100-24	715	1.1	0.9		8.1	4.4
SCF-0.4-100-24	668	1.3	1.1		10.4	5.1
SCF-0.6-100-24	591	1.8	1.7		15.9	10.9
SCF-1-100-24	547	2.2	2.1		21.2	11.2
SCF-1-70-24	631	1.5	1.4		13.8	6.1
SCF-1-80-24	561	1.7	1.6		16.4	7.9
SCF-1-90-24	493	1.8	1.7		16.7	10.8
SCF-1-100-12	571	2.1	2.0		19.3	8.6
SCF-1-100-42	549	2.8	2.7		25.4	13.4
SCF-1-100-60	451	2.2	2.1		24.3	15.1
SCF-1-120-24	168	1.8	0.72	0.91	52.8	34.3
SCF-2-100-24	240	2.8	0.31	2.77	57.9	39.7
SCF-2-100-42	217	2.5	0.56	1.91	61.3	38.7
SCF-3-100-24	198	3.2	0.27	2.5	74.2	39.1
SCF-3-100-42	223	2.4	0.38	1.99	62.2	39.4
SCF-3-120-24	165	1.6	0.23	1.37	50.9	44.4

Table 5.2 Surface textual properties of the synthesised SCF materials.





Fig. 5.2 Effect of precursor chemistry and preparation conditions on the surface textural properties of SCF material samples.

The surface area of the synthesised materials, depended heavily on the preparation conditions, varying from 714 m<sup>2</sup>/g for the sample SCF-0-100-24 where no TMB was
used, to just 165 m<sup>2</sup>/g for the sample SCF-3-120-24 prepared at 120 °C and a TMB/P123 ratio of 2. As expected, the surface areas were found to decrease significantly as the pore volumes increased with TMB concentration and aging temperature. This is, in principle, because the resultant enlarged windows cost disproportionately a larger fraction of the surface areas of the enlarged cells. Indeed, all the samples synthesised at 120 °C and those at 100 °C but with high TMB/p123 ratios ( $\geq 2$ ) were found to have the lowest surface areas, generally well below 250 m<sup>2</sup>/g but with largest pore diameters and window sizes (Table 5.2). In particular, the sample (SCF-3-120-24) prepared at an aging temperature of 120 °C with a TMB/P123 ratio of 3 was found to have the largest window size of 44.4 nm but the lowest surface area of only 165 m<sup>2</sup>/g and the smallest pore volume of 1.6 cm<sup>3</sup>/g. This further highlights the enhanced silica condensation as a result of accelerated hydrolysis of TEOS at high aging temperature and TMB concentration, leading to increased cell diameter with reduced cell cavity and enlarged pore opening.

Schmidt-Winkel et al. (Schmidt-Winkel, 2000) found that the cell cavity or pore size is in a linear relationship with the cubic root of TMB/P123 mass ratio, being in contrast to the direct linear relationship with the TMB/P123 ratio observed in a latter investigation by Sridhar et al. (Sridhar et al., 2014). However, no such linear relations were obtained across the whole wider range of TMB/P123 and aging temperatures examined in our investigation while our synthesised cellular foams were found to have significantly larger pore diameters and much lower surface areas compared to those obtained in previous investigations (Schmidt-Winkel, 2000, Sridhar et al., 2014, van Grieken, 2002). Regarding the effect of precursor chemistry and preparation conditions on SCF wall thickness, van Grieken et al. and Schmidt-Winkel et al. found that enhanced silica condensation is directly responsible for increased wall thickness (Schmidt-Winkel, 2000, van Grieken, 2002), which contradicts the findings by Srihar et al. that increased wall thickness is not a result of enhanced silica condensation but by shrinked pore size and a transition of pore geometry from being spherical to cylindrical (Sridhar et al., 2014). However, the findings revealed by Fig. 5.2, Table 5.2 and the imaging analyses below indicates that a combination of enhanced silica condensation and pore geometry transition coupled with the aggregation of smaller TMB-cored micelles due to reduced surface tensions is the most likely cause of the formation of larger cells with reduced cell cavity and enlarged window sizes at higher aging temperatures and TMB concentrations. The transition of pore hysteresis from H2 to H1 type as shown in Fig. 5.1 also corroborates the analysis above.

Fig. 5.3 and Fig. 5.4 show the morphological features at different microscopic scales of the typical cellular foams synthesised. As shown in Fig. 5.3 (a, b), due to the extensive random aggregation observed among the smaller spheres of variable sizes, the siliceous particles prepared at lower aging temperatures and/or shorter aging times exhibit assembled coral-like cylindrical morphologies, which are somewhat similar to those of SBA-15 (Subagyono et al., 2011). In contrast, the formation of significantly larger, more uniform and less packed spherical particles is evident when increasing the aging temperature from 80 to 100 °C (Fig. 5.3 (a, c)) or the aging time from 12 to 60 hours (Fig. 5.3 (b, d)). A further transformation from spherical to ellipsoidal particles that tend to assemble into larger spherical aggregates can be seen with further increase in aging temperature from 100 to 120 °C and/or TMB/P123 ratio from 1 to 3. Closer examinations of the particle morphologies, as shown in Fig. 5.4, reveals the open polygonal networks framed by silica struts, being characteristic of the structural feature of siliceous cellular foams (Schmidt-Winkel, 1999, Schmidt-Winkel, 2000). Some deformations of the spherical cells are evident, probably caused by the unfavourable packing of the spherical micelles or the collapse of micellar cores during the packing due to their polydispersity. It can be seen that with increasing TMB concentration and aging temperature, the polygonal network structures became more developed and interconnected with increasingly more dense silica struts or thicker framework walls, while their sizes were found to be considerably less uniform with the formation of large empty voids or much greater cellular structures (Fig. 5.4 (d,e)). By and large, the morphological transformation is consistent with the variation of surface areas and pore size distributions with TMB concentration and aging temperature as shown in Table 5.2 and Fig. 5.2 (d,e).



Fig. 5.3 SEM images of representative SCFs synthesized under different conditions.



Fig. 5.4 Microscopic SEM analyses of representative SCF particles synthesized under different conditions.

#### 5.3.2 CO<sub>2</sub> adsorption-desorption of the amine-modified sorbents

#### 5.3.2.1 Quasi-static CO<sub>2</sub> adsorption study

To examine the variation of  $CO_2$  uptake with temperature and hence to identify the optimal adsorption temperature, quasi-static  $CO_2$  adsorption tests were first conducted for PEI-modified SCF adsorbents at temperatures between the ambient and 120 °C with a heating rate of 0.5 °C/min. The use of such a low heating rate is to facilitate near equilibrium  $CO_2$  adsorption at individual adsorption temperatures in the range. Fig 5.5 shows the results from the quasi-static tests for selected samples. As can be seen from Fig. 5.5, the  $CO_2$  uptake first increased and then deceased with adsorption temperature for all the samples examined, and the differences between the  $CO_2$  uptakes were significantly larger at lower adsorption temperatures. Meanwhile, the optimal adsorption temperature giving rise to the highest  $CO_2$  uptake also varied considerably for different samples, despite their same level of PEI loading at 60 wt%. Sample SCF-3-120-24 was found to have the lowest optimal adsorption temperature of ca.71 °C, compared to 75 °C for SCF-1-100-24 and SCF-2-100-24 and the highest optimal of 80 °C observed for the sample SCF-0-100-24, respectively.



Fig. 5.5 Quasi-static CO<sub>2</sub> adsorption tests of selected PEI (60%)-modified SCF adsorbents in simulated flue gas (15% CO<sub>2</sub> in N<sub>2</sub>). Conditions: Heating rate of 0.5  $^{\circ}$ C /min from ambient to 120  $^{\circ}$ C; Content of PEI-600: 60 wt%.

Thermodynamically, low temperature favours the CO<sub>2</sub> adsorption of amine-modified sorbent materials, but increasing adsorption temperature can help overcome the kinetic barrier of CO<sub>2</sub> adsorption due to the accordingly improved mobility and hence diffusivity and accessibility of the impregnated PEI molecules (Builes, 2012, Li et al., 2015, Xiaoliang Ma, 2009, Xu et al., 2003). The considerable differences observed in the optimal adsorption temperatures and CO2 uptakes reveal the different mass transfer limitations or diffusivity of CO<sub>2</sub> in the amine sorbents. It is evident that irrespective of the pore volumes, the SCF materials synthesised at higher TMB concentrations or aging temperatures, which generally had larger pore diameters and wider window sizes, also have lower optimal adsorption temperatures in general. In addition, the results also show that although the differences between the variations of CO<sub>2</sub> uptake with temperature diminished significantly at higher-than-the-optimal temperatures, the  $CO_2$ uptake of the samples with higher optimal adsorption temperatures generally decreased more rapidly with temperature, being indicative of the lower diffusional resistance of the desorbed  $CO_2$  when diffusing out through the pores and the bulk phase of immobilised amines during the desorption at higher temperatures. Presumably, for a given level of PEI loading, this is because larger pore and window sizes in an interconnected porous network can facilitate greater thermo-mobility and hence kinetic behaviour of the immobilised amines through the pores such as to enhance the exposure of unreacted amine groups to CO<sub>2</sub> or facilitate the CO<sub>2</sub> diffusion deeper into the immobilised polymer amines, leading to higher amine efficiency or CO<sub>2</sub> uptake of the sorbents. By and large, the results from the quasi-equilibrium adsorption tests are generally in good agreement with the findings by Sakwa-Novak et al (Sakwa-Novak, 2015) that improved amine mobility by adding additives can significantly increase the temperature sensitivity of immobilised amines for CO<sub>2</sub> capture and hence the amine efficiency due to the resultant higher probability of intra-chain CO<sub>2</sub> adsorption events. Builes and Vega (Builes, 2012) also found that high mobility of immobilised amines can facilitate the creation of a diffusive network of micro-cavities within the bulk phase of the amines that favours the diffusion of CO<sub>2</sub> molecules in and out of the amines within the pores. Taking into account of the surface textural properties shown in Table 5.2 and Fig. 5.2, the above results indicate that the formation of the diffusive network of micro-cavities can be better facilitated in the cellular materials with larger window sizes and somewhat greater pore diameters.

#### 5.3.2.2 CO<sub>2</sub> adsorption capacity of SCF-supported amine adsorbents

Fig. 5.6 shows the adsorption profiles of representative PEI-modified SCF adsorbents for each series of SCF materials synthesised. Despite the considerable variation of optimal adsorption temperatures for different SCFs, the CO<sub>2</sub> adsorption capacities were all measured at the same temperature of 75 °C for the sake of consistent comparison. As can be seen from Fig. 5.6, all SCF samples showed significantly faster adsorption kinetics and higher CO<sub>2</sub> capacities than the commercial benchmark silica (PQ Silicas), which is a highly meso-structured siliceous material with its pore volume, pore diameter and window size being similar to or even greater than those of the SCFs (Table 5.2). The times taken for the SCF adsorbents to achieve 80% and 90% of equilibrium CO<sub>2</sub> capacity were found to be just ca. 1.5 min and 3 mins, which is nearly 8 times faster than the ca. 12 and 23 mins obtained for the commercial silica, respectively. This highlights the novel accessibility of the immobilised amines to CO<sub>2</sub>, facilitated by the high levels of pore network connectivity in the SCF materials.



Fig. 5.6 CO<sub>2</sub> adsorption profiles of representative PEI-impregnated SCF adsorbents in 15% CO<sub>2</sub>/N<sub>2</sub> at 75 °C.

Table 5.3 compares the  $CO_2$  adsorption performance for all PEI-600-modified SCF materials at different PEI loading levels, while Fig. 5.7 shows the variation of  $CO_2$  uptake with the precursor chemistry and preparation conditions used. All PEI-modified

SCF adsorbents showed increased CO<sub>2</sub> uptake capacities with increasing levels of PEI but with great variations in CO<sub>2</sub> capacity, determined by the preparation conditions. Among all the materials, SCF-3-120-24 gave rise to the highest CO<sub>2</sub> adsorption capacity of 180.8 mg/g at a PEI content of 70 wt%, followed by SCF-2-100-42 (178.4 mg/g) and SCF-3-100-42 (176.5 mg/g), which are significantly higher than those obtained previously for amine-modified MCFs (Subagyono et al., 2011, Subagyono et al., 2014, Yan et al., 2011) and virtually any other 2D mesoporous silica materials(Hicks, 2008, Son et al., 2008, Ünveren et al., 2017, Zeleňák et al., 2008, Zhou et al., 2014). At 50% and 60 wt% PEI, however, the highest CO<sub>2</sub> uptake was instead obtained for SCF-1-100-60 at 150.4 and 168 mg/g, respectively. It is noteworthy that with a total pore volume of just  $1.1 \text{ cm}^3/\text{g}$ , the SCF material prepared without the pore-expanding agent (SCF-0-100-24) also achieved a higher CO<sub>2</sub> capacity of 138 mg/g) than that of the baseline PQ silica material (127.4 mg/g) with over 50% higher meso-pore volume  $(1.7 \text{ cm}^3/\text{g})$ , highlighting the importance of the 3D pore connectivity of SCF materials. It appears that for the SCF materials prepared with lower TMB concentrations, there generally exists a maximum PEI loading level beyond which the CO<sub>2</sub> adsorption capacity decreases, being consistent with previous findings on amine-modified MCFs (Yan et al., 2011, Zhao et al., 2012). However, the same trend was not observed for those prepared with higher TMB concentrations or aging temperatures, which showed much lower CO<sub>2</sub> uptake capacities but with a sharp continuous increase with increasing PEI contents up to 70 wt%. Nevertheless, no further appreciable increases in CO<sub>2</sub> uptake or even CO<sub>2</sub> capacities were obtained when increasing PEI content to higher than 70 wt% while the SCF adsorbents became pasty.

Samples	CO <sub>2</sub> uptake, mg/g				
	50 xyt%	60 wt%	70 xx/t0/	Max. CO <sub>2</sub> uptake	
	JU w170	UU W170	70 W170 _	mg/g-ads	mg/g-PEI
SCF-0-100-24	118.2	139.4	107.1	139.4	232
SCF-0.4-100-24	125.2	143.2	140.2	143.2	239
SCF-0.6-100-24	134.9	157.9	143.7	157.9	263
SCF-1-100-24	128.7	148.9	162.7	162.7	271
SCF-1-70-24	85.3	103.5	67.8	103.5	173
SCF-1-80-24	91.6	128.4	119.5	128.4	214
SCF-1-90-24	100.6	138.4	154.7	154.7	221
SCF-1-100-12	113.3	139.2	151.0	151.0	215
SCF-1-100-42	137.3	151.3	173.9	173.9	248
SCF-1-100-60	150.4	172.1	144.4	172.4	287
SCF-1-120-24	134.4	156.7	166.2	166.2	237
SCF-2-100-24	113.1	156.2	167.3	167.3	239
SCF-2-100-42	101.3	146.2	178.4	178.4	255
SCF-3-100-24	115.9	146.4	172.5	172.5	246
SCF-3-100-42	112.4	149.8	176.5	176.5	252
SCF-3-120-24	116.7	156.4	180.8	180.8	258
PQ mesoporous silica	127.4	113.8	104.7	131.4	255

Table 5.3  $CO_2$  uptake capacities of PEI-impregnated SCF adsorbents with different PEI-600 contents at 75 °C in simulated flue gas (15%  $CO_2$  in  $N_2$ ).



Fig. 5.7 Variation of  $CO_2$  uptake of SCF materials with precursor chemistry and other preparation conditions (continued).



Fig. 5.7 Variation of CO<sub>2</sub> uptake of SCF materials with precursor chemistry and other preparation conditions.

Fig. 5.7 indicates that increasing TMB concentration and aging temperature and time led to increased CO<sub>2</sub> adsorption capacity for all SCF materials, but the trend varied significantly for different individual conditions and PEI loading levels. As can be seen from Fig. 5.7(a), the effect of TMB concentration appears to depend on the amount of PEI immobilised in the SCF materials. At relatively lower PEI loading levels ( $\leq 60$ wt%), the  $CO_2$  uptake first sharply increased with increasing TMB/P123 ratio from 0 to 1.0 and then deceased significantly when the ratio was further increased from 1 to 3. This instead led to lower CO<sub>2</sub> capacities or amine efficiencies for the bestperforming SCF materials that were synthesised all with high TMB/P123 ratios ( $\geq 2$ ), compared to those prepared with lower TMB concentrations, as shown in Fig. 5.7(a). However, at the higher PEI loading level of 70 wt%, no such trend was observed as can be seen from the continuous increase of the CO<sub>2</sub> uptake with TMB concentration. This is clearly because of the variable maximum PEI-accommodating abilities, which were lower for the SCF materials synthesised with lower TMB concentrations and aging temperatures or times (Table 5.3). A similar trend was also observed on the effect of aging time, namely an increase in aging time led to reduced CO<sub>2</sub> capacity or amine efficiency at lower PEI contents for the SCF substrates synthesised from using

high TMB/P123 ratios. In comparison, all SCF materials showed a continuous increase in CO<sub>2</sub> uptake with aging temperatures at all PEI loading levels, as indicated in Fig. 5.7(b). However, it is noteworthy that despite the variable trends observed, the SCF materials prepared with higher TMB/P123 ratios ( $\geq$ 2) and aging temperatures (>100 °C) all exhibited the highest CO<sub>2</sub> adsorption capacities among all the materials.



Fig. 5.8 Effect of total pore volume, pore diameter and pore window size on the maximum  $CO_2$  uptake capacity of the SCF materials synthesised in different conditions (continued).



Fig. 5.8 Effect of total pore volume, pore diameter and pore window size on the maximum  $CO_2$  uptake capacity of the SCF materials synthesised in different conditions.

In theory, given the similar nature of the SCF materials all with interconnected 3D porous structures, the  $CO_2$  capacity of the range of SCF-based adsorbents should be proportional to the amount of PEI impregnated onto the SCF substrates, which is in

turn determined by the total pore volume of the substrates. Previous investigations have found that the total pre volume was the decisive factor affecting the  $CO_2$  uptake at high amine loading levels particularly for meso-structured support materials with 2D hexagonal symmetries (Veneman et al., 2012, Xu et al., 2003, Yan et al., 2011, Yue et al., 2008). Fig. 5.8 shows that variation of the CO<sub>2</sub> uptake capacity as a function of the surface textural properties of the SCF materials. It is evident that the CO<sub>2</sub> uptake capacity increased dramatically with the total pore volume, pore diameter and window size of the SCF substrates increasing, particularly for the SCF materials synthesised at lower TMB concentrations and/or aging temperatures. In addition, close-to-linear relationships can also be observed between the CO<sub>2</sub> uptake and the total pore volume for the SCF substrates with pore volumes lower than 2.2  $\text{cm}^3/\text{g}$  and pore diameters/window sizes below 28 nm as shown in Fig. 5.8 (a,c). For the SCFs with larger pore volumes or pore diameter/window sizes, the CO<sub>2</sub> uptake deviated from the linear relationship toward lower CO<sub>2</sub> uptakes, indicating the lower amine efficiencies or that the pores could not possibly be fully impregnated with PEI to give higher CO<sub>2</sub> capacity.

However, it needs to be emphasised that all the best-performing SCF materials, which were the macro-structured siliceous foam materials synthesised with high TMB/P123 ratios ( $\geq 2$ ) and aging temperatures (120 °C) or long aging times (>24 hours), all interestingly exhibited the lowest CO<sub>2</sub> capacities or amine efficiencies at low PEI impregnation levels but their CO<sub>2</sub> uptake capacities were found to increase much more sharply with PEI impregnation, instead giving rise to the highest CO<sub>2</sub> capacities at high PEI loading levels among all the materials as shown in Table 5.3 and Fig. 5.7(a,b). These anomalies were found to be largely responsible for the significant data scattering observed in the above correlations (Fig. 5.8) where SCF-2-100-42, SCF-3-100-42 and SCF-3-120-42 were excluded. For instance, SCF-3-120-24, which had the lowest total pore volume of only 1.6 cm<sup>3</sup>/g and surface area of 165 m<sup>2</sup>/g, had one of the lowest CO<sub>2</sub> uptakes at 116.7 mg/g (233 mg-CO<sub>2</sub>/g-PEI) at 50 wt% PEI but achieved the highest CO<sub>2</sub> uptake of 180.8 mg/g (258 mg-CO<sub>2</sub>/g-PEI) at 70 wt% PEI among all the SCF materials, compared to SCF-1-100-24 which has a higher capacity of 128.7 mg/g (257.4 mg-CO<sub>2</sub>/g-PEI) at 50wt% PEI but much lower capacity of 162.7 mg/g (232 mg-CO<sub>2</sub>/g-PEI) at 70 wt% PEI. Meanwhile, SCF-3-100-24, which had the largest pore volume of 3.2 cm<sup>3</sup>/g, gave rise to a CO<sub>2</sub> uptake of just 172.5 mg CO<sub>2</sub>/g-ads being

considerably lower than that of SCF-3-120-24 and other materials with much lower pore volumes. Similar comparisons can also be drawn between SCF-3-100-42 and SCF-1-100-42, SCF-2-100-42 and SCF-1-100-60, and SCF-3-120-24 and SCF-1-100-24. The findings that macro-structured siliceous foams perform better in CO<sub>2</sub> uptake than their meso-structured counterparts have never been observed in previous investigations which were mostly focused on meso-structured MCFs (Subagyono et al., 2011, Subagyono et al., 2014, Yan et al., 2011) and other silica materials (Hicks, 2008, Son et al., 2008, Ünveren et al., 2017, Yue et al., 2008, Zeleňák et al., 2008, Zhou et al., 2014). In addition, Yan et al. (Yan et al., 2011) found that window size, when larger than 8.6nm, is no longer an important factor affecting the impregnation and distribution of PEIs and hence the CO<sub>2</sub> capacity of PEI-modified MCFs, which clearly cannot be generalised to the SCF materials in this investigation probably because of the small number of samples or conditions examined in the previous investigation.

Clearly, the exceedingly high CO<sub>2</sub> uptake performance of the highly macroporous SCF materials cannot be accounted for solely by their greater porosities and pore geometries. Closer examinations of the surface textual results shown in Table 5.2 and Fig. 5.2~4 reveal that the SCF materials prepared at increased aging temperatures and aging times with high TMB concentrations all expectedly had increased pore diameters and/or window sizes but with drastically reduced surface areas (Table 5.2). In addition, it seems that the effect of aging temperature and time on the surface textural properties of SCF materials depends on the TMB concentrations used in the synthesis. Further, as shown in Table 5.2 and Fig. 5.2, the effect of aging temperature and time on the surface textural properties at high TMB concentrations was also found to differ from the effect at low TMB concentrations in that at high TMB concentrations, further increase in aging time from 100 to 120 °C or aging times from 24 to 42 hours led to significantly reduced, rather than increased, pore volumes and macro-pore sizes (e.g. SCF-3-120-24 vs SCF-3-100-24 and SCF-3-100-42 vs SCF-3-100-24) with boosted silica struts or cell wall thickness as shown in Fig. 5.4 (e.f). This essentially led to the formation of mixed meso/macro-cellular SCFs with relatively wider but regular pore size distributions as shown in Fig. 5.1 (b,d). It is therefore believed that the formation of the ordered meso/macro-porous SCF materials with enhanced silica strut structures, which serves as the framework platforms for impregnation, can facilitate higher levels

PEI impregnations and more importantly, greater mobility or diffusivity of the immobilised bulk amines which is vital in boosting their accessibility to  $CO_2$  molecules. This hypothesis is strongly supported not only by the high amine efficiencies achieved of these SCFs at high impregnation levels but also their lower optimal adsorption temperatures, which act as an indicator of the amine mobility, and the fast adsorption kinetics at high PEI loading levels, which indicates the low  $CO_2$  diffusion resistance within the bulk phase of the supported PEI amines, as shown Fig. 5.5. However, the significantly lower surface areas of the highly meso/macro-cellular SCFs, which reduced from typically over 500 m<sup>2</sup>/g-ads to below 250 m<sup>2</sup>/g-ads, may lead to lower  $CO_2$  uptake capacities at low PEI loading levels due to the disproportionately reduced larger number of available top surface amine sites due to accordingly increased coating thickness, which cannot be offset by the increased amine mobility of the bulk impregnated PEI at low loading levels.

5.3.2.3 CO<sub>2</sub> adsorption capacity of SCF materials modified with varying molecule weight PEIs

To further improve the CO<sub>2</sub> adsorption performance of the amine-modified SCF adsorbents, the best performing SCF materials, including SCF-3-100-24 and SCF-3-120-24, were selected for binary impregnation. The results above suggest that the accessibility of the bulk phase of impregnated PEIs play a vital role in determining the CO<sub>2</sub> uptake capacity of the PEI-SCF adsorbents, which is affected heavily by both the surface textural and the morphological properties of the SCF materials that govern the distribution state of the impregnated PEIs. Previous investigations have confirmed that the use of surfactants in amine impregnation can facilitate additional CO<sub>2</sub> pathways within the bulk phase of immobilised amines and hence improve the mobility and accessibility of the amines for higher amine efficiencies and CO<sub>2</sub> capture capacities, and CO<sub>2</sub>-unreactive surfactants were typically used, such as sodium dodecylsulfate (Starkie et al., 2014), P123, STAB and SPAN80 (Wang et al., 2012) and CTAB and polyethylene glycol of different molecular weights (Sakwa-Novak, 2015). Instead of using CO<sub>2</sub>-unreactive surfactants, tetraethylenepentamine (TEPA), which is a type of low molecular weight PEI was used as the substitute for surfactants to prepare the binary PEI adsorbents via co-impregnation with the two selected SCF materials, namely SCF-3-120-24 and SCF-3-100-24. Fig. 5.9 presents the CO<sub>2</sub> uptake performance for the binary SCF adsorbents.



Fig. 5.9 CO<sub>2</sub> adsorption profiles of binary amine-modified SCF adsorbents at 75 °C in simulated flue gas (15% CO<sub>2</sub> in  $N_2$ ).

As can be seen from Fig. 5.9, the binary amine-modified SCF adsorbents achieved significantly higher CO<sub>2</sub> uptake for both SCF materials examined at an amine loading level 70 wt%. The TEPA-PEI modified SCF-3-120-24 reached an exceedingly high CO<sub>2</sub> capacity of 198.2 mg/g, 10% higher than its PEI-modified counterpart (180.8 mg/g). Similar increase in CO<sub>2</sub> uptake by approximately 10% was also obtained for SCF-3-100-24, from 172.5 mg/g for PEI impregnation to 190 mg/g for PEI-TEPA co-impregnation. The CO<sub>2</sub> capacities obtained for the binary SCF adsorbents represent

the highest ever reported under similar conditions (Zhang et al., 2013, Dao, 2015, Ojeda et al., 2017).

Nevertheless, it appears that at the early stage of adsorption, the binary coimpregnation resulted in somewhat slower adsorption kinetics, as opposed to the faster kinetics expected for the lower viscosity and more reactive amine groups of TEPA compared to the higher molecular weight PEI-600. For SCF-3-100-24, the time taken to achieve 80% of equilibrium capacity increased from 1.4 min for PEI impregnation to 3.2 min for the PEI/TEPA co-impregnation whereas for the SCF-3-120-24 material, the time increased from 1.6 to 2.4 min, respectively. Meanwhile, the peak adsorption time  $(t_{max})$  increased from 0.6 to 1.0 min for SCF-3-100-24 and slightly from 0.7 to 0.9 min for SCF-3-120-24, respectively, when the impregnation changed from to PEI-600 to the mixture of TEPA and PEI-600. The results differ from the previous findings that the use of blended amines, such as TEPA and DEA for impregnation resulted in faster rates of adsorption kinetics in addition to higher capacities. Presumably, the lower rate of adsorption kinetics of the binary SCF adsorbents is because of the potentially more dense bulk phase packing of the binary amines as the much less viscous and smaller TEPA molecules can penetrate into the micro-cavities created by the larger PEI-600 molecules as ever observed by (Builes, 2012), leading to steric crowding within the bulk phase of the impregnated mixed amines and hence increased diffusion resistance for CO<sub>2</sub> migration. This kind of effect may not be pronounced in the case of the co-impregnation of TEPA and DEA because of their similar molecular sizes and when the adsorption take place at low temperatures (Dao, 2015, Zhang et al., 2013).

As well as the co-impregnation of amines of different molecular weights, attempts were also made to examine the suitability of the synthesised SCF materials for impregnating higher molecular mass PEIs as a measure to improve the thermal stability of the adsorbents. The development of amine-impregnated adsorbents for CO<sub>2</sub> capture has so far been mostly limited to the use of low molecular weights mass amines, such as TEPA, DEA and PEIs with molecular mass typically below 1800, because they are less viscous and can facilitate faster adsorption kinetics and higher adsorption capacity

at the same impregnation levels. However, the supported lower molecular mass amines usually have lower thermal stability, giving rise to inevitable amine loss due to evaporation or even thermal decomposition in long term operations (Sanz et al., 2013). To this end, higher molecular mass PEIs do offer some considerable advantages. However, in terms of adsorption capacity and kinetics, the CO<sub>2</sub> adsorption performance of higher molecular mass PEIs can be sluggish due to their higher viscosities and tertiary amine contents (Li et al., 2014), and thus more robust porous support materials are required to mitigate the negative impact. To further investigate the ability of the synthesised SCF materials to accommodate higher molecular weight PEIs as means to improve the thermal stability of low molecular mass PEI-modified SCF materials, the meso-structured SCF-1-100-24 was selected as the support for the impregnation of higher molecular mass PEIs. Fig. 5.10 shows the CO<sub>2</sub> adsorption performance in comparison with the baseline 2D meso-structured PQ silica material.

As expected, the results demonstrate that the  $CO_2$  capacity decreased considerably for both the SCF and the baseline 2D meso-porous PQ silica as the molecular weight of PEI increased. At 50% PEI content, the CO<sub>2</sub> adsorption capacity of the PQ silica dropped from 127.4 to 95 mg/g as the molecular mass of PEI increased from 600 to 60,000, whereas the capacity of SCF-1-100-24 with 60 wt% PEI content decreased from 148.9 mg/g to 127 mg/g, respectively. It is important to highlight that the mesostructured siliceous cellular foams facilitated significantly higher CO<sub>2</sub> capacities than the PA silica for all the higher molecular mass PEIs at all impregnation levels examined, with its CO<sub>2</sub> capacity increasing significantly with increasing levels of impregnation. At 60 wt% PEI content, the PEI-modified SCF adsorbent reached gave rise to impressive capacities of 126 and 97.3 mg/g for PEI-10000 and PEI-60000, respectively, which are even significantly higher than those reported for PEI-1800 modified PQ silica (Zhang et al., 2014) and PEI-2500 modified-MCF (Subagyono et al., 2014). In contrast, the CO<sub>2</sub> adsorption capacity of the PQ silica decreased sharply with increasing content of the PEIs and no appreciable capacities could be measured at 60wt% PEI-60000 loading. This highlights that the SCF materials can be used to prepare high molecular mass PEIs-modified adsorbents with significantly improved thermostability at a modest cost of CO<sub>2</sub> capacities.



Fig. 5.10 Comparison of  $CO_2$  adsorption performance of the SCF materials modified with different molecular mass PEIs measured at 75 °C in simulated flue gas (15%  $CO_2$  in N<sub>2</sub>).

5.3.2.4 Cyclic adsorption-desorption performance testing of PEI-modified SCF materials

The regenerability or adsorption-desorption performance of  $CO_2$  adsorbents is critical in determining their life-time importance in practical applications. Therefore, some of the best-performing PEI-600-modified SCF adsorbents are selected for cyclic adsorption-desorption performance testing in TGA in simulated flue gas conditions. As shown in Fig. 5.11, no appreciable changes in  $CO_2$  uptake were observed from the 50 adsorption-desorption cycles, highlighting the novel thermos-stability and fully reversible  $CO_2$  adsorption of the adsorbents. The negligible losses observed in the early few cycles were believed to be mainly associated with the evaporation loss of small quantities of some lower molecular mass PEI components present in the PEI. In addition, it seems that the SCF materials prepared at higher aging temperatures or longer aging times present slightly better thermal stability.



Fig. 5.11 Cyclic adsorption-desorption profiles of PEI-600-modified SCF materials for CO<sub>2</sub> uptake in simulated flue gas conditions (15% CO<sub>2</sub> in N<sub>2</sub>). Conditions: Adsorption temperature: 75 °C; Desorption temperature: 130 °C; Heating rate: 15 °C /min.

# 5.4 Conclusions

A wide range of meso, hybrid meso/macro and macro-structured siliceous cellular foam (SCF) materials have been tailor-designed and fabricated for preparing PEI-modified highly efficient adsorbent materials for CO<sub>2</sub> capture. The results demonstrate that while all the SCF materials exhibited higher capacities and faster adsorption kinetics in comparison with conventional meso-structured materials with 2D hexagonal pore geometries, all best-performing SCF materials are the hybrid meso/macro and macro-structured materials prepared from using high TMB concentrations, high aging temperatures and longer aging times despite their drastically reduced surface areas. The CO<sub>2</sub> uptake capacities of the SCF materials reached up to 180.2 mg/g (5.85 mmol/g-amine) for PEI impregnation and was further improved to 198.2 mg/g (6.44 mmol/g-amine) for the hybrid impregnation of PEI-TEPA at 75 °C in simulated flue gas (15% CO<sub>2</sub> in N<sub>2</sub>), which are significantly higher than the previously reported under similar or comparable conditions. The macro- and hybrid meso/macro-structured SCF materials were also found to be particularly suitable for preparing high molecular weight PEI-modified adsorbents with

significantly improved thermo-stability and at 60 wt% PEI loading, the CO<sub>2</sub> capacity reached 126 and 97.3 mg/g for PEI-10000 and PEI-60000, respectively, which are the highest ever reported. The PEI-modified adsorbents displayed superior thermo-stability with fully reversible CO<sub>2</sub> adsorption as no appreciable changes were observed during the 50 cycles lifetime performance testing.

Relating the CO<sub>2</sub> adsorption performance to the surface textural and morphological properties of the SCF materials reveals that the pore volume, pore diameters and window size of the SCF substrates collectively determines the CO<sub>2</sub> uptake capacity of the PEI-modified adsorbents while for the macro- and hybrid meso/macro SCFs, the morphology particularly the thickness of cell walls or framework silica struts also plays a vital role in facilitating higher levels of PEI impregnation with enhanced PEI mobility and accessibility for higher CO<sub>2</sub> uptake capacities. Differing from previous findings, no particularly favourable pore diameters or windows sizes for PEI impregnation or optimal CO<sub>2</sub> adsorption are observed for the wide range of SCF materials examined, although close to linear relationships appears to exist between  $CO_2$  uptake capacity and total pore volume for the SCF materials if with pore volumes below 2.2 cm<sup>3</sup>/g and pore diameters/window sizes below 28 nm.

# Chapter 6 Life-Time Performance Testing, Degradation Behaviour and Strategies to Mitigate the Degradation of Supported Polyamine CO<sub>2</sub> Adsorbents

# 6.1 Introduction

As has been discussed in Chapter 5, dry sorbent looping technology has widely been recognised as a viable alternative carbon capture technology to the state-of-the-art aqueous amine scrubbing, which has the potential to significantly reduce the energy penalty with improved capture efficiency and the avoidance of a range of operational issues associated with amine scrubbing, such as excessive foaming and fouling, unacceptably high corrosion rates and difficulties in the disposal of large volumes of corrosive and toxic aqueous waste streams (Choi, 2009, Gray et al., 2008, Sjostrom and Krutka, 2010). Among many CO<sub>2</sub> adsorbent materials currently under development (Choi, 2009), supported polyamines, including both grafted and impregnated polyamines has been one of the most investigated categories of CO<sub>2</sub> capture materials, due to their high capture capacity, fast adsorption kinetics, high selectivity and desirable operational temperature windows (50 ~ 75 °C) which essentially requires no flue gas cooling for typical flue gas streams (Choi et al., 2016, Han et al., 2015, Jiang et al., 2011, Jung et al., 2017, Kishor and Ghoshal, 2016, Wilfong et al., 2016). However, similar to aqueous amine solvents, polyamines-based CO2 adsorbents are also liable to variable degrees of thermal and oxidative degradation, depending on the types of the amines used, flue gas compositions and  $CO_2$ adsorption/desorption conditions (Ahmadalinezhad and Sayari, 2014, Bali et al., 2013, Bollini et al., 2011a, Heydari-Gorji and Sayari, 2012, Li et al., 2016). Drage et al., Sayari et al. and Jung H et al. investigated the thermal degradation behaviour of different types of supported-polyamines under different adsorption and desorption conditions, and it was found that the irreversible formation of urea species, which take place particularly during the desorption or sorbent regeneration process at temperatures higher than 120 °C or 130 °C depending on the types of PEIs used, was responsible for the thermal degradation of the supported polyamine adsorbents(Drage et al., 2008, Jung et al., 2017, Sayari et al., 2012). For oxidative degradation of polyamines, previous investigations revealed that the degree of oxidative degradation of polyamines is determined by the oxygen content in the flue gas streams, with the oxidative degradation products typically including amide and imine species and a

variety of products with different oxygen-containing functional groups, such as hydroxyl, carbonyl and carbonate ester (Bali et al., 2013, Bollini et al., 2011a, Heydari-Gorji et al., 2011a, Li et al., 2010). Approaches that have been examined to improve the thermo-oxidative performance of polyamines or PEIs-based adsorbents include 1) the use of higher molecule weight and/or linear PEIs with a higher molecule weight, and replacing branched PEI with linear PEI; 2) adding moisture into the flue gas; 3) using polyamines with more secondary or tertiary amine sites; and 4) the use of additives, such polyethylene glycol (PEG) or cross-linker to protect or stabilize the amine sites. Li et al. tested different molecule weight branched PEIs and linear PEIs and found that linear PEIs and higher molecule weight PEI have greater cyclic stability in the same adsorption and desorption condition, although linear and higher molecule weight PEIs have lower CO<sub>2</sub> uptake and adsorption rates (Li et al., 2014). Zhang et al and Sayari et al. showed that the presence of water vapour in flue gas can effectively reduce the PEI thermal degradation (Sayari et al., 2012, Zhang et al., 2014). Most recent investigations also revealed that the use of cross-linker, such as 1,2epoxybutane (Choi et al., 2016), poly(vinyl alcohol) (Zhai and Chuang, 2017), 1,3butadienediepoxide (Jung et al., 2017) to crosslink the impregnated amines or the use of polyamines with longer alkyl linker length (e.g. propyl) (Pang et al., 2017) can significantly improve the resistance of polyamines adsorbents to thermo-oxidative degradation.

However, it appears that the use of additives and/or cross-linker could lead to considerably reduced CO<sub>2</sub> capture capacities, due to the 'diluting' effect of the additives and/or cross-linkers on the relative contents of active amine groups in the amine sorbents. In addition, these approaches may have the potential to mitigate the thermo-oxidative degradation though at cost of capture capacity but they do not deal with the already degraded polyamines or the disposal of the degraded solid amines at the end of their working life. Little work has been conducted on how or if the degraded amines can be effectively rejuvenated or converted to other value-added products. In this Chapter, the life-time performance or the cyclic adsorption-desorption behaviour of the supported PEI adsorbents was first evaluated under different conditions for adsorption and desorption and subsequently, approaches that may have the potential to improve the lifetime performance were explored, with a particular focus on the rejuvenation of degraded supported-PEI adsorbents. However, it is noteworthy that

due to the large quantities of silica materials required for preparing the supported-PEI adsorbents and the preparation limit of laboratory facilities, a commercially available meso-structured silica material (PQ Silicas) was used instead of the SCF materials developed in Chapter 5 for the sorbents preparation in relatively large quantities for the range of tests and characterisations.

#### 6.2 Experimental

#### 6.2.1 Preparation of PEI-silica Adsorbent

The preparation of PEI-silica adsorbents followed the same procedure as described in Chapter 4 (Section 4.1.2) and Chapter 5 (Section 5.2.1), and different types of PEIs with different molecular weights (MW) varying from 600 to 10,000 were used, but the majority of the PEI sorbents were prepared with PEI-600.

To examine the effectiveness of additives in improving the anti-degradation performance of The PEI sorbents, a variety of inorganic hydrate compounds, including calcium metaborate (CaB<sub>2</sub>O<sub>4</sub>), sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), magnesium phosphate (Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) and calcium sulphate (CaSO<sub>4</sub>) were selected as the additives to dope the PEI-silica sorbents during the preparation process following the same procedure as used for preparing normal PEI-silica sorbents without the additives. All additives percentage in PEI-PQ silica adsorbent with additive is 10%. In a typical preparation, pre-defined amount of each individual additive was first dissolved in a fixed predefined amount of water under stirring conditions at ambient temperature and then, the calculated amount of PEI was dissolved in the solution with continuous stirring. The new solution was further stirred for 30 mins before the addition of the calculated amount of the PQ silica support substrate under vigorous stirring conditions to yield the final mixture. After stirred overnight, the mixture was left to dry in N<sub>2</sub> to remove the free water before they were dried in a vacuum oven at 40 °C to yield the final sorbent materials ready for characterisation.

#### 6.2.2 Accelerated degradation tests and preparation of degraded PEI

The accelerated degradation tests were designed to 1) speed up the lifetime performance testing and obtain the ultimate degradation profiles of the PEI adsorbents

in extreme thermal and/or thermos-oxidative environments and 2) prepare the degraded PEI adsorbents in significant quantities for use in subsequent rejuvenation treatments of the degraded sorbents.

For the accelerated oxidative degradation tests, a fixed amount of the PEI (40%)–silica adsorbent, typically 200 grams, was placed in a horizontal tube furnace (HTF) and heated up to 120 °C at a heating rate of 10 °C /min in a flow of N<sub>2</sub> (500 ml/min) to remove the moisture contained in the sorbent. After the moisture removal, the furnace temperature was then decreased to 75 °C (the optimal adsorption temperature of the PEI sorbents) with the gas flow switched to air. The PEI sorbent was sampled for different duration times of the oxidative degradation treatment, typically 1, 2, 3, 4, 5, 6, 10, 15 and 20 days. Similar procedures were used for the thermo-oxidative degradation treatments, but with the atmosphere changed from air to a flow of simulated gas-fired flue gas (500 ml/min) with 5% CO<sub>2</sub> and 12% O<sub>2</sub> in N<sub>2</sub>. The treated PEI adsorbents was sampled after different duration times of the thermo-oxidative treatment, typically 1, 2, 3, 4, 5, 6 and 10 days.

The treated PEI adsorbents collected from different duration times of the treatments were then characterised with TGA to determine their CO<sub>2</sub> adsorptive properties. To obtain the degraded PEIs for different rejuvenation treatments, the degraded PEI adsorbents was first subjected to Soxhlet extraction with methanol for overnight, and the resultant methanol solutions obtained for different degraded PEI samples were then dried via vacuum evaporation at 40 °C to obtain the degraded PEI for subsequent use.

#### 6.2.3 Rejuvenation treatments of degraded PEI

The potential of using catalytic hydrogenation and aqueous reforming to rejuvenate the heavily degraded PEI sorbents prepared from accelerated degradation tests was examined. The rejuvenation tests were carried out in a fix-bed hydropyrolysis (HyPy) reactor and autoclave as described in Chapter 4, and supported platinum (Pt) was used as the catalyst.

#### 6.2.3.1 Preparation of hydrogenation catalyst

The silica-supported Pt (10% w/w) catalyst was prepared using a recipient wet impregnation method. In a typical preparation, pre-calculated amount of platinum (Pang et al.) nitrate solution (Alfa Aesar, Pt 15% w/w) was added dropwise while stirring to the silica support, which was pre-dried and calcined at 400 °C before use. The mixture was first air-dried overnight in ambient conditions and then heated to 120 °C at 10 °C /min and held at this temperature for 2 hours to remove the moisture. The Pt-silica catalyst was then subjected to calcination at 500 °C in air for 5 hours, followed by a reductive treatment at 300 °C in H<sub>2</sub> (100 ml/min) for 2 hours to yield the final Pt-silica catalyst.

For each hydrogenation test conducted on the degraded PEIs, a calculated amount of 0.5g degraded PEI, which was obtained from the Soxhlet extraction of the heavily degraded PEI adsorbents, was impregnated onto 0.5g of the Pt-silica catalyst, following the same procedure as used for preparing the PEI-silica sorbents. The obtained Pt-PEI-degraded PEI mixture was then dried at 40 °C in vacuum for use in different rejuvenation treatments.

#### 6.2.3.2 Rejuvenation of heavily degraded PEI adsorbents

#### Catalytic hydrogenation treatment

The catalytic hydrogenation was performed in a fixed-bed HyPy reactor, and the details of the reactor can be found in Chapter 4. In each hydrogenation experiment, about 0.1 g of the prepared Pt–PEI–degraded PEI mixture was loaded to the reactor and was heated in a flow of H<sub>2</sub> (3 MPa, 5 litre/min) to a pre-set target reaction temperature varying from 175 to 250 °C. In a typical run, the hydrogenation lasted for about 30 min at the selected hydrogenation temperature, and the treated PEIs were recovered for analysis from the cold trap once it cooled down to ambient conditions.

# Catalytic aqueous reforming

The catalytic aqueous reforming was performed in an autoclave reactor. In a typical CAR run with the autoclave, about 0.1g of the prepared Pt–PEI–degraded PEI mixture and pre-calculated volumes of water or ammonium water (typically 5 ml) was first

loaded to the autoclave, which was then subsequently purged firstly  $N_2$  to displace the air, followed by further purge with a flow of  $H_2$  to displace the  $N_2$ . The autoclave reactor was then pressurised with  $H_2$  to a pre-set pressure before it was heated to a selected reaction temperature under different reaction atmospheres. After each CAR treatment, which lasted for about 30 min, the treated PEI was then recovered for analysis. The reaction temperatures varied from 175 °C to 250 °C, being similar to those used in the HyPy tests.

#### 6.2.4 Characterisation

#### CO<sub>2</sub> adsorption and desorption

Same methodologies as described in details in Chapter 4 and Chapter 5 were used both for the measurements of CO<sub>2</sub> adsorption capacity of the rejuvenated PEIs and for the cyclic life-time performance testing of the PEI-silica adsorbents under different flue gas and adsorption/desorption conditions. In the temperature-programmed CO<sub>2</sub> adsorption-desorption cycles used for the lifetime performance testing of the materials, the adsorption cycle was performed at 75 °C in two different types of simulated flue gas streams i.e. 15% CO<sub>2</sub>/N<sub>2</sub> for coal- and 5% CO<sub>2</sub>/N<sub>2</sub> for natural gas fired flue gas, respectively. Desorption cycle took place at a higher temperature of 130 °C in either N<sub>2</sub> or pure CO<sub>2</sub>. For selected runs, moisture and O<sub>2</sub> were also introduced into the gas streams used in order to assess the impact of flue gas oxygen and moisture on the performance of the adsorbent materials.

#### Other characterisations

Other characterisation tools, such as Raman spectroscopy, FTIR and nuclear magnetic resonance spectroscopy (NMR), were also used where necessary to characterise the properties of the PEI adsorbents before and after different treatments.

## 6.3 **Results and Discussion**

# 6.3.1 Temperature-programmed cyclic adsorption–desorption performance in CO<sub>2</sub>/N<sub>2</sub> and N<sub>2</sub> gas conditions.

In addition to required high  $CO_2$  capture capacity and fast adsorption-desorption kinetics, the thermo-oxidative stability of a  $CO_2$  adsorbent is also critical in determining its overall techno-economic performance for  $CO_2$  capture as it directly determines the replacement rates of the sorbents and the cost to deal with the disposal the ceased sorbent materials. The degradation profiles or lifetime performance of the PEI-silica adsorbents was therefore evaluated using cyclic adsorption–desorption tests.



Fig. 6.1 Cyclic adsorption-desorption performance of 40% PEI-600-silica sorbent. Conditions: Adsorption in15%  $CO_2/N_2$  at 75 °C and desorption in N<sub>2</sub> at 130 °C.

Fig. 6.1 shows the result of a typical cyclic CO<sub>2</sub> adsorption-desorption test for the 40% PEI-600-silica adsorbent in 15% CO<sub>2</sub>/N<sub>2</sub>. In general, the CO<sub>2</sub> uptake capacity remained relatively stable during the fifty cycles, with a relatively insignificant drop of 1.1% from 10.3 wt% in the 1<sup>st</sup> cycle to 9.2 wt% in the 50<sup>th</sup> cycle. As can be seen from Fig. 6.1, the baseline of the cyclic adsorption-desorption profiles was found to decrease continuously for each cycle particularly during the early cycles, and the baseline drifting reached approximately -3.0% in the 50<sup>th</sup> cycle. Similar phenomena

were also found for other PEI sorbents but with the degree of drifting being dependent on the types of PEI amines as shown hereinafter. Blank runs confirmed that the cause of the baseline drifting is not due to the malfunctioning of the TGA used but the evaporation loss of the PEIs during the adsorption-desorption cycles. Therefore, amount of negative baseline drifting can be reasonably approximated as the apparent PEI evaporation loss, although thermo-oxidative degradation of PEI may make the real evaporation loss seemingly lower, as it usually causes positive baseline drift. For the 40% PEI-600-silica sorbent, the average evaporation loss of PEI per cycle was approximately 0.06 wt% on the basis of the bulk sorbent and 0.15 wt% of the PEI contained in the sorbent. The majority of the loss occurred during the desorption process at higher temperatures and although no further tests at higher desorption temperatures were carried out, it is expected that the PEI evaporation loss will increase significantly as desorption temperature increases.



Fig. 6.2 Cyclic adsorption-desorption performance and PEI evaporation loss of PEI adsorbents prepared with different levels of PEI loading. Conditions: adsorption at 75 °C in 15%  $CO_2/N_2$  at 75 °C; desorption at 130 °C in N<sub>2</sub>.

Fig. 6.2 shows that the evaporation loss of the PEI-600 adsorbent increased almost proportionally to the PEI contents in the adsorbents, with the PEI loss being increased to 4 wt% of the adsorbent and 6.7 wt% of the sorbent-contained PEI in 50 cycles for

the 60% PEI-600-silcia sorbent. Although the 60% PEI-600-silica sorbent has a lower  $CO_2$  capacity due to the excessive loading of PEI in the silica substrate material, its PEI evaporation loss provides a meaningful information on the relationship between the content and evaporation loss of the PEIs in the sorbents. It is envisaged that PEI emissions could be a potential issue of the PEI-based  $CO_2$  adsorbents that will have to be adequately dealt with due to the toxic and corrosive nature of the emissions.

Fig. 6.3 compares the cyclic adsorption-desorption performance of the CO<sub>2</sub> sorbents prepared with different MW PEIs at the same PEI content of 40 wt%, while Fig. 6.4 shows the profile of PEI evaporation loss for the sorbents. Clearly, an increase in the molecular weight of the PEI used led to increased thermal stability of the PEI sorbent. The CO<sub>2</sub> adsorption capacity of the 40% PEI-10000-silica sorbents remained essentially unchanged during the 50 adsorption-desorption cycles with negligible PEI evaporation losses, and this compares to the PEI-600 and PEI-1800, which all gave rise to variable but continuous decrease in CO<sub>2</sub> capacity and increase in PEI evaporation loss. Closer examinations unveiled that in the O2-free adsorption conditions, the loss in  $CO_2$  capacity is almost proportional to the evaporation loss of PEIs during the 50 adsorption-desorption cycles (Fig. 6.4), suggesting that thermal chemical degradation of the PEIs is insignificant and the thermal evaporation loss of the PEIs is the primary cause of the loss of CO<sub>2</sub> capacity during the cycles. However, as can be seen from Fig. 6.3, it is evident that the improved thermal stability of higher molecular weight PEIs took place at a cost of  $CO_2$  capacity. The cycle-averaged  $CO_2$ capacity decreased from 9.6 wt% for the 40% PEI-600-silica sorbent, to 8.9 wt% for

40% PEI-1800 and 8.74 wt% for 40 PEI-1800, respectively. The decrease in CO<sub>2</sub> capacity with increasing PEI molecular weight is due to the growing number of tertiary

amine sites as PEI molecular weight increases, which always occurs at a cost of primary and secondary amine sites. Tertiary amines cannot react with  $CO_2$  in the absence of water or moisture and even in the presence of moisture, the reaction is also kinetically unfavourable. Clearly, when the selection of PEIs of different molecular weights is concerned, there is surely a trade-off between the  $CO_2$  capacity and thermal stability of the polyamines-based  $CO_2$  sorbents. The results shown in Fig. 6.2 and 6.3 imply that although the lower molecular weight PEIs may have considerably higher initial  $CO_2$  capacities, the sorbents prepared with PEI-10,000 could instead offer significantly better lifetime performance and drastically reduced environmental impact due to its potentially near zero PEI emissions.



Fig. 6.3. Cyclic adsorption-desorption performance of PEI adsorbents prepared with different molecular mass weight PEIs. Conditions: adsorption in 15%  $CO_2/N_2$  at 75 °C; desorption in N<sub>2</sub> at 130 °C.



Fig. 6.4. Profile of PEI evaporation loss of the adsorbents prepared with different molecular weight PEIs at 40 wt% loading level. Conditions: adsorption at 75 °C in 15%  $CO_2/N_2$  at 75 °C; desorption at 130 °C in N<sub>2</sub>.

# 6.3.2 Effect of CO<sub>2</sub> partial pressure in the flue gas on cyclic adsorptiondesorption performance

Fig. 6.5 and 6.6 shows the CO<sub>2</sub> adsorption-desorption performance and the profile of PEI evaporation loss of the 40% PEI-600-PQ silica at different CO<sub>2</sub> partial pressures, respectively. As expected, the  $CO_2$  adsorption capacity decreased with decreasing  $CO_2$ partial pressure, from 10.3 wt% in 15% CO<sub>2</sub>/N<sub>2</sub> to ca. 9.0 wt% in 5% CO<sub>2</sub>/N<sub>2</sub> for the adsorbent tested. In general, the profile of CO<sub>2</sub> capacity loss and that of PEI evaporation loss are both comparable to those observed in Fig. 6.1 ~ Fig. 6.4. However, it was interestingly found that the lower CO<sub>2</sub> partial pressure led to considerably higher losses both in CO<sub>2</sub> capacity and the PEI content during the 50 adsorption-desorption cycles, being contradictory to the envisaged results that lower CO<sub>2</sub> partial pressures might result in lower CO<sub>2</sub> capacity and PEI evaporation losses, due to the potentially lower degrees of thermo-degradation particularly in terms of urea formation. Again, the results suggest that thermochemical degradation, which is usually characterised by the formation of urea species, is not the major cause of  $CO_2$  capacity loss but the loss of PEI content due to evaporation. The considerably lower PEI evaporation losses observed at higher CO<sub>2</sub> partial pressures imply that the carbamate formation, which accounts for the reversible CO<sub>2</sub> adsorption process of polyamine adsorbents, has a shielding or stabilising effect to the impregnated PEIs during both the adsorption and desorption processes. The higher PEI evaporation loss observed in 5% CO<sub>2</sub>/N<sub>2</sub> is due to the reduced formation of carbamates (i.e. lower CO<sub>2</sub> adsorption capacity) and hence less stabilising effect that can be derived accordingly.



Fig. 6.5 Effect of flue gas  $CO_2$  partial pressure on the cyclic adsorption-desorption performance of PEI sorbents. Conditions: adsorption at 75 °C; desorption at 130 °C in N<sub>2</sub>.



Fig. 6.6 Effect of flue gas  $CO_2$  partial pressure on PEI evaporation loss of the 40% PEI-600-silica adsorbent. Conditions: adsorption at 75 °C; desorption in N<sub>2</sub> at 130 °C.
#### 6.3.4 Effect of O<sub>2</sub> in the flue gas on the cyclic adsorption-desorption performance of PEI adsorbents

All combustion flue gases contain variable levels of oxygen due to the use of excess air or oxygen to maximise the combustion efficiency. The presence of excess  $O_2$  can potentially lead to oxidative degradation of  $CO_2$  adsorbents. In this session, simulated natural gas combustion flue gas containing 5%  $CO_2$  and 12  $O_2$  in  $N_2$  was used to evaluate the oxidative degradation of the supported PEI (40%) adsorbents. The adsorption-desorption performance of the PEI adsorbents was compared in Fig. 6.7, and the profile of PEI loss was presented in Fig. 6.8.



Fig. 6.7 Effect of  $O_2$  in the flue gas on the cyclic adsorption-desorption performance of the 40% PEI-600-silica adsorbent. Conditions: adsorption at 75 °C in 5% CO<sub>2</sub>/12 %  $O_2$  in N<sub>2</sub>; Desorption in N<sub>2</sub> at 130 °C.

As can be seen from Fig. 6.7, the effect of  $O_2$  on  $CO_2$  adsorption was negligible in the first few adsorption–desorption cycles but the effect accelerated rapidly with increasing cycles, with the  $CO_2$  capacity decreased by 27%, from 9.03 wt% in the 1<sup>st</sup> cycle to just 6.6 wt% in the 50<sup>th</sup> cycle, giving rise to an averaged  $CO_2$  capacity loss of 0.5% per cycle which was significantly higher than the capacity loss in any other adsorption conditions examined. Being consistent with the accelerated  $CO_2$  capacity loss, the apparent PEI loss as measured by the baseline drifting also accelerated rapidly

and simultaneously from the few cycles, giving rise to a cumulative apparent PEI loss of 5.2 wt% of the sorbent or 13 wt% on the basis of the sorbent-contained PEI in the 50 cycles. The PEI content of the 40% PEI-600-silica sorbent at the end of the cyclic test, which should be more appropriately called the content of total organic matter as it also included the degradation products, was measured at 37.7 wt% (or 5.7 wt% in sorbent weight loss), which is comparable to that obtained from the TGA baseline 'drifting'. Presumably, the weight losses obtained in the cyclic tests was mainly due to the thermal evaporation loss of the undegraded PEIs remaining in the sorbent in Fig. 6.8, based on the results obtained in the O<sub>2</sub>-free adsorption conditions as discussed earlier. However, the contribution of PEI degradation products to the total weight loss obtained could not be ruled out, this would be relatively small given the low adsorption and desorption temperatures. Previous investigations revealed that the products from the oxidative degradation of PEIs are mainly a range of amides and imines and other species with different oxygen functionalities, such as hydroxyl, carbonyl and carbonate ester (Bali et al., 2013, Bollini et al., 2011a, Heydari-Gorji, 2011, Heydari-Gorji and Sayari, 2012, Lepaumier, 2009, Li et al., 2010). In addition, it must also be noted that the loss of CO<sub>2</sub> capacity was caused not only by the thermal evaporation loss but also by the thermo- oxidative degradation of the impregnated PEI. However, it seems that in addition to its direct effect on CO<sub>2</sub> capacities, the oxidative degradation during the adsorption process is also linked to the accelerated PEI evaporation loss due to the decreased stabilising effect as a result of the reduced formation of carbamate species, namely lower CO<sub>2</sub> capacities.



Fig. 6.8 Profile of PEI loss during the cyclic adsorption-desorption cycles of the 40% PEI-600-silica. Conditions: adsorption at 75 °C in 5% CO<sub>2</sub>/12 % O<sub>2</sub> in N<sub>2</sub>; Desorption in N<sub>2</sub> at 130 °C.

To further investigate the oxidative degradation, accelerated oxidative degradation tests were conducted in the simulated gas-fired flue gas stream (5% CO<sub>2</sub>/12% O<sub>2</sub> in N<sub>2</sub>) at a temperature of 75 °C, using a horizontal furnace with large quantities of the 40% PEI-600-silica sorbent (200 grams). The sorbent materials were sampled periodically for CO<sub>2</sub> adsorption measurements. Fig. 6.9 shows that the CO<sub>2</sub> capacity decreased continuously during the 20 days of the accelerated degradation tests, while the sorbent changed in colour from white to dark brown in just 10 days. The CO<sub>2</sub> uptake capacity decreased by nearly 30% in just 6 days, from its initial capacity of 9.5 % to 6.8 %. There appears to be a sharp decrease in CO<sub>2</sub> uptake when degradation reached a critical stage. The CO<sub>2</sub> uptake of the PEI adsorbents decreased drastically from 6.8 wt% to 2.8 % when the duration time of the accelerated test increased from 6 days to 15 days, and to just 1.3 wt% when the duration time increased to 20 days. This gave rise to a cumulative loss in CO<sub>2</sub> capacity of 86% in 20 days, an average loss of 4.3 % per day, highlighting the severe oxidative degradation of the PEI adsorbents in the simulated gas-fired flue gas stream. Therefore, anti-oxidative degradation measures must be taken to mitigate the impact of the oxidative flue gas conditions, particularly

for the natural gas fired power plants where the excess  $O_2$  levels are usually significantly higher than those of coal-fired power plants.



Fig. 6.9 Variation of CO<sub>2</sub> adsorption capacity with duration times of the accelerated degradation test with large quantities of PEI adsorbents in a horizontal furnace at 75 °C in 5% CO<sub>2</sub>/12% O<sub>2</sub> in N<sub>2</sub> (500 ml/min).

Fig. 6.10 presents the Fourier transform Raman spectra for the 40% PEI-600-silica adsorbent after subjected to different period of the thermo-oxidative degradation in 5%  $CO_2/12\% O_2/N_2$  at the typical adsorption temperature of 75 °C. It indicates that a variety of functionalities arising from the thermo-oxidative degradation were observed and with their intensity increasing with increase in the duration times of the degradation treatment, including the cyclic urea (1663 cm<sup>-1</sup>), open-chain urea (1628 cm<sup>-1</sup>), oximes/imines (1600 cm<sup>-1</sup>, R<sup>1</sup>R<sup>2</sup>C=NOH and R<sup>1</sup>R<sup>2</sup>C=N), hydroxyl (900-1200 cm<sup>-1</sup>) and carboxylic groups (1256 cm<sup>-1</sup>) etc. It is noteworthy that the formation of carboxylic groups became significant after the PEI adsorbent was subjected for 6 days to the thermo-oxidative adsorption environment. This finding is consistent with the results shown in Fig. 6.9 where the loss in CO<sub>2</sub> capacity was found to accelerate dramatically also after 6 days treatment.



Fig. 6.10 Fourier transform FTIR Spectra of the PEI sorbents after subjected to different periods of thermo-oxidative degradation in 5%  $CO_2/12\% O_2/N_2$  at 75 °C.

To further reveal the chemical constitution of the degradation products, aqueous NMR spectroscopy was used to characterise the degraded PEI isolated via Soxhlet extraction with methanol from the PEI sorbent after the thermo-oxidative treatment for 10 days. Fig. 6.11 shows the <sup>13</sup>C NMR spectra for the selected samples. Being consistent with the FTIR results, a range of carboxylic and amide compounds or functionalities were identified in the PEI extracts, as shown by the peaks between 160 and 180 ppm. . Carboxylic groups acidify the sorbent surface and/or react with amine groups to form amides, thus de-activating the PEI sorbent. In addition, compared to the undegraded PEI, the amine functional groups present in the degraded PEI sorbent also appeared to be chemically altered as can be seen from the complex peaks obtained, which may also inevitably impact the CO<sub>2</sub> adsorption performance.



Fig. 6.11 Aqueous 13C NMR spectra of PEI adsorbent before and after the thermooxidative treatment in 5% CO<sub>2</sub>/12% O<sub>2</sub>/N<sub>2</sub> at 75 °C.

# 6.3.5 Effect of desorption conditions on cyclic adsorption-desorption performance of PEI adsorbents

Temperature wing adsorption (TSA) process is widely recognised as being the major viable process for solid adsorbent based CO<sub>2</sub> capture systems. In a TSA process, the selection of suitable sorbent regeneration is critical in determining the purity of recovered CO<sub>2</sub> and associated techno-economic performance of an adsorption-based CO<sub>2</sub> capture system. In conventional TSA applications, the solid adsorbent is often regenerated by direct purging with a hot non-adsorbing and non-adsorbate gas, such as steam, air, and N<sub>2</sub>. However, for carbon capture, because the adsorbate is the target products, the use of non-adsorbing purge or stripping gas can result in great dilution of the desorbed product CO<sub>2</sub> gas, which may need additional costly separation treatment. Indeed, the investigation conducted by Tlili et al. (Tlili et al., 2009) reveals that the use of hot N<sub>2</sub> even only as a sweep gas can still significantly dilute the final CO<sub>2</sub> product. The use of hot steam as a sweep gas has been successfully tested in fluidized bed systems with solid sorbents for CO<sub>2</sub> capture(Beaver and Sircar, 2010, Park et al., 2011, Sjostrom et al., 2011), but sorbent regeneration with direct steam stream stripping is not considered as a favourable option due to the detrimental effect on CO<sub>2</sub> adsorption capacity of most CO<sub>2</sub> adsorbents already developed or currently under development (Radosz, 2008, Li et al., 2009). It is therefore desirable if hot CO<sub>2</sub> gas, which is the product of sorbent regeneration, can be used as either the stripping gas and/or sweep gas in a TSA process. Despite the fact the CO<sub>2</sub> working capacity of an adsorbent can be reduced due to the CO<sub>2</sub> adsorption equilibria at the desorption temperature with CO<sub>2</sub>, this sorbent regeneration strategy can least ensure that the highest obtainable CO<sub>2</sub> purity under the given adsorption-desorption conditions can be best maintained and with the potentials of significant energy savings (Grande, 2010). However, the potential impact of using hot CO<sub>2</sub> either as the sweep gas and/or stripping gas on the lifetime performance of a PEI adsorbent has still not been well investigated. In this session, temperature swing adsorption-desorption cycles with CO<sub>2</sub> as being the purge or desorption gas was conducted to evaluate the lifetime performance of the PEI adsorbents, with the results shown in Fig. 6.12 and Fig. 6.13 for the 40% PEI-600silica sorbent.

Due to the adsorption equilibrium during the desorption process in CO<sub>2</sub>, some of the CO<sub>2</sub> adsorbed at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub> cannot be completely desorbed at the higher desorption temperature of 130 °C and will hence remain as the residual CO<sub>2</sub> in the adsorbent in the next cycle. Consequently, a seemingly sharp decrease in CO<sub>2</sub> capacity was observed in the 2<sup>nd</sup> adsorption-desorption cycle, as shown in Fig. 6.12. Therefore, the measured cyclic  $CO_2$  capacity is essentially the working  $CO_2$  capacity of the TSA cycle with CO<sub>2</sub> as being the purge gas, namely the difference of the CO<sub>2</sub> adsorption capacity at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub> minus the capacity at 130 °C in pure CO<sub>2</sub> for each cycle. As can be seen from Fig. 6.12, compared to the desorption in N<sub>2</sub> at 130 °C, the desorption in CO<sub>2</sub> at the same temperature led to nearly 50% loss in CO<sub>2</sub> capacity for the 40% PEI-600-silica sorbent, giving rise to a CO<sub>2</sub> working capacity of just 5.3 wt%. It is evident that the use of CO<sub>2</sub> as the purge gas in desorption led to rapid de-activation of the PEI sorbent in CO<sub>2</sub> adsorption, with the working capacity rapidly decreased from 5.3 wt% in the 2<sup>nd</sup> cycle to ca. 2.0 wt% in 15<sup>th</sup> cycle and just 1.0 wt% at the end of the 50 cycles test. This means that the PEI sorbent was essentially destroyed completely. As there is no O<sub>2</sub> present in the adsorption-desorption cycles, thermooxidative degradation is clearly the cause of the sorbent deactivation.



Fig. 6.12 Effect of desorption conditions on the cyclic  $CO_2$  adsorption-desorption performance of the 40% PEI-silica adsorbent. Conditions: (1) adsorption at 75 °C in 15%  $CO_2/N_2$ , desorption at 130 °C in N<sub>2</sub>; 2) adsorption at 75 °C in 15%  $CO_2/N_2$ , desorption at 130 °C in CO<sub>2</sub>.

As shown in Fig. 6.13, positive baseline 'drifting' or sorbent weight gain is evident when  $CO_2$  was used as the purge gas in desorption, and the baseline weight gain increased continuously with the adsorption-desorption cycles. This is in sharp contrast to the baseline weight loss (negative baseline 'drifting') observed with N<sub>2</sub> as the purge gas. It was found in previous investigations (Lee et al., 2011, Li et al., 2014, Sayari et al., 2012, Wang et al., 2014b) and also as shown in Fig. 6.10 that the irreversible formation of different types of urea species, including cyclic and open-chain urea, is the major cause of thermo-deactivation of amine-based adsorbents during adsorption and particularly the desorption process at higher temperatures. Fig. 6.14 shows the mechanisms of urea formation proposed by Sayari et al. (Sayari et al., 2012). Based on the mechanism, the sorbent is expected to gain weight from CO<sub>2</sub>-induced urea formation, which can be calculated at 28 g per mole of urea formed. Therefore, it is evident that the weight gain profile obtained with CO<sub>2</sub> as the purge gas is somewhat quantitatively indicative of the greatly enhanced CO<sub>2</sub>-induced urea formation. However, the actual baseline weight gain attributable to urea formation is in fact much higher than that shown in Fig. 6.12, which represents the net effect of urea formation plus the residual  $CO_2$  minus the evaporation loss of PEIs, whereas the latter two components are both expected to decrease with increasing cycles. In fact, it can be reasonably envisaged that virtually all the PEIs has been converted to urea at the end of the 50 cycles test, given the absence of oxidative degradation and the negligible remnant of  $CO_2$  capacity (ca. 1 wt% as shown in Fig. 6.11) that could arise mainly from physical adsorption of the degraded PEI sorbent due to its physical porosity.



Fig. 6.13 Effect of desorption conditions on adsorption (TGA) baseline 'drifting' during the adsorption-desorption cycles of the 40% PEI-silica sorbent. Conditions: (1) adsorption at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub>, desorption at 130 °C in N<sub>2</sub>; 2) adsorption at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub>, desorption at 130 °C in CO<sub>2</sub>.

Mechanism A: Formation of open-chain ureas



Fig. 6.14 Mechanisms of CO<sub>2</sub>-induced thermal degradation of supported polyamines (Sayari et al., 2012).

# 6.4 Exploratory investigation of potential strategies to improve the lifetime performance of supported-PEI adsorbents for CO<sub>2</sub> capture

As has been discussed above, the ultimate lifetime performance of supported amines for  $CO_2$  capture essentially determines not only their techno-economic performance but also their environmental performance due to the concerns over the potential emission of corrosive and toxic emissions of PEI and their degradation products. Clearly, measures that can effectively improve the thermo-oxidative degradation behaviours of polyamines-based  $CO_2$  adsorbents will benefit their overall performance for  $CO_2$  capture. In this section, potential anti-degradation approaches are explored to improve the lifetime performance of supported amines, using the PQ silica supported PEI as the adsorbents.

## 6.4.1 The Efficacy of moisture in mitigating thermo-oxidative degradation of supported PEI sorbent

The CO<sub>2</sub>-induced irreversible urea formation, which serves as the main cause of thermo-degradation of amines, involves an essential step of the dehydration of carbamate acid and/or ammonium carbamate formed from CO<sub>2</sub> adsorption, as shown in following schematic diagram. This implies that if the dehydration can be supressed via measures such as the provision of moisture in the adsorption and desorption process, the urea formation shall be depressed or even inhibited. Inspired by this, the potential efficacy of using moisture to suppress the urea formation was examined via the cyclic adsorption-desorption performance testing of the PQ silica supported PEI sorbents with the presence of 10% v/v moisture in the gas streams for both adsorption and desorption. Fig. 6.15 and Fig. 6.16 show the test results for the simulated coal and natural gas fired flue gas streams under the wet and dry conditions, respectively.



Fig. 6.15 Temperature swing adsorption-desorption profiles of 40% PEI-600-silica sorbent under wet and dry gas conditions. Conditions: Adsorption at 75 °C in 15% CO<sub>2</sub> in N<sub>2</sub>, desorption at 130 °C in CO<sub>2</sub> desorption condition; Moisture content: 10% v/v in both adsorption and desorption (black).



Fig. 6.16 Temperature swing adsorption-desorption profiles of 40% PEI-600-silica sorbent under wet and dry gas conditions. Conditions: Adsorption at 75 °C in 5% CO<sub>2</sub>

/ 12%  $O_2$  /  $N_2$ , desorption at 130 °C in  $N_2$ . Moisture content: 10% v/v in both adsorption and desorption (black).

Similar to the results shown in Fig. 6.12, the sharp decrease in CO<sub>2</sub> capacity observed in the  $2^{nd}$  cycle, as shown in Fig. 6.15, were not due to degradation but the adsorption equilibria when the desorption was in pure CO<sub>2</sub>. It can be seen from Fig. 6.15 that with the presence of 10% water vapour in the gas streams for adsorption and desorption, virtually no changes in CO<sub>2</sub> capacity were observed throughout the 50 cycles of tests for the simulated coal-fired flue gas, highlighting the efficacy of moisture in inhibiting or supressing the CO<sub>2</sub>-induced degradation via the pathway of urea formation. Similar results were also observed for the simulated gas-fired flue gas with 10% v/v O<sub>2</sub>, as shown in Fig. 6.16. However, for the O<sub>2</sub>-containg natural fired flue gas, a gradual decrease in CO<sub>2</sub> capacity was observed and showed an increase with increasing cycles, which is believed to be caused by the oxidative degradation of the PEI sorbent due to the presence of  $O_2$  in the flue gas. Nevertheless, it is noteworthy that the loss in  $CO_2$ capacity due to the oxidative degradation was obviously much less significant when 10% v/v water vapour was present, suggesting that the presence of water vapour was able to not only suppress the urea formation but interestingly also the oxidative degradation, being consistent with previous findings (Heydari-Gorji and Sayari, 2012, Lepaumier, 2009). As the oxidative degradation of PEI usually involves the formation of ketone groups (-C=O), water and ammonia (Heydari-Gorji and Sayari, 2012)., it is believed that the presence of water might make this oxidation reaction harder to proceed kinetically, thus suppressing the oxidative degradation.

It is well known that in the absence of water, tertiary amines cannot react with  $CO_2$  and hence do not contribute to  $CO_2$  adsorption. As an addition benefit, it is interesting to note, however, that the presence of water vapour in the gas streams also enable the tertiary mine sites present in the PEI sorbent to adsorb  $CO_2$ , as highlighted by the considerably higher  $CO_2$  capacities obtained in the wet conditions than in dry conditions (Fig. 6.16).

Encouraged by the promising results obtained on the suppressing effect on thermooxidative degradation of the supported PEI sorbent, a selected heavily degraded PEI sorbent sample, which was prepared from 20 days' thermo-oxidative treatment in 5%  $CO_2/12\% O_2/N_2$  (Fig. 6.9), was selected for steam treatments in an autoclave. Table 1 presents the results obtained under different conditions. As can be seen from Table 1, the results are very disappointing, and the steam treatments even in the presence of H<sub>2</sub> or ammonia gave rise to no appreciable improvements under all conditions examined and at slightly higher temperatures, the treatments even led to further degradation or loss in  $CO_2$  capacity. Sayari et al.(Sayari, 2010) found that deactivation of nonoamine and tri-amine containing sorbents via formation and accumulation of urea groups can be completely reversed via hydrolysis of such groups under steam conditions. It is evident that the urea groups present in degraded polymeric PEIs, including cyclic and openchain urea, is much more stable than those formed from mono and triamines (Heydari-Gorji and Sayari, 2012).

Conditions	Temperature	Measured PEI	CO <sub>2</sub> uptake
	°C	content wt %	wt%*
PEI-600 (40%) silica sorbent		43.4	9.2 (21.3)
Heavily degraded PEI sorbent		41.9	1.4 (3.3)
$H_2O / H_2$	175	54.1%	1.3 (2.4)
$H_2O / H_2$	200	53.9%	1.7 (3.2)
$H_2O / H_2$	225	36.7%	1.2 (3.3)
$H_2O / H_2$	250	31.4%	0.6 (1.9)
$H_2O / H_2$	275	40.0%	0.2 (0.5)
$H_2O / NH_3$	200	49.5%	2.8 (5.7)
$H_2O / NH_3$	225	49.1%	2.8 (5.7)
$H_2O / NH_3$	250	42.2%	1.1 (2.5)
$H_2O / NH_3$	275	43.2%	0.8 (1.9)

Table 6.1 CO<sub>2</sub> uptake capacities of degraded PEI sorbent before and after the stream treatment under different conditions

\*Note: The CO<sub>2</sub> uptake in bracket is measured on the basis of PEI content

## 6.4.2 Efficacy of inorganic hydrate dopants in mitigating thermo-oxidative degradation of supported amines

As has been discussed earlier, the presence of water vapour during adsorption and desorption can suppress the CO<sub>2</sub>-induced thermal degradation via urea formation and also improve the anti-oxidative degradation performance of supported PEI sorbents. Therefore, it is envisaged that use of suitable inorganic hydrates as the dopants may also serve the same purpose or even better. The hydration water can be released simultaneously at suitable temperatures to facilitate instantaneous suppression on urea formation. It is also expected that even if the hydration water cannot be released due to temperature, it may still be able to create some local humidity that may still be of some significance in supressing urea formation. Meanwhile, the loss of water in the hydrates at the higher desorption temperatures can be automatically replenished with flue gas moisture during the adsorption process at lower temperatures. Therefore, in this session, the potentials of using inorganic hydrates as the additives to improve the anti-degradation performance of PEI sorbents are explored.

6.4.2.1 Effect of different inorganic doping on CO<sub>2</sub> adsorption of PEI adsorbents Four inorganic dopants were examined, including calcium sulphate (CaSO<sub>4</sub>), magnesium phosphate (Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), calcium borate (CaB<sub>2</sub>O<sub>4</sub>) and sodium borate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). In the aqueous PEI sorbent preparation process, different hydrates of these compounds are formed and dispersed into the PEI sorbents but with the number of hydration water in the hydrates being determined by the adsorption and desorption temperatures. It proves extremely difficult to accurately measure the hydration water content in the prepared PEI sorbent and in the sorbent before and after each adsorptiondesorption cycle, due to the multiple changing variables. Nevertheless, it is estimated that the number of hydration water varies between 1–2 for CaSO<sub>4</sub>, 4–5 for Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, 1–2 for CaB<sub>2</sub>O<sub>4</sub> and 3–6 for Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, provided that humid gas streams are used in adsorption at 75 °C and desorption at 130 °C. However, to avoid further complicating adsorption measurements, the cyclic adsorption–desorption testing in TGA was carried out in dry conditions for the hydrate-doped PEI sorbents. Fig. 6.17 presents the CO<sub>2</sub> adsorption profiles for the PEI-sorbents doped with 10 wt% of the selected additives. It can be seen that compared to the undoped PEI (40 wt%) adsorbent, at a doping level of 10 wt%, the addition of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> led to a significant increase in CO<sub>2</sub> capacity by over 10% whereas the CO<sub>2</sub> capacity decreased by nearly 30% for CaSO<sub>4</sub> and 12% for CaB<sub>2</sub>O<sub>4</sub>, respectively. In companion, no obvious effect of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> doping was found. The unexpected significant decreases in CO<sub>2</sub> capacity observed for the doping of CaSO<sub>4</sub> and CaB<sub>2</sub>O<sub>4</sub> are believed to be due to the weak acidity of the two dopants, which tend to neutralise the basicity of the impregnated PEI due to their variable liabilities to hydrolysis. However, significantly faster adsorption kinetics were observed for all the dopants examined particularly at the early stages of adsorption, with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> giving rise to the best result. These suggest that irrespective of their effect in CO<sub>2</sub> capacity, the addition of the impregnated PEIs, leading to decreased mass transfer resistance for CO<sub>2</sub> adsorption.



Fig. 6.17 CO<sub>2</sub> adsorption profiles of additive-doped PEI-silica sorbent an adsorption temperature of 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub>.



Fig. 6.18 Variation of CO<sub>2</sub> uptake capacity with the dopant content of sodium borate in PEI-silica sorbent an adsorption temperature of 75 °C in 15%  $CO_2/N_2$ .

Given the great increase in CO<sub>2</sub> capacity with improved adsorption kinetics observed for the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> dopant, the effect of the doping concentration of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> was further investigated and with the results shown in Fig. 6.18. It was found that the CO<sub>2</sub> capacity increased firstly with increasing concentration of the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> dopant up to 20 wt%, and this was followed by a decrease in  $CO_2$  capacity with further increase in  $Na_2B_4O_7$ content. Fig. 6.19 compares the CO<sub>2</sub> capacities of the PEI sorbent with different levels of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping in a comparison with other dopants, and it is evident that Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> gave rise to the best results both in terms of the CO<sub>2</sub> capacity and related adsorption kinetics. At a 20% doping level of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, the CO<sub>2</sub> capacity was increased by over 30% to 13.3 wt%, from 10.2 wt% for the as-prepared undoped PEI sorbent. Sodium borate can be classified as a weak base, with a pH value of 9.24 for its 1 wt% aqueous solution. Although it is unlikely to measure the number of hydration water in the sodium borate doped in the Pei sorbent, the sodium borate hydrate may potentially serves as solid solution with weak basicity. Presumably, the great positive effect of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping on CO<sub>2</sub> adsorption of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped PEI sorbent arose from the additional basic sites in the sorbent. However, excessive doping of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> along with the PEI impregnated can cause pore blockade to the produced sorbents, leading to sharp decrease in CO<sub>2</sub> capacity as observed at 30% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping levels with 40 wt% PEI (Fig. 6.18 ~ 6.19).



Fig. 6.19.  $CO_2$  adsorption capacity of PEI-600 (40 wt%)-silica sorbent doped with different dopants. Conditions: adsorption temperature at 75 °C in 15%  $CO_2/N_2$ .

6.4.2.2 Effect of  $Na_2B_4O_7$  hydrate doping on the cyclic adsorption-desorption performance of PEI adsorbents with desorption in  $N_2$ 

Fig. 6.20 presents the cyclic adsorption-desorption profiles for the 40 wt% PEI-600silica sorbents doped with different levels of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, while the related baseline weight change profiles during the cyclic tests are compared in Fig. 6.20. As can be seen from Fig. 6.19, all Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped sorbents displayed significantly higher cyclic CO<sub>2</sub> uptake capacities with superior cyclic adsorption-desorption performance, with the CO<sub>2</sub> capacity depending on the doping level of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.



Fig 6.20. Temperature swing adsorption-desorption profiles of 40% PEI-600-silica with different dopants. Conditions: Adsorption at 75 °C in 15%  $CO_2/N_2$ , desorption at 130 °C in N<sub>2</sub>.

Similar to the earlier results obtained for the cyclic tests with desorption in  $N_2$  (Fig. 6.2, 6.4, 6.6 and 6.8.), negative baseline "drifting" or baseline weight losses were also observed as shown in Fig. 6.21, due to the weight losses as a result of the evaporation loss of PEI and that of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water. It is important to note that no significant differences in the baseline weight losses were obtained between the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped and undoped PEI adsorbents, despite the significant differences in the doping levels ranging from as low as 1 wt% to 20 wt%. It had been expected that the evaporation losses of the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-deoped PEI sorbents would be significantly higher

than those of the undoped PEI sorbent, because of the considerable amount of  $Na_2B_4O_7$ -contained hydration water in the sorbent. Compared to the undoped PEI sorbent, the considerably lower-than-expected evaporation losses obtained for the  $Na_2B_4O_7$ -doped PEI sorbents are suggestive of the synergistic effects that may exist between the impregnated PEI and doped  $Na_2B_4O_7$ , which appeared to help preserve the hydration water while mitigate the thermal degradation of PEI, including the evaporation loss of PEI and CO<sub>2</sub>-induced urea formation. However, this does not mean that there is no hydration loss of  $Na_2B_4O_7$  hydrates in the sorbent, as can be seen from Fig. 6.21 that the overall evaporation loss increased with increasing the doping levels of  $Na_2B_4O_7$  though much less proportionally.



Fig. 6.21. Baseline weight change profiles of 40 wt% PEI-silica with different dopants during cyclic adsorption-desorption tests. Conditions: Adsorption at 75 °C in 15%  $CO_2/N_2$ , desorption at 130 °C in N<sub>2</sub>.

6.4.2.3 Effect of  $Na_2B_4O_7$  hydrate doping on the cyclic adsorption-desorption performance of PEI adsorbents with desorption in  $CO_2$ 

Fig. 6.22 shows the cyclic adsorption-desorption profiles of  $Na_2B_4O_7$ -doped PEI adsorbents. Again as mentioned earlier (Fig. 6.10 and 6.15), sharp decreases in CO<sub>2</sub> capacity were evident, due to the adsorption equilibria in CO<sub>2</sub> when desorption took place in CO<sub>2</sub> as opposed to N<sub>2</sub>. It is obvious that compared to the undoped PEI sorbent,

the doping of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> hydrate led to significantly higher cyclic CO<sub>2</sub> capacities even at a negligible level of just 1 wt%, and that the cyclic adsorption-desorption performance remained virtually unchanged during the 50 cycles test when the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping levels were in the range of 5 ~ 10 wt%. However, at the higher doping level of 20 wt%, a considerable decrease in CO<sub>2</sub> capacity was observed with increasing adsorption-desorption cycles, which is attributable to the loss of the hydration water present in the doped PEI sorbent. In fact, it is envisaged that the actual CO<sub>2</sub> uptake capacities of the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped adsorbents should be even higher than the measured with TGA, because the weight gain measured with TGA actually represented the difference of CO<sub>2</sub> adsorption-induced weight gain minus the chronic evaporation loss of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water during the cyclic tests in dry gas conditions. Nevertheless, the chronic evaporation loss of the hydration water could not possibly be measured with the existing TGA configurations used.



Fig. 6.22. Temperature swing adsorption-desorption profiles of 40% PEI-600-silica with different doping levels of  $Na_2B_4O_7$  hydrate dopants. Conditions: Adsorption at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub>, desorption at 130 °C in CO<sub>2</sub>.

Fig. 6.23 presents the TGA-recorded baseline 'drifting' or baseline weight change during the cyclic tests for different Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped PEI adsorbents. The sharp positive baseline weight again represents the residual CO<sub>2</sub> surviving desorption process in CO<sub>2</sub>

at 130 °C in the 1<sup>st</sup> cycle, due to a combination of the adsorption equilibria and relatively short desorption duration times (15 mins) used in the accelerated cyclic tests. As can be seen from Fig. 6.23, both the undoped PEI and the sorbent doped with 1 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> saw a gradual weight gain with increasing adsorption-desorption cycles, which is largely due to CO<sub>2</sub>-induced urea formation as have been discussed earlier in Session 6.5.1. At higher doping levels of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, however, negative rather than positive baseline weight gains started to emerge and become more pronounced with increasing Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> levels, being indicative of the supressed urea formation particularly during the desorption cycle in CO<sub>2</sub> at the higher desorption temperature of 130 °C. One may argue that the baseline weight losses was caused by the evaporation loss of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–contained hydration water, but they cannot wholly accounted for the large differences observed between the absolute baseline weight changes of the doped and undoped PEI sorbents ( $\Delta W_{doped} - \Delta W_{undoped}$ ), which ranged from -2.2 wt% for the 1 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped PEI sorbent, -2.6 wt% for the 5 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped to -3.79% for the 20 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>–doped PEI sorbents respectively.



Fig. 6.23 Positive TGA baseline drifting (baseline weight gain) profiles of PEI adsorbent doped with different levels of  $Na_2B_4O_7$  hydrate during cyclic adsorptiondesorption tests with desorption in dry CO<sub>2</sub>. Conditions: Adsorption at 75 °C in 15% CO<sub>2</sub>/N<sub>2</sub>, desorption at 130 °C in CO<sub>2</sub>.

As has been discussed earlier in Session 6.5.1, dehydration of the carbamate acid, which is the intermediate product of the reversible reaction of  $CO_2$  with nitrogencontaining amine groups, is an essential step of  $CO_2$  adsorption induced urea formation and the presence of water vapour can effectively supress the urea formation. The above test results tend to suggest that the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water might have played an important role in suppressing the urea formation with either the water vapour produced from dehydration (ex-situ suppression) and/or directly via the bound hydration water which is in close contact with the amine sites (in-situ suppression).



Fig. 6.24 Chemical structures of tetrtaborate ion present in borate hydrates (Nies, 1964)

Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> hydrates typically present in two different forms, namely borax decahydrate Na<sub>2</sub>(B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>).8H<sub>2</sub>O and pentahydrate Na<sub>2</sub>(B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub>).3H<sub>2</sub>O, with the borate ions in the borax structure having the chemical formula of B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub><sup>-2</sup>, known as tetraborate ion. The representative chemical structures of tetraborate ion are shown in Fig. 6.24. In both of the two sodium borate hydrates, two moles of water molecules per mole of the borate hydrates are structurally incorporated the borate structure as hydroxyl groups (Fig. 6.24) and cannot be easily dehydrated at temperatures below 200 °C. Sodium borate decahydrate can easily lose 3 water molecules at temperatures below 70 °C to convert to sodium borate pentahydrate, whereas the complete dehydration of pentahydrates take place at temperatures 140 °C (E. Akbay, 2017, Hammar, 1969). Sodium pentahydrate has a vapour pressure of 17.7 kPa at equilibrium at 59 °C and converts to the form of dihydrate at an equilibrium vapour pressure of 0.26 kPa at 88 °C (R. Thompson and A. J. E. Welsh, 1980). Therefore, based on the above discussions and according to the adsorption and desorption temperatures used in the cyclic tests, it can be reasonably anticipated that the number of hydration water in the sodium borate hydrate varied from a minimum of 2 to a maximum of 5 water molecules per mole of sodium borate doped and they are unlikely to disappear quickly but rather gradually decay at an evaporation rate, which is determined by its vapour pressure at different temperatures varying from 75 to 130 °C. Clearly, the above test results indicates that the in-situ slowly released water vapour along with the remaining water molecules in the hydrate enabled the remarkable suppressing effect observed on CO<sub>2</sub>-indiced urea formation during both the cyclic adsorption and particularly the desorption cycles. This highlights the novel efficacy of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping in improving not only the CO<sub>2</sub> capacity but also the thermal stability of PEI-based adsorbents.

6.4.2.4 Effect of  $Na_2B_4O_7$  hydrate doping on the cyclic adsorption-desorption performance of PEI adsorbents with adsorption in oxidative gas conditions The cyclic adsorption-desorption performance of the 40% PEI-600-silica sorbent and related baseline weight change profiles before and after the doping of  $Na_2B_4O_7$  hydrate are compared in Fig. 6.25 and Fig. 6.26, respectively. In general, the results obtained for the oxidative gas-fired flue gas stream containing 5% CO<sub>2</sub> and 12 % O<sub>2</sub> in N<sub>2</sub> are comparable to those shown in Fig. 6.20 and Fig. 6.21 for the simulated coal-fired flue gas stream but with no excess O<sub>2</sub> present.



Fig. 6.25 Cyclic adsorption-desorption profiles of 40% PEI-600-silcia adsorbents before and after the doping of  $Na_2B_4O_7$  hydrate at different levels.

Adsorption/desorption conditions: Adsorption in 5%  $CO_2/12\% O_2/N_2$  at 75 °C; desorption in N<sub>2</sub> at 130 °C.

Compared to the undoped sorbent, significantly higher cyclic CO<sub>2</sub> capacities were obtained for all the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped PEI adsorbents, with the CO<sub>2</sub> capacity of the bestperforming 20 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped sorbent being nearly 30% higher than that of its undoped counterpart at the end of the 50 cycles test. In addition to the higher  $CO_2$ capacities, all Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped sorbents also exhibited much higher thermo-oxidative stabilities than the undoped original PEI sorbent. For instance, the CO<sub>2</sub> capacity of undoped PEI sorbent decreased by nearly 30% in the 50 cycles test, much greater than the 10% drop obtained for the PEI sorbent doped with 20 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. The desirable effect of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping on thermo-oxidative stability of PEI sorbents can be further highlighted by the significantly lower baseline weight losses observed for the doped PEI sorbents as shown in Fig. 6.26, which represents the evaporation and oxidative losses of the impregnated PEI, as has been discussed earlier in this Chapter. It had been envisaged that the total baseline sorbent weight loss of the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-doped PEI sorbents could be significantly higher, as opposed to lower than the undoped sorbent, due to the additional losses of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water at high doping levels. This further highlights the novel capacity of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping in improving the thermo-oxidative stability of impregnated PEI sorbents in the oxidative adsorption conditions.



Fig. 6.26 Baseline weight change profiles of cyclic  $CO_2$  adsorption-desorption of PEI-600-silica adsorbent before and after  $Na_2B_4O_7$  doping at different levels. Adsorption/desorption conditions: Adsorption in 5%  $CO_2/12\%$   $O_2/N_2$  at 75 °C; desorption in  $N_2$  at 130 °C.

#### 6.4.3 Rejuvenation of degraded PEI adsorbents with catalytic hydrogenation

All amine-based adsorbents for  $CO_2$  capture will ultimately reach their working life, despite the improved thermo-stability that can be potentially achieved with various types of measures that have examined above and in other investigations (Zhang et al., 2014, Pang et al., 2017, Zhai and Chuang, 2017). Therefore, effective measures that can be potentially used to rejuvenate the spent amine adsorbents is of great importance to further improve both the economic and environmental performance of carbon capture technologies. However, no such investigations have been carried out to the best of our knowledge to date. In this session, an exploratory investigation has been performed to examine the potentials of using catalytic hydrogenation to rejuvenate the spent PEI adsorbents under relatively mild conditions. A fixed-bed reactor and autoclave, which have been described in the Experimental Chapter, was used in this exploratory investigation.

**6.4.3.1** Determination of optimal hydro-treating conditions and validation of the efficacy of hydrogenation

Initial tests were undertaken to ascertain the temperature window available for the rejuvenation of degrade PEI sorbent within the HyPy reactor without causing any unintended decomposition or further degradation of the polymer chain. Fig. 6.27 shows the total ion chromatogram (TIC) from the GC-MS analysis of the products recovered in the cold trap from the HyPy treatment of PEI loaded at 40% onto a porous silica support without catalyst added.

As the polymeric PEI itself is not amenable for analysis by GC-MS, the peaks shown are only for the products recovered from the cryo-trap of the HyPy. Undertaken with a hydrogen flow through the reactor of 5 L/min (and so a residence time of  $H_2$  in the reactor of just seconds), the results show that at 300 °C the PEI became thermally labile, with significant amounts of products being produced. Although the contribution from the evaporation of smaller constituents in the PEI could not be ruled out, the products were more likely to be from the hydro-cracking or decomposition of the PEI chains.



#### PEI stability under different HyPy conditions

Fig. 6.27. GC-MS TIC of products recovered from the HyPy of a PEI sorbent with increasing temperature at a H<sub>2</sub> pressure of 3 MPa.

The results from the 250 and 200 °C runs were more promising, with the traces shown on the same scale as that for the 300 °C test with a very low abundance of products being apparent. Thus, at temperatures below 250 °C, it appears that PEI is thermally stable and sufficiently involatile to be held within the HyPy reactor. Therefore, experiments could be conducted without a continuous flow of H<sub>2</sub> gas through the reactor with the oxidised PEI held within the reaction zone. This avoids potential issues with products transport through the rig and allows for greater residence time of the samples to be in contact with the catalyst to promote deoxygenation of the oxidsed PEI. Clearly, the rejuvenation of degraded PEI should ideally be conducted at temperatures below 250 °C.

The second test was to assess the efficacy of a Pt-based catalyst for reducing oxygen functionalities while the performance of the catalyst is not affected by the presence of PEI. To do this, we used cholestenol as a model compound, with the aim of reducing the hydroxyl functional group to the corresponding alkane cholestane. This was done using a carbon-supported 5% platinum as per a previous study (Meredith et al., 2006). The de-oxygenation reaction involved in the reduction of this model compound is similar, if not the same, to those required for the rejuvenation of the oxidatively degraded amines. The aim of the test was also to identify the best temperature window for the rejuvenation of degraded PEI sorbents.

Fig. 6.28 shows the catalytic performance of the carbon-supported platinum catalyst, with complete conversion of the cholestanol to cholestane obtained with the PEIimpregnated catalyst. No unreacted cholestanol was present, and neither were intermediary compounds such as cholestanone. It was also apparent that no significant isomerisation took place all the products have the original  $\alpha\alpha\alpha R$  configuration instead of the more thermally stable  $\beta\alpha\alpha R$  configuration which would have been the case if the presence of PEI induced a reduced rate of reaction.

However, with the carbon-supported catalyst, the required temperature of 300 °C for the complete de-oxygenation of cholestanol to form corresponding cholestane was found to be too high for the hydro-treatment of PEI sorbent as shown in Fig. 6.27. It was therefore decided to test the effectiveness of the silica-supported Pt catalyst system at lower temperatures to find the mildest possible temperatures at which complete reductive removal of oxygen-bearing functionalities can be achieved for degraded PEI sorbents.



Model compound deoxygenation - HyPy at 300°C – GCMS (TIC)

Fig. 6.28 GC-MS TIC of products from the treatment of cholestenol in the presence of PEI showing 100% de-oxygenation of the cholestanol to the corresponding cholestane without significant isomerisation

Fig. 6.29 shows the results for the tests at 150, 200 and 250 °C (final temperature hold for 10 mins) for the silica-supported Pt catalyst (5 wt%). These results show that despite the higher degree of isomerisation observed at higher temperatures, the silica-supported Pt catalyst was clearly significantly more active, with the complete reduction temperature decreased remarkably to as low as 150 °C.



Fig. 6.29 GC-MS TIC of the products from the hydropyrolysis of cholestanol on the silica-supported Pt catalyst system, which indicate that a temperature of 150  $^{\circ}$ C is required for complete reduction.

6.4.3.2 Rejuvenation of heavily degraded PEI adsorbents with catalytic hydrogenation Two of the heavily degraded PEI sorbent samples were selected for rejuvenation, including the one from the 4 days thermo-oxidative treatment (silica-PEI-600-4) and another from the 15 days' treatment (silica-PEI-600-15) in 5% CO<sub>2</sub>/12% O<sub>2</sub>/N<sub>2</sub> at 75 °C. The degraded PEI amine were first recovered from the silica support by washing with methanol and the recovered PEI amine from each sample was then subjected to HyPy with the above mentioned silica-supported Pt as the catalyst. The rejuvenated PEI amine was then re-used for preparing the silica-PEI sorbent following the same procedures as used for preparing the original PEI sorbent.

Fig. 6.30 shows the performance of rejuvenated samples. It can be seen that for the less degraded amine sample, silica-PEI-4, the CO<sub>2</sub> uptake performance can be largely restored with the capacity increased from 7.8 wt% to ca. 9.3 wt%, which is essentially equal to that of the original sorbent sample (ca. 9.5 wt%). For the more heavily degraded sample of silica-PEI-15, a much greater performance improvement was obtained, with its CO<sub>2</sub> capacity increased remarkably to 6.2 wt% after the rejuvenation with HyPy, more than doubled the 2.8 wt% of the original degraded sample before rejuvenation. However, it must be noted that despite the great improvement, the CO<sub>2</sub> uptake capacity of the rejuvenated silica-PEI-15 sample is still significantly lower than that of the original sorbent before degradation (9.47 wt%). This indicates that higher reaction temperatures may be needed to effectively remove the oxygen and other functionalities present in the heavily degraded sample, but this may risk the amine groups being removed altogether or the amines being totally destroyed at higher hydrogenation temperatures. It is therefore believed that the functionalities formed at early stages of degradation may undergo transformation to form more stable structures as the degradation proceeds further. Though more investigations are clearly needed, the above results along with those presented in Table 1 demonstrate that once heavily degraded, such as the one silica-PEI-600-15, the PEI-based adsorbents could be more difficult to rejuvenate, compared to degraded lower molecular mass amines that could be easier to restore their  $CO_2$  adsorption performance via potential measures, such as steam treatment (Sayari, 2010). Therefore, for heavily degraded silica-supported PEI adsorbents, it may be more economical to recover the porous silica substrate that can be re-used for sorbent preparation with fresh PEIs.



Fig 6.30 CO<sub>2</sub> uptake performance of degraded PEI amines before and after rejuvenation with catalytic HyPy at different temperatures.

Aqueous <sup>13</sup>C NMR spectroscopy was applied for the structural characterisation of selected PEI samples from the catalytic rejuvenation tests, and Fig. 6.31 shows the <sup>13</sup>C NMR spectra for the selected samples, including the undegraded PEI-600 and the degraded samples before and after the catalytic hydrotreatments.

As shown in Fig. 6.31(A), the undegraded PEI contained a range of aliphatic primary amine (40-43 ppm), secondary amine (50-53 ppm) and tertiary amine functional groups (54-60 ppm) (Pretsch, 2000). It is evident from Fig. 6.30(B) that the 15 days' thermo-oxidative treatment of PEI (PEI-600-15) in 5% CO<sub>2</sub>/12% O<sub>2</sub>/ N<sub>2</sub> led to the formation of a variety of new functionalities exhibiting peaks between 160 and 180 ppm, including carboxylic acids and carboxamides and ketones, while the chemical

constitution of the amine functionalities in the degraded PEI became much more complicated. Fig. 6.31(C, D) indicate that the majority of degradation-derived carboxyl and amide groups were removed after the catalytic hydro-treatment and the presence of these functionalities became negligible when the hydrogenation temperature increased from 225 to 275 °C. However, it was also found that despite the mild hydrogenation conditions used, the loss of some of the amine functionalities appeared to inevitable as highlighted by the formation of a range of alkyl groups, which increased with increasing hydrogenation temperatures. This explains, at least partly if not wholly, why the CO<sub>2</sub> capacity of the heavily degraded PEI sorbents could not be fully restored, despite the near complete removal of the degradation-derived functionalities under the mild conditions used.



Fig. 6.31 Aqueous <sup>13</sup>C NMR spectra for selected degraded PEI samples before and after catalytic hydro-treatments.
## 6.5 Concluding remarks and recommendations

In this Chapter, the lifetime performance of PQ silica supported PEI adsorbents for  $CO_2$  capture has been evaluated under various conditions for both adsorption and desorption, using temperature-swing cyclic adsorption-desorption cycles in TGA. Based on the lifetime performance testing results, an exploratory study has been conducted to examine the effectiveness of a range of potential approaches that can be used to improve the anti-degradation performance of PEI adsorbents.

The lifetime performance testing results demonstrate that irrespective of the adsorption and desorption conditions, PEI degradations were observed at various levels for all conditions examined. The comprehensive performance evaluation led to the following conclusions:

- In adsorption-desorption cycles with  $N_2$  as being the purge gas (desorption in  $N_2$ at a higher temperature), the evaporation loss of the supported PEI amines was found to be the major pathway of thermal degradation, although CO<sub>2</sub>-inudced urea formation could also play a rule particularly during the desorption process at higher temperatures than adsorption. In general, however, the CO<sub>2</sub>-induced thermal degradation was not found to occur significantly. The evaporation loss of PEI increase with the temperatures for adsorption and desorption increase and decreases with increasing molecular weight of the PEI used. Novel thermostability was observed for the high boiling PEI with a molecular weight of 10,000, which showed negligible evaporation loss in both coal and gas fired flue gas conditions though at a modest cost of CO<sub>2</sub> capacity. In addition, the evaporation loss of PEI was also found to be significantly affected by the CO<sub>2</sub> partial pressures. The significantly lower evaporation loss of PEI obtained for adsorption taking place at higher CO<sub>2</sub> partial pressures suggests that the reversible carbamate formation resulting from the CO<sub>2</sub> adsorption can help preserve and thereby mitigate the evaporation loss of the supported amines.
- Severe PEI degradations were observed in temperature-swing adsorptiondesorption tests when adsorption condition took place in the simulated gas-fired flue gas streams containing 5% CO<sub>2</sub> and 12% O<sub>2</sub> in N<sub>2</sub>. It seems that oxidative degradation and thermal degradation affect each other in vicious cycles, with the supported amine sorbent losing its CO<sub>2</sub> capacity completely in the 50 cycles test,

which lasted approximately 120 hours. In the  $O_2$ -containg flue gas, the evaporation loss of PEI in each individual adsorption-desorption cycle was found to be much greater than in the  $O_2$ -free baseline gas conditions, due to the gradual loss of the stabilising effect as a consequence of reduced carbamate formation because of the oxidative degradation of PEI in the  $O_2$ -bearing flue gas.

The use of dry CO<sub>2</sub> either as the purge gas and/or stripping gas has been proposed as being a potentially viable option for sorbent regeneration while producing high purity CO<sub>2</sub> stream with improved process efficiency and energy savings. However, the results from temperature-swing adsorption-desorption cycles demonstrate that the use of CO<sub>2</sub> as the purge gas could lead to 1) drastically reduced CO<sub>2</sub> capacity due to the CO<sub>2</sub> adsorption equilibria at the higher desorption temperature and 2) rapid de-activation of supported amines, due to severe CO<sub>2</sub>-induced thermal degradation i.e. urea formation during the desorption cycles.

To sum up, the results from lifetime performance testing indicate that the evaporation loss of supported PEI adsorbent, a type of PEI thermal degradation, could be a major concern in terms of both the techno-economic performance and environmental impact should the PEI sorbent be used for  $CO_2$  capture, while oxidative degradation due to the presence of  $O_2$  in the flue gas should be concerned where flue gas contains high levels of excess  $O_2$ . Consequently, effective measures must be taken to mitigate both the thermal or thermo-oxidative degradation and the potential toxic PEI emissions, particularly for the flue gas streams having low  $CO_2$  partial pressures and high levels of excess  $O_2$ , such as the flue gas streams of combined cycle gas turbine (CCGT) power plants.

Based on the results from the comprehensive lifetime performance tests, examinations of the potential measures or strategies that can be used to improve the lifetime performance of impregnated PEI sorbents have led to the following conclusions and recommendations:

- CO<sub>2</sub>-induced urea formation as one of the major causes of PEI thermal degradation can be effectively mitigated or even eliminated with the presence of water vapour or moisture in the gas streams during adsorption and particularly the desorption cycles. This potentially make it possible to use moisturised hot CO<sub>2</sub> gas as the either stropping or purge gas to regenerate the amine-based CO<sub>2</sub> adsorbents without causing significant  $CO_2$ -incluced thermos-degradation in a  $CO_2$ -rich environment.

- It was also found that as a co-benefit of reduced urea formation, the presence of moisture in the adsorption/desorption streams can also improve the antioxidative degradation performance of PEI sorbents as the accordingly improved carbamate formation as a result of reduced urea formation can help protect the PEI from getting evaporated and/or oxidised during the adsorption process.
- The exploratory investigation into the efficacy of inorganic hydrate doping in improving the anti-degradation of PEI sorbents reveals that due to the desirable weak basicity and unique hydration and dehydration characteristics, the doping of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> hydrates even at very low doping levels can greatly increase the cyclic adsorption-desorption lifetime performance of PEI adsorbents for CO<sub>2</sub> capture, in terms of not only the CO<sub>2</sub> adsorption capacity but also more importantly, the performance against thermo-oxidative degradation. The great effect of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping was ascribed to the slow release of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water, though not found at significant quantities. More importantly, the gradual loss of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water can be easily replenished by the moisture present in the flue gas streams during adsorption.
- The exploratory investigation also found that catalytic hydrogenation could be effectively used to rejuvenate the spent PEI sorbents and for some degraded PEI sorbent samples, the loss of CO<sub>2</sub> capacity due to the formation and accumulation of urea and other thermo-oxidative degradation products which can be largely restored. However, for severely degraded PEI sorbents, the sorbent de-activation appears to be unlikely to be reversed with catalytic hydrogenation due to the inevitable loss of functional amine groups during hydrogenation even under mild conditions. Therefore, it may become uneconomical to rejuvenate the heavily degraded PEI sorbents. As a result, the recovery of the porous silica substrate for preparing new PEI sorbent materials, rather the rejuvenation of the supported PEIs, could be more economical.

# CHAPTER 7 Novel Reductive Rejuvenation Approaches for Degraded Amine Solvents from PCC in Power Plants

## 7.1 Introduction

Aqueous amine scrubbing was developed for natural gas treatment and is currently considered to be the current best available technology for post-combustion capture (IPCC) of CO<sub>2</sub> from both pulverised fuel (Romanos et al.) and natural gas combined cycle (NGCC) power plants(Dutcher et al., 2015, Molina and Bouallou, 2017, Yan et al., 2017). A major issue is the severe thermo-oxidative degradation of alkanoamine solvents that occurs in PCC compared to natural gas processing (Fig. 7.1), with the problem being compounded by the presence of acid gases that lead to the formation of heat stable salts (HSS) (Thompson, 2014). The accumulation of degradation products is known to reduce CO<sub>2</sub> capture efficiency and cause excessive foaming and fouling and unacceptably high corrosion rates (Tanthapanichakoon, 2006).

Current measures to compensate for degradation involve purging spent solvent for reclamation, makeup with fresh amine and the addition of anti-foam and oxidation/corrosion inhibitors (Chakma, 1995, Rochelle, 2009, Rochelle, 2012, Teeradet Supap, 2006). Reclaimer technologies based on distillation, ion-exchange and elecrodialysis (Chakma, 1995) have been developed to deal primarily with HSS where distillation has the advantage of removing both the HSS and their anions. However, these technologies do not deal with the majority of the other degradation products, particularly those arising from thermo-l oxidative degradation where Table 1 shows those obtained from monoethanolamine degradation (Teeradet Supap, 2006, Gouedard et al., 2012). Further, MEA also forms polymeric products, such as N-(2-hydroxyethyl)-ethylenediamine (HEEDA), which may continue to degrade in the presence of  $CO_2$  to form longer substituted ethlyenediamines. In distillation, these and the higher boiling degradation products remain in the residues with the HSS that then require disposal.



Fig. 7.1 the severe thermo-oxidative degradation of alkanoamine solvents: (a) degraded amines produced from  $CO_2$  capture test by Tel-Tek, the sticky brown liquid contains more than 90% amine waste and the dark brown liquid in the corner is amines in a paster-like phase; (b) amines degradation observed from an industrial pilot amine capture plant, leading to complete destruction of the amine solvent.

A recent IEA study estimates that the cost of reclaimer technologies is in the range of \$1 per tonne of CO<sub>2</sub> captured (Davison, 2014). However, the estimated costs of amine replacement arising from thermo-oxidative loss is considerably higher estimated at between \$1.5-4.0 per tonne of CO<sub>2</sub> captured (0.5-2.0 kg of amine) (Goff, 2004) and this figure does not include disposal costs. Clearly, processes that can convert the degraded amines back to hydroxylamine solvents or, alternatively, saleable products will potentially reduce this cost considerably.

Oxidative degradation products	Thermal degradation products
N- glycylglycine	Oxazolidin- 2- one (OZD)
N- (2- hydroxyethyl)oxamic acid	N,N- bis- (2- hydroxyethyl)urea
N (2 hydrovethyl)imiderale (UEI)	N- (2- hydroxyethyl)-
	diethylenetriamine
N- (2- hydroxyethyl)piperazin- 2-	N- (2- hydroxyethyl)ethylenediamine
one	(HEEDA)
N- (2- hydroxyethyl)formamide	N- (2- hydroxyethyl)imidazolidin-
(HEF)	2- one (HEIA)
N (2 hydroyyothyl)acatomida	N,N- bis(2-
(HEA)	hydroxyethyl)imidazolidin- 2- one
(nea)	(BHEI)
N- (2- hydroxyethyl)piperazin- 3-	N- [2- [(2- hydroxyethyl)amino]
one (HEPO)	ethyl]imidazolidin- 2- one
N.N. big(2 bydroyyothyl)oyalamida	N- (2- aminoethyl)- N- (2-
	hydroxyethyl)imidazolidin- 2- one
(BILOX)	(AEHEIA)
N- (2- hydroxyethyl)ethylenediamine	
(HEEDA)	
2- Hydroxy- N- (2-	
hydroxyethyl)acetamide (HHEA)	
N,N- bis(2-	
hydroxyethyl)ethylenediamine	
(BHEEDA)	
N- (2- hydroxyethyl)- 2- (2-	
hydroxyethylamino)acetamide	
(HEHEAA)	

Table 7.1 Selected typical MEA degradation products (Gouedard et al., 2012)

This exploratory study has been aimed to investigate the feasibility or capability of using a range of reductive approaches, such as hydrolysis and catalytic hydrotreatments at modest temperatures and pressures, which can be collectively called aqueous reforming, to effectively rejuvenate the spent amine solvents or convert them into other highly value-added products. The original objectives are repeated here as follows:

- (i) To apply the hydrogenation/ hydropyrolysis and hydrothermal treatments to a number of individual compounds found in degraded solvents, including 1-(2-hydroxyethyl)-2-imidazolidone (HEIA), HEPO and HEEDA (Table 7.1).
- (ii) Based on the model compound results, to conduct experiments on actual fractions from degraded amine solvents containing the degradation products.
- (iii) To use the results to define the overall benefits hydrogenation, hydropyrolysis and hydrothermal treatments in solvent rejuvenation and a basis for planning the subsequent research needed to take forward these new treatments, in terms of identifying how these treatments can best be conducted continuously.

## 7.2. Experimental

#### 7.2.1 Preparation of Catalysts

Three catalysts, including supported platinum (Pt) and nickel (Ni) and molybdenum oxysulfides were used in the hydrotreatment and hydrothermal treatments.

*Preparation of activated carbon or silica supported Pt and Ni catalyst\_*A wet impregnation method was used in preparing the supported catalysts containing 10 wt% active metals. In a typical preparation of supported catalysts e.g. silica-supported Pt, a calculated amount of 757 mg of platinum (IV) nitrate solution (15 wt%, Alfa Aesar) and 1 g PQ silica (PQ company) were first added to 5 ml deionized water, and the mixture was then stirred overnight at room temperature. Following drying in a vacuum oven at 40 °C for 24 hours, the mixture was calcined in air at 500 °C for 4 hours. The solid product yielded was then reduced at 600 °C in H<sub>2</sub> to give the highly active silica-supported Pt metal for use in hydrotreat tests.

**Preparation of molybdenum-based catalyst** 2 g of ammonium molybdate tetrahydrate (Sigma-Aldrich) was dissolved in 9 ml of ammonium sulphide solution (20% in water, Sigma-Aldrich), with the solution stirred in an ice bath for 30 minutes. The resulting precipitate of ammonium dioxydithiomolybdate [(NH<sub>4</sub>)<sub>2</sub>MoO<sub>2</sub>S<sub>2</sub>], was recovered via filtration and then dried in a vacuum oven at 50 °C for 1 hour. As with the Pt-based catalyst, the precipitate was also reductively treated to yield catalytically active oxysulfide Mo species, although MoS<sub>2</sub> would not be formed until approximately 400 °C (Meredith et al., 2015).

#### 7.2.2 Hydrogenation and Hydrothermal Treatment tests

## 7.2.2.1 Hydrogenation tests

**Batch-wise tests in autoclave** A closed micro-autoclave system rated to 30 MPa at 420 °C. The reactor is heated by a fluidized sand bath, which was controlled by an external temperature controller. Temperature is monitored by an additional K-type thermocouple and is recorded every 10 seconds by a coupled computer. Compressed air is transferred into the bottom of the sand bath through a gas distributor and evenly bubbled inside container to mix the sand, and so evenly distributed the heat through the sand bath. The sand bath is pre-heated to the required temperature and left for 10

minutes to equilibrate. When the experiment finished, the reactor is removed from the sand bath immediately, with compressed air used to cool the reactor to room temperature in order to prevent secondary reactions before product recovery.

Individual samples were prepared by dissolving 0.5 g of the model MEA degradation compounds or degraded MEA solvent samples in 5 g water. This solution was first mixed with 0.05 g of catalyst before transferred to the autoclave. The autoclave was then sealed and pressurised to 3 MPa with hydrogen. After leak test, the autoclave was then transferred to the heated sand bath and left to run for a pre-set duration of time, which has been typically around 30 mins at a given temperature. The temperature investigated in the hydrotreatments in autoclave varied from 170 to 300 °C, with the pressure in the closed system ranging from 9 to 12 MPa for an initial pressure of 3 MPa. For the tests with ammonia, the water initially charged to the reactor was replaced instead with 10 g 30% ammonium hydroxide solution.

*Hydrogenation tests in a fixed-bed reactor* The fixed-bed hydrogenation reactor is an open reaction system where continuous flows of high pressure hydrogen (up to 15 MPa) is used for the catalytic selective de-functionalisation of the model compounds, such as steroids and carboxylic acids (Meredith et al., 2004, Sephton et al., 2005b, Meredith et al., 2006). Compared to the autoclave reaction system where hydrogenation takes place in hydrothermal conditions, the hydrogenation tests in the open fixed-bed reactor is essentially under dry hydrogen conditions as the sample is pre-uploaded onto the solid catalysts used and any moisture produced is removed in the hydrogen flow. The sample/catalysts mixture is located within the centre of the hot zone between the heating connectors on the rig. In each hydrogenation test, the sample once loaded into the reactor was rapidly heated from ambient to a maximum of 550 °C at a heating rate of up to 300 °C/min. A hydrogen pressure of up to 15 MPa and a flow of up to 5 L/min was used to reduce the sample while the formed products were recovered into a downstream dry ice cold trap filled with silica (Meredith et al., 2004). The short residence time of only seconds preserves the structural integrity of the products as it can minimize or even prevent any secondary reactions.

*Hydrogenation tests in continuous flow reactor system* A PID Effi Microactivity reactor (Fig. 4. 4), which is an advanced continuous flow reactor system that can allow

the continuous feeding and collection of reactants and products in a catalytic reaction system. The aqueous sample was continuously fed at a constant rate of 5 ml/min while the hydrogen pressure was controlled at 2 MPa with a flow rate of 50 ml/min and the reaction temperature examined varied from 200 °C to 350 °C. The liquid products were collected from the liquid outlet of the reactor.

Hydrous or hydrothermal treatment tests were conducted all in a small autoclave as described above, following the procedures that were essentially the same as for the hydrogenation tests in the autoclave.

#### 7.2.3 Product characterisation

A Varian CP-3800 gas chromatograph (GC) equipped with a Zebron ZB-1701 fused silica capillary column (60 m x 0.25 mm (i.d.), 0.25  $\mu$ m thickness), which is interfaced to a Varian 1200 mass spectrometer (MS), was used to characterise the liquid products from the hydrogenation and hydrothermal treatments.

The CO<sub>2</sub> absorption of the aqueous MEA solvent samples before and after treatment was assessed using a small gas washer connected to a CO<sub>2</sub> analyser. A simulated flue gas steam containing 15% CO<sub>2</sub> in N<sub>2</sub> was introduced at a flow rate of 5 ml/min into the gas washer containing 2 ml of original and treated aqueous solvent samples. The CO<sub>2</sub> concentration of the outlet gas stream was continuously monitored until it reached the inlet concentration of 15% CO<sub>2</sub>.

## 7.3 Results and Discussion

#### 7.3.1 Sample Preparation and Characterisation

The following six model degradation compounds sourced from Sigma-Aldrich were selected for hydrotreatments and/or hydrolysis tests.

N-(2-Hydroxyethyl)-ethylenediamine

Glycylglycine (Gly-Gly)





MW: 104



MW: 87 1-(2-Hydroxyethyl)-imidazole



MW: 112

MW: 132

1-(2-Hydroxyethyl)-2-imidazolidinone



MW: 130

N-Acetylethanolamine or N-(2-hydroxy-ethyl)-acetamide





The efficacy of the hydrogenation technique together with the proposed silica/catalyst support was also tested with cholestenol (Sigma-Aldrich), which has previously been used as a model compound for de-functionalisation of steroids (Will Meredith, 2015).

In addition, an industrial sample of a heavily degraded MEA solvent was sourced from E.ON from its Ratcliffe-on-Soar power station which was prepared from the cold wall by 5 weeks at 60 °C and 5 week at 120 °C. Detailed characterisation of the degraded solvent samples has been conducted as part of an EngD project (Lewis, 2017). The most heavily degraded MEA solvent sample was used directly in all hydrotreatments tests without further pretreatment, due to the heavy degradation and the difficulties to

remove the MEA without altering the original chemical constitution of the degraded solvent. In brief, the most heavily degraded MEA solvent selected for the rejuvenation tests still contained ca. 10 wt% MEA, with the major degradation products identified including hydroxyl acetamides, hydroxyl succinimide and alkyl hydrazones.

#### 7.3.2 Catalytic Hydrogenation or Hydropyrolysis (HyPy)

#### 7.3.2.1 MEA model compounds

For each experiment approximately 10 mg of each model compound was dissolved in methanol and adsorbed to 80 mg of the silica-Pt (5% wt%). Held in a glass tube made from a cut down Pasteur pipette plugged top and bottom with quartz wool, the sample was then introduced to the reactor. A constriction within the reactor tube holds the sample directly between the electrical connectors and directly below the control thermocouple. The system was then heated from ambient temperature to 150 °C at 150 °C/min, and then to the final temperature of 300 or 350 °C at 10°C/min. The final temperature was held for 30 mins before the system was allowed to cool. A H<sub>2</sub> pressure of 3 MPa was maintained within the system at all times, with a gas flow of 2 L/min used to transfer any volatised products from the reactor to the trap.

For two of the model compounds, including N-(2-hydroxyethyl)ethylenediamine and 2-oxazolidinone, experiments were repeated at 15 MPa  $H_2$  pressure and 350 °C. It revealed that increasing the pressure had very limited effect on the distribution of products so this variable was not tested for the remaining model compounds.

The products were recovered from the trap silica by desorbing in 5 ml aliquots of dichloromethane and methanol, with the two fractions combined before analysis. Results for all model compounds are shown in Fig. 7.2. The Pt catalyst residue was also desorbed in methanol after each experiment, with the eluent analysed to ensure that all of the starting material was converted to volatile products, and this was found to be the case for all the model compounds tested.

## N-(2-Hydroxyethyl)ethylenediamine (Fig. 7.2a)

Complete conversion of starting material was achieved at temperatures  $\geq 300$  °C (boiling point 240 °C) with none of the starting material detected on the catalyst residue after HyPy. The products are shown to be limited only to alkylated piperazines, with no apparent effect observed with increasing the temperature to 350 °C. The consistency of product distribution results from the lack of secondary reactions, probably due to the very limited residence of time (in the order of seconds) of the hydrogen and also the volatilised model compound within the reactor.

## 2-Oxazolidinone (Fig. 7.2b)

As with the N-(2-hydroxyethyl)-ethylenediamine, there was complete mobilisation of the starting material by 300 °C, with all of the starting material volatilised. However, complete conversion was not apparent with much of the starting material found to be unreacted following treatment at 300 °C. Products at 300 °C included a number of alkyl hydrozones. Increasing the temperature to 350 °C gave rise to increased conversion of the starting material with alkylated piperazines as being the major products as seen for N-(2-hydroxyethyl) ethylenediamine. This indicates interestingly that the higher temperature employed promoted the cyclisation of the products even under the reductive environment of high pressure H<sub>2</sub>.

## 1-(2-Hydroxyethyl)-2-imidazolidinone (Fig. 7.2c)

This MEA degradation product was also found to be very reactive. Most of the model compound can be effectively converted at 300 °C and with complete conversion achieved at 350 °C. Products at both temperatures are composed of a range of alkyl-imidazolidinones and alkyl-hydrazones.

## 1-(2-Hydroxyethyl)imidazole (Fig. 7.2d)

Treatment at 300 °C resulted in the complete conversion of the starting material with the removal of the hydroxyl group to form 1-ethyl imidazole. A very small amount of 1 methyl imidazole is also formed, with similar results found at 350 °C. Again no

secondary reactions were observed at either reaction temperature, highlighting the high degree of selectivity of the defunctionalisation via HyPy.

## <u>N-Acetylethanolamine (Fig. 7.2e)</u>

Acetylethanolamine was reduced to a series of alkylated acetamides, although a final temperature of 350 °C was required to convert all of the starting material. In addition, a large peak at the very start of the chromatogram was apparent that could not be identified. The presence of this compound explains the relatively low intensity of the acetamide peaks and suggests that a large portion of the starting material was converted to very low molecular weight components, which will require further analysis under a different GCMS programme to fully characterise.

## Gly-Gly (not shown)

The treatment of Gly-Gly did not result in any recoverable products from either within the reactor or from the cryo-trap. Either this model compound was reduced to very low molecular weight products of great volatility which could not be trapped on the silica within the cryo-trap, or less likely, the products bound so strongly to the silica-Pt catalyst that they could not be recovered in solvent after the experiment.



Fig.7.2 GC-MS TIC of the products from hydropyrolysis of the MEA model compounds. Note Gly-Gly resulted in no recoverable product (continued).



Fig.7.2 GC-MS TIC of the products from hydropyrolysis of the MEA model compounds. Note Gly-Gly resulted in no recoverable product (continued).



Fig.7.2 GC-MS TIC of the products from hydropyrolysis of the MEA model compounds. Note Gly-Gly resulted in no recoverable product (continued).



Fig.7.2 GC-MS TIC of the products from hydropyrolysis of the MEA model compounds. Note Gly-Gly resulted in no recoverable product (continued).



Fig.7.2 GC-MS TIC of the products from hydropyrolysis of the MEA model compounds. Note Gly-Gly resulted in no recoverable product.

#### 7.3.2.2 Degraded MEA solvent & mixture of all 6 model compounds

In order to get an appreciation for the overall efficacy of catalytic HyPy for the reduction of the thermal and oxidative degradation products of MEA, experiments were performed with both a mixture of the six model compounds, as a representation of a simple mixture of degraded MEA solvent together with the actual degraded solvent from Ratcliffe-on-Soar power station, which was clearly more compositionally complex. Despite the dark colour indicating the severity of degradation, the degraded MEA solvent still contains some amount of MEA (ca. 10 wt%). Experiments were performed using the silica-Pt catalyst at 550 °C (with a final hold time of 20 mins) under 3 MPa H<sub>2</sub>.

The use of higher hydrogenation temperatures than those used previously ( $\leq 350$  °C) is to speed up the catalytic hydrotreatment process and to examine the potential effect of hydrogenation temperature on the composition of products. The results shown in Fig. 7.3 demonstrate that the composition of the products produced at higher hydrogenation temperatures are generally similar to those produced at lower temperatures, but with higher quantities of five-membered nitrogen-containing aromatic products (e.g. imidazoles) being produced.

The compositions shown in Fig. 7.3 are similar for both mixture samples, with the products composed largely of alkylated pyrazines, piperazines, acetamides and imidazoles. No actual MEA was recovered in either case, implying that the remaining MEA in the degraded solvent were destroyed completely in the applied hydro-treatments.

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Fig. 7.3 Catalytic hydrogenation of degraded MEA: (a) the mixture of the 6 model compounds; (b) the degraded MEA solvent with the silica-Pt catalyst at 550 °C and 3 MPa  $H_2$ . (Continued)



Fig. 7.3 Catalytic hydrogenation of degraded MEA: (a) the mixture of the 6 model compounds; (b) the degraded MEA solvent with the silica-Pt catalyst at 550 °C and 3 MPa  $H_2$ .

To investigate if the high degree of activity of the Pt catalyst had a significant influence on the product distribution, the experiment on the degraded MEA solvent was repeated using a less active molybdenum catalyst and a lower maximum temperature of 350 °C. The results are shown in Fig. 7.4. While the products again contain large quantities of alkyl-pyrazines, the formation of a greater range of compounds, including acetamides, pyrrolidinediones and piperazinones, are apparent.



Fig. 7.4 Catalytic hydrogenation of the degraded MEA solvent with a Mo catalyst at  $350 \ ^{\circ}C$  and  $3MPa H_2$ .

## 7.3.2.3 Summary of findings from catalytic hydropyrolysis (HyPy) experiments

Catalytic hydrogenation (via the HyPy system) has been shown to effectively transform amine degradation products into deoxygenated products at extremely high conversion efficiencies. The products from individual model compounds are highly selective, with in some cases just one or two individual compounds generated. While MEA itself was shown not to be formed in any of the experiments, compound classes such as piperazines, acetamides, inidazolidinones and hydrazones were found for the individual model compounds and their mixtures and from the actual degraded MEA solvent.

#### 7.3.3 Hydrous Pyrolysis or Hydrothermal Treatments

Hydrothermal experiments were undertaken with both hydrous hydrogen and ammonia in a batchwise autoclave reactor. Catalysts used included the same silica-Pt catalyst as used for the catalytic hydrogenation in the HyPy system, and also nickel on PQ silica.

#### 7.3.3.1 Silica-Pt catalyst

#### (a) Model degradation compounds

## <u>N-(2-Hydroxyethyl)ethylenediamine</u>

In a hydrogen/water system at 250 °C, N-(2-Hydroxyethyl)ethylenediamine is converted to a number of smaller amines, including the cyclic structure of piperazine (Fig. 7.5). In addition, larger compounds are also formed from the ring formation from the cyclic and straight chained products, yielding compounds with increased molecular weight. Increasing the temperature to 300 °C resulted in the suppression in the amount of MEA formed.

With the less reductive treatment under an ammonia solution, alkylated pyrazines are instead the major products identified, with complete conversion and de-oxygenation being apparent.

#### <u>Gly-Gly</u>

Gly-Gly was found to be fully converted under all conditions examined (Fig. 7.6), with 3 MPa hydrogen resulting in the generation of a range of alkyl piperazinediones. Increasing the temperature to 300 °C promoted the reduction of these compounds to a range of piperazinones and pyrimidinones. Replacing the hydrogen with ammonia solution supressed the formation of these compounds with the piperazinediones formed at 250 °C, which was further converted to alkyl acetamides and acetic acid at 300 °C.



Fig. 7.5 Total ion chromatograms (TIC) for the rejuvenation tests of N-(2-Hydroxyethyl) ethylenediamine and peak assignments from the GC-MS for the rejuvenation tests of N-(2-Hydroxyethyl) ethylenediamine.

Table 7.2 Table of peak assignments from the GC-MS for the rejuvenation tests of N-(2-Hydroxyethyl) ethylenediamine

Peak #	Compound Name	Mw	Chemical Structure
1	N-(2- Hydroxyethyl)ethylenediamin e	104	HO NH <sub>2</sub>
2	Monoethanolamine (MEA)	61	HO NH <sub>2</sub>
3	Ethylaminoethanol	89	N OH H
4	Piperazine	86	HNNH
5	1,3-Bis(dimethylamino)butane	144	N N
6	1-Piperazineethanol	130	HNNOH
7	1-Acetylpiperidine	127	
8	1,4-Bis(2- hydroxyethyl)piperazine	174	но
9	N-Methylpiperazine	100	HNN
10	N,N'-Dimethylpropylene urea	128	
11	2-Methylpyrazine	94	N N
12	2-Ethylpyrazine	108	N
13	2,3-Dimethylpyrazine	108	
14	2-Ethyl-3-methylpyrazine	122	

15	2,3-Diethylpyrazine	136	
16	N-Methylacetamide	73	O NE



Fig. 7.6 Total ion chromatograms (TIC) from the GC-MS of the rejuvenation tests on Gly-Gly.

Peak #	Compound name	Mw	Chemical structure
1	Gly-Gly	132	
2	1-methyl-1,3-diazinane-2,4- dione	128	O N O
3	γ-Decalactone	170	
4	Butanal dimethyl hydrazone	114	_N_N
5	Ethylhydrazine	60	H <sub>2</sub> N <sup>H</sup> N
6	Monomethylacetamide	73	O H H
7	N-Ethylacetamide	87	O N H
8	N,N-Dimethylguanidine	185	_N_NH₂ NH
9	N,N'-Dimethylpropyleneurea	128	
10	Acetamide	59	O NH <sub>2</sub>
11	2-Methylpiperazine	100	NH HN
12	Butanal dimethyl hydrazone	114	

Table 7.3 Table of peak assignments from the GC-MS for the rejuvenation tests of Gly-Gly.

## 2-Oxazolidinone

2-Oxazolidinone was found to be highly reactive in a hydrogen atmosphere and the presence of water, with almost complete conversion apparent for all temperatures in excess of 200 °C (Fig. 7.7). While no MEA was produced at all conditions examined, 1-(2-hydroxyethyl)-2-imidazolidinone, a reagent for synthesis of HIV-1 integrase

inhibitors, was found to be the major product at lower temperatures. At higher temperatures (300 °C), alkylated piperazines became increasingly the major products. For the hydrolysis with ammonium water, alkylated pyrazines and a group of heterocyclic aromatic compounds increasingly became the major products with increasing temperatures. Enhanced aromatisation was observed with increasing temperatures under the hydrothermal conditions of ammonia water, highlighting the lower reactivity of NH<sub>3</sub>.



Fig. 7.7 Total ion chromatograms (TIC) of the rejuvenation tests on 2-oxazolidinone under both hydrogen and ammonia and the peak assignments from the GC-MS of the rejuvenation tests on 2-oxazolidinone under both hydrogen and ammonia.

Table 7.4 Table of peak assignments from the GC-MS of the rejuvenation tests on 2oxazolidinone under both hydrogen and ammonia

Peak #	Compound Name	Mw	Chemical Structure
1	2-Oxazolidinone	87	O NH
2	N-Ethyl-3-piperidinol	129	но
3	1-(2-Hydroxyethyl)piperazine	130	HNNNOH
4	N,N'-Dimethylpropylene urea,	128	O N N
5	2-Propanone, dimethylhydrazone	100	N_N_
6	1-(2-Aminoethyl)piperazine	129	HNNNH2
7	DL-Asparagine	132	
8	2-Imidazolidone	86	
9	2-Ethylpyrazine	108	N N
10	2,3-Dimethylpyrazine	108	N
11	2-Ethyl-3-methylpyrazine	122	N
12	2,3-Diethylpyrazine	136	
13	1-Aminopiperidine	100	N-NH <sub>2</sub>
14	1,3-Diazine	80	N
15	2-Methylpyrazine	94	N N

## 1-(2-Hydroxyethyl)-2-imidazolidinone

While unreactive at 250 °C, 1-(2-Hydroxyethyl)-2-imidazolidinon was found to readily loose its hydroxyl group at 300 °C to form a suite of cyclic amines (Fig. 7.8). As some of the product compounds still contain oxygen groups, higher temperatures or longer residence times appear to be needed to fully de-oxygenate this compound. This compound was clearly unreactive at 250 °C in an ammonia solution. However, at 300 °C, it was found to be significantly more reactive than in the  $H_2/H_2O$  hydrothermal system, with full reductive conversion to alkyl pyrazines along with the functionalised intermediates as seen with hydrogen.



Fig. 7.8 Total ion chromatograms (TIC) from the GC-MS of the rejuvenation tests on 1-(2-hydroxyethyl)-2-imidazolidinone

Table 7.5. Table of peak assignments from the GC-MS for the rejuvenation tests of 1-(2-hydroxyethyl)-2-imidazolidinone.

Peak #	Compound Name	Mw	Chemical Structure
1	1-(2-Hydroxyethyl)-2- imidazolidinone	130	HN_N_OH
2	N-Aminoethylpiperazine	129	HNNNH <sub>2</sub>
3	5-Aminouracil	127	
4	Succinimide	99	o H o
5	Pyrimidine	80	N
6	2-Methylpyrazine	94	N N
7	Ethylpyrazine	108	N N
8	2,3-Dimethylpyrazine	108	N N
9	N-Methylacetamide	73	O NH
10	2-Ethyl-3-methylpyrazine	122	N
11	1,2-Dimethylimidazole	96	N N
12	N,N'-Dimethylethyleneurea	114	N N
13	4-(2- Aminoethyl)morpholine	130	ONNH <sub>2</sub>
14	Succinimide	99	0 K O
15	N-Methylsuccinimide	113	0 N O

## 1-(2-Hydroxyethyl)imidazole

1-(2-hydroxyethyl)-2-imidazolidinone was found to be more reactive in the  $NH_3/H_2O$  than in the  $H_2/H_2O$  hydrothermal conditions. Increasing the temperature to 300 °C led to complete de-oxygenation of this MEA degradation product to form a variety of alkyl imidazoles (Fig. 7.9). As expected, the five-membered aromatic ring structure remained intact under the relatively mild reductive hydrothermal conditions.



## 1-(2-hydroxyethyl)-2-imidazolidinone

Fig. 7.9 Total ion chromatograms (TIC) from the GC-MS of the rejuvenation tests on 1-(2-hydroxyethyl) imidazole.

Table 7.6. Table of peak assignments from the GC-MS for the rejuvenation tests of 1-(2-hydroxyethyl)imidazole..

Peak #	Compound Name	Mw	Chemical Structure
1	1-(2- Hydroxyethyl)imidazole	112	N-OH
2	N-Methylimidazole	82	N N
3	N-Ethylimidazole	96	N N
4	Imidazole	68	NH
## N-Acetylethanolamine

As shown in Fig. 7.10, complete de-hydroxylation was achieved at temperatures between 250 and 300 °C in both hydrothermal conditions but the oxygen-bearing carbonyl group retained in different forms of the product species produced.

Alkyl piperazines dominated the products formed in the  $H_2/H_2O$  reaction system, followed by alkyl acetamides. For the  $NH_3/H_2O$  hydrothermal system, however, no cyclisation reactions were observed and the major products, including acetic acid and a range of alkyl acetamides, appeared to be from the hydrolysis of the model compound after de-hydroxylation.



Fig. 7.10 Total ion chromatograms (TIC) from the GC-MS of the rejuvenation tests on N-acetylethanolamine.

Table 7.7. Table of peak assignments from the GC-MS for the rejuvenation tests of N-acetylethanolamine.

Peak #	Compound name	Mw	Chemical Structure
1	N-Acetylethanolamine	103	О
2	N,N'- Dimethylpropyleneurea	128	
3	N,N-Dimethylacetamide	87	O N
4	N,N-Diethylacetamide	115	O N
5	N-Acetylpiperidine	127	
6	1-Methylpiperazine	100	HNN
7	Triethylamine	101	N L
8	1,3,5-Trimethylpyrazole	110	N-N
9	Pyrimidine	80	N
10	Acetamide	60	ОН
11	Ethylpyrazine	108	N
12	Acetamide	59	O NH <sub>2</sub>
13	Acetylmethylamine	73	O NH NH
14	N-Ethylacetamide	87	O NH

15	1,2-Dimethylimidazole	96	N N
			<u>~</u> N

## (b) Degraded MEA solvent

Two industrial samples of degraded MEA solution from its Ratcliffe-on-Soar power station (60 °C and 120 °C) were treated in the autoclave under an initial H<sub>2</sub> pressure of 3 MPa in the presence of the silica-Pt catalyst at 250 °C (final pressure of 9 MPa) and 300 °C (final pressure 12 MPa) for 30 minutes. Hydrothermal tests with NH<sub>3</sub>-H<sub>2</sub>O was also performed under the conditions similar to those used in the H<sub>2</sub>-H<sub>2</sub>O hydrothermal reaction system.

The heavily degraded solvent samples, which was very dark in colour (Fig. 7.11), still contained a considerable amount of MEA but the overall composition was already heavily dominated by the degradation products, such as hydroxyl acetamides, hydroxyl succinimide, alkyl hydrazones (Fig. 7.3). It was found that the heavily degraded solvent samples decoloured significantly after the hydrotreatments (Fig. 7.10), being indicative of the high efficiency of the mild reductive hydrothermal treatments in cleaning up the degarded solvents or removing at least the highly polar degradation products. GC-MS characterisation (Fig. 7.12) shows that a wide range of cyclisation reactions took place during the hydrothermal treatments. Characteristically, alkyl piperazines were found to be the dominant products formed in the H<sub>2</sub>-H<sub>2</sub>O reaction system whilst for the NH<sub>3</sub>-H<sub>2</sub>O system, the hetero-aromatic alkyl pyrazines were the major products instead.



Fig. 7.11 Photographs showing the reduction in the dark colour of the degraded amine solvent following hydrothermal treatment.



Fig.7.12 Total ion chromatograms (TIC) and table of peak assignments from the GC-MS of the hydro-thermal rejuvenation tests on the degraded amine solvent.

Table 7.8 Table of peak assignments from the GC-MS for the rejuvenation tests of degraded MEA

Peak #	Compound Name	Mw	Chemical Structure
1	Monoethanolamine (MEA)	61	HO NH2
2	Trimethylamine	59	, N
3	Dihydroxyacetone	90	Ю
4	2,5-Pyrrolidinedione	99	0 H O

_	2-Propanone,		N
5	dimethylhydrazone	100	N N
6	dl-Aspartic acid	133	
7	1,3-Diazine	80	N
8	2-Methylpyrazine	94	
9	2-Ethylpyrazine	108	
10	2,3-Dimethylpyrazine	108	Ň
11	N-Methylacetamide	73	N
12	2-Ethyl-3-methylpyrazine	122	
13	1-Methylimidazole	82	N-N-
14	2,3-Diethylpyrazine	136	
15	1-Ethylimidazole	96	N N
16	1,2,4 trimethylpiperazine	128	N
17	1,4-dimethylpiperazine	87	N_N_
18	1,4, Diethyl-2-piperazione	156	

#### 7.3.3.2 Silica-supported Nickel catalyst (silica-Ni)

The nickel-based catalyst has been examined as an economical alternative to the Ptbased catalyst. The tests with the silica-supported Ni catalyst were conducted under essentially the same conditions used for the hydro-treatments with silica-Pt catalyst except that the reaction time was increased to 30 minutes. The test results are shown in Fig. 7.13.

Nickel-based catalyst is known to have lower catalytic activity as a hydrogenation catalyst. However, as shown in Fig. 7.13, essentially complete conversion was achieved for all of the model degradation compounds except 1-(2-hydroxyethyl)-2-imidazolidinone, which remained unconverted at the hydro-treatment temperature of 300 °C. It is noteworthy that the lower catalytic activity of nickel catalyst appeared to be beneficial for the conversion of 1-(2-hydroxyethyl)imidazole, 2-oxazolidinone, 1-(2-hydroxyethyl)-2-imidazolidinone and N-acetylethanolamine to imidazoles and piperazines with extremely high selectivity and few secondary reactions, being similar in some respects to what was observed for the catalytic HyPy with silica-Pt as the catalyst.



Fig. 7.13 GC-MS TIC of the products from the hydrothermal treatment of model degradation compounds in  $H_2/H_2O$  with silica-Ni as the catalyst. Gly-Gly produced no recoverable product

## 7.3.3.3 Summary of the findings from the hydrothermal treatments

The hydrothermal treatment under both hydrogen and ammonia water conditions with platinum and nickel catalysts has been demonstrated to transform amine degradation products into deoxygenated products at extremely high conversion efficiencies. Depending on the conditions employed, the products from individual model compounds are highly selective, with just one or two individual compounds generated in some cases. While MEA itself was shown not to be formed in any of the experiments, compound classes such as pyrazines, piperazines, acetamides, imidazolidinones and imidazoles were formed in the hydrothermal treatments of both the individual model compounds and the degraded MEA solvent. Under hydrothermal conditions, pyrazines were often found to be favoured over piperazines (as seen with HyPy), especially when ammonia water solutions was used as the media for hydrothermal treatment.

# 7.3.4 Catalytic hydrotreatments in continuous PID Microactivity Reactor system

The PID micro-reactivity reactor, as a continuous flow system, is a highly-advanced modular laboratory system for continuously measuring the activity and selectivity of catalysts and catalytic reactions. In this case, it was used to assess the hydrothermal conversion or rejuvenatability of degraded MEA solvent under selected hydrothermal conditions. Fig. 7.14 shows the test results.



Fig. 7.14 GC-MS TIC of the products from the catalytic reductive hydrothermal treatment of the degraded MEA solvent using a continuous reactor system (PID

Microactivivity Effi Reactor). Reaction conditions: liquid flow rate, 0.5 ml/min;  $H_2$  flow rate, 50 ml/min; Reaction pressure, 2 MPa; reaction temperatures, 300 ~ 350 °C.

The successful results from the tests with the continuous flow reactor are indeed very encouraging. Despite the short residence times in an order of a few seconds, the catalytic hydrotreatments in the hydrothermal media (steam) facilitated in the continuous reactor system was found to give rise to complete conversion or de-oxygenation of the MEA degradation products, which are generally comparable to those obtained from the batchwise HyPy and hydrothermal treatments with autoclave. The products are extremely dominated by alkyl piperazines. It is evident that the formation of fully saturated compounds, such as piperazines rather than the unsaturated pyrazines was greatly favoured in the continuous hydrothermal reactor which can facilitate shorter residence times and faster heating rates.

#### 7.3.5 Preliminary Process Assessment

## 7.3.5.1 CO<sub>2</sub> absorption test

It proves to be extremely difficult to draw a "like-for-like" comparison of the CO<sub>2</sub> absorption performance before and after the rejuvenation of degraded MEA solvent, because 1) the degraded solvent still contains some amount of MEA at ca. 10 wt%, which is hard to be removed without impacting the original chemical compositions and 2) the MEA remaining in the original degraded solvent is eliminated during the hydro-treatments. To draw relatively meaningful comparison, the hydro-treated degraded solvent was doped with MEA at the similar concentration of 10 wt%. Due to the difficulty in collecting enough quantities of the hydro-treated aqueous sample, a simple gas washer containing 20 ml of the treated solvent collected from the continuous reactor was used for the absorption test. Fig. 7.15 shows the results of the absorption tests using 15% CO<sub>2</sub> in N<sub>2</sub> at a flow rate of 2.0 ml/min.



Fig. 7.15 Breakthrough curves of  $CO_2$  absorption of the heavily degraded MEA solvent before and after hydrothermal treatment at 300 °C and 2 MPa H<sub>2</sub> with silica-Pt as the catalyst (absorption temperature: ambient)

It was found that compared to the untreated sample, the hydro-treated degraded solvent sample displayed a significantly higher  $CO_2$  absorption capacity. Although the  $CO_2$ breakthrough time obtained for the hydro-treated degraded solvent was just slightly longer than that of the untreated solvent (2.5 versus 1.9 min), the equilibrium absorption capacity of the treated sample was significantly greater than that of the untreated sample as indicated by its significantly longer time required to reach equilibrium absorption (18 mins for the treated versus 10 mins for the untreated). The slightly slower absorption kinetic rate of the rejuvenated solvent, as shown by the longer time needed to reach equilibrium, is in agreement with the compositional profile of the treated solvent sample, which is composed of mainly tertiary amines with some quantities of secondary amines (Fig. 7.13). Stoichiometrically, tertiary amines can have much higher equilibrium absorption capacities but with lower reaction rates in general, due to their different reaction mechanisms (carbonate/bicarbonate reaction route rather than the carbamate route for primary and secondary amines). To improve the absorption performance in terms of both absorption capacity and kinetics, further investigations are needed to optimise the rejuvenation process in terms of the relative formation of secondary and tertiary amines.

#### 7.3.5.2 Preliminary process assessment and design

Based on the results obtained above, it is clear that both catalytic hydrogenation and reductive hydrothermal treatments can be effectively used to transform degraded amine solvents to different categories of de-oxygenated products with very high selectivity and efficiency. The formation of products from different processes appears to be quite characteristic and generally irrespective of the starting degradation products. In general, the results suggest that catalytic hydro-treatment in both H<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O with shorter residence times favour the formation of piperazines with high selectivity whilst in less reactive hydrothermal conditions (e.g. in ammonia water), pyrazines are instead formed preferentially with high efficiency. It appears that the product mixtures from hydrogenation and hydrothermal treatments can be relatively easily processed to yield valuable individual products. A simple search revealed that many of the products produced, such as the piperazines and pyrazines, are valuable feedstock or precursor chemicals widely used in pharmaceutical and chemical industries, due to their antitumor, anti-helmintic, anti-HIV, antibiotic and diuretic activities.

In terms of the scope and efficacy for using these approaches for rejuvenating the degraded amine solvents, the characteristic selective formation of piperazines in catalytic hydro-treatments especially the results obtained from using the continuous reactor system is particularly encouraging. The use of piperazines as alternative solvents to MEA, which can be used either as a standalone solvent or mixed with other amines to form mixed amine solvents for CO<sub>2</sub> separation, has received increasing attention in recent years due to the benefits of energy savings, higher absorption capacity, greater degradation resistance and lower corrosivity (Chowdhury et al., 2013, Rayer and Henni, 2014, Zheng et al., 2014, Norouzbahari et al., 2016, Zhang et al., 2016b) (Norouzbahari et al., 2016; Zheng et al., 2014; Rayer and Henni, 2014; Chowdhury, 2013; Zhang et al., 2016). The higher CO<sub>2</sub> absorption capacity of the hydro-treated solvent suggests that the catalytic hydro-treatment under relatively mild condition can be effectively used as a novel solvent rejuvenation technology to produce superior mixed amine solvents from heavily degraded MEA solvents or waste

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sludge. Fig. 7.16 shows a schematic process flow diagram for conducting the catalytic reductive treatments on a continuous basis.



Fig. 7.16 Schematic process flow diagram for conducting reductive hydro-treatments on a continuous basis.

# 7.4 Conclusions

Catalytic hydrotreatments and hydrothermal treatments, including both hydrous pyrolysis and hydrogenation or hydropyrolysis (HyPy) under different conditions, have been investigated as the potential reductive approaches for rejuvenating degraded solid and aqueous amine sorbents or converting them into value-added products. Six model MEA degradation compounds and three spent MEA solvent samples obtained from industrial pilot capture facilities were selected for the tests. Three different catalysts, including molybdenum oxysulfides and platinum (Pt) and nickel (Ni) supported onto activated carbon and/or silica materials were used. The results demonstrate that the reductive rejuvenation or conversion of the MEA degradation compounds was governed not only by the types of the degradation products but also by the conditions used in the reductive hydrotreatments. The main scientific highlights are summarised as follows:

- 1. Catalytic hydrogenation and reductive hydrothermal treatments can both be effectively used to transform amine degradation products into deoxygenated products at extremely high conversion efficiencies.
- No appreciable quantities of MEA was obtained at all conditions examined, highlighting the impossibility or difficulties to produce MEA from its thermooxidative degradation products.
- 3. Despite the dependence of the compositions of the products on hydro-treating conditions, the results tend to suggest that regardless the types of MEA degradation products, the products generated from the hydro-treatments of both the model compounds and degraded MEA solvent are overall comparable:
  - For catalytic hydrogenation, the major products are piperazine and their alkylated derivatives.
  - For less reductive hydrothermal treatment or hydrous pyrolysis, the products are mainly pyrazine and its methylated derivatives.
- 4. The predominant formation of piperazines from the hydrous pyrolysis under less reductive conditions is encouraging as piperazine and its derivatives are generally considered to be better alternative solvent for CO<sub>2</sub> capture, which can be used either as a standalone solvent or as additives to other amine solvents.
- 5. Pyrazines and piperazines produced from the hydro-treatment of degraded MEA solvent can potentially have a high valuable use as a feedstock for chemical and pharmaceutical industries. Some of pyrazine derivatives identified are widely used in pharmaceutical industries, due to their antitumor, anti-helmintic, antibiotic and diuretic activities.

## **CHAPTER 8** General Discussion and Conclusion

## 8.1 General discussion

#### 8.1.1 Regeneration heat of PEI adsorbent

The regeneration heat can determine the operational costs and energy efficiency of carbon capture technology in power plant, which includes sensible heat, heat of adsorption and vaporization heat (Zhang et al., 2016b). The regeneration heat of adsorbent can be calculated by Equation 8.1 (Zhang et al., 2017). Acceding to the Equation 8.1, the regeneration heat and carbon capture ability of adsorbent have an inverse relation. Zhang et al. reported that the regeneration heat of PEI-silica adsorbent is just 2.46 GJ/tCO<sub>2</sub> with 1.35 mmol/g working capacity, which is lower than the typical aqueous MEA system (3.9 GJ/tCO<sub>2</sub>) and advance MEA system (3.3 GJ/tCO<sub>2</sub>) (Zhang et al., 2016b). In Chapter 5, 70% PEI-SCF-3-120-24 has the maximum CO<sub>2</sub> uptake (180.8mmol/g), which maybe has lower than 2.46 GJ/tCO<sub>2</sub> regeneration heat of PEI adsorbent with additive may be increase due to hydration water.

$$Q_r = \frac{1 - \alpha}{q_w} C_{ps} (T_{de} - T_{ad}) + (1 - \beta) \Delta H_a + (1 - \gamma) \frac{Q_v \int H_2 O}{q_w}$$
(8.1)

Where  $Q_r$  (Gt/tCO<sub>2</sub>) is the regeneration heat of adsorbent;  $q_w$  (wt%) is the working capacity of adsorbent;  $C_{ps}$  (kJ/kg K) is the specific heat of adsorbent;  $T_{de}$  and  $T_{ad}$  (K) are the temperature of adsorption and desorption process respectively;  $\Delta H_a$  is the absolute value of heat of adsorption;  $Q_v$  (kJ/kg) is 2257.6 kJ/kg, which is the vaporization heat of water;  $\int H_2O$  is (wt%) is the mass fraction of evaporated water content;  $\alpha$ ,  $\beta$ ,  $\gamma$  are the fractions of heat recovered from sensible heat, heat of adsorption and vaporization heat, respectively.

#### 8.1.2 Comparison of moisture and additives in mitigation of PEI degradation

Both of adding moisture in flue gas and adding additives in adsorbent can mitigate the degradation of PEI adsorbent. For the CO<sub>2</sub>-induced thermos-degradation, it is evident that the CO<sub>2</sub> uptake of adsorbent shows negligible decrease with the presence of moisture in the gas streams in Fig 6.15. However, there is a drop of CO<sub>2</sub> uptake for all PEI adsorbent with additive in Fig 6.22. Furthermore, for the oxidative degradation of

PEI adsorbent, Fig 6.25 shows approximately 10%  $CO_2$  uptake drop of PEI adsorbent doped with 20 wt% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, which is close to  $CO_2$  uptake drop of PEI adsorbent with the presence of moisture as shown in Fig. 6.16. Thus, the presence of moisture in the gas stream can clearly help mitigate PEI degradation and hence to extend the lifetime performance of PEI-based adsorbents for  $CO_2$  capture.

However, water adsorption and evaporation occur in with the in adsorption-desorption cycles presence of moisture, which lead to the regeneration heat increase according to the Equation 8.1. Meanwhile, the regeneration heat should not increase significantly for PEI adsorbent doped with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> due to Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>-contained hydration water slow release in adsorption-adsorption-desorption cycles. Furthermore, PEI adsorbent doped with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> reveal higher CO<sub>2</sub> capacity and faster adsorption kinetics than undoped PEI adsorbent in Fig 6.17 and Fig 6.17. Moreover, moisture in flue gas can cause the corrosion problem. Therefore, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> should have higher potential for industrial application.

## 8.2 Overall conclusions

In this project, the author intends to develop new solid adsorbent materials with higher  $CO_2$  capture capacity capacities and fast adsorption kinetics, to investigate the degradation of PEI adsorbents, to improve the adsorption-desorption lifetime performance of PEI adsorbent, to investigate effective measures effectively prevent the thermal and oxidative degradation of the sorbent materials the degradation of PEI adsorbents and to investigate approaches that can rejuvenate the degraded amine sorbent or convert them to high value-added materials. The main conclusions can be summarised as follows:

- The investigation of porous siliceous cellular foam (SCF) reveals that (1) The increasing of TMB/P123 ratio lead to narrower pore size distribution and larger pore diameters; (2) Both the cell diameters and the window sizes of SCFs increase significantly with increasing of TMB/P123 ratio, aging time and aging temperature; (3) The increasing of TMB/P123 ratio and aging temperature can result into the surface area of SCF decreasing and pore volumes incline; (4) SCF-3-100-24 have the highest pore volume (3.2 cm<sup>3</sup>/g) and largest pore size (74.2 nm) and SCF-3-120-24 have the largest window size (44.4 nm).
- 2. All the SCF adsorbent exhibited high CO<sub>2</sub> adsorption capacity and fast adsorption kinetics. The results of CO<sub>2</sub> adsorption capacity test of SCF-supported amine adsorbents shows: (1) The optimal adsorption temperature of SCF adsorbent decrease with the pore diameters and windows sizes increasing; (2) the pore volume, pore diameters and window size of the SCF substrates collectively determines the CO<sub>2</sub> uptake capacity of the PEI-SCF adsorbents, and 70%PEI-600-SCF-3-120-24 have the highest CO<sub>2</sub> adsorption ability (180.2mg/g) in all PEI-SCF adsorbents at 75 °C in 15% CO<sub>2</sub> in N<sub>2</sub> gas condition; (3) The thickness of cell walls also plays an important role in facilitating higher levels of PEI impregnation with enhanced PEI mobility and accessibility; (4) The TEPA-PEI hybrid impregnated SCF-3-120-24 can reach an exceedingly high CO2 capacity of 198.2 mg/g. (5)
- 3. The regenerability or adsorption-desorption performance of CO2 adsorbents is critical in determining their life-time importance in practical applications. The evaporation loss of PEI molecule was the main pathway of thermal degradation,

in pure  $N_2$  desorption gas condition. There is no appreciable change in  $CO_2$  uptake for PEI-600-modified SCF adsorbents after 50 adsorption-desorption cycles. Furthermore, The PEI loss increase with adsorption and desorption temperature increasing and PEI molecule weight decreasing.

- 4. When the adsorption gas took place in the simulated gas-fired flue gas streams containing 5% CO<sub>2</sub> and 12% O<sub>2</sub> in N<sub>2</sub>, oxidative degradation is the main reason which lead to CO<sub>2</sub> adsorption ability almost completely lost after 50 adsorption-desorption cycles. Meanwhile, the PEI loss increase In the O<sub>2</sub>-containg flue gas due to the stabilizing effect loss by oxidative degradation of PEI. Furthermore, when adsorption condition took place in pure CO<sub>2</sub>, there is a dramatically drop of CO<sub>2</sub> adsorption ability of PEI adsorbent due to the severe CO<sub>2</sub>-induced thermal degradation i.e. urea formation during the desorption process.
- 5. The presence of moisture in the adsorption/desorption streams can improve the anti-thermal degradation performance of PEI sorbents by suppressing the urea formation. Furthermore, the moisture can protect PEI from oxidative degradation with improving carbamate formation.
- hydrates slow 6.  $Na_2B_4O_7$ can release the hydration water in adsorption/desorption cycles. The doping of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> hydrates can greatly improve the anti-degradation of PEI adsorbent, because of the the desirable weak basicity and unique hydration and dehydration characteristics. 40% PEI-PQ silica with 15% Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> showed best thermal and oxidative stability in all PEI adsorbent with additive. Meanwhile, the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> doping also improve the CO<sub>2</sub> adsorption ability of PEI adsorbent and 40% PEI-PQ silica with 20%  $Na_2B_4O_7$  have highest CO<sub>2</sub> adsorption capacity (13.3%).
- **7.** Catalytic hydrotreatments and hydrothermal treatments, including both hydrous pyrolysis and hydrogenation or hydropyrolysis (HyPy) under different conditions. Catalytic hydrogenation could be effectively used to rejuvenate the spent PEI sorbents and for some degraded PEI sorbent samples. In the catalytic hydrogenation process, thermo-oxidative degradation products can be largely restored. The CO<sub>2</sub> adsorption ability of rejuvenated PEI adsorbent can reach approximately 65% of the CO<sub>2</sub> uptake of fresh PEI adsorbent. Meanwhile, in hydrous pyrolysis test, the CO<sub>2</sub> capture capability of rejuvenated PEI was improved to half of fresh PEI CO<sub>2</sub> capture capability.

8. Catalytic hydrogenation and reductive hydrothermal treatments can both be effectively used to transform amine degradation products into deoxygenated products at extremely high conversion efficiencies. For catalytic hydrogenation, the major products are piperazine and their alkylated derivatives. Meanwhile, the products are mainly pyrazine and its methylated derivatives for less reductive hydrothermal treatment. Piperazines and pyrazines are a type of important pharmaceutical intermediates. Especially, some of pyrazine derivatives identified are widely used in pharmaceutical industries, due to their antitumor, anti-helmintic, antibiotic and diuretic activities. Unfortunately, no appreciable quantities of MEA was obtained at all catalytic hydrogenation and reductive hydrothermal treatments.

## 8.2 Future Work

Potential future work identified during this project is summarised under 3 heading listed below:

1. SCF preparation improvement

In the previous SCF preparation, the aging temperature was limit to 100 °C due to the limit of equipment. However, 120 °C maybe not the optimum aging temperature. Then, it is necessary to increase aging temperature by advanced equipment. Furthermore, the TEOS is too expensive for preparation in kg level. Therefore, a relatively cheaper silica source need to replace TEOS. Furthermore, the regeneration heat of adsorbent with SCFs need to be calculated for the further industrial application.

2. Fluidised bed testing for PEI-MCF adsorbent and PEI adsorbent with additives

The previous results of PEI-MCF adsorbent and PEI adsorbent with additives were all carried out in lab-scale. It is necessary to scale up the preparation of adsorbents form several grams to kg level, so as to test the adsorption of adsorbent and the life time of PEI adsorbent with additives with simulated gas components as coal-fired or natural gas power plant.

3. Catalytic hydrotreatments improvement

There are three aspects to improvement the catalytic hydrotreatment: catalyst and product purification. Although Ni-based catalyst can used as catalyst under  $H_2$  reaction gas condition, Ni-based catalyst is no effective under ammines gas condition, it is necessary to prepare one relatively cheaper catalyst for the degraded MEA rejuvenation test. Furthermore, the products of catalytice hydrotreatment is necessary to be separated to extract the piperazine derivatives and pyrazine derivatives.

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## APPENDICES

## APPENDIX A LIST OF PUBLICATIONS

## Published manuscripts during PhD:

 Zhang, W., Liu, H., Sun, Y., Cakstins, J., Sun, C. and Snape, C.E., 2016. Parametric study on the regeneration heat requirement of an amine-based solid adsorbent process for postcombustion carbon capture. *Applied Energy*, *168*, pp.394-405

## **Prepared manuscripts:**

- 1. Yuan Sun, Xin Liu, Chenggong Sun, Waleed Al-Sarraf, Khai Zhen Foo, Yang Meng, Stevens Lee, Hao Liu and Colin Snape. Synthesis and functionalisation of spherical meso-, hybrid meso/macro- and macro-porous cellular silica foam materials with regulated pore sizes for CO2.*Journal of Materials Chemistry A* (Under Review)
- Yuan Sun, Chenggong Sun, Hao Liu, Colin E. Snape. Life-Time Performance Testing, Degradation Behaviour and Strategies to Mitigate the Degradation of Supported Polyamine CO2 Adsorbents. (To be submitted soon)
- Yuan Sun, Will Meredith, Chenggong Sun, Hao Liu, Colin E. Snape. Novel Reductive Rejuvenation Approaches for Degraded Amine Solvents from PCC in Power Plants. One step synthesis of rice husk based activated carbon for carbon capture. (To be submitted soon)