

DEPARTMENT OF CHEMICAL & ENVIRONMENTAL

ENGINEERING

EFFECTIVE CARBON ADSORBENTS OF SOLID LOOPING TECHNOLOGIES FOR POST COMBUSTION CARBON CAPTURE

By

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I, Jingjing Liu, confirm that all the content presented in this thesis is based on my own work. Where information is from the literatures or work by collaborators, I confirm that these have been referenced and acknowledged in the thesis.

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Date

Abstract

Carbon Capture and Storage (CCS) has been considered as one of the most promising techniques to reduce anthropogenic CO_2 emissions in the atmosphere. As an alternative to replace the traditional technology of aqueous amine scrubbing, solid adsorbents looping technology (SALT) has attracted growing attention. Among various solid adsorbent materials, carbon-based materials with unique properties such as wide availability, relatively low cost, highly porous structure ease of regeneration, and stable cyclic performance, have been considered as promising candidates at both low pressure and moderate to high partial pressure. In this PhD research, activated carbon spheres derived from two different precursors, which are phenolic resin and coal-tar pitch, have been prepared and modified with potassium intercalation to improve CO_2 capture performance for post combustion carbon capture. The project aims to investigate the factors that affect CO_2 adsorption performance for post combustion carbon capture.

Firstly, series of spherical activated carbon beads (with a uniform diameter of ca. 0.6-0.8 mm) derived from phenolic resin have been developed and characterised. The results show that the surface polarity can be enhanced by potassium intercalation. The intercalation of potassium significantly increased the CO₂ capacity of the AC beads by a factor of up to 2 at 0.15 bar while the effects of the treatment on their mechanical strength and morphological features were negligible at KOH/AC mass ratios of 0.3 and below. The factors other than adsorption that affect the performance of phenolic resin derived carbon spheres were also investigated in terms of adsorption kinetics, cyclic performance, heat of adsorption, the effect of moisture, and regeneration heat.

Secondly, coal tar pitch derived activated carbons, with uniform spherical diameter of 1-2 mm were synthesised via two different activation approaches, which is firstly an initial steam activation followed by KOH activation, and secondly one-step KOH activation, both with mild KOH/carbon mass ratios. Samples prepared with one-step KOH activation method had shown a better microporous structure and a higher CO₂ adsorption capacity. Owing to the narrow micropores and K-doping, the samples demonstrated outstanding CO₂ capacities at relatively low CO₂ partial pressure. Multicycle stability was examined over 50 cycles of adsorption and desorption, and both samples present excellent adsorption kinetics and regeneration ability. Finally, the volumetric CO₂ uptake of best performing samples were also calculated and compared with other candidates.

Based on our previous results, further investigation towards the influence of precursor materials and correlation between microporosity pore size ranging from 0.4 nm to 2 nm and CO_2 uptakes have been carried out. Future work on how to improve the CO_2 sorption performances of the studied materials has been proposed.

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CHAPTER 1 Introduction

1.1 Background

Tackling climate change is set to be the greatest humanitarian challenge facing the world, due to the soaring energy demand and the continual dominance of fossil energy in our energy landscape. The emissions of carbon dioxide that is known as the major contributor of greenhouse gases (GHG), from combustion of fossil fuels (such as coal, natural gas, and petroleum), accounts for more than 85% of anthropogenic GHG emissions (De Coninck and Benson, 2014). CO₂ could persist over time, which results in irreversible (where irreversible is defined as a time scale exceeding the end of the millennium in year 3000) climate change (Solomon et al., 2009). According to the fifth report from Intergovernmental Panel on Climate Change (IPCC) 2014 (Pachauri et al., 2014), the total anthropogenic GHG emissions between 2000 and 2010 demonstrated a faster discharge compared with that in previous three decades. More specifically, the average growth of GHG emissions per year was by 2.2% (1.0 Gt CO₂ eq) from 2000 to 2010, while the figure was 1.3 % (0.4 Gt CO₂ eq) from 1970 to 2000, as shown in Fig. 1.1 (Pachauri et al., 2014). Since the time of industrial revolution, the atmosphere CO_2 concentration as a result of anthropogenic CO_2 emission, has risen from the value of ~280 ppm to 379 ppm in 2005 and ~390 ppmv currently; by the year 2100, the atmosphere may contain up to 570 ppmv, and the global temperature is possibly to rise between 1.4-5.8 °C compared to 1990, if no effective actions were undertaken (Rogner et al., Samanta et al., 2012, Stewart and Hessami, 2005, McMichael et al., 2004). Moreover, thermal expansion of the warming ocean provides a conservative lower limit to irreversible global average sea level rise of at least 0.4-1.0m if CO₂ concentrations exceed 600 ppmv (Solomon et al., 2009).

On the other hand, it has been found that more coal-fire or natural gas power plants have been built in the past decade than ever. For example, between 2010 and 2012, the generating capacity of around 89 gigawatts per year (GW yr⁻¹) for new coal plants was added, compared to 66 GW yr⁻¹ during 2000-2009 time period (Davis and Socolow, 2014). Based on the above research, it can be seen that the demand to reduce CO_2 concentrations so as to relieve the global warming circumstances has become more and more urgent world-wide.



Total Annual Anthropogenic GHG Emissions by Groups of Gases 1970-2010

Fig. 1.1 Total annual anthropogenic GHG emissions (Gt $CO_2 eq / yr$) by groups of gases 1970–2010: carbon dioxide (CO₂) from fossil fuel combustion and industrial processes; CO₂ from Forestry and Other Land Use (FOLU); methane (CH₄); nitrous oxide (N₂O); fluorinated gases covered under the Kyoto Protocol (F-gases). At the right side of the figure, GHG emissions in 2010 are shown again broken down into these components with the associated uncertainties (90 % confidence interval) indicated by the error bars (Pachauri et al., 2014).

Generally, there are three methods to control or reduce CO_2 emissions into the atmosphere (Yang et al., 2008). Firstly, the direct option is to reduce energy intensity, indicating improving the energy efficiency. The second option is to reduce carbon intensity, i.e., replacing fossil-fuels with renewable energy resources such as solar energy, wind, nuclear, hydrogen, biomass, etc. The third option is to enhance the sequestration of CO_2 , which means to capture and sequester CO_2 with advanced technologies.

Although switching to renewable energies is an exciting and promising way in the long-term situation, it is not realistic for most governments and companies to apply these clean energies as a result of high costs in the present stage. Based on the fact that among the anthropogenic CO_2 emission sources, fossil-fuel power plants account for approximately one third of the emissions (Choi et al., 2009), carbon capture and storage has been widely regarded as a most viable technology system to mitigate CO_2 emissions from fossil fuel combustion.

 CO_2 capture and storage involves three related processes in terms of capturing the CO_2 arising from the combustion of fossil fuels (in power generation), or from the preparation of fossil fuels (in natural-gas processing), transporting the CO_2 , and finally storing the gas in a site where it can be stably stored for a long period instead of being released back into atmosphere (Metz, 2005). Normally, the CO_2 could be placed into oil reservoirs with the aim of enhancing the oil recovery, or into abandoned gas fields or into deep saline aquifers (Gibbins and Chalmers, 2008). One can see the life-cycle chain of fossil fuel use regarding carbon capture and storage in Fig. 1.2. The IPCC estimates that CO_2 emissions to the atmosphere could be reduced

by 80-90 % for a modern conventional power plant equipped with carbon capture and storage technology (D'Alessandro et al., 2010a).



Fig. 1.2 Diagrammatic representation of the life-cycle chain of fossil fuel use. CO_2 separation and capture at power plants enables storage of CO_2 in porous rocks deep below ground (Haszeldine, 2009).

During the process, the carbon capture technology plays a dominating role because it consumes the most energy and results in the highest cost which approximately occupies half or two thirds of the total costs (Bode and Jung, 2006). During the past decades, significant efforts have been contributed to the progress of carbon capture technology, especially from the aspect of large-scale application.

As the main generators of CO_2 , fossil-fuel power plants in terms of Pulverized Coal combustion (PC), Natural Gas Combined Cycle (NGCC) and Integrated coal Gasification Combined Cycle (IGCC) are also considered as the leading candidates

for carbon capture technology. The technologies of CO_2 capture will be reviewed in detail in Chapter 2.

Low temperature solid adsorbents looping technology (SALT) is widely considered to have the potential to be a viable capture technology to overcome many of the shortcomings of the state-of-art aqueous amine scrubbing systems, such as high energy penalty, solvent degradation and corrosion. However, the success of the solid looping technology depends on the successful development of high performing solid adsorbents. A number of adsorbents are currently under development and some have been demonstrated at small pilot scale, including supported and immobilized amines, functionalised carbon materials and zeolites (Choi et al., 2009, Wang et al., 2014). Among these adsorbents, activated carbon materials exhibit promising adsorption performance, especially for post-combustion carbon capture.

On one hand, as is known, activated carbons have already been applied in carbon capture by temperature swing adsorption (TSA) and/or pressure swing adsorption (PSA) cycles, due to their wide availability, high specific surface area, low adsorption heat and excellent mechanical and thermal stability (de Souza et al., 2013, Pevida et al., 2008a, Sun et al., 2013a, Drage et al., 2009a, Thote et al., 2010). However, while carbon-based adsorbents can usually adsorb a large volume of CO₂ at ambient temperature, their capacity decreases markedly at elevated temperatures and low CO₂ partial pressures. One way to improve the selective CO₂ affinity of carbon materials is to incorporate basic nitrogen functionalities into carbon matrix using different preparation and activation strategies (Hao et al., 2010, Plaza et al., 2007a, Zhu et al., 2014, Yang et al., 2008, Ahmadpour and Do, 1997, Caturla et al., 1991) that can lead to incremental improvement in adsorption performance. In this case, chemical activation with potassium hydroxide (KOH) was always involved during preparation.

Another way to increase the CO_2 uptakes of carbon adsorbents at low CO_2 partial pressure was to design the adsorbent material with tailored pore size, *i.e.*, ultramicropores below 0.8 nm, so as to enhance the micropore filling mechanism (Marco-Lozar et al., 2014).

On the another hand, another challenge for carbon-based sorbents for practical application lies in relatively low bulk density which will normally lead to low CO_2 uptakes on a volumetric basis.

As a result, as for activated carbon materials, it is urgent and essential to investigate tailored activated carbon spheres that are ready to use with high bulk density as well as enhanced CO_2 capture capacities at low CO_2 concentrations that are suitable for post combustion carbon capture.

1.2 Aims and objectives

Based on the previous introduction, in order to overcome the current shortcomings of activated carbons, the aim of this work is to develop and optimise effective solid carbon adsorbents with sound CO₂ adsorption properties for post-combustion carbon capture where the CO₂ partial pressure is *ca*. 0.15 bar. More specifically, due to the ease of modification in spherical form as well as high bulk density, two different precursors of the targeting carbon materials, which are phenolic resin and coal-tar pitch have been chosen as the parent material for activation carbon spheres. Therefore, this research can be generally divided into mainly two sections, *i.e.*, firstly the development of potassium intercalated carbon beads derived from phenolic resin (PR) as well as its potential application in industry, and secondly the development and characterisation of pitch-based carbon spheres.

The activated carbon (AC) beads prepared from phenolic resins used an integrated and mild KOH activation process. The specific objectives are:

- To investigate the effect of potassium intercalation for phenolic resin-based carbons on the CO₂ adsorption performance;
- To understand the fundamental mechanisms of CO₂ adsorption in the potassiumintercalated carbon adsorbents;
- To test the mechanical strength of PRACs compared with the original carbon beads as well as the regenerability over multi-cycles with Thermogravimetric Analysis (TGA);
- To study the heat of adsorption and specific heat capacity of potassium intercalated carbon beads, so as to estimate the techno-economic assessment of the SALT-fluidised bed process;
- To investigate the influence of moisture on CO₂ adsorption behaviour using a fixed bed reactor (modified TGA);

Similarly, the AC spheres derived from coal-tar pitch were prepared with various activation methods. The objectives can be seen as follows:

- To investigate the CO₂ adsorption capacities of pitch-based carbon spheres with different activation methods;
- To study the influence of structural properties of pitch-based carbons on CO₂ adsorption properties;
- 3) To test the mechanical strength of pitch-carbons compared with the original carbon beads as well as the regenerability over 50 accelerated cycles with TGA;
- To discuss the bulk density, mechanical strength and volumetric CO₂ uptakes of selected activated pitch spheres.

CHAPTER 2 Literature review

As mentioned before, Carbon Capture and Storage (CCS) have been considered as an important technology of transition from fossil fuel energy to renewable and nuclear energies. In this chapter, a literature review relevant to CCS will be given. Basically, the first two sections have addressed an introduction of carbon capture technologies in terms of post-combustion, pre-combustion and ox-fuel combustion, as well as separation technologies for post-combustion. More importantly, the review of development of solid adsorbent will be included in Section 2.3, where the recent progress and status quo in CO₂ capture using solid adsorbents has been carried out to obtain a thorough understanding of the features of different solid sorbents.

2.1 Carbon capture technologies

2.1.1 Post-combustion

There are three different approaches to capture CO_2 from fossil-fuel based power plants: post-combustion, pre-combustion and oxy-fuel combustion (Herzog, 2001, Gibbins and Chalmers, 2008, Zamzow, 2009, Metz, 2005, Yang et al., 2008) (Fig. 2.1).

Post-combustion capture technology could be applied directly to the existing fossil-fuel power plants, indicating its high potential in the very short term of the utilization. As shown in Fig. 2.1, after combustion of the fuel and air, the flue gases, including both residuary and new generated gases, are transferred to the " CO_2 separation section" before following processes in terms of CO_2 dehydration, compression, transport and storage. The main disadvantage for this technology lies in the low concentration of CO_2 (typically

less than 15 %), resulting from using air in the combustion stage (Figueroa et al., 2008, Pires et al., 2011). Correspondingly, solid adsorbent materials that are capable of capturing CO₂ at low concentrations, in another words, with relatively high CO₂ affinity to CO₂ molecules, will be much preferred for this technology.



Fig. 2.1 Technology concepts for CO₂ capture (Pires et al., 2011)

2.1.2 Pre-combustion

Unlike post-combustion, the capture of CO_2 occurs prior to combustion in precombustion technology. To achieve this, a mixture of CO and H₂, namely "synthesis gas", is obtained via reforming (for natural gas) or gasification (for coal) process (Yang et al., 2008). Then, the reaction (2.1) takes place in the "water-gas shift" sector where CO is converted to CO_2 with added steam. Additionally, more H₂ is generated apart from the original synthesis gas (Figueroa et al., 2008, Gibbins and Chalmers, 2008). Finally, CO_2 could be separated from the H₂-rich fuel gases which contribute to heat and power production in the next step.

$$C0 + H_2 0 \Leftrightarrow CO_2 + H_2 \tag{2.1}$$

From the above description of Pre-combustion, one can see that this technology has obvious advantages, i.e., concentrated in CO₂, relatively higher CO₂ partial pressure, and potential for decrease in compression costs (Figueroa et al., 2008). Additionally, the main output hydrogen gas has a high calorific value and the feature of being totally environmentally friendly. A new approach called integrated gasification combined cycle (IGCC) to generate electricity with synthesis gas is commonly considered as one of the most promising replacements of traditional coal-fired power plants in the long term. However, since IGCC could only be applicable to mainly new plants, it is still not realistic currently as a result of its complicated constructions and extensive supporting systems requirements (Folger, 2010, Bohm et al., 2007).

2.1.3 Oxy-fuel combustion capture

Oxy-fuel combustion technology is another alternative for carbon capture. In this process, almost pure oxygen is produced via an integration of air separation from Nitrogen before combustion (Pfaff and Kather, 2009). Combustion in pure oxygen can result in a very high temperature which is beyond the bearing capacity of the boiler. Therefore, there is a need to use recycled flue gas to solve the problem by cooling down the combustion section and also generates a high concentration of CO_2 (with values above 80 % v/v) (Olajire, 2010) in the output steam, as seen in Fig. 2.1. CO_2 and H_2O are the two main components of the ox-fuel combustion flue gas, while H_2O could be easily removed as condensed water. Another advantage for oxy-fuel combustion is the absence of a harmful

pollutant, NO_X , and markedly reduced amount of gas to be dealt with in gas desulphurisation plant.

The dominant drawback of this technology is the expensive cost of air separation unit. Commercially, the method of cryogenic distillation is applied to separate nitrogen and oxygen in air but this consumes a large amount of energy (Bolland and Undrum, 2003). With the state of art, air separation technologies, for example, a hybrid system of membrane and cryogenic distillation, the energy required for air separation can be significantly reduced (Burdyny and Struchtrup, 2010).

2.2 Carbon separation technologies for post-combustion capture

Based on the post-combustion technology which is the main topic of this thesis, there are several categories of carbon separation technologies that are currently being developed at different scales (Wong and Bioletti, 2002):

- (1) Chemical and physical absorption
- (2) Cryogenic separation
- (3) Membrane separation
- (4) Solid adsorption

Generally, the process of gas sorption can be various and the forms of sorbents can be either solid or liquid. For instance, CO_2 can react with sorbents to form new compounds or be adsorbed on the surface of sorbents, or even just physically mixed with the material, determined by the varying technologies and sorbents (D'Alessandro et al., 2010b).

2.2.1 Absorption

As mentioned above, there are basically two different methods in absorption technologies, namely, chemical and physical absorption.

As chemical absorption is commonly used in various industry processes, it is considered as the most mature approach for post combustion carbon capture (Yang et al., 2008). In this process, the chemical compounds such as TEA (Triethanolamine), MDEA (Methyl diethanolamine) and MEA (Monoethanolamine) can absorb CO₂ and generate other carbon compounds. Since the flue gases usually are composed of many other gas components such as N₂, other than pure CO₂, good selectivity for CO₂ with the chemical compounds is of great importance. As for amine scrubbing technology, amine-based liquid-solvents are most applied to react with acidic CO₂ gas, during which an intermediate compound is formed with weak chemical bonds (Olajire, 2010). The chemical reaction is reversible so that the newly formed compound could release CO₂ when the temperature increases and the amines can be regenerated again for the following cycle. Fig. 2.2 demonstrates a typical amine adsorption unit (Wong and Bioletti, 2002).

Among various amine solvents, monoethanol amine (MEA) has been the traditional choice and commercialized for over 70 years, especially in natural gas industry due to its minimum cost, lowest molecular weight and highest theoretical absorption capacity. However, MEA absorption has many shortcomings such as low CO₂ loading capacity, severe corrosion situation, and high energy consumption (Fauth et al., 2005). For instance, Idem reported that the regeneration heat of MEA absorption accounts for up to 70 % of the total operating energy cost (Idem et al., 2006). Moreover, typical MEA absorption which uses 20-30 wt% of aqueous MEA to absorb CO₂, results in 80 % increase in the cost of electricity for coal-fired power plants (Rao and Rubin, 2002). Therefore, further improvements have to be made for amine-based absorption if it is to be widely used to capture CO₂ from power plants.



Fig. 2.2 Typical amine absorption unit for CO₂ recovery from flue gas. (Wong and Bioletti, 2002)

The theory of physical absorption is based on Henry's Law. The absorbents interact with CO₂ molecules through weak physical intermolecular forces such as Van de Waals and electrostatic force, instead of chemical bonds. Technically, the absorption occurs at relatively high CO₂ partial pressures and low temperatures to obtain higher CO₂ capacities. The solvents can be regenerated by either pressure or temperature swing process. Since an IGCC system supplies the syngas at an elevated pressure (approx. 40 bars) in the gasification section, it is ideal for physical absorption. Selexol (dimethylether of polyelene glycol) and Rectisol (cold methanol) are commonly used for physical absorption in industry (Sircar, 2006).

2.2.2 Cryogenic separation

The cryogenic method mainly involves a physical distilling process in which CO_2 is separated from other gases in a low temperature (normally lower than -73.3 C) (Olajire, 2010). The cooling process, in another word, condensation, aims at inducing a phase change of CO_2 while other components remain invariable in the mixture. From the description of this technology, one can tell that the main advantage of cryogenic separation is that a relatively high concentration of CO_2 in the form of liquid is obtained so that CO_2 could be directly transferred and stored in ship and pipelines without any chemical absorbents/ adsorbents.

However, cryogenic separation is barely utilised for flue gas from coal/natural gas fired power plants because this method requires streams with high CO_2 concentrations (typically over 50 %). There are many by-products produced such as NO_x and SO_x and water vapour near atmosphere pressure, which is harmful in cryogenic process because cryogenic separation is very sensitive to corrosive gases and moisture environment. Based on the limitations above and another dominant drawback, which is highrefrigeration cost, at this stage, the method is not ideal for carbon capture, especially postcombustion (Mondal et al., 2012). Anyhow, cryogenic separation has great potential in pre-combustion and oxy-fuel combustion decarbonisation processes which supply high CO_2 concentration and elevated pressure gases as well.

2.2.3 Membrane separation

Due to the fact that membranes are semi-permeable barriers, there are various mechanisms in terms of solution-diffusion, adsorption-diffusion, molecular sieve and ionic transport, etc. Regarding to CO₂ capture, two different mechanism, i.e., gas separation membrane and gas absorption membrane are selected, as seen in Figs. 2.3, 2.4 (McKee, 2002). The principle for membrane separation based on the solution-diffusion model can be described as follows: different gases can selectively penetrate when passing by the membrane, in which the gas molecule is firstly absorbed to the surface, sequentially dissolved and finally desorbed from the other side of the membrane. The

force of penetration depends on the permeability, selectivity and different partial pressure of the components at both sides of the membrane.

Membrane separation is considered as a very promising technology as a result of its inspiring advantages. Firstly, relatively low cost, simple design and easy handle-ability (no regeneration section is required) are associated with this method; secondly, it is especially applicable for retrofitting and process optimization since it has no requirements for positioning. Currently, most commercial applications are dominated by polymeric membranes but actually, two other major categories also exist, namely, inorganic membranes and hybrid organic/inorganic membranes (Ebner and Ritter, 2009). Similar to cryogenic separation, membrane separation works more efficiently with high CO₂ partial pressure, hence it is more suitable for oxy-fuel combustion and pre-combustion (especially IGCC) processes.

The main drawbacks of membrane separation lie in that its performance lacks of longterm stability. It is impossible currently for most membranes to have the resilience under industrial conditions (Zhang et al., 2013a).



Fig. 2.3 Principle of gas separation membrane (McKee, 2002)



Fig. 2.4 Principle of gas absorption membrane (McKee, 2002)

2.2.4 Solid adsorption

Among various CO_2 separation approaches, solid adsorption has attracted increasingly attention in the last two decades due to its remarkable advantages for energy efficiency. Basically, this adsorption method uses novel solid materials to interact with CO_2 in the feed gases and ideally, only CO_2 should be captured. For the interaction between gas molecules and solid materials, it can be divided into physical adsorption (physisorption), in which van der waals forces play a dominant role; and chemical adsorption (chemisorption) which relies on covalent bonding. Nevertheless, in most cases, both of the adsorptions are involved during the progress. After the desorption, the adsorbed CO_2 could be separated and transferred while solid adsorbents would be regenerated through certain treatments including TSA or PSA so that the whole system can be recycled. With a typical TWA process, by elevating the temperature, the adsorbed CO₂ can be released so as to regenerate the adsorbents (Hedin et al., 2013). TWA is considered as particularly promising for post combustion capture because the relatively low-pressure and large volume of flue gases, it makes the equipped pressure swing more difficult to be realised; and secondly, heating during TSA can be partly applied in the regeneration, which reduces energy consumption (Ishibashi et al., 1996). TWA can be applied to both physical sorption and chemical sorption. With regard to physisorption, the relatively weak interactions which are involved at interfaces between gas and solid will be eliminated by raising the kinetic energy of CO₂ molecules. While as for chemisorption, since the chemical reaction occurs between adsorbents and CO₂, more energy and higher temperature over physisorption is normally required to break the chemical bonds and release CO₂ so as to accomplish regeneration. Fig. 2.5 illustrates the diagram of a simple TSA process for post—combustion carbon capture (Mason et al., 2011). As can be seen in Fig. 2.5, the flue gas contains mainly N₂ (blue) and CO₂ (green), after adsorption of CO_2 , the adsorbents in fixed bed will be saturated with CO_2 . Then when the temperature increases to desorption temperature (T_d), CO₂ will be desorbed and purged by N₂ from the adsorbents. The bed is ready to use for next cycle while cooled down to adsorption temperature.



Fig. 2.5 Schematic diagram of a simple temperature swing adsorption (TSA) process for post-combustion carbon capture (Mason et al., 2011)

PSA is also a very common technique to separate CO₂ from other flue gases by changing the applied pressure. PSA has been frequently used for gas separation in H₂ production or air purification (Ho et al., 2008). In a typical PSA process, the CO₂ is adsorbed by adsorbents at pressures that are higher than atmospheric pressure, while desorbed at lower pressure (normally atmospheric pressure) in a parallel desorption bed (Yu et al., 2012). It is preferred that high-concentration CO₂ such as in pre-combustion carbon capture be used, for the sake of generating high purity separated CO₂; however, for the application in low-CO₂-concentration such as post-combustion capture, the development of highly performed adsorbents with better selectivity, higher adsorption capacity, lower heat of adsorption and so on requires improvement for PSA utilisation (Chue et al., 1995). One advantage of PSA is the cycling time can be greatly shortened by switching between high and low pressure via simply introducing or evacuating abundant gas into the PSA chamber. The driving force for CO₂ desorption is determined by the pressure ratio of the high adsorption pressure to the low desorption pressure (Ho et al., 2008). In summary, both TSA and PSA have their own advantages and disadvantages. However, the key factor of success no matter which technology is employed is largely dependent on the performance of adsorbent materials.

Compared with the traditional absorption process, for instance, solid adsorption presents such characteristics as (D'Alessandro et al., 2010a):

- (1) Reduced energy for regeneration,
- (2) Higher capacity,
- (3) Higher CO₂ selectivity,
- (4) Ease of handling.

As mentioned above, in traditional amine-based absorption method, a large amount of aqueous solvent is required and hence desorption of CO₂-loaded amines consume a large amount of energy while solid adsorption uses solid materials without the presence of water. It is well known that CO₂ capacity is one of the most important factors to estimate carbon capture performance. Although absorption has been widely used for a long time, various novel adsorption materials have shown relatively higher CO₂ capacity and selectivity. Further efforts have been contributed to improve adsorbents' comprehensive capture behaviours. Solid adsorption technology is more suitable for large-scale applications, especially post-combustion because of its ease of handling and good regeneration properties.

There are still many shortcomings for solid adsorption. For example, each kind of adsorbent materials has its own characteristics in terms of CO_2 capture capacity and selectivity, regenerability, kinetics of adsorption and desorption, etc. New capture materials with excellent characteristics and ideal properties for practical application will be in great demand and need to be developed in the near future. This thesis is focusing

on solid adsorption for post-combustion and various adsorbents will be discussed in detail in next section. Fig. 2.6 demonstrates existing CO₂ capture methods/materials in the context of post-combustion, pre-combustion and oxy-fuel combustion.



Fig. 2.6 Materials for CO_2 capture: post-combustion, pre-combustion and oxy-fuel combustion.

2.3 Adsorbents

2.3.1 Criteria for selecting adsorbent materials

What makes a good adsorbent? As mentioned before, many parameters of adsorbents are concerned for practical applications. There are no absolute standards for selecting adsorbents because the strength and weakness also depend on the operating conditions. However, with regard to industrial application, adsorbents with both operational and economical characteristics are more preferable, the criteria items are listed as follows (Yang, 2003, Yong et al., 2002, Sayari et al., 2011):

- (1) Adsorption capacity. Normally, the higher of adsorption capacity, the better of the adsorbents. With given amount of flue gases, the value of CO_2 uptake obviously determines the amount of solid adsorbents and reduces the cost of raw materials furthermore. In addition, smaller quantity of adsorbents could benefit the design process for the equipment. The carbon capture capacity stated before in this thesis refers to the equilibrium capacity rather than working capacity, which is the most relevant parameter for practical applications defined for a shorter adsorption time.
- (2) Adsorption/desorption kinetics. It is of great importance of solid adsorbents to have fast adsorption/desorption kinetics because it could shorten the recycling time and improve efficiency significantly. The kinetics has a close connection with inner structure of adsorbents. Physisorption materials with porous structures have a relatively fast kinetics, which usually include diffusional transport mechanisms in micro-pores and macro-pores. On the other hand, chemisorption is always accompanied with a slower kinetics owing to the chemical reaction between the functional group and carbon dioxide.

For instance, Guerrero (Serna-Guerrero et al., 2010) developed an equilibrium model to describe the adsorption behaviour on amine-grafted mesoporous silica. A semi-empirical was applied in which two independent mechanism was employed, i.e., for the amine-functional groups, chemical adsorption played the dominant role while physical adsorption mainly occurred on the surface of the adsorbent. The results turned out to have an excellent agreement with experimental data.



Fig. 2.7 Comparison between kinetic model predictions and experimental data at several temperatures in isothermal condition (Monazam et al., 2011).

Monazam et al (Monazam et al., 2011) investigated the performance and kinetics of a solid amine adsorbent. They studied the effects of the loading of amine, reaction temperature and particle diameters. It was found that the maximum CO_2 uptake had a linear relationship with the reaction temperature. The kinetic model used to simulate the fractional conversion at various temperatures exhibited similar results as experimental data, as shown in Fig. 2.7.

- (3) CO₂ selectivity. Due to the fact that the flue gas produced from power plants contain many other gases such as N₂, O₂, H₂O in addition to CO₂, it is necessary for adsorbents to be highly selective towards CO₂. Additionally, CO₂ captured in this step has a profound influence to the downstream stages of the CCS chain, namely, CO₂ transportation and sequestration. Hence, a high selectivity for CO₂ is required to obtain CO₂ flows with satisfied purity level.
- (4) Regeneration and recycling stability. With regard to regeneration, there are two parameters that need to be taken into consideration. First of all, the energy consumed during this process, which is directly related to the heat of adsorption.

As for a typical physisorption, the heat of adsorption is approximately (-25) - (-50) kJ/mol; but it is in the range of (-60) - (-90) kJ/mol for the case of chemisorption (Samanta et al., 2012). In addition, adsorbents have different intrinsic adsorption/desorption temperatures which affect the required energy and operating adsorption/desorption windows dramatically in the practical process. Another key factor that a good adsorbent should have is the stable recycling performance which means that the material particles should not only remain an effective microstructure and morphology after multi-cycling adsorption and desorption steps but also have constant mechanical strength via trenchant operating conditions such as that in TSA or PSA.

- (5) Tolerance to impurities. The flue gases from power plants always contain contaminants, e.g., SO_X, NO_X, water vapour and other species (such as O₂). Consequently, it will limit the practical use if the solid materials are affected negatively by the contaminants or lack the resistance to the impurities. Additionally, chemical tolerance to oxygen is also of great importance and required for the adsorbents as flue gases always contain a certain amount of O₂.
- (6) Adsorbents costs. The price of materials is another factor that needs to be considered. According to Tarka et al., (Tarka et al., 2006) it is more advantageous if the price of the adsorbents is below \$ 10 /kg, comparing to traditional carbon capture materials. Moreover, if the cost of adsorbent is over \$ 15 /kg, it would not be considered as economical or a good scenario (Tarka et al., 2006).

Although a number of factors have been described and discussed in this section, it is impossible to develop/find an ideal situation for adsorbents with no drawbacks. When selecting an adsorbent for practical application, the conditions must be taken into account via a comprehensive assessment of the adsorbent performance under these
conditions. Generally speaking, an excellent adsorbent should be effective, reliable and economical during the whole carbon capture process.

2.3.2 Classification for different adsorbents

There are many ways to classify different solid adsorbents. For example, according to working (adsorption/desorption) temperature, adsorbents can be classified as High-temperature, Intermediate-temperature and Low-temperature as shown in Fig. 2.8. Solid adsorbents can also be grouped by the adsorption type, namely physisorbents and chemisorbents, as illustrated in Fig. 2.9.



Fig. 2.8 Category for solid adsorbents from the working temperature



Fig. 2.9 Category for solid adsorbents from adsorption type

In the following sections, some of the promising adsorbents will be selected as objectives and the CO_2 capture behaviours of selected adsorbents will be discussed in full details.

2.3.3 Zeolites

Many zeolites have been tested as adsorption materials for separation applications, as early as 1961 (Li et al., 2013). Zeolites have very unique structural characteristics including a crystalline aluminosilicates consisted of TO₄ tetrahedra (T= Si, Al) (Walton et al., 2006). Via connection between T atoms and oxygen, a well-defined molecular sieving structure is formed. There are free pore spaces in the original negative-charges contained framework (because of the presence of aluminium atoms) such that when other exchangeable cations (normally alkali cations, e.g. Na⁺) are introduced, the framework can be tuned to obtain different pore sizes or adsorption characteristics. The steric effect as well as polarity, magnetic susceptibility and polarizability of the molecule can affect the selectivity of zeolites, so as to influence adsorption properties (Tarka et al., 2006). It is illustrated in Fig. 2.10 that Faujasite cage structure contains sodalite cage where site I, I' are located and super cage where site III is located. Site II can be found at the hexagonal rings inside the cavities.

Similar to ACs, zeolites are typical physisorbents which are sensitive to temperature and pressure and usually work with an elevated pressure. Although zeolites have a relatively high CO₂ capacity among other adsorbents, the capacity decreases dramatically when the temperature goes up above 30 $\,^{\circ}$ C (Inui et al., 1988). More recently, X, Y-type Faujasite zeolites and 13X (Maurin et al., 2005, Harlick and Sayari, 2006) are intensively investigated, indicating a better selectivity of CO₂ than N₂. The results from the work of Siriwardane et al. revealed that optimization of 13X could also obtain promising capacity and high purity of the components even under low feed pressure during PSA approach.



Fig. 2.10 The framework of faujasite zeolites: (a) sodalite cages and super cages;(b) main crystallographic sites (I, I', II, and III) for the extra-framework cations.Modified from reference (Maurin et al., 2005).

The limit for application of zeolites should be the strong influence of water vapour in the feed gases, i.e., with the presence of H_2O , the CO_2 capture capacity of zeolites descends

dramatically. Generally speaking, how to eliminate the negative influence of water vapour, so as to maintain high CO_2 capture capacity under practical conditions should be the main challenge for zeolite materials.

2.3.4 Alkali metal-based adsorbents

Alkali metal oxides such as CaO and MgO can be used as adsorbents for CO_2 as a result of this reaction (2.2):

$$MO(s) + CO_2(g) \leftrightarrow MCO_3(s)$$
 (2.2)

Where M represents alkali metal: Mg, Ca, Sr, Ba, etc.

In this section, we will focus on carbonation-calcination loop of CaO/CaCO₃ for which the principle is described in Fig. 2.11 (Grasa and Abanades, 2006). One of the most significant advantages of CaO is the wide availability in nature, which reduces the portion of adsorbent materials cost. From the diagram, one can see that flow of carbonationcalcination loop is relatively simple, which indicates more opportunities for industrial application in terms of ease-handling and design.



Fig. 2.11 Flow diagram of CaO/CaCO₃ carbonation-calcination loop (Grasa and Abanades, 2006)

Additionally, reaction (2.2) reveals that CO_2 can be adsorbed with a molar ratio to CaO of 1:1, and the maximum theoretical value of CO_2 uptake is 17.8 mmol/g (Choi et al.,

2009). Hence, the kinetics and regeneration ability plays very important roles. According to previous research (Abanades, 2002), the kinetics depend on the rate of the chemical reaction. The carbonation of calcium oxide takes place initially at a fast rate, and then in the second stage, the chemical reaction slows down until it reaches the maximum conversation. It is proved that both partial pressure of CO₂ and temperature have an important impact on the chemical reaction (Oakeson and Cutler, 1979, Li et al., 2012). With the increase of pressure and/or temperature, the initial carbonation becomes faster at the first stage. However, the second stage is relatively slow and barely influenced by pressure/temperature conditions.

As for regeneration ability, it turned out that the CO_2 capacity reduced after multi-cycles of carbonation/calcination. Abanades (Abanades and Alvarez, 2003) and Lu (Lu et al., 2006) explained that the main reason was the blockage and collapse of the pore structure.

At atmosphere pressure, the adsorption temperature for calcium oxide is around 650 °C while desorption temperature maintains at approximately 900 °C, which is not realistic for post-combustion capture because of the intensive energy consumption. Furthermore, the extreme operating conditions requires strict standard of equipment in terms of high pressure/temperature.

2.3.5 Alkali-metal carbonate-based adsorbents

It is commonly accepted that alkali metal carbonate-based adsorbents (M_2CO_3 , where M can be K, Na, Li, etc.) are one of the most potential solid materials for post-combustion. This regenerable class of adsorbents has an adsorption/desorption temperature below 200 ° C, which well suits post-combustion process. The recycling chemical reactions include two steps, namely carbonation and decarbonation, shown as follows (Samanta et al., 2012):

Carbonation:

Decarbonation:

 $M_2CO_3 + H_2O + CO_2 = 2MHCO_3 \tag{2.3}$

$$\Delta H = \begin{cases} -135 \ kJ \ mol^{-1} & M = Na \\ -141 \ kJ \ mol^{-1} & M = K \end{cases}$$

$$2MHCO_3 = M_2CO_3 + H_2O + CO_2 \tag{2.4}$$



Fig. 2.12 Effect of the temperature on the efficiency of CO_2 capture by alkali-metal carbonates. Feed gas composition: 13.8 % CO_2 , 10 % H₂O, and balance (Hayashi et al., 1998)

It can be seen from the chemical reaction (2.3) that water vapour is the necessary component of adsorption, which makes good use of the water vapour from the feed gases in the adsorption period. As for the CO₂ capacity, in theory, the maximum is 9.43 mmol g^{-1} for Na₂CO₃ and 7.23 mmol g^{-1} for K₂CO₃, respectively. Hayashi et al. compared the performance of different alkali-metal carbonate-based adsorbents and found that K₂CO₃ could maintain a stable CO₂ uptake at 60-80 °C, see Fig. 2.12 (Hayashi et al., 1998).

Actually, many groups of researchers have further investigated and improved the adsorption/desorption performance of K_2CO_3 over the recent years. It is very common

for this adsorbent category to be loaded on porous supports so that an optimum CO₂ capacity could be obtained and regenerated as well. For example, a Korean group had researched different supports such as ACs, TiO₂, MgO, Al₂O₃ prepared by impregnation method (Lee et al., 2006). The results showed that K₂CO₃/AC and K₂CO₃/TiO₂ could be completely converted to the original K₂CO₃ phase so that the adsorbent systems performed stable regenerable adsorption with high CO₂ capacity (around 1.82-2.27 mmol/g) as well. However, the CO₂ uptake of K₂CO₃/MgO and K₂CO₃/Al₂O₃ after regeneration decreased dramatically because of the formation of KAl(CO₃)₂(OH)₂, $K_2Mg(CO_3)_2$, and $K_2Mg(CO_3)_2 \cdot 4(H_2O)$, which hindered the conversion to the original K₂CO₃ phase. Their work clarified the importance of the formation of KHCO₃ crystal structure after CO_2 adsorption. More recently, based on the above work, Lee et al (Lee et al., 2011) has developed a new alumina-modified adsorbents, in which a CO₂ capacity of 2.91 mmol/g was obtained with 60 wt% K₂CO₃ on Al₂O₃ as a support. During the experiments, K₂CO₃ was prepared in the presence of CO₂, which insures that only a KHCO₃ phase was formed during CO₂ adsorption. The results of this alumina-modified adsorbent stayed stable in regeneration after 10 cycles at even low regeneration temperature of 130 °C. Another group (Zhao et al., 2009) in China who also focused on structural characteristics in potassium carbonate adsorbents concluded that it was more effective for K_2CO_3 with a hexagonal structure rather than monoclinic structure, resulting from the resemblance in crystal structure between K₂CO₃ (hexagonal) and KHCO₃.

Zhao's research group had systematically investigated the CO₂ capture behaviours of K_2CO_3/Al_2O_3 in flue gases from power plants (Zhao et al., 2012a). They applied the carbonation conversion (η) to assess the degree of the complete conversion of K_2CO_3 to KHCO₃, as shown in equation (2.5).

$$\eta = \frac{M_{K_2CO_3}(w(t) - w(0))}{aw(0)(2M_{\text{KH}CO_3} - M_{K_2CO_3})} \times 100\%$$
(2.5)

Where t refers to the reaction time, w(t) and w(0) are the weights of the sorbent at time t and the start, while α is the loading amount of K₂CO₃. Zhao et al.'s research has analysed the effect of temperature, gas composition, and pressure on the experiments and the results revealed that a high CO₂ capacity of K₂CO₃/Al₂O₃ and its carbonation conversion maintained 68.3-91.8 % in 20 min, under 0.1 MPa of pressure, the reaction temperature of 55-75 °C, CO₂ concentration of 5-20 % and H₂O concentration of 12-21 %. More specifically, the increase of CO₂ and H₂O concentrations has a positive effect on the carbonation conversion while it is the opposite with the increase of temperature and pressure. For instance, Fig. 2.13 presents the effect of water concentration on carbonation conversion rate.



Fig. 2.13 Effect of water concentration on carbonation conversion rate (Zhao et al.,

2012a)

Li et al (Li et al., 2011) developed a novel adsorbent, i.e., dry $K_2CO_3/MgO/Al_2O_3$, and tested it in a fluidized-bed reactor. According to their work, the total CO₂ adsorption capacity of this novel material was 2.49 mmol/g in the bubbling regime at 60 °C, and maintained performance after 6 cycles with regeneration temperature at 480 °C.

Overall, as a typical chemisorbent, alkali-metal carbonate based materials, especially K_2CO_3 , performed promising CO_2 capacity at ideal adsorption/desorption temperature below 200 °C with modified porous supports. It is worth further efforts in the future to improve the recycling stability and persistence under realistic conditions for industrial applications.

2.3.6 Supported Polyethleneimine (PEI) adsorbents

PEI-containing adsorbents have drawn increasingly attention in carbon dioxide separation for decades (Hicks et al., 2008, Kresge et al., 1992, Beck et al., 1992, Xu et al., 2003). Compared with traditional aqueous amine scrubbing, PEI-containing adsorbents display many advantages such as high CO₂ capacity and selectivity, persistent performance with water vapour, favourable adsorption/desorption temperature for post-combustion and low energy consumption. (Heydari-Gorji et al., 2011, Sjostrom and Krutka, 2010, Qi et al., 2011) It is well known that PEI could be supported by various supports, among which, silica exhibits promising performance as a result of its highly porous structure and compatibility with PEI.

Pirngruber et al (Pirngruber et al., 2009) compared two methods of immobilization of amines including grafting of aminosilanes and impregnation of polyamines separately. Based on the adsorption isotherms and kinetic data in the VSA/PSA process, adsorbents prepared from impregnation could adsorb more CO₂ than that from grafting, however, one issue for impregnated PEI/silica is to maintain stability after regeneration. Colin Snape's research group had investigated cyclic performance of PEI/silica via thermal swing regeneration in the presence of pure CO_2 (Drage et al., 2008). The results indicated that due to the formation of urea type linkage, CO_2 capacity decreased dramatically above 135 °C.

Very recently, Sayari's group (Heydari-Gorji and Sayari, 2012) examined the comprehensive behaviours of PEI-impregnated mesoporous silica in various conditions including dry/humid streams in adsorption/desorption cycling at different adsorption/regeneration temperatures. In addition, in their research, they supplied three different gaseous streams in terms of carbon-free air (CFair), simulated flue gas (SFG) and different $CO_2/O_2/N_2$ mixtures with a SBA-15 silica support. The results of their work can be summarised as follows:

- (1) The amine-containing adsorbent displayed much better stability in CO₂ capacity over 66 cycles with the presence of water vapour than under the dry condition, as seen in Fig. 2.14.
- (2) PEI was relatively stable at mild temperatures after long term exposure to dry CO₂. The experiments of continuous exposure to dry 5 % CO₂/N₂ for 10 h at different temperatures demonstrated that the deactivation increased with the increasing temperature. More specifically, the CO₂ uptake at 5 % CO₂/N₂ at 75 °C decreased from 12.8 wt% for the fresh sample, to 12.5 wt% for sample exposed at 85 °C and 4.1 wt% for sample exposed at 120 °C.
- (3) The results of oxidative degradation showed that the PEI-impregnated materials maintained a stable behaviour over long term exposure to wet CO₂ and O₂containing gas mixtures. This could be explained by the presence of CO₂ which could protect the amine groups from oxygen attack, due to effective conversion of amine groups to carbonate and bicarbonate.



Fig. 2.14 CO₂ uptake during non-isothermal CO₂ adsorption/desorption cycling over SBA-15PL-600 (55) in both dry and humid conditions (Heydari-Gorji and Sayari, 2012)

2.3.7 Carbon

Carbon-based materials with micro/meso-porous structures, such as activated carbons, carbon nanotubes, graphenes, carbon molecular sieves, have been under intensive investigations for decades as a result of their wide applications in industry such as water treatment, gas purification, gas storage hosts, hydrogen storage and gas separation (Sevilla and Mokaya, 2014, Ma et al., 2013, Jones and Koros, 1994, Ren et al., 2011, Drage et al., 2009b, Ghosh et al., 2008, Ruthven, 1984, Crittenden and Thomas, 1998). Among the most-studied materials as candidates for CO₂ adsorption, carbon-based materials are attractive because of their advantages of the low cost, wide availability (e.g.,

coal, wood, biomass sources and so on) (Davini, 2002, Sircar et al., 1996), ease of regeneration and good thermal and chemical stabilities. In general, the synthesis methods of carbon materials can be divided into two stages, namely "carbonisation" and "activation". To be more specific, regarding to carbonisation, high temperature treatment within an inert gas atmosphere such as N₂ is normally involved, in some cases, however, a pre-treatment like slow oxidation of carbon materials at relatively lower temperature may be required. The purpose of high temperature treatment is to increase the weight ratio of carbon. The obtained carbons will then proceed with activation where steam, ZnCl₂, and KOH/NaOH are the most mentioned agents, aiming at enhancing the porous structures and enlarging the surface area (Marsh and Reinoso, 2006).

Activated carbons (ACs), as one of the representatives of carbon-based materials, with high surface area of more than 1000 m²/g (Otowa et al., 1993, Ahmadpour and Do, 1997, Lillo-Ródenas et al., 2003), are well known as typical physical adsorbents. The mechanism of carbon capture with ACs can be simply described as the addition of CO₂ to porous surface of ACs. The kinetics is relatively fast, normally within a few minutes to reach 90 % of equilibrium capacity and revisable desorption is available during multicycling process. At low CO₂ partial pressures (below 1 bar), the adsorption capacity is determined by the developed porous structure of ACs, especially ultra microporosity (<0.8 nm) (Wei et al., 2012, Sun et al., 2015). On the other hand, when it goes to high pressure, the total pore volume, rather than microporosity, plays a more important role in CO₂ capacity (Sun et al., 2013a). In industry, the application of ACs is normally accompanied by PSA to achieve the regeneration of the adsorbents (Chue et al., 1995, Siriwardane et al., 2001, Sircar and Golden, 1995). Due to the nature of physical adsorbents at low CO₂ partial pressures. It is of great importance to keep ACs in a stable operating

temperature because another shortcoming of ACs is the sensitivity to temperature changes, i.e., CO_2 capacity decreases dramatically when the temperature increases. The main challenges for CO_2 capture with ACs can be summarised as follows:

- (1) How to improve the CO₂ selectivity. Due to the nature of physisorption, ACs have wide adsorption abilities towards all types of gases including other components in the feed gases apart from CO₂. The solution could be modification of the surface functionalities of ACs before the adsorption/desorption period. Many groups are contributing to improve adsorption properties via impregnation or high temperature treatment (Plaza et al., 2007b, Yang et al., 2008, Wang et al., 2014, Neel et al., 2009).
- (2) The influence of water vapour. Water vapour is considered as a big issue for physisorbents since the steam has a comparable ability to be adsorbed by ACs. A recent study (Wang et al., 2008a) shows that below the pressure of 25 bar, H₂O has a significant negative impact on the CO₂ capacity, while the CO₂ capacity displays an increase along with the increase of H₂O concentration under higher pressure (Fig. 2.15). This phenomenon is even more obvious in microporous than mesoporous ACs.



Fig. 2.15 The CO₂ isotherms in coconut shells carbon at 275K: (1) $R_W=0$, (2) R_W =1.74, (3) R_W =1.32, (4) R_W =1.65 (Wang et al., 2008a) (R_W represents ratio of water)

(3) Mechanical strength of ACs. In principle, adsorbents should have good mechanical strength to remain effective in recycling and oxidizing environments. Hence, the physical form of ACs plays an important role in industrial use. Rather than AC powders, AC beads or other bulk morphology are more acceptable for practical application.

In order to enhance the surface affinity of ACs towards the acidic CO₂ molecules so as to increase CO₂ capacities at low CO₂ partial pressures, many investigations have been carried out by using various activation methodologies, manipulating the precursor materials, or surface modification such as hetero-atom doping (Wahby et al., 2010, Jiménez et al., 2012, Silvestre-Albero et al., 2011a). The influence of activation methods, different precursors, hetero-atom modifications will be discussed in detail in the following part of this section.

2.3.7.1 Activation mechanism

As mentioned above, NaOH and KOH are both common activation agents for carbon to effectively obtain high surface area. The mechanism is quite similar, although KOH is considered as more efficient, resulting from that the activation temperatures for KOH over NaOH is relatively lower (Raymundo-Piñero et al., 2005, Lillo-Ródenas et al., 2003), leading to a lower energy penalty in application.

Take KOH activation for carbon as an example, KOH activation involves a variety of chemical reactions as reactions 2.6-2.15, with the significance of the individual reactions varying with temperatures and KOH/carbon mass ratios. During the activation, KOH acts in three simultaneous/consecutive ways: 1) The catalyst to accelerate the gasification reactions which are shown in reactions (2.6)-(2.8) and (2.10). Otowa et al. (Otowa et al., 1993) proposed the reactions of carbon with CO₂ and H₂O (steam) produced from KOH decomposition at temperatures from ca.400 °C, as shown in reactions (2.6)-(2.8). However, recent work by Linares-Solano and his colleagues (Lillo-Ródenas et al., 2003, Raymundo-Piñero et al., 2005, Lozano-Castello et al., 2007) had observed that carbon can react directly with KOH as shown in reaction (2.10) at temperatures from ca. 400 °C as the standard Gibbs free energy of this reaction turns negative from this temperature, and this has been vindicated by the formation of H₂ and K₂CO₃ at temperatures below 700 °C with no appreciable amount of CO and CO_2 being produced (Lillo-Ródenas et al., 2003); 2). The formation of metallic potassium particularly at temperatures higher than 700 °C can readily be mobilised and intercalated to the carbon matrix during the porosity development, largely due to the high volatility of metallic potassium (the melting and boiling point for metallic K are 63 and 759 °C, respectively), see in reactions (2.10) and (2.12) - (2.14); and 3) The formation of potassium carbonate layer as shown in reactions

(2.9) and (2.10), which can effectively prevent the carbon from over consumption, although the carbonate can also be partly or wholly consumed in reactions (2.11) and (2.14), depending on the KOH/carbon ratios used. It is believed that the intercalated K is most likely associated with the formed oxygen functionalities (as shown in reaction (2.15)) within the carbon matrix structures via the formation of quasi-chemical bonds, giving rise to the residual potassium species that cannot be readily removed by the routine washing with excessive water.

$$2KOH \to K_2 O + H_2 O \tag{2.6}$$

$$C + H_2 O(steam) \to CO + H_2 \tag{2.7}$$

$$CO + H_2O \to CO_2 + H_2 \tag{2.8}$$

$$K_2 O + C O_2 \to K_2 C O_3 \tag{2.9}$$

$$6KOH + 2C \to 2K + 3H_2 + 2K_2CO_3 \tag{2.10}$$

$$K_2 C O_3 \rightarrow K_2 O + C O_2 \tag{2.11}$$

$$K_2 0 + H_2 \to 2K + H_2 0$$
 (2.12)

$$K_2 0 + C \rightarrow 2K + C0 \tag{2.13}$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{2.14}$$

$$K_2 0 + C \to K + C \cdot O \cdot K \tag{2.15}$$

The surface area or microporosity of KOH-activated carbons is determined by a combination of activation temperature and the KOH/AC mass ratio.

2.3.7.2 Precursors

There are various carbon-containing materials which can be carbonised and activated into resulting ACs, herein, we group the precursors into four main categories: biomass, coal-based carbons, synthetic materials, and others.

A. Biomass

Due to the low cost and wide availability, biomass waste has been seen as very sustainable for the production of ACs. Many investigations have proved that highly porous and large surface area ACs can be obtained from biomass waste such as corn cobs (Tsai et al., 1997), olive stones (Minkova et al., 2001), fruit stones and nutshells (Aygün et al., 2003), grape seeds (Savova et al., 2001), coconut (Kadirvelu and Namasivayam, 2003, Hu and Srinivasan, 1999), and bamboo (Hameed et al., 2007). The biomass-derived ACs can usually exhibit good microporous structure so as to obtain high CO₂ uptake. For instance, Deng *et al.* (Deng et al., 2015) just reported that ACs prepared from peanut shell and sun flower seed shell with KOH/carbon mass ratio of 1:1 demonstrated CO₂ uptake of 1.54 and 1.46 mmol/g at 25 °C and 0.15 bar CO₂.

B. Coal-based carbons

Coal-based material including brown coal (Pietrzak et al., 2007), bituminous coal (Hsu and Teng, 2000), pitches (Silvestre-Albero et al., 2011b) and so on, which has a high carbon-content, has been used for the production of ACs for a long time (Munoz-Guillena et al., 1992). Hsu et al. (Hsu and Teng, 2000) studied the influence of different chemical reagents in terms of ZnCl₂, H₃PO₄ and KOH on the texture properties of obtained ACs and found that the maximum surface areas for ACs were 960, 770 and 3300 m²/g, respectively, indicating KOH is more suitable to produce high porosity carbons from bituminous coal. Silvestre-Albero and his co-workers (Silvestre-Albero et al., 2011b, Wahby et al., 2010) reported that the carbon molecular sieves from petroleum pitch using KOH as activation agent had extremely high surface areas of up to 2895 m²/g, and obtained the CO₂ adsorption capacity at 50 bar and 25 ° C as high as around 500 cm³ STP per cm³, which is one of the best among all porous solid sorbents reported in the literature.

The high adsorption capacity was ascribed to the well-developed network of this new material.

2.3.7.3 Hetero-atoms modification

A. Nitrogen-atoms modification

In order to enhance the surface affinity of ACs towards the acidic CO₂, many investigations have been carried out by surface modifications (Pevida et al., 2008b, Figueiredo et al., 1999, Chingombe et al., 2005, Shafeeyan et al., 2010). Among all the methods, nitrogen-doping has been reported to be an effective means to increase the CO₂ adsorption capacity (Zhu et al., 2014, Wei et al., 2013, Plaza et al., 2007b, Hao et al., 2010). Basically, nitrogen can be doped into carbon matrix by either nitrogen-containing precursors or post-treatment like thermal or ammonia treatment. Fig. 2.16 illustrates different types of nitrogen surface functional groups including: amide group, imide group, loctame group, pyrrolic group, and pyridinic group. The mechanism of interaction between nitrogen-containing functional groups and acid molecules which is CO₂ in this case, is based on the generation of dipole-dipole, H-bonding, covalent bonding and so on (Shen et al., 2008).

The advantage of using nitrogenous precursors to introduce nitrogen lies in the *in-situ* retention of nitrogen functional groups, which makes this method more promising comparing with post-treatment. For example, Sevilla *et al.* (Sevilla et al., 2011) reported N-doped polypyrrole-based activated carbons by KOH activation and they found that carbons with milder KOH activation conditions of KOH/matrix=2 at activation temperature of 600 °C over that of KOH/matrix=4 can lead to resulting sample CP-2-600 with a larger number of nitrogen functional groups (up to 10.1 wt.%) and narrower micropore sizes. In addition, due to the nitrogen functionalities as well as ultra-

microporous structure, a very high CO_2 uptake of 6.2 mmol/g at 0 °C and 3.9 mmol/g at 25 °C was achieved for sample CP-2-600.



Fig. 2.16 Types of nitrogen surface functional groups: (a) pyrrole, (b) primary amine, (c) secondary amine, (d) pyridine, (e) imine, (f) tertiary amine, (g) nitro, (h) nitroso, (i) amide, (j) pyridone, (k) pyridine-N-oxide, (l) quaternary nitrogen (Pietrzak, 2009).

B. Metal-atoms modifications

Surface modification with other atoms doping instead of nitrogen-doping has achieved very limited success. Zhao and his co-workers (Zhao et al., 2012b) had investigated a novel microporous carbon material, namely KNC-A-K, and proposed that K^+ play an vital role in enhancing CO₂ adsorption by electrostatic interactions. According to the electrostatic potential surfaces, as shown in Fig. 2.17, they pointed out that the reason why K ions could promote CO₂ adsorption capacity was because the highly ionic K-O bonds could lead to strong polarization and charge separation within the carbon cluster, which can markedly enhance the capacity at low CO₂ partial pressures. Their best

candidate had obtained a high CO_2 capacity of 1.62 mmol/g at 25 °C and 0.1 bar, much higher compared with that of other reported carbon materials tested at the same CO_2 partial pressure. However, due to the involvement of N precursor, it is difficult to exclude the impact of nitrogen on the CO_2 adsorption behaviour; thus, further investigation is still required.

Apart from potassium, some other metal atoms have also been attempted to modify the carbon framework, such as copper or nickel (Jang and Park, 2012, Kim et al., 2010). However, the efficacy in enhancing adsorption capacity of CO_2 is not eliminated from other factors.



Fig. 2.17 Electrostatic potential surfaces of carbon terminated with different functional groups: -PyN, -NH₂, -OK, -PyN·HCl, -NH₂·HCl, and –OH. The electrostatic potential is mapped onto the electron density (isovalue = 0.0008 au), both of which were calculated at the ω B97XD/6-311++g (2d,p) level. In all surfaces, the contour range of the electrostatic potential is from +0.03 to -0.03 au, with red signifying a value greater than or equal to the minimum in negative potential and blue signifying a value greater than or equal to the maximum in positive potential (Zhao et al., 2012b).

CHAPTER 3 Methodologies

In this chapter, the experimental methodologies and techniques was given in detail. It could be divided into two sections including sorbents preparation and characterisation. More specifically, sorbents preparation described the synthesis methods in terms of preparation of raw carbon matrix and post-treatments of carbon beads for both phenolic resin-based and pitch-based carbon spheres. On the other hand, sorbents characterisation illustrated the techniques of measurements on CO_2 capture capacity, textural properties, elemental analysis as well as thermodynamic properties, *etc*.

3.1 Sorbents preparation

3.1.1 Preparation of phenolic resin-based activated carbon (AC) beads

3.1.1.1 Preparation of the raw activated carbon (AC) beads

The AC beads using phenolic resins as precursor were synthesised and provided from Institute of Coal Chemistry, Chinese Academy of Science (ICC, CAS). The synthesis method could be described as: a solution of hexamethylenetetramine and novolac-type phenolic resins were dissolved in methanol, followed by mixing in aqueous polyvinyl alcohol (PVA), and then the mixture was heated to 130 °C under stirring (400 RPM) in an autoclave for 1 h. After washing with abundant deionised water, the resulted resin beads were dried at 110 °C for overnight before they were carbonised at 830 °C in N₂ (1 bar, 1 L/min) for 1 h followed by steam activation for another 1 h at the same temperature to obtain the parent raw AC beads (denoted as PR0).

3.1.1.2 KOH treatment

5g of the raw AC beads were impregnated with 50 ml aqueous solution of KOH for 24 h. After drying in a vacuum oven at 70 °C for overnight, which ensures that all the samples were completely evaporated, the samples were heated in a horizontal tube furnace from ambient to a pre-selected treatment temperature at 3 °C /min and maintained at the temperature for 1 h. The samples were then washed with deionized water with a filter until neutral filtrate was obtained. Different KOH/AC mass ratios for impregnation and various chemical activation temperatures used in the preparation are summarised in Table 3.1 along with sample designations.

Number	Sample	Initial KOH/AC mass ratio for impregnation	Chemical activation temperature (°C)
1	PR0	0	None
2	PR1_600	0.1:1	600
3	PR1_700	0.1:1	700
4	PR1_800	0.1:1	800
5	PR2_600	0.3:1	600
6	PR2_700	0.3:1	700
7	PR2_800	0.3:1	800
8	PR3_600	0.5:1	600
9	PR3_700	0.5:1	700
10	PR3_800	0.5:1	800
11	PR4_600	1:1	600
12	PR4_700	1:1	700
13	PR4_800	1:1	800

Table 3.1 Preparation conditions and designation of the AC bead samples

3.1.1.3 Soxhlet extraction

Some of the samples were further treated by exhaustive Soxhlet extraction using deionised water to obtain samples with variable contents of intercalated potassium contents (PR3_700_*x*h, where *x* stands for the extraction duration in hours). Detailed procedures of Soxhlet extraction with deionised water include: 1) The extraction thimble which contained the carbon bead sample was loaded into the main chamber of Soxhlet extractor; 2) Connect the Soxhlet exactor with distillation flask and reflux condenser; 3) Heat the distillation flask to 100 °C and maintain at this temperature for different periods of extraction. By controlling the extraction time, carbons containing different levels of intercalated potassium can be obtained in order to evaluate the importance of intercalated potassium at different levels.

3.1.2 Preparation of pitch-based carbon spheres

3.1.2.1 Preparation of raw carbon spheres

The raw coal tar pitch with softening point of 280 °C was blended with 30 wt% of naphthalene under stirring, followed by heat treatment at 150 °C for 1 hour under N₂ atmosphere (0.5 MPa, 2L/min). Then the blended pitch was pulverised into particles of ca. 0.15-1.0 mm. The spherical pitch beads were synthesised via an emulsion method: firstly the blended pitch was stirred in polyvinyl alcohol solution in a sealed autoclave with a rotation rate of 250-300 r/min, and secondly, with a heating rate of 5 °C /min, the solution was heated to 145 °C and isothermal for 0.5 h, and finally the pitch spheres were washed in de-ionised water and dried in a vacuum oven. Sequentially the beads were filtered and dried in oven at 70 °C after impregnation in n-heptane for 24 h. In order to increase the property of thermal setting for the pitch beads, the pitch beads were placed in horizontal tube furnace in air with a heating rate of 0.5 °C /min up to 300 °C and held for 5 h. The stabilised pitch spheres were then carbonised at 900 °C for 0.5 h after heating

from room temperature to 900 °C at a heating rate of 10 °C /min in nitrogen (1 bar, 1 L/min). The obtained pitch carbon beads were so called raw pitch spheres, PAC0.

3.1.2.2 Preparation of activated pitch spheres

Physical and chemical activation are both standard approaches for carbon based materials to produce large surface area and abundant pores. It is widely known that chemical activation have many advantages such as higher yield, lower activation temperature and shorted activation time. On the other hand, physical activation are beneficial because of less expensive, and exemption of washing stage (Maciá-Agulló et al., 2004). So as to compare the impact of different activation methods, the raw pitch spheres were separated into two batches: the first batch of samples were firstly steam activated at high temperatures ranging from 600 to 800 °C and followed by KOH activation of carbon matrix so as to obtain high bulk density.

3.1.2.2.1 Steam activation

The steam activation of the as-prepared raw pitch spheres were carried out in a modified Horizontal Tube Furnace, as shown in Fig. 3.1. 10 g of raw sample were placed into the central heated area of the quartz tube, followed by ramping temperature to targeting temperatures (600, 650, 700, 750, 800 °C) at a rate of 10 °C/min in 100 % N₂ atmosphere (1 bar, 100 mL/min). Then water was pumped into the tube furnace with a flowing rate of 1.63 mL/min. The steam activation was maintained for 2 h then the water pump was switched off. Then the samples were taken out until naturally cooled down in N₂ atmosphere.



Fig. 3.1 Modified Horizontal Tube furnace for steam activation

3.1.2.2.2 KOH activation

The KOH activation of pitch based carbons applied is similar to the KOH treatment mentioned in 3.1.1.2, but slightly different on the selected KOH/carbon mass ratios and activation temperature. 5g of pitch spheres (raw or steam activated) were impregnated in KOH solution containing 5/10 g KOH (indicating KOH/ carbon mass ratio of 0.5:1 and 1:1) and 50 mL of de-ionised water for overnight. Then the impregnated spheres were dried in the oven at 70 °C for 24 hours, followed by heat treatment at 700 °C for one hour with a heating rate of 3 °C/min in 100 % N₂ atmosphere (1 bar, 1 L/min). The obtained carbon beads were then washed with abundant amount of de-ionised water until pH

reaches neutral. Finally, the samples were dried in the oven at 70 °C overnight to remove the moisture.

3.2 Sorbents characterisation

3.2.1 TGA analyses

CO₂ adsorption of the AC beads was also investigated by using a thermogravimetric analyser (TGA, Q500, TA instruments). The sample was first dried at 150 °C in pure N₂ (1 bar, 100 mL/min) for 45 minutes to remove any physisorbed moisture and/or CO₂, the temperature was then cooled to the adsorption temperature (25 °C). After the temperature stabilized, a flow of 100 mL/min of a simulated flue gas containing 15 % CO₂ in N₂ at 1 bar was introduced into the sample chamber at the adsorption temperature for 60 mins and the sample weight was recorded in order to calculate the CO₂ uptake. After adsorption, the gas atmosphere was switched to N₂ and the temperature was increased to 150 °C at a heating rate of 30 °C/min to desorb the CO₂. Up to 50 adsorption-desorption cycles were performed to evaluate the stability of the adsorbent samples.

3.2.2 Textural properties

The textural properties of adsorbents in terms of BET surface area, pore volume and pore size distribution, play a vital role in sample characterisation. In this section, both of the method and algorithms for porosity calculation will be introduced.

3.2.2.1 General information

Physical adsorption of N₂ at -196 °C was carried out on a Micromeritics ASAP 2420 analyser. Prior to any measurements, all samples were degased at 120 °C for overnight. The apparent surface area (S_{BET}) was calculated according to the method suggested by Parra *et al.* (Parra Soto et al., 1995). The cumulative pore volumes (V_{total}) were calculated

from the amount of nitrogen adsorbed at P/P_0 of *ca*. 0.99, and the average pore volume was calculated by $4V_{total}/S_{BET}$. The micropore volume (V_{micro}) and micropore surface area (S_{micro}) were determined by the t-plot method. Specially, the pore size distribution for pitch-based carbons were determined by Non-Local Density Functional Theory (NLDFT) method.

3.2.2.2 Algorithms for porosity calculation

A. Classification of N2 adsorption isotherms

It is well known that according to different N_2 adsorption isotherms, one can analyse the materials with different pore structures (Webb and Orr, 1997). IUPAC (International Union of Pure and Applied Chemistry) classification has been widely used and accepted to define the isotherms (Sing, 1985). Based on IUPAC, adsorption isotherms generally follow six main types of N_2 isotherms, as can be seen in Fig. 3.2 (Sing, 1985).

Type I illustrates that the adsorbents having very small pores which are micropores in most cases, which can be indicated from the fact that the adsorbents adsorb a large amount of N_2 at low relative pressures and reach a plateau at high pressures. This type usually presents relative small external surfaces, such as activated carbons and zeolites. The limiting uptake is determined by the accessible micropore volume, instead of the internal surface area (Sing, 1985).

Type II is generally similar to Type IV, indicating the material with either non-porous structure or large macro-porous structures. For both types, point B usually means the ending of monolayer and the beginning of multilayer adsorption. For Type IV, the characteristic feature is the obvious hysteresis loop, suggesting the mesoporous structures of the adsorbents, which can be explained by the gas condensation.



Fig. 3.2 Six basic adsorption isotherm types (Sing, 1985)

Type III and Type V both demonstrate a convex relationship between relative pressure and adsorption amount, which is indicative of stronger interaction of adsorptive molecules with one another as compared with the weak adsorbent-adsorbate interactions. Similarly, to Type IV, the hysteresis loop existed in Type V is ascribed to mesopores. It is worthy to note that neither Type III nor Type V is common.

Type VI shows many plateaus during the whole range, which results from stepwise multilayer adsorption on a non-porous surface. This type is very rare since it requires fairly uniform or homogenous surface.

B. BET theory

For porous material, BET theory is commonly applied to calculate the specific surface area. BET is named after the surnames of its three originators, namely Brunauer, Emmett and Teller (Brunauer et al., 1938). Based on Langmuir theory, in which it is assumed that gases can form monolayer on the solid (Langmuir, 1918), they proposed the concept of multi-molecular layer adsorption. To apply BET equation, the fundamental assumption is that the forces active in the gas condensation are also accountable for the binding energy during the process of multi-molecular layer adsorption. The assumptions can be summarised as:

- The adsorption rule obeys that one adsorbent site can only adsorb one adsorbate molecular and in BET theory, the surface of the adsorbent is homogenous;
- (2) No other interactions are involved but one-to-one adsorbate-adsorbent interaction. Furthermore, the interaction between the surface of adsorbent and first layer of gas molecules is much stronger than that of the second layer. The interaction of adsorbate and adsorbate can be ignored;
- (3) The rate of condensation of gas molecules onto an already adsorbed layer equals the rate of evaporation from that layer. When we sum for an infinite number of layers, the BET equation is then obtained:

$$V_a = \frac{V_m CP}{(P_0 - P) \left[1 + (C - 1) \frac{P}{P_0} \right]}$$
(3.1)

Where V_{α} is the quantity of gas adsorbed at pressure P, V_m is the quality of gas adsorbed while the entire surface of adsorbent is occupied by a monomolecular layer. C is a constant, and Po is the saturation pressure of the gas. The value of C in the simplest terms is:

$$\mathcal{C} \infty \exp \frac{q_1 - q_L}{RT} \tag{3.2}$$

Where q_1 is the heat of adsorption for the first layer, and q_L is liquefaction of the adsorptive, R is the ideal gas constant (8.314 J/ (K·mol)), and T is the absolute temperature.

We can rewrite Equation 3.1 into the linear form:

$$\frac{P}{V_a(P-P_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{P}{P_0}\right)$$
(3.3)

In Equation 3.3, the values of $P/[V_a(P_0-P)]$ can be plotted against P/P_0 , and the intercept 1/ (V_mC) and slope (C-1)/(V_mC) can be obtained. It is well accepted that the relative pressure P/P_0 are taken between the values of 0.05-0.35, where the linear BET plot can be produced. However, in some cases, for example, for materials with microporous structures, lower relative pressure area is normally employed to ensure the accuracy of the calculation of surface area. The software of MicroActive Version 3.00 by Micromeritics Instrument Corporation, USA was used to process the BET data, details can be found in the literature (Webb and Orr, 1997).

After taking or selecting the multiple data points on a N_2 sorption system, intercept i (1/(V_mC)) and the slope s, which is (C-1)/(V_mC) can be easily determined from the BET plot, as the surface area S can be calculated by the following equation:

$$S = \frac{V_m N A_{cs}}{M w} \tag{3.4}$$

Where N is the Avogadro's number, which is 6.02×10^{23} molecules/mole, A_{cs} is the cross sectional area of the adsorbate molecule, M is the molecular weight of the adsorbate molecule, w is the sample weight. And V_m can be calculated from Equation 3.5:

$$V_m = \frac{1}{s+i} \tag{3.5}$$

C. Pore size and total pore volume

Pore size distribution and pore volume are very important parameters to assess the texture properties of the porous adsorbent materials, so as to understand the mechanism of the performance of CO₂ adsorption, especially for physical adsorbents such as activated carbons. Pore size is defined as the diameter of the opening (for cylindrical structure) or the width/ half-width of the slit. IUPAC proposed how to classify pores by the internal pore diameters or slit width, that is, Micropore represents internal width less than 2 nm; Mesopore with internal width for 2-50 nm; and Macropore with internal width larger than 50 nm (Lowell et al., 2012). The schematic illustration of adsorption potential of micropore, mesopore and nonporous surface can be found in Fig. 3.3 (Lowell et al., 2012).



Fig. 3.3 Schematic of illustration of adsorption material, ε , on (a) planar, nonporous surface; (b) mesopore; (c) micropore (Lowell et al., 2012, Sing, 1985)

There are different models as to describe the pore size distribution dependant on adsorbent with different structures. In the present work, the t-plot and Non-Local Density Functional Theory (NLDFT) method were applied for microporous materials to calculate the micropore volume and pore size distribution. Detailed description of the theories can be found elsewhere (Lastoskie et al., 1993, Barrett et al., 1951, Rouquerol et al., 1994).

Total pore volume refers to that the volume of all the cracks, fissures, holes, channels and so on, within the body of particles or of larger objects (Webb and Orr, 1997). It can be calculated according to the following Equation 3.6, in which the total pore volume is obtained with the amount of adsorbed gas at a relative pressure when the pores are fully occupied with adsorbate molecules. Take N₂ sorption isotherm for an instance, since the temperature used for characterisation is -196 °C (the same as liquid N₂ bath), the volume of adsorbed liquid N₂ molecules that fills the pores at -196 °C can be obtained by converting from the volume of N₂ at Standard Temperature and Pressure (STP).

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT} \tag{3.6}$$

In Equation 3.6, V_{liq} , which stands for the volume of liquid Nitrogen, is the targeting total pore volume. P_{α} 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 cm³/mol), R is the ideal gas constant and T is the ambient temperature.

In general, to characterise the textural properties of the activated carbon materials related in this work, N₂ sorption isotherms were carried out at -196 °C using a Micromeritics ASAP 2420 instrument to test the porosity and textural structure of samples. Prior to analysis, samples were degassed at 150 °C for 15 h. The surface area was calculated by BET (Brunauer-Emmett-Teller) method from the N₂ adsorption isotherm data within the relative pressure ranging from 0.01 to 0.10 P/P₀ to give positive BET 'C' parameters. Since N₂ molecules have difficulty entering narrow micropores (< 0.8 nm), CO₂ adsorption isotherms at 0 °C were carried out and joined to N₂ adsorption isotherms (beginning at 0.00001 P/P₀) using Microactive V3.0 software. Narrow microporosity for pitch-based carbon was calculated using cumulative pore volume from NLDFT carbon slit pore model at 0.8 nm, total micropore volume at 2 nm and total pore volume at 100 nm.

3.2.3 Elemental characterisation using X-ray fluorescence (XRF)

spectrometry

The theory behind X-Ray Fluorescence (XRF) is to excite a material by bombarding using high-energy X-rays or gamma rays, resulting in the emission of characteristic "secondary" (or fluorescent) X-rays which then gives elemental and chemical information. X-ray can be applied for routine, relatively non-destructive chemical analyses on targeting materials, and in this thesis, the tests of the selected samples were carried out on a Bruker S8 Tiger Spectrometer. For each test, around 5 g of each sample was placed in the sample holder and the test was repeated twice for each sample to make sure the results are reliable. One advantage of this test is the carbon beads could be recycled as no pre-treatment was required.

3.2.4 Inductively Coupled Plasma (ICP)

To determine the quantity of remaining potassium for ACs after washing, the samples were ashed using a thermogravimetric analyser (TGA, Q600, TA instruments; samples were first dehydrated at 120 °C in N₂ for 20 mins, and then changed gas to air and heated to 600 °C with a ramping rate of 20 °C/min, followed by an isothermal period for 40 mins in air. The resultant ashes were analysed by an Inductive Coupled Plasma Optical Emission Spectrometer (Perkin-Elmer Optima 33-DV ICP-OES, USA).

3.2.5 Elemental Analysis (EA)

The chemical contents of samples were obtained by using Elemental Analysis (EA) through a LECO CHN 628 Series to detect elements N, C and H and S. Prior to the test, about 100mg of each sample were grounded to powder and then put in the alumina crucible for elemental analysis. Three tests for each sample were conducted and the reported results were the average value of the three tests.

3.2.6 Scanning Electron Microscope and Energy Dispersive X-ray

spectroscopy

The morphologies of the materials were observed on a FEI Quanta 600 Scanning Electron Microscope (SEM) and the Energy Dispersive X-ray spectroscopy (EDX) software is called Esprit 1.9 which is produced by Bruker.

In a typical SEM test, a beam of electrons is used to scan across the specimen in synchronism with the spot of a cathode ray tube (CRT) (Goldstein et al., 2012). This incident beam leads to elastic and inelastic scattering of electrons, as well as variations of electromagnetic radiation. As a result, a host of secondary signals that can be observed, including secondary electrons, backscattered electrons, Auger electrons or X-rays (Flegler et al., 1993). Generally, the intensity of the secondary signal is dependent on the surface morphology, chemistry, physical state and so on.

X-ray emission consequent to the interaction of the primary electron beam with the sample, can also be detected by an EDX within the SEM. As the resulting X-ray energies

are characteristic of the atomic structure of the element they originated from, the spectra generated can be used to identify the constituent elements.

Before the tests, samples were fixed to conductive carbon tabs onto SEM sample holders and then gold coated to avoid electron charging. In order to image their cross-sectional morphology, some of the samples were cut by a scalpel before the imaging.

3.2.7 Transmission Electron Microscope

A JEOL 2100F Transmission Electron Microscope (TEM) was also applied to obtain the morphologies of the materials.

Typically, an electron source at the top of the microscope emits electrons that travel through a vacuum in the column of the microscope. To focus the electrons into a very thin beam, the electromagnetic lenses are applied. Then the thin beam can be directed through the area of the sample of interest. The detector can be reflected of the information when the electrons pass through the sample. Normally the bright field imaging relies on incident electrons being scattered and disappearing from the beam depending on the compositional density and crystal orientation of the sample (Flegler et al., 1993). As a result of the difference of density of different parts of the sample, the corresponding image hence will be displayed with varied darkness and the intensity of un-scattered electrons leads to a rise to a "shadow image". Similarly, the chemical compositions as well as elemental mapping can be detected by an integrated EDX.

To conduct the TEM imaging, samples were prepared as ground, suspended in methanol and agitated by an ultrasonicator to achieve uniform suspension. A drop of the suspension was placed onto a carbon-film coated copper grid (300 mesh) and then dried in vacuum before being loaded into the TEM.

3.2.8 X-ray powder Diffraction

In order to detect the if the form of K-spices in the carbon materials, a Siemens D500 X-ray powder Diffraction (XRD) was used with a Cu K-alpha radiation source, 1-40kV range.

XRD is a commonly used technique for phase identification of a crystalline material and it is based on constructive interference of monochromatic X-rays and the sample (Warren, 1969). XRD is consist of three basic elements in terms of an X-ray tube, a sample holder and an X-ray detector. Typically the X-rays are produced by a cathode ray tube, and after filtered to generate monochromatic radiation and collimated to concentrate, the X-rays are directed to the sample (Klug and Alexander, 1954). When the conditions satisfy Bragg's Law:

$$n\lambda = 2d\sin\theta$$

The wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline samples. Then the diffracted X-rays can be detected, processed and counted. The sample will normally be scanned through a range of 2θ angels so that all possible diffraction directions of the lattice can be attained.

In this work, the detected carbon beads (around 1 g) were finely ground and placed in the central of the sample holder (which is made of glass), and data is collected at 2θ from ~5 ° to 70 °. In addition, the process was in full computer control with DIFFRAC-PLUS Measurement and DIFFRAC-PLUS Evaluation software packages.

3.2.9 X-ray Photoelectron Spectroscopy

The surface analysis of selected samples in the work was conducted by Kratos AXIS ULTRA DLD X-ray Photoelectron Spectroscopy (XPS). XPS has been intensively applied to define the surface elemental composition and chemical functional groups of
solid materials (within the first 10 nm) (Van der Heide, 2011). Typically, under an ultrahigh vacuum condition, a beam of X-ray is irradiated to the surface of the sample. Due to the photoelectric interaction between monoenergetic X-rays and the solid sample, electrons with discrete kinetic energies will be ejected from the surface. As the kinetic energy corresponding to discrete electron "lines" can be quantitatively observed, the binding energy of the electron can be calculated by (Hollander and Jolly, 1970):

$$E_{hv} = E_k + E_{\phi} + E_{B(i)}$$

Where $E_{h\nu}$ is the energy of X-ray, E_k represents the photoelectron kinetic energy, E_{ϕ} is a small correction for solid effects (work function, etc.), and $E_{B(i)}$ is the electron binding energy of the *i*th level. The binding energies of electrons in different electron orbitals are known for different chemical elements. Hence, it is easy to identify atoms/ions of specific elements in a sample.

In order to obtain a photoelectron spectrum, a plot of "counts per second" (which indicates the number of photoelectrons observed by the spectrometer) vs. binding energy could be drew (Van der Heide, 2011). The characteristic peaks in the spectrum can be used to identify the chemical elements as well as the compositions of detected elements. Additionally, due to the fact that the same element can exist in different forms such as chemical functional groups, sometimes the peaks need to be deconvoluted into sub-peaks.

Before XPS test, a double sided adhesive tape glued to one end of the sample holder and place the sample powder on the top end of the tape using a clean, dry spatula over small area (0.5 cm * 0.5 cm) for XPS analysis. The sample size is approximately 20 mg. Following this, a clean alumina foil can be used and gently pressed on the sample area to ensure the firmness on the taped holder.

3.2.10 Heat of adsorption measurements

The heat of adsorption and the specific heat capacity of the AC carbon materials were determined using a SENSYS evo TG-DSC instrument (Setaram) under the conditions similar to those used in adsorption tests using a mixture of CO_2 and nitrogen. Since this instrument simultaneously provides mass changes and heat flows, the heat of adsorption can then be deduced in terms of the heat released per mole of CO_2 adsorbed.

3.2.11 Mechanical strength testing

The mechanical strengths of the samples were measured using a DMA Q800 dynamic mechanical analyser (TA instruments, USA). The dynamic force exerted on the sample allows the change in deformation with temperature to be monitored. Each sample was tested more than ten times during which one carbon bead was randomly selected every time to ensure the accuracy of the results. The average values from the repeat tests for each sample are reported.

3.2.12 Bulk density

Bulk density measurements were acquired by using a Micromeritics AutoPore IV 9500 series Mercury Intrusion Porosimeter. Approximately 0.3 g of sample was dried in a vacuum oven at 0.03 mbar at 70 °C for 24 h prior to analysis. The AC bead samples were placed into powder penetrometer (5 ml sample volume, 1.06 ml intrusion volume). Only low pressure analysis was carried out, with bulk density being calculated at 0.034 bar from total weight of mercury in penetrometer, density of mercury, sample weight and total penetrometer volume.

CHAPTER 4 KOH activated carbon spheres derived from phenolic resin

4.1 Introduction of phenolic resin based AC spheres

As mentioned before, among the most studied potential solid adsorbents, activated carbon materials have been characterised by several advantages such as low cost, easy to regenerate and stable cyclic performance. Therefore, they have long been considered as promising candidates for CO_2 adsorption. The general conclusion from open literature is that the surface affinity of carbon-based materials towards the acidic CO_2 can be enhanced by involving alkali functionalities, however, the major adsorption mechanism for carbon material is still physical adsorption. Therefore, the adsorption capacities of carbon materials are largely determined by their texture properties, i.e. highly developed microporosity is decisive for the adsorbents to have high adsorption capacities. In other words, the adsorption of CO_2 on carbon adsorbents follows a pore-filling mechanism, namely the CO_2 molecule exists as a liquid-like phase in the pores, and pores are filled gradually from smaller ones to larger ones with an increase in CO_2 pressure (Juan and Ke-qiang, 2009), and this indicates that significant adsorption capacities can be obtained at high pressures but capacities at low pressures need further improvements.

It was only recently that carbon-based materials with enhanced CO₂ adsorption capacities (ca. 1.0-1.8 mmol/g at 0.15 bar CO₂ and 25 °C) at relatively low pressure were reported (Silvestre-Albero et al., 2011a, Wang et al., 2012a, Xia et al., 2011, Zhao et al., 2010, Zhao et al., 2012b, Zhu et al., 2014). Most of the adsorbents in these investigations were prepared by involving nitrogen-containing functionalities, and in many cases coupled with chemical activation by KOH (Lozano-Castello et al., 2001, Presser et al., 2011, Sevilla et al., 2011, Wang and Kaskel, 2012, Yoon et al., 2004). These protocols appeared

to be effective in enhancing CO_2 adsorption capacities, however the nitrogen-containing precursors were usually expensive and the obtained samples were highly porous powders with very low densities. In practical CO_2 capture facilities where either fix-bed or fluidized-bed adsorbers are used, these fine powders need to be re-shaped to pellets or beads with the aid of binders or other additives, which can reduce the adsorption capacities significantly.

Nonetheless, the basic principle to promote low pressure CO_2 uptake of carbon-based adsorbents can be deduced from previous investigations: a polarized surface is of great importance to enhance its interaction with the quadrupole moment of CO_2 . Encouraged by this, a novel idea to enhance the surface polarity of the carbon materials by involving K^+ -O⁻ ionic-like structures, instead of nitrogen-containing functionalities that are covalent-like structure with lower electron separation tendency, is investigated in the present study. Based on the spherical activated carbon (AC) beads development in this work, potassium species were intercalated into the carbon framework successfully following by a facile method. The obtained materials were evaluated for CO_2 adsorption at low pressures and fully characterized to clarify the important role of potassium intercalation in enhancing CO_2 adsorption.

In this work, activated carbon beads with diameter of 0.6-0.8 mm that were prepared from phenolic resin were produced using fairly mild KOH post-treatment. The AC samples exhibited excellent sorption capacity under low CO₂ particle pressure. The experiment results also indicate how intercalated K species effectively enhance the CO₂ adsorption performance over 50 cycles.

4.2 Characterization of the K-containing activated carbon beads

4.2.1 Chemical composition

Before KOH post-treatment, the chemical composition of raw AC spheres were tested by Elemental Analysis, as shown in Fig. 4.1. The result shows that the parent carbon bead sample (PR0) was free from Nitrogen (less than 0.01 wt%) and inorganics, which was expected as the sample was derived from pyrolysis of a phenolic resin containing negligible impurities compared with coal and biomass-derived ACs.

Table 4.1 Elemental analysis results for the parent PRAC spheres (PR0)

	Elemental Analysis (wt%)						
	C ^a	H ^a	N ^a	O ^a	N/C ^b	O/C ^b	
PR0	93.6	0.52	0.00	5.84	0.000	0.062	

On the other hand, after KOH activation, information from XPS of selected samples has indicated the surface information of potassium distribution, as presented in Fig. 4.1 and Table 4.2. Coincidentally, one can also observe similar results by SEM-EDX in Fig. 4.2 and Table 4.3, in which there is an obvious peak of elemental K. The nomination of PRAC samples can be found in Table. 3.1.



Fig. 4.1 XPS analysis of PR1_700 showing the K and C peaks

	Table. 4.2 Surface K	concentrations results	for PR0, PR1	700 and PR3	700 from XPS
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Sample	KOH/AC mass ratio	K concentration	
	-	Atom. (at%)	Norm. (wt%)
PR0	0	0.0	0.0
PR1_700	0.1:1	2.9	8.5
PR3_700	0.5:1	3.1	9.2



Fig. 4.2 SEM-EDX analysis of PR1_700 showing the K, C and O peaks

Element	Norm. (wt.%)	Atom. (at.%)
Carbon	68.9	78.6
Oxygen	20.7	17.7
Potassium	10.4	3.7

Table 4.3 EDX results of K concentration for PR1_700

Table 4.4, which is the XRF results, depicts the concentration of K in the bulk for PRAC samples activated at 700 °C. It is worth to note that XRF indicates that the PRAC samples activated at 700 °C have concentrations of K in the range of 14-22 wt%. However, XPS data as well as SEM-EDX reports suggest that the surface K concentrations are considerably lower, being around 10 wt%. This reveals that most of the K species have been effectively intercalated within the carbon beads. It was difficult to precisely link the amount of intercalated K with the KOH/carbon mass ratios used in the preparation method as the formation of some crystalline potassium compound clusters on the outer surface of the carbon beads is evident (see Fig. 4.3). However, it must be stressed that the materials prepared using the same procedure and conditions are fairly reproducible, for

which the repeating adsorption behaviour for different batches of sample will be presented in the following section.

Sample	KOH/AC mass ratio	K concentration (wt%)
PR0	0	0.0
PR1_700	0.1:1	13.9
PR2_700	0.3:1	18.4
PR3_700	0.5:1	21.7
PR4_700	1:1	15.1

Table 4.4 XRF results of K concentration for PR0, PR-AC activated at 700 °C



Fig. 4.3 SEM image of the PR1_700 sample showing the formation of clustered potassium compounds on the outer surface of the treated carbons during the drying process

4.2.2 Textural properties

The N_2 adsorption isotherms are illustrated in Figs. 4.4-4.7. Despite the small hysteresis loops observed for some of the samples due to the relatively minor development of mesoporous structures, all isotherms can be generally classified as type I according to IUPAC classification (Sing, 1985), suggesting that the spherical carbons are mainly microporous.



Fig. 4.4 N₂ isotherms of comparisons between sample PR0 and PR1 under different activation temperatures



Fig. 4.5 N₂ isotherms of comparisons between sample PR0 and PR2 under different activation temperatures



Fig. 4.6 N₂ isotherms of comparisons between sample PR0 and PR3 under different activation temperatures.



Fig. 4.7 N₂ isotherms of comparisons between sample PR0 and PR4 under different activation temperatures

Table 4.5 summarises the specific BET surface areas, pore volumes, microporosities for all the samples derived from N₂ (-196 °C) adsorption data. The initial AC bead sample (PR0) exhibits a BET surface area of 1128 m^2/g , which is typical for phenolic resin based

activated carbons (Oya et al., 1995, Tennison, 1998). The micropore surface area (S_{micro}) calculated by the t-plot method is fairly close to the BET surface area, consistent with the dominant microporosity. However, it is interesting to note that despite prolonged washing with water, considerably lower BET surface areas and total pore volumes were observed for most of the PRACs, particularly the PR3 series. These results are in sharp contrast to those reported in the literature where enhanced porosity of carbons was obtained via KOH activation (Lillo-Ródenas et al., 2003, Wang and Kaskel, 2012, Yoon et al., 2004). Therefore, it appears that the carbon matrix structures inherited from the earlier steam activation has been further modified leading to intercalation of K species but with the loss of some microporosity.

Table 4.5 Texture	properties of the carbon beads
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Sample

	$S_{BET}(m^2/g)$	V _{total} (cm ³ /g)	Average Pore Diameter (nm)	S _{micro} (m ² /g)	V _{micro} (cm ³ /g)
PR0	1128	0.45	1.59	1115	0.43
PR1_600	972	0.39	1.60	958	0.37
PR1_700	943	0.38	1.61	930	0.36
PR1_800	1047	0.42	1.61	1029	0.40
PR2_600	758	0.31	1.63	748	0.29
PR2_700	902	0.36	1.61	892	0.35
PR2_800	963	0.41	1.70	939	0.38
PR3_600	857	0.35	1.64	843	0.34
PR3_700	826	0.34	1.63	815	0.32
PR3_800	820	0.35	1.69	804	0.32
PR4_600	983	0.40	1.64	963	0.38
PR4_700	1071	0.44	1.65	1050	0.42
PR4_800	1171	0.50	1.76	1150	0.47

Previous investigations (Raymundo-Piñero et al., 2005, Romanos et al., 2012, Neel et al., 2009, Wang and Kaskel, 2012, Lozano-Castello et al., 2007, Otowa et al., 1993) have revealed that KOH activation involves a variety of chemical reactions as detailed below, with the significance of the individual reactions varyin g with temperatures and KOH/carbon mass ratios. Details of the mechanism of KOH activation has already been fully discussed in Section 2.3.7.1.

The surface area or microporosity of KOH-activated carbons is determined by a combination of activation temperature and the amount of KOH used. As shown in Table 4.5, however, the considerably lower surface areas obtained for most of the samples from the secondary KOH activation of the original steam-activated carbon bead sample (PR0), which has a considerably higher surface area of 1128 m² g⁻¹, tend to suggest that the potential extra microporosity developed from the secondary KOH activation was offset by the even larger porosity loss as a consequence of the simultaneous potassium intercalation that can potentially lead to complete or partial occlusion of the micropores. It was found that at the same KOH/AC mass ratios, the surface areas of all the PRAC bead samples increased significantly with increasing activation temperatures, highlighting the temperature-dependent reactivity of carbon with KOH. At the same activation temperature, however, the surface areas of the PRACs were found to decline first with elevating KOH/AC mass ratios from 0.1:1 to 0.5:1 and then incline with further rise in KOH/AC ratios from 0.5:1 to up to 1:1, indicating the relative significance of porosity development and simultaneous potassium intercalation during the chemical activation process.

4.2.3 Morphology

The morphology of the carbon beads was investigated by both SEM and TEM. Fig. 4.8 shows the images from SEM. Figs. 4.8 (a-e) confirm that the AC samples have well-

developed spherical forms with uniform diameters of 0.6-0.8 mm. Fig. 4.8 (a-e) shows the comparison between original AC bead, as seen in Fig. 4.8 (a), and the AC samples with the increase of initial KOH/AC loading, which is ranging from 0.1:1 to 1:1. More importantly, the macroscopic morphology of the samples shows little change after the incorporation of K; the desired spherical form has been preserved. Specifically, cracks and randomly distributed large holes are present on the outer surface, especially for sample PR4_700. Figs. 4.8 (f-j) show the cross-sectional images for the carbon beads where the presence of large number of µm-scale pores and some interior hairline channels are evident. For samples with KOH/AC loadings lower than 0.5:1, the pore structures are almost maintained. If we compare sample PR3_700 and PR4_700, it is obvious that even though there are some cracks present in sample PR3 700, no serious and thorough cracks can be found. However, when KOH/AC mass ratio reaches 1:1 (sample PR4_700), the cracks became severe. This gives evidence for the results of mechanical strength for AC samples, which will be discussed in Section 4.3.1. TEM images in Fig. 4.9 reveal the amorphous nano-structures with graphite layers being observed. The fact that no crystallized K species were found reflects their superior uniform distribution, which is of great importance to form highly polarized surfaces to enhance CO₂ capture. This will be further discussed in Section 4.4.



Fig. 4.8 SEM images of (a) original PR0, (b) PR1_700 (KOH/AC mass ratio of 0.1:1), (c) PR2_700 (KOH/AC mass ratio of 0.3:1), (d) PR3_700 (KOH/AC mass ratio of 0.5:1), (e) PR4_700 (KOH/AC mass ratio of 1:1), and their corresponding cross-sectional images (f-j).



Fig. 4.9 High resolution TEM images of the activated carbon beads (sample PR3_700)

4.2.4 Element mapping

The distribution of the K species was obtained from SEM element mapping which is depicted in Fig. 4.10, where red colour represents the existence of K with the brightness indicating concentration. As can be seen from Fig. 4.10 a, no K was detected for the initial AC, PR0, as expected. It can also be seen that, according to Figs. 4.10 (b-e), the K-intercalation treatment led to relatively even distributions of K with no obvious segregation for all the samples, rather than an ascending K concentration for samples with increasing KOH/AC mass ratios from 0.1:1 to 1:1. This can be ascribed to the washing procedure with large amount of de-ionised water after KOH activation. More specifically, Fig. 4.11 gives the K mapping of PR0, PR3_700 and its cross-section images, implying that the incorporated K is highly dispersed throughout the carbon beads. It is worth noting

that abnormal sharp highlighted red area, as shown in Fig. 4.10 (b), can be observed, indicating the formation of clustered potassium on the outer surface of carbon beads during the drying process.



Fig. 4.10 SEM images of potassium mapping: (a) sample PR0, (b) sample PR1_700, (c) sample PR2_700, (d) sample PR3_700, (e) sample PR4_700



Fig. 4.11 SEM images of potassium mapping: (a) sample PR0, (b) sample PR3_700, (c) cross-section of sample PR3_700

For KOH activated carbons, it is generally recognised that all the residual K species can be removed by subsequent washing with acid (normally HCl solution), by which the porosity in the carbon samples can be recovered (Ahmadpour and Do, 1997, Kierzek et al., 2004, Lillo-Ródenas et al., 2003, Wickramaratne and Jaroniec, 2013, Zhu et al., 2011). In the present case, however, deionised water was used as a "soft" washing procedure to successively remove first the "free" and then the intercalated K. In other words, we are attempting to enhance the surface polarity of the carbon beads by potassium intercalation into the carbon frameworks as will be discussed later. Therefore, the distribution of potassium and oxygen on the surface in microscopic scale plays an important role in promoting CO₂ adsorption capacities. To further investigate the distributions of K and O in relation to C, TEM mapping was carried out, and the results (Fig. 4.12) suggest that the C, K and O elements are evenly distributed and appear to be interlinked to each other, which suggests that the surface modification was achieved successfully. The presence of potassium species can also be evidenced by the weak diffraction peak in the XRD pattern (Fig. 4.13).



Fig.4.12 TEM images of PR3_700, showing the distribution of different elements: (a) original image, (b) carbon mapping, (c) potassium mapping, (d) oxygen mapping.

As mentioned above in 4.2.3, according to the chemical reactions between C and KOH during the chemical activation, metallic K and quasi-chemical bonds of C-O-K as new surface functionalities can be formed at over 700 °C and efficiently intercalated into the carbon framework structures. When washing with excessive water, most of free surface potassium species, such as K_2CO_3 and K_2O formed during the activation at high temperatures, can be readily removed while intercalated potassium species or related functionalities (e.g. the –O-K chemical or quasi chemical bonds) remain in the carbon matrix structures. The element mapping shown in Fig. 4.12 illustrates a high consistency between the surface distributions of K and O, further suggesting that the intercalated K is most likely associated with the formed oxygen functionalities via the formation of quasi-chemical bonds, giving rise to highly polarized carbon surfaces.



Fig. 4.13 XRD pattern of sample PR3_700

4.3 CO₂ adsorption behaviour on the carbon beads

4.3.1 Static adsorption measurement

As the most used method for adsorbent evaluation, the CO_2 isotherms of the carbon beads were measured both at 0 and 25 °C by a Sieverts apparatus (volumetric method) to obtain the CO_2 adsorption capacities. The results can be seen in Fig. 4.14 and corresponding CO_2 uptakes at both temperatures at 0.15 and 1.0 bar can be found in Table 4.6. It is intuitive that the CO_2 capacities at 0 °C are relatively higher than that at 25 °C, as a result of the reduced kinetic energy of CO_2 molecules at lower temperatures.

As mentioned before, all the samples display a type I isotherms and from the CO_2 isotherms, one can see a sharp adsorption uptake at the early adsorption stage in the low relative pressure region, suggesting that the carbon beads are mainly microporous materials. At atmospheric pressure, sample PR0 adsorbs 4.45 and 2.80 mmol CO_2 /g at 0 and 25 °C, respectively, being consistent with those reported elsewhere for phenolic resin derived carbons not modified by nitrogen treatments (Sun et al., 2013b). For better comparison, the CO_2 adsorption capacities measured at different temperatures and partial pressures are summarised in Table 4.6 while a comparison with those reported in the literatures for KOH activated carbons is presented in Table 4.7.



Fig. 4.14 CO₂ adsorption isotherms of samples PR0-PR4 series, tested at 0 and 25oC from 0.1 to 1 bar

As expected, all of the KOH-activated carbon bead samples showed substantially higher adsorption capacities at both temperatures, especially at relative low pressures. It was found that at the same activation temperatures, the adsorption capacity of PRACs increased with the KOH/AC mass ratios used in the chemical activation. However, no obvious correlation was found between the adsorption capacity and the surface area or porosity of the carbon samples derived from different conditions (Table 4.6), especially at lower CO_2 partial pressures.

~ .	KOH/AC mass —	CO ₂ capacity (mmol/g)				
Sample		0°C		25	°C	
	ratio	0.15bar	1.0bar	0.15bar	1.0bar	
PR0	0	1.52	4.43	0.79	2.78	
PR1_600	0.1:1	1.92	4.45	1.14	3.02	
PR1_700	0.1:1	2.07	4.77	1.23	3.17	
PR1_800	0.1:1	2.06	4.74	1.26	3.27	
PR2_600	0.3:1	2.06	3.95	1.38	2.97	
PR2_700	0.3:1	2.19	4.58	1.40	3.28	
PR2_800	0.3:1	1.83	4.25	1.12	2.91	
PR3_600	0.5:1	2.18	4.29	1.43	3.18	
PR3_700	0.5:1	2.33	4.59	1.51	3.35	
PR3_800	0.5:1	1.95	4.25	1.23	3.06	
PR4_600	1:1	2.16	4.78	1.36	3.35	
PR4_700	1:1	2.35	5.13	1.52	3.72	
PR4_800	1:1	2.00	5.07	1.25	3.47	

Table 4.6 CO₂ uptakes of PR-ACs at 0 and 25°C under 0.15 and 1.0 bar of CO₂ partial

pressures using BET ASAP 2420

At 25 °C and a CO₂ partial pressure of 0.15 bar, the original steam-activated sample (PR0), which has the highest surface area of 1128 m²/g and micropore volume of 0.43 cm³/g, adsorbed approximately only half of the amount of CO₂ adsorbed by the K-intercalated PR3_700 sample (1.51 mmol/g), which has a considerably lower surface area of 826 m²/g

and micropore volume of 0.32 cm³/g, highlighting the importance of potassium intercalation for enhanced CO₂ adsorption performance of the carbons. Similar phenomenon was also observed for other PRAC samples. For each series of samples obtained from using the same KOH/AC ratios in activation, the adsorption capacity of the activated samples at 800 °C was found to be lower than that of the samples activated at 700 °C, despite the higher surface areas of the activated samples at the higher activation temperatures. Similarly, samples activated at 600 °C showed a better performance than that at 800 °C with KOH/AC mass larger than 0.1:1. For all the KOH/AC mass ratios examined, the PRAC samples activated at 700 °C exhibit the best performance for CO₂ uptake.

adsorbents					
Materials	Precursor	S_{BET} (m ² /g)	Uptake at (mmol/	25 °C * /g)	Ref.
			0.15bar	1 bar	-
PC-2	Agaricus	1479	0.88	3.46	(Wang et al., 2012a)
KNC-A-K	P-diaminobenzene	614	1.81	4.04	(Zhao et al., 2012b)
IBN9-NCI-A	P-diaminobenzene	890	1.62	4.50	(Zhao et al., 2012c)
VR-93	Vacuum residue	2895	1.02	4.83	(Silvestre- Albero et al., 2011a)
CEM-750	N-doping carbon	3360	0.98	4.38	(Xia et al., 2011)
RFL-500	Resorcinol, formaldehyde and lysine	467	1.50	3.21	(Hao et al., 2010)
CSA-700	Poly (acrylonitrile- co-acrylamide)	1231	1.61	3.75	(Zhu et al., 2014)
PR3_700	Phenolic resin	826	1.51	3.35	This work

Table 4.7 Comparison on the adsorption capacities of PR3_700 and other carbon

* All results are measured by static volumetric method.

Although carbon beads derived from a nitrogen-free phenolic resin was deliberately used in this study in order to eliminate the effects of any other heteroatoms in the precursors, a comparison of the PRACs with the nitrogen-enriched carbons reported in the literature (Table 4.7) shows that the CO₂ adsorption capacities of our PRAC samples are overall comparable to the nitrogen-enriched carbons reported in literature, despite their significantly lower surface areas (hence potentially higher capacities on a volumetric basis) and the absence of nitrogen functionalities (Tables 4.5 and 4.7). More importantly, all the PRAC beads were measured as produced with desirable spherical diameters typically varying between 0.6 and 0.8 mm.

As already been described that although various AC adsorbents have been reported with high CO₂ adsorption capacities, most of the reported carbons were produced in powder forms via processes that often require sophisticated post-treatments, such as HNO₃ oxidation and/or NH₃ activation, leading to significantly increased production costs and reduced carbon yields. Further, carbons produced in fine powder forms cannot usually be used in moving-bed or fluidized bed reactors and will have to be further engineered via palletisation or granulation to form different types of shapes with required particle sizes, and this can sharply reduce the adsorption capacity and kinetics of the carbon adsorbents (Sun et al., 2013b).

As indicated in Table 4.8, the K intercalation treatment as a means to improve adsorption performance only has a relatively small impact on the mechanical strength of the carbon beads. The addition of 0.1 and 0.3 KOH mass ratio to the carbon beads only reduces the mechanical strength by ca. 10 and 20 %, respectively. This reduction is easily tolerated for fluidised bed operation given the high mechanical strength of the initial beads.

Sample	KOH/ AC mass ratio	Maximum Load (N)	
PR0	0	3.08	
PR1_700	0.1:1	2.86	
PR2_700	0.3:1	2.47	
PR3_700	0.5:1	2.21	
PR4_700	1:1	1.75	

Table 4.8 Mechanical strength of PRACs (activated at 700 °C)

One should also bear in mind that while the adsorption capacity on a weight basis is important in terms of the scale-up of the adsorption-based CO₂ capture process, the form and density of the activated carbons will also be critical, with the adsorption capacity on a volumetric basis instead ultimately determining the size and process efficiency of the adsorbent bed. Therefore, it is evident that the overall performance of the adsorbents will be a compromise between adsorbent materials having high surface area and microporosity while having sufficient density to maximize the volumetric adsorption capacity. To this end, the phenolic resin derived activated carbon beads from the present study are highly advantageous over the reported carbons, given their significantly lower porosity, higher bulk density (0.39 g/cm^3) and much easier-to-handle spherical forms for practical applications. Scaled-up production of these novel carbon bead adsorbents is underway in order to further evaluate their performance for CO₂ capture on a volumetric basis using a kg-adsorbent scale fluidized bed reactor (Zhang et al., 2014c).

4.3.2 Adsorption isotherms fitting using the dual-site Langmuir model

According to Myers and others (Krishna, 2012, Myers and Monson, 2002), absolute loadings are needed for thermodynamic processing such as isotherm fitting and adsorption enthalpy calculations, therefore the obtained excess CO₂ uptakes were converted to absolute uptakes by using Peng-Robinson equation of state (the original data can be seen in Appendix B.(1-13)) (Robinson et al., 1985, Robinson and Peng, 1978). For simplicity, Exc and Abs loadings are used to represent initial excess CO₂ uptakes and absolute uptakes respectively.

In this work, the dual-site Langmuir (DSL) equation was used to fit the adsorption isotherms of all PRAC samples as the one-site Langmuir equation is no longer applicable due to the surface heterogeneity of the carbon surface as a result of potassium intercalation (Mason et al., 2011, Herm et al., 2012). Indeed, recent investigations have proposed that DSL equation is a better model to fit the adsorption isotherms of carbons with high surface heterogeneity (Ben et al., 2012, Mahurin et al., 2014). The DSL equation (4.1) can be expressed as follows:

$$q = \frac{q_{s,A} \times b_A \times P}{1 + b_A \times P} + \frac{q_{s,B} \times b_B \times P}{1 + b_B \times P}$$
(4.1)

Where $q_{S,A}$ and $q_{S,B}$ are the mono-layer capacity of site A and B, b_A and b_B are the adsorption equilibrium constants for site A and B. During the fitting of isotherms, one must note (Lu et al., 2013):

1) use absolute adsorption capacities;

2) $q_{S,A}$ and $q_{S,B}$ should be kept constant at all temperatures to fulfil their physical meanings;

3) b_X (X=A or B) usually decreases with increasing adsorption temperature and is related to a temperature-independent constant, $b_{0,x}$ by the Arrhenius equation (4.2).

$$b_x = b_{0,x} exp(\frac{E}{RT}) \tag{4.2}$$

In Eqn. 4.2, E can be used to indicate the average adsorption heat. Since the fitted isosteric heat of adsorption was obtained as a function of adsorbed CO_2 in which case Q_{st} represents the average of all adsorption sites that can be potentially occupied at a certain coverage level (McDonald et al., 2011, Mathias et al., 1996), the calculated heat of adsorption corresponds to the values at initial coverage (at a CO_2 uptake level of 0.01 mmol/g). However, it is noteworthy that the calculated adsorption heat may differ from the isosteric heat (Q_{st}) of adsorption, but the difference should be quite small (Mathias et al., 1996).

After plotting with the absolute loadings, we fit the curves from dual-site Langmuir isotherm equation for all the samples at 0 and 25 °C, which can be seen in Fig. 4.15 (0 °C) and Fig. 4.16 (25 °C). The results show that the fitted curves agree very well with the experimentally measured value (shown as dots in the Figs. 4.15-4.16). The parameters such as $q_{S,A}$, $q_{S,B}$, b_A and b_B and standard error for each plotting can be found in Appendix C.



Fig. 4.15 CO₂ adsorption isotherms of the carbon beads at 0 $^{\circ}$ C (symbols represent the measured values and lines are the fitted values with the dual-site Langmuir isotherm equation)



Fig. 4.16 CO_2 adsorption isotherms of the carbon beads at 25 °C (symbols represent the measured values and lines are the fitted values with the dual-site Langmuir isotherm equation)

4.4 The role of intercalated potassium in CO₂ adsorption

The results in the previous sections demonstrate that K intercalation can significantly improve the CO₂ adsorption performance of the phenolic resin derived carbon beads. It can be reasonably assumed that the increased CO₂ adsorption capacity arose from either increased micro-porosity or modified surface chemistries or a combination of both. As Table 4.5 indicates, however, a considerable decrease rather than an increase in surface area and microporosity was observed for all the K intercalated carbon samples under the conditions used, despite the washing with excessive quantities of de-ionised water. This suggests that the improved CO₂ adsorption of the PRACs cannot be accounted for by the surface textual properties but by the modified surface chemistries. It has been well established that KOH activated carbons are usually enriched in different surface oxygen functionalities (Bleda-Martínez et al., 2005, Pandolfo and Hollenkamp, 2006, Frackowiak, 2007), but the presence of the surface functionalities alone is not sufficient to explain the significant increase in CO₂ capacities according to the results reported elsewhere (Drage et al., 2009b, Zhu et al., 2014). It is therefore considered that the intercalated K is responsible for the enhanced CO₂ adsorption performance of the PRACs. To provide further insight, an exhaustive Soxhlet extraction at 100 °C with deionised water as the solvent was used to remove the intercalated potassium in the PRAC samples to different levels. This was used to evaluate the variation of CO₂ adsorption with different levels of potassium intercalation and hence to determine the minimal content of intercalated potassium that is required to achieve appreciable improvement in CO₂ adsorption. One of the PRAC samples, the PR3_700 which exhibited the highest CO₂ capacity at 25 °C and a CO₂ partial pressure of 0.15 bar, was selected for the exhaustive Soxhlet extraction for different extraction times. The samples produced from different

periods of extraction were then subjected to CO₂ adsorption tests and other characterisation.

Table 4.9 summaries the textural properties of the extracted samples and their CO₂ adsorption capacities measured at both 0 and 25 °C and a CO₂ partial pressure of 0.15 bar. As expected, the amount of K present decreased with increasing extraction time and after 20 hours extraction, the potassium content was reduced from 9.25 % to only 0.57 % on a weight basis. As can be seen from Table 4.9, the BET surface area of the carbon sample increased considerably with increasing removal of the intercalated potassium from the carbons, particularly at the early stages of Soxhlet extraction. This confirms that the lower surface areas obtained for the PRAC samples (Table 4.5) was due to the potassium intercalation which led to partial or even complete occlusion of micropores.

Measurements of CO₂ adsorption capacity before and after the Soxhlet extraction, presented in Table 4.9 and Fig. 4.17, demonstrate that the capacity shows no significant change with decreasing residual potassium content from *ca*. 9.2 to 2.8 wt%, but a sharp decrease was observed when potassium content was further reduced to below 1 wt%. It appears that there is a critical concentration of potassium above which the excess residual potassium contributes little to CO₂ adsorption capacity. It can be reasonably assumed that the hard-to extract residual quantities of K are deeply intercalated into the fine carbon structure in the form of extra-framework K⁺ cations. Previous investigations (Liu et al., 2012, Zhao et al., 2012b) showed that stronger CO₂ adsorption sites of zeolite, MOF adsorbents reside predominantly around unsaturated framework metal cations. Therefore, it is believed that the significantly improved CO₂ adsorption as a result of the intercalation of K cations is due to the involvement of stronger electrostatic forces created by the exposed framework K⁺ ions on the surface, with the strength of the electrostatic interaction being determined by the surface density and nature of the extra-framework K^+ ions, an adsorption mechanism similar to that observed for the MOF-based CO₂ adsorbents (Liu et al., 2012, Zhao et al., 2012b). Indeed, strong electrostatic properties were observed in handing the PRAC samples which were found to be easily attached to the interior surface of the sample cell and showed appreciable repulsion behaviour between different PRAC carbon beads while similar phenomena were not observed for the parent carbon beads.

It is very likely that the strong electrostatic interaction may lead to the formation of labile carbonate-like complexes upon CO₂ adsorption around the extra-framework cations (Martin-Calvo et al., 2014). As highlighted in the following cyclic adsorption/desorption tests in dry gas conditions, the enhanced CO₂ adsorption of the PRACs, does not require the participation of water or moisture in the adsorption process unlike the K₂CO₃-based adsorbents where the presence of significant quantities of moisture in the gas stream is essential to the CO₂ adsorption (Lee et al., 2008).



Fig. 4.17 The influence of K concentration (determined by ICP) on the CO₂ capacities for deionised water extracted samples from PR3_700

Sample	$S_{BET} (m^2 g^{-1})$	K wt%	CO ₂ capacity at 0.15bar (mmol/g)	
			0 °C	25 °C
PR3_700_1.5h	892	9.25	2.18	1.36
PR3_700_2.5h	984	2.79	2.16	1.34
PR3_700_4.0h	1053	0.96	2.15	1.32
PR3_700_20h	1074	0.57	1.91	1.08
PR0	1128	< 0.01	1.54	0.80

Table 4.9 Characterization results for the extracted samples from PR3_700 (K concentrations determined by ICP)

4.5 Conclusions

The use of potassium intercalation via relatively mild KOH activation has been investigated as a novel effective means to boost the adsorption performance of activated carbons for post-combustion carbon capture. A nitrogen-free phenolic resin derived spherical carbon material with desirable spherical diameters (0.6~0.8 mm) which is suitable for direct practical applications without further palletisation or granulation treatment has been used so that the enhanced CO₂ adsorption achieved by potassium intercalation could be delineated from any other effects. The results demonstrated that the intercalation of K significantly increased the CO₂ capacity of the AC beads by a factor of up to 2 at 0.15 bar CO₂ partial pressure while the effects of potassium intercalation on the mechanical strength and morphological features of the carbon beads were small at KOH/AC mass ratios of ≤ 0.3 .

The results suggest that the enhanced CO_2 adsorption of potassium-intercalated carbons, is closely related to the formation of carbon framework or extra-framework K⁺ cations, which can lead to the potential formation of $K^{\delta^+}-O^{\delta^-}$ zwitterion-like structures that can boost the electrostatic interaction of the carbon surface with CO₂. In addition, there appears to be a low critical K concentration, which is not much more than *ca*. 1 wt% in the case of the carbon beads examined, below which the beneficial effect of K intercalation on CO₂ adsorption becomes negligible. The results also demonstrate that due to the mild KOH loadings, the K-intercalated carbons with KOH/AC mass ratio lower than 1:1 showed relatively high methanical strength.

The significantly increased CO₂ adsorption capacity, fast kinetics and good mechanical strength augurs extremely well that the PRAC adsorbents could provide a sound alternative to the most studied polyethyleneimine-based sorbents for improved energy penalty of post-combustion capture using low temperature solid adsorbent looping technology.

CHAPTER 5 Factors other than adsorption that affect the adsorption performance of PRACs for pulverised fuel CO₂ postcombustion capture

In the previous chapter, K-intercalated carbon beads derived from phenolic resin have shown high CO_2 capacity at low CO_2 partial pressure, indicating potential applications for post combustion carbon capture. This has already changed the traditional image of activated carbon materials that are considered as a preferable candidate for carbon capture at high pressures. However, it is of great importance to take other essential factors that could affect the adsorption performance for the PRACs in industrial application. In this chapter, determinants other than adsorption that also play important roles of an adsorbent candidate for practical application for carbon capture were investigated, in terms of kinetics, cyclic performance (life time), heat of adsorption, specific heat, and the influence of moisture. Additionally, the heat capacity and regeneration heat of PRACs as well as the impact of moisture on the CO_2 uptakes have been fully investigated.

5.1 Adsorption kinetics study of phenolic resin-based adsorbents

The rate of adsorption has always been considered as an important parameter to evaluate an adsorbent as fast kinetics enables maximised CO₂ capacity within a limited gas-solid contact time for practical application (Abanades et al., 2004). Another promising adsorbent with fast kinetics, PEI/silica (with 40 % PEI loading), which is a chemical adsorbent, was chosen for comparison. To analyse the adsorption kinetics, a few parameters are defined as follows:

t_x: Time when the CO₂ adsorption capacity achieved x % of equilibrium CO₂ capacity; where x= 30, 60, 90, 95;


Fig. 5.1 CO₂ adsorption isotherm for (a) PEI/Silica, (b) PR0 and PR3_700 with a display of adsorption time when the CO₂ capacity reached 30 %, 60 %, 90 %, 95 %, under 15 % CO₂ atmosphere

Fig. 5.1 has illustrated the CO₂ adsorption isotherm in the initial 10 mins for 40% PEI/Silica, PR0 and PR3_700 under 15 % CO₂ and 85 % N₂. Also t_{30} , t_{60} , t_{90} , t_{95} were clearly displayed in the plot at the corresponding CO₂ capacities. The details of adsorption time of relevant adsorption capacity for PEI/silica, PR0 and PR3_700 under

different CO₂ concentrations can be found in Table 5.1. The initial adsorption stage for PEI/Silica was fast, as indicated by that it took only 2.94 min to adsorb 90 % of equilibrium CO₂ capacity. However, it took a much longer time, *i.e.* 5.54 min, for PEI/Silica to adsorb from 90 % to 95 % of CO₂ capacity, which can be explained by the nature of chemical adsorption (Wang et al., 2012b). If we compare PEI/Silica with PRO, it can be found that PRO demonstrated a first-order trend at entire adsorption stage, with a similar adsorption time as PEI/Silica from 0- 90 %, but a much faster kinetics from 90 % to 95 % of CO₂ capacity. After surface modification with K species, PR3_700 depicted a very interesting result as the adsorption behaviour was more "chemical", indicated by the fact that it took 4.96 and 22.38 min to achieve 90 % and 95 % of CO₂ capacity. This can be explained by that the surface chemistry has been changed due to the formation of the K^{δ+}–O^{δ-} zwitterion-like structures. The adsorption of PR3_700 revealed a combination of physical adsorption contributed by microporous structure and "chemical" adsorption through interaction between –OK groups and CO₂ molecules which needs higher reaction energy than pure physical adsorption.

Sample	Adsorption time under 15 % CO ₂				Adsorption time under 100 % CO ₂			
	(min)			(min)				
	t ₃₀	t ₆₀	t90	t95	t ₃₀	t ₆₀	t 90	t95
PEI/Silica	0.57	0.98	2.94	8.48	0.63	1.01	2.40	6.64
PR0	0.53	0.98	2.41	3.44	0.40	0.73	1.86	2.51
PR3_700	0.29	0.75	4.96	22.38	0.48	0.81	2.01	2.85

Table 5.1 Comparison of adsorption time for 40 % PEI/Silica and PR samples

On the contrary, with higher CO₂ concentration, both PR0 and PR3_700 showed a much faster kinetics than PEI/Silica under 100 % CO₂. For instance, PR0 and PR3_700 achieved 95 % of total CO₂ capacity within 2.51 and 2.85 min respectively, while

PEI/Silica took 6.64 min to achieve the same level. This phenomenon was due to that under high CO₂ concentration, physical adsorption played a dominant role for PR3_700, whereas –OK species are more sensitive under low CO₂ partial pressure.

Although the introduction of –OK surface groups slows the adsorption kinetics as a compromise for much enhanced CO₂ uptakes under low CO₂ partial pressure, the PR3_700 material still presented a fast and comparable kinetics to PEI/Silica. For example, and PR3_700 could achieve 90 % of equilibrium CO₂ capacity within 5 min. Actually, the working capacity, rather than equilibrium capacity is more important for practical application because of limited gas-solid contact time (Zhang et al., 2014a).

5.2 Cyclic adsorption/desorption and stability testing of phenolic

resin-based adsorbents

Good stability, regenerability and long lifetime are indispensable factors to determine a potential solid adsorbent. Before multi-cycle testing of sample PR3_700, we have investigated the optimal adsorption temperature of the materials under both 15 % and 100 % CO₂ atmosphere with a slow heating rate (0.2 °C/min) method which ensures the PR3_700 reaches equilibrium capacity at every individual temperature. The results can be seen in Fig. 5.2. According to Fig. 5.2, after potassium intercalation, when temperature increases from 25 to 150 °C, the CO₂ uptakes of sample PR3_700 present an almost linear inverse proportion relationship with the temperature at both atmospheres. The optimal adsorption temperature for PR3_700 is shown as 25 °C.



Fig. 5.2 Slow heating adsorption for sample PR3_700 at both 15% and 100% CO2

Fig. 5.3 presents the adsorption/desorption characteristics of one of the K/AC samples (PR3_700) obtained from TGA at a temperature of 25 °C and a CO₂ partial pressure of 0.15 bar (N₂ balance). As shown in Fig.5.3 (a), a final equilibrium CO₂ adsorption capacity of 1.9 mmol/g is obtained with approximately 90 % of the equilibrium capacity achieved in 5 minutes under the TGA test conditions. Notably, the CO₂ capacity tested by TGA is higher, if we compare this value with that tested by BET ASAP 2420 (1.51 mmol/g for sample PR3_700 at 25 °C under 0.15 bar CO₂ partial pressure), which can be explained by that TGA is a dynamic testing process which detects the mass change lively while the method applied in BET ASAP 2420 is a static volumetric method. This highlights the high capacity and fast adsorption kinetics of the PRAC beads, although it takes a slightly longer time for the PRACs to reach equilibrium adsorption compared to the parent ACs. Fig. 5.3 (b) shows the cyclic adsorption/desorption testing results under 15 % CO₂ concentration for the PR3_700 carbon bead sample. The cyclic life-time performance testing demonstrates the excellent reversible adsorption performance of the

K-intercalated carbon beads, despite the slight decrease in CO_2 capacity in the first 5 cycles, which appears to be attributable to the irreversible CO_2 adsorption on non-intercalated potassium species (as shown by bright red spots in Fig. 4.10(b)) in the dry flue gas conditions. The CO_2 capacities for the first and 50th cycle are 1.92 and 1.68 mmol/g respectively, revealing that the CO_2 uptake can maintain 87.5% compared with initial cycle.





Fig. 5.3 (a) The CO₂ adsorption curve of PR0 and PR3_700; (b) 50 cycles of the adsorption and desorption for PR3_700; both under an atmosphere of 15 % CO₂ and 85 % N_2 at 25 °C.

Additionally, we have also tested the CO₂ adsorption behaviour of sample PR3_700 under 100 % CO₂ concentration, as shown in Fig. 5.4. As expected, owing to higher CO₂ concentration, PR3_700 can adsorb 3.21 mmol/g for the first cycle, compared to the CO₂ capture capacity of 2.82 mmol/g for PR0. Similarly, PR3_700 demonstrate minor reduction of CO₂ capacity with an even more excellent regenerability of 98.8 % over 50 cycles at 100 % CO₂ concentration at 25 °C. More specifically, the CO₂ uptake for sample PR3_700 can still maintain 3.17 mmol/g, compared with the starting value of 3.21 mmol/g. However, the CO₂ capacity of the sample under 100 % CO₂ partial pressure did not benefit from potassium incorporation as much as that under lower CO₂ concentration (15 % CO₂), which further validate that the surface chemistry plays an more important role in adsorption behaviour at relatively low CO₂ concentration.



Fig. 5.4 50 cycles of the adsorption and desorption for PR3_700 under an atmosphere of 100% CO₂ at 25 $^{\circ}$ C

Apart from overall stability in multi-cycle tests, the regeneration energy needs to be considered in order to evaluate the efficiency and cost-effectiveness of the PRAC samples as CO₂ adsorbents. The required regeneration heat for potential industrial application and comparison of energy required with commercial MEA will be thoroughly discussed in the following chapter.

5.3 Measurement of heat of adsorption and specific heat capacity

Heat of adsorption is an important thermodynamic parameter for describing the adsorption behaviour of an adsorbent and evaluating the energy performance of a process of adsorption and desorption, such as the pressure swing and temperature swing gas separations. Isosteric heat of adsorption (Q_{st}) can be used to indicate the surface affinity

of an adsorbent towards an adsorbate. It is usually estimated by using the Clausius– Clapeyron equation:

$$Q_{st} = -RT^2 \left[\frac{\partial \ln P}{\partial T}\right]_q \tag{5.1}$$

Where R represents specific gas constant; q stands for the adsorption capacity and T, P is the temperature and pressure, respectively. By fitting the obtained experimental isotherms at different temperatures with isotherms equations, one can acquire the pressure (P) needed to reach the same adsorption capacity (q) at different temperatures (T), and then Q_{st} can be calculated by fitting the Clausius–Clapeyron equation.

Fig. 5.5a illustrates the calculated Q_{st} for both the parent and KOH-intercalated carbon beads at a CO₂ uptake level of 0.01 mmol/g. Generally, except sample PR4_800, a considerable increase in isosteric adsorption heat was observed for all K-intercalated carbon bead samples comparing with the parent carbon beads (PR0). For instance, the calculated isosteric adsorption heat of K-intercalated PR1 and PR3 series carbons increased by up to 60 % to *ca.* 36-42 kJ/mol CO₂ from 26 kJ/mol CO₂ for the parent carbon beads (PR0), respectively. This highlights the effectiveness of K intercalation in improving the surface affinity of the carbons for CO₂ adsorption particularly at low CO₂ partial pressures.



Fig. 5.5(a) Fitted isosteric adsorption heat at a CO_2 uptake level of 0.01 mmol/g for all the carbon beads; (b) Fitted isosteric adsorption heat of PR0 and PR3 series as a function of absolute CO_2 loading using dual-site Langmuir model

Isosteric adsorption heat is also used to indicate the degree of surface heterogeneity of the adsorbent or different interactions between adsorbent and adsorbate. For energetically heterogeneous surfaces, the isosteric heat of adsorption will decrease with increasing quantities of adsorbed substances due to the occurrence of different types of active adsorption sites. Fig. 5.5(b) shows the isosteric adsorption heat both for the parent (PR0) and K-intercalated carbons (PR3 series) at different CO₂ uptake levels. The calculated isosteric adsorption heats are by and large close to the upper range of the reported adsorption heats for carbon-based adsorbents (Bansal and Goyal, 2010, Himeno et al., 2005, Shen et al., 2010). While higher isosteric adsorption heats were obtained for all PRACs, the variation of isosteric heat of adsorption with the quantities of CO₂ adsorbed is much higher for the PRACs than for the initial carbon beads with the isosteric adsorption heat remaining relatively constant. This demonstrates that the porous surface of the K-intercalated carbons becomes energetically much more heterogeneous, being indicative of the incorporation of new active adsorption sites (Fig. 4.12) that led to higher interaction energy of CO₂ with the surface.

In order to validate the calculated isosteric heat of adsorption with the dual-site Langmuir model, TGA-DSC has been used to experimentally measure the adsorption heat of the carbon beads. Given that the measured value by TGA-DSC represents the averaged adsorption heat integrated from the DSC heat flow corresponding to the adsorption capacity of a carbon adsorbent, the following equation (5.2) (Bülow et al., 2002) was used to derive the integral adsorption heat values from the isosteric heat of adsorption. The integral adsorption values correspond to the defined ranges of sorption-phase concentration from 0 to n, where n equals to the equilibrium CO₂ adsorption capacity obtained by TGA-DSC in a calorimetric analysis.

$$Q_{int} = \frac{1}{n} \int_0^n Q_{st} \, dn \tag{5.2}$$

The calculated adsorption heat was then validated by the adsorption heat experimentally measured by TGA-DSC. As shown in Table 5.2, the measured and calculated adsorption heats for the original steam-activated carbon beads are almost identical while for the K-

intercalated carbons, the calculated adsorption heat values appears to be slightly lower by 1~6 kJ/mol CO₂, compared to the values measured by TGA-DSC. The good agreement obtained between the calculated and measured adsorption heat for most of the carbon bead samples confirms the suitability of the DSL modelling for evaluating the adsorption behaviour of surface-modified carbons.

	and measured DSC near of	adsorption
Sample	Analytical integral heat of	Experimental measured heat of
	adsorption by DSL model (kJ/mol)	adsorption by TG-DSC
		(kJ/mol)
PR0	26.0	26.7
PR1_600	34.1	33.9
PR1_700	36.9	39.7
PR1_800	30.6	33.7
PR2_600	35.6	38.2
PR2_700	31.4	35.1
PR2_800	29.6	33.0
PR3_600	33.3	38.8
PR3_700	33.3	35.5
PR3_800	32.4	34.2
PR4_600	33.2	34.9
PR4_700	31.6	34.7
PR4_800	25.3	31.3

 Table 5.2 Comparison between analytical integral heat of adsorption by DSL model

 and measured DSC heat of adsorption

The specific heat capacity of a targeting sorbent plays an essential role in the process design for the calculation of, which includes, on one hand, the heat demand in the regenerator; on the other hand, the heat flux in the heat exchangers for recycling the sensible heat contained in the hot sorbent. One main advantage of solid adsorbent to traditional liquid amine, for instance MEA, lies in that the sensible heat will be largely decreased because of the absence of water in the solvent systems (Yokoyama, 2012). Carbon materials, usually present a relatively low heat of capacity (less than 1.0 J/g·K) (DeSorbo and Tyler, 1953, Kano et al., 1997, Hepplestone et al., 2006) over a temperature range between room temperature and 120 °C, which is ideal for carbon capture regarding to regeneration heat. Hence, it is interesting to investigate how K intercalation would

affect the heat capacity of PRAC samples, compared with the raw carbon beads. The general results are displayed in Fig. 5.6. As expected, raw sample PR0 demonstrate an average heat capacity of around 0.96 J/g·K over temperature range between 30 and 130 °C, which agrees with the values that are reported in the literature for activated carbons. However, after mild KOH treatment, even with greatly increased CO₂ capacities, the heat capacities for all other PRAC samples maintained low values (within 20 % of increase compared to PR0) except sample PR3_600. This can be explained by that heat capacity is considered as the instinct feature of the material, although after KOH treatment, there are intercalated K, the matrix of PRACs are still carbon.



Fig. 5.6 Average heat capacity of PR0 and PRAC samples after KOH treatment (over temperature range of 30-130 °C)



Fig. 5.7 DSC measurement of heat capacity for sample PR3 series and comparison with PR0

The DSC measurements of heat capacity of PR0 and PR3 series activated at different temperatures can be seen in Fig. 5.7. For sample PR0, the heat capacity barely changes with the temperature; on the other hand, the heat capacities for PR3 samples tend to increase as temperature increases. Take PR3_700 for an example, the heat capacity from 30 to 130 °C, has risen from around 1.00 to 1.19 J/g·K. To summarise, that the PRAC beads developed in this study have maintained the low specific heat capacity after K intercalation.

5.4 The effect of moisture on adsorption behaviours

Flue gas streams generated from fossil-fuel fired power plants do not only contain CO_2 , but also many other components, as shown in Table 5.3 (Drage et al., 2012). Among all the impurities, H₂O accounts for a comparative value to that of CO_2 . It is essential that the adsorbent candidate is capable of showing high capacity as well as selectivity for CO₂ in the presence of significant amounts of moisture in the flue gas. According to the literature (Wang et al., 2008b, Samanta et al., 2011), as a typical physical adsorbent, ACs usually exhibit low selectivity as a result of the competitive adsorption of water, which may negatively affect the CO₂ capacity. Moreover, with existence of moisture, the surface of ACs can be oxidised gradually, leading to a decrease of CO₂ adsorption capacity (Choi et al., 2009). However, the above are based on activated carbon materials without surface modifications. As is known, the ACs reported in this work have been incorporated with potassium intercalation, which has enhanced the surface affinity of adsorbents with CO₂ molecules and hence, the adsorption mechanism has become more "chemical". Would potassium intercalation positively affect the CO₂ capacities of PRACs? In this section, the moisture adsorption, the effect of moisture on PRACs and the adsorption kinetics of moisture and CO₂ will be investigated.

Table 5.3 Example flue gas composition from coal and gas combustion (values are quoted as vol% unless otherwise stated) (Drage et al., 2012)

Component	Coal ^a (no FGD/DeNO _x)	Coal (after FGD/DeNO _x)	Natural Gas
N ₂	75-80%	75-80%	74-80%
CO ₂	12-15%	12-15%	3-5%
SO ₂	1800 ppm	10-70 ppm	<10ppm
NO _x	500 ppm	50-100 ppm	50 ppm
H ₂ O	5-7%	5-14% ^b	7-10%
O ₂	3-4%	3-4%	12-15%
CO	<100 ppm - occasionally	<100 ppm - occasionally	<5 ppm
	5000 ppm	5000 ppm	
Hg/As	ppb	ppb	0
Particulates	10-20 mg Nm ³	10-20 mg Nm ³	Not present
Pressure	0.1	0.1	0.1
CO ₂ partial pressure	0.012-0.015	0.012-0.015	0.005-0.01
(MPa)			

a Based on a medium to high sulphur coal. *b* The moisture content of post FGD flue gas will depend on whether a wet or dry technology is used. Wet FGDs (such as the common limestone/gypsum technology) typically produce a flue gas at outlet with between 10-14 vol% H₂O.

5.4.1 Modification of TGA to introduce moisture

In order to test the moisture uptake dynamically using TGA, the instrument has been modified by extending the gas line to bypass the moisture generator before contacting the sample in the furnace. The flow diagram can be seen in Fig. 5.8 (a), while the layout of modified instrument can be found in Fig. 5.8 (b).





Fig. 5.8 (a) the flow diagram of designed moisture introduction into TGA; (b) the layout of modified TGA with moisture

As shown in Fig. 5.8, basically the gas line has been separated into two flow directions, when the three-way valve points to right (white gas line), the gas will go directly to the furnace as normal; however, when the valve points to left (black gas line), the gas will be bypassed through a moisture generator for which the temperature could be controlled by the water bath. To avoid the moisture condensation, a heated line was also added from the exit of moisture generator to the entrance of furnace. The calibration has been carried out and the results displayed in Table 5.4 have illustrated fairly stable moisture contents from 3 to around 17 vol % at the temperature range of the water bath between 30 to 60 $^{\circ}$ C.

Sample	Duration (h)	Temp of water bath (°C)	Temp of heated line (°C)	Calculated moisture (vol %)	Average moisture content (vol %)
	0.5			2.81	
01	1.0	30	50	3.01	
	0.5			3.08	
02	1.0	30	50	3.08	3.00
03	0.5	40	60		
05	1.0	40	00	4.97	5.27
04	0.5	40	60	5.36	
04	1.0	40	00	5.36	
	0.5			8.41	
05	1.0	50	70	10.93	
	0.5			8.41	
06	1.0	50	70	8.78	9.67
	0.5			18.51	
07	1.0	60	80	15.30	
	0.5			19.77	
08	1.0	60	80	16.32	17.48

Table 5.4 Moisture calibration using modified TGA

5.4.2 Moisture uptake

The hydrophobic nature of activated carbon materials decides that the adsorption of water vapour in the flue gas should be taken into consideration for post combustion CO_2 capture (Choi et al., 2009). Plaza et al. (Plaza et al., 2014) have investigated the influence of water vapour on CO_2 adsorption using a biomass-based carbon and found out that although water vapour could be co-adsorbed, the CO_2 capacity was not decreased. However, it is still of great importance to study moisture uptake as a result of the high energy consumption for moisture evaporation during regeneration process. In this section,

the moisture uptake and its competition with CO₂ adsorption for PRAC samples will be discussed.



Fig. 5.9 Water vapour adsorption isotherm for sample PR0 and PR3_700 at 25 $^{\circ}$ C and a moisture content of 9.67 vol% in N₂ at ambient pressure

There are many reports addressing the influence of water on CO₂ adsorption for activated carbon materials. For instance, Wang and his colleagues (Wang et al., 2008b) had found that compared with activated carbons with mesoporous structure, the CO₂ capacities of microporous activated carbons were more negatively influenced due to more severe water adsorption. However, this phenomenon does not suit the case of PRACs samples. The candidate sample PR3_700 has a well-developed microporous structure (details can be found in Chapter 4, Table 4.5) with a surface area of 826 m²/g and around 94 % of microporosity (the ratio of micropore volume to total pore volume). On the other hand, before KOH treatment, sample PR0 has an even higher surface area (1128 m²/g) as well as microporosity of 96 %. Actually, if we look at the curve of water adsorption for both sample PR0 and PR3_700 is a lot faster than sample PR0. More specifically, after

moisture was introduced for 5 mins, the adsorbed moisture for PR0 and PR3_700 is 3.8 and 11.5 wt% respectively, revealing that PR3_700 is more sensitive to moisture. It is well known that the interaction between the carbon surface and water molecules is relied on the hydrogen bonding. The adsorption of moisture for activated carbons usually happens where oxygen groups behave as the first adsorption sites for water molecules by hydrogen bonding, followed by adsorption of more water molecules by hydrogen bonds supplied by adsorbed water molecules as second sites. And then, due to the increase of water vapour pressure, water clusters will be formed followed by capillary condensation in micropores (Dubinin, 1980, Rodriguez-Reinoso et al., 1992, Qi and LeVan, 2005). As a result, the reason of higher adsorption kinetics of PR3_700 can be possibly ascribed by the increasing surface functional groups of –OK species, which offer more adsorption sites to accomplish the interaction between oxygen and hydrogen. This phenomenon agrees with the theory previously proposed by Rodriguez-Reinoso et al. that the surface chemistry of the carbon, rather than microporosity, plays the dominant role on the water adsorption when relative pressure is below 0.3 (Rodriguez-Reinoso et al., 1992).

As to investigate the influence of water content on the kinetics of moisture adsorption, we have applied a wild range from around 3 to 17.48 vol% (shown in Fig. 5.8) on sample PR3_700. The water content was controlled by changing the temperature of water bath (as detailed in Table 5.3).



Fig. 5.10 The influence of water vapour on the water adsorption for sample PR3_700 at 25 $^{\rm o}C$ in N_2

According to Fig. 5.10, it is obvious that the relative pressure of moisture has a direct proportional relationship with the water uptake at room temperature. More specifically, as marked in Fig. 5.10, the water uptakes for PR3_700 at different water contents, *i.e.*, 3.00, 5.27, 9.67, 17.48 vol% are 1.25, 1.58, 1.65 and 2.08 wt% at 1st min and 7.47, 8.52, 9.28, 10.22 wt% at 5th min, respectively. Although after about 30 mins, regardless of initial water content, all of the samples reach similar equilibrium capacity of about 26 wt% (not shown in the fig). However, in reality, only the water uptakes in the first few minutes are of great interest as the PRACs would have a limited residence time in the order of a few minutes in the adsorber. If we compare the dynamics of water and CO₂ adsorption, as shown in Fig. 5.11, the CO₂ adsorption is much faster than that of moisture. For instance, at 1 min, the adsorption of CO₂ for sample PR3_700 is 22 % higher than that of water adsorption. Both of the adsorption for water and CO₂ reaches the same value of 6.5 wt% at 2.25 min, and water uptake surpasses CO₂ uptake afterwards. As both CO₂

adsorption and moisture adsorption affect the regeneration heat, a good balance between CO_2 capacity and moisture adsorption needs to be achieved in order to minimise the regeneration heat. Options to realise the balance include increasing the hydrophobicity of adsorbents, restricting the residence time and so on.



Fig. 5.11 Dynamic weight uptake of both CO₂ and H₂O adsorption in the initial 5 mins for PR3_700 in 15% CO₂, 85% N₂ on the dry basis and 9.67 vol% of water vapour

5.5 Calculation of regeneration heat

The regeneration energy, which is one of the most important criteria in terms of practical applications, needs to be considered in order to evaluate the efficiency and cost-effectiveness of the PRAC samples as CO_2 adsorbents. As is known, the most mature aqueous amine based absorbent has been criticised as a result of the high energy penalty, that could lower the power generation efficiency of the power plant by around 10 % (Rao et al., 2006). The regeneration heat for the typical aqueous amine based absorbent was about 3.9-4.2 GJ/tonne CO_2 (Chapel et al., 1999, Abu-Zahra et al., 2007), but the state-

of-art advanced MEA capturing system with optimised process design could reduce the regeneration heat to a value of 3.3 GJ/tonne CO₂ (Veneman et al., 2013), which is used as a benchmark for the evaluation of the performance of the PRACs.

The required regeneration energy of a solid adsorbent is the sum of the sensible heat that is required to heat the adsorbent from the adsorption temperature to the regeneration temperature and the latent heat (heat of adsorption) that is required to overcome the bonding energy to remove CO_2 from the adsorbent in the desorption process and last but not least, the latent heat contributed by the vaporisation of water that is contained in the solvent or adsorbed by the adsorbent materials (Zhang et al., 2014a). The formula (5.3) of calculation of regeneration heat can be found as follows:

$$Q_{r} = \frac{1-\alpha}{q_{w}} C_{p,s} \left(T_{de} - T_{ad} \right) + \left(1 - \beta \right) \Delta H_{a} + (1 - \gamma) \frac{Q_{v} f_{H20}}{q_{w}} \quad (5.3)$$

Qr (kJ/kgCO₂): regeneration heat;

- α : recovery ratio of sensible heat;
- β : recovery ratio of heat of adsorption;
- γ : recovery ratio of vaporisation heat;
- $q_w(wt\%)$: working capacity of the adsorbent;
- $C_{p,s}$ (kJ/kg·K): specific heat capacity of the adsorbent;
- $T_{de}(K)$: desorption temperature;
- T_{ad} (K): adsorption temperature;
- ΔH_a (kJ/kgCO₂): heat of adsorption;

Q_v (kJ/kgCO₂): vaporisation heat of water (2257.6 kJ/ kg under ambient pressure);

 f_{H2O} : mass fraction of moisture which was adsorbed simultaneously with CO₂ adsorption

and has to be evaporated at desorption temperature;

From the above equation one can see that there are many variables that can affect the value of regeneration heat. Those variables can be divided into three categories; one is the distinct parameters that depend on the physical properties of the adsorbent materials, such as $C_{p,s}$ and ΔH_a ; while the second one is related with process design, such as α , β and T_{de} , T_{ad} and so on; and thirdly, parameters that are relevant with both distinct parameters and physical properties, for example, q_w and f_{H20} .

5.5.1 Preferences of heat recovery fractions α , β and γ

Heat recovery fractions α , β and γ represent thermal energy recovered from sensible heat, latent heat and vaporisation heat that are all process design related parameters. There are few literatures discussing how to determine the percentage in terms of carbon materials, however, as to make synthetic comparison with the benchmark advanced MEA, to simplify here, we employed the same values of α and γ as calculated in advanced MEA system reported elsewhere (Veneman et al., 2013). To be more specific, α and γ refer to 0.75 and 0.5 respectively. β for MEA and carbons are different because the adsorption temperature varies from around 75 °C for MEA to 25 °C for carbons respectively. Hence, β that we applied for MEA was 0.25 and 0 for carbons as the recovery ratio of heat of adsorption for carbon materials are low grade.

5.5.2 Working capacity q_w

The difference between equilibrium capacity and working capacity can be explained by that the former is obtained when the CO_2 adsorption for a specific adsorbent reaches equilibrium, normally without extra weight uptake with time extensions; on the other

hand, for practical application, there is not enough time for adsorbents to reach equilibrium because the adsorbents will be circulated in cycles between adsorber and desorber, in which case, working capacity is the actual CO_2 uptakes in reality. Working capacity q_w equals the value that the reduced CO_2 loading from the end of adsorption to desorption. For simplification, tests the working capacity is assumed to be 75 % of the equilibrium capacity determined by TGA is applied in this report.

5.5.3 Moisture content f H20

Owing to the introduction of oxygen functional groups, potassium intercalated activated carbon beads tend to have a stronger affinity to water than the raw activated carbons. As mentioned before, the flue gas generated from industry usually have a certain amount of moisture, 5-14 vol% for coal fired power plants and 7-10 vol% for natural gas fired power plants (Drage et al., 2012). By and large, the amount of moisture adsorbed has a directly proportional impact on the additional requirement of vaporisation heat during regeneration. As explained above, the moisture adsorbed during adsorption period depends on the residence time. Take PR3_700 for an example, in Fig. 5.9, after adsorption time of 1 min, the sample can adsorb 5.31 wt% of CO₂, compared with 4.37 wt% of H₂O. Moreover, at 2.25 min, both uptakes of CO₂ and H₂O have reached a capacity of 6.5 wt%. As assumed working capacity is 75 % of the equilibrium capacity for PR3_700, the working capacity would be about 6.18 wt% considering the equilibrium capacity for PR3_700 is 8.24 wt%. Hence, the f _{H2O} here would be 5.67 wt% when the adsorption time is around 1.73 min according to Fig. 5.9.

5.5.4 Calculation of regeneration heat

PR3_700 has been chosen as the best candidate among all the PRAC samples. The

nominal values of all the parameters have been listed in Table 5.5, the heat of adsorption Δ H_a and heat capacity C_{p,s} for PR3_700 were those measured by TG-DSC as described in previous section 5.2.

Parameter	Value	Notes
Δ H _a (kJ/mol)	35.5	Measured by TG-DSC
$C_{p,s}$ (kJ/kg.K)	1.1	Measured by TG-DSC
Δ T (K)	95	$T_{ad} = 25^{\circ}C, T_{de} = 120^{\circ}C$
Qv (kJ/kg)	2257.6	
$q_w (mmol/g)$	1.404	6.18 wt%
f_{H2O}	0.0567	5.67 wt%
α	0.75	
β	0	
γ	0.5	

Table 5.5 Nominal parameters adopted for calculation regeneration heat for PR3_700

After applying all the parameters into equation 5.5, regeneration heat and its individual components can be calculated as seen in Table 5.6. To summarise, the total regeneration heat of PR3_700 demonstrated a value of 2.27 GJ/ tonne CO₂, compared with that of 3.3 GJ/ tonne CO₂ for the benchmark, advanced MEA. Sample PR3_700 shows an outstanding advantage in the potential application in industry for post combustion carbon capture.

Table 5.6 Calculation of regeneration heat for sample PR3_700					
Types of heat (GJ/ tCO2)Sample PR3_700					
Sensible heat	0.423				
Heat of adsorption	0.807				
Vaporisation heat	1.036				
Total regeneration heat	2.27				

It is worth noting that according to Table 5.6, the vaporisation heat accounts for almost half of the regeneration heat for sample PR3_700. In order to further investigate the effect

of moisture vaporisation on the regeneration heat, we have calculated the values of regeneration heat as a function of moisture adsorption (f_{H2O}) , see Fig. 5.12. The regeneration heat of advanced MEA has been shown as a comparison, which demonstrated that for potassium intercalated carbon beads, as long as the moisture adsorption (f_{H2O}) that contributed to vaporisation heat is within 9 wt%, PRACs still have the superior advantage with lower value of regeneration heat to the advanced MEA.



Fig. 5.12 Effect of moisture vaporisation on regeneration heat; the dot line in the middle shows the regeneration heat of benchmark of advanced MEA (3.3 GJ/tonne CO₂)

5.6 Conclusion

The potential application for K intercalated PRACs for pulverised fuel CO_2 postcombustion capture has been systematically investigated in this chapter. The results show that the best-performing sample PR3_700 has a fast adsorption kinetics at both low and high CO_2 concentrations, as well as good regenerablity over 50 adsorption/desorption cycles. The PRAC beads developed in this study have fairly low heat of adsorption, and low specific heat capacity (*e.g.* 35.5 kJ/mol, 1.1kJ/kg.K for PR3_700) and but markedly enhanced CO₂ capacities after K intercalation, which has beneficial effect on the regeneration heat. For example, PR3_700 demonstrate a value of 2.27 GJ/ tonne CO₂, which is much lower than traditional aqueous amine (3.9-4.2 GJ/ tonne CO₂) as well as advanced MEA (3.3 GJ/ tonne CO₂).

The influence of moisture on adsorption behaviours and regeneration heat has also been investigated. The results show that PRACs have become more hydrophilic due to the introductions of oxygen functional groups through K intercalation. In addition, the vaporisation heat, resulting from the adsorbed moisture accounts for nearly half of the regeneration heat for PR3_700. Consequently, the biggest challenge for PRAC samples in the future is how to effectively decrease the moisture adsorption, for instance, through surface hydrophobic modifications.

CHAPTER 6 Preparation and characterisation of pitch-based activated carbon spheres

In this chapter, CO_2 adsorption performance of coal tar pitch-based activated carbon was investigated. Similar to phenolic resin-based carbons, the K intercalation also plays an important role in enhancing the CO_2 uptakes for pitch based carbon adsorbents and the effects will be studied in this chapter. However, owing to the special features for each category of materials, different from that in the previous chapters, the analysis for pitch based adsorbents also focuses on other parameters in terms of the influence of activation methods, ultra-microporous structures and volumetric CO_2 capacities.

Coal tar pitches are considered to be important raw materials in carbon manufacturing industry as a result of their low cost and flexibility to design carbons with various characteristics relying on different synthesis conditions (Fernández et al., 1995). The structure of coal-tar pitch is very complicated, and the predominate component is highly condensed aromatic units (Kershaw, 1993) that are linked by aliphatic side chains with various functional groups (Jalilov et al., 2015). In order to maintain high bulk density of activated pitch beads, in this chapter, we have applied different activation methods including steam and mild KOH activation to optimise the CO₂ adsorption performance of activated pitch beads. The influence of activation methods, structural properties, and CO₂ adsorption performance of series of pitch based adsorbents will be fully analysed.

Additionally, one significant advantage of coal tar pitch is relatively compact structure and high bulk density and hence normally have high volumetric CO_2 capacity. This is of great importance for practical application of post combustion carbon capture as under flue gas stream conditions, the adsorbent materials are normally placed in a very limited volume of the adsorber such as fixed or fluidised bed. However, most reported solid adsorbents were only tested in gravimetric CO_2 uptakes instead of volumetric CO_2 uptakes, in which case, it may not realistic to apply them in industry as a result of low bulk density. Hence, in this chapter, the CO_2 uptake of pitch based adsorbents will also be investigated on a volumetric basis.

6.1 Nomination of pitch-based carbon spheres

Sample	Initial KOH/carbon mass	Steam activation	KOH activation	
	ratio for impregnation	temperature (°C)	temperature (°C)	
PAC0	0	None	None	
PAC0.5_700	0.5:1	None	700	
PAC1.0_700	1:1	None	700	
PBS600	None	600	None	
PBS650	None	650	None	
PBS700	None	700	None	
PBS750	None	750	None	
PBS800	None	800	None	
PBS850	None	850	None	
PBSK600	0.5:1	600	700	
PBSK650	0.5:1	650	700	
PBSK700	0.5:1	700	700	
PBSK750	0.5:1	750	700	
PBSK800	0.5:1	800	700	
PBSK850	0.5:1	850	700	

Table 6.1 Preparation conditions and designation of the pitch AC beads

The details of preparation and activation methods have been described in Section 3.1.2. Table 6.1 illustrates the nomination of investigated pitch spheres. As is shown, PAC0 is the raw pitch beads without activation. Sample PAC0.5_700 and PAC1.0_700 were synthesised via one-step KOH activation without steam activation, both at 700 °C with KOH/carbon mass ratio of 0.5:1 and 1:1; while samples PBSK*x* were firstly steam activated at different temperatures where *x* represents steam activation temperature, and then activated by KOH with a consistent KOH/carbon mass ratio of 0.5:1 and 700 °C. It

is worthy to note that PBSx were also listed that represent samples only with steam activation at *x* temperatures from parent pitch beads.

6.2 Chemical properties of pitch-based spheres

The chemical compositions of pitch-based carbons were determined by Elemental Analysis, as summarised in Table 6.2. The elemental composition of parent pitch sample PAC0 is consist of 91.6 wt% of C, 1.5 wt% of N, 3.4 wt% of H, 0.7 wt% of S and 2.8 wt% of O, which is similar to that for pitch based carbons investigated by other researchers (Fernández et al., 1995, Alcañiz-Monge et al., 1997, Petrova et al., 2005). Due to the consumption of carbon matrix and KOH during pore producing process at high temperature, which is 700 °C in this case, the content of carbon for all other samples decreased markedly after KOH activation. Meanwhile, the results showed that there was a certain amount of potassium left in carbon after water washing, 6.3 wt% and 5.9 wt% for PAC0.5_700 and PAC1.0_700 respectively. The remaining potassium was most possibly in the form of surface species C-O-K which was produced by reaction between the formed K₂O and carbon at high temperature of 700 °C shown in reaction (Viswanathan et al., 2009) as follows (Detailed process of KOH activation has been demonstrated in Chapter 3) :

$$K_2 0 + C \rightarrow K + C - O - K$$

This reaction indicates that the remaining amount of potassium could possibly exist in the form of surface species of C-O-K, rather than crystal K-compounds, which can be further revealed by the calculation of the residual amount of K after adequate water-washing, as shown in Table 6.2. As a result, the increased amount of O content can be partly explained by the formation of C-O-K, while the rest of O was mainly contributed by O-containing surface functional hydroxyl groups.

Sampla	Chemical compositions (wt%)						
Sample _	С	Ν	Н	S	O^*	K ⁺	
PAC0	91.6	1.5	3.4	0.7	2.8	0.0	
PAC0.5_700	83.9	1.1	0.8	0.6	7.3	6.3	
PAC1.0_700	83.6	1.2	0.5	0.6	8.2	5.9	
PBSK600	84.9	1.6	0.8	0.6	5.8	6.3	
PBSK650	85.6	1.6	0.8	0.6	5.0	6.4	
PBSK700	82.1	1.6	0.8	0.5	8.5	6.5	
PBSK750	80.0	1.0	1.0	0.1	11.3	6.6	
PBSK800	79.4	1.0	1.4	0.3	13.1	4.8	
PBSK850	76.9	1.2	0.8	0.4	15.5	5.2	

 Table 6.2 Chemical compositions of pitch-based spheres

⁺ The content of potassium was determined by XRF.

^{*} The content of oxygen was obtained by difference.

The elemental analysis of samples PBSK series with steam as well as KOH activation can also been seen in Table 6.2. Generally speaking, along with the increase of steam activation temperatures from 600 to 850 °C, the consumption of the carbon matrix became more and more significant, leading to a decrease of carbon content and an uptrend of oxygen content. The compositions of N, H, and S were in a reasonable range for both PAC and PBSK samples. However, the content of potassium for PBSK800 and PBSK850 was slightly lower compared with other samples, which can be explained by that the preconsumption of the carbon matrix in steam activation, due to the generation of a larger proportion of micropores at higher activation temperatures; as a result, the following KOH activation could not engage an effective potassium intercalation into carbon layers.

6.3 Structural characterisation of pitch-based spheres

The N_2 adsorption isotherms at -196 °C for KOH activated pitch beads are all illustrated in Fig. 6.1. All of the plots demonstrate a sharp increase of adsorbed volume at low relative pressure, which agrees with the typical shape of type I (IUPAC classification), revealing that the structures of activated pitch beads are generally microporous. The N_2 isotherm for PBS samples with steam activation can also be categorised as Type I, which was not shown here.



Fig. 6.1 N₂ adsorption isotherms of activated pitch spheres with steam activation (Sample PBSK600-850) and without steam activation (Sample PAC0.5_700 and PAC1.0_700)

The individual N_2 adsorption/desorption isotherms can be seen in Fig. 6.2 for steam activated pitch spheres PBSK600-850; while Fig. 6.3(a) shows one-step KOH activated samples PAC0.5_700 and PAC1.0_700. According to Fig. 6.1, it can be concluded that on one hand, for steam activated samples, the adsorbed volume was generally enhanced along with the increase of temperatures of steam activation from 600 to 850 °C. On the other hand, samples PAC0.5_700 and PAC1.0_700 have demonstrated faster kinetics of N_2 adsorption at relatively low pressure, which can be indicated by the sharper increase of adsorbed volume before reaching the plateau than that for PBSK600-850.



Fig. 6.2 N_2 adsorption/desorption isotherms of steam activated pitch spheres PBSK600-850

The texture properties of pitch carbon spheres are shown in Table 6.3. It can be seen that the solid pitch beads became porous materials after activation. According to the previous research (Molina-Sabio et al., 1996, San Miguel et al., 2003), the development of porosity is mainly dependent on three factors in terms of precursor, process temperatures and activation agent. The differences within the steam activated PBS samples can be explained by activation temperature which plays a dominant role in the development of porosity. It has been revealed from previous publications that steam activation was an effective approach to generate micropores for carbons, at lower activation temperature such as 600 °C, smaller micropores were formed, while with increase of activation temperatures, it is a process of pore widening and enhancement of activation (Pastor-Villegas and Duran-Valle, 2002). In addition, the external surface area and development of total micropore volume illustrated a linear relationship with the degree of activation (San Miguel et al., 2003). The surface area increased from 467 m²/g for sample PBS600 to 1188 m²/g for sample PBS850, compared to 1 m²/g of parent pitch beads. The average pore diameter generally has also shown a gradual rise with the increase of steam activation temperatures.

Chemical properties of PBSK600-850 from Table 6.2 could give an indicative result of degree of activation by the decrease of carbon contents. However, it is very interesting to see that compared with PBS samples, the surface area and pore volume of PBSK samples have decreased but the average pore size has increased after KOH activation. Take samples PBS850 and PBSK850 for examples, the surface area and total pore volume were decreased from 1188 m²/g and 0.415 cm³/g to 990 m²/g and 0.357 cm³/g after KOH activation, but with an increase of pore size from 1.40 nm to 1.74 nm. Similar to the discussion of PRAC samples in Chapter 4, the considerably lower surface area obtained for PBSK samples from the secondary KOH activation of the original steam-activated pitch bead, PACO, indicated that the potential extra microporosity developed from KOH activation was offset by the even larger loss in porosity as a consequence of the simultaneous potassium intercalation that has led to partial blockage of the micropores. The increase of average pore size from around 1.36-1.40 nm of PBS samples to 1.52-1.74 nm has proved the efficacy of KOH activation of development of porosity. The texture properties of PBSK series present in Table 6.3 can be summarised as, surface area and total pore volume increase gradually from 133 m^2/g and 0.053 cm^3/g for PBSK600 to 990

 m^2/g and 0.357 cm³/g for PBSK850. Furthermore, the average pore size has risen from 1.52 nm for PBSK650 to 1.74 nm for PBSK850.

Sample					
	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	Average Pore Diameter (nm)	V _{micro} ^a (cm ³ /g)	V _{narrow} ^b (cm ³ /g)
PAC0	1	-	-	-	-
PAC0.5_700	714	0.285	1.52	0.280	0.244
PAC1.0_700	974	0.381	1.57	0.378	0.331
PBS600	467	0.161	1.36	0.149	-
PBS650	480	0.167	1.36	0.154	-
PBS700	538	0.185	1.38	0.173	-
PBS750	652	0.221	1.38	0.211	-
PBS800	849	0.288	1.39	0.277	-
PBS850	1188	0.415	1.40	0.396	-
PBSK600	133	0.053	1.57	0.042	-
PBSK650	102	0.041	1.52	0.032	-
PBSK700	198	0.071	1.53	0.064	-
PBSK750	552	0.194	1.57	0.181	-
PBSK800	768	0.266	1.62	0.251	-
PBSK850	990	0.357	1.74	0.326	-

Table 6.3 Texture properties of pitch carbon spheres

^a Pore volume of micropores (2 nm) was calculated by cumulative pore volume using NLDFT model. ^b Pore volume of narrow micropores (< 0.8 nm) which was calculated by cumulative pore volume using NLDFT model.

Secondly, compared with multi-step activation, it seems that the approach of one-step KOH activation has a significant advantage in producing smaller micropores and narrower pore size distribution of activated samples. As for sample PAC1.0_700 and PBSK 850, it is obvious that the adsorbed volume of PAC1.0_700 reached equilibrium with P/P₀ less than 0.1, whilst PBSK850 did not reach equilibrium until P/P₀ was above

0.2, as shown in Fig. 6.1. Although external surface area for PAC1.0_700 is smaller than that of PBSK850 (974 m²/g for PAC1.0_700 and 990 m²/g for PBSK850), the total volume for PAC1.0_700 (0.381 cm³/g) is larger than that of PBSK850 (0.357 cm³/g). Moreover, the micropore volume for PAC1.0_700 is as high as 0.378 cm³/g, however, for PBSK850, it is only 0.326 cm³/g. In order to calculate the narrow micropores which are less than 0.8 nm, a NLDFT model has been applied to indicate the narrow micropore volume, as displayed in Table 6.3. It has been found that for steam activated carbons, there were barely micropores with diameter below 0.8 nm. Nevertheless, the narrow micropores dominated samples synthesised by one-step KOH activation samples, i.e., 85.6 % for PAC0.5_700 and 87.6 % for PAC1.0_700.

The results of microporosity of PAC0.5_700 and PAC1.0_700 were so outstanding that a further study has been discussed. Fig. 6.3(b) demonstrates the pore size distribution of K-treated pitch spheres. Basically, both prepared samples have two dominant uniform pore size distributions around 0.4 nm and 0.6nm. Although a small peak around 1.1nm and 1.2nm for PAC0.5_700 and PAC1.0_700 respectively was also found in the plot, it is too small in volume that we can validate our previous observation of texture properties that the micropores are mainly narrow micropores smaller than 0.8 nm. This phenomenon is even more obvious when we see the plots of cumulative pore volume against pore width for PAC0.5_700 and PAC1.0_700. Additionally, the cumulative pore volume is mainly contributed by narrow micropores, which possess a value of 0.23 cm³/g out of the total value of 0.26cm3/g for sample PAC0.5_700, and 0.32 cm³/g out of the total value of 0.34 cm³/g for sample PAC1.0_700, respectively.


Fig.6.3 (a) N_2 isotherms at -196 °C and (b) pore size distributions for PAC0.5_700 and PAC1.0_700; the inner picture in (b) shows the relationship of d V/d W and Cumulative pore volume against pore width for PAC0.5_700 and PAC1.0_700

In comparison, PAC1.0_700 activated with higher KOH/C ratio had larger surface area and pore volume, which means that more KOH was helpful to further develop the porosity. But it was also worth noticing that the small pores were widened and the pore size distribution slightly shifts to a larger size with the increase of KOH loading. Compared to other reported activated carbons with considerably larger surface areas (normally larger than 2000 m²/g (Neel et al., 2009, Raymundo-Pinero et al., 2005, Otowa et al., 1997)), the prepared pitch beads were generally activated carbons with relatively lower surface area and pore volumes. However, the advantages of one-step KOH activation lie in the fact that the obtained pitch beads were developed with extremely high microporosity. V_{micro}/ V_{total} is as high as 98 % for PAC0.5_700 and 99 % for PAC1.0_700 respectively. In addition, by employing NLDFT model, the result shows that a high narrow microporosity (which is defined as: V_{narrow}/V_{micro}) of 87 % for PAC0.5_700 and 88 % for PAC1.0_700 were also obtained. That will be beneficial for post combustion CO₂ adsorption.



Fig. 6.4 SEM images of (a) original pitch sphere PAC0; (b) PAC0.5_700 with KOH/carbon mass ratio of 0.5:1; (c) PAC1.0_700with KOH/carbon mass ratio of 1:1; and (d) close up view of PAC1.0_700; EDX elemental mapping of K of PAC1.0_700 for (e) carbon beads and (f) cross-section

The cross section of raw pitch beads was shown by SEM images in Fig. 6.4(a), from which the cracks or tunnels across the bead can be observed. After KOH activation, as shown in Figs. 6.4(b)-(d), it is evident that the cracks or tunnels become more severe with the increase of KOH/carbon mass ratio from 0.5:1 for PAC0.5_700 to 1:1 for PAC1.0_700. The enlarged close-up view of PAC1.0_700 illustrated in Fig. 6.4(d) reveals that the initial worm-like tunnels have supplied a platform for KOH to react with the pitch matrix at activation temperatures as to form numerous micropores. It means that the prepared samples have hierarchical macro-micropore structure. The existence of interconnecting macropores or tunnels could be beneficial for gases like CO₂ to facilitate diffusion into the micropores.

6.4 CO₂ adsorption performance of pitch-based spheres

6.4.1 Static adsorption measurement

To evaluate CO₂ adsorption performance of pitch-based spheres from both multiactivation and one-step KOH activation methods, a static volumetric method (measured by BET ASAP 2420) was also applied to possess the CO₂ adsorption capacities. The CO₂ adsorption isotherms for all the activated pitch carbons were illustrated in Fig. 6.5, and detailed CO₂ capacities at 0.15 bar and 1.0 bar at both 0 and 25 °C could be found in Table 6.4. It is fairly obvious that the CO₂ uptakes for PAC0.5_700 and PAC1.0_700 are much higher than that for PBSK samples, regardless of adsorption temperatures and relative pressure. This can be mainly ascribed to the much larger narrow micropore volume that is below 0.8 nm of samples PAC0.5_700 and PAC1.0_700. The differences of CO₂ uptakes among PBSK samples are quite small. Specifically, at 0 °C, the CO₂ uptakes for PBSK samples are around 2 mmol/g at 0.15 bar and 3-4 mmol/g at 1.0 bar.



Fig. 6.5 CO₂ adsorption isotherms of activated pitch spheres at (a) 0 °C and (b) 25 °C

A similar trend can also be found for CO₂ uptakes at 25 °C for PBSK samples. The results seem to be very strange since micropore volume varies greatly with the increase of steam activation temperatures. For instance, at 0 °C, sample PBSK600 and PBSK800 could possess a similar CO₂ uptake of 3.55 mmol/g and 4.15 mmol/g at 1.0 bar; however, at 0.15 bar, PBSK600 obtained an even higher CO₂ uptake of 2.24 mmol/g, compared to 2.00 mmol/g for sample PBSK800. The reason for this can be explained by the fact that at low partial pressure, smaller micropore plays a more important role in increasing the

 CO_2 adsorption for adsorbents. Under this condition, it is possible that KOH intercalation is less adoptable as a result of the pre-formation of micropore structures by steam activation, rather than KOH activation.

If we compare sample PAC0.5_700 and PAC1.0_700, at 0 °C and 1 bar, the CO₂ capacity value of PAC0.5_700 is 5.16 mmol/g, while it is even higher for PAC1.0_700 which is 6.10 mmol/g. Since both samples were activated at the same temperature of 700 °C, the reason that PAC1.0_700 has a higher CO₂ uptake may be ascribed to higher KOH/carbon mass ratio that leads to a larger surface area and micropore volume. As mentioned before, a highly microporous, especially narrow microporous structure for both samples has been generated during activation process. More specifically, according to pore size distribution shown in Fig. 6.3, the K-treated samples have a dominant proportion of micropores with a pore width of around 0.4 and 0.6 nm, which plays a critical role in CO₂ uptakes (Zhang et al., 2013b, Sethia and Sayari, 2015).

Sample	CO ₂ capacity at 0 °C (mmol/g)		CO ₂ capacity at 25 °C (mmol/g)	
	0.15 bar	1 bar	0.15 bar	1 bar
PBSK600	2.24	3.55	1.37	2.66
PBSK650	1.81	3.10	1.30	2.48
PBSK700	2.06	3.42	1.40	2.70
PBSK750	2.01	3.64	0.84	2.23
PBSK800	2.00	4.15	1.15	2.80
PBSK850	1.70	3.93	0.99	2.56
PAC0.5_700	3.13	5.16	1.86	3.95
PAC1.0_700	3.15	6.00	1.83	4.03

Table 6.4 CO₂ adsorption capacities of the carbon beads

So as to compare our best performing samples with reported activated carbons, CO_2 capacities of PAC0.5_700 and PAC1.0_700 were listed with other N-doped porous carbons at 0 and 25 °C with a CO_2 partial pressure of 0.15 bar and 1 bar. PBSK800 was

also selected as a typical sample to represent steam activated pitch beads. It can be concluded that at 0.15 bar, the CO₂ capacities for our samples are one of the highest recorded among reported carbon adsorbents. Take PAC0.5_700 for an example, the CO₂ uptakes are 3.13 and 1.86mmol/g at 0 and 25 °C, respectively. It is worth to note that even the CO₂ uptakes at CO₂ pressure of 1 bar for PAC samples are much lower than that for other N-doped sorbents listed in Table 6.5, whereas at 0.15 bar, PAC0.5_700 and PAC1.0_700 demonstrated superior adsorption capacities than those of other adsorbents. However, the texture properties could only be one of the reasons to explain the extraordinary CO₂ uptakes. As for N-free samples, the only efficacy is from the K compounds left in the carbon lattice. The distribution of K in carbon was done by elemental mapping for PAC1.0_700 that was illustrated in Figs. 6.4(e) and (f), where the intensity of red colour represents the concentration of potassium. It is clearly shown that potassium is uniformly dispersed over the carbon framework. The formation of surface C-O-K group acting like extra framework in zeolites, MOFs, and POPs enhanced the electrostatic force of the surface that had positive effect on CO₂ capture.

Our previous work has already proposed that the effect of intercalated potassium in enhancing the CO₂ adsorption behaviours for carbon-based materials (Liu et al., 2015). KOH was considered as a commonly used activation agent; however, the mechanism of K-doping has been ignored for a long time. According to our results, the influence of Kdoping on CO₂ uptakes is, if not better than, quite comparable to nitrogen enrichment for carbon materials, particularly at low CO₂ partial pressures. Hence, K-doping pitch-based spheres with highly narrow microporous structures have shown great potential in application for post combustion carbon capture.

	CO ₂ capacity at 0 °C		CO ₂ capacit	CO ₂ capacity at 25 °C	
Sample	(mmo	ol/g)	(mmo	ol/g)	
	0.15 bar^*	1 bar	0.15 bar^*	1 bar	
CP-2-600	2.10	6.20	1.08	3.90	(Sevilla et
					al., 2011)
CEM750	1.70	6.92	0.98	4.38	(Xia et al.,
					2011)
CSA-700	2.38	5.75	1.64	3.80	(Zhu et al.,
					2014)
S-2N-2P	3.15	8.99	1.51	4.57	(Ma et al.,
					2014)
NAC-1.5-600	2.95	7.2	1.70	5.38	(Hong et
					al., 2016)
PBSK800	2.00	4.15	1.15	2.80	This work
PAC0.5_700	3.13	5.16	1.86	3.95	This work
PAC1.0_700	3.15	6.00	1.83	4.03	This work

Table 6.5 Comparison of CO2 adsorption capacities for different carbon adsorbents

All results are measured by static volumetric method.

*Some of CO₂ uptakes at 0.15 bar were measured from the graph.

6.4.2 Dynamic adsorption measurement

Dynamic adsorption measurement employing TGA is another common evaluation methodology of CO_2 uptakes for solid adsorbents. In order to simulate conditions for post combustion carbon capture, a mixture gas of 15 % CO_2 and 85 % N_2 was employed to test the dynamic and cyclic performance of activated pitch samples. Fig. 6.6 shows CO_2 adsorption isotherms for steam activated carbon spheres which have two categories: (1) before KOH activation, which are PBS600-850 shown in Fig. 6.6 (a) and (2) samples PBSK600-850 after KOH activation. The equilibrium CO_2 uptakes have also been summarised in Fig. 6.7.

The plots of PBS samples in Fig. 6.6 have demonstrated very fast adsorption kinetics as a result of the porous nature after steam activation, which can be validated by that the sample obtained more than 90 % of equilibrium CO₂ uptakes within the 1st min after the

inlet of 15 % CO₂ gas. The CO₂ uptakes followed a parabolic curve as a function of steam activation temperatures. More specifically, the CO₂ uptake gradually increased from 0.67 mmol/g for PBS600 to 0.93 mmol/g for PBS750, and then decreased to 0.73 mmol/g for PBS850. This phenomenon can be contributed by the enhancement of microporosity when temperature rises from 600 to 750 °C, however, when temperatures were above 750 °C, a significant proportion of larger micropores or even meso/macro- pores were generated, which had a detrimental effect on CO₂ uptakes at low partial pressure.

After KOH activation, the CO₂ uptakes were generally markedly increased and the kinetics was slightly decreased but still maintained more than 85 % of equilibrium CO₂ uptakes after CO₂ adsorption of 1 min, as shown in Fig. 6.6 (b). The decrease in kinetics was due to the formed K species acting as surface functional groups that could enhance the surface affinity to CO₂ molecules, so as to make the carbon materials more "chemical". As a result of the potassium intercalation, the CO₂ uptakes were approximately double that of the PBS samples. For instance, sample PBSK600 could adsorb 1.55 mmol/g, compared with 0.67 mmol/g before KOH activation, see Fig. 6.7. Specifically, PBSK600, rather than PBSK750 possessed the highest CO₂ adsorption capacities. Again, this is due to that the potassium intercalation, instead of microporosity plays a dominant role in the CO₂ capacities.



Fig. 6.6 CO₂ adsorption isotherms of samples (a) PBS series and (b) PBSK series at CO₂ partial pressure of 0.15 bar and 25 $^{\circ}$ C from TGA



Fig. 6.7 Comparison of equilibrium CO₂ uptakes of sample PBS and PBSK series at 25 $^{\rm o}C$ and 15 % CO₂ in N₂ from TGA

On the other hand, the CO₂ adsorption isotherms of activated pitch spheres prepared with one-step KOH activation were displayed in Fig 6.8. Similar to PBSK samples, the PAC samples have a relative fast adsorption kinetics. However, PAC0.5_700 and PAC1.0_700 possessed a superior CO₂ uptake than that of PBSK samples. As shown in Fig. 6.8, the CO₂ uptakes for PAC0.5_700 and PAC1.0_700 can reach 89 and 92 % of the equilibrium capacities in initial 5 mins, which are 1.60 mmol /g and 1.71 mmol /g respectively, compared to 1.80 mmol /g and 1.85mmol /g as the equilibrium capacities. It is believed that the hierarchical structure in pitch beads enables fast diffusion system of CO₂ adsorption, i.e., the macroporous and mesoporous interconnecting tunnels can be considered as express way for CO₂ molecules to reach the micropores. It is obvious that although PAC1.0_700 has slightly faster adsorption kinetics, this can be explained from

having a larger micropore volume, PAC0.5-700 presents a fairly comparable CO₂ uptake with much reduced KOH loadings.



Fig. 6.8 CO₂ adsorption isotherms of PAC0.5_700 and PAC1.0_700 at CO₂ partial pressure of 0.15 bar and 25 $^{\circ}$ C

Generally speaking, compared with PBSK samples, although with slightly lower adsorption kinetics of CO₂, PAC0.5_700 and PAC1.0_700 with one-step KOH activation had demonstrated significant advantage with superior CO₂ uptakes at 0.15 bar at room temperature, which is typical for post combustion capture. Consequently, in the following sections, PAC0.5_700 and PAC1.0_700 have been selected to study the regeneration ability and volumetric basis of CO₂ uptakes to assess their application for industry.

6.5 Cyclic adsorption/desorption and stability testing of selected

activated pitch spheres

As is known, good stability and regeneration ability is essential for good adsorbents. PAC0.5_700 and PAC1.0_700 have been chosen as the best candidates to evaluate its adsorption over multiple cycles. Fig. 6.9 demonstrates CO₂ adsorption and desorption performance of PAC samples in 50 cycles, and the procedures can be found in Section 3.2.1. In general, both samples illustrate very stable adsorption capacities in long term. For instance, PAC0.5_700 can maintain 92 % of CO₂ uptake after 50 cycles by temperature swing, while PAC1.0_700 can possess 94 % over 50 cycles. The slight decrease for PAC1.0_700 may be due to the irreversible CO₂ adsorption on K-containing compounds such as KOH and K₂CO₃ that were not intercalated into carbon layers. The high CO₂ capacity and good regenerability for pitch-based samples further proves that they are promising candidates for post combustion CO₂ capture applications.



Fig. 6.9 The CO₂ adsorption of PAC0.5_700 and PAC1.0_700 in a 15 vol % CO₂ and 85 vol % gas flow at 25 °C in 50 cycles of adsorption and desorption

6.6 Volumetric CO₂ uptakes of selected activated pitch spheres

In this section, the volumetric CO_2 uptakes of PAC samples were calculated and discussed. Given the fact that under flue gas stream conditions, the adsorbent materials

will be located in the adsorption reactor with limited space, it is beneficial that adsorbents have a higher volumetric CO_2 uptake. Hence, from the aspect of practical application, it is essential for solid sorbents to convert from gravimetric CO_2 uptakes to volumetric CO_2 uptakes by measuring bulk densities of the samples.

	1		
Sample	Description	Form	Bulk density (g/cm ³)
R2030 ^a	Norit carbon purchased	powder	0.52
	from Sigma Aldrich		
MPPY2600 ^b	Polypyrrole	pellets	0.85
PR3_700 ^c	Phenolic Resin	spheres	0.39
PEI/silica ^d	40 %PEI loading	powder	0.60
PAC0	Raw coal tar pitch	spheres	1.14
PAC0.5_700	Coal tar pitch	spheres	1.00
PAC1.0_700	Coal tar pitch	spheres	0.76

Table 6.6 Comparison of bulk density of pitch spheres and other adsorbents

a: Data from reference(Woodward et al., 2014), b: Data from reference (Adeniran and Mokaya, 2015), c: Data from reference (Liu et al., 2015) d: Data from reference (Zhang et al., 2016)

Table 6.6 listed the bulk densities of different adsorbents for comparison. One can see that carbons with different precursors were chosen, and PEI/silica was considered as benchmark employed in fluidised bed reactor (Zhang et al., 2016). The bulk density of raw pitch beads PR0 without KOH activation was found to possess the highest value of 1.14 g/cm³. Although PAC0.5_700 and PAC1.0_700 demonstrated a slight decrease in density with the increase of KOH/carbon mass ratios, 1.00 and 0.76 g/cm³ respectively, they can still maintain higher figures than others. The results were in line with that of BET surface areas and SEM images. The data suggests that PAC0.5_700 presents even higher density than sample MPPY2600 that was prepared by compactivation via a mechanical compression step (Adeniran and Mokaya, 2015).

The gravimetric and volumetric CO_2 uptakes for adsorbents listed in Table 6.6 were summarised in Fig. 6.10. There were quite a few candidates demonstrated a comparable, or even higher gravimetric CO_2 uptake than PAC0.5_700 and PAC1.0_700. For instance, the CO₂ uptake at 25 °C and 0.15 bar of MPPY2600, PR3_700 and PEI/silica are 92.4, 79.2 and 101.2 mg/g, compared to 81.8 mg/g for PAC0.5_700 and 80.5 mg/g for PAC1.0_700. However, when we consider the volumetric CO₂ uptakes, thanks to high bulk density, PAC0.5_700 shows a superior value of 81.8 g/L, while MPPY2600, PR3_700 and PEI/silica achieved a volumetric CO₂ uptake of 78.5g/L, 79.2 g/L and 60.7 g/L, respectively. As a result of lower bulk density, the volumetric uptake for PAC1.0_700 was also smaller (61.2 g/L) than that of PAC0.5_700. It can be concluded that PAC0.5_700 is very promising for post combustion carbon capture as a result of its outstanding volumetric CO₂ uptake.



Fig. 6.10 Comparison of gravimetric and volumetric CO_2 uptakes at 25 °C and 0.15 bar for different adsorbents

Table 6.7 has also presented the mechanical strength for PAC0.5_700 and PAC1.0_700. As comparison, the data of activated spheres derived from phenolic resin (data are also available in Section 4.3.1) were also listed in the table. From the results one can see that owing to more compact structure, pitch-based samples demonstrated an overall much higher mechanical strength than that of phenolic resin-based samples. For example,

before activation, parent PAC0 could stand a maximum load of 12.19 N, which is almost 4 times of parent PR0. With the same KOH loading, PAC0.5_700 could still possess a maximum load of 8.31 N, compared with a value of 2.21 N for PR3_700. Although a severe KOH loading has led to a dramatic decrease of mechanical strength for PAC1.0_700, it is still comparable to PR0. By and large, sample PAC0.5_700 was proven to be the best candidate for post combustion carbon capture.

Table 6.7 Comparison of mechanical strength of activated carbon spheres derived from phenolic resin and coal tar pitch (all activated at 700 °C)

Sample	KOH/ AC mass ratio	Maximum Load (N)
PR0	0	3.08
PR3_700	0.5:1	2.21
PR4_700	1:1	1.75
PAC0	0	12.19
PAC0.5_700	0.5:1	8.31
PAC1.0_700	1:1	3.02

6.7 Conclusions

Coal tar pitch derived activated carbons with ideal spherical form with a diameter of 1-2 mm were synthesised via two different activation approaches, which is firstly an initial steam activation followed by KOH activation, and secondly one-step KOH activation, both with mild KOH/carbon mass ratios. The results show that compared with the samples prepared with the first method, the activated pitch spheres with one-step KOH activation, which were denoted as PAC0.5_700 and PAC1.0_700, possessed superior performance characteristics for post combustion carbon capture.

As for the steam and KOH activated pitch samples PBSK600-850, it had been found that low activation temperatures was beneficial for generation of smaller micropores; combining with potassium intercalation, the CO₂ uptakes could be increased

markedly compared to the samples only with steam activation. However, owing to the existence of narrow micropores smaller than 0.7 nm, samples prepared with the one-step KOH activation, which were PAC0.5_700 and PAC1.0_700 had been found to have superior CO₂ adsorption performance. Highly microporous structure of 98 % and 99 % of microporosity and 87 % and 88 % of narrow-microporosity for PAC0.5_700 and PAC1.0_700 were developed with a uniform distribution of pore sizes. Owing to the narrow micropores and K-doping, the samples demonstrated outstanding CO₂ capacities at relatively low CO₂ partial pressure. PAC0.5_700 possessed a CO₂ uptake of 1.86 mmol/g while PAC1.0_700 obtained that of 1.83mmol/g at 25 °C at 0.15bar.

In order to select the best performing candidate for industrial application, PAC0.5_700 and PAC1.0_700 were further characterised and analysed in terms of regeneration ability, volumetric CO₂ uptake and mechanical strength. Under typical conditions of post combustion carbon capture, at 0.15 bar and 25 °C, 50 cycles of adsorption and desorption were carried out and both samples showed excellent adsorption dynamics and regeneration efficiency. From the results of CO₂ uptakes on a volumetric basis and comparing with other candidate adsorbents reported previously, it was revealed that PAC0.5_700 maintained a high bulk density and volumetric CO₂ uptake, 81.8 g/L, which is among the highest for solid adsorbents reported so far. In addition, PAC0.5_700 also shows a superior mechanical strength, which is 4 times higher as activated carbon spheres derived from phenolic resin. These superior performances of PAC0.5_70 0 indicate it has the potential to be the best solid adsorbent for post combustion carbon capture.

CHAPTER 7 General discussion and conclusion

7.1 General discussion

Two types of spherical activated carbons derived from different precursors, namely phenolic resin and coal-tar pitch, have been characterised in terms of CO_2 capture capacities under post-combustion capture conditions. The results have indicated that structural properties, preparation process, and K intercalation play important roles in the CO_2 adsorption behaviours of resulting activated carbon materials.

It is well known that activated carbons have significant advantages as a result of their relatively low cost, wide availability and porous structure and ease of modifications of surface chemistries. Apart from above, there are a few other reasons to choose phenolic resin and coal-tar pitch as the precursors. Firstly, super microporous carbon spheres can be produced using simple preparation method with relatively high bulk density, which provides potentials for practical application such as fluidised-bed testing. Secondly, the as-obtained carbon beads have high level of resistance to KOH chemical activation. This helps the carbon spheres maintain spherical form, and good mechanical strength after activation hence being superior than other carbon spheres, for example, those prepared by polyacrylonitrile, which is called "CSA-700" (Zhu et al., 2014) showed an outstanding CO_2 adsorption performance; but with the mechanical strength so low that the beads were too fragile to remain spherical form for fluidised bed testing. Thirdly, the resulting materials from both precursors contain a very low level of Nitrogen (< 0.1 wt% for phenolic resins and < 1.6 wt% for pitch beads), which eliminated potential interference from nitrogen functionalities, and proved the beneficial effects of K-intercalation to enhance the CO₂ adsorption capacities. Although KOH was applied as the activation agent to produce activated carbon materials, the residual K compounds were always

removed by washing by acid. Even in some cases, the K species remained in carbon matrix when using water as washing agent, the effect of K species in promoting CO₂ capture capacities were also unfortunately ignored in most previous publications.

Furthermore, to compare the potentials of industrial applications of these two activated carbon adsorbents, cyclic adsorption/desorption performance, heat of adsorption, as well as volumetric adsorption capacities will be systematically discussed in the following sections.

7.1.1 Comparison of the precursor materials

Table 7.1 presents chemical compositions of two parent carbon spheres: PR0 (derived from phenolic resin) and PAC0 (derived from coal-tar pitch). Both samples showed a high composition of C and a very small amount of N. Due to the existence of large amount of aromatic rings, PAC0 possessed with a higher level of H and a lower amount of O.

Table 7.1 Chemical properties of parent phenolic resin spheres (PR0) and pitch spheres (PAC0)

Sample	Elemental analysis					
	С	Ν	Н	S	0	
PR0	93.6	0.0	0.5	0.1	5.8	
PAC0	91.6	1.5	3.4	0.7	2.8	

As standard polymeric precursors, phenolic resins comprise simple chemical components. One superior advantage of synthetic polymeric materials, which is phenolic resin in this case, lies in that the chemical composition can be precisely controlled, including morphology and pore structures. On the other hand, coal-tar pitch materials usually have complex structure, and the predominated content is highly condensed aromatic units that are linked by aliphatic side chains with various functional groups. Compared with phenolic resin precursors with amorphous structure, this fairly compact structure of the pitch is beneficial for the formation of graphitic structures after carbonisation or even chemical activation by KOH. As a result, pitch-based carbon spheres usually have a higher resistance to KOH attack than that of phenolic resin-based carbons, owing to the stable aromatic ring structure. This also explains the fact that carbon spheres from coaltar pitch have obtained higher mechanical strength and higher bulk density than phenolic resin carbons.

As mentioned in previous Chapters, many samples were investigated with both types of carbon materials. For example, samples were prepared with different KOH/carbon ratios and different activation temperatures (from 600 to 800 °C) for phenolic resin-based carbons; while the pitch-based carbons were prepared with different processing methods including two step method of physical steam activation, chemical activation and one step KOH activation. To make simple and valid comparison of their characteristics and CO₂ capture performance, samples prepared under the chemical conditions of a mass ratio of 0.5:1 and 1:1 of KOH/carbon, activation temperature of 700 °C, *i.e.* PR0, PR3_700, PR4_700 and PAC0, PAC0.5_700, PAC1.0_700 were selected for further discussion in the next section.

7.1.2 Specific surface area and pore volume

According to the results of N₂ isotherms at -196 °C for PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700, described in Chapter 4 and 6, all of the samples can be categorised as Type I isotherms, which is microporous materials. The parent sample PR0 was already activated before KOH activation; hence it had obtained a surface area of 1128 m²/g. On the contrast, PAC series began from little porosity for PAC0 to a surface area of around 1000 m²/g for both PAC0.5_700 and PAC1.0_700. Owing to the blockage of K intercalation, the surface area of PR3_700 and PR4_700 decreased slightly to 826

and 1071 m²/g. In fact, after KOH activation at 700 °C, sample PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700 possessed a similar surface area.

	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} ^a (cm ³ /g)	V _{narrow} ^b <0.8nm (cm ³ /g)	V _{narrow} ^c <0.6nm (cm ³ /g)	V _{narrow} ^d <0.4nm (cm ³ /g)
	1100	0.411	0.407	0.051	0.010	0.042
PR0	1128	0.411	0.407	0.251	0.218	0.042
PR3_700	826	0.300	0.273	0.240	0.227	0.119
PR4_700	1071	0.405	0.389	0.282	0.252	0.114
PAC0	1	-	-	-	-	-
PAC0.5_700	714	0.267	0.261	0.225	0.225	0.169
PAC1.0_700	974	0.351	0.349	0.322	0.300	0.154

Table 7.2 Texture properties of selected carbon beads

Sample

^a Pore volume of micropores (<2 nm) was calculated by cumulative pore volume using NLDFT model. ^{b, c, d} Pore volume of narrow micropores (< 0.8 nm, 0.6 nm and 0.4 nm respectively) was calculated by cumulative pore volume using NLDFT model.

As it is known, the adsorption behaviour of porous carbons follows a micropore filling mechanism, rather than monolayer adsorption. The smaller the pore size, the higher the adsorption potential for porous carbons. CO₂ molecules prefer to be adsorbed at smaller micropores because of their stronger interaction with CO₂. As a result, narrow micropores are considered as a determining factor to enhance the filling system, so as to promote the CO₂ capacities at relatively low CO₂ partial pressures. Based on the theory above, the pore volume of narrow micropores including below 0.8 nm, 0.6 nm and 0.4 nm were calculated using NLDFT carbon slit pore model, and the results were presented in Table 7.2. The data shows that PR0 has the highest pore volume of total pores and micropores (< 2 nm). However, samples PR3_700 and PR4_700 after KOH activation possessed higher ultra-micropore volume (smaller than 0.4 nm and 0.6 nm) than sample PR0. In

addition, although PAC0.5_700 and PAC1.0_700 showed a relatively lower total pore volume and micropores, the volume of narrow pores below 0.6 nm were already quite comparable to PR3_700 and PR4_700. This phenomenon is more obvious for narrow micropore below 0.4 nm. This result suggests that one-step KOH activation is beneficial to produce narrower microporosity.



Fig. 7.1 Pore size distributions for sample PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700

The pore size distributions of PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700, was clearly demonstrated in Fig. 7.1. For narrow micropores below 0.4nm, the proportion which can be indicated by the strength of peak for dV/dW pore volume for each sample follows this order: PAC0.5_700 > PAC1.0_700 > PR3_700 > PR4_700 > PR0. Sample PR0 has a wider range of pore size distribution with three main peaks at 0.35 nm, 0.5 nm and 1.2 nm, while for other samples, the peaks of pore width are mainly compared on around 0.35 nm and 0.5 nm. Fig. 7.2 reveals the cumulative pore volume against the pore

width for sample PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700. In order to give more intuitive information about the proportion of main pore sizes, here we define two terms namely microporosity (Micro%) and narrow microporosity (Nm%), where the former one equals to the percentage of the micropore volume in the total pore volume, while the later indicates the percentage of the narrow micropores smaller than a certain pore width (0.8 nm, 0.6 nm, 0.4 nm) in the micropore volume. The results are displayed in Table 7.2.



Fig. 7.2 Cumulative pore volume against pore width for sample PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700 using a CO₂ isotherm at 0 °C linked to a N₂ isotherm at - 196 °C

From Table 7.3 one can see that, all of the samples were within a high Micro% of more than 90 % as well as a high Nm% (< 0.8 nm). However, with the decrease of the pore width from 0.8 nm to 0.6 nm, PR3_700 and PAC0.5_700 showed highest Nm% (< 0.6 nm), which are 83.2 % and 80.4 % respectively; and PAC0.5_700 showed highest Nm% (< 0.4 nm) which is 60.4 %.

	Micro% ^a (%)	Nm% ^b <0.8 nm (%)	Nm% ^c <0.6 nm (%)	Nm% ^d <0.4 nm (%)
PR0	99.5	61.4	53.3	10.3
PR3_700	91.0	87.9	83.2	43.6
PR4_700	96.0	72.5	64.8	29.3
PAC0.5_700	98.2	87.1	80.4	60.4
PAC1.0_700	99.2	87.6	79.4	40.7

Table 7.3 Micropososity and narrow microporosity of selected carbon beads

^a Micro% = V_{micro}/V_{total} ; ^{b, c, d} Nm% (< 0.8 nm, 0.6 nm, 0.4 nm)= $V_{narrow (< 0.8 nm, 0.6 nm, 0.4 nm)}/V_{micro}$;

7.1.3 Specific CO₂ uptake vs porosity

Sample

We have analysed the surface area and pore volume, especially narrow micropore volumes below 0.8 nm, 0.6 nm and 0.4 nm in the previous section. In this section, the relationship between the porosity and CO_2 capacities will be fully discussed.

Correlations between the CO₂ uptakes for PR0, PR3_700, PR4_700, PAC0.5_700 and PAC1.0_700 at 0.15 bar and porosities including total pore volume, micropore volume and narrow micropore volume are presented in Fig. 7.3, 7.4. More specifically, the CO₂ adsorption capacities under different adsorption temperatures (0 and 25 °C) and CO₂ partial pressures (0.15 and 1.0 bar) were discussed as a function of the volume fraction of micropore smaller than a critical size, here, 0.8 nm, 0.6 nm and 0.4 nm. Regardless of CO₂ partial pressure, CO₂ uptakes do not seem to have linear relationships with the total pore volume or the total micropore volume smaller than 2 nm, see Fig. 7.3 (a, b) and Fig. 7.4 (a, b). At relatively low CO₂ partial pressure, *i. e.*, 0.15 bar, CO₂ uptakes present a

considerably low coefficient of determination with the narrow micropore volume smaller than 0.8 nm or 0.6 nm. For instance, R^2 equals around 0.14 and 0.27 at 25 °C and with a narrow micropore volume smaller than 0.8 nm and 0.6 nm respectively. However, the CO₂ uptakes have shown a fairly linear relationship with the volume fraction of micropores below 0.4 nm, with a R^2 of 0.98 at 25 °C and 0.96 at 0 °C. On one hand, if we compare two different adsorption temperatures, it is obvious of the preference of CO₂ to smaller micropores at higher adsorption temperature. For example, the coefficient (R^2) is 0.27 at 25 °C, compared with 0.32 at 0 °C, both with narrow pore volume smaller than 0.6 nm. That is to say, along with the increase of adsorption temperature, the critical pore size that determines the CO₂ uptakes decreased. Similar conclusion could be also conducted from the results at CO₂ partial pressure of 1.0 bar, shown in Fig. 7.4.

On the other hand, if we compare two different CO_2 partial pressures, there are mainly two findings. Firstly, similarly, with the increase of the partial pressure of CO_2 adsorption, the critical pore size decreases. For example, both at adsorption temperature of 0 °C and with small micropore volume smaller than 0.8 nm, R^2 rises from 0.19 under 0.15 bar to 0.76 under 1.0 bar. Secondly, it is also not difficult to find that the smaller narrow micropores from pore size smaller than 0.8 nm, the more linear the correlation between CO_2 uptakes and the fraction of the pore size.

Generally speaking, at higher temperatures and lower pressures, the CO_2 molecules are more active and struggling to leave the carbon surface, hence CO_2 adsorption requires stronger adsorption force which decreases with the pore width. This is due to the superposition extent of the van der Waals force produced by two adjacent walls of slit pores. This study reveals that smaller micropores, especially smaller than 0.4 nm, plays an dominant role in CO_2 capture at higher adsorption temperatures and lower CO_2 partial pressures for porous carbon materials.



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Fig. 7.3 Relationships between CO_2 uptake and porosities: (a) Total pore volume, (b) Micropore volume, (c) Narrow micropore volume < 0.8nm, (d) Narrow micropore volume < 0.6nm, (e) Narrow micropore volume < 0.4nm; CO_2 uptakes at 0.15 bar were measured by static volumetric method



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Fig. 7.4 Relationships between CO_2 uptake and porosities: (a) Total pore volume, (b) Micropore volume, (c) Narrow micropore volume < 0.8nm, (d) Narrow micropore volume < 0.6nm, (e) Narrow micropore volume < 0.4nm; CO_2 uptakes at 1.0 bar were measured by static volumetric method

7.1.4 Mechanical strength, bulk density and volumetric CO₂ capacity

As a more ideal form than pulverous activated carbon, spherical carbon beads have a superior advantage for industrial application such as fluidised-bed reactor testing. The carbon spheres derived from the two precursors in this project have shown high CO_2 capacities at a relatively low CO_2 partial pressure of 0.15 bar corresponding to the case

of post combustion carbon capture with coal-fired power plants. However, a good mechanical strength to minimise abrasion during fluidisation and high bulk density and volumetric CO_2 capacity to maintain high CO_2 uptake in a given/ limited adsorption column are also of great importance in reality. In this section, the two batches of carbon adsorbents will be compared regarding to their potential in practical applications.

Table 7.3 compares the mechanical strength and bulk density of the PR and PAC samples. The K intercalation treatment as a means to improve CO₂ adsorption capacity has a general negative impact on the mechanical strength as well as the bulk density of the carbon beads. In terms of mechanical strength, 72 % and 57 % could be maintained for the PR samples, while only 59 % and 35 % were presented for the PAC samples, when the raw samples were KOH activated with the KOH/AC mass ratio of 0.5:1 and 1:1 respectively. This reveals that the phenolic resin samples have better resistance to KOH activation. However, the mechanical strength of PAC1.0_700 is still higher than that of the raw PR0. By contrast, the KOH treatment has a smaller impact on the bulk density of the PAC samples have an overall higher bulk density than that of the PR samples.

Sample	KOH/ AC mass	Maximum Load (N)	Bulk density (g/cm ³)
	ratio		
PR0	0	3.08	0.49
PR3_700	0.5:1	2.21	0.39
PR4_700	1:1	1.75	0.31
PAC0	0	21.44	1.14
PAC0.5_700	0.5:1	12.64	1.00
PAC1.0_700	1:1	7.51	0.76

Table 7.4 Mechanical strength and bulk density of selected carbon beads

The gravimetric and volumetric CO_2 uptakes at 25 °C and 0.15 bar for adsorbents listed in Table 7.4 were further illustrated in Fig. 7.5. Solid adsorbent PEI/ silica developed at Nottingham (Zhang et al., 2016) was also presented in Fig. 7.5 for comparison as it has been considered as promising material to be employed in Solid Adsorption Looping Technologies. One can see from Fig. 7.5 that PR3_700, PR4_700 shows competitive gravimetric CO₂ uptake to PAC0.5_700 and PAC1.0_700. However, volumetric CO₂ uptake of the PR samples decrease markedly smaller than those of the PAC samples. PAC0.5_700 and PAC1.0_700 showed a superior value of 81.8 g/L and 61.2 g/L, while PR3_700 and PR4_700 achieved a volumetric CO₂ uptake of 25.9 g/L, 20.7 g/L, respectively. Due to the higher bulk density, PAC samples also have a superior volumetric CO₂ uptake than that of PEI/silica, although the gravimetric CO₂ uptake for PEI/silica is higher than that of the PAC samples.



Fig. 7.5 Comparison of gravimetric and volumetric CO_2 uptakes at 25 °C and 0.15 bar for carbon beads and PEI/silica

In conclusion, PAC0.5_700 and PAC1.0_700 are more promising than the PR samples for post combustion carbon capture as a result of their exceptional volumetric CO₂ uptake.

7.2 Conclusions

In this project, the author has developed effective carbon-based porous solid adsorbents of solid looping technologies for post combustion carbon capture. A range of carbon spheres derived using two different precursors have been developed, characterised and compared in order to determine their potential in industrial application. The effects of K intercalation as well as microporosity on CO₂ adsorption behaviours were investigated and analysed. The main conclusions can be summarised as follows:

1. The investigation of phenolic resin-based carbon spheres reveals that (1) Nitrogen-free spherical carbon beads, PR series with a uniform diameter of ca. 0.6-0.8 mm can be easily prepared by hydrothermal synthesis, and the intercalation of K significantly increased the CO₂ capacity of the AC beads by a factor of up to 2 at 0.15 bar while the effects of the treatment on their mechanical strength and morphological features are small at KOH/AC mass ratios of 0.3 and below. (2) The results suggest that the enhanced CO₂ adsorption of potassiumintercalated carbons, as highlighted by their higher isosteric heat of adsorption, are closely related to the formation of extra-framework K⁺ cations. The measured heats of adsorption for the PRAC beads were between 32 and 40 kJ/mol, compared to 27 kJ/mol for the raw AC. This provides evidence of significantly increased electrostatic interactions of the carbon surface with CO₂ molecules. The formation of K^{δ^+} -O^{δ^-} zwitterion-like surface functional groups gives rise to a greater surface affinity towards CO_2 to enhance adsorption capacity. (3) There appears to be a low critical K concentration, which is not much more than ca. 1 wt% in the case of the carbon beads examined, below which the beneficial effect of K intercalation on CO_2 adsorption becomes negligible. (3) The results also demonstrate that the dual-site Langmuir model can be used to effectively characterise the adsorption behaviours of porous K-intercalated carbon PR samples where there is high heterogeneity existing in this material. (4) The relatively low heats of adsorption, coupled with the CO₂ uptakes achieved, fast kinetics and excellent mechanical strength means that the performance of the PRACs for Pulverised Fuel Post-Combustion Capture in terms of the overall energy penalty is potentially superior to strongly basic adsorbents, such as those based on polyethyleneimine.

2. In the study of coal-tar pitch-based carbon adsorbents, (1) microporous carbon spheres with a diameter ranging from 1-2 mm and high bulk density and volumetric CO₂ capacity have been prepared and characterised using nitrogenfree precursors, namely PAC series and PBSK series. (2) Different activation methods including physical and chemical activation have been carried out and indicated that one-step KOH activation showed advantage to develop carbon adsorbents with maintaining the microporous structure, i. e., pore size smaller than 0.8 nm. PAC0.5_700 and PAC1.0_700 have obtained a well-designed microporous structure with a microporousity 98 % for PAC0.5_700 and 99 % for PAC1.0_700 respectively. By employing NLDFT model, the result shows that a high narrow microporosity (which is defined as: Vnarrow/ Vmicro) of 87 % for PAC0.5_700 and 88 % for PAC1.0_700 were also obtained. (3) The results also prove that owing to the narrow micropores and K-doping, the samples demonstrated superior to current reported data of CO₂ capacities at relatively low CO₂ partial pressure. For instance, PAC0.5_700 possessed a CO₂ uptake of 3.13 mmol/g and 1.86 mmol/g at 0 °C and 25 °C at 0.15bar, while PAC1.0_700 obtained that of 3.15 mmol/g and 1.83mmol/g at the same conditions. (4) 50 cycles of adsorption and desorption were also carried out and both samples PAC0.5_700 and PAC1.0_700 showed excellent adsorption dynamics and regeneration efficiency. (5) The comparison of the bulk density and volumetric CO_2 capacity between the samples PAC and the carbon materials reported in the literature indicates the great potential of PAC samples for post combustion carbon capture.

3. The performance of selected carbon spheres derived from different precursors have been compared and characterised. It has been concluded that at higher adsorption temperatures and lower CO₂ partial pressures, micropore that is smaller than 0.4 nm plays a dominant role in CO₂ uptakes. Along with the increase of adsorption temperature and CO₂ partial pressure, the critical pore size decreases markedly for the porous carbon materials. In addition, according to the comparisons of the mechanical strength, bulk density and volumetric capacity between the PR samples and PAC samples, PAC samples appear to have greater potential for post combustion carbon capture.

7.3 Future work

7.3.1 Modification of porous carbon spheres

The porous carbon spheres, the PR and PAC samples reported in this thesis have both shown their potential for post combustion carbon capture. However, they have their own corresponding problems for fluidised bed testing.

As for phenolic resin-based PR samples, although they have ideal spherical form with a diameter of 0.6-0.8 mm, the mechanical strength needs to be enhanced during preparation process. As a typical polymeric material, it is well known that the mechanical strength of the carbon material is determined by the polymer sphere. One way to solve this is to replace the precursor with monomer that has a higher molecular weight, resulting in the

increase of average molecular weight of resulting parent sample. Alternatively, in order to conduct K intercalation, more mild activation agents such as potassium oxalate can be employed, rather than strong alkaline KOH.

As for coal-tar pitch-based PAC samples, although it has superior mechanical strength and bulk density, in reality, how to achieve balance with the volumetric CO₂ uptake and a relatively small minimum fluidisation velocity (Umf) will be the biggest challenge for this material. For fluidised bed testing, an appropriate minimum fluidisation velocity does not only meet the requirement of good mixing of particles in the adsorber, but also need to keep the adsorbents in situ, rather than flying to the pipeline, as well as taking the purge flow of the flue gas into consideration. To reduce the diameter as well as increase the porosity of pitch-based spheres during preparation process is the easiest way to minimise the minimum fluidisation velocity for pitch-based carbon spheres. In the preparation of raw pitch spheres, a few of parameters of stabilisation could be optimised. More specifically, it is reasonable to reduce the heating rate from 0.5 to 0.1-0.2 °C/min and increase the duration of stabilisation at 300 °C to conduct thorough mild oxidation in air. Another alternative is to employ n-heptane with as-obtained pitch beads over night before stabilisation, so as to increase the thermosetting property.

7.3.2 Electrostatic force analysis of K-intercalated carbon spheres

In this thesis, the results have proven the extraordinary effect of K intercalation on the CO_2 capacity, especially at low CO_2 partial pressures. Combined with data from soxhlet extraction and Elemental mapping, it was found only slightly more than *ca*. 1 wt% of K is required to give the maximum benefit from intercalation that increases the surface polarity and the affinity towards CO_2 to enhance adsorption capacity. It is assumed that

the promotion of K intercalation was essentially as a result of the electrostatic interactions of phenolates, which is -OK in this case. Therefore, as a consequence, it is of great importance to further analyse on the design of an adsorption model of K-carbon spheres of CO_2 and to measure the electrostatic force to give information on the surface of the carbon spheres before and after K intercalation.

It is well known that Atomic Force Microscopy (AFM) or Electrostatic Force Microscopy (EFM) is capable of measuring the electrostatic force. The difference between carbon spheres before and after K intercalation in terms of electric potential and electrostatic force could be obtained. In addition, if we could modify the equipment by injection CO₂ in situ, the dynamic changes of adsorption of CO₂ of K-intercalated carbon adsorbent could be detected. The results will provide direct evidence of the effect of K- intercalation and supply valuable reference on the dynamic adsorption behaviours for porous carbon materials.

7.3.3 Fluidised bed testing of K-intercalated carbon spheres

The previous results of K-intercalated carbon materials were all carried out in lab-scale. It is necessary to scale up the preparation of K treatment of carbon adsorbents from several grams to kg level, so as to test the adsorption behaviours with simulated gas components as coal-fired or natural gas power plant. Fig. 7.6 (Zhang et al., 2014b) displays the bubbling fluidised bed reactor in our research group that is designed and manufactured to assess solid adsorbents for CO₂ capture with simulated flue gases under low to medium adsorption/desorption temperatures conditions.




Fig. 7.6 (a) Schematic and (b) a photograph of the bubbling fluidised bed reactor

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APPENDICES

APPENDIX A

LIST OF PUBLICATIONS

Published manuscripts during PhD:

- Jingjing Liu, Nannan Sun, Chenggong Sun, Hao Liu, Colin E. Snape, et al. Spherical potassium intercalated activated carbon beads for pulverised fuel CO₂ post-combustion capture. Carbon 94, 243-255, 2015.
- 2. Nannan Sun, Chenggong Sun, Jingjing Liu, Hao Liu, Coin E. Snape, et al. Surface modified spherical activated carbon materials for pre-combusiton carbon dioxide capture. RSC Advances 5 (42), 33681-33690, 2015.
- Bingjun Zhu, Kaixi Li, Jingjing Liu, Hao Liu, Chenggong Sun, et al., Nitrogenenriched and hierarchically porous carbon macro-spheres-ideal for large-scale CO₂ capture. Journal of Materials Chemistry A 2(15), 5481-5489, 2014.
- Nannan Sun, Chenggong Sun, Jingjing Liu, Lee Stevens, Trevor Drage, et al. Synthesis and Characterisation and evaluation of activated spherical carbon materials for CO₂ capture. Fuel, 113, 854 - 862, 2013.

Prepared manuscripts:

- Jingjing Liu, Luis Jaimes, Xin Liu, Yuan Sun, Chenggong Sun, Hao Liu, Colin E. Snape. CO₂ adsorption performance of chia seed-derived activated carbons for post combustion capture. (To be submitted soon)
- Jingjing Liu, Xin Liu, Lee Stevens, Chenggong Sun, Hao Liu, Colin E. Snape. Superior volumetric CO₂ adsorption capacity of pitch-based carbon spheres for post combustion capture. (To be submitted soon)
- 3. Xin Liu, Jingjing Liu, Chenggong Sun, Hao Liu, Colin E. Snape. *One step synthesis of rice husk based activated carbon for carbon capture.* (To be submitted soon)

APPENDIX B

DUAL SITE LANGMUIR MODELING DATA

	PR0 at 0°C		F	PR0 at 25°C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00103	0.02427	0.02429	0.00122	0.01018	0.01020
0.00129	0.02927	0.02930	0.00139	0.01112	0.01114
0.00182	0.03890	0.03894	0.00204	0.01565	0.01569
0.00245	0.05026	0.05031	0.00300	0.02263	0.02268
0.00350	0.07009	0.07016	0.00428	0.03252	0.03260
0.00485	0.09566	0.09575	0.00635	0.04818	0.04830
0.00678	0.13162	0.13175	0.00950	0.07127	0.07144
0.00953	0.17990	0.18009	0.01412	0.10426	0.10451
0.01330	0.24232	0.24258	0.02096	0.15048	0.15086
0.01862	0.32323	0.32359	0.03081	0.21288	0.21344
0.02583	0.42333	0.42384	0.04534	0.29835	0.29917
0.03599	0.55072	0.55144	0.06667	0.41294	0.41415
0.05006	0.70845	0.70944	0.09799	0.56430	0.56608
0.06960	0.90166	0.90304	0.14410	0.76132	0.76393
0.09663	1.13537	1.13729	0.21162	1.01253	1.01638
0.13438	1.41800	1.42066	0.31112	1.32928	1.33494
0.18670	1.75266	1.75637	0.46598	1.74123	1.74971
0.26700	2.18439	2.18969	0.68608	2.21892	2.23142
0.37113	2.64811	2.65549	1.01123	2.77845	2.79690
0.51822	3.18520	3.19551			
0.00103	0.02427	0.02429			
0.00129	0.02927	0.02930			

Table B.1 Excess and absolute loadings for PR0

PR1_600 at 0°C			PR1_600 at 25°C		
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00049	0.09194	0.09195	0.00063	0.04501	0.04502
0.00085	0.12360	0.12362	0.00075	0.05152	0.05154
0.00094	0.13410	0.13411	0.00099	0.06019	0.06020
0.00136	0.15951	0.15953	0.00140	0.07130	0.07132
0.00183	0.19576	0.19579	0.00197	0.08539	0.08542
0.00264	0.23630	0.23634	0.00290	0.10568	0.10573
0.00348	0.27623	0.27629	0.00431	0.13421	0.13428
0.00504	0.33710	0.33719	0.00641	0.17091	0.17101
0.00675	0.39440	0.39452	0.00948	0.21808	0.21823
0.00952	0.47498	0.47514	0.01398	0.27792	0.27814
0.01305	0.56282	0.56305	0.02083	0.35558	0.35590
0.01839	0.67607	0.67639	0.03050	0.44867	0.44915
0.02568	0.80620	0.80664	0.04485	0.56651	0.56722
0.03566	0.95718	0.95779	0.06630	0.71395	0.71500
0.04982	1.13675	1.13761	0.09740	0.89275	0.89429
0.06917	1.34205	1.34324	0.14373	1.11289	1.11515
0.09633	1.58304	1.58469	0.21151	1.37738	1.38071
0.13446	1.86269	1.86501	0.31118	1.69423	1.69913
0.18707	2.18165	2.18487	0.46535	2.08575	2.09309
0.26711	2.57563	2.58023	0.68495	2.52492	2.53574
0.37153	2.99131	2.99771	1.01281	3.03017	3.04620
0.51699	3.45741	3.46633			
0.72371	3.97873	3.99123			
0.00049	0.09194	0.09195			

Table B.2 Excess and absolute loadings for PR1_600

	PR1_700 at 0°C		PR	1_700 at 25°C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00053	0.11977	0.05239	0.00075	0.05239	0.05239
0.00077	0.14924	0.06929	0.00116	0.06929	0.06929
0.00093	0.16626	0.08000	0.00142	0.08000	0.08000
0.00129	0.19413	0.09450	0.00197	0.09450	0.09450
0.00175	0.23413	0.12021	0.00292	0.12021	0.12021
0.00262	0.28289	0.15168	0.00434	0.15168	0.15168
0.00347	0.32909	0.19246	0.00639	0.19246	0.19246
0.00508	0.39842	0.24561	0.00946	0.24561	0.24561
0.00671	0.45984	0.31197	0.01400	0.31197	0.31197
0.00927	0.54183	0.39405	0.02063	0.39405	0.39405
0.01310	0.64616	0.49657	0.03034	0.49657	0.49657
0.01842	0.76820	0.62570	0.04497	0.62570	0.62570
0.02561	0.90656	0.78085	0.06617	0.78085	0.78085
0.03579	1.06900	0.97025	0.09739	0.97025	0.97025
0.04972	1.25499	1.19987	0.14359	1.19987	1.19987
0.06953	1.47378	1.47524	0.21160	1.47524	1.47524
0.09679	1.72323	1.80346	0.31174	1.80346	1.80346
0.13506	2.01202	2.20582	0.46564	2.20582	2.20582
0.18814	2.34131	2.65500	0.68609	2.65500	2.65500
0.26257	2.71798	3.16530	1.00991	3.16530	3.16530
0.37233	3.16576	3.17201			
0.51868	3.64200	3.65071			
0.72421	4.16703	4.17921			
0.00053	0.11977	0.05239			

Table B.3 Excess and absolute loadings for PR1_700

	PR1_800 at 0°C		PR	1_800 at 25°C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00036	0.06536	0.06536	0.00088	0.06570	0.06571
0.00053	0.08500	0.08501	0.00102	0.07230	0.07231
0.00071	0.11079	0.11080	0.00139	0.08727	0.08729
0.00100	0.13387	0.13389	0.00198	0.10271	0.10274
0.00131	0.15716	0.15718	0.00292	0.12619	0.12624
0.00189	0.19113	0.19116	0.00439	0.15736	0.15743
0.00253	0.22801	0.22805	0.00627	0.19343	0.19353
0.00365	0.28212	0.28219	0.00948	0.24595	0.24611
0.00493	0.33493	0.33502	0.01399	0.31025	0.31049
0.00684	0.40464	0.40476	0.02083	0.39442	0.39477
0.00937	0.48379	0.48396	0.03061	0.49679	0.49731
0.01316	0.58652	0.58676	0.04503	0.62535	0.62612
0.01848	0.70992	0.71026	0.06641	0.78518	0.78631
0.02577	0.85183	0.85230	0.09769	0.97963	0.98129
0.03572	1.01522	1.01588	0.14395	1.21721	1.21965
0.04986	1.20994	1.21086	0.21213	1.50342	1.50702
0.06941	1.43483	1.43611	0.31233	1.84393	1.84923
0.09669	1.69541	1.69720	0.46043	2.24487	2.25269
0.13474	1.99534	1.99783	0.68815	2.72595	2.73766
0.18752	2.33635	2.33982	1.01096	3.24584	3.26306
0.26182	2.72657	2.73142			
0.37201	3.19227	3.19916			
0.51791	3.67965	3.68926			
0.00036	0.06536	0.06536			
0.00053	0.08500	0.08501			

Table B.4 Excess and absolute loadings for PR1_800

	PR2_600 at 0°C		PR	2_600 at 25°C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00045	0.14966	0.14966	0.00070	0.13403	0.13404
0.00049	0.22207	0.22208	0.00093	0.16614	0.16616
0.00077	0.25908	0.25909	0.00134	0.19196	0.19198
0.00092	0.29403	0.29404	0.00201	0.22997	0.23000
0.00138	0.34067	0.34069	0.00293	0.26651	0.26655
0.00176	0.37872	0.37875	0.00443	0.31780	0.31786
0.00263	0.43817	0.43820	0.00657	0.37219	0.37228
0.00342	0.48774	0.48779	0.00960	0.43805	0.43817
0.00479	0.55758	0.55765	0.01369	0.51023	0.51040
0.00669	0.63768	0.63777	0.02003	0.60131	0.60156
0.00941	0.73008	0.73021	0.02974	0.71134	0.71172
0.01310	0.83247	0.83264	0.04506	0.85195	0.85251
0.01837	0.95156	0.95181	0.06492	0.99330	0.99411
0.02514	1.07657	1.07692	0.09469	1.16288	1.16406
0.03517	1.22283	1.22331	0.14075	1.36945	1.37121
0.04854	1.38080	1.38147	0.21436	1.62376	1.62644
0.06809	1.56768	1.56861	0.31481	1.89175	1.89570
0.09522	1.77430	1.77560	0.46373	2.19946	2.20527
0.13244	2.00093	2.00274	0.68432	2.54877	2.55736
0.19142	2.28464	2.28726	1.01002	2.93635	2.94905
0.26642	2.56961	2.57325			
0.36917	2.88080	2.88585			
0.51737	3.23634	3.24343			
0.00045	0.14966	0.14966			
0.00049	0.22207	0.22208			

Table B.5 Excess and absolute loadings for PR2_600

PR2_700 at 0 ^o C			PR2_700 at 25 ^o C		
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00035	0.09555	0.09556	0.00073	0.11077	0.11078
0.00036	0.11231	0.11232	0.00106	0.13036	0.13038
0.00054	0.13336	0.13337	0.00133	0.14649	0.14651
0.00068	0.16647	0.16648	0.00202	0.17101	0.17104
0.00103	0.20161	0.20162	0.00305	0.20295	0.20299
0.00126	0.22420	0.22422	0.00438	0.23642	0.23648
0.00181	0.26937	0.26940	0.00636	0.28085	0.28094
0.00249	0.31320	0.31324	0.00943	0.34163	0.34177
0.00356	0.37692	0.37698	0.01413	0.41937	0.41957
0.00491	0.44395	0.44402	0.02070	0.51154	0.51184
0.00664	0.51781	0.51792	0.03067	0.62662	0.62706
0.00940	0.61678	0.61693	0.04511	0.76507	0.76572
0.01308	0.72878	0.72898	0.06671	0.93299	0.93396
0.01843	0.86114	0.86143	0.09826	1.13144	1.13287
0.02556	1.00765	1.00806	0.14475	1.36885	1.37095
0.03582	1.18045	1.18102	0.21376	1.64770	1.65081
0.04992	1.37405	1.37484	0.31469	1.97444	1.97902
0.06993	1.59779	1.59890	0.46438	2.35350	2.36026
0.09774	1.84896	1.85051	0.68428	2.77903	2.78900
0.13646	2.13334	2.13551	1.00918	3.24443	3.25916
0.19075	2.45360	2.45663			
0.26604	2.81008	2.81430			
0.37133	3.21116	3.21706			
0.00035	0.09555	0.09556			
0.00036	0.11231	0.11232			
0.00054	0.13336	0.13337			

Table B.6 Excess and absolute loadings for PR2_700

	PR2_800 at 0 ^o C		P	R2_800 at 25 ^o C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.000428	0.058032527	0.05804	0.000934	0.051284128	0.0513
0.000693	0.09966885	0.099681	0.001089	0.057275023	0.057293
0.000987	0.10875634	0.108774	0.001365	0.063597295	0.06362
0.001259	0.118482445	0.118505	0.002059	0.07492196	0.074956
0.001771	0.139946095	0.139978	0.002974	0.092477798	0.092527
0.002561	0.170147759	0.170194	0.004259	0.116579258	0.11665
0.003515	0.212376712	0.21244	0.006286	0.15041279	0.150517
0.00503	0.271726106	0.271817	0.009252	0.195126945	0.19528
0.006849	0.331733177	0.331857	0.013806	0.255143811	0.255372
0.0094	0.404912245	0.405082	0.020342	0.328820098	0.329157
0.013305	0.501306075	0.501546	0.029988	0.418587712	0.419084
0.018216	0.604502561	0.604831	0.043578	0.530656152	0.531377
0.025421	0.732120827	0.73258	0.06539	0.680953347	0.682035
0.035358	0.880636699	0.881275	0.095979	0.855265643	0.856854
0.049322	1.05504635	1.055937	0.14168	1.069178596	1.071524
0.068752	1.256910147	1.258152	0.208877	1.324373816	1.327834
0.095798	1.48868625	1.490417	0.314842	1.646393649	1.65161
0.133374	1.753667771	1.756078	0.463945	2.004725124	2.012417
0.186213	2.057778039	2.061144	0.685528	2.422711478	2.434091
0.266139	2.429670684	2.434485	1.011493	2.895159835	2.911984
0.370797	2.821223892	2.827935			
0.518368	3.263598246	3.272991			
0.723324	3.747947273	3.761071			
1.009842	4.268966092	4.287327			

Table B.7 Excess and absolute loadings for PR2_800

	PR3_600 at 0 ^o C		PR	3_600 at 25 ^o C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00037	0.12616	0.12616	0.00070	0.12297	0.12298
0.00060	0.18859	0.18860	0.00094	0.13803	0.13804
0.00075	0.21590	0.21591	0.00136	0.15900	0.15902
0.00092	0.24814	0.24816	0.00199	0.18303	0.18306
0.00144	0.29112	0.29114	0.00302	0.22177	0.22181
0.00177	0.32353	0.32356	0.00464	0.26956	0.26962
0.00259	0.38321	0.38325	0.00647	0.31705	0.31714
0.00347	0.43613	0.43619	0.00931	0.37916	0.37929
0.00480	0.50598	0.50605	0.01382	0.46280	0.46300
0.00682	0.59629	0.59640	0.02054	0.56402	0.56431
0.00959	0.69718	0.69733	0.03000	0.67845	0.67888
0.01321	0.80508	0.80528	0.04401	0.81713	0.81775
0.01846	0.93583	0.93611	0.06522	0.98475	0.98567
0.02561	1.07910	1.07950	0.09586	1.17696	1.17831
0.03531	1.23688	1.23742	0.14117	1.40272	1.40471
0.04919	1.42109	1.42184	0.20862	1.66583	1.66878
0.06921	1.63420	1.63527	0.31561	1.98802	1.99248
0.09578	1.86141	1.86288	0.46451	2.33192	2.33850
0.13362	2.12139	2.12345	0.68490	2.71894	2.72865
0.18671	2.41152	2.41441	1.01119	3.14495	3.15931
0.26618	2.75535	2.75946			
0.37136	3.10838	3.11411			
0.51799	3.49368	3.50169			
0.00037	0.12616	0.12616			
0.00060	0.18859	0.18860			

Table B.8 Excess and absolute loadings for PR3_600

PR3_700 at 0 ^o C			PR3_700 at 25 ^o C			
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs	
Pressure	-	-	Pressure	-	loading	
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)	
0.00042	0.14321	0.14322	0.00073	0.11166	0.11167	
0.00070	0.16650	0.16652	0.00131	0.14348	0.14350	
0.00092	0.21532	0.21533	0.00135	0.14830	0.14832	
0.00135	0.26133	0.26135	0.00213	0.17872	0.17875	
0.00176	0.32171	0.32174	0.00291	0.21255	0.21259	
0.00245	0.37295	0.37298	0.00458	0.26583	0.26589	
0.00341	0.45193	0.45198	0.00644	0.31805	0.31814	
0.00484	0.53358	0.53365	0.00952	0.39179	0.39192	
0.00659	0.61635	0.61645	0.01381	0.47264	0.47283	
0.00937	0.72500	0.72514	0.02010	0.57386	0.57414	
0.01315	0.84825	0.84844	0.03014	0.70367	0.70409	
0.01848	0.99001	0.99028	0.04379	0.84536	0.84596	
0.02507	1.13157	1.13194	0.06451	1.01874	1.01963	
0.03486	1.30358	1.30411	0.09510	1.22240	1.22371	
0.04874	1.50221	1.50294	0.13999	1.46004	1.46197	
0.06805	1.72414	1.72516	0.21346	1.76200	1.76494	
0.09447	1.96907	1.97049	0.31295	2.07905	2.08335	
0.13210	2.24777	2.24975	0.46151	2.44522	2.45157	
0.18998	2.58775	2.59060	0.68158	2.85830	2.86768	
0.26519	2.93514	2.93911	1.00994	3.32505	3.33898	
0.36880	3.31807	3.32361				
0.51624	3.73744	3.74519				
0.72089	4.18330	4.19415				
0.00042	0.14321	0.14322				

Table B.9 Excess and absolute loadings for PR3_700

	-				
	PR3_800 at 0 ^o C		PR	.3_800 at 25 ^o C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00058	0.04837	0.04838	0.00067	0.03632	0.03633
0.00073	0.12435	0.12436	0.00100	0.05020	0.05021
0.00096	0.14086	0.14088	0.00155	0.07352	0.07355
0.00127	0.18851	0.18853	0.00197	0.08522	0.08525
0.00188	0.22703	0.22705	0.00292	0.11647	0.11651
0.00250	0.26908	0.26912	0.00456	0.15878	0.15885
0.00354	0.31821	0.31827	0.00671	0.20892	0.20902
0.00480	0.37113	0.37120	0.00924	0.25407	0.25420
0.00683	0.44279	0.44290	0.01480	0.33763	0.33784
0.00939	0.52019	0.52033	0.02094	0.41548	0.41578
0.01320	0.61608	0.61628	0.03067	0.52036	0.52079
0.01821	0.72508	0.72536	0.04531	0.65138	0.65202
0.02577	0.86494	0.86534	0.06407	0.78963	0.79053
0.03615	1.01869	1.01925	0.09432	0.97416	0.97549
0.04962	1.18643	1.18719	0.14011	1.20031	1.20229
0.07010	1.39768	1.39876	0.21320	1.48517	1.48818
0.09786	1.63380	1.63531	0.31507	1.79839	1.80285
0.13172	1.86912	1.87115	0.46440	2.15969	2.16627
0.18982	2.19883	2.20176	0.68516	2.57143	2.58114
0.26541	2.54251	2.54660	1.01131	3.02800	3.04236
0.37035	2.92575	2.93147			
0.51607	3.34842	3.35640			
0.72227	3.81222	3.82341			
0.00058	0.04837	0.04838			

Table B.10 Excess and absolute loadings for PR3_800

PR4_600 at 0 ^o C			PR4_600 at 25 ^o C		
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00042	0.02459	0.02459	0.00067	0.05096	0.05097
0.00055	0.10789	0.10790	0.00107	0.06659	0.06661
0.00076	0.12604	0.12605	0.00144	0.08084	0.08087
0.00092	0.16727	0.16729	0.00200	0.09965	0.09968
0.00136	0.19662	0.19664	0.00291	0.12794	0.12799
0.00178	0.23593	0.23596	0.00429	0.16410	0.16417
0.00257	0.28633	0.28638	0.00626	0.20938	0.20948
0.00349	0.34340	0.34346	0.00933	0.27174	0.27189
0.00518	0.42267	0.42276	0.01400	0.35158	0.35180
0.00669	0.48439	0.48451	0.02051	0.44614	0.44647
0.00964	0.58608	0.58625	0.03037	0.56616	0.56665
0.01305	0.68451	0.68474	0.04483	0.71062	0.71135
0.01810	0.80929	0.80961	0.06595	0.88289	0.88395
0.02551	0.95992	0.96037	0.09713	1.08938	1.09095
0.03526	1.12415	1.12477	0.14334	1.33540	1.33771
0.04931	1.31939	1.32026	0.21123	1.62443	1.62784
0.06859	1.54135	1.54256	0.31163	1.96308	1.96812
0.09598	1.79764	1.79933	0.48255	2.40826	2.41607
0.13333	2.08343	2.08578	0.70270	2.84751	2.85889
0.18645	2.41375	2.41704	1.01052	3.31738	3.33377
0.26747	2.81726	2.82198			
0.37124	3.22931	3.23587			
0.51716	3.69058	3.69972			
0.00042	0.02459	0.02459			
0.00055	0.10789	0.10790			

Table B.11 Excess and absolute loadings for PR4_600

	PR4_700 at 0 ^o C		PR	4_700 at 25 ^o C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs
Pressure			Pressure		loading
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00040	0.12814	0.12814	0.00069	0.07111	0.07112
0.00053	0.15231	0.15232	0.00103	0.09979	0.09980
0.00072	0.18678	0.18679	0.00136	0.11327	0.11329
0.00099	0.21209	0.21210	0.00208	0.14370	0.14373
0.00130	0.24459	0.24462	0.00293	0.17370	0.17375
0.00180	0.28617	0.28620	0.00428	0.21889	0.21896
0.00246	0.33414	0.33419	0.00629	0.27346	0.27357
0.00355	0.40094	0.40100	0.00938	0.34568	0.34585
0.00487	0.46814	0.46823	0.01393	0.43380	0.43405
0.00677	0.55319	0.55333	0.02046	0.53852	0.53888
0.00975	0.66210	0.66229	0.03009	0.66739	0.66792
0.01300	0.76404	0.76429	0.04467	0.82592	0.82671
0.01838	0.90471	0.90506	0.06548	1.01066	1.01182
0.02547	1.05970	1.06019	0.09669	1.23498	1.23669
0.03553	1.24127	1.24196	0.14228	1.49918	1.50171
0.04939	1.44881	1.44977	0.20994	1.81263	1.81636
0.06889	1.68889	1.69022	0.31538	2.19908	2.20469
0.09589	1.96181	1.96367	0.46425	2.62623	2.63450
0.13375	2.27515	2.27774	0.68478	3.11849	3.13069
0.18633	2.62974	2.63336	1.00934	3.66785	3.68587
0.26744	3.07031	3.07550			
0.37230	3.52700	3.53423			
0.51862	4.03653	4.04662			
0.00040	0.12814	0.12814			
0.00053	0.15231	0.15232			

Table B.12 Excess and absolute loadings for PR4_700
· · · · ·	PR4_800 at 0 ^o C		PR	4_800 at 25 ^o C	
Measured	Exc loading	Abs loading	Measured	Exc loading	Abs loading
Pressure			Pressure		
(bar)	(mmol/g)	(mmol/g)	(bar)	(mmol/g)	(mmol/g)
0.00059	0.05524	0.05526	0.00062	0.03303	0.03305
0.00069	0.06581	0.06582	0.00062	0.03418	0.03419
0.00094	0.08175	0.08177	0.00104	0.04462	0.04464
0.00129	0.10858	0.10861	0.00149	0.05512	0.05515
0.00184	0.13439	0.13443	0.00212	0.07512	0.07516
0.00251	0.16771	0.16776	0.00333	0.10108	0.10115
0.00358	0.21112	0.21120	0.00426	0.12065	0.12074
0.00475	0.25465	0.25476	0.00630	0.15807	0.15820
0.00687	0.32318	0.32333	0.00943	0.20874	0.20893
0.00954	0.39961	0.39982	0.01394	0.27334	0.27362
0.01340	0.49658	0.49687	0.02062	0.35612	0.35654
0.01818	0.60006	0.60046	0.03036	0.45953	0.46014
0.02549	0.73819	0.73875	0.04462	0.58932	0.59022
0.03569	0.90285	0.90364	0.06575	0.75209	0.75341
0.04950	1.09320	1.09429	0.09674	0.95223	0.95418
0.06887	1.32171	1.32323	0.14232	1.19843	1.20130
0.09616	1.59133	1.59345	0.20950	1.49889	1.50312
0.13329	1.89998	1.90291	0.31506	1.88396	1.89033
0.18580	2.26499	2.26909	0.46333	2.32057	2.32994
0.26562	2.72168	2.72754	0.68391	2.84153	2.85538
0.37015	3.21128	3.21945	1.00689	3.43694	3.45736
0.51635	3.77366	3.78508			
0.72134	4.40063	4.41659			
0.00059	0.05524	0.05526			

Table B.13 Excess and absolute loadings for $PR4_800$

APPENDIX C

PARAMETERS FOR DUAL SITE LANGMUIR MODEL

Sample	q s,A		QS,B		bA		b _B	
	value	Standard Error	value	Standard Error	value	Standard Error	value	Standard Error
PR0	7.66988	0.05284	0.96037	0.0349	8.54196E-6	2.19719E-7	1.42116E-4	5.45549E-6
PR1_600	5.97168	0.15147	0.81812	0.05853	1.60373E-5	1.25624E-6	0.00108	1.63501E-4
PR1_700	-0.03383	1.46559E15	54.92735	10258.1836	-5.89179E-8	2.55271E9	0.12278	12.37212
PR1_800	-0.00967		62.21655	17850.8995	-1.46175E-8		0.11138	16.97338
PR2_600	4.23854	0.13173	0.92883	0.05556	2.49104E-5	2.56818E-6	0.0032	5.18129E-4
PR2_700	5.4153	0.14543	0.97597	0.06768	1.99589E-5	1.81621E-6	0.00148	2.29731E-4
PR2_800	5.68797	0.14966	0.91648	0.06955	1.42393E-5	1.23655E-6	6.24956E-4	8.4169E-5
PR3_600	4.71	0	0.97	0	8.9525E-6	2.15435E-7	5.68798E-4	4.83492E-5
PR3_700	5.07458	0.12089	1.09814	0.06204	2.22812E-5	1.88887E-6	0.00169	2.19468E-4
PR3_800	5.26812	0.12727	0.85212	0.05615	1.83562E-5	1.4623E-6	0.00129	1.84158E-4
PR4_600	5.7709	0.13992	0.99207	0.06303	1.78751E-5	1.43841E-6	0.00116	1.55201E-4
PR4_700	6.36277	0.18259	1.0114	0.07216	1.84524E-5	1.67139E-6	0.00153	2.52374E-4
PR4_800	7.61104	0.17745	0.94686	0.06618	1.19274E-5	8.23458E-7	5.30306E-4	6.42827E-5

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