

CRANFIELD UNIVERSITY

BASIL WADI

CO₂ SEPARATIONS AND THE ROLE OF SURFACE
FUNCTIONALITY

SCHOOL OF WATER AND ENERGY

Energy and power

MSc BY RESEARCH

Academic Year: 2019 –2020

Supervisor: Ali Nabavi

Associate Supervisor: Vasilije Manovic

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ABSTRACT

To curb irreversible environmental effects of climate change, urgent measures must be taken to limit anthropogenic emissions and achieve net-zero carbon goals by 2050. Carbon capture technology to meet these goals is wide ranging, with novel methods directed at biogas upgrading or direct air capture. Biogas is produced from the anaerobic digestion of biological waste and considered a valuable renewable energy source; to produce biomethane for use interchangeably with natural gas. However, widespread use of established separation processes is limited, primarily due to low CO₂ selectivity or high energy demands of cyclic operation. One method to tackle these issues is the development of novel sorbents for use in pressure swing adsorption, targeting maximum CO₂ capacity and selectivity, while minimising regeneration energy penalties. Adsorbents incorporated with amines can meet one of these criteria, selectively adsorbing CO₂, but require high regeneration energies. Herein, the adsorption performance of a diverse range of amines grafted on mesoporous silica at varying densities is studied, to understand developing adsorption mechanisms, and identify the ideal degree of functionalisation for gas separations. It was found that although high amine densities led to the highest enhancement in CO₂ capacity and selectivity, moderate levels have comparable selectivity and capacity in isothermal adsorption-desorption conditions, standing out are di- and secondary amines. Diamine loadings achieved an adsorption capacity of 1.12 mmol/g, a heat of adsorption of 35-50 kJ/mol, and an IAST selectivity of 374 at CO₂ partial pressures of 40 kPa. Secondary amines had a low capacity of 0.67 mmol/g, but a higher heat of adsorption comparatively. The optimal binder formulation for pellet preparation of amine grafted silicas was also studied, a necessary step in conducting laboratory scale fixed-bed adsorption studies. When applying amines for ambient air adsorption, very high amine loadings result in slow adsorption kinetics, rendering the advantage of their high capacity debatable. Moderate loadings of primary and triamine under humid conditions have higher adsorption rates >250 µg/g/min, making them more suited for fast cycle processes.

Keywords:

Carbon capture, mesoporous silica, SBA-15, amine functionalisation, biogas upgrading, direct air capture, pellet formation

ACKNOWLEDGEMENTS

I would like to thank Howard Smith, Euan Hakon, Jane Hubble, Maria Biskupska, and Richard Andrews, Christine Kimpton, Peter Clough and Fatih Gulec for their help and support during the entire experimental work. Additionally would like to thank Ayub Golmakani for his support in specific experimental and theoretical work relevant to this research. Additionally, I would like to thank the team from Aston University which include Anisa Mahomed, and Amin Osatiashtiani, who aided in running certain experimental work for material testing. I would also like to thank my supervisor Ali Nabavi for guiding me through the unique norms and standards of the academic world.

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LIST OF ABBREVIATIONS

IT	Information Technology
AEAPT	3-(2-aminoethylamino)propyltri-methoxysilane
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
BAPT	(N-butylamino)propyl-trimethoxysilane
BdB-FHH	Broekhoff-de Boer - Frenkel-Halsey-Hill
BJH	Barrett-Joyner-Halenda
CA	Combined amine
CCS	Carbon capture and storage
DAC	Direct air capture
DFT	Density functional theory
DMA	Dynamic mechanical analysis
DMAPT	dimethylaminopropyl)trimethoxysilane
DT	Diethylene-triamine
EA	Elemental analysis
FTIR	Fourier transform infrared spectroscopy
GHG	Greenhouse gases
IAST	Ideal adsorption solution theory
IGCC	Integrated gasification and combined cycle
IR	Infrared
LJ	Lennard Jones
MM	Molecular mechanics
MOF	Metal organic framework

NET	Negative-net emissions technology
NMR	nuclear magnetic resonance
PEI	Polyethylenimine
SA	Single amine
SEM	Scanning electron microscope
SSNMR	Solid state nuclear magnetic resonance
TAEPT	3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane
TEPA	Tetraethylenepentamine
TGA	Thermogravimetric analysis
TMAP	([trimethoxy[3-(methylamino)propyl]silane)
TSA	Temperature swing adsorption
UFF	Universal forcefield
VdW	Van der Waals

1 INTRODUCTION

1.1 Background

The concentration of carbon dioxide in the atmosphere has continuously accelerated over the last century, increasing by 22 ppm from 1900 to 1960 compared to 100 ppm from 1960 to 2020, with 2020 reaching a record annual median of 414ppm^{1,2}. The Paris Agreement outlining actions to mitigate climate change has led to a global consensus; that anthropogenic warming must be limited to 1.5°C by 2100, accomplished through net-zero emissions by mid-century to avoid irreversible or long-term environmental damage^{3,4}. Global greenhouse (GHG) emission from energy use account for ~72% of the total, with industrial sources and buildings making up more than half of that total. Targeting CO₂ emissions from these mentioned point sources through carbon capture is a key step towards net-neutrality goals. These methods encompass a diverse range of technology: some of which are flue gas treatment of post combustion products, or pre-combustion capture such as syngas treatment in steam-methane reforming plants⁵. However, much of the current technology is under continuous development due to economic downsides, for example, carbon capture and storage (CCS) energy penalties in post-combustion capture implemented on existing plants can reach as high as 40% of net kWh of plant output⁶. While in processes such as methane reforming, the syngas is often treated to produce high purity hydrogen and CCS implementation into these processes continues to be under study^{7,8}. This has made integrated gasification and combined cycle (IGCC) one of the few current alternative that completely aims for CCS integration, however, IGCC is subject to high capital costs compared to post combustion process implementation and operational costs that are almost equivalent^{9,10}.

In short, carbon capture technology continue to be under study, and the current benchmark process for carbon capture from lower CO₂ partial pressure gas streams remains to be amine scrubbing, but is a process that imposes high operational costs due to regeneration energy penalties^{11,12}. Consequently, to

reduce the regeneration energy, the employment of solid adsorbent in pressure swing adsorption (PSA) processes has gained increasing interest, but current state-of-the-art adsorbents suffer from low selectivity and low product recovery^{13–15}.

1.2 Motivation

PSA processes separate feed components via cyclic operation by modulating the pressure, and adsorbents that physisorb CO₂ are more commonly used in these arrangements¹⁶. Examples of low CO₂ partial pressure employment of separation materials include zeolites in CO₂/CH₄ separations, which selectively adsorb CO₂ through pore sizes tailored to the kinetic diameter of CO₂ rather than CH₄. Zeolites offer benchmark adsorption capacity and selectivity, but they are sensitive to moisture and result in low CH₄ recovery due to the similarity in the kinetic diameter of CO₂ and CH₄ of only 0.05 nm^{17,18}. On the other hand, in ultra-low CO₂ partial pressure gases such as air, physisorption is insufficient in selectively capturing CO₂, and make chemisorption by amine functionalities a strong contender as a material for direct air capture. Consequently, the incorporation of functional groups such as amines to selectively interact with CO₂ and enhance the recovery of CH₄ in biogas, or selectively separate ultra-low concentrations of CO₂ from an air stream is the focal topic of this thesis¹⁹.

When incorporating amines in adsorbents, maximising the quantity of amines leads to very highly selective CO₂ adsorption performance, but requires significant regeneration energy input to desorb the CO₂ captured. Since the selectivity of an adsorbent is dependent on the principle adsorption mechanism and the adsorbent-adsorbate interactions, tailoring the amine functionalities of an adsorbent can aid in the synthesis of a balanced adsorbent. This work probes the resulting selectivity, capacity, and energy efficiency of different amine groups at different surface loadings, and aims to make conclusions on the ideal amine type and level of functionality that can be incorporated into an adsorbent to provide an enhancement in the selective adsorption of CO₂, at a minimal impact on regeneration energy. On the other hand, in targeting CO₂ capture from ambient

air, the adsorbent's kinetics and capacity must be balanced to optimise air capture processes for continuous and cyclic operation, and this is similarly probed within this work.

1.3 Aims and objectives

The aim of this research is to investigate the effectiveness of amine functionalised silicas for CO₂ separations, for CO₂ removal from binary gas mixtures of partial pressures below 50 kPa. This is carried out in two main steps: by narrowing down the influence of amines on CO₂/CH₄ separation efficiency, and by preparing pelletised materials that can be used in high throughput fixed bed adsorption processes. Additionally, the suitability of amine functionalities in direct air capture (DAC) applications, which require effectiveness in ultra-low CO₂ partial pressures, has been assessed. Figure 1.1 outlines the sections of the thesis that aim to address the following research questions and objectives:

1. Synthesise amine functionalised mesoporous silicas using reagents demonstrating individual and combined amine moieties at different surface loadings.
2. Measure and compare the adsorption performance of the synthesised adsorbents using parameters of adsorption capacity, selectivity, and heat of adsorption of CH₄ and CO₂ gases. Objectives 1 & 2 are linked to the following research questions:
 - a. What changes in CH₄ and CO₂ adsorption interactions develop by primary, secondary, and tertiary amines up to 100 kPa? To what extent is the change in selectivity a factor of amine-CH₄ interactions?
 - b. How do CH₄ and CO₂ adsorption mechanisms change from combining amine moieties at different loadings, and through experimental and molecular simulation approaches, how does it relate to the intramolecular and intermolecular interactions taking place?

- c. Assessing the combined performance of the range of amines studied, what is the optimal amine loading for CO₂/CH₄ separations in isothermal conditions, and how does it compare to non-isothermal conditions?
3. Produce a pelletised version of the powdered mesoporous silica adsorbent that maintains a similar adsorption capacity as the powdered samples, while having strong mechanical integrity and is capable of amine functionalisation. This objective is linked to the following research question:
 - a. What is the optimal pellet binder composition of raw and functionalised SBA-15 that enhances mechanical strength, while having a minimal effect on the total CO₂ uptake?
4. Classify the effectiveness of amine functionalised silicas as CO₂ adsorbents for ambient air adsorption.
 - a. What is the adsorption capacity and kinetics arising from primary, diamine, and triamine grafted SBA-15 in DAC applications?

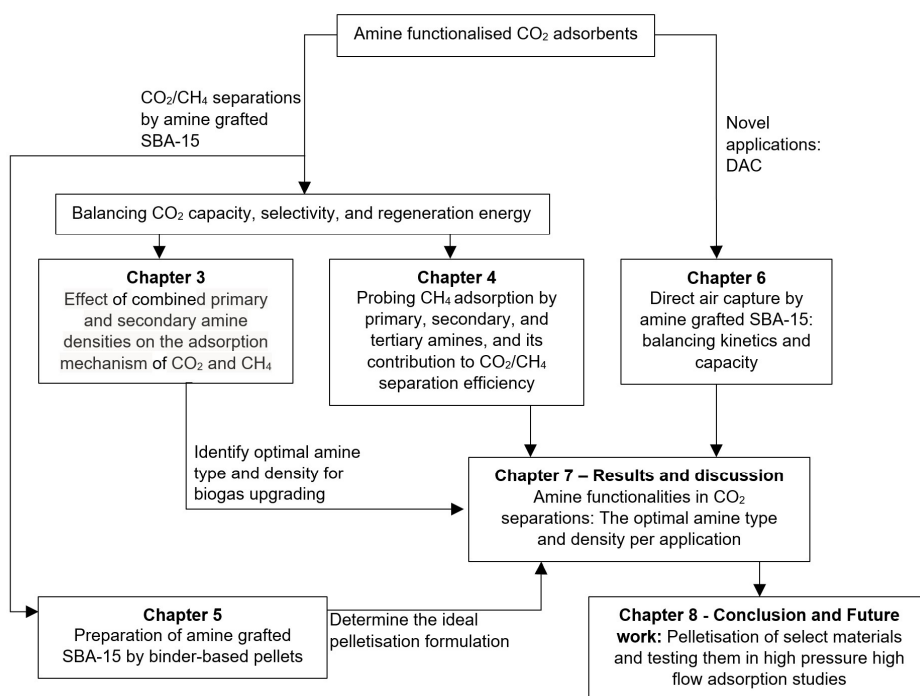


Figure 1.1. Outline of the sections of the thesis and the connections between them.

1.4 Novelty

Historically, amines have been successfully incorporated into a variety of adsorbent mediums, including zeolites, metal organic frameworks (MOF), carbons, silicas, and polymers^{20–23}. In the development of effective amine functionalised adsorbents, mesoporous silicas are often studied due to their adjustable yet uniform cylindrical pore distributions, high pore volume and high specific surface area, allowing for wide range of amine functionalisation^{18,24–28}. Additionally, the mesoporosity of these materials means excess void space, permitting the detailed study of adsorbate-amine interactions. Although with plenty of scientific work exploring the tailor-ability of silicas with amines, majority of studies concentrate on the maximum enhancement of CO₂ capacity by densely grafting amines on mesoporous silicas. Although superior capacities result from these materials, they lead to high energy penalties for the material's regeneration.

There is a gap in knowledge in understanding the change in adsorption performance as the degree of functionalisation increases, specifically in conditions at lower CO₂ partial pressures relevant to CO₂/CH₄, and DAC separations. This directly relates to the effect of amine functionalities on the adsorption capacity of CO₂, CO₂/CH₄ selectivity, and the regeneration energy demands at each level of functionalisation. Mapping this dependency of adsorption performance on the extent of functionalisation is key in developing novel amine functionalised adsorbents, which can be tailored to meet process specifications on an application specific basis.

The first step in this study was to graft SBA-15 using single amine and combined amine reagents at different surface loadings, and evaluate the ideal amine functionalisation density that balances the CO₂ adsorption capacity, the CO₂/CH₄ selectivity, and the associated energy demands for regeneration. Additionally, important conclusions on the effect of amine functionalities on CH₄ adsorption can be deduced from this step.

The second step was to investigate the effect of binder composition on the formation of a pellet from the powdered materials synthesised. There is little research into the effective pelletisation of powdered silica adsorbents, specifically in amine grafted materials, which is an essential step towards commercial carbon capture utilisation of these developed materials. A range of pellet formulations were prepared and were assessed based on their amine grafting efficiency, structural integrity, and CO₂ adsorption capacity.

The last step included a preliminary assessment of DAC applications by densely grafted SBA-15. These are novel operations that are recently finding relevance, and this study compares the resulting CO₂ capture and adsorption rates of different amine types for insight on which materials are the most advantageous for humid ambient air CO₂ capture.

1.5 Layout of thesis

A summary of the sections of this thesis is as follows: the introduction is presented in Chapter 1, the literature review in Chapter 2, Chapter 3 to 6 include the results of the research. Chapter 3 and 4 are papers currently under-review in a peer-reviewed journal, while Chapter 5 and 6 will be submitted for publication.

- Chapter 1 encompasses an introduction on the topic, an overview of the motive for this research. This is followed by highlighting the research aim, objectives, novelty, and structure of the thesis.
- Chapter 2 starts with an overview on carbon capture and the relevance of adsorbent development to biogas upgrading, followed by a critical comparison of amine functionalisation methods in silicas, and then by a detailed discussion of amine induced adsorption mechanisms, and a parametric evaluation of their applicability for CO₂/CH₄ separations. Additionally, included is a brief discussion on the current methods of adsorbent pelletisation, and DAC applications of amine functionalised silicas.

- Chapter 3 studies the effect of combined amine organ silane branches, and the combined effect of amine moieties and loadings on efficiency of CO₂/CH₄ separations. In this work, the unique intramolecular and intermolecular interactions that arise from multi amine containing organ silane branches are analysed. Additionally, the isothermal and non-isothermal operation is compared as a function of amine type and loading, giving insight into how to best utilise amine functionalities for these separations.
- Chapter 4 concentrates on single amine organ silane branches, important in isolating amine moiety influences on adsorbate interactions. In this study, the individual amine dependent influences on CO₂ and CH₄ adsorption were studied, with a specific concentration on the affinity of CH₄ to adsorb, and whether is it a factor of strictly steric influences or entropic ones, aided by molecular simulation methods.
- Chapter 5 explores various binder formulations, with a specific concentration on bentonite and LUDOX® as potential materials for the pellet formation of powdered SBA-15. These materials were prepared and tested to narrow down the most effective composition that balances structural integrity, while maintaining a close to equal adsorption capacity as the powdered material.
- Chapter 6 focuses on the added advantage of densely grafted SBA-15, showing exceptional enhancement of CO₂ uptake at CO₂ pressures found in air. A preliminary study was carried out on the feasibility of amine grafted mesoporous silicas for direct air capture (DAC), and whether they could offer a balance in adsorption capacity and kinetics not found in amine impregnated silicas.
- Chapter 7 includes a brief discussion combining the results of the research presented here.
- Chapter 8 presents the overall conclusions of the research and highlights suggested future studies.

1.6 Peer-reviewed publications

1. Wadi, B., Golmakani, A., Manovic, V. & Nabavi, A. Effect of combined primary and secondary amine loadings on the adsorption mechanism of CO and CH. *Chem. Eng. J.* (2021).
2. *Under review in Journal of Industrial and Engineering Chemistry*: Wadi, B., Golmakani, A., Manovic, V. & Nabavi, A. Probing CH₄ adsorption by primary, secondary, and tertiary amines, and its contribution to CO₂/CH₄ separation efficiency. *J. Colloid Interface Sci* (2021).
3. *Under review in Journal of Industrial and Engineering Chemistry* : Wadi, B., Golmakani, A., Manovic, V. & Nabavi, A. Direct Air Capture by Amine Grafted SBA-15: Balancing Kinetics and Capacity
4. *Accepted for Publication in the Journal of Powder Technology on July, 17, 2021*: Wadi, B., Mahomed, A., Ostatishtiani, A., Manovic, V. & Nabavi Preparation of amine grafted SBA-15 by binder-based pellets

2 LITERATURE REVIEW: AMINE FUNCTIONALISED SILICAS FOR CARBON CAPTURE AND BIOGAS UPGRADING

Abstract

There has been a continuous interest into research for the mitigation of climate change through carbon capture and storage (CCS) as applied to pre combustion, post combustion, air capture, and upgrading processes. This review encompasses the use of amine functionalised silicas within a broader context of carbon capture applications, slowly narrowed down to CO₂/CH₄ separations and biogas upgrading. In the pursuit of understanding the effects of amine functionalities on gas separations, a specific discussion on the adsorption mechanisms arising from amine's has been included. Additionally, the pelletisation of these adsorbents for commercial applications has been discussed. Finally, the discussion relates back to novel applications of amine functionalised silicas and their feasibility for DAC processes.

2.1 Introduction

In carbon capture applications, amine functionalities can enhance the CO₂ selectivity of adsorbents in a variety of gas mixtures, and the development of amine incorporated adsorbents for biogas upgrading has the potential of producing a higher CH₄ recovery and high purity CO₂ purge compared to non-functionalised adsorbents^{29,30}. However, within the literature, most studies of amine functionalised silicas target the incorporation of higher quantities of amines, leading to superior adsorption capacity but additional demands on the regeneration energy required of these adsorbent formulations^{20,31–34}. Within these studies are a few that seek to understand the molecular mechanisms dictating amine promoted adsorption of CO₂, but it is limited to these high amine loading materials or do not relate the performance to CO₂/CH₄ separation efficiency. Since the principal adsorption mechanism in an adsorbent dictates the desorption energy required to regenerate an adsorbent, it is important to

understand the changes in adsorption mechanisms resulting from incorporating different amine types within a range of loadings in CO₂/CH₄ separations^{35,36}. The gap in knowledge is a lack of data on the developing relationship in the observed CO₂ adsorption capacity, CO₂/CH₄ selectivity, and desorption energy efficiency because of different amine functionalities.

This review is divided into the following sections: Section 2.1 starts off by giving an overview on carbon capture and its relationship to biogas upgrading. Section 2.2 discusses the role of amines in CO₂ capture processes and the methods of amine functionalisation, with a brief comparison on the advantages and disadvantages of each. Section 2.3 concentrates on the adsorption mechanisms and molecular interactions of amine functionalised silicas, specifically for CO₂ adsorption. Section 2.4 relates the discussion back to CO₂/CH₄ separations, and the work that has been carried out amine functionalised silicas for these applications. Section 2.5 covers the adsorbent pelletisation, an essential part of real-world applications. Finally, Section 2.6 explores novel DAC applications of amine functionalised silicas and the related literature.

2.2 Carbon Capture

2.2.1 General Overview

As reported in 2020 by the National Centre for Environmental Information (NCEI), the average global surface temperatures in 2019 were the second highest since 1880, with an estimated anthropogenic warming between 0.1 and 0.3 °C per decade^{37,38}. This increase has been partially attributed to global atmospheric carbon dioxide concentrations, which averaged 414 ppm in 2020 as reported by the National Oceanic & Atmospheric Administration (NOAA)². Today's atmospheric CO₂ concentration is in stark contrast to the 300 ppm maximum average over the past 800,000 years reported from paleoclimatology data by The NCEI³⁹. In response, there has been a strong push towards establishing a long-term plan for decarbonisation. In the UK, the Climate Change Act was released in 2008, requiring that emissions be reduced by at least 80% by 2050 compared

to the 1990 baseline emissions. It should be noted that in 2019 the value was amended to 100% by 2050 as compared to the 1990 baseline emissions, emphasizing the urgency and feasibility of net-zero carbon emissions⁴⁰.

To meet the goals outlined by governmental regulations for a cleaner future, a balance must be found between the economic implications and the implemented transition towards cleaner technologies. Currently fossil fuels dominate energy production as well-established and cheap methods of energy generation, in 2017 they accounted for about 81% of usage worldwide as reported by IEA⁴¹. This has resulted in directing research initiatives towards the development of CCS technologies that can work in unison with currently running industrial processes, giving rise to several classifications of carbon capture technology.

Carbon capture technology can target pre-combustion or post-combustion sources; the processes utilized are dependent on the type of combustion process that will emit CO₂ into the environment⁵. Post combustion technologies are widely used in treating flue gas after combustion, but several complications arise leading to heavy energy costs for CO₂ capture. The low CO₂ partial pressure means high equipment costs because of the high-volume throughput, as well as heavy costs for the compression and storage of extracted CO₂. In addition, when using the well-developed Monoethanolamine (MEA)-based liquid scrubbing technology, the difference in temperature between adsorption and regeneration to remove the captured the CO₂ places a heavy energy requirement on the overall plant utilities^{11,12,42}.

pre-combustion technologies treat gases produced from the gasification of coal and from steam reforming of natural gas. Both processes lead to the formation of syngas which is further treated for the removal of CO₂ through absorption (solvent-gas contact) or adsorption (solid-gas contact) processes, with high adsorption or absorption efficiency facilitated by the higher pressure of the feed⁴³. Within the context of renewable energy, an additional category for carbon capture applications is biogas upgrading and will be the subject of discussion in the next section.

2.2.2 Biogas Upgrading

Biogas, produced through the anaerobic digestion of organic waste, has gained traction throughout the years as an alternative and sustainable form of energy world-wide⁴⁴. Since the year 2000, biogas production within the European Union has gone up by 87% from 2,186 ktoe to 16,838 in 2018⁴⁵. This percentage increase was levelled as a result of slower growth from 2016 onwards, but Biomethane plant production recovered in 2018, and they have shown a 51% increase in the number of plants by 2020⁴⁶.

There is a strong growing trend for Biogas usage in a variety of applications that include heat production and fuel for electric cars through purified biomethane, but stricter regulations for the better overall management of the use of land and food crops have affected the biogas sector's growth over the past few years^{47,48}. As a result, a shift towards the development of more efficient processes for biogas uses is necessary to achieve decarbonisation initiatives and ensure a continuous transition to cleaner energy.

The composition of biogas varies depending on the raw material and process utilized. In general, the anaerobic digestion and gasification of biomass produces a mixture of primarily carbon dioxide, methane, and small amounts of sulphur, nitrogen, and water vapour^{49,50}. Sulphur and water vapour are readily removed through well-established processes⁵¹. Nitrogen is expensive to remove, it is therefore addressed by minimizing sources that could produce it from the very beginning⁵¹.

This leaves a mixture of methane and carbon dioxide ranging in value from 53-70% and 30-47% respectively⁵⁰. The percentage of methane to carbon dioxide has a direct effect on the energy content of biogas, since methane is the only contributor to calorific value in the mixture (Table 1)^{52,53}. Standards for Biogas specifications vary between countries, but the general requirements for grid injection and vehicle fuel utilization are designed around Natural Gas specifications, and make raw Biogas inadequate for these applications⁵¹.

Table 2-1 Calorific values of natural gas, biogas, and biomethane^{52,53}

	Units	Natural Gas (85-92%, 9% Heavy HC)	Biogas(60-70% CH ₄ , 30-40% CO ₂)	Biomethane (97% CH ₄)
Calorific value(lower)	MJ/m ³	39	23	34
Wobbe index (higher)	MJ/m ³	55	27	45
Density (NTP)	kg/m ³	0.82	1.1	0.72
Energy (Per 1 Nm³)	kWh	11	~6-7	9.7

One of the limitations of Biogas for its potential use as a sustainable energy source includes increasing its calorific value and has led to many different biogas upgrading technologies. These technologies range from Membrane separation, Pressure Swing Adsorption (PSA), Absorption without chemical reaction, Absorption with chemical reaction, Cryogenic removal of carbon dioxide, and supplementary upgrading⁴⁹. Some of these methods have been effective at the removal of carbon dioxide to values below 3%, but require high operating costs, and lead to losses of methane within the reject stream, lowering product recovery and overall process efficiency⁴⁹.

The most utilized biogas upgrading technologies include PSA, amine scrubbing, and water scrubbing processes⁵⁴. Organic solvent scrubbing technologies such as Selexol or Genosorb have a strong grounding in H₂/CO₂ separation, but demonstrate a lower CH₄/CO₂ selectivity and higher operational costs within a biogas context⁵⁵⁻⁵⁷.

Amine scrubbing has been proven to provide the highest CH₄ purity at concentrations greater than 99%, with high CH₄ recovery compared to alternative technologies since CO₂ reacts preferentially with the solvent⁵⁸⁻⁶⁰. Although amine scrubbing has led in performance, PSA technology can minimize capital costs compared to scrubbing, even when CH₄ losses are higher in the product stream¹³⁻¹⁵. Cycle arrangement, operational conditions, as well as adsorbent type are several of the factors that can affect separation efficiency, and as a result, extensive research into the improvement of CH₄ recovery using PSA has been

underway^{13–15}. This includes not only PSA, but also Vacuum Swing Adsorption, Temperature Swing Adsorption (TSA), or a combination of them using commercial and novel adsorbents. These processes aim to tackle the shortcomings faced by conventional PSA processes while benefiting from the lower capital costs associated with it^{13–15}. The advantages of amine scrubbing's direct targeting of CO₂ by forming chemical bonds combined with swing adsorption has given rise to amine functionalisation of a variety of adsorbent bases. This includes commercial materials such as activated carbons (AC)⁶¹, zeolites⁶², or mesoporous silicas⁶³ as well as novel formulations that involve polymers^{22,64}, or metal organic frameworks⁶⁵ (MOFs). The development of these adsorbents and their adsorption performance is one of the key factors in gas separation processes, and the functionalisation of mesoporous silicas with amines will be focal point of discussion in the next section.

2.3 Overview of amine functionalised silicas

2.3.1 Methods of functionalisation

Amines can be introduced onto sorbents by several methods, some of which are grafting, in-situ doping, or impregnation. Amine impregnation involves the deposition of an amine reagent into the adsorbent pores. The amine, of monomeric or polymeric form, interacts with the adsorbent surface by weak intermolecular forces such as van der Waals or hydrogen bonding⁶⁶. Some examples of amines used for impregnation include Tetraethylenepentamine TEPA (a pentaamine) and Polyethylenimine PEI (a polymeric amine), illustrated in **Figure 2.1a and b**.

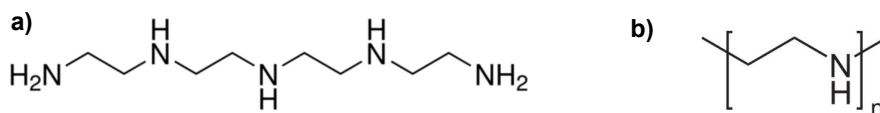
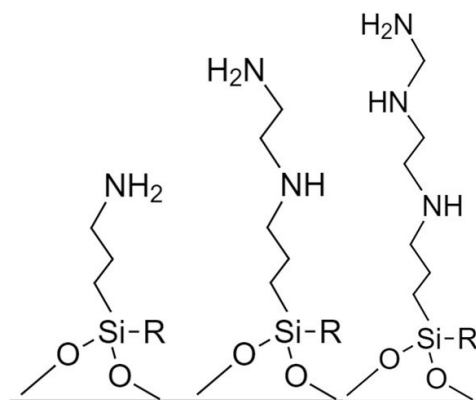


Figure 2.1 Chemical formula of a) TEPA molecule b) PEI molecule

Since amine impregnation primarily relies on the available pore volume for maximum loading, many studies have employed it on mesoporous silicas with a

narrow and uniform pore distribution, like SBA-15 or MCM-41. These materials have been shown to load up polyethylenimine (PEI) up to 70 wt%, although diffusional resistance arising from pore filling limits the optimal value to 50-60 wt%^{24,67,68}. The adsorbent performance of amine impregnated silicas varies because of the structural characteristics of the mesoporous base. In general, as higher amine densities are deposited and enhance the adsorption capacity, slower adsorption rates result due to diffusional limitations. Additionally, leaching of the amine may occur under cyclic adsorption-desorption as no bonds are formed between the amine and the surface of the adsorbent^{23,32,69,70}.

In contrast, grafting of amines makes use of amino organ silane reagents, presented in **Figure 2.2**, to form a silane bond between the adsorbent surface and the amine's silane^{71,72}. Consequently, this form of functionalisation can only be carried out on silica surfaces for the silane bonding reaction to proceed, it is also limited by the available surface area of the adsorbent for bond formation. Amine impregnation therefore leads to much higher loadings of amines in an adsorbent and in certain instances a slightly superior enhancement in adsorption capacity compared to grafted amines. Regardless of the method of functionalisation and adsorbent base, many studies concentrate on high amine loadings to maximise the chemisorption of CO₂ by the amines, adsorption performance at high degrees of impregnation is facilitated by temperatures over 60°C, becoming ideal materials for post-combustion conditions³¹⁻³⁴.



(a) (b) (c)

Figure 2.2 Examples of amino organ silanes branches grafted on mesoporous silicas, R represents a methyl, ethyl, or OH group. (a) APTES, (b) AEAPT, and (c) TAEPT.

2.3.2 Amine impregnation

Although amine impregnation can be carried out in a variety of adsorbent mediums, they are most often investigated on mesoporous silica, a preferred medium due to the structural morphology discussed earlier^{24,67,73–75}. Their results demonstrate an increase in amine efficiency - defined as moles of CO₂ adsorbed per gram of amine - up to a certain amine loading before diffusional limitations take over. Sanz et al.^{68,74} showed that with PEI, the amine efficiency past an amine loading of 30% begins to decrease due to pore blockage. **Figure 2.3** presents their results for CO₂ adsorption at varying PEI loadings on SBA-15 up to 6 bar and at 318K, with clear indications of the decrease in percent improvement as amine loading increases. This had been previously confirmed by Xu et al.²⁴ on PEI functionalized MCM-41 material, in which they correlated the adsorption and desorption of CO₂ with PEI loading in MCM-41, as seen in **Figure 2.4**.

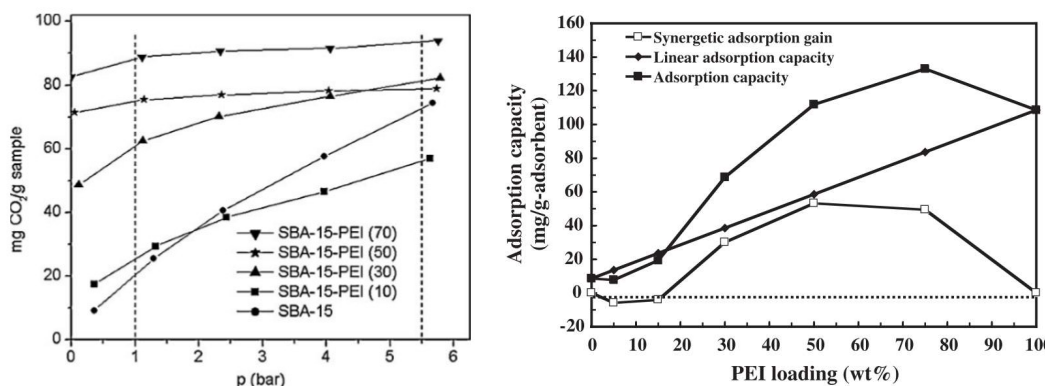


Figure 2.3 CO₂ adsorption isotherms up to 6 bar at 45°C by different percentage of loaded PEI on SBA-15⁶¹. **Figure 2.4** CO₂ adsorption capacity up to 1 bar and 75°C as a function of PEI loading on MCM-41²⁴. *The Synergetic adsorption gain is defined as the amount adsorbed by PEI functionalized MCM-41 subtracted from unfunctionalized MCM-41*

Although Sanz et al.^{68,74} confirmed that although amine efficiency decreases past 30%, there is still an enhancement in total CO₂ for PEI impregnation at higher loadings. The findings by Sanz et al. and Xu et al. indicate that amine impregnation within the range of 30-50 wt% minimizes diffusion limitations while still enhancing the total uptake.

2.3.3 Amine grafting

When grafting amines, different amine moieties or combination thereof can be used for adsorbent functionalisation. The resulting extent of performance enhancement is dependent not only on the loading but also the amine type used. Hiyoshi et al.⁶⁹ investigated the relationship between amine type, loading and the resulting CO₂ adsorption amount. In their study, they grafted a range of loadings of primary, diamine and triamines on SBA-15 and their adsorption performance was studied at 60°C and a CO₂ partial pressures of 1, 5, and 15 kPa balanced by N₂ for a total pressure of 100 kPa. The primary amine, APTES had the highest capacity when compared to equivalent amine loadings of diamine and triamine per gram of SBA-15, as presented in **Figure 2.5**. They also reported an enhanced capacity of 10-14% by densely grafted diamine and triamine in the presence of moisture. However, the maximum amine loading for APTES was 2.61 N mmol/g compared to 4.61 and 5.80 N mmol/g for AEAPT (diamine) and TAEPT (triamine), respectively. This meant that although primary amines offer the highest amine efficiency for CO₂ adsorption, diamines and triamines allow for a significantly higher grafting density of amines per gram of adsorbent, and max loadings lead to superior overall CO₂ capacities. The low pressures studied may have been directed towards flue gas treatment, but this pressure region is dominated by the

chemisorption of CO₂ and can be used to elucidate the role of chemisorption in amine-initiated adsorption of CO₂.

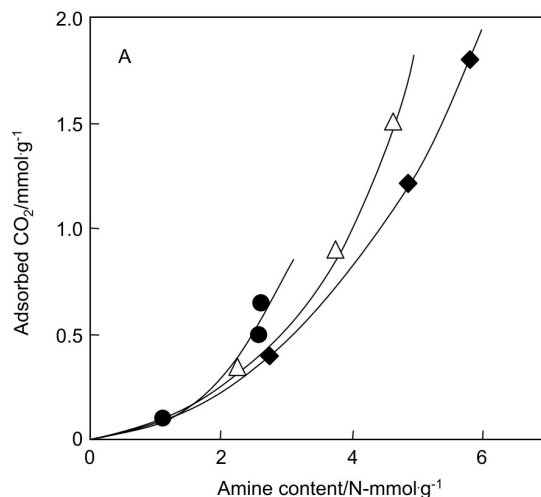


Figure 2.5 Adsorption capacity at 15 kPa CO₂ and 60°C as a function of amine loading of (●) Primary Amine, (△)Diamine, and (◆) Triamine grafted on SBA-15⁶⁹.

More recently, Hori et al.⁷⁶ analysed the differences imparted on amine efficiency, capacity, and kinetics by the different pore sizes of MCM-41 and SBA-15. They concluded that smaller pore sizes contribute towards better amine efficiency by primary amines. In comparison, larger pore sizes are better utilized for longer triamine molecules and result in higher adsorption kinetics and efficiency. These results agree with investigations of pore expanded MCM-41 for triamine grafting, primarily carried out by Sayari and coworkers³⁴, showing that expanding the pore volume from 1 cm³/g to 2 cm³/g enhances amine efficiency of triamine by up to 50% at an adsorption temperature of 110°C. Amine efficiency, in a manner like impregnation, is therefore dependent on pore volume and amine loading, with pore filling having a significant effect on adsorption kinetics and available amines for CO₂ adsorption.

Amine efficiency in 'ambient' temperatures

The previous studies discussed provide key information on amine efficiency in CO₂ capture, but the conditions studied are specific to flue gas or post-

combustion carbon capture. In an analysis of design considerations for CO₂ capture at 25°C, Ko et al.⁷⁷ grafted primary, secondary, and tertiary amines on SBA-15 and related the adsorption and desorption of each to the associated basicity. The resulting adsorption uptake by each amine type measured by TGA is presented in **Figure 2.6**. They found that although primary amines result in the highest CO₂ uptake because of its higher basicity, secondary amines require a lower energy for their regeneration, in-line with its lower basicity compared to primary amines. Tertiary amines have been shown to chemisorb very little CO₂ in dry conditions (<0.01 mmol/g), and therefore had the lowest uptake and regeneration demands⁷⁸. This provides key information on the effectiveness of secondary amines in balancing both a high capture capacity while minimizing the heat duty associated with cyclable applications, although the regeneration conditions studied were limited to 110°C, and so represent TSA process arrangements and do not encompass a wider range of conditions.

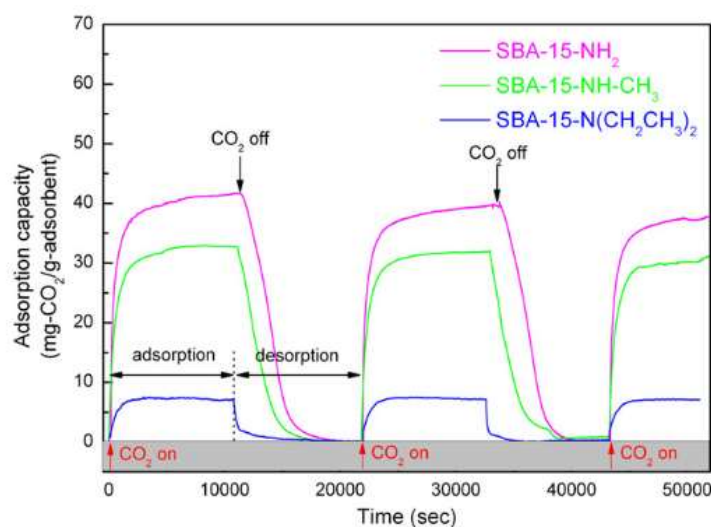


Figure 2.6 CO₂ adsorption at 25°C and desorption at 110°C of primary (SBA-15-NH₂), secondary (SBA-15-NH-CH₃), and tertiary (SBA-15-N(CH₂CH₃)₂) amines measured by TGA⁷⁷.

2.3.4 Cyclability of amines

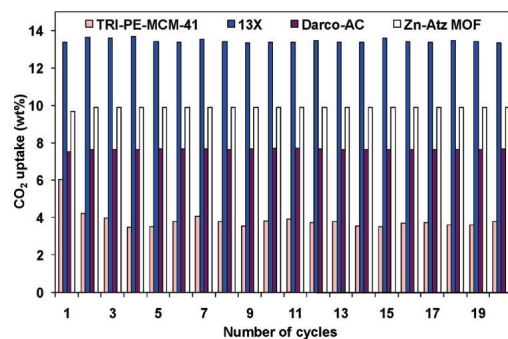
Although studies with amine impregnated mesoporous silica at various quantities have demonstrated the possibility of superior selective CO₂ adsorption with adsorption capacities reaching over 2.5 mmol/g, they have slower adsorption kinetics and are subject to a decrease in capacity under cyclic adsorption-desorption^{69,70,79}. On the other hand, Hiyoshi et al.⁸⁰ showed no decrease in adsorption capacity for Triamine grafted at maximum surface coverage on SBA-15 over 50 cycles, employing an adsorption condition of 50°C and 0.15 bar and desorption at 100°C. Perez et al.⁸¹ further confirmed the stability of grafted amines by comparing PEI impregnated MCM-41 to Diethylene-triamine (DT) grafted MCM-41. They reported that through temperature swing adsorption and over 10 cycles - at an adsorption of 45°C and desorption at 110°C - impregnated MCM-41 showed a loss of 12% in capacity compared to 4% loss for DT grafted MCM-41. In a separate study, they demonstrated that TEPA impregnated MCM-41 showed an even larger drop of 13.7% at the same conditions³².

Rao et al.⁷⁰ tested the cyclic stability of PEI impregnated MCM-41 under vacuum desorption conditions at 100°C and adsorption at 1 bar and 25°C of pure CO₂. The decline in capacity was reported as 14.22% for 50% PEI impregnated MCM-41, while only 5.19% for 50% APTS grafted MCM-41. Zhao et al.⁶⁷ had already studied the cyclability of TEPA impregnated SBA-15, and his results matched theirs, with a 10% adsorption capacity drop of CO₂ after 10 cycles at 75°C adsorption and 100°C desorption conditions.

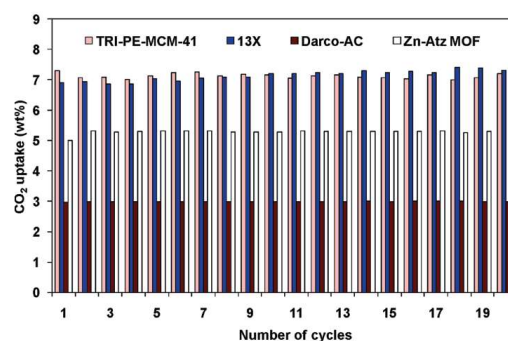
Cyclability is an important characteristic that adsorbents should have for long-term operation, and amine grafting clearly provides a more stable continuous operation compared to impregnation. Belmbakhout et al.³³ investigated the feasibility of industrial employment of amine grafted silicas and studied the cyclic capacity of triamine grafted MCM-41 under different PSA conditions for flue gas treatment, presented in **Figure 2.7**. They primarily compared the resulting cyclic performance under vacuum versus atmospheric desorption conditions in a range of temperatures. The working capacity over several cycles at 70°C suggested

competitive performance with commercial zeolite and activated carbon adsorbents under vacuum desorption conditions, but this was not the case at 25°C. Additionally, 70°C adsorption cycles with 7.5% RH in the feed gas, the performance of triamine MCM-41 outperformed both Zeolite 13x and Darco AC, mainly due to the resistance of amine grafted silicas to performance degradation by moisture, a quality lacking in zeolites (**Figure 2.7**). From these studies, it's clear that amine grafting provides a balance of capacity, selectivity, and cyclability in combination with a moisture resistance that is lacking in zeolitic materials. For this reason, the proceeding section will concentrate specifically on amine grafted mesoporous silica, and the resulting adsorption mechanisms.

a.



b.



c.

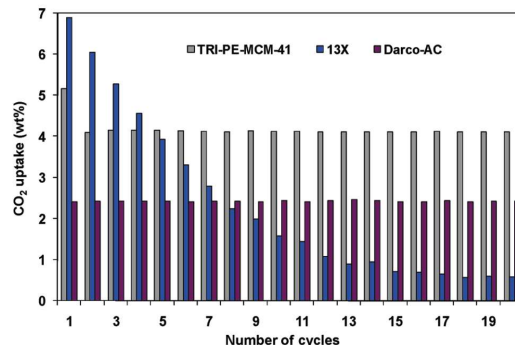
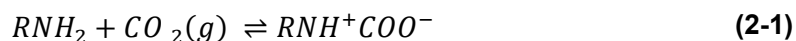
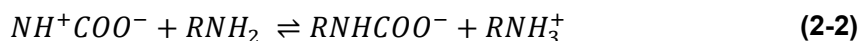


Figure 2.7 Cyclic stability studies at various isothermal conditions for tri-amine grafted pore expanded MCM-41. (a) Vacuum desorption at 25°C, (b) Vacuum desorption at 70°C, and (c) Atmospheric desorption at 70°C in the presence of 7.5%RH in the adsorption feed flow³³.

2.4 Adsorption mechanisms of amine functionalities

Understanding the principle mechanism by which amines adsorb CO₂ is key in designing adsorbents that efficiently utilise the amines grafted, which is often a trade-off between physisorption and chemisorption active sites. This results from the inherent mode of chemisorption by amines, believed to follow a two-step zwitterion mechanism in anhydrous conditions, presented in Eq.(2-1) and.(2-2)⁸²⁻⁸⁴. Enhancement of capacity by chemisorption in dry conditions thus requires two amine moieties per CO₂ molecule, but the grafting of amino organ silanes occupies the adsorbent's specific surface area and therefore physisorption sites, especially by isolated amines that cannot chemisorb CO₂ due to stoichiometry. These two modes of adsorption are prevalent at very low pressures of CO₂ adsorption (<20 kPa), but the overall amine-adsorbate mechanism of adsorption, whether at low or higher pressures, is not limited only to them^{63,85}. This section summarises the literature work covering the structural, amine, and process condition influences on adsorption mechanisms, separated by the methodologies used to elucidate them.



2.4.1 Adsorption mechanism from bulk interactions

The available surface area pre and post grafting affects intermolecular and intramolecular interactions, which are influential on the adsorption mechanisms and thus the CO₂ adsorption capacity. Belmabkhout and Sayari⁸⁶ further sought to quantify the principle adsorption mechanism in densely grafted triamine on Pore Expanded MCM-41 (PE-MCM-41). At maximum surface coverage of

triamine on PE-MCM-41, the CO₂ capacity exceeded the unfunctionalized material up to 8 bar at 25°C, attributed to the initial chemisorption of CO₂ followed by a limitation on physisorption at higher pressures. This was deduced from the isosteric heat of adsorption at below 2.5 mmol/g uptake, which presented a steep slope that exceeded 40 kJ/mol, indicating chemisorption as the principle adsorption mechanism⁸⁷. Referring to **Figure 2.8**, as the uptake increased the slope begins to flatten out, indicating a combination of both chemisorption and physisorption prior to the complete transition to physisorption. The transition to physisorption coincides with approximately 40-50 kPa of pressure, depending on the adsorption temperature, and can be seen in the isotherm profile presented in **Figure 2.8b**.

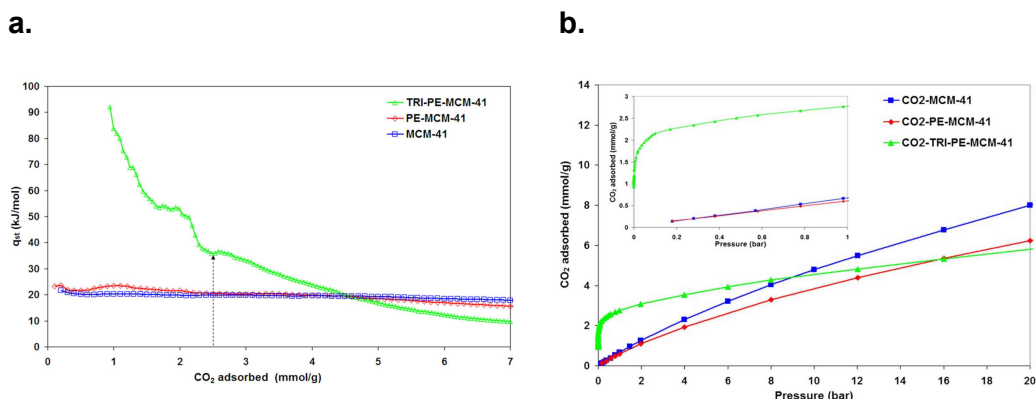
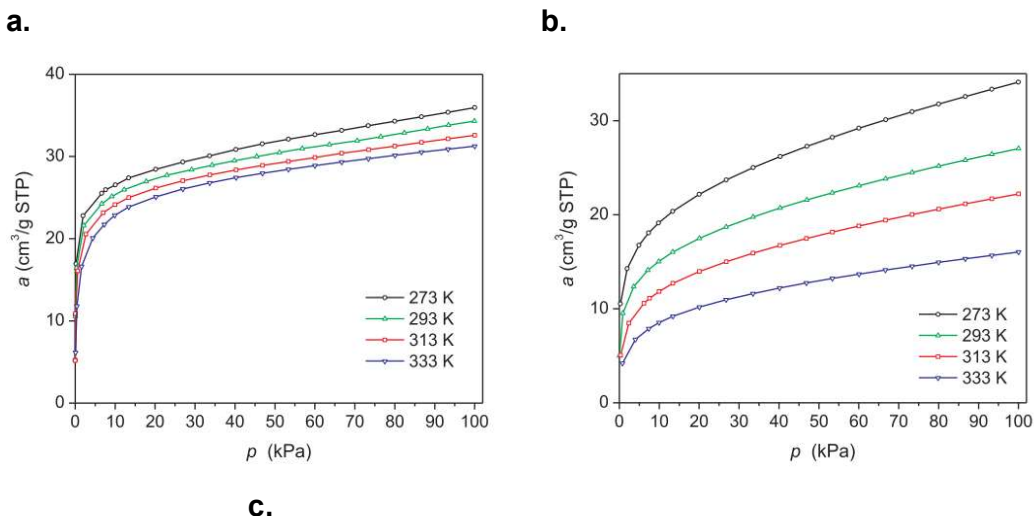


Figure 2.8 Triamine grafted pore expanded MCM-41 studied by Belmabkhout et al. for (a) Isothermic heat of adsorption versus CO₂ adsorbed, and (b) CO₂ adsorption isotherm at 25°C⁸⁶.

Watabe and Yogo⁸⁸ further expanded these results by calculating the heats of adsorption of densely grafted silica that included primary, secondary, tertiary, diamine, and triamine reagents. They found that diamine functionalities result in the lowest heats of adsorption at equivalent capacities of other amine reagents, further confirmed by the lower required heat of regeneration for adsorption-desorption cycles. Secondary amines may have had the lowest isosteric heat of adsorption up to 0.5 mmol/g, but underperformed compared to primary, diamine, and triamine, which reached adsorption capacities >1.0 mmol/g at 40°C

adsorption. Although Watabe and Yogo elucidated key information on the ease of regeneration based on amine type, their study concentrated on flue gas treatment, and targeted densely loaded amines only.

In comparison to Watabe and Yogo, Zelenak et al.⁸⁹ densely grafted primary, diamine, and triamine on SBA-15 to clarify the effect amine basicity has on the isosteric heats of adsorption, and therefore the principal adsorption mechanisms. Starting at adsorption temperatures of 25°C and up, triamine was found to offer enhanced capacity at higher temperatures of 60°C compared to primary and diamine; explained by the higher contribution by physisorption to the adsorption of CO₂ by primary or diamine organ silanes. This is a consequence of the longer triamine molecule, which hinders diffusion through the pores to a greater extent and results in a consistent adsorption capacity that is maintained at higher temperatures compared to primary amines and even diamines (**Figure 2.9**). Zelenak et al.'s study elucidated the temperature dependency of amine types on CO₂ adsorption, but was limited to only densely grafted SBA-15, and therefore did not account for mechanisms that may arise from intramolecular and intermolecular interactions between amines, the adsorbent surface, and the adsorbates.



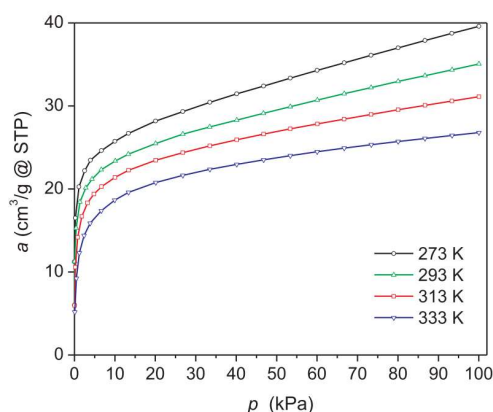


Figure 2.9 CO₂ adsorption at 60°C of pore expanded MCM-41 grafted with (a) triamine, and (b) primary amine⁸⁹.

2.4.2 Adsorption mechanism from molecular interactions

To further scrutinize the mechanism of adsorption while identifying chemisorbed species formed from amine-CO₂ interactions, in-situ IR studies as well as density functional theory (DFT) methods have been utilised within the literature. Hiyoshi et al.⁶⁹ showed that the preferential formation of ammonium carbamate occurs on neighbouring amines rather than single amines, confirming that densely grafted amines facilitate chemisorption by providing the necessary 2:1 stoichiometry for adsorption in dry conditions. Hahn et al.⁹⁰ combined DFT simulation with IR spectroscopy to visualise the chemisorbed species formed by low pressure CO₂ adsorption at 50°C. They studied primary, secondary and diamine grafted silica at an amine loading of ~3.3 mmol/g. They found a susceptibility of secondary amines, whether in a single branch or part of diamine, to form surface hydrogen bonds making them unavailable for CO₂ capture. This is especially prominent at low amine surface coverage, which gives way to a high number of adjacent surface silanol hydroxyl groups. This leads to a 25% amine efficiency in diamine compared to 50% in primary or secondary amine reagents, due to the un-reactive secondary amines that are inaccessible due to carbamate formation on the primary moieties of diamine (**Figure 2.10**). Additionally, through DFT, it was

concluded that secondary amines tend to form less stable carbamic acid species instead of ammonium carbamate that are formed by primary amines.

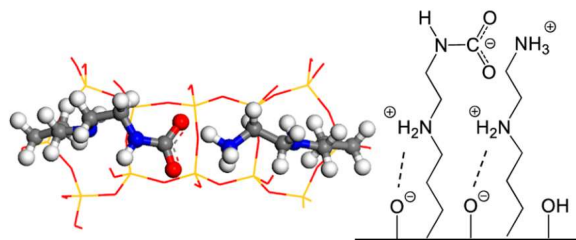


Figure 2.10 Expected molecular interactions of diamine with surface silanol hydroxyl groups and adjacent amines⁹⁰.

Mafra et al.⁹¹ utilised solid-state nuclear magnetic resonance (SSNMR) and DFT to reveal detailed information on chemisorbed CO₂ species as well as physisorbed formed on amine grafted SBA-15. They found that carbamic acid may form under certain conditions in both primary and secondary amine moieties, the identified species are illustrated in **Figure 2.11**. Their findings would support the observed partial reversibility of chemisorbed CO₂ by pressured modulation, rather than being only dependent on temperature modulation for adsorbent regeneration. The detection of carbamic acid formation in primary amines stabilised by hydrogen bonds was also prominently seen in low density grafting; indicating that the possibility of low amine grafted silicas to provide an enhancement in capacity with lower regeneration energy compared to dense grafting, and should be further explored. In another related study utilising the same methodology, Mafra et al.⁹² showed that physisorbed CO₂ can form multiple hydrogen bonds with grafted amines and chemisorbed species (**Figure 2.12**). This supported the hypothesis that the enhancement in adsorption by amine functionalisation is not strictly a result of chemisorption enhancements.

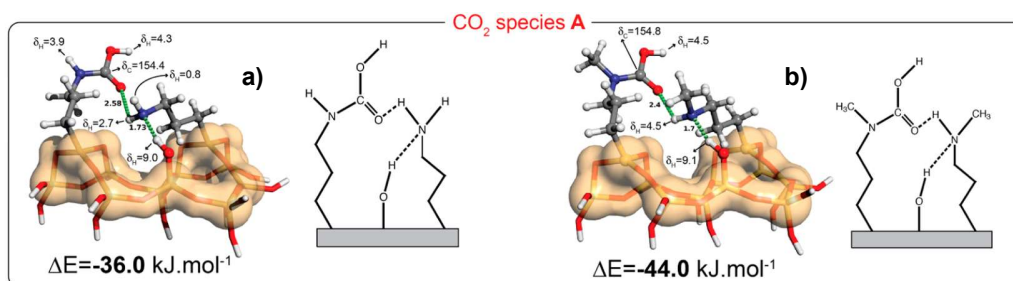


Figure 2.11 One of the identified species of chemisorbed CO₂ stabilised by nearby hydrogen bonds for (a) primary and (b) secondary amines⁹¹.

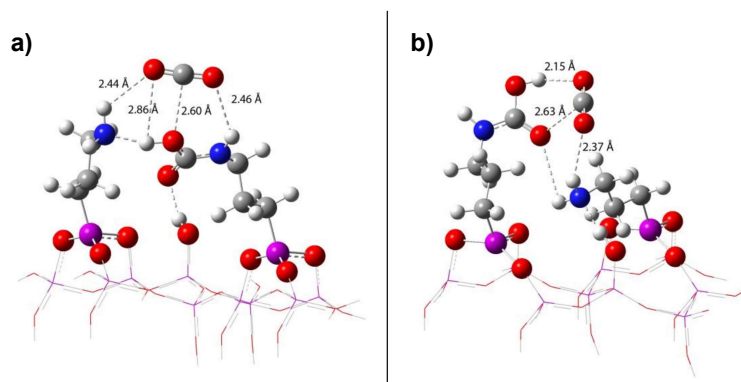


Figure 2.12 Representation of the possible physisorbed CO₂ arrangements and their interaction with ammonium carbamate species identified at different experimental peaks of (a) 163 ppm and (b) 154 ppm by ¹³C cross polarized – magic angle spinning (CPMAS) NMR spectra⁹².

Yoo et al.⁹³ functionalised SBA-15 with very low loadings of amines (<0.45 mmol/g) to investigate the role that surface silanols and amine spacing plays in the adsorption of CO₂. They confirmed that surface silanols are essential for the chemisorption of CO₂ at low amine loadings. Additionally, the intramolecular adsorption of CO₂ by triamine was shown to be much more efficient compared to diamine (**Figure 2.13a**). That is to say, at low amine loadings in which sufficient spacing separates adjacent amine branches, amines along the same chain in triamine are more prone to interact amongst each other to adsorb CO₂ (**Figure 2.13b**).

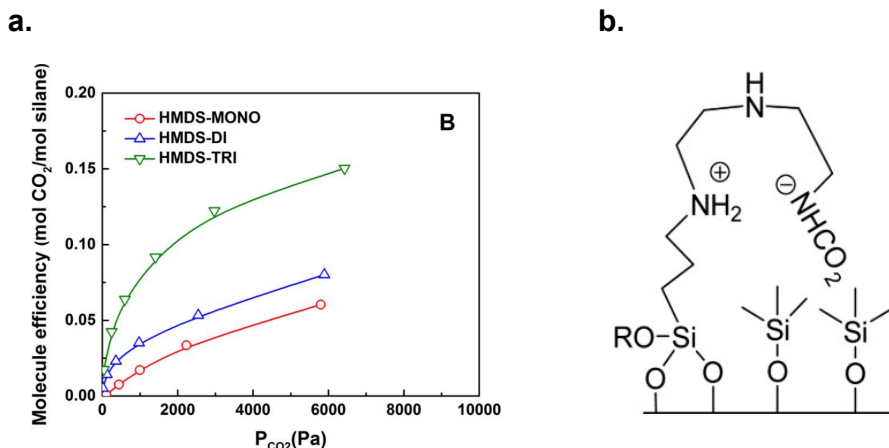


Figure 2.13 (a) Amine efficiency of CO₂ adsorption by primary (MONO), diamine (DI), and triamine (TRI) with capped surface silanols at low amine surface coverage. (b) The proposed method of the stabilisation of CO₂ adsorption and stabilisation of triamine in the absence of surface hydroxyl groups and adjacent amines⁹³.

2.5 CO₂/CH₄ separations by amines

Although many studies have explored amine functionalized adsorbent's feasibility in flue gas applications, not many tackle their applicability for biogas upgrading. However, as regulations for carbon dioxide emissions have become stricter, it has become more relevant to design biogas upgrading adsorbents that maximise the purity of the produced biomethane, while maintaining a high purity carbon dioxide purge for further storage or usage. This can be carried out by maximising CO₂ selectivity over CH₄ while simultaneously maintaining a cyclable and high working capacity comparable to current benchmark materials (Zeolite 13x). Belmabkhout et al.⁶³ had already demonstrated that the selectivity of triamine grafted MCM-41 through breakthrough experiments competes with 5A zeolite and BPL carbon and Zeolite 13X adsorbents⁹⁴.

Mafra et al.⁹² explored the feasibility of using amine grafted SBA-15 in biogas upgrading by VPSA/PSA processes. They studied the adsorption of CO₂ and CH₄ up to 10 bar by densely grafted primary, diamine, and secondary amines and the selectivity in a binary mixture of CO₂/CH₄ was calculated using ideal adsorption solution theory (IAST) methods, presented in **Figure 2.14**. The maximum

selectivity achieved by the diamine AEAPT was 15000 compared to 1114 for the secondary amine ([trimethoxy[3-(methylamino)propyl]silane) (TMAP) and 25 for the primary amine APTES. In agreement with previous studies discussed on triamine grafted MCM-41, amine functionalised SBA-15 exceeded the CO₂ capacity of unfunctionalized SBA-15 but was limited to lower pressures, in this case below 3 bar at a temperature of 25°C. Additionally, they compared the working capacities of the various amine grafted samples in isothermal desorption conditions at 10 kPa (representative of VPSA), and 100 kPa (representative of PSA) following an adsorption step at 10 bar (**Figure 2.15**). This was only a preliminary analysis, but the capacity of all materials decreased below the unfunctionalised sample following desorption. Nonetheless, the working capacity in these conditions was highest for primary amines and showed potential of this type of amine in enhancing capacity, and selectivity simultaneously. The narrow range of process conditions studied shows potential of amine utilisation for biogas upgrading, but further work should be carried out to build up on their findings, such as the dependency of working capacities on the maximum adsorption pressure, temperature, and amine loading.

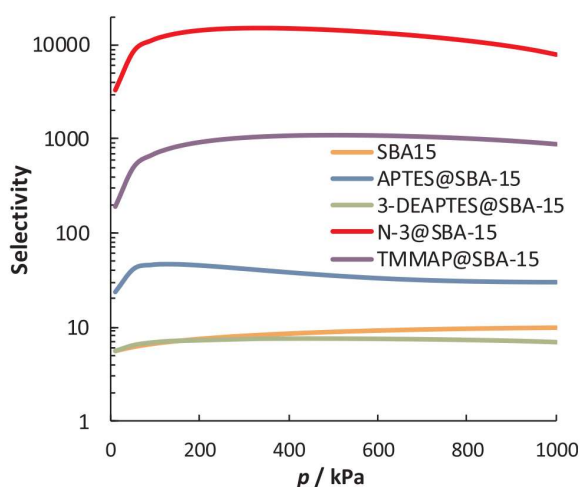


Figure 2.14 Selectivity of various amines grafted on SBA-15 in a binary mixture of CO₂/CH₄ at 25°C⁹².

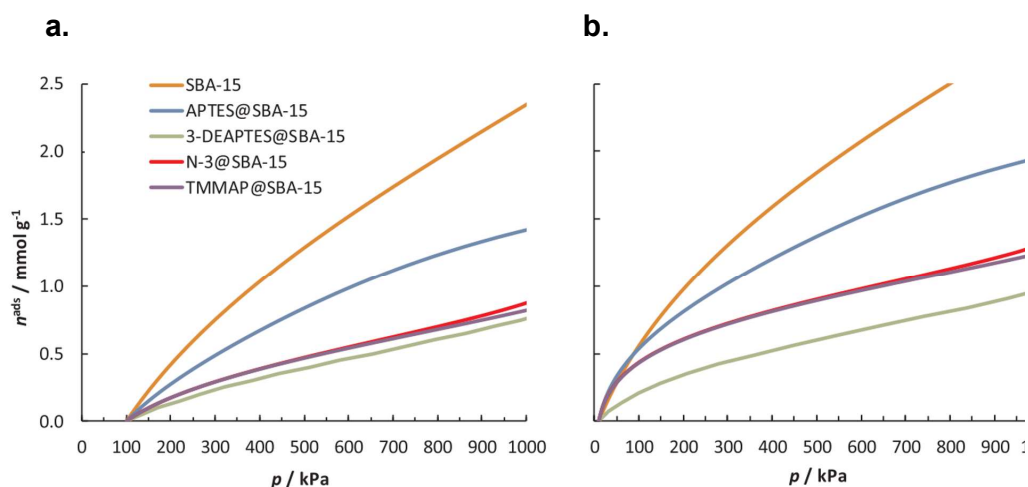


Figure 2.15 Working capacity at 25°C of various amines after a desorption of (a) 100 kPa, and (b) 10 kPa⁹². Where APTES is the primary amine (Aminopropyl)triethoxysilane, 3-DEAPTES is the tertiary amine [[3-(diethylamino)propyl]tri- methoxysilane, N-3 is the diamine - ([N-[3-(trimethoxysilyl)propyl]ethylenediamine, and TMMAP is the secondary amine ([trimethoxy[3-(methylamino)propyl]silane)

Villarrasa-Garcia et al.⁹⁵ conducted CO₂/CH₄ studies on APTES functionalized SBA-15, comparing the effect of pore expanded SBA-15 on the grafted loading of APTES and the resulting capacity and selectivity. They found that a 35% increase in APTES loading could be achieved, leading to an approximately 10% increase in the CO₂ capacity compared to unaltered SBA-15, and a CO₂/CH₄ selectivity of up to 200 at a CO₂ partial pressure of 20 kPa and 25°C. Although pore expansion enhanced capacity and selectivity, the adsorption kinetics of these materials suffered due to larger pore diameters and diffusion limitations from the densely grafted amines. Additionally, the selectivity was not affected significantly, and their study did not consider amine-CH₄ interactions but attributed the decrease in CH₄ uptake as a direct result of pore blockage.

Lourenco et al.⁹⁶ studied through DFT the molecular interactions of CO₂ and CH₄ on low loaded functionalised mesoporous phenylene-silicas (Ph-PMO) by a variety of primary amine moieties. The silica studied incorporated amines in two

methods: by conventional grafting through inert reflux, such as (3-aminopropyl)trimethoxysilane (APTMS) illustrated in **Figure 2.16**, and by a two-step chemical reaction with strong acids to incorporate moieties such as -NH_2 , presented in **Figure 2.17**. They confirmed that the interaction energy of CH_4 varies with amine moiety, with a clear increase in functionalised Ph-PMO by APTMS (by -0.9 kJ/mol), $\text{-CH}_2\text{NH}_2$ (by -2.3 kJ/mol), and isopropylamine (by -4.7 kJ/mol) compared to unfunctionalized Ph-PMO. These results were similarly seen in the CH_4 uptake of APTMS and $\text{-CH}_2\text{NH}_2$ at 25°C (**Figure 2.18**). Although they quantified the energy of CH_4 -amine interactions and the implications to selectivity, the adsorption effects were limited to primary amine moieties. Additionally, the phenylene bridge in the silica base is unique to Ph-PMO's and may influence the uptake and selectivity.

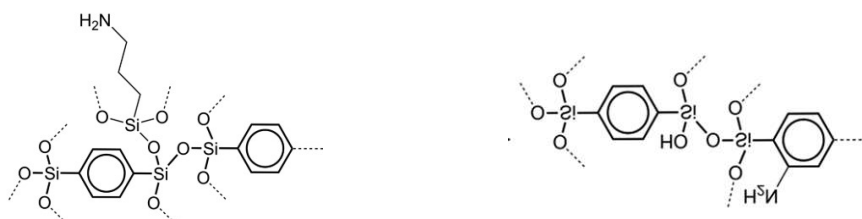


Figure 2.16 Chemical formula of APTMS-Ph-PMO⁹⁶ **Figure 2.17** Chemical formula of NH_2 -Ph-PMO⁹⁶

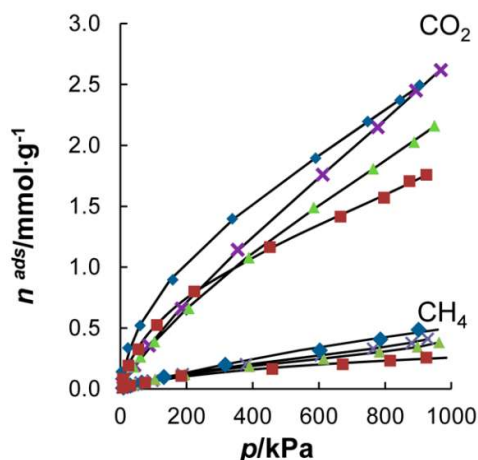


Figure 2.18 CO₂ and CH₄ adsorption isotherms at 25°C of various functionalised Ph-PMO adsorbent⁹⁶ Legend: ▲ *Ph-PMO*, × *NH₂-Ph-PMO*, ◆ *APTMS-Ph-PMO*, and ■ *APTMS-NH₂-Ph-PMO*

The focal point of adsorption studies in biogas upgrading and carbon capture has continuously shifted over the years because of external factors. Amine modifications have been shown to enhance CO₂ selectivity and capacity, while having a range of regeneration energy implications depending on the amine type and separation technology employed.

However, there is a lack of data on the changes in the CO₂ adsorption mechanism as a function of amine type and loading at values below full surface coverage, while targeting processes conditions around ambient temperatures and partial pressures of CO₂ over 15 kPa. Understanding the developing mechanism as a function of amine loading is key in accounting for the regeneration energy and elucidating if lower loadings could provide a competitive working capacity under isothermal conditions. Similarly, to fully harness the potential of amine incorporation on various adsorbent bases, it is important to understand the changes to CO₂/CH₄ selectivity as a function of amine loading. This can be accomplished by an evaluation of the CH₄ uptake and the selectivity, and to what extent amine-adsorbate interactions contribute to the observed CH₄ loading. Understanding these underlying mechanisms can provide a full picture of the

feasibility of amine applications in biogas upgrading, choosing the appropriate degree of functionalisation to balance adsorption capacity, selectivity, and energy efficiency on a per process basis.

2.6 Molecular Simulations in carbon capture

With the rise in computational processing power, molecular simulation (MS) can be a key tool in studying adsorbate-adsorbent interactions. However, the appropriate simulation method for each system must be carefully chosen based on type of molecular interactions, and the feasibility of accurately modelling them using MS tools. As a result, a combined set of techniques are necessary for a full picture of adsorption mechanism in gas applications, which encompass experimental as well as computational methods, especially when chemisorption is considered. This section reviews the various methods of MS available, specifically as applied to mesoporous silicas and amine functionalities, to make conclusions on whether they can be applied to this work in elucidating the amine-adsorbate interactions of the material's studied.

2.6.1 Simulation Methods

Molecular simulation relies on statistical thermodynamics to define each molecules position and state of existence⁹⁷. In Monte Carlo and Molecular Dynamic simulations, a subset of molecular mechanics (MM), the translation of molecules is based on concepts of Brownian motion, defined as the random motion of particles at a microscopic level⁹⁸. The average of this movement at equilibrium can provide realistic information on the macroscopic properties of a sample. Compared to quantum chemical methods, MM simulations provide less accuracy in predicting structures and exact energies but are significantly less computationally demanding and therefore convenient approximations⁹⁹. In MM modelling, the molecular energy is defined by both inter and intramolecular forces that are dictated by user assigned force field parameters. The following section discusses the fundamentals of these force fields and major factors to consider for their use.

2.6.1.1 Molecular Mechanics methods

The rise of higher computational power has opened opportunities for the better use of simulation software in providing insights to adsorption mechanisms both at a molecular and macro scale. At the molecular scale, Molecular Mechanics is often used to simulate fluid movement within specified boundary conditions. Molecular dynamic (MD) is a subset of Molecular Mechanic (MM) simulations and relies on Newton's law of motion to simulate the movement of particles within a system.¹⁰⁰ This follows an integration of Newton's equation of motion across a specified time step:

$$\vec{F}_i = m_i \frac{d^2 \vec{r}_i}{dt^2} \quad (2-3)$$

Where F is the force, m_i is mass, r_i is the position of the particle, and t is time.

The movement of particles follows user specified inputs and can include the insertion/deletion of particles, however this specific removal can affect the continuity of Newton's equation, and limits MD simulations in being applied for gas adsorption studies since the Grand Canonical Ensemble (GCMC) cannot be utilized⁹⁷. MD is thus used for diffusion and heat transfer behaviour through transport phenomenon analysis; by maintaining the total of the energy of the system constant the above equation is solved through the micro-canonical ensemble expressed as NVE⁹⁷.

When applying MD in gas adsorption, there are only hybrid methods to simulate the changing energy within the system, while maintaining a constant chemical potential or fugacity. This makes MD simulations not as straightforward in reproducing experimental gas adsorption behaviour compared to GCMC.

In the next section Monte Carlo (MC) calculations will be discussed. MC is a powerful sampling method used in molecular simulation software to re-create experimental adsorption data through the employment of the GCMC ensemble and producing essential thermodynamic information over a wide range of process conditions.

Forcefields in Molecular Mechanics

In replicating intramolecular interactions of a system, an expanded forcefield equation that accounts for all atomic contributions within a certain system is used^{97,101}. This equation describes internal molecular energy contributions and is parametrized through a rigorous procedure that fits thermodynamic data to forcefield parameters and can include bond length, bond angle, bond torsions, and any further contributions deemed influential to replicate experimental properties. The accuracy of the system is affected by the decision of which key elements are included within the force field (FF) equation; there are many forms of the FF equation utilizing either generic or specific parameter fitting and Eq. (2-4) is one representative example of energy contributions within a forcefield^{101,102}. The first three terms represent internal or intramolecular energy contributions while the last term applies to external or non-bonded influences. It is important to note that electron properties are not taken into account, and therefore reactions and interactions involving the exchange of electrons are not modeled¹⁰³.

$$U = E_{Bond} + E_{Angle} + E_{Torsion} + E_{NonBonded} \quad (2-4)$$

$$E_{Bond} = \frac{1}{2}k(r - r_0)^2 \quad (2-5)$$

$$E_{Angle} = \frac{1}{2}k_\alpha(\theta - \theta_0)^2 \quad (2-6)$$

$$E_{Torsion} = \frac{1}{2}k(1 - \cos(2\chi)) \quad (2-7)$$

$$E_{NonBonded} = E_{VdW} + E_{Coulomb} \quad (2-8)$$

Where r_0 is the reference bond length, k is the force constant, θ_0 is the reference bond angle, k_α is the α force constant, and χ is the out-of-plane angle.

In modelling the intermolecular forces from the dispersion and repulsive energy of a non-bonded (E_{VdW}) interacting set of atoms within a system, the Lennard-Jones (LJ) potential is often used to represent the Van Der Waals (VdW) contributions. The LJ potential equation has two forms designated as the 12-6 and 9-6 potential and the form used depends on the forcefield chosen and

modelling method. Emami et al.¹⁰⁴ prepared a database for modelling silica surfaces and demonstrated the inability of generalizing LJ parameters for varying force fields, in order to accurately model real systems they assigned different LJ potential values based on the energy equation or force field being used¹⁰⁴.

In the LJ equation presented in Eq. 2-9, the repulsive force is represented by $(\sigma_{ij}/r_{ij})^{12}$ and the attractive forces by $(\sigma_{ij}/r_{ij})^6$. The adjustment of the power variable in the 9-6 form of the equation decreases the contribution of repulsive forces to the energy calculation, however, the 12-6 form is more often found in Monte Carlo software and used for gas adsorption studies, and is expressed with the following equation:

$$E_{vdW} = \sum_{\substack{i,j \\ i < j}} 4 \varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \quad (2-9)$$

Where σ in Angstrom is the distance at which intermolecular potential is zero, ε is the depth of potential well or how strong two particles attract each other, and r is the interatomic distance in Angstrom.

To reconstruct the interaction parameters σ , ε , and r for two atoms, a combination rule must be chosen. The Lorentz-Berthelot (LB) mixing rule is widely used in CO₂ gas adsorption studies, but has been shown to be outperformed by the Kong rule in certain systems, such as n-alkane-CO₂ mixtures¹⁰⁵. A simple calculation testing each combination rule can demonstrate their effect on results, Delhommelle and Millie¹⁰⁶ demonstrated the variation between LB, Kong, and Wadlman-Hegler (WH) combination rules in predicting equilibrium properties of Neon, Argon, and Krypton gases. They showed that the Kong combination rule predicted the closest results of liquid properties and co-existence curves for the listed gases.

LB rule¹⁰⁷:

$$\sigma_{ab}^{LB} = \frac{\sigma_{aa} + \sigma_{bb}}{2} \quad (2-10a)$$

$$\varepsilon_{ab}^{LB} = \sqrt{\varepsilon_{aa}\varepsilon_{bb}} \quad (2-10b)$$

Kong rule¹⁰⁸:

$$\sigma_{ab}^K = \left\{ \frac{\left[(\varepsilon_{aa}\sigma_{aa}^{12})^{\frac{1}{13}} + (\varepsilon_{bb}\sigma_{bb}^{12})^{\frac{1}{13}} \right]^{13}}{2^{13} \sqrt{\varepsilon_{aa}\sigma_{aa}^6 \varepsilon_{bb}\sigma_{bb}^6}} \right\}^{\frac{1}{6}} \quad (2-11a)$$

$$\varepsilon_{ab}^K = \frac{2^{13} \varepsilon_{aa}\sigma_{aa}^6 \varepsilon_{bb}\sigma_{bb}^6}{\left[(\varepsilon_{aa}\sigma_{aa}^{12})^{\frac{1}{13}} + (\varepsilon_{bb}\sigma_{bb}^{12})^{\frac{1}{13}} \right]^{13}} \quad (2-11b)$$

WH rule¹⁰⁹:

$$\sigma_{ab}^{WH} = \left[\frac{\sigma_{aa}^6 + \sigma_{bb}^6}{2} \right]^{\frac{1}{6}} \quad (2-12a)$$

$$\varepsilon_{ab}^{LB} = \frac{2\sigma_{aa}^3\sigma_{bb}^3}{\sigma_{aa}^6 + \sigma_{bb}^6} \sqrt{\varepsilon_{aa}\varepsilon_{bb}} \quad (2-12b)$$

In the approximation of electrostatic and quadrupole contributions, atomic partial charges are used to represent them directly through Coulombs law.

$$E_{Coulomb} = \sum_{\substack{i,j \\ i < j}} \frac{1}{4\pi\varepsilon_o} \frac{q_i q_j}{r_{ij}} \quad (2-13)$$

In Eq. (2-13), q_i and q_j represent the partial charges of the interacting atom pair, r_{ij} is the separation distance, ε_o is the vacuum permittivity defined as permittivity of free space and is a constant equal to $8.85419 \times 10^{-12} \text{ C}^2/\text{n-m}^2$. Considering that many simulation techniques account for intermolecular forces by only including parameters of partial charge and LJ potentials, polarization energy is thus accounted for in MC and MD simulations through the specific values assigned to these variables¹¹⁰.

Generic Forcefields in Molecular Mechanics

The dependency of simulation results on the parameters chosen has led to focused study into the approximation of forcefield parameters, and many all-purpose forcefields have emerged, with some carefully fitted to specific systems such as the MM2, Dreiding, UFF, AMBER, OPLS, and TraPPE¹¹¹.

The Dreiding¹¹² and UFF¹¹³ forcefields are examples of generic forcefields parameterized for a broad set of molecules and systems. They have been shown to successfully predict structural geometries of crystals as well as adsorption capacity and selectivity in a variety of adsorbent types^{114,115}. In the case of silicas, simulations have shown the effectiveness of the MM2 forcefield¹¹⁶, which was parameterized specifically for silanes and polysilanes through experimental data to reliably predict heats of formation. Whether it is the MM2, Dreiding, or UFF forcefields being used for adsorbent representations, the choice of which to use is system dependent and requires careful study. Different forcefields have been successfully used to the same end such as the parameterization of the MCM-41 adsorbent by Dreiding or by MM2 by Zhuo et al.¹¹⁵ and Williams et al.¹¹⁷, respectively.

In more specific cases such as functionalized surfaces or tailorable MOFs these generic forcefields become inadequate and custom forcefields or combinations of FFs are employed¹¹⁸. Such an example is seen by Schumacher et al.¹¹⁹ and Williams et al.¹¹⁷ who modelled amine chains on the surface of MCM-41 using OPLS¹²⁰, denoted as the optimized potential for liquid simulations, developed for proteins and incorporated into models representing water. In some instances, such as in IR-MOF-1 and Zeolitic imidazolate framework simulation studies by Babarao et al.¹²¹ and Pellitero et al.¹²², the LJ potentials were adjusted from the standard UFF values through a correction factor fitted from experiment, and their transferability ensured on similar frameworks and under different adsorbates^{114,122}.

In the parameterization of Carbon Dioxide gas in adsorption, EPM2¹²³ is a model that is often used. Developed by Harris and Yung¹²³, it models the molecule

through point charges and LJ parameters centred at each atom. EPM2 has been shown to predict CO₂ critical properties accurately with only a 1-2% error in liquid coexistence loadings predictions. This model has been shown in several studies to accurately represent the CO₂ adsorption in Mesoporous silica adsorbents¹²⁴, Single Walled carbon nanotubes^{125,126}, Carbon Nanotubes^{127,128}, Zeolite NaY¹²⁹ silicalite (Si/Al) based adsorbents¹³⁰, and hybrid adsorbents¹³¹.

For methane adsorbates or methylene chains in amino-silanes, the TraPPE-UA¹³² forcefield was developed specifically for alkanes to reproduce the critical properties and liquid loadings through a single interaction site on the Carbon atom. The TraPPE forcefield's applications were broadened by Potoff et al.¹⁰⁵ to accurately model CO₂ and N₂ in a mixture with alkanes. In this model, the CO₂ quadrupole is represented similarly to the EPM2 model by a partial charge at each atomic site to represent its quadrupole moment¹³³. The TraPPE forcefield has also been optimized for Nitrogen through a 3-site representation and is commonly employed for CO₂/N₂ mixtures for a variety of adsorbent and functional group interactions^{134–138}.

These forcefields have standardized LJ potentials in molecular simulation. Although with certain limitations, a creative approach to adapting them to each unique system has been proven and becomes an important part of employing them within the broader context of MM simulations.

2.6.2 Monte Carlo

Monte Carlo (MC) methods are statistical methods used by a variety of disciplines to tackle complex deterministic problems, at the root MC methods rely on random sampling of a system to solve the thermodynamic equations of its components. The metropolis method introduced in 1953 was the first computational application of MC in the determination of the properties of an interacting system¹³⁹. When applied to equilibrium systems, MC calculations are based on the choice of an ensemble that holds certain thermodynamic properties constant to determine the remaining properties of a system at these given conditions. The following

thermodynamic relationship applies: The ensemble chosen determines the fluctuating variables of the system and an integration across the finite possibilities over a systems probability distribution will provide the average properties of a system¹⁴⁰. Coinciding with this is an assigned value for the number of cycles of repeated calculations that determine the density of system sampling, the higher the number of repeated probabilistic calculations, the lower the standard deviation becomes, and the more accurate the result. (**Figure 2.19**)

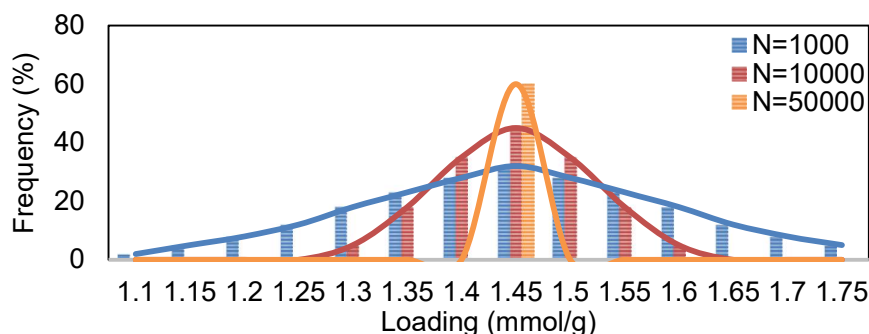


Figure 2.19 Monte Carlo probability distribution of a hypothetical adsorbent loading based on the frequency of sampling represented by N.

The choice of calculation ensemble is specific to each topic studied, and in the case of adsorption, Grand Canonical Monte Carlo (GCMC) is the most effective in simulating adsorption isotherms and therefore will be the focus of this section. The GCMC ensemble, also known as the μ VT ensemble, holds the chemical potential (μ), volume, and temperature constant while fluctuating the energy and number of molecules at thermal equilibrium. The chemical potential is related to the fugacity of the adsorbate components and is derived from it. The ensemble is applicable to a unit cell input dictated by the framework of the system, while the thermodynamic limitations apply to both the framework and the adsorbate components. **Figure 2.20** illustrates as an example the unit cell of a mesoporous silica structure, and the periodic boundaries applied to it in GCMC calculations to simulate the full adsorbent structure observed experimentally.

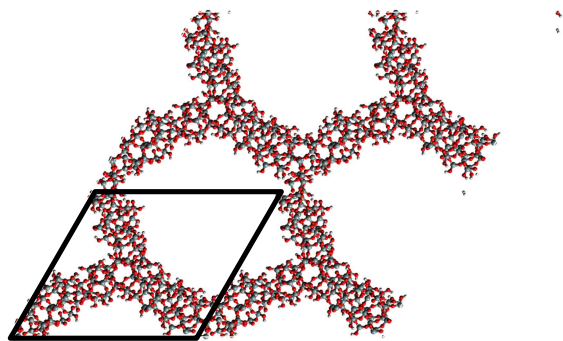


Figure 2.20 Mesoporous silica MCM-41 Unit Cell and periodic structure visualization for GCMC calculations¹⁴¹.

Once the process variables are set and held constant, a Monte Carlo software applies prespecified moves for each component within the system, such as insertion/deletion, translation, and rotation (**Figure 2.21**). Each move is accepted or rejected based on a program's acceptance rules, while the user specified total number of cycles determine the accuracy. The higher the level of sampling, the more accurate and repeatable simulation results become¹⁴².

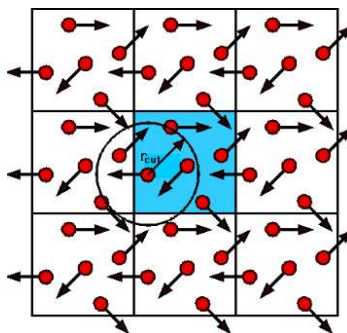


Figure 2.21 Periodic boundary conditions as applied to component translation moves¹⁴³.

2.6.3 Quantum Mechanics

Considering the limitations of MM, Quantum chemistry addresses this by describing electron distributions and particle motions through Schrödinger's

equation, also known as the wave function (Eq. (2-14), which theoretically solves to a probability of finding a particle in a point in space ¹⁴⁴.

$$\mathcal{H}\Psi_i = E_i\Psi_i \quad (2-14)$$

where $\mathcal{H}$ is the Hamiltonian operator, Ψ_i is the wave function corresponding to the i-th electronic state and E_i is the energy of the ith electronic state. To calculate energy and other related properties of compounds, this equation must be solved. The exact solution of the equation is only possible for a helium atom or for a H_2^+ molecule. For other molecules, approximate solutions must be used. Solving the equation often requires a balance between accuracy and cost, in terms of computational processing power, and the methods used can vary based on the system being studied. These can include, among others, ab initio methods such as MP2, which provide a balance of accuracy versus cost, or Density Functional Theory (DFT), offering faster calculations at adequate accuracies. Nonetheless, the choice of method is often system based, and should therefore be chosen on a per-application basis. In this work, DFT will be the main method discussed as a starting point for molecular simulation applications.

The complexity of solving the wave function led to the use of DFT, a method based on the Kohn-Sham equation which simplifies the Schrodinger wave equation through a simulated non-interacting electron representation of a given system. This system solves to the same density of an interacting system solving for a probability density distribution of the system. As the Schrodinger wave function is a many-body problem and an N-dimension equation with 3 dimensions for each electron within the system, the computational power necessary for a system of more than a few atoms is at a level beyond realistic computational power¹⁴⁵.

With the introduction of the Hohenberg and Kohn theorem¹⁴⁶ (1964) and the KS equation in 1965¹⁴⁷, it allowed the reduction of the 3N functions of Eq. (2-15) below based on the spatial coordinates of each particle and its spin $[\Psi(r1, r2, \dots, rN, t)]$ to be defined by only $\Psi(n(r))$, with $n(r)$ representing the electron density¹⁴⁸. Eq. (2-16) breaks down the variables involved in calculating the ground state

energy, the first term represents the electron kinetic energies, $V(r)$ describes electron-nuclei interactions, $V_H(r)$ describes electron-electron coulomb repulsions, and $V_{XC}(r)$ is the exchange correlation which includes all additional interaction forces and whose approximated form or value dictates the accuracy of the DFT calculation¹⁴⁹.

$$[\hat{T} + \hat{V} + \hat{U}]\Psi = E\Psi \quad (2-15)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2-16)$$

Where $\hat{T}$ is the Kinetic energy, $\hat{V}$ is the external potential (from atomic nuclei), $\hat{U}$ is the electron-electron interaction energy, E is the energy.

As DFT relies on mathematical short-cuts, the ground state energies calculated are inherently uncertain, and there is currently no clear method of calculating the magnitude of this deviation. This is carried over to excited state energies from DFT calculations, and they are considered even less accurate compared to ground state energy calculations¹⁴⁵. MP2 calculations can be employed to offer the highest level of accuracy for describing dispersion energies, but they are significantly more computationally expensive.¹¹⁰ In addition, vdW interactions are not accounted for in DFT functionals, and must be incorporated into hybrid DFT calculations. Rana et al.¹⁵⁰ developed such functionals for CO₂ adsorption in MOFs, they showed higher level of accuracy in CO₂ binding enthalpies but a trade-off was made with a decreased accuracy in predictions of metal-CO₂ bond length¹⁵¹.

As for the general considerations in DFT, computational limitations for large systems lead to simulation models that only address single adsorbate or surface group interactions with the adsorbent surface. With respect to amine functionalization, this treatment requires detailed knowledge of the possible species existing before, during, and after adsorption. Narrowing down the state of each molecules that could exist at a certain point adds to the complexity of DFT applications. In general, the choice of functional, basis set and system size

for DFT calculations is a science in itself, and a trade-off between calculation accuracy and computational cost is always present^{101,145,152}.

2.6.4 Parameterization of mesoporous silicas for GCMC

Mesoporous silica adsorbents have been extensively studied experimentally for their simple modification and high amine loading capacity as a result of their large surface area and pore volume^{23,79}. Studies utilizing simulation software for deeper insight into the adsorption mechanism of mesoporous silica are many, but the methodologies used vary depending on the author and study criteria.

Most studies target a deeper understanding of adsorption of CO₂ in flue gas, by functionalised and unfunctionalized silicas. The few that explore the effect of amine functionalities on the adsorbate-adsorbent interactions are discussed in a separate section (section 2.6.5), which is dedicated to modelling chemisorption of amine functionalities.

Forcefield considerations

As the choice of forcefield is one of the major decisions in molecular simulations, there has been research that targets an understanding of the ideal LJ parameter values to approximate interaction energies for more accurate simulations. Emami et al.¹⁰⁴ developed ideal LJ parameters, bond length, and partial charges for amorphous silica nanoparticles accurately reproducing bulk and interfacial properties, allowing their incorporation into common forcefields for biomolecules and materials. However, these values are not tailored for gas adsorption systems, and exclude interactions that play an important part in mesoporous silica's gas adsorption capacity. For mesoporous silica, LJ parameters chosen to represent the framework and simulate experimental isotherms usually coincide with the well-known Dreiding generic forcefield or the MM2 forcefield. However, their values are at times fine-tuned on a per study basis to ensure the experimental and simulated isotherm match.

Structural considerations

MCM-41, introduced by Beck et al.²⁸ from the Mobil Research group, are a class of adsorbents characterized as mesoporous molecular sieve types with pore diameters above 2 nm, a high surface area and a uniform distribution. Their advantages gave rise to the novel synthesis of the similarly structured and tailorable mesoporous silica adsorbents used in this work, SBA-15¹⁵³.

Although a pore distribution across a range of pore diameters is observed in mesoporous silicas^{28,153}, their characterization through Nitrogen adsorption allows for accurate measurement of mesoporous silica's pore diameters distribution, with the pronounced peak around the primary pore diameter¹⁵⁴. The preparation of a simulation unit cell replicating the structure of MCM-41, MCM-48, and SBA-15 has been carried out in a variety of methods and successfully shown to mimic experimental gas adsorption tests, under certain process conditions. It is important to note the challenges associated with preparing a unit cell with the large pore diameters associated with these adsorbents. At pore diameters above 4 nm, the number of atoms within a unit cell can go over 1000 leading to computational issues in rendering the structure for visualization with open source software such as Avogadro¹⁵⁵. Software such as VMD¹⁵⁶ are designed to analyse large biomolecules and therefore are efficient in rendering a high quantity of atoms, but is not compatible with periodic crystal structural files limiting their potential to be fully used for structural preparation.

The remaining subsections separate the different methodologies employed in applying GCMC to these silicas; each subsection highlights the techniques used to build the structure, the associated forcefield parameters chosen, and the results gathered to validate and produce valuable data to compliment experimental results.

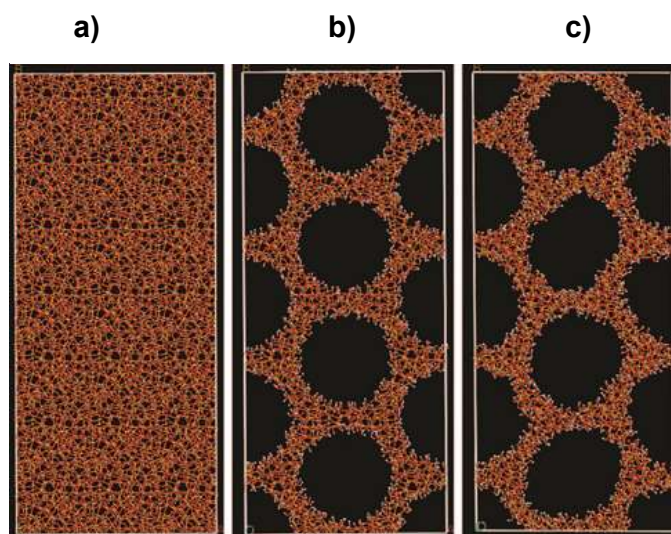


Figure 2.22 Steps in the construction of the MCM-41 model – a) Amorphous Silica b) Carving Cylindrical Pores c) Post geometric optimization by MM¹¹⁵.

2.6.4.1 Preparing a structure from an amorphous silica matrix

The pore diameter distribution of MCM-41 was used by Zhuo et al.¹¹⁵ to prepare an MCM-41 adsorbent model from a pre-set crystal database structure of amorphous silica with cylindrical pores carved into it (**Figure 2.22**). The pore diameter was set at 14.38 Ang with a Connolly surface of 1047 m²/g and a surface density of hydroxyl groups at 7-8 OH/nm². They compared the simulation to the experimental sample of MCM-41 with a BET of 1013.7 m²/g and radius of 13.48 Ang. Experimental studies by Landmesser et al.¹⁵⁷ designated a value of 4.43 mmol/gram to hydroxyl groups in hydrated MCM-41 adsorbent, which coincides to 2.63 OH/nm² in the aforementioned sample. This experimental value can be considered reasonable as Van der Voort et al.⁷² demonstrated the presence of a maximum of 1.7 OH/nm² of free hydroxyl groups with a total of 5 OH/nm² of both bridged and free hydroxyl groups on silica gel. In the study by Zhuo et al.¹¹⁵, they allocated Dreiding forcefield parameters for LJ potentials as well as partial charges for the Silica, Oxygen, and Hydrogen framework atoms. The charge distribution was calculated by DFT geometric optimization followed by Electrostatic Potential (ESP) method on three different clusters of amorphous Silica (**Figure 2.23**). The simulation isotherms agreed with experimental results

for both CO₂ and N₂, giving insight into the adsorbate distribution of CO₂ and selectivity of CO₂ to N₂ across a range of temperatures.

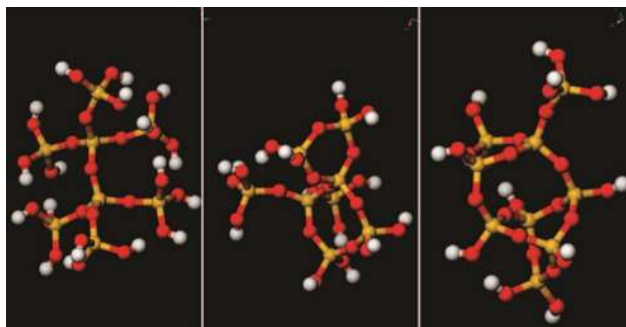


Figure 2.23 Three different Amorphous Silica clusters used for ESP partial charge determination¹¹⁵.

The parameters presented in the study by Zhuo et al.¹¹⁵ are seen repeatedly used in subsequent MCM-41 studies by Jing et al.¹⁵⁸, Ngoc Ho et al.¹²⁴, Zhu et al.¹³⁶, and Chang et al.¹⁵⁹. Although with hydroxyl groups higher than experimentally studied, the treatment of the structure and the allocation of partial charges through ESP proved adequate in recreating gas isotherms for several studies within a reasonable error, as in the study by Jing et al.¹⁵⁸ a correction factor was included to match experimental results.

2.6.4.2 Preparing a structure with only oxygen FF contributions

In comparison to the method for structural preparation presented in the previous section, Yun et al.^{160,161} suggested the assignment of LJ parameters for only the oxygen atom within the structure, with no Coulombic effects considered. This method referred to a study by Bezus et al.¹⁶² in 1978 which assumes the adsorbate-adsorbent interactions of the structure are represented by the oxygen only. This claim is attributed to the dependence of the polarizability of oxygen on the Si/Al ratio in a zeolite, making their contribution negligible, as well because of the surface coverage of the structure with oxygen.

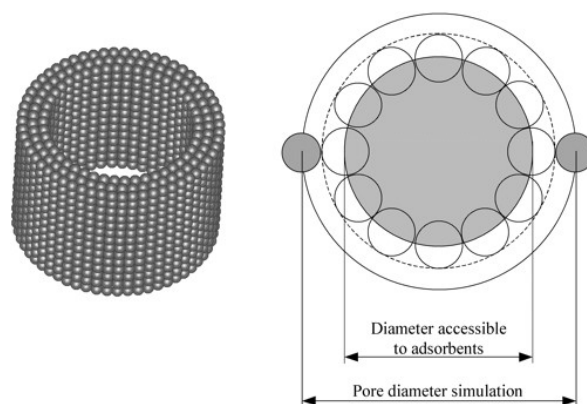


Figure 2.24 Yun et al.'s model of MCM-41, with the structure composed of only oxygen atoms¹⁶⁰.

In the above model, Yun et al.¹⁶⁰ accurately re-created adsorption isotherms across a range of temperatures of pure methane, while predications for ethane had a larger margin of error as temperatures increased, although they remained within an 'acceptable' range. **(Figure 2.24)** The applicability of the simple model is only accurate at higher pressures, due to the simplification of the heterogeneity of experimentally synthesized MCM-41 to only an oxygen surface **(Figure 2.24)**, and can be seen in the pressure range of 0-250 kPa of **Figure 2.25**. These results echoed the study by Maddox et al.¹⁶³ which had previously shown the inadequacy of a simple model in recreating low pressure nitrogen isotherms, but its effectiveness at higher pressures due to multilayer adsorption as the interactions of the gas shift from the adsorbent surface to the adsorbate layer.

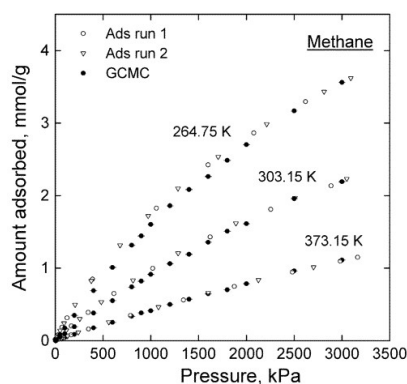


Figure 2.25 Comparison of experimental and simulated Methane pure component Isotherms by Yun et al.¹⁶⁰

The construction and validation of the model by Yun et al.¹⁶⁰ is important as a similar methodology that includes coulombic effects was used for CO₂ adsorption studies by Schumacher et al.^{119,164,165}, and Williams et al.¹¹⁷ modelling surface group modified MCM-41 and will be discussed in the next section. Additionally, the allocation of LJ parameters to only oxygen for MCM-41 was repeated by C. Williams et al.¹⁶⁶ for a silica matrix prepared through MD methods utilizing melt-quench techniques. This method mapped an automated procedure to prepare an MCM-41 structure of varying wall thickness and pore diameter and validated it through experimental results. Their results showed variations at higher pressures but at lower pressures accurate isosteric heats and loading data was collected for CO₂.

2.6.4.3 Preparing a structure from a Cristoballite matrix

He and Seaton¹⁶⁷ demonstrated the important role surface heterogeneity plays in adsorption of CO₂ at lower pressures by modelling MCM-41 with only oxygen LJ contributions but including Silica atoms in the structure and assigning partial charges to them without LJ parameters. Their findings in combination with studies by Coasne and Pellenq¹⁶⁸ were developed on by Sizova et al.¹⁶⁹ in adsorption studies of CO₂/CH₄ and CO₂/N₂ on SBA-15 with respect to moisture effects on the interaction mechanism. The structure used was p-cristoballite for the skeletal model, and random movements were imposed on the atoms to re-create the amorphous quality of SBA-15 with a cylindrical pore carved through the centre. In this study, the pore diameter of SBA-15 was modelled as smaller than typical experimental data, but they concentrated on the effect of water on adsorption. Therefore, they modelled the molecular wall formed by water on SBA-15, and only validated it through experimental data. In their study, they demonstrated that even with discrepancies in the prepared unit cell structure and experimental counterpart, relevant conclusions could still be made on the system being studied.

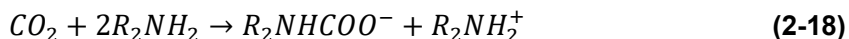
2.6.4.4 Preparing a structure by simulating the synthesis procedure

To accurately target a structure that replicates the exact internal morphology of MCM-41 and SBA-15, Battacharya et al.¹⁷⁰ developed a method through the reproduction of synthesis procedure involving template removal through configurational bias Monte Carlo (CBMC), thus creating an uneven surface roughness model. This method was originally developed by Pellenq and Levitz¹⁷¹ using TEM data correlations to recreate the internal structure of mesoporous adsorbents, further applied to MCM-41 by Coasne et al.¹⁷² The uneven pores were imposed on a p-cristobalite crystal structure to prepare the simulation unit cell. This structure showed agreement with experimental data for Argon adsorption at 77K, but overestimated values at low to intermediate pressures and no results were reported for CO₂. In comparison to smoother surface roughness, both models exhibited acceptable agreement with experiment, although higher surface roughness coincided with more accurate data at longer simulation cell lengths.

2.6.5 MS methods to account for chemisorption

The incorporation of surface groups onto mesoporous silica substrate has been shown to significantly enhance the selectivity of the adsorbent to CO₂, as well as the total loading at a range of pressures and temperatures^{33,61,70,92,173}. Grafted amino silanes have been shown to have realistic cyclability compared to impregnated amines onto mesoporous silica due to the covalent bonds formed with the surface^{33,70,81}. Primary, Secondary, Tertiary, Diamines, and Triamines have all been deeply studied, with experimental studies showing Primary and Triamine competitively enhancing CO₂ adsorption capacity at 1 bar and temperature range of 298-343K^{33,68,69,92}.

However, as mentioned previously, chemisorption cannot be directly modelled through MC or MD simulations. In order to accommodate the chemisorption of CO₂ on amines, which follows the reaction route in Eq. 2-17 and 2-18^{174,175}, various methods are utilized to include its contribution in GCMC simulations.



Zhu et al.¹³⁶ used a combination of DFT and GCMC to simulate and study CO₂/N₂ isotherms on MCM-41 functionalized with primary amines at 8, 12, 16, and 24 wt% amine coverage. The standard LJ potential parameters for CO₂ and amine interactions were redefined to account for a stronger interaction energy through a simple equation that accounts for all the energies of the molecules involved in the formation of carbamic acid.

$$E_{interaction} = E_{amine+CO_2} - (E_{amine} + E_{CO_2}) \quad (2-19)$$

The variable $E_{interaction}$ in Eq. 2-19 is based on a straightforward DFT energy calculation for CO₂, amine, and the carbamic acid and then incorporated into the GCMC model. The rest of the system maintained a Dreiding generic potential parameters and the LB mixing rule. This method was able to accurately predict CO₂ capacity and CO₂/N₂ isotherms up to 1 bar. The simulation provided density profiles of CO₂/N₂ across the surface, mapping the active sites for CO₂ versus N₂ adsorption, but the imposed interaction energy imposes a stronger physical interaction that may cast doubt on the accuracy of the atomic density profiles.

The inability of modelling electron exchange by Monte Carlo simulation led to the development of a diverse set of methods to model the chemisorption of CO₂ on amine surface groups. Builes and Vega¹³⁷ completely ignored chemisorption, and specifically modelled and analysed the intra and intermolecular interactions of carbamate moieties with pure component CO₂ gas. The amine chains were generated under a coupled-decoupled configurational bias (CDCB) algorithm to allow re-growing of amine chains thus accounting for bending/torsion contributions in the simulation.

Williams et al.¹¹⁷ and Schumacher et al.¹¹⁹ both concentrated only on higher pressures to better understand interactions of functional groups with CO₂. Schumacher et al.^{119,165} modelled aminopropyl modified MCM-41 for only

physical interactions between CO₂ and NH₂ moieties up to 20 bar. Williams et al.¹¹⁷ employed a similar procedure to investigate a multitude of surface groups with a range of functional moieties and surface coverage up to 50 bar. In both studies, only physisorption was modelled as at higher pressures it has been previously shown that in amine functionalized adsorbents physisorption is the leading adsorption mechanism once all chemisorption sites are occupied^{18,85}. The exact pressure threshold depends on the process conditions, type of amine, and surface coverage, but both studies demonstrate the transition at below 0.5 bar. Schumacher et al.¹¹⁹ confirmed the validity of their model at higher pressures by comparing the experimental and simulation results of CO₂ adsorption in 10% AP functionalized MCM-41 at -10°C (**Figure 2.26**). On sampling a multitude of functional groups, they concluded that an amine surface group containing an aromatic ring such as diaminophenyl (**Figure 2.27**) would be the optimal functional group for CO₂/N₂ applications. This was a result of two things: (1) Projecting the amine moieties or polar groups into the pore space enhances selectivity. (2) The formation of hydrogen bonds between the surface groups and the adsorbent surface can decrease adsorption sites for CO₂.

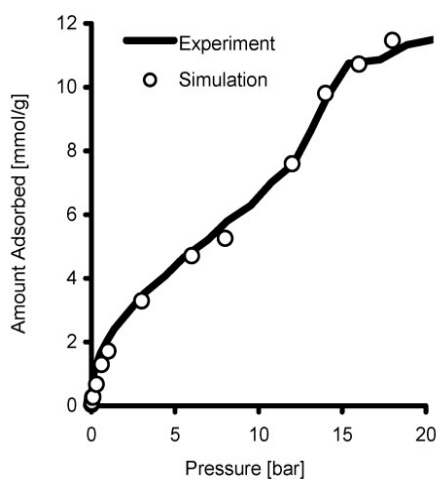


Figure 2.26 CO₂ Isotherm on Aminopropyl modified MCM-41¹¹⁹ at -10°C, and AP:Si = 0.1

Through GCMC, Williams et al.¹¹⁷ built on the previously presented data and investigated the CO₂ loading capacity and selectivity data for a variety of functional groups - some of which are presented in **Figures 2.27 to 2.29** - at a surface coverage of 25%, 50%, 75%, and 100%. However, it's important to note that the temperature studied was below 0°C, and therefore it is unclear if their methods and analysis can be carried over at higher temperatures that are more applicable to year-round ambient temperatures. Additionally, in their extensive analysis of surface groups, hexaminoterphenyl (HEP) (**Figure 2.28**) modified MCM-41 showed competitive selectivity to SAPO-34, and zeolite Y, with a type I isotherm ideal for PSA applications at an enhanced capacity compared to raw MCM-41. Although showing promise, there was no mention of the ease of experimentally grafting HEP, and whether it can be accomplished in a cost-effective manner.

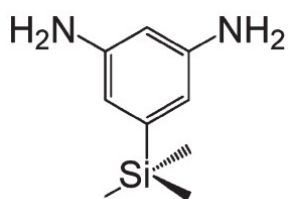


Figure 2.27 structure of diaminophenyl with silanol bond¹¹⁷

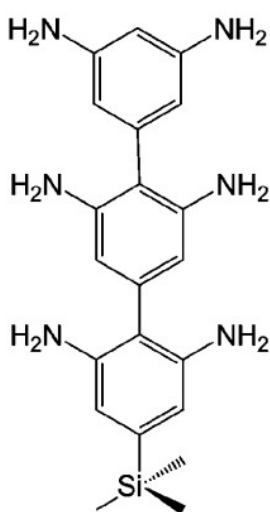


Figure 2.28 Chemical formula of Hexaminoterphenyl¹¹⁷

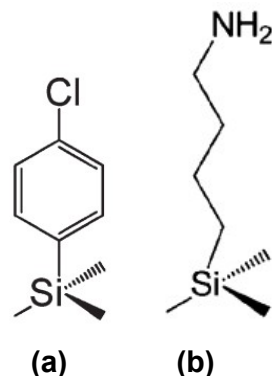


Figure 2.29 Examples of surface groups tested by Williams et al.¹¹⁷
(a)Chlorophenyl (b)Butylamine

2.6.5.1 DFT in amine Functionalized mesoporous silicas

With DFT, Computational studies simulating the chemisorption of CO₂ adsorption on functionalized mesoporous silica are possible, but an accurate representation

of the adsorbent structure and functional groups will contain over 1000 atoms, and the computational cost and time is unfeasible. Consequently, DFT becomes a tool to understand single Adsorbent-adsorbate interactions within the system, or to develop parameters for the system to be used in GCMC simulations.

Mafra et al.^{91,92} studied the chemical species formed from CO₂ adsorption in CO₂/CH₄ mixtures on amine functionalized SBA-15 through DFT analysis coupled with SSNR characterization. The silica surface cluster in the simulation was based on an alpha-quartz, and functional amine groups were placed on the surface to replace dangling -OH bonds. **Figure 2.30** shows an example of the model for Primary amine (APTES) used on the studied surface.

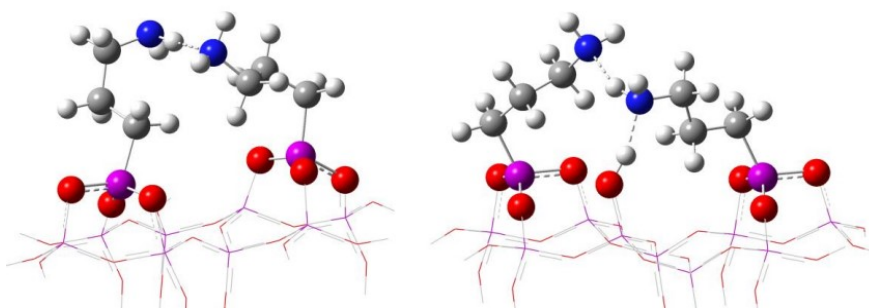


Figure 2.30 Several structures of APTES modified silica surface, post DFT geometric optimization¹.

By employing this C NMR and DFT methodology, they narrowed down the entities of chemisorbed CO₂ species on amine moieties as a factor of the neighbouring atoms and therefore surface loadings of the amines. The three possible species formed with APTES functionalized silica can be referred to in **Figure 2.31**. This multifarious method confirmed the possibility of the formation of carbamic acid moieties stabilized by Hydrogen Bonding for certain conditions, structures that had been previously thought to be unstable. This was confirmed by calculating dissociation energies and correlated them to NMR resonances under adsorption/desorption conditions; in this manner they demonstrated that the existence of these species was possible. This explained the fast reversibility of CO₂ adsorption under low pressure and provided insight on enhanced physisorption because of amine functionalization in CO₂/CH₄ applications.

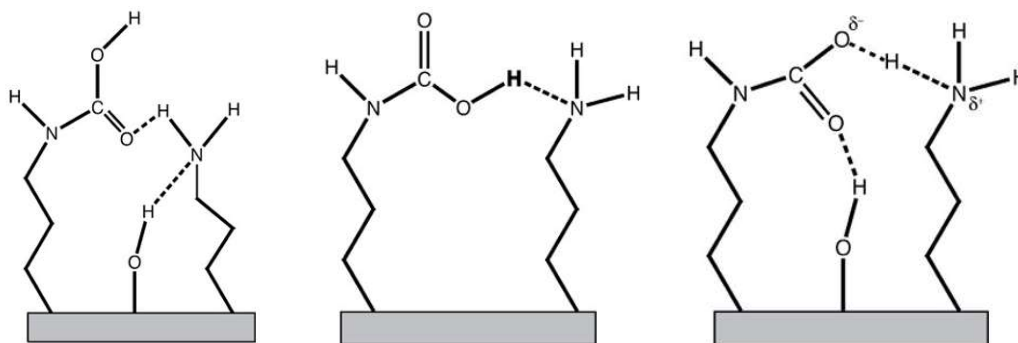


Figure 2.31 Structures of species formed by carbamic acid interaction with adsorbent surface and neighbouring molecules¹.

2.6.6 Feasibility of employing MS methods in this work

In conclusion, screening functional groups on mesoporous silica through GCMC molecular simulation can lead to a collection of extensive physisorption data, as was presented in the previous section^{117, 101, 119, 143}. However, referring to the diverse methodologies used in this section, the process of preparing a mesoporous structure and ensuring its accuracy can vary greatly, making it difficult to ascertain that a structural and FF parameter set can be carried over to different process conditions. This is further complicated when amine functionalities are involved and chemisorption exists, as it cannot be modelled by standard GCMC. This leads to a laborious process of structural validation and requires several assumptions to be made in modelling the system. These factors make applying GCMC methods to mesoporous systems a time-consuming process, and put the conclusions drawn from an only GCMC simulation in question.

DFT simulations are subject to different limitations, in that the interaction energies calculated do not solely account for adsorption conditions such as temperature and pressure^{130, 134}. However, DFT calculation methods have been extensively

optimised, and can be an effective and time efficient tool for a comparative study of the interaction energies arising from different molecular structures and moieties. Consequently, this work employs only DFT calculations to aid in the rationalisation of differences in adsorption performance by the different amines grafted.

2.7 Pelletisation

To practically employ adsorbents at a larger scale, considerations for the diffusion mass resistance and the pressure drop across the adsorbent bed must be considered. The most studied mesoporous silicas are SBA-15 and MCM-41; however, adsorption data is often reported for their powder form. This is because they more readily synthesized or sold in powder form. Pelletised forms of these adsorbents are also sold, but they are not as common and can be quite expensive (381 GBP for 5 g from SigmaAldrich, UK). Within the literature, there are very few works that explore alternative methods for the pelletisation of silica materials like the one used here. Rezaei et al.¹⁷⁶ pelletised SBA-15 post-amine functionalisation by a carver press under ~7 MPa and 34 MPa pressures. Their goal was to understand the effect of pelletisation pressure on the measured CO₂ capacity. Pressures of 7 MPa were found to prepare significantly better pellets, having no effect on the adsorption capacity of PEI impregnated SBA-15 and only a 13% decrease of the APTES grafted SBA-15, but no results on the adsorption kinetics were reported. Additionally, although the resulting pellets showed exceptional adsorption capacity, the formed spherical pellets were of 250 and 500 µm in size, which remains too small a particle size to predict their structural integrity as larger pellets and in continuous industrial level pressure cycling processes.

Klinthong et al.¹⁷⁷ introduced a new method of pelletising SBA-15, by using polyallylamine with NaOH solution. The resulting pellets showed acceptable structural integrity of 0.4 MPa and the APTES functionalised sample maintained 90% of the capacity of powdered samples. This showed promising results, but

the cost of the polyallylamine is quite high, being sold for ~100 GBP for 5 g of material, making the scale-up of this method economically difficult.

In another study, Sharma et al.¹⁷⁸ prepared pellets using bentonite as a binder, a cheap and commercially available material. They investigated the effect of adding activated carbon to the binder solution, and whether it could minimise the reduction in capacity post-pelletisation. They found that a composition of 20% bentonite and 5% activated carbon (AC) helped maintain the adsorption uptake, a result of the expansion of AC during the calcination step. However, the expansion of AC altered the internal morphology of SBA-15, and likely changing the dynamic adsorption of the pellets, a factor that was not discussed within their study. In this work, I have built on Sharma et al.'s study to investigate the optimal quantity of an only bentonite binder composition, thus minimising any internal morphology changes while maintaining a reasonable adsorption capacity, structural integrity, and surface area for functionalisation. Additionally, LUDOX®, a colloidal silica, was used as a co-binder to see if it could aid in the pellet's structural strength, while also providing replacement/additional hydroxyl sites for functionalisation.

2.8 Novel applications of amine grafted silicas

Projections estimate that to maintain a maximum of 1.5°C increase in global temperatures relative to the pre-industrial period, it is necessary to limit atmospheric CO₂ to 430 ppm by 2100¹⁷⁹. Nevertheless, related studies show that this maximum is not achievable without negative-net emission technology (NETs)^{3,180}. The development of “negative carbon technology”, such as DAC, have thus become ever more necessary.

2.8.1 Direct Air Capture

In the design of adsorbents for air capture, specific conditions must be considered, primarily, the low CO₂ partial pressure (0.04%) and the presence of water vapour. The utilisation of established physisorbents for DAC may be

considered an attractive option, as they selectively adsorbed CO₂/N₂, even at partial pressures relevant to air capture, while requiring low regeneration energy¹⁸¹. What they lack is selectivity of CO₂ over H₂O, with studies showing zeolite 13x and MOF-74 being heavily affected by relative humidity in their overall capacity and cyclability^{181–183}. In these same studies, MOFs have even been shown to degrade structurally upon exposure to water vapour¹⁸⁴. Amine functionalised silicas offer a viable alternative that provides CO₂/N₂ selectivity and CO₂ capacity, while resisting or being enhanced by the presence of moisture^{33,185,186}.

When employing amines for DAC, the amine efficiency for CO₂ adsorption has been shown to change in response to the relative humidity (RH) and low CO₂ partial pressure in air. This was demonstrated by Didas et al.¹⁸⁷, in which primary amines showed a much higher hydrophilicity compared to secondary amines at low CO₂ partial pressures. The contribution from moisture in primary amines led to an amine efficiency of 0.20 mol of CO₂/ mole amine in primary amines compared to 0.07 mole of CO₂/ mole amine in secondary. Although this might be the case, many studies concentrated on maximising the adsorption capacity by densely functionalising mesoporous silica, sometimes using impregnation to achieve this goal. Choi et al.¹⁸⁸ prepared PEI impregnated silica and simulated dry ambient air adsorption conditions (at 25°C), and one of the synthesized materials achieved a capacity up to 2.36 mmol/g. Although an impressive capacity for such low CO₂ partial pressures, the adsorption halftime for uptakes between 2.0 to 2.36 mmol/g was estimated to be range from 200 to 300 minutes. Additionally, the desorption conditions were performed under nitrogen at 110°C for 3 hours, causing a decrease in capacity in one material by up to 0.7 mmol/g in only a few cycles. Brillman et al.¹⁸⁹ showed promising results with TEPA impregnated silica, achieving uptakes of up to ~2.49 mmol/g at 35 wt% TEPA impregnation. Although with exceptional uptake, the time of exposure used was 16 hours, implying very long adsorption times associated with the reported uptake, and providing no insight into the kinetics of adsorption. From these

studies, amine impregnated silicas may offer high capacities, but they are subject to long adsorption rates and possible deterioration over cyclic operation.

For amine grafted silicas, Belmabkhout et al.¹⁸⁶ investigated the feasibility of triamine grafted MCM-41 in CO₂ capture, in both humid and dry conditions. They found that a 26% RH enhanced the adsorption from 0.9 mmol/g to 1.19 mmol/g. The adsorption period was reported as a total breakthrough time, reaching 328 minutes. Although promising, Wagner et al.¹⁹⁰ grafted triamine at a loading of 7.3 mmol/g on MCM-41 and then left it overnight outdoor for ambient air capture cycles. However, after two desorption cycles held for 2 hours at 75°C by humid air or humid N₂, the adsorption capacity dropped by 100% in both cases. In their case, the humidity in the desorption conditions plus the extended time frame for it contributed to the deterioration in performance, and so do not reflect the full extent of triamine grafted silicas in air adsorption applications. Compared to impregnated materials, triamine grafted silicas show promise for DAC applications. It should be considered that multi-amine containing branches may show very high CO₂ uptake in air, but they are limited by their slower adsorption rates compared to shorter amine branches and lower functionalisation loadings¹⁸⁹. Additionally, there is some evidence that multi amine moieties may be affected by the presence of moisture and forming bicarbonate, thus limiting desorption efficiency¹⁹¹. To maximise the overall CO₂ uptake while minimising the time required for its adsorption/desorption, it is important to further investigate different amine types grafted on silica, and their resulting adsorption capacity and kinetics under humid conditions. Can moderate to highly grafted amines on silicas match the reported CO₂ capture capacities of impregnated amines? Can this requirement be met at faster adsorption rates?

2.9 Conclusion

From the discussed literature, it's clear that the adsorption uptake and regeneration capabilities of grafted amines outweigh impregnated amines, especially for conditions more relevant to CO₂/CH₄ separations. However, there is no such study that has correlated the changing performance expected in

CO₂/CH₄ separations because of different amine types at different loadings. Considering the energy demands associated with regenerating materials with high amine loadings, this mapped out relationship is essential in understanding how to best employ amines onto adsorbent bases, in mesoporous silicas and beyond. There is a similar lack of research into the pelletisation of powdered materials, with very few that target larger pellets that can avoid carry over, minimise differential pressure across a bed, and maintain integrity at higher operating pressures, conditions very relevant to commercial applications. Finally, as the necessity to achieve negative carbon footprint rises, novel applications such as CO₂ removal from air by DAC are only recently gaining interest. Much work is required in understanding the optimal amine types for capture from ambient air, specifically when considering continuous and time efficient adsorption of the low CO₂ partial pressure present in air.

3 CO₂/CH₄ ADSORPTION MECHANISMS FROM COMBINED AMINE FUNCTIONALITIES

Effect of combined primary and secondary amine loadings on the adsorption mechanism of CO₂ and CH₄ in biogas

ABSTRACT

Biomethane, produced by biogas upgrading, is a promising energy source that can play a key role towards net-zero emissions targets. The incorporation of amine functionalities into adsorbents for biogas upgrading can facilitate the selective adsorption of CO₂, but their effect has not been comprehensively studied within the context of CH₄ mixtures. In this work, the effectiveness of amine functionalities in selectively separating CO₂ from biogas, is investigated. Primary, diamine, and triamine organo-silanes grafted at various loadings on SBA-15 were used to study the adsorption mechanisms associated with amine functionalities for CO₂:CH₄ gas mixtures. The successful incorporation of amines was confirmed with thermogravimetric analysis (TGA), Fourier Transform Infrared (FTIR), and elemental analysis (EA). The different amine reagents and loadings resulted in an alteration of adsorption mechanism that provided key information on the developing relationship between adsorption capacity, selectivity, and energy efficiency. Diamine with an amine loading of 2.5 mmol/g and a moderate silane coverage of 1.54 molecules/nm² was found to provide the best balance of an enhanced CO₂ adsorption capacity (1.12 mmol/g), a superior selectivity to densely grafted primary amines, and the lowest isosteric heat of adsorption of ~25 kJ/mol at 1.12 mmol/g compared to ~41 kJ/mol for primary and triamine materials. Amongst all the samples, a lower amine loading on the bare adsorbent enhanced CO₂ adsorption capacity and selectivity while minimising the heat duty associated with adsorbent regeneration. Moreover, under isothermal desorption conditions at 25 °C, some samples achieved working capacities comparable to higher amine loaded materials.

Introduction

Atmospheric carbon dioxide (CO₂) concentrations reached a record high in 2020, with global averages reaching 414 ppm, being largely responsible for a global warming of $\sim 1\text{ }^{\circ}\text{C}$ ². To minimise severe consequences of climate change, it has become necessary to limit the extent of global warming to $1.5\text{ }^{\circ}\text{C}$ from pre-industrial times by 2100, which would require meeting a net-zero emissions target by 2050^{3,192}.

Energy from fossil fuels continues to be the primary source of worldwide usage, but as a major contributor to greenhouse gases, has diverted research towards alternatives such as biogas⁴¹. Biogas, depending on the feedstock and upstream process, is a renewable energy source that can potentially be carbon neutral. Biogas is produced through anaerobic digestion, is primarily made up of CH₄ and CO₂, and is produced through processes that provide much lower lifecycle CO₂ footprints compared to fossil fuels^{193,194}. This qualifies biogas as a feasible source of energy towards the UK's net-zero target. Moreover, upgrading biogas to biomethane for an increased calorific value while producing a high-purity CO₂ tail gas for storage can drive this initiative towards a negative-emissions energy source¹⁷.

Amine scrubbing is a well-proven carbon capture technology that selectively absorbs CO₂. However, the energy demand for regeneration is high which leads to a large energy penalty^{11,12}. An alternative to scrubbing that potentially imposes lower energy demand for regeneration is swing adsorption technology. Swing adsorption processes utilise solid adsorbents and come with the added benefit of flexibility in process arrangements allowing for a wide range of operating conditions for a diverse set of applications^{13,14,195}. The favourable characteristics of amine scrubbing and swing adsorption can be combined through amine functionalisation of a variety of sorbent materials, although each material presents its own challenges and sensitivity to moisture, some examples include activated carbon⁶¹ (AC), zeolites⁶², mesoporous silica⁶³, and polymers^{22,64}. The incorporation of amines into solid adsorbents can be carried out in a variety of

methods, including grafting, impregnation, or in-situ doping, with various studies aiming to maximise the capacity of adsorbents through amine functionalisation utilising a wet-impregnation method on mesoporous silica such as MCM-41. This material has a high pore volume and can load up to 70 wt.% of polyethyleneimine (PEI) or tetraethylenepentamine (TEPA), with an optimal value of 50%-60% to minimise diffusional resistance^{24,67,68}. Amine impregnation has been shown to enhance capacity and selectivity at low pressures, and due to the dominating effects of chemisorption at low CO₂ partial pressures, has been investigated for applications in flue gas treatment^{31,32,196}. However, as the amine loading increases the required regeneration temperature, the cyclability of these adsorbents is limited due to leaching. This is primarily caused by the absence of bonds between amine groups and the adsorbent surface^{32,69,70}. In comparison, grafted amino organ silanes on mesoporous silicas form a covalent bond with the surface allowing for better cyclability. However, the maximum capacity is limited by the accessible surface silanols for amino-silane bond formations^{71,72}. Whether by impregnation^{67,68,95} or grafting^{34,70,95,197,198}, many studies target high amine coverage to maximise adsorption capacity. These studies are mainly applied for post-combustion conditions, where the performance under CO₂/N₂ gas mixtures or in the presence of typical flue gas components is explored³¹⁻³⁴. Hiyoshi et al.⁶⁹ studied SBA-15 with a range of surface functionalities on the adsorption of CO₂ in CO₂/N₂ mixtures. However, they focused on adsorption temperatures of 60°C and limited the CO₂ pressure to 15 kPa, conditions specific to flue gas. Alkhabbaz et al.¹⁹⁹ used calorimetry to understand the entropic and enthalpic contributions to the heats of adsorption of SBA-15 functionalised with 3-aminopropyltrimethoxysilane (APS) and several secondary amine structures. They deduced the importance of entropic factors in adsorbent CO₂ capture efficiency and showed the superiority of primary amines compared to secondary amines in achieving high CO₂ uptakes at ultra-low pressures, up to 10 kPa. Overall, there is a limited number of studies with respect to CO₂ adsorption efficiency ascribed to different amine functionalities and surface loadings in CO₂/CH₄ mixtures.

Mafrá et al.^{29,91} and García et al.⁹⁵ both demonstrated the enhanced selectivity of CO₂ to CH₄ in amine-grafted SBA-15 at maximum grafting loadings. However, cyclic studies of SBA-15 functionalised with a high level of amines showed a lower working capacity for all amine types compared to raw SBA-15, at desorption conditions of 100 kPa and 10 kPa at 25 °C²⁹. Similarly, in a cyclic stability study of triamine-functionalised SBA-15 in dry conditions, Belmabkhout et al.³³ reported a 67% loss in capacity under atmospheric desorption and a 20% loss under vacuum desorption at 25 °C. Although underperforming in dry conditions, in the same study they demonstrated the superior performance and cyclability of triamine-grafted MCM-41 at 7.5% relative humidity compared to zeolite 13x and Darco-AC commercial adsorbents. Belmabkhout et al.^{63,85} also showed that at ambient temperatures, CH₄ interacts to a higher degree with functionalised and raw MCM-41 compared to N₂. For a fully functionalised MCM-41 with triamine, they reported a molar selectivity of 28 for CO₂/CH₄ compared to 308 for CO₂/N₂ at 100 kPa CO₂ partial pressure. Xu et al.²⁰⁰ studied the adsorption of CO₂, CH₄, and N₂ mixtures on a monoethanolamine-modified β -zeolite from 5% to 60% functionalisation. They showed that at functionalities above 15%, selectivity is enhanced and a lower uptake of all components including CO₂ is observed. The adsorbent's specific surface area reaches 17 m²/g at this degree of amine functionalisation, which makes it difficult to determine the principal causes of the change in adsorption behaviour. This rationalises the need to utilise mesoporous media at low coverage to scrutinise the adsorbate-amine interactions to a greater degree. The lower coverage can provide essential information on the inter- and intra-molecular interactions at play while isolating them from diffusional limitations due to high loadings. The changes in inter- and intra-molecular interactions were analysed by Yoo et al.⁹³ through the heat of adsorption of mono-, di-, tri- and tetra-amines. They found that in certain cases, surface hydroxyl groups can interact with nearby amines to facilitate the chemisorption of CO₂. Their findings highlighted the potential utilisation of low amine loadings for CO₂ sorption. Nonetheless, the study was limited to ultra-low coverage and was not extended towards the selectivity of gas mixtures.

Limitations in the isothermal cyclic utilisation of amine-functionalised adsorbents, and the concentration of most studies on maximum amine loadings, highlight the necessity to understand the developing relationship between the level of functionality and adsorbent performance for these materials. In CO₂/CH₄ gas separations, further studies are required that scrutinise the developing relationship between amine loading, amine type, and the resulting separation efficiencies achievable.

In this work, a fundamental understanding of the change in adsorption mechanisms and separation efficiency with amine type and loading were studied, up to atmospheric pressure. This encompasses the initial pressure region in which the adsorption mechanisms of amine functionalised SBA-15 is undergoing a transition between chemisorption and physisorption. The effects of amine functionality on the adsorption of CO₂/CH₄ mixtures was thus investigated by grafting primary amine, di- and tri-amine organo-silanes on SBA-15 at varying amine loadings. The CO₂ and CH₄ capture capacity and selectivity of each amine type at different surface coverage was studied. This aided in the identification of amine-adsorbate interactions and elucidated important considerations in employing amine functionality for CO₂/CH₄ separations. Additionally, the isosteric heat of adsorption was calculated to understand the governing adsorption mechanisms as a function of amine type and amine loading. Finally, isothermal, and non-isothermal adsorption-desorption cycles were used to compare the implications of amine type and loading for low pressure adsorption, or temperature swing adsorption (TSA) applications.

3.1 Material and methods

3.1.1 Materials

As synthesised SBA-15 mesoporous silica was purchased in powder form from XFNANO®. The chemical reagents (3-aminopropyl)triethoxysilane (APTES), 3-(2-aminoethylamino)propyltri-methoxysilane (AEAPT), 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (TAEPT), toluene (99.8%), and methanol

(HPLC grade) were purchased from Sigma-Aldrich, UK. All gases were supplied by BOC, UK with a purity above 99.99% for nitrogen, carbon dioxide, and methane.

3.1.2 Material Synthesis

For each sample, 1 g of SBA-15 was dried at 110 °C under vacuum (40 mbar) for 1 h to remove moisture and ensure minimal polymerisation of silane branches during grafting^{71,91}. Once cooled, the system was purged with nitrogen, prepared for inert reflux, and 80 mL of toluene was introduced into the flask containing the SBA-15 powder. Subsequently, a given amount of amino organ silane was added as per Table 1 (0.1-2 cm³ of amine per gram of SBA-15) and the mixture was heated to 70°C for 18 h under reflux. The grafted SBA-15 was then filtered under vacuum suction and washed with an abundance of toluene and methanol. It is reported that drying of the sample in air can result in the oxidation of amino groups at elevated temperatures⁷⁴. Therefore, the powder was left to dry in air for 24 h at room temperature. Each sample is designated as S-x-y, with x representing the amine type and y the amine loading.

3.1.3 Characterisation methods

3.1.3.1 Estimation of amine content

The quantity of amine grafted on each sample was estimated by thermogravimetric analysis (TGA 8000, PerkinElmer) and C and N elemental analysis (vario EL III, Elementar). The TGA measurement was carried out with a sample weight of 8-10 mg, under nitrogen flow from 30 °C to 800 °C at a rate of 20 °C /min, with a 10 min hold at 120 °C under nitrogen flow and a 5 min hold at 800 °C under air flow. Elemental analysis (EA) for C and N quantity was measured by a thermal conductivity detector through thermal combustion analysis.

3.1.3.2 Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectra of samples over the range of 1000 - 3800 cm^{-1} were measured using a Shimadzu Attenuated Total Reflection (ATR) spectrometer to confirm the successful grafting of the amine branches and assess the gradual increase of functional moieties across all samples. Each sample was scanned 20 times at a resolution of 4 cm^{-1} .

3.1.3.3 Pore structure analysis

The structural properties were calculated from nitrogen adsorption isotherms at -196 °C using a 3P Meso 222 sorption analyser (3P Instruments). For each test, 0.2-0.3 g of sample was degassed at 90 °C for up to 2 h under vacuum. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method in the relative pressure of 0.05 to 0.2⁸⁷. The pore volume was calculated from the volume of adsorbed nitrogen at $p/p^0 = 0.95$ using the Barrett-Joyner-Halenda (BJH) method¹⁵⁴. The pore size distribution (PSD) was determined by the Broekhoff-de Boer (BdB) method simplified using the Frenkel-Halsey-Hill (FHH) approximation denoted as BdB-FHH²⁰¹. Specific surface area, pore volume, and average pore size of samples are summarised in **Table 3-1**.

3.1.3.4 Volumetric gas adsorption measurement

CO₂ and CH₄ isotherms were measured using the 3P Instrument's sorption analyser. For each test, 0.25-0.3 g of sample was degassed under the same procedure previously described for nitrogen physisorption analysis. The adsorption temperature was maintained at 25, or 40 °C by submerging the sample tube in an anti-freeze liquid bath (3P Instruments). All measurements were taken up to 100 kPa.

The ideal gas adsorption theory (IAST)²⁰² method was employed to estimate the adsorption selectivity. It is important to note that the use of IAST is subject to certain limitations when applied to systems exhibiting energetic surface heterogeneity, or when one component adsorbs substantially more than the other^{203,204}. Depending on the degree of functionalisation of the samples, surface

heterogeneity may exist, especially at very low CO₂ pressures. This is due to unreacted amine moieties, chemisorption sites, or chemisorbed species distributed across the surface. Considering these limitations, this model is used as a comparative tool of the various functionalised samples relative to each other, providing insight on the different influences on CO₂/CH₄ selectivity, particularly concentrating at CO₂ partial pressures > 40 kPa, when chemisorption is no longer the principle adsorption mechanism.

The IAST selectivity ($\hat{S}$) was calculated using Eq (3-1):

$$\hat{S} = \frac{q_i/P_i}{q_j/P_j} \quad (3-1)$$

where q (mmol/g) and P (kPa) are equilibrium adsorption capacity and partial pressure of the gas species, respectively.

3.1.3.5 Gravimetric gas adsorption measurement

Gravimetric CO₂ adsorption and desorption for chosen samples were measured by TGA (TGA 8000, Perkin Elmer). A sample of 8-12 mg was degassed under a nitrogen flow of 60 mL/min at 110 °C for 30 min to ensure moisture is stripped away. The sample temperature was then stabilised at 25 °C and exposed to a flow of 60 mL/min of CO₂ for 25 min. The gas was then switched to nitrogen at 60 mL/min, and the temperature was kept at 25 °C for 30 min or increased at a rate of 15 °C/min to 40 °C and was maintained at 40 °C for 30 min.

3.2 Results and discussion

3.2.1 Surface analysis

Nitrogen adsorption-desorption isotherms of samples at -196 °C are given in **Figure 3.1**. All samples exhibited a type IV isotherm with an H1 type hysteresis loop, indicating a narrow distribution of uniform mesopores, a typical feature of SBA-15²⁰⁵. The introduction of amino organ silanes led to a reduction in adsorbent pore volume and specific surface area as the amine loading increases. In agreement with previous studies^{32,80}, the effect of grafted amine loading on the

pore volume and specific surface area is more pronounced as the amine moieties per organ silane branch increase in number, with TAEPT having the most considerable effect at lower silane loadings followed by AEAPT and APTES. In the case of AEAPT (diamine), 22% more nitrogen loading was achieved at a comparable surface area of 308 and 317 m²/g and pore volume of 0.78 and 0.81 cm³/g for APTES and AEAPT, respectively. This is similarly seen with TAEPT, showing a 38% increase in nitrogen loading at a comparable surface area of 308 and 333 m²/g and pore volume of 0.78 and 0.87 cm³/g for APTES and TAEPT, respectively. Additionally, the affinity of each organ silane towards the formation of surface bonds varied based on the reagent used. Surface grafting occurred more readily at lower reagent volumes of 0.45 mL in the order of APTES > AEAPT > TAEPT, inversely proportional to the molecular length of each reagent.

The change in the pore size distribution with an increasing amount of grafted functional groups was calculated from the N₂ isotherms up to P/P₀=0.85, which marks the final saturation plateau, and presented in **Figure A.1** in the Supplementary Information^{29,87,176,206}. It demonstrates the likely heterogeneous distribution of silane molecules within the pores of SBA-15, and clustering of amines or single isolated amines may both be present and should be considered when analysing the amine dependent CO₂ adsorption behaviour. The peak pore size for all functionalised samples was estimated from the nitrogen desorption branch showing a starting maximum pore diameter for raw SBA-15 of 7 nm.

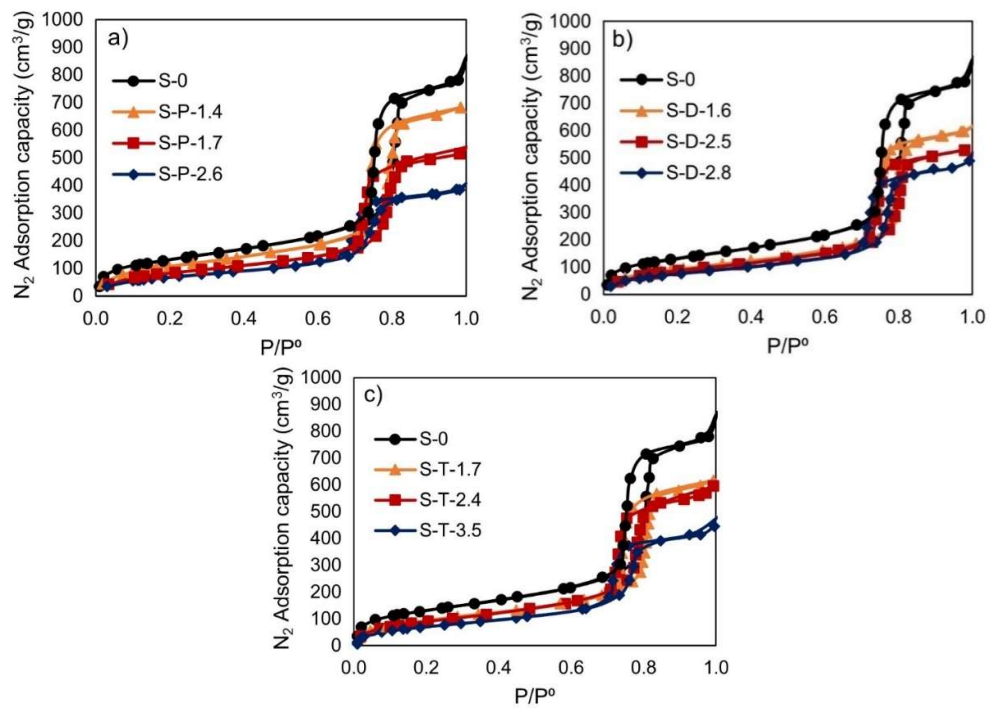


Figure 3.1 Nitrogen adsorption-desorption isotherms at $-196^\circ C$ for functionalised samples with (a) APTES, (b) AEAPT, and (c) TAEPTs, in comparison with raw SBA-15.

Table 1. Physical and chemical properties of raw and functionalised SBA-15

Sample	Reagent type	Reagent quantity(mL)	Amine type(S)	Amine loading (mmol/g)					S_{BET} (m ² /g)	Vp (cm ³ /g)	Dp (nm)
				TGA – Tridentate/Biden-OH*	TGA-Bidentate [†]	Elemental Analysis	Silane loading [§]	Silane Molecule/nm ² ‡			
S-0	-		-	-	-	-	-	-	490	1.20	7.0
S-P-1.4	APTES	0.45	Primary	1.49	0.99	1.46	1.46	1.79	406	1.04	6.4
S-P-1.7	APTES	1.00	Primary	1.78	1.19	1.71	1.71	2.10	308	0.78	6.3
S-P-2.6	APTES	2.00	Primary	2.42	1.62	2.60	2.60	3.19	267	0.63	5.7
S-D-1.6	AEAPT	0.25	Primary Secondary	1.84	1.6	1.59	0.79	0.98	340	0.89	6.5
S-D-2.5	AEAPT	0.35	Primary/ Secondary	2.40	2.09	2.47	1.23	1.54	317	0.81	6.3
S-D-2.8	AEAPT	0.45	Primary/ Secondary	2.95	2.57	2.78	1.39	1.71	288	0.74	6.2
S-T-1.7	TAEPT	0.19	Primary/ 2 Secondary	2.09	1.89	1.70	0.56	0.70	352	0.92	6.8
S-T-2.4	TAEPT	0.23	Primary/ 2 Secondary	2.61	2.36	2.40	0.78	0.98	333	0.87	6.4
S-T-3.5	TAEPT	0.45	Primary/ 2 Secondary	3.90	3.53	3.52	1.17	1.44	274	0.66	6.3

* Estimate of amine loading from TGA data for tridentate-type bonding with the adsorbent surface or bidentate with an -OH side chain.

[†] Estimate of amine loading from TGA data for bidentate-type bonding with the adsorbent surface with a methyl/ethyl branch remaining on the unsubstituted portion of the amino organ silane.

[§] Silane loading calculated from the elemental analysis of each sample

‡ Calculated amine surface coverage from the effective surface area of raw SBA-15 sample S-0 and the total measured amine loading in mmol/g.

3.2.1.1 Chemical properties

The measured infrared (IR) spectra of the functionalised samples (**Figure 3.2a**) confirm the successful grafting of the amino organ silanes on the surface of SBA-15. There is an increase in peak intensity at 1045 cm^{-1} coinciding with Si-O-Si bond vibrations within the range of $1130 - 1000\text{ cm}^{-1}$. According to **Figure 3.2b**, the samples with the lowest loadings exhibit shallow peaks due to the small percentage of organics grafted (7%-10%). Nonetheless, there are clear peaks for NH_2 bending vibrations at around 1641 cm^{-1} for all primary amines. This is accompanied by the broad, yet weak band at 1566 cm^{-1} for organic silica containing a primary amine moiety. The presence of secondary amine moieties is more difficult to distinguish, but a magnification of the relevant IR regions associated with APTES, AEAPT, and TAEPT is provided in **Figure A.2** in the Supplementary Information.

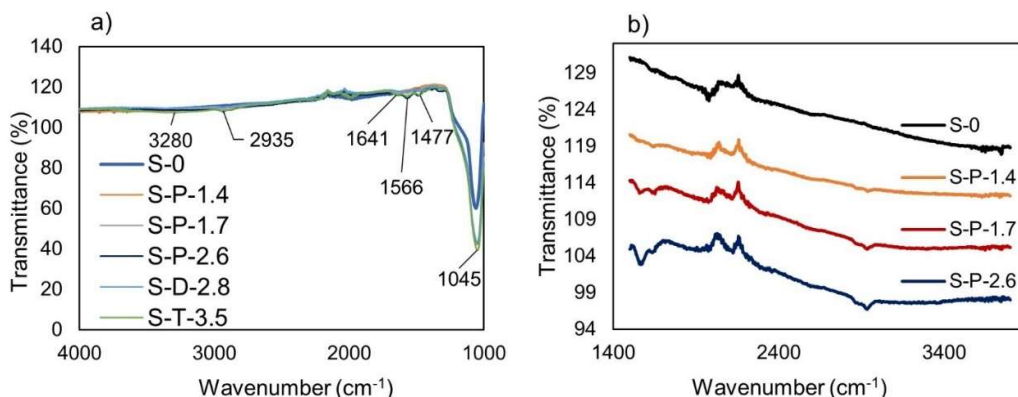


Figure 3.2. IR spectra for (a) selected functionalised samples and (b) primary amine-functionalised samples offset and magnified from 1500 to 3500 cm^{-1} , compared to raw SBA-15.

TGA results presented in **Figure A.3** provide the total mass of grafted organic content. However, to accurately estimate the amine loading by TGA, an understanding of the bond type formed with the surface silanols is required. The possible variation in amine loading for different bonds between the organ silane and the surface can be seen in **Table 3-1**, as TGA – Bidentate and TGA-Tridentate. Bidentate refers to the formation of two bonds between the organ

silane and the adsorbent surface while tridentate refers to grafting by forming three bonds. The R group in a bidentate surface bonding may exist as a methoxy in AEAPT and TAEPT, or ethoxy in APTES, or hydroxyl group for all amine reagents (**Figure 3.3**)^{71,207}. It is important to note that the bidentate amine loading in **Table 3-1** only refers to the presence of methyl or ethyl on the R-group. On the other hand, the calculated amine loading, for a hydroxyl R-group, is considered as a tridentate bond.

For all amine types, the IR bands that coincide with the lateral methyl and ethyl branches, substituted during the grafting, are difficult to distinguish as they peak within 1075-1190 cm⁻¹ and are masked by the sharper Si-O-R peak. The type of surface bonding was therefore estimated from a combined input of measured data, using both elemental analysis and TGA measurements. This was carried out using the total weight change attributed to organic content measured by TGA, and then correlated to the reported nitrogen content by EA. The weight measured by TGA can indicate different loadings of amines on the adsorbent' surface, and depends on the type of surface bond formed, which can be bidentate with a hydroxy, methoxy, or ethoxy side chain, or surface tridentate bonds^{29,197}. The conversion of organic weight burnt off by TGA to amine loaded in mmol/g requires the molecular weight of the species bonded to the surface, which will vary depending on the type of bond formed between the amino organ silanes and the surface. Since the concentration of N and C from EA give an accurate total quantity of amines grafted, this can be related to the calculated amine loading from the TGA data, which will vary depending on different surface bonds and their respective molecular weight, giving an indication to the principal bond type formed. In this manner, the amine concentration measured from the Elemental Analysis can be correlated to the likelihood of a certain bond type. APTES data agrees with previous ¹H-²⁹Si heteronuclear correlation solid-state nuclear magnetic resonance (ssNMR) analysis by Mafrá et al.⁹¹, indicating a susceptibility for tridentate grafting with SBA-15 for this type of amine. In comparison, some of the diamine and triamine EA results can potentially indicate a higher quantity of bidentate bond types compared to primary amine-grafted samples. The method

used limits definitive conclusions on the type of bonding due to possible silane polymerisation, shown to primarily result from the presence of moisture within the system^{71,208}. Although the synthesis procedure was formulated to ensure a moisture-free environment, there remains a possibility of polymerisation as suggested by previous research by Vrancken et al. of APTES grafted silica gel.

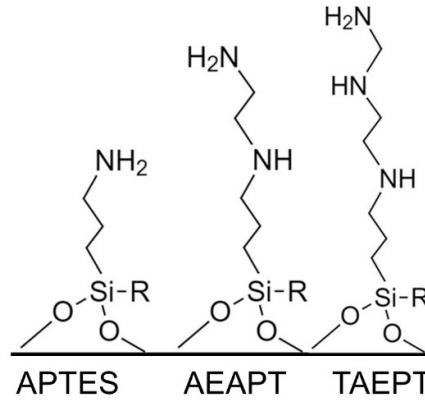


Figure 3.3 Silica surface grafted organo-silanes. R represents the methoxy or ethoxy or hydroxyl group in bidentate grafting. For tridentate grafting, all three silane branches are bonded to the surface of SBA-15 and R represents surface Si-O-Si bonds.

3.2.2 Adsorption mechanisms of CO₂ and CH₄

The measured CO₂ and CH₄ isotherms of the APTES, AEAPT, and TAEPT samples at 25 °C and 40 °C are provided in **Figures 3.4 to 3.6**, respectively. A summary of measured adsorption data, and estimated selectivity and heat of adsorption of samples are tabulated in **Table A.1**. The measured CO₂ adsorption isotherms were fitted using the modified two-site Toth isotherm model, developed by Serna-Guerrero et al.²⁰⁹, Eq. 2, and CH₄ adsorption isotherms were fitted by the Henry model, Eq. 3²¹⁰. The individual isotherm parameters for each sample and the R squared representing the accuracy of the regression models fitted to experimental data is presented in **Appendix C**.

$$q = \left[\frac{n_s b_1 P}{(1 + (b_1 P)^{t_1})^{1/t_1}} \right] + \left[\frac{n_{s2} b_2 P}{(1 + (b_2 P)^{t_2})^{1/t_2}} \right] \quad (3-2)$$

$$q = KP \quad (3-3)$$

where n_s , b , and t are the Toth isotherm parameters with the 1 or 2 subscripts indicating the adsorption site. The variable K represents the Henry isotherm constants. To understand the adsorption mechanisms as a function of amine loading, the isosteric heat of adsorption of each sample was calculated using the Clausius Clapeyron equation, Eq. 3-4 (**Figure 3.7**)

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{Ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3-4)$$

where H_{Ads} is the isosteric heat of adsorption, T_1 and T_2 are the isotherm temperatures of the relative pressures of P_1 and P_2 , and R is the universal gas constant.

For APTES samples (containing only a primary amine), an increase in amine loading from 1.4 N (S-P-1.4) to 1.7 N (S-P-1.7) caused a significant rise in the heat of adsorption (**Figure 3.7**). However, the increase in heat of adsorption was moderate when amine loading was increased from 1.7 N to 2.6 N mmol/g (S-P-2.6). S-P-1.4, with the lowest loading, has the lowest heat of adsorption starting at ~ -50 kJ/mol then drops to -40 kJ/mol as q increases from 0.1 to 0.3 mmol/g. Compared to the raw sample S-0, there is an approximate increase of 20 kJ/mol in the heat of adsorption of S-P-1.4. Chemisorption can be characterised by heats of adsorption of > -40 kJ/mol with binding energies that separate chemisorption from physisorption at about 48 kJ/mol^{35,36}. As a result, it can be concluded that S-P-1.4 shows a minimal enhancement of adsorption through chemisorption, but with a 62% increase in adsorption capacity compared to non-functionalised S-0 at 100 kPa and 25 °C (**Figure 3.4a**). In comparison, an increase in amine loading from 1.4 mmol/g (S-P-1.4) to 1.7 mmol/g (S-P-1.7) resulted in a 33% increase in adsorption capacity at 100 kPa but was accompanied by a considerable rise in the heat of adsorption (121 kJ/mol at 0.3 mmol/g). This is likely a result of the higher availability of adjacent amine sites in the S-P-1.7 sample, satisfying the

2:1 amine-to-CO₂ ratio expected for chemisorption to occur under dry conditions and the formation of carbamate or carbamic acid^{175,211}.

A further increase in amine loading from 1.7 mmol/g (S-P-1.7) to 2.6 mmol/g (S-P-2.6) did not have a significant effect on the heat of adsorption but enhanced the CO₂ capacity by 30% at 100 kPa (146 kJ/mol at 0.3 mmol/g). This may be a result of the initial fast reaction between CO₂ and the readily available amine sites, resulting in a strong interaction between adsorbate and amine, and a higher heat of adsorption at loadings below 0.4 mmol/g. This initial spike in adsorption is followed by a more uniform distribution of CO₂ on the remaining active sites in a manner comparable to S-P-1.7 and subject to similar interaction strengths.

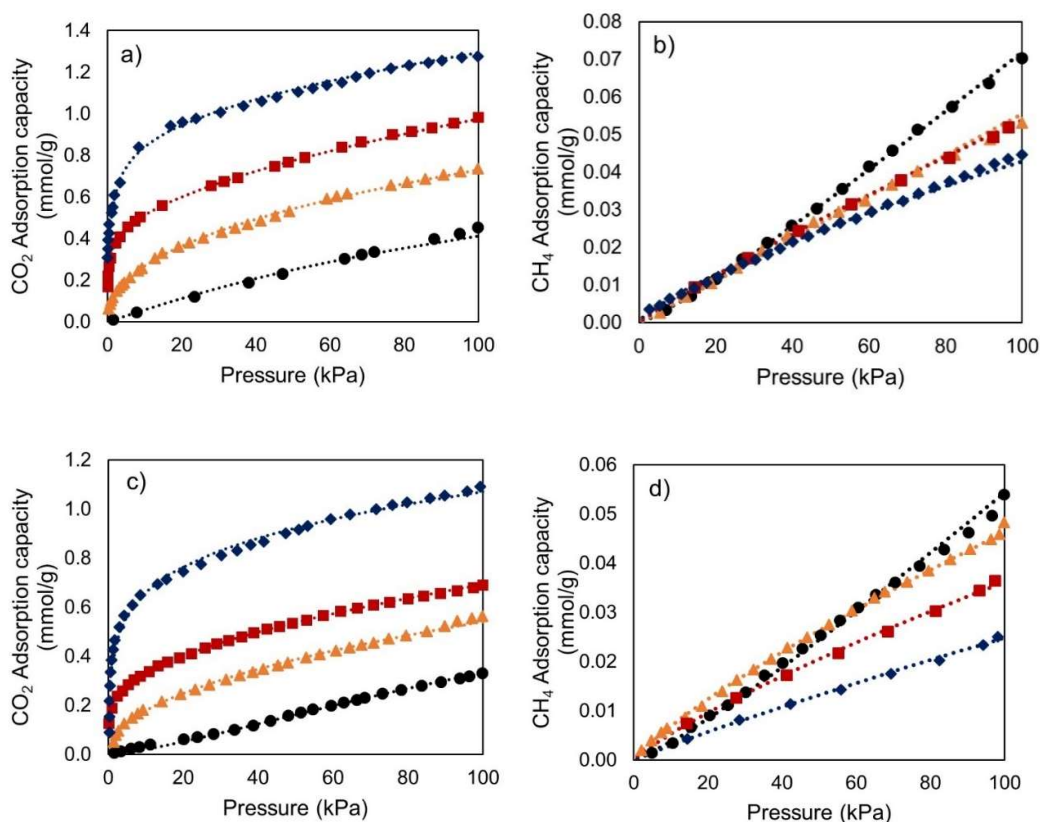


Figure 3.4 APTES adsorption isotherms for (a) CO₂ at 25 °C and (b) CH₄ at 25 °C, (c) CO₂ at 40 °C and (d) CH₄ at 40 °C (●) S-0, (▲) S-P-1.4, (■) S-P-1.7, (◆) S-P-2.6. The dotted lines represent the model predictions.

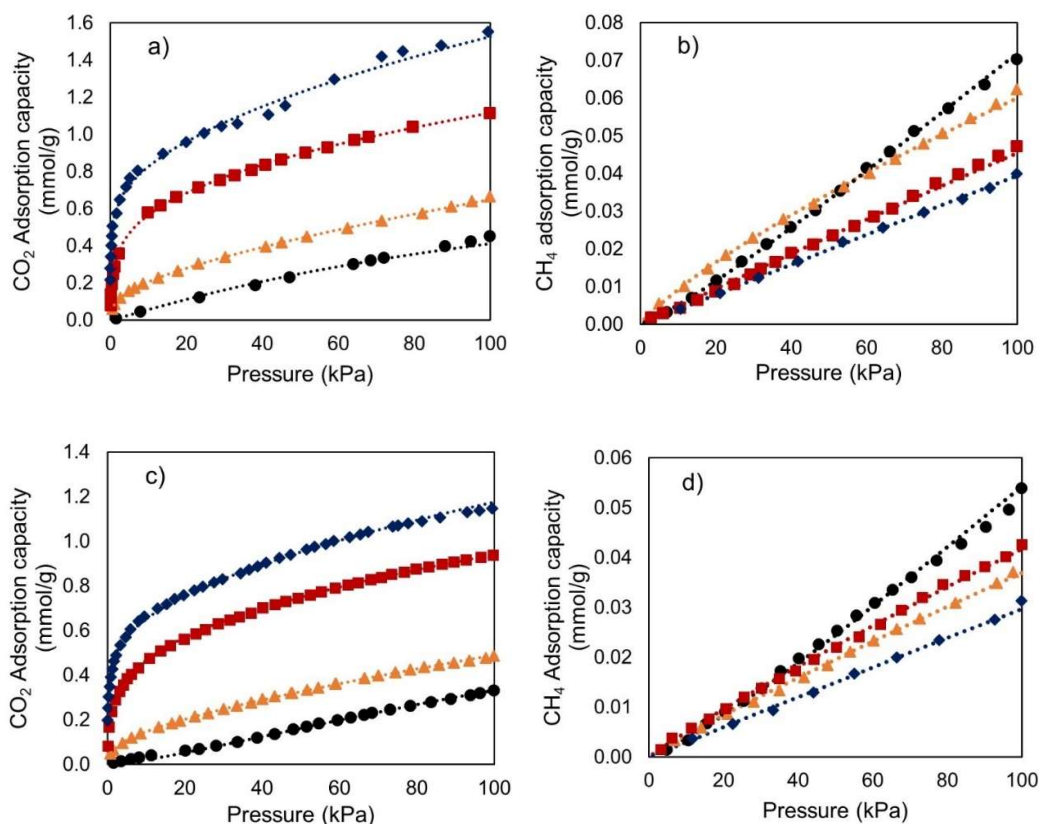
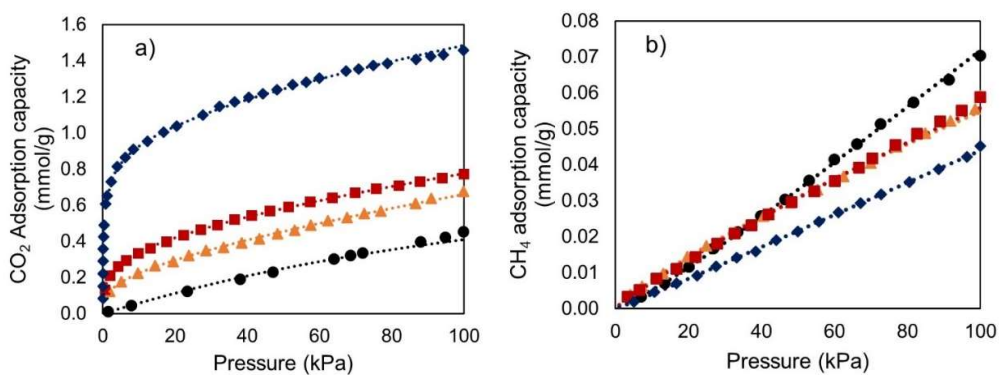


Figure 3.5 AEAPT adsorption isotherms for (a) CO₂ at 25 °C and (b) CH₄ at 25 °C, (c) CO₂ at 40 °C and (d) CH₄ at 40 °C (●) S-0, (▲) S-D-1.6, (■) S-D-2.5, (◆) S-D-2.8. The dotted lines represent the model predictions.



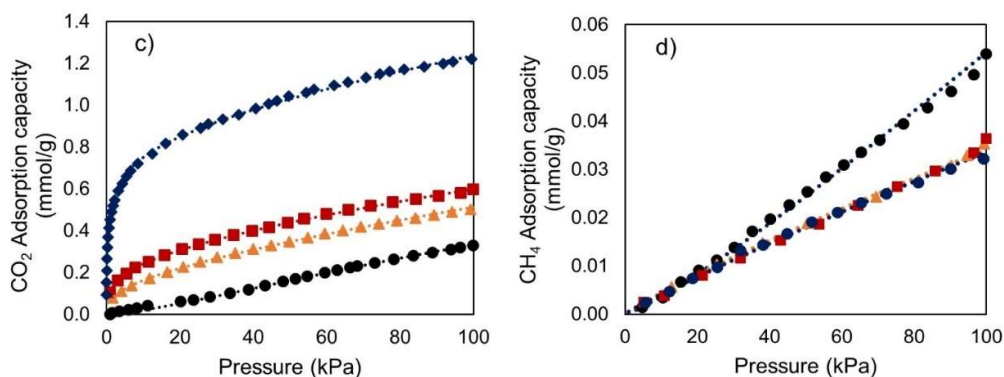


Figure 3.6 TAEPT isotherms for (a) CO₂ at 25 °C and (b) CH₄ at 25 °C, (c) CO₂ at 40 °C and (d) CH₄ at 40 °C (●) S-0, (▲) S-T-1.7, (■) S-T-2.4, (◆) S-T-3.5. The dotted lines represent the model predictions.

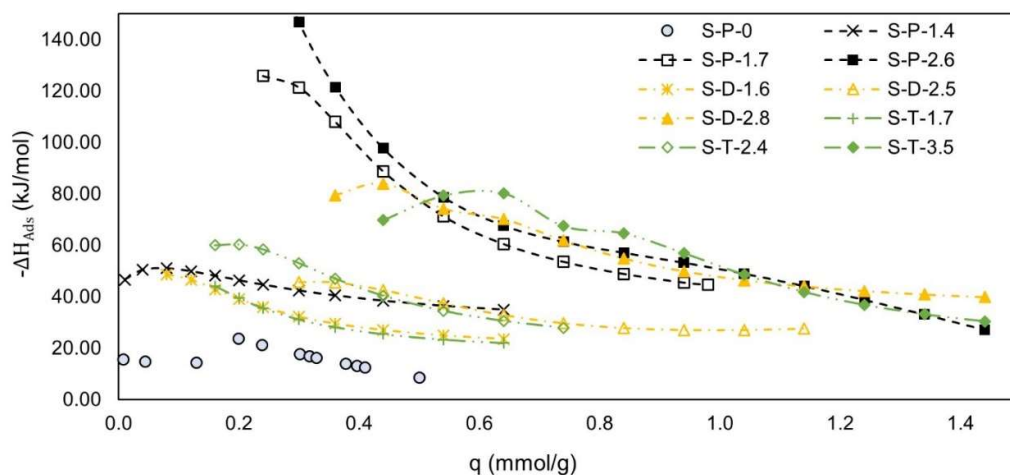


Figure 3.7 Isosteric heat of adsorption for raw SBA-15 and functionalised samples

For AEAPT samples (containing one primary and one secondary amine), an increase in amine loading from 1.6 (S-D-1.6) to 2.5 N mmol/g (S-D-2.5) caused a considerable enhancement in adsorption capacity from 0.3 to 0.6 mmol/g (**Figure 3.5a**), while only a slight rise in heat of adsorption (~ 15 kJ/mol) was observed (**Figure 3.7**). This response is distinctive compared to the APTES samples since S-D-2.5 achieves an adsorption capacity across all pressures that exceeds S-P-1.7 but with a heat of adsorption closer to S-P-1.4 (60 to 25 kJ/mol). Similar performance has been previously reported for secondary amine

containing amino organo-silanes and can be explained by the formation of lower stability carbamic acid, and the availability of two amine pairs along the same silane chain to satisfy the 2:1 requirement for the chemisorption of CO₂ while minimising the occupation of active sites for physisorption on the adsorbent surface^{89,199}.

For TAEPT samples (containing one primary and two secondary amines), a contrasting trend was observed with S-T-1.7, S-T-2.4, and S-T-3.5: they have higher nitrogen loadings than their diamine counterparts yet lead to a noticeably smaller enhancement in adsorption capacity at an equivalent $-\Delta H_{\text{Ads}}$ (**Figure 3.5a and c, Figure 3.6a and c, Figure 3.7**). A comparison of S-T-2.4, S-D-2.5, and S-P-2.6 highlights the effects of increasing amine moieties at similar amine loadings, and indicates that at this level of coverage, CO₂ uptake reaches 0.78 mmol/g, 1.12 mmol/g, and 1.29 mmol/g, respectively.

The sorbents with high loading of primary, diamine, and triamine agree with Zelenak et al.⁸⁹ work. Primary and diamine samples having similar heats of adsorption along a wider range of CO₂ loadings. In their work triamine grafted at 3.6 mmol/g presented an overall lower heat of adsorption than both primary and diamine. However, in their case the S_{BET} and pore volume was much smaller than presented samples in this study. For materials with lower loading, Yoo et al.²¹² presented calorimetric data of diamine and triamine grafted at 0.85 mmol/g and 1.2 mmol/g of amine, showing similar heats of adsorption starting at 80 kJ/mol and following a decreasing profile similar to the one presented in **Figure 3.7**.

These results demonstrate that a higher amine efficiency is obtained from only primary amine-grafted samples compared to a mixture of secondary and primary amine moieties. Triamine, which contains two secondary amines per each primary amine, leads to a less efficient utilisation of amine moieties for chemisorption, even at low amine loadings. This has been attributed to steric hindrances that reduce the total number of accessible secondary amines^{69,80}. There is also a limitation on the intramolecular interaction of adjacent amines, which hampers the realisation of a 2:1 stoichiometric ratio of amine to CO₂ for

carbamate formation under dry conditions^{77,211,213}. Additionally, recent studies by Cendak et al.²¹⁴ confirmed the presence of isolated CO₂ species in APTES modified SBA-15 with controlled amine spacing creating isolated APTES branches. Their study combined with the higher amine efficiency observed by APTES in this work indicates that secondary amines may similarly enhance the adsorption of CO₂, evidenced by the low heat of adsorption observed in diamine and triamine.

For Chemisorption of CO₂ by diamine and triamine branches, there are many possible amine-amine and amine-adsorbent interactions, shown most recently through NMR spectroscopy by Szego et al.²¹⁵. However, it has been reported by Hahn et al.⁹⁰ and Mafra et al.⁹¹ that there is a tendency for a secondary amine to be protonated and stabilised by surface hydrogens (from hydroxyl groups), in place of chemisorbed CO₂ (as carbamate or carbamic acid), thus lowering the available amine sites for CO₂ adsorption. Additionally, triamine organ silanes have the longest molecular length, and Hahn et al.⁹⁰ and Zelenak et al.⁸⁹ proposed that a primary amine moiety and a secondary amine moiety can interact to adsorb CO₂ along one amine branch. This is more likely to occur in the absence of lateral amines and at low grafted amine coverage. This leaves the lower secondary amine unpaired, and prone to be stabilised by surface bonds, making it unavailable for CO₂ chemisorption at the pressures studied. Results here confirm hypothesis by Zelenak et al.⁸⁹, which attributes a smaller contribution from chemisorption as the molecular length of the organ silane increases, and a larger influence of physisorption in the adsorption of CO₂ as pressure increases.

Figures 3.4c, 3.5c, and 3.6c present the CO₂ adsorption isotherms of APTES, AEAPT, and TAEPT at 40 °C. Although amines primarily interact with CO₂ via chemisorption, a mechanism that is assisted by higher operating temperatures, a decrease in total capacity was observed as the adsorption temperature increased from 25 to 40 °C. This observation is in agreement with studies by Sayari and co-workers^{209,213} on primary- and triamine-functionalised MCM-41 from 25 to 55 °C. Investigating the decrease in capacity observed for primary amine shows a 0.28 mmol/g decrease in S-P-1.7 compared to 0.19 and 0.21

mmol/g for S-P-1.4 and S-P-2.6, respectively. There is also a clear shift from a flatter slope in initial CO₂ uptake towards a much steeper rise as amine loading increases. The larger decrease in adsorption capacity by S-P-1.7 indicates the availability of more physisorption sites compared to S-P-2.6, due to the higher dependency of adsorption on temperature. Since S-P-1.4 did not demonstrate an equivalent decrease in capacity, these physisorption sites in S-P-1.7 are likely caused by polarised chemisorbed species acting as physisorption sites, as has been previously suggested by Mafra et al.^{29,91} This may additionally be attributed to the distribution of active amine sites along the length of the adsorbent's cylindrical pores, a higher amine loading closer to the adsorbent surface hinders the diffusion of CO₂ into the pores, leading to a larger drop in capacity at higher temperatures^{216,217}. To further explore this hypothesis, adsorption data measured by TGA for CO₂, across the varying loadings of primary amine grafted SBA-15, is presented in **Figure A.4**. There is initial faster adsorption by S-P-1.7, indicating more accessible amine sites for CO₂-amine interactions compared to S-P-1.4 and S-P-2.6. There may be additional factors involved, but results presented here show the larger role physisorption has in S-P-1.7 compared to S-P-2.6, and is supported by the similarities in the heat of adsorption for both samples at CO₂ loadings above 0.4 mmol/g, as presented in **Figure 3.7**.

Figures 3.4c, 3.5c, and 3.6c present the CO₂ adsorption isotherms of APTES, AEAPT, and TAEPT at 40 °C. Although amines primarily interact with CO₂ via chemisorption, a mechanism that is assisted by higher operating temperatures, a decrease in total capacity was observed as the adsorption temperature increased from 25 to 40 °C. This observation is in agreement with studies by Sayari and coworkers^{209,213} on primary- and triamine-functionalised MCM-41 from 25 to 55 °C. Investigating the decrease in capacity observed for primary amine shows a 0.28 mmol/g decrease in S-P-1.7 compared to 0.19 and 0.21 mmol/g for S-P-1.4 and S-P-2.3, respectively. There is also a clear shift from a flatter slope in initial CO₂ uptake towards a much steeper rise as amine loading increases. Higher temperatures, favoured by chemisorption, aid in the diffusion of CO₂ into the pores, implying that changes in all samples should be almost similar^{87,218}. The

difference in S-P-1.7 may be attributed to the distribution of active amine sites along the length of the adsorbent's cylindrical pores, a higher amine loading closer to the adsorbent surface hindering the diffusion of CO₂ into the pores, leading to a larger drop in capacity at higher temperatures^{216,217}. This phenomenon shows the larger role physisorption has in S-P-1.7 compared to S-P-2.6 and is supported by the similarities in the heat of adsorption for both samples as shown in **Figure 3.7**.

In the case of AEAPT, from 25 to 40 °C the adsorption capacity of both S-D-1.6 and S-D-2.5 at 100 kPa decreases by 0.17 mmol/g (26% and 16%, respectively). The largest drop in capacity of 0.40 mmol/g (a further 26%) is seen for S-D-2.8, the densest sample with the smallest pore volume (0.74 cm³/g). Comparable to S-P-1.7 ($V_p = 0.78$ cm³/g), this may be a consequence of diffusion effects from the longer AEAPT molecule, due to localised clustering of the organ silanes within the adsorbent pores. The CH₄ adsorption capacity and selectivity (separation factor) can highlight the effects of amine type and surface coverage on the performance of grafted adsorbents. It was found that in all samples, an increase in amine surface coverage caused a reduction in the total adsorbed CH₄, and the highest amine loading showed the largest decrease in CH₄ adsorption capacity. The decrease in adsorption capacity was dependent on the type of amine employed, with a minimum and maximum decrease (from raw SBA-15) of 11% for S-D-1.6, and 42% for S-D-2.8. The similarity in uptake can be attributed to the overall weak affinity of the adsorbent towards CH₄ molecules below 100 kPa. The individual contribution of porosity and intermolecular interactions can be scrutinised by correlating the available pore volume and silane surface coverage to changes in adsorbate uptake (**Figure A.5**). It is important to note that at lower silane loadings the overall effect on CH₄ adsorption is weak, especially at 40 °C; this can potentially lead to similar CH₄ uptake amongst some samples such as AEAPT samples presented in **Figure 3.5d** for S-D-1.6 (silane loading of 0.79 mmol/g) and S-D-2.5 (silane loading of 1.23 mmol/g) at 40 °C.

However, the evidently weak intermolecular forces at this temperature between diamine and CH₄ accentuate the different adsorption behaviour of each amine

type, with APTES demonstrating a smaller variation in uptake at 25 °C instead of 40 °C (**Figure 3.4b and d**). For triamine at 40 °C, the extent of reduction in CH₄ adsorption was limited to a minimum; all three samples adsorbed almost the same quantity of CH₄ of ~0.033 mmol/g, a 38% decrease from S-0 (**Figure 3.6d**).

At equivalent silane surface coverage, triamine and diamines exhibit a similar CH₄ uptake (**Figure A.6b**). This is not the case for primary amine, as its shorter molecular length leads to a higher uptake at a similar level of molecules/nm². Investigating the effect of pore volume, as presented in **Figure A.5a**, S-P-2.6 and S-T-3.5 with high amine functionalisation led to similar adsorption capacities, likely attributed to the pore blockage from the low pore volume of 0.63 and 0.66 cm³/g, respectively. At moderate coverage, S-P-1.7 ($V_p = 0.78$ cm³/g) achieved an uptake 18% higher than S-D-2.5 ($V_p = 0.81$ cm³/g) and 3.7% lower than S-T-2.4 ($V_p = 0.87$ cm³/g). The association of available effective surface area and CH₄ adsorption is especially pronounced in the higher coverage samples (S-P-2.6, S-D-2.8, and S-T-3.5) as can be seen in **Figure 3.4b, 3.5b, and 3.6b**, and in adsorption isotherms at 40 °C for APTES and AEAPT (**Figure 3.4d and 3.5d**). It is not clear if electrostatic interactions between CH₄ and primary and secondary amines play a part in the change in CH₄ adsorption due to different amine coverage. Further experiments should be carried out at higher pressures to better understand the role of amine grafting in CH₄ adsorption mechanism, whether it is a result of electrostatic forces between the amine groups and CH₄, a decrease in pore volume and effective surface area, or a combination of both.

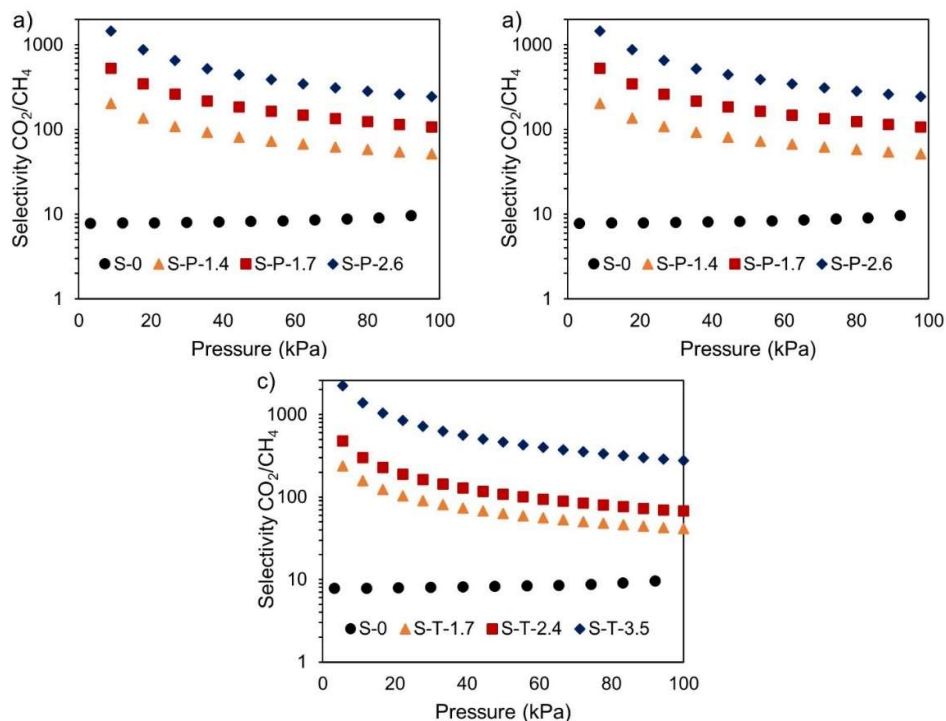


Figure 3.8 CO₂/CH₄ IAST selectivity (log scale) at 25 °C up to 100 kPa pressure of a 60:40 CH₄:CO₂ mixture for raw SBA-15 with (a) APTES, (b) AEAPT, and (c) TAEPT at different amine loadings.

Figure 3.8 presents the CO₂/CH₄ selectivity of all samples at 25 °C. All samples become more selective towards CO₂ as the amine quantity increases. At a CO₂ partial pressure of 40 kPa (**Figure 3.9**), the primary amine with the lowest loading (S-P-1.4) shows a higher selectivity (51) compared to S-D-1.6 (34) and S-T-1.7 (41), even though all have similar amine loadings. On the other hands, for the samples with the highest CO₂ uptake, S-P-2.6 had the lowest selectivity of 240, compared to 374 for S-D-2.5 and 276 for S-T-3.5.

Referring to **Figure 3.9**, there is a linear increase in selectivity as amine loading increases, which may indicate similar molecular interactions between CH₄ and the amine moieties. This interaction can be associated with a primary or secondary moiety, depending on the distribution of the organ silane branches and the accessibility of the CH₄ molecule to the amine moiety. This is seen by S-D-2.8, which is more linearly related to the APTES samples, indicating similar

primary amine interactions. While in comparison, S-T-3.5 is more linearly related to the remaining AEAPT and TAEPT materials, indicating a combined contribution of primary and secondary amine interactions with CH₄, coupled with likely steric influences. Simultaneously, accessible amines act as active sites for CO₂ adsorption, through both chemisorption and physisorption interactions. Thus, the linear relationship can be attributed to the same accessible amine moieties, influencing both CO₂ and CH₄ adsorption, with a much stronger effect on the former adsorbate.

At a higher temperature of 40 °C (**Figures A.6 and A.7**), the selectivity follows a similar order, and referring to APTES and TAEPT functionalised samples with high CO₂ adsorption capacities, the selectivity of S-P-1.7, S-P-2.6 and S-T-3.5 increase by almost equivalent magnitudes. Comparatively, AEAPT functionalised samples both showed a decrease in the selectivity, especially in S-D-2.8. At this temperature, S-P-1.4, S-D-1.6, and S-T-1.7 all have very similar selectivity values ranging from 31 to 41. The effect of temperature on the selectivity of higher-loaded samples can be a result of the lower quantity of CO₂ physisorption active sites in S-P-2.6 and S-T-3.5, in these materials, the temperature increase has a smaller effect on CO₂ adsorption, indicating a lower quantity of CO₂ adsorption by Van der Waals forces.. Additionally, at both temperatures, the effect of molecular interactions between amines and the octupole moment of CH₄ should be considered. Low to moderate loadings of APTES may indicate a higher degree of CH₄ adsorbate-amine interactions compared to AEAPT and TAEPT, even when pore volume contributions are considered, as discussed previously.

At very low CO₂ partial pressures, chemisorption is the dominant adsorption mechanism in all functionalised samples, but the selectivity remains a relevant parameter for the comparison of the extent of separation. At a pressure of 11 kPa of a 40:60 CO₂:CH₄ mixtures, the IAST selectivity of S-P-2.6, S-D-2.5, and S-T-3.5 are 1317, 2251, and 1390, respectively. The deviation in selectivity amongst these samples at this pressure follows the same trend as at 40 kPa CO₂ partial pressure, but with larger differences in selectivity that continue to rise as pressure

decreases below 5 kPa, coinciding with the initial high CO₂ uptake via chemisorption.

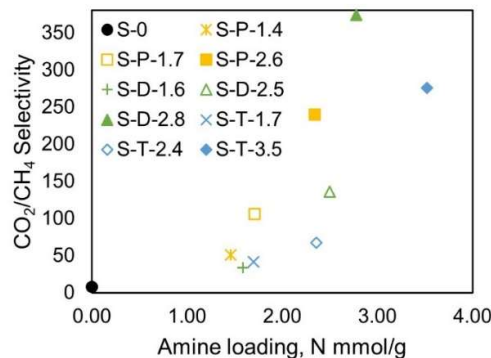


Figure 3.9 CO₂/CH₄ selectivity as a function of amine loading of samples at CO₂ partial pressure of 40 kPa and 25 °C.

The CO₂/CH₄ adsorption characteristics of prepared samples in this work, in comparison with other adsorbents in literature are provided in **Table A.2**. The low CH₄ adsorption capacity and high CO₂/CH₄ selectivity of presented samples can be considered superior to most benchmark adsorbents, even at low amine loadings of 1.4-1.7 mmol/g. Calgon BPL and Norit C carbon-based adsorbents were shown to be limited to a selectivity of ~3, with CH₄ capacities > 0.45 mmol/g²¹⁹. Zeolite 13x was shown to adsorb similar quantities of CH₄ to the carbon based adsorbents (~ 0.5 mmol/g), but has a larger molar selectivity of 13-15 due to the higher CO₂ (4.5 mmol/g)^{220,221}. MOFs, such as MIL-53 (Cr) and MOF-508b, have CH₄ capacities of 0.4-0.5 mmol/g, with CO₂ capacity of 1.2-1.6 mmol/g in equimolar CO₂/CH₄ breakthrough experiments at 100-200 kPa and 30°C^{222,223}. A more recent study by Golmakani et al.¹⁷ on novel polymeric adsorbents, showed slightly higher CH₄ adsorption of 0.12 mmol/g compared to the adsorbents presented here, with CO₂ adsorption capacity of 0.6 mmol/g. Higher CH₄ adsorption capacities result from the adsorbents presented here compared to low-moderate amine grafted SBA-15, which in this study show significantly lower CH₄ adsorption of ~0.05 – 0.06 mmol/g, at CO₂ adsorption capacities that range from 0.68 to 1.11 mmol/g. However, it should be noted that

the enhanced selectivity of amine functionalities imposes energy penalties of regeneration, which is what makes this study scrutinizing the correlation between amine loading and separation efficiency necessary to further advance the development of state-of-the-art adsorbents.

3.2.3 Isothermal versus non-isothermal operation

Isothermal and non-isothermal performance can provide valuable information on the regeneration efficiency for each amine type and surface loading. The presented data aims to support conclusions made from the calculated heat of adsorption, while comparing the efficacy of the prepared materials to desorb CO₂, either by temperature modulation or by CO₂ partial pressure modulation (using a purge gas). These results are the first step towards narrowing down the energy dependency of each amine type and loading for commercial pressure swing processes, following the pelletisation of the utilised SBA-15 powder. The desorbed quantity of CO₂ can confirm the conclusions made from the equilibrium adsorption data and the heats of adsorption. **Figure 3.10** presents the adsorption uptake per amine loading (molar quantity of adsorbed CO₂ per mmol of nitrogen per gram of adsorbent), under isothermal adsorption-desorption at 25 and 40 °C (**Figure 3.10a and c**), and non-isothermal conditions with adsorption carried out at 25 °C and desorption at 40 °C (**Figure 3.10b**), measured by TGA. S-P-2.6 has the highest adsorption efficiency as a function of amine quantity. However, referring to **Figure 3.11**, which summarises the molar fraction desorbed per molar fraction adsorbed (C_{Des}/C_{Ads}), it loses almost 46% of its adsorption capacity after the first cycle under atmospheric desorption at 25 °C. This can indicate that functionalisation to a maximum extent is not always beneficial at these operating conditions. This is highlighted by the isothermal cycle at 40 °C, in which desorbed quantities are equivalent to the 25 °C isothermal cycle for all samples, except S-P-1.4 and S-T-2.4. This loss of capacity makes S-P-1.4, S-P-1.7 and S-D-2.5 comparable alternatives under isothermal operating conditions; they provide a working capacity and amine efficiency equivalent to S-P-2.6 and S-D-2.8 while outperforming S-T-2.4 and S-T-3.5. Under a higher desorption temperature of 40

°C the samples with higher loading, specifically S-P-2.6, S-P-1.7 and S-D-2.8, achieve the highest adsorption per amine efficiency by a large margin. The difference between S-P-2.6 and S-P-1.7 is small, suggesting that amine efficiency does not increase proportionally with amine loaded, and moderate functionalities may provide better performance under cyclic low-temperature operation.

According to **Figure 3.4a**, under equilibrium adsorption at 100 kPa and 25°C, S-P-1.4 achieved a capture capacity of 0.74 mmol/g compared to 0.45 mmol/g for S-0. The increase in adsorption capacity is a result of the incorporation of amines which enhance adsorption of CO₂ primarily by chemisorption. However, in **Figure 3.11**, under isothermal desorption, the enhancement in capacity is still significant, as only a 0.15 mmol/g loss in capacity is measured at 25°C compared to the 0.29 mmol/g enhancement in total adsorption for S-P-1.4. This quality is shared by all the samples with a lower amine loading, demonstrating a lower heat of adsorption. The results from isothermal desorption at 25 °C under nitrogen flow support studies by Mafra et al.^{29,91}. They concluded that under certain conditions less stable carbamic acid species are formed and stabilised by surface hydrogens. These formed entities are more readily desorbed under milder conditions. This may imply that a right balance of amine functionalisation for effective isothermal desorption and cage-like internal morphology for a pressure dependence of adsorption-desorption cycles would provide the ideal adsorbent formulations for PSA and pressure vacuum swing adsorption (PVSA) applications.

To further progress the work towards commercial pressure swing application, the future research should focus on the functionalisation of palletised SBA-15 based on the outcomes of this work, in order to enable fixed bed breakthrough measurement using binary gas mixtures, and under isothermal/non-isothermal desorption conditions.

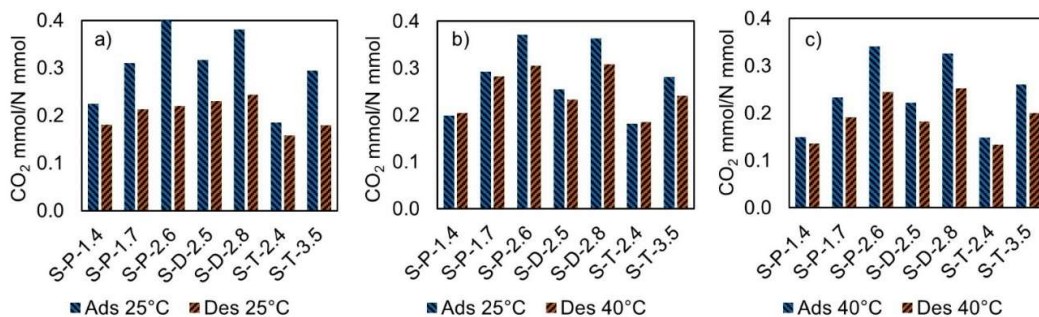


Figure 3.10 CO₂ molar capacity per amine molar loading at (a) isothermal adsorption-desorption cycle of 25 °C, (b) non-isothermal adsorption-desorption from 25 °C to 40 °C, and (c) isothermal adsorption-desorption cycle of 40 °C.

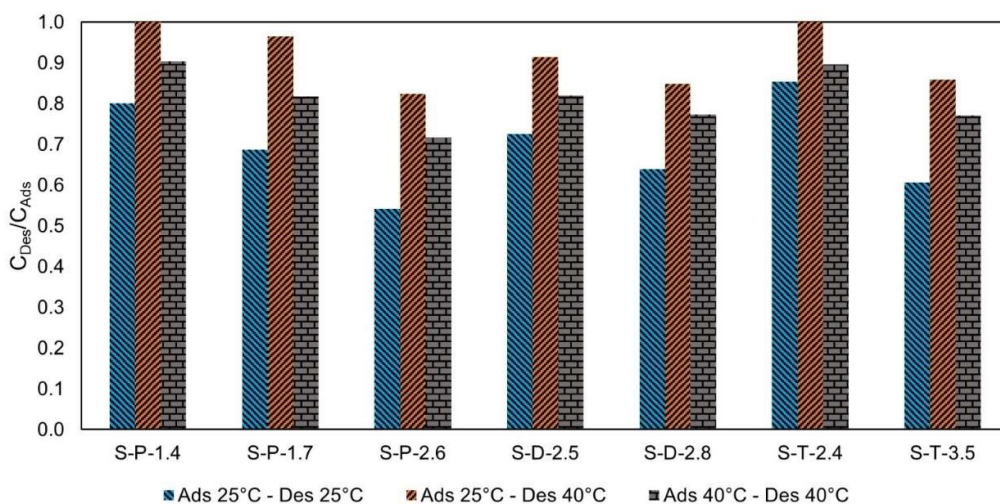


Figure 3.11 Ratios of desorbed CO₂ per total adsorbed CO₂ (C_{Des}/C_{Ads}) under isothermal and non-isothermal conditions.

In comparison with typical liquid absorbers in amine scrubbing, such as 30wt% MEA and DEA ²²⁴, all the grafted samples in this work presented a lower equilibrium capacity. However, MEA 30 wt% was reported to have a heat of adsorption of ~89 kJ/mol, which is higher compared to some of the samples presented here. For example, S-D-2.8's calculated heat of adsorption corresponding to CO₂ loadings above 1.0 mmol/g was ~45 kJ/mol. Similarly, isothermal desorption studies of low-moderate amine loaded SBA-15, such as S-P-1.4 or S-D-2.5, showed a very efficient desorption of CO₂, reported to be

between 70 to 90% when purged. Results here summarise the advantages of using sorbents for carbon capture, but a full techno-economic analysis is required for more practical comparison, which draws upon fixed-bed studies of amine functionalised sorbents

3.3 Conclusions

Different amine types and loadings lead to distinct trends in the adsorption of CO₂ and CH₄, providing key insights on the interactions between the adsorbent surface and adsorbates. The elucidation of the resulting interactions provides necessary information on process and adsorbent design considerations for amine incorporated adsorbents in CO₂/CH₄ separations. In this study, primary amine, diamine, and triamine were grafted on SBA-15 and characterised through structural and chemical morphology by TGA, FTIR, EA, and nitrogen adsorption measurements. It was found that low amine loadings enhanced the adsorption capacity of CO₂ and its selectivity in CO₂/CH₄ mixtures, while minimising the heat of adsorption associated with chemisorption. Diamine-grafted samples with a moderate surface coverage maintained a low CH₄ adsorption and demonstrated a balance of capture capacity and heat of adsorption that is comparable to high-coverage primary amines. In a similar manner, moderately-grafted primary amine desorbed CO₂ at an efficiency equivalent to densely-grafted primary amines. The variation in amine loading and resulting performance implies that optimal grafting quantities can potentially exist below the maximum surface coverage of an adsorbent base, showing superior uptake and selectivity to CO₂ from CH₄ at atmospheric conditions. They show promise as materials for low pressure processes such as vacuum swing adsorption (VSA). The interaction of CH₄ with amines can be concluded as negligible at around 25-40 °C and 100 kPa, but further studies at higher pressures should be employed to confirm the mode of electrostatic interactions dictating CH₄ adsorption for different amine concentrations. Furthermore, in conventional commercial biogas upgrading by pressure swing processes, the adsorption step occurs at high pressure (>5 bar) to maximise the adsorbed quantity of CO₂. Therefore, exploring the effect of

different amines and their functionalities on adsorption at elevated pressure is essential to further advance adsorbents for biogas upgrading, across a wider range of operating processes and conditions.

The presented data indicates that adsorbents with lower amine loadings can balance the distribution of adsorption mechanisms between chemisorption and physisorption, providing an enhancement in adsorbents for the separation of CO₂/CH₄ mixtures while minimising implications on adsorbent regeneration for cyclic applications. Moreover, although moderately amine-grafted sorbents can benefit from higher kinetics and lower heat of adsorption, compared to those that are grafted to maximum loading, their adsorption capacity is lower. Therefore, their cyclic performance for biogas upgrading needs to be further evaluated and optimised using dynamic PSA simulations.

Nomenclature

Parameter	Description	Unit
b	Toth isotherm parameter	1/kPa
b_{μ}	Sips isotherm parameter	1/kPa
C_{Des}	Desorption capacity	mmol/g
C_{ads}	Adsorption capacity	mmol/g
D_p	Pore diameter	nm
n	Sips isotherm exponent	-
n_s	Toth isotherm parameter	mmol/g
$n_{\mu s}$	Sips isotherm parameter	mmol/g
P	Pressure	kPa
Q	Molar uptake	mmol/g
R	Ideal gas constant	J/mol-K
$\hat{S}$	Selectivity	-
S_{BET}	BET surface area	m ² /g
T	Temperature	K
t	Toth isotherm parameter	-
V_p	Pore volume	cm ³ /g
ΔH_{Ads}	Isosteric heat of adsorption	J/mol

4 CONTRIBUTION OF INDIVIDUAL AMINE MOIETIES TO CO₂/CH₄ SEPARATIONS

Probing CH₄ adsorption by primary, secondary, and tertiary amines, and its contribution to CO₂/CH₄ separation efficiency

ABSTRACT

Sustainable energy sources such as biogas play an essential role in the path towards net-zero carbon emissions. In designing amine-incorporated adsorbents for biogas upgrading, it is essential to understand the individual effects that amine moieties have on the separation of CO₂/CH₄ mixtures. In this work primary, secondary and tertiary amines are moderately grafted on SBA-15 to scrutinise factors affecting adsorption of CO₂ and CH₄ and assess their suitability for biogas separations. The materials were characterised by thermogravimetric and elemental analysis, and their performance measured by volumetric and gravimetric gas adsorption. An amine loading of 1.6-1.7 mmol/g in secondary and tertiary amines showed an equivalent CH₄ uptake of <0.04 mmol/g at 25°C, while primary amines adsorbed up to 0.05 mmol/g, indicating stronger interaction forces with CH₄. In terms of selectivity, primary and secondary amines grafted at 1.3-1.4 mmol/g had similar values, unaffected by amine type and temperature. At an amine loading of ~1.7 mmol/g, an increase in temperature from 25 to 40°C at a CO₂ partial pressure of 40 kPa resulted in a decrease in the selectivity of primary amines from 33 to 29, with no change in the selectivity of secondary amine. In isothermal adsorption-desorption conditions, moderately grafted secondary amines have an equal working capacity to primary amines, making them viable components for CO₂/CH₄ separations.

4.1 Introduction

Atmospheric CO₂ concentrations continue to rise yearly with the National Oceanic and Atmospheric Administration reporting an annual median of 414 ppm in 2020^{2,225–227}. The increase in atmospheric concentrations of CO₂ from post-industrial

anthropogenic emissions has caused reported global warming of $\sim 1.0^{\circ}\text{C}$ ³. There is thus a clear need to decrease greenhouse gas (GHG) emissions to avoid irreversible environmental damage. Sustainable energy sources such as biogas play an essential role in the path towards net-zero carbon emissions. As a result, there has been an increasing interest in utilising cyclic processes that employ Pressure Swing Adsorption (PSA), or Vacuum Swing Adsorption (VSA) for biogas separations. Compared with temperature swing sorption processes, pressure swing cycle processes benefit from lowered required energy demand, if the utilised adsorbent can offer maximised CH_4 recovery and minimised regeneration energy^{228–230}.

In the development of novel adsorbents for carbon capture, the incorporation of amines onto a variety of adsorbents has been shown to enhance CO_2 capacity and selectivity by the chemisorption of CO_2 for process conditions up to 100°C and 10 bar^{20,92,231}. However, many of these applications concentrate mainly on CO_2 adsorption from flue gases in the power and industrial sectors^{20,232,233}. This is because the chemisorption of CO_2 is favoured by partial pressures below 20 kPa and higher temperatures from $60\text{--}100^{\circ}\text{C}$, conditions that make elevated amine loadings on adsorbent bases more effective for flue gas treatment^{20,87}. With respect to CO_2/CH_4 and biogas mixtures, amines have the potential to offer exceptional selectivity of CO_2/CH_4 , but to the best of our knowledge, only a limited number of studies exploring the direct relationship between amine functionalisation and separation efficiency are available^{61,92,95}.

Garcia et al.⁹⁵ studied the separation of CO_2/CH_4 on amino-grafted silicas, representing a non-interacting adsorbent base. However, their work was limited to high-density functionalisation, and mainly focused on the adsorption behaviour resulting from different synthesis routes of mesoporous silica. Belmabkhout et al.⁶³ explored the selectivity of triamine grafted at a high loading of 7.9 mmol/gram on MCM-41 through breakthrough experiments. They found that this material achieved an uptake of 1.89 mmol/g with a fast-initial breakthrough of CH_4 in seconds, a selectivity comparable with commercial adsorbents such as Zeolite 5A and BPL activated carbon. Despite this, their study was limited to a $\text{CO}_2:\text{CH}_4$

mixture of 1:99 at 100 kPa and mainly focused on only one amine reagent (triamine) targeting maximum adsorption enhancement. In a more recent study, Mafra et al.⁹² investigated the adsorption of a binary mixture of CO₂/CH₄ across a range of pressures on SBA-15 grafted with a high loading of primary, secondary, and diamines and quantified the selectivity of each amine type. They found that secondary amine provided the highest selectivity at high surface coverage compared to primary amine, but it was outperformed by primary amines due to the loss in capacity under isothermal desorption conditions of 10 or 100 kPa. They concluded that at the high loadings studied, primary amines provided an enhancement in capacity and selectivity that can be potentially applied for PSA/VSA processes. Lourenco et al.⁹⁶ prepared phenylene-silicas (Ph-PMO) functionalised by various primary amine groups through two methods, including conventional grafting or by strong acid-promoted chemical bonding. They studied the CO₂ and CH₄ interactions by density functional theory (DFT) and found that -CH₂NH₂ functionalities on Ph-PMO provide the optimal enhancement of CO₂ uptake without affecting CH₄ adsorption. Although insightful, the work was limited to primary amine groups, while probing the interactions of different amines is yet to be explored.

In terms of functional groups and their effect on CO₂ adsorption, Ko et al.²³⁴ compared the adsorption and desorption behaviour of CO₂ in primary-, secondary-, and tertiary-amine-functionalised SBA-15 at 25°C, and found that adsorption capacity decreased in the order of Primary>Secondary>Tertiary while desorption followed the opposite trend. In their study, the grafted density was ~3 mmol/g, indicating full surface coverage. Additionally, they used the quantity of CO₂ adsorbed per gram of amine grafted to compare the different amine types, which is representative but does not account for amine spacing and diffusion effects on adsorption efficiency. Moreover, the research was solely based on a pure stream of CO₂, and the effect of adsorption by additional molecules in a binary gas mixture is yet to be explored.

Studies up to this point on the CO₂/CH₄ capture efficiency of amines have shown their potential as adsorbent components that enhance CO₂ capacity and

selectivity. However, they have either concentrated on only primary amines, or on densely grafting different amine types. This work aims to build on this by targeting the individual contribution of each amine moiety or organ silane branch to CH₄ and CO₂ adsorption performance in CO₂/CH₄ mixtures. This is accomplished by grafting primary, secondary, and tertiary amines at different loadings on SBA-15 and analysing the effects on CO₂/CH₄ selectivity, CH₄ adsorption, isosteric heats of adsorption, and the regeneration energy implications of each amine type. Similar grafting loadings have been targeted for an equivalent comparison of the underlying CO₂ adsorption mechanisms and the resulting CH₄ interactions with different amine types to narrow down amine/CH₄-specific influences.

4.2 Material and methods

4.2.1 Materials

The different chemical reagents (3-aminopropyl)triethoxysilane (APTES), dimethylaminopropyltrimethoxysilane (DMAPT), toluene (99.8%), and methanol (HPLC grade) were purchased from Sigma-Aldrich, UK. Additionally, (N-butylamino)propyl-trimethoxysilane (BAPT) was purchased from fluorochem. SBA-15 powder was purchased from XFNANO. The methane, nitrogen, and carbon dioxide (99.99% purity) gases were purchased from BOC, UK.

4.2.2 Material synthesis

The functionalisation of SBA-15 followed a dry grafting procedure under inert reflux. First, 1 g of SBA-15 powder was dried in a flask under vacuum (40 mbar) at 110°C for 1 hour. The flask and reflux apparatus were then purged with nitrogen, and 80 mL of toluene was added to the flask followed by the required quantity of amine reagents illustrated in **Fig. 4.1** and **Table 4-1**. The system was heated to 70°C and left under reflux for 18 h. The grafted SBA-15 powder was recovered by filtering under vacuum suction and washed with ample toluene and methanol. Finally, the samples were left to dry in air at room temperature for 24 h. The samples were labelled as S-x-y with x as type of amine (P-Primary, Sec-

Secondary, Te-Tertiary), and γ the amine loading as measured by elemental analysis (EA), **Table 4-1**.

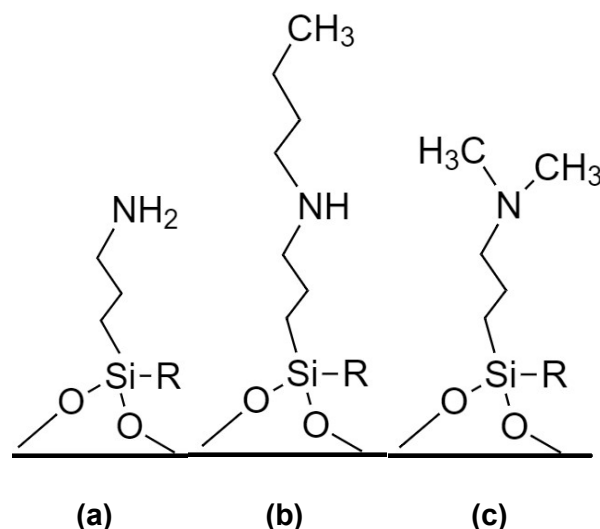


Figure 4.1 Silica surface-grafted organo-silanes. R represents the methoxy or ethoxy or hydroxyl group in bidentate grafting. For tridentate grafting, all three Silane branches are bonded to the surface of SBA-15 and R represents surface Si-O-Si bonds. (a) APTES, (b) BAPT, and (c) DMAPT.

4.2.3 Material characterisation

Thermogravimetric analysis (TGA 8000, PerkinElmer) and C and N elemental analysis (vario EL III, Elementar) were used to determine the grafted amine loading on SBA-15 samples. In the case of TGA, 8-10 mg of each material was exposed to nitrogen at 60 mL/min and heated at a rate of 20°C/min from 30°C to 120°C, held for 10 minutes, and then increased to 800°C under the same heating rate. At 800°C the gas was switched to air and held for an extra 5 min. The weight percent of C and N grafted on SBA-15 was measured by Elemental analysis by thermal combustion analysis using a 10 mg sample.

Structural properties of the samples were estimated from nitrogen adsorption isotherms and are summarised in **Table 4-1**. Nitrogen adsorption-desorption isotherms at -196°C were measured using a 3P Meso 222 sorption analyser (3P Instruments). Each sample (0.2-0.3 g) was degassed by heating it under vacuum

for 2 h at 90°C. The Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05 to 0.2 was used to calculate the effective surface area ⁸⁷. The Barrett-Joyner-Halenda (BJH) method was used to calculate the pore volume of each sample at $p/p^0 = 0.95$ ¹⁵⁴. The Broekhoff-de Boer (BdB) method simplified by the Frenkel-Halsey-Hill (FHH) approximation was used for pore size distribution (PSD) estimations ²⁰¹.

4.2.4 Adsorption measurements

Gravimetric CO₂ adsorption and desorption measurements at 25 and 40°C were taken by TGA (TGA 8000, Perkin Elmer) to measure the dynamic uptake of materials. Each sample (8-12 mg) was degassed at 110°C for 30 min by a 60 mL/min flow of nitrogen and then cooled to 25°C or 40°C, depending on the condition required. Upon stabilisation of the temperature, the feed gas was switched to CO₂ at 60 mL/min for 25 min. For the desorption step, the gas was switched to nitrogen at 60 mL/min and the temperature was maintained at 25 or 40°C for 30 min. For measurements of adsorption at 25°C and desorption at 40°C, the temperature was increased to 40°C at a rate of 15°C/min and held for 30 min.

CO₂ and CH₄ volumetric adsorption measurements for equilibrium data were carried out using the 3P Meso 222 sorption analyser. Each sample (0.25-0.3 g) was degassed under the same procedure previously described for nitrogen adsorption. The sample tube was submerged in a liquid bath (3P Instruments), at a temperature of 25 or 40°C. A modified form of the two-site Toth isotherm model was applied to fit CO₂ gas adsorption isotherms ²⁰⁹, Eq. (4-1), and the Henry model was used for CH₄ due to the linearity of the adsorption profiles ^{235,236}, Eq. (4-2): The individual isotherm parameters for each sample and the R squared representing the accuracy of the regression models fitted to experimental data is presented in **Appendix C**.

$$q = \left[\frac{n_s b_1 P}{(1 + (b_1 P)^{t_1})^{1/t_1}} \right] + \left[\frac{n_{s2} b_2 P}{(1 + (b_2 P)^{t_2})^{1/t_2}} \right] \quad (4-1)$$

$$q = KP \quad (4-2)$$

where n_s , b , and t are the Toth parameters with a subscript to distinguish each adsorption site. The variable K represents the Henry constant. q and P are the molar uptake and pressure.

The isosteric heat of adsorption was calculated using the measured isotherms at 25 or 40°C and based on the Clausius Clapeyron equation²³⁷:

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{Ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4-3)$$

The isosteric heat of adsorption is represented by H_{Ads} , T_1 and T_2 are the isotherm temperatures of the relative pressures of P_1 and P_2 , and R is the universal gas constant.

4.2.5 Density functional theory (DFT) modelling

Computational modelling was performed using the NWChem software²³⁸ and employed the B3LYP hybrid functional^{239–241} with basis set 6-31G²⁴². The interaction energies were calculated from a final structure prepared by first imposing a single CH₄ molecule at a ~1 Å distance from an amine or methyl group, and then optimising the geometry.

4.3 Results and discussion

4.3.1 Physiochemical properties

The BET surface area, pore volume, and maximum encountered pore size of samples are summarised in **Table 4-1**. Nitrogen adsorption at -196°C of raw SBA-15 and functionalised samples resulted in a type IV isotherm associated with mesoporous silicas such as SBA-15 and MCM-41^{205,210} (**Fig. 4.2**). The PSD maximum confirms the continued mesoporosity of SBA-15 post-functionalisation with a narrow variation in the measured values, displaying a range of 5.6 to 7.0 nm.

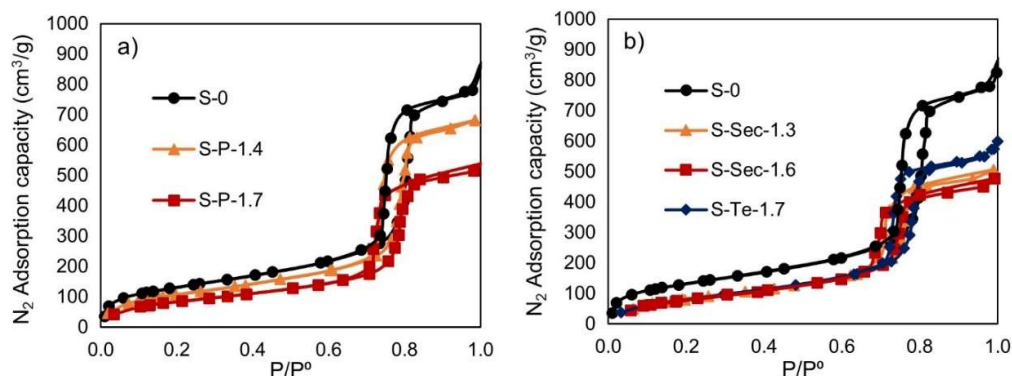


Figure 4.2 Nitrogen adsorption-desorption isotherm at -196°C for raw and (a) APTES, and (b) BAPT and DMAPT functionalised SBA-15.

Table 4-1 Physical and chemical properties of raw and functionalised SBA-15.

Sample	Reagent type	Amine type	Reagent Added (mmol)	Amine Loading (mmol/g)		S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)	Silane Molecules/ $\text{nm}^2 \pm$
				TGA – Tridentate*	Elemental				
S-0	-	-	-	-	-	490	1.2	7.0	-
S-P-1.4	APTES	Primary	2.0	1.49	1.45	406	1.04	6.4	1.79
S-P-1.7	APTES	Primary	4.0	1.78	1.71	308	0.78	6.3	2.10
S-Sec-1.3	BAPT	Secondary	2.0	1.31	1.32	316	0.75	5.8	1.62
S-Sec-1.6	BAPT	Secondary	4.0	1.56	1.56	302	0.69	5.6	1.92
S-Te-1.7	DMAPT	Tertiary	2.0	1.68	1.72	326	0.85	6.3	2.11

‡ Amine coverage calculated from the surface area of S-0 and the total amine loading

* Amine loading for tridentate surface bonding from TGA

Amino organo-silanes can bond with the surface by forming bidentate or tridentate bonds (**Fig. 4.1**)^{71,208}. From TGA and EA measurements, APTES, BAPT, and DMAPT are more prone to form tridentate bonds under the synthesis conditions used here, as presented in **Table 4-1**. For all samples, the grafted loadings and surface coverage are in-line with previous studies employing similar materials and grafting conditions^{76,88,92,243}. The surface coverage of silane molecules per nm^2 was calculated using the effective surface area of raw SBA-15 and the silane loading of each sample.

Although S-P-1.4, S-P-1.7, and S-Te-1.7 have a higher organo-silane loading compared to S-Sec-1.3, and S-Sec-1.6, a smaller effect on pore volume and specific surface area was observed. The occupation of more pore space by similar loadings in the secondary amines is a result of the difference in molecular length between amine types. The overall molecular length was measured using Avogadro (V1.2) based on a Universal Force Field (UFF) geometry optimisation from the base silica to the nitrogen or carbon atom at the end of the molecule. For BAPT, the distance was around 0.89 nm, while it was 0.54 and 0.55 nm for APTES and DMAPT, respectively. Consequently, BAPT occupies more open pore space for similar nitrogen loadings. The inherent structure of BAPT limited the achievable grafted loading to a maximum of 1.56 mmol/g, compared to 2.6 mmol/g for APTES, as previously reported ²⁴⁴.

4.3.2 Adsorption performance

The adsorption isotherms measured for CO₂ and CH₄ at 25 and 40°C are presented in **Fig. 4.3**. The change in the CH₄ adsorption profile of the different functionalities provides a comparative analysis of the effects of porosity and amine type on adsorbent performance in CO₂:CH₄ mixtures (**Fig. 4.3b and d**). A clear decrease in CH₄ uptake is seen as amine surface loading increases. However, the extent of the reduction depended on amine types. To scrutinise the reason for these differences, the CH₄ capacity at 25°C and 100 kPa of all the materials is correlated with the pore volume and silane surface coverage and is presented in **Fig. 4.4**. Referring to **Fig. 4.4a and b**, the adsorption capacity of primary amines at similar surface coverage deviated from the rest of the samples. In primary amine samples, the increase in silane functionalisation from raw SBA-15 did not decrease CH₄ adsorption to the same degree as secondary and tertiary amines. Although, at a higher temperature of 40°C (**Fig. 4.4b**), the differences between the primary and secondary amines are less pronounced, due to the lower overall uptake from weak interactions between the adsorbent/amines and CH₄. The differences in the adsorption of CH₄ by APTES could be attributed to the shorter overall molecular length which would create more pore space under

similar loadings. To further scrutinise the parameters affecting CH₄ adsorption, the CH₄ uptake at 100 kPa correlated with each sample's pore volume at 25 and 40°C is presented in **Fig. 4.4c and d**. From the scattered distribution of CH₄ uptake in **Fig. 4.4c**, there is no definite effect caused by only pore volume at these conditions (100 kPa and 25°C). The pore volume at similar loadings is in the order of S-Te-1.7>S-P-1.7>S-Sec-1.6, but the quantity of adsorbed CH₄ is highest for S-P-1.7 and lowest for S-Sec-1.6.

Similarly, within the same amine types, there is a greater decrease in CH₄ uptake when amine loading increases in secondary amines compared to primary amines. From S-Sec-1.3 to S-Sec-1.6, the pore volume decreased by 0.06 cm³/g, while from S-P-1.4 to S-P-1.7 it decreased by 0.26 cm³/g. The small volume change in BAPT resulted in a decrease in CH₄ uptake by 37% in S-Sec-1.3 and by 47% in S-Sec-1.6. For APTES, despite a larger variation in pore volume observed from S-P-1.4 to S-P-1.7, the difference in CH₄ uptake was negligible. At this temperature, the small change in CH₄ uptakes may indicate that methane has a higher interaction with APTES moieties, compared to BAPT and DMAPT.

For adsorption at 40°C, an imposed linear average can be drawn amongst all samples, indicating that a relationship exists between the adsorbed CH₄ and the pore volume (**Fig. 4.4d**). Higher adsorption temperatures affect physisorbed molecules following Le Chatelier's principle, by shifting the equilibrium away from the adsorbent surface and towards the gas phase. This is partially due to an increase in the internal energy of adsorbate molecules at higher temperature that weakens electrostatic interaction with the adsorbent. CH₄ does not contain a quadrupole moment, but there is a surface interaction between adsorbate and adsorbent due its octupole moment. This makes CH₄ a weakly adsorbing molecule, but the changes in the adsorption profile with temperature amongst different amine reagents can allow scrutiny of the intermolecular interactions between amine and CH₄. For APTES, the increase in temperature resulted in a decrease in the uptake of S-P-1.7 from S-0 by 47%. This reduction is considerably higher compared to S-sec-1.3 and S-sec-1.6, decreasing 15% and

33%, respectively. The effect on CH₄ uptake at 40°C between the functionalised and raw SBA-15 is thus weaker compared to 25°C. The higher dependency on temperature of CH₄ uptake by APTES may indicate a stronger interaction between CH₄ and primary amine moieties compared to secondary amines. This is facilitated by the accessibility of CH₄ to surface amine moieties in APTES due to its location at the tip of the organ silane branch instead of in the middle as is the case with BAPT. It's important to note that at the lowest APTES loading (S-P-1.4) the change of temperature resulted in the same uptake as S-Sec-1.3. This is likely a result of the large pore volume of S-P-1.4, and any possible changes to electrostatic forces affecting CH₄ adsorption are less distinguishable.

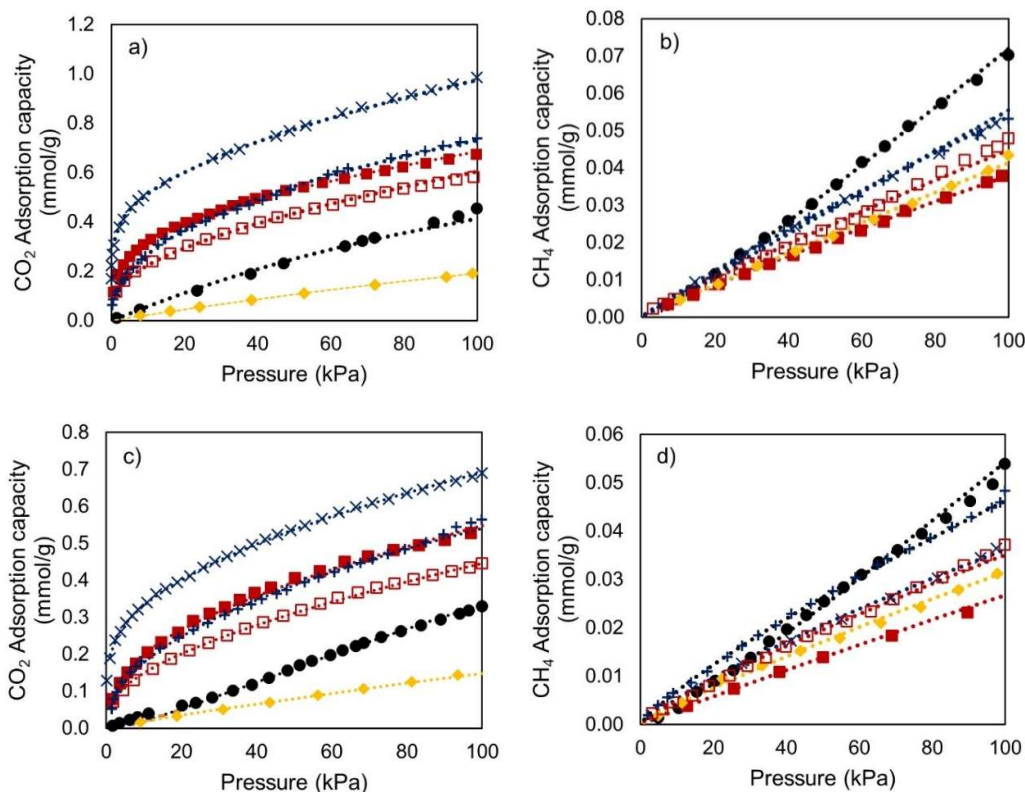


Figure 4.3 Adsorption isotherms of functionalised materials for (a) CO₂ and (b) CH₄ at 25°C, and (c) CO₂ and (d) CH₄ at 40°C. *The lines represent the model fit and the following markers represent the experimental data: (●) S-0, (+) S-P-1.4, (x) S-P-1.7, (□) S-Sec-1.3, (■) S-Sec-1.6, (◆) S-Te-1.7*

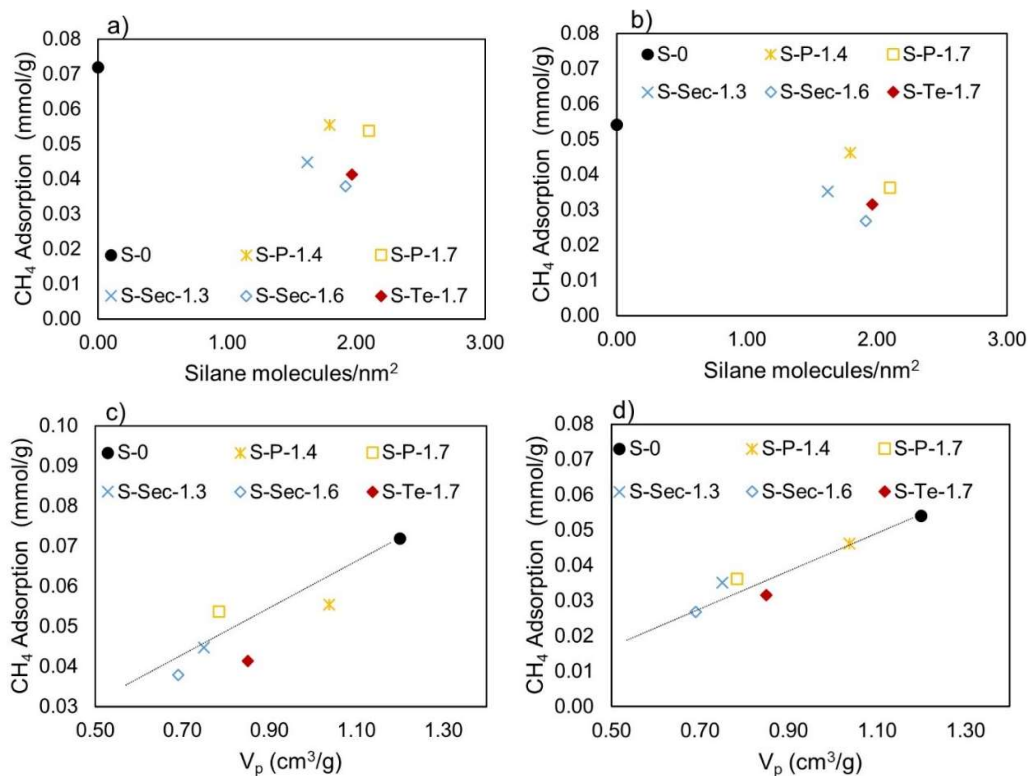


Figure 4.4 Relationship between CH_4 equilibrium capacity at 100 kPa with (a) silane surface coverage at 25°C and (b) silane surface coverage at 40°C, and with (c) pore volume at 25°C and (d) pore volume at 40°C. (●) S-0, (✱) S-P-1.4, (□) S-P-1.7, (x) S-Sec-1.3, (◇) S-Sec-1.6, (◆) S-Te-1.7

The interactions of methane are primarily a result of induced dipole effects or London dispersion forces, but due to the non-polar nature of methane, uncertainties can arise as to the exact extent of the molecular interactions ²⁴⁵. In response, DFT calculations were performed to assess the possible interaction energies that may result. This was accomplished by imposing a single CH_4 molecule onto the amine and methyl moieties of APTES and BAPT organ silanes, and then relaxing the structure. The interaction energy (ΔE_{int}) and optimised structures studied are presented in **Fig. 4.5**. The insertion of the CH_4 molecule closer to the amine moieties in both organ silanes shows almost equivalent interaction energies. However, considering the molecular length of BAPT at equivalent loadings of APTES, a larger percentage of CH_4 may be interacting with the methyl group at the end of the BAPT molecule, which results in smaller

interaction energies, as is presented in **Fig. 4.5c**. This may explain the differences in CH₄ uptake seen; however, in our studies the surface of SBA-15 was not considered, and neither was the influence of adjacent amine branches.

These findings are in agreement with a recent study by Lourenco et al.⁹⁶, performing DFT analysis on the interaction energy of CH₄ with primary amines grafted on Ph-PMO. They found noticeable changes do result in the degree of interactions based on the type of amine. Further studies scrutinising various shapes, interactions, and surface contributions will be the subject of future work.

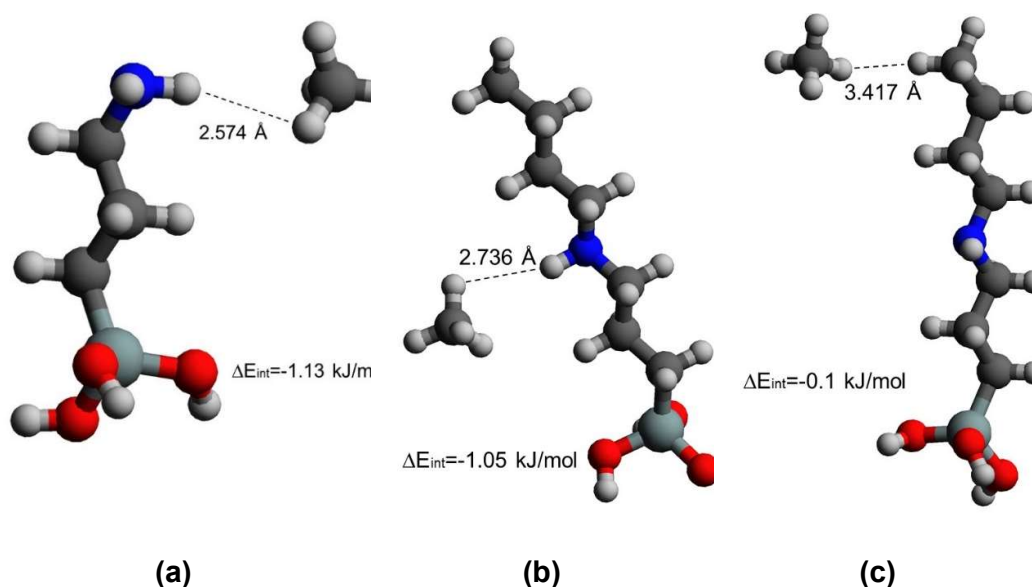


Figure 4.5 Studied DFT structures relaxed after imposing a CH₄ molecule near the respective moieties specified in the atomic distance. (a) APTES, (b) and (c) BAPT.

With respect to the CO₂ adsorption behaviour of the synthesised materials, the similar quantities of grafted total amines among APTES, BAPT, and DMAPT allows for a like-for-like comparison of the adsorption behaviour resulting from each amine type (**Fig 4.3a and c**). Ko et al.²³⁴ previously compared the performance of these amines using amine efficiency, defined as CO₂ adsorbed per N mmol grafted. However, closely examining CO₂ adsorption between amines under equal amine loading can clarify contributions not just from chemisorption but also the physisorption of CO₂. Comparing S-Sec-1.6 and S-P-1.7, the primary

amine outperforms secondary amine-grafted samples, showing higher amine efficiency in primary amines at this loading and in agreement with results by Ko et al.²³⁴. The tertiary amine, S-Te-1.7, adsorbed a lower quantity of CO₂ than raw SBA-15 and, therefore, a limited number of measurements were carried out for it. It has been shown that tertiary amines could adsorb CO₂ and form bicarbonate in “dry” conditions but at negligible quantities of <0.01 mmol/g⁷⁸. This results in a low capture capacity due to the reduced surface area and hinders any physisorption seen in raw SBA-15.

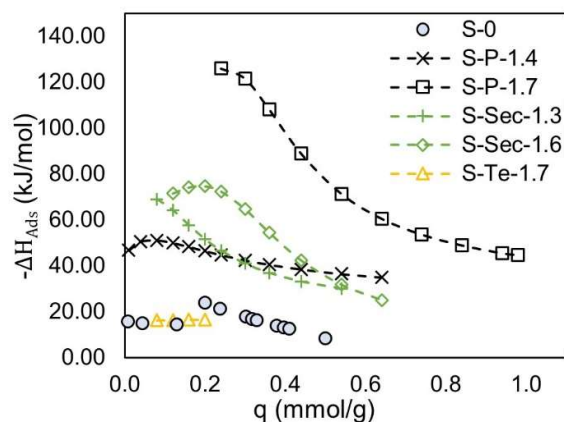


Figure 4.6 CO₂ isosteric heat of adsorption of the functionalised materials.

The samples with lower amine loading, S-P-1.4 and S-Sec-1.3, present almost identical adsorption capacity below 13 kPa (at 25°C) before S-Sec-1.3 diverges into a gentler slope. This behaviour is similarly seen at 40°C but the divergence commences at a lower pressure (**Fig. 4.3c**). The widening gap in CO₂ uptake between the two samples is likely a result of diffusion hindrance caused by the bulkier BAPT molecules and lower silane surface coverage. The lower quantity of adjacent amines in S-Sec-1.3 provides fewer active sites for the pair-wise chemisorption of CO₂ and a faster transition to physisorption. During this transition to physisorption, the lower pore volume hinders CO₂ diffusion and rationalises the increasing difference in uptake between S-Sec-1.3 and S-P-1.4 as pressure increases. This is supported by the calculated heat of adsorption in **Fig. 4.6**, in which S-Sec-1.3 crosses S-P-1.4 at a CO₂ loading above 0.2 mmol/g, indicating a larger contribution from physisorption within this region.

From these results, it can be concluded that primary and secondary amines at low coverage can lead to the same adsorption capacity at low CO₂ pressures. The lower quantity of adjacent amines in S-Sec-1.3 provides fewer active sites for the pair-wise chemisorption of CO₂. Additionally, it has been proposed by Hahn et al.²⁴⁶ that energetically less favoured carbamic acid is more likely to form at low loadings of primary and secondary amines as adjacent amine pairs decrease in number, meaning they undergo similar adsorption mechanisms regardless of the amine type. This implies that the efficiency of amines in capturing CO₂ may not always agree with higher adsorbent loadings and pressures.

4.3.3 Adsorption selectivity

To understand the effect of amine functionalisation on the selective adsorption of CO₂, the developing CO₂/CH₄ static selectivity ($\hat{S}$) with CO₂ partial pressure was calculated using **Eq. (4-4)** at 25°C, up to 100 kPa, and is presented in **Fig. 4.7**.

$$\hat{S} = \frac{q_i/P_i}{q_j/P_j} \quad (4-4)$$

All the functionalised secondary and primary amine samples have a similar rate of decrease in selectivity as partial pressure of CO₂ increases. At a CO₂ partial pressure of 40 kPa, the selectivity of S-P-1.4, S-P-1.7, S-Sec-1.3, and S-Sec-1.6 is 22, 33, 23, and 32, respectively, a significant increase from S-0 of 7.5. When considering the selectivity at lower CO₂ partial pressures, representing dynamic adsorption along an adsorbent bed in which lower partial pressures are expected near the bed outlet, S-P-1.7 and S-Sec-1.3 overcome their respective samples at similar loadings, achieving 252 and 108 at P_{CO2} = 3 kPa compared to 192 and 95 in S-Sec-1.6 and S-P-1.4, respectively. From this, it can be surmised that at this level of functionalisation and at this temperature, there is a negligible effect on selectivity between APTES and BAPT at pressures above 15 kPa.

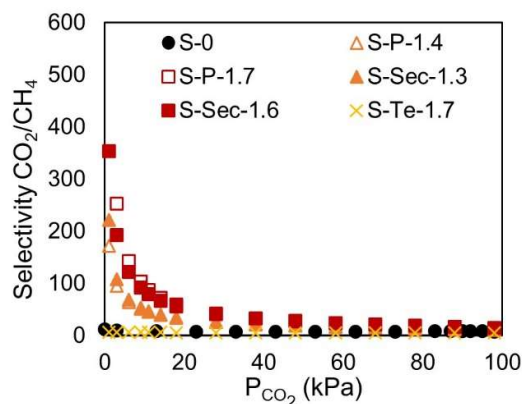


Figure 4.7 Selectivity at 25°C of APTES, BAPT and DMAPT.

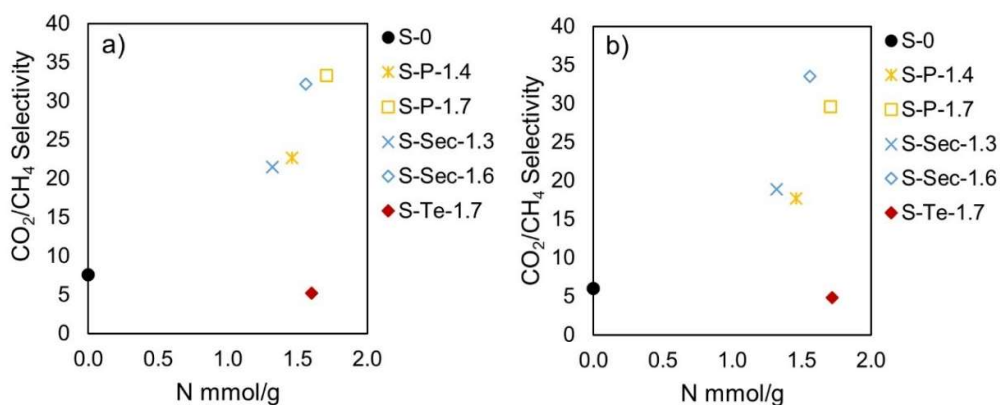


Figure 4.8 Effect of amine loading on CO_2/CH_4 selectivity at a CO_2 partial pressure of 40 kPa (a) 25°C, and (b) 40°C.

Referring to **Fig. 4.8**, in both primary and secondary amines, there seems to be a correlation between amine loading and selectivity, regardless of amine type. The selectivity at 25°C increases in the order of $\text{S-Sec-1.3} < \text{S-P-1.4} < \text{S-Sec-1.6} < \text{S-P-1.7}$, which seems only dependent on the amine loading regardless of the amine type. The primary contributions to the change in selectivity are illustrated in **Fig. 4.9**, which compares the calculated selectivity with the pure gas adsorption of CO_2 and CH_4 at pressures of 40 and 60 kPa, respectively. When APTES and BAPT are grafted at similar loadings, the ratio of CO_2 to CH_4 adsorbed is mirrored, causing the similarity in selectivity observed.

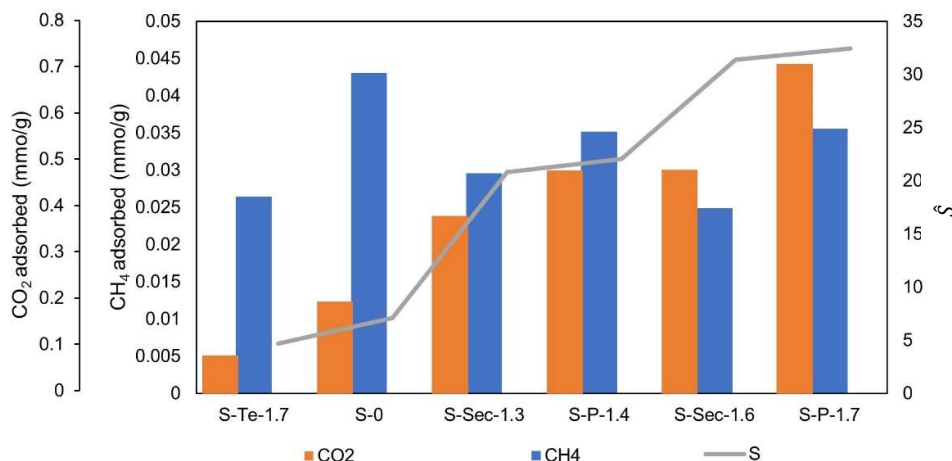


Figure 4.9 The CO₂ and CH₄ adsorption capacity at 40 kPa and 60 kPa from pure gas adsorption isotherms compared to the calculated selectivity at P_{CO₂} of 40 kPa and 25°C. S represents selectivity.

At 40°C, the order of increase in selectivity is altered towards S-P-1.4 (18)<S-Sec-1.3 (19)<S-P-1.7 (29)<S-Sec-1.6 (33), and is presented in **Fig. 4.8b**. Although by a small fraction, the selectivity of primary amines decreased on a higher magnitude compared to secondary amines. The previous section demonstrated that temperature had a greater effect on the CH₄ adsorption of APTES-functionalised materials. Additionally, at higher temperatures primary amines showed the largest decrease in CO₂ adsorption at a partial pressure of 40 kPa. The combined effect of a lower CO₂ and CH₄ uptake at higher temperatures explains the greater effect on selectivity seen in APTES-functionalised samples.

4.3.4 Regeneration efficiency

Grafted samples with maximum loading of primary amines allow reaching the highest CO₂ adsorption capacity and selectivity. On the other hand, it significantly increases the heat of adsorption, and in turn energy demand for regeneration of adsorbents. This is reflected in the adsorption-desorption cycles under isothermal and non-isothermal conditions presented in **Fig. 4.10** and **Table 4-2**. S-P-1.7 has a higher CO₂ uptake (0.53 mmol/g) compared to S-Sec-1.6 (0.4 mmol/g) but an

equivalent quantity of 0.36 mmol/g of CO₂ under atmospheric conditions is desorbed. Additionally, the desorption kinetics of S-Sec-1.6 are the fastest and lead to the highest fraction of adsorbent 'regeneration' (C_{Des}) under isothermal conditions at 25°C (**Fig. 4.10**). At non-isothermal conditions from 25 to 40°C (**Table 4-2**) S-P-1.7 outperforms the secondary amine and desorbs 0.48 mmol/g compared to 0.39 mmol/g for S-Sec-1.6. This is a result the formation of carbamates with a strong intramolecular stabilisation in primary amines. The existence of these species has been shown to be a characteristic of chemisorption by densely grafted primary amines⁹⁰. The stronger stabilisation of chemisorbed species leads to higher heats of adsorption and a greater dependency on temperature for desorption. This is in agreement with previous studies showing the secondary amine [3-(methylamino) propyl] trimethoxysilane (MAPTMS) required a lower energy for regeneration compared to (3-aminopropyl) trimethoxysilane (APTMS) under similar conditions²³⁴. The combination of energy efficiency and the enhanced selectivity towards CO₂ of secondary amines can make them a competitive option for biogas separations in a VPSA/PSA arrangement.

The low calculated heats of adsorption, faster desorption kinetics, and ease of desorption make secondary amines an interesting component to consider for future adsorbent development. The low regeneration duty is accompanied by an enhanced capacity and selectivity that at the right surface coverage could be applied to biogas separation applications. Nonetheless, further studies exploring the adsorption profiles of low to moderately functionalised adsorbent at higher pressures should be undertaken. The moderate loadings could make isothermal regenerations more effective in employing amine functionalisation. Moderate functionalisation provides a balanced level of enhancement in capacity and selectivity while minimising capacity loss in cyclic operations.

Table 4-2 Isothermal and non-isothermal adsorption-desorption runs of selected samples

	S-Sec-1.6		S-P-1.4		S-P-1.7	
	A ₂₅ -D ₂₅	A ₂₅ -D ₄₀	A ₂₅ -D ₂₅	A ₂₅ -D ₄₀	A ₂₅ -D ₂₅	A ₂₅ -D ₄₀
q _{Ads} (mmol/g)	0.40	0.39	0.33	0.30	0.53	0.50
q _{Des} (mmol/g)	0.36	0.39	0.26	0.30	0.36	0.48
C _{Des}	0.90	1.00	0.80	1.00	0.69	0.96

q_{Ads} – CO₂ adsorbed at 30 min of CO₂ flow

q_{Des} – CO₂ desorbed after 30 min of N₂ flow

C_{Des} – Fraction of adsorbed CO₂ that is desorbed (q_{Des} / q_{Ads})

A₂₅ and A₄₀ : Adsorption at 25°C and 40°C, respectively.

D₂₅ and D₄₀: Desorption at 25°C and 40°C, respectively.

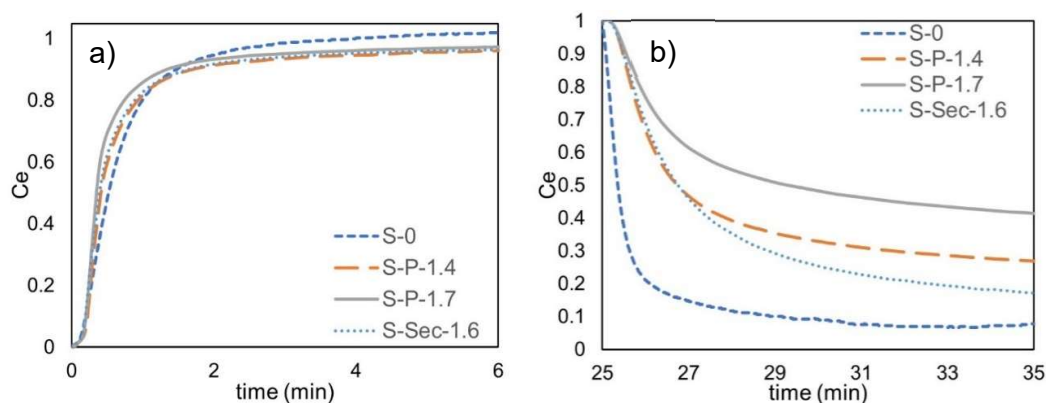


Figure 4.10 CO₂ (a) adsorption and (b) desorption curves at 25°C and 100 kPa. Ce represents the fractional uptake of CO₂ out of a total adsorption of q_{Ads}.

4.4 Conclusions

This analysis on the resulting effects different amines and loadings have on the adsorption mechanism, selectivity, and associated energy demands provides key insight on the implications expected by incorporating different amine moieties for CO₂ and CH₄ separations and, therefore, for biogas upgrading in the path towards net-zero carbon emissions. A comparison of the adsorption capacity of CO₂ on primary and secondary amines at similar loadings showed that an amine's adsorption efficiency is affected by CO₂ partial pressure; low amine loadings give

rise to similar CO₂ adsorption capacities along pressures below 10 kPa. For CH₄ adsorption, secondary and tertiary amines at similar surface coverage showed small differences in CH₄ uptake, indicating that for these materials, the distribution of amine branches along the adsorbent surface is the main influence on CH₄ adsorption. When comparing primary amines with secondary and tertiary amines, a smaller decrease in CH₄ adsorption results, indicating a higher degree of amine-adsorbate interactions between CH₄ and primary amines. The primary amine studied also showed the largest increase in CH₄ uptake and selectivity as temperature decreased from 40 to 25°C, supporting the presence of stronger interaction energies. Overall, for primary and secondary amines, the effect of amine type on the selectivity of CO₂ at partial pressures of 40 kPa up to 100 kPa was negligible, displaying instead a correlation with amine loading. Although primary amines have been shown to have the highest CO₂/CH₄ selectivity and capacity, the associated desorption and energy demands for regenerations reduces their efficiency for vacuum swing adsorption applications. For moderately grafted amines under isothermal applications, secondary amines are viable alternatives that provide comparable capacity and superior selectivity, while simultaneously maintaining a lower energy penalty for CO₂/CH₄ separations.

Nomenclature

Parameter	Description	Unit
S_{BET}	BET surface area	m^2/g
V_{p}	Pore volume	cm^3/g
D_{p}	Pore diameter	Nm
$\hat{S}$	Selectivity	-
ΔH_{Ads}	Isosteric heat of adsorption	J/mol
T	Temperature	K
P	Pressure	kPa
R	Ideal gas constant	J/mol-K
n_{s}	Toth isotherm parameter	mmol/g
b	Toth isotherm parameter	1/kPa
t	Toth isotherm parameter	-
K	Henry constant	$\text{mol}/(\text{m}^3 \cdot \text{Pa})$
C_{Des}	Fraction desorbed	-
C_{e}	Fractional uptake	-
A_{x}	Adsorption condition at $X^\circ\text{C}$	-
D_{x}	Desorption condition at $X^\circ\text{C}$	-
q	Molar uptake	mmol/g

5 FROM POWDER ADSORBENT TO PELLET

Preparation of amine grafted SBA-15 by binder-based pellets

ABSTRACT

Amine functionalised mesoporous silicas are promising adsorbents for the development and optimisation of carbon capture processes. However, they are often studied in powder form, and need to be formed into pellets if their feasibility for commercial use is to be assessed. In this study, pellets were prepared from SBA-15 powder using a range of bentonite and LUDOX concentrations, aiming to narrow down the ideal binder composition that minimises any deteriorating effects on adsorption performance. Thermogravimetric analysis, scanning electron microscopy, and dynamic mechanical analysis were used to structurally characterise the pellets, and then, the synthesised pellet's CO₂ adsorption isotherms pre and post triamine grafting were measured by volumetric sorption. Bentonite was found to be an effective single binder that forms tough pellets and retains up to 85% of CO₂ capacity of the base adsorbent. When LUDOX was added as a co-binder, there was no noticeable advantage; the hardness of the pellets was lower than bentonite only binders, caused more pore blockage, and resulted in a larger decrease in the CO₂ capacity. Out of the binder formulations studied, 25% bentonite was found to provide pellets with post triamine functionalisation CO₂ capacity equivalent to powder SBA-15, at an amine efficiency of 0.41 mol CO₂/mol, while minimising pore blockage and maintaining a compressive strength of 1.5 MPa.

5.1 Introduction

Carbon capture using adsorbents has been a promising approach to tackling anthropogenic CO₂ emissions, with their potential to be utilised in swing adsorption to reduce operational energy demands of established processes, such as amine scrubbing^{247,248}. Within the subgroup of adsorbents, amine functionalised mesoporous silicas have shown promise, providing enhanced CO₂ capacities with highly selective separations from N₂ and CH₄ containing gas

mixtures^{30,92}. However, these mesoporous silica adsorbents are often synthesised and functionalised as powders, and cannot be practically employed in conventional fixed bed contactors due to several reasons, which include the carryover of fines, high pressure drop, and diffusion mass resistance across the adsorbent bed^{249–251}. Hung et al.²⁵² quantified the difference in pressure drop and showed that the powder form of a MCM-41 material can reach a pressure drop of 7000 mBar/g, while in their formed beads of 1.7 mm sizes, it was almost negligible at equivalent superficial velocities. As the pressure drop across an adsorbent bed increases, the operational and capital costs of the associated compressor increases, it is therefore important to minimise any contributions to it by the adsorbent material.

The preparation of pellets from mesoporous silica is an important part of employing them for commercial separations, with the optimisation of binder formulations a crucial step in minimising the changes to performance. Rezaei et al.¹⁷⁶ utilised different pressing pressures of 7 MPa and 34 MPa to prepare SBA-15 pellets post amine functionalisation to sizes of 0.25 and 0.5 mm. They found that the change in performance was highly dependent on the pressing pressure used, with higher pressures of 34 MPa causing a 40% decrease in adsorption capacity of both impregnated and grafted SBA-15 materials. This change in performance is material specific, as Yang et al.²⁵³ recently showed that pressing pressures of 40 MPa to form zeolite beads of 1.1-1.4 mm had no effect on their CO₂ adsorption performance. The negligible effect on adsorption was similarly demonstrated in MOF materials by Peterson et al.²⁵⁴. 0.25 and 0.5 mm. Klinthong et al.¹⁷⁷ introduced a new method that uses polyallylamine with NaOH solution to prepare pellets, showing a minimal decrease in capacity of 10%. Although promising, polyallylamine is an expensive chemical, and makes large scale production economically unfavourable. Comparatively, Sharma et al.¹⁷⁸ studied the effect of using bentonite, a readily available chemical used for a variety of applications including as an adsorbent and catalyst binder, as a primary binder to pelletise SBA-15^{255–259}. The adsorption studies were carried out on amine impregnated mesoporous silica pellets made up of 20% bentonite and 5%

activated carbon (AC). The pellets tested showed no change in adsorption uptake compared to the powdered alternatives, but the activated carbon used to prepare them affected the internal morphology by expanding during the calcination step, and therefore possibly affected the dynamic performance of the pellet material.

To the best of our knowledge, there are no studies that investigate the change in adsorption performance as the binder concentration changes, specifically in amine grafted mesoporous silicas, which rely on available surface silanols for amine functionalisation. Accordingly, this study aimed to identify the optimal range of binder composition, using bentonite as the primary binder and LUDOX® as a co-binder. Bentonite is readily used to provide mechanical strength to a variety of materials²⁶⁰. LUDOX® is a commercial chemical made up of amorphous silica dispersed in water, commonly used for the manufacture of binders, catalyst support, and as a silica source for zeolites²⁶¹. We assessed each binder formulation's mechanical integrity, and the resulting CO₂ adsorption performance, to narrow down the interdependency of adsorption capacity and pellet toughness resulting from the binders prepared. Additionally, LUDOX® was investigated as a co-binder that could provide surface silanols for amine grafting, that replace active sites blocked by bentonite. Finally, the efficiency of grafting amines on the pellets prepared and the resulting CO₂ adsorption capacity was quantified.

5.2 Materials and methods

5.2.1 Materials

SBA-15 adsorbent was supplied by XFNANO. The chemicals 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (triamine), toluene (99.8%), methanol (HPLC grade), LUDOX®, Methyl cellulose (4,000 cP at 2%), bentonite, and poly(vinyl alcohol) (Mw 13,000-23,000) were purchased from Sigma-Aldrich, UK. The gases nitrogen and carbon dioxide were purchased from BOC, UK and were of a purity above 99.99%.

5.2.2 Pellet Synthesis

The preparation of the SBA-15 pellets followed a modified version of a procedure previously described by Sharma et al.¹⁷⁸; bentonite or a mixture of bentonite and LUDOX® were used as the permanent binder, while methyl cellulose and PVA acted as temporary binders. First, 3 g of SBA-15 was mixed with a given quantity of bentonite, and methyl cellulose, as per **Table 5-1**. The produced powder mixture was then placed in a rotary mixer for 2 hours. For some samples, the quantity of LUDOX® as per Table 1 was added. Further, 5% PVA, acting as a temporary binder, was dissolved into water, and used to make a paste which was then extruded into thin cylindrical shapes. Finally, the extrusions were left to dry in air for 24 hours and then placed in an oven at a heating rate of 2.5°C/min up to 550°C and for 10 hours to calcine. The synthesised pellets had an equivalent diameter of ~2 mm with lengths of 5-10 mm. The pelletised samples were denoted as (x)BE(y)LU, where x is the fraction of bentonite and y the fraction of LUDOX® added.

5.2.3 Amine grafting

SBA-15 powder and selected pelletised materials were grafted with triamine under an inert reflux procedure through a detailed method described elsewhere²⁴⁴. In short, 4 mmol/g of triamine was added to 1 g of SBA-15 and refluxed for 4 hours at 90°C in toluene solvent. The grafted pellets were washed with plenty of toluene and methanol then filtered under vacuum suction and left to air dry under a fume hood for 24 hours.

5.2.4 Characterisation methods

5.2.4.1 Determination of amine loading

Thermogravimetric analysis (TGA 8000, PerkinElmer) was used to estimate the quantity of amine grafted on each pelletised sample. 10-15mg of sample was subjected to a nitrogen flow of 80ml/min and heated up to 800°C at 20°C /min. A 10-minute hold was carried out at 120°C and a 5-minute hold under air flow at 800°C.

5.2.4.2 Pore morphology

Each material's internal pore structure was determined from nitrogen adsorption at -196°C using a 3P Meso 222 volumetric sorption unit (3P instruments). A sample weight of 0.3g was used for each run and outgassed for 2 hours under vacuum at 90°C . The surface area (S_{BET}) was estimated using the Brunauer-Emmett-Teller (BET) in the pressure range of $0.05 < p/p^{\circ} > 0.3$. The pore volume was evaluated by the Barrett-Joyner-Halenda (BJH) method at $p/p^{\circ}=0.95$. The pore size distribution (PSD) was determined by the BJH method using the Broekhoff-de Boer (BdB) ²⁰¹.

Scanning electron microscopy (SEM) was used to capture images of the surface topography of the materials and used the TESCAN S8000G system. The samples were held onto an aluminium SEM stub and coated with a 10nm of gold in a Quorum sputter coater, and then imaged at a magnification and conditions shown in the image presented.

5.2.4.3 Pellet mechanical strength

The compressive strength of the formed pellets was measured using an electro-mechanical driven universal testing machine Instron® 5965 5kN test system equipped with a 50N cell. The pellets were mounted between compression plates and the test conducted at a crosshead speed of 0.5 mm/min. The displacement and force, from which the stress-strain curve was derived, was recorded once the total force exceeded 0.1 N.

5.2.4.4 CO₂ adsorption measurements

CO₂ adsorption was measured using the same 3p meso unit used above, with each material (0.25-0.3g) undergoing the same outgassing procedure described in section 2.4.2. The temperature was held at 25°C using an anti-freeze bath (3P instruments).

Table 5-1. Structural characteristics compositional make-up of the pelletised materials compared to powder SBA-15 (SBA-P).

Sample	$S_{\text{BET}}(\text{m}^2/\text{g})$	$V_p(\text{cm}^3/\text{g})$	$D_p(\text{nm})$	Fraction Added	
				Bentonite (%)	LUDOX® (%)
SBA-P	490	1.2	7.8	-	-
20BE0LU	395	1.017	7.1	20	0
20BE5LU	398	0.984	7.6	20	5
25BE0LU	391	0.938	7.5	25	0
25BE5LU	395	0.907	7.5	25	5
30BE0LU	391	0.919	7.8	30	0
20BE10LU	384	0.888	8	20	10

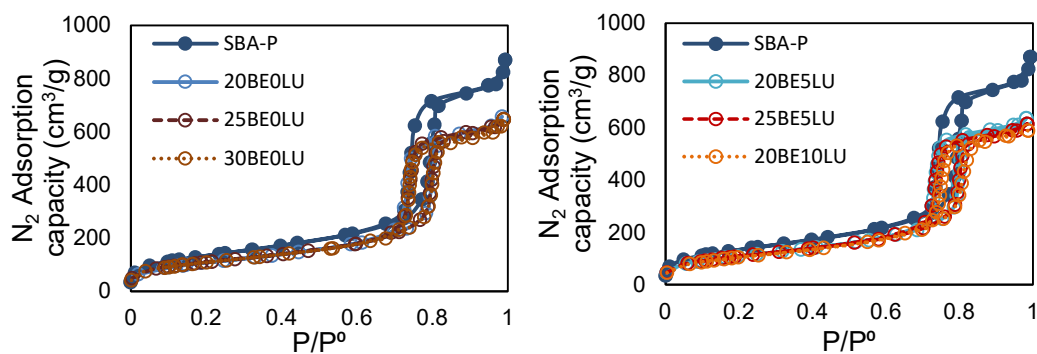


Figure 5.1 N₂ adsorption isotherms of pelletised materials at -196°C.

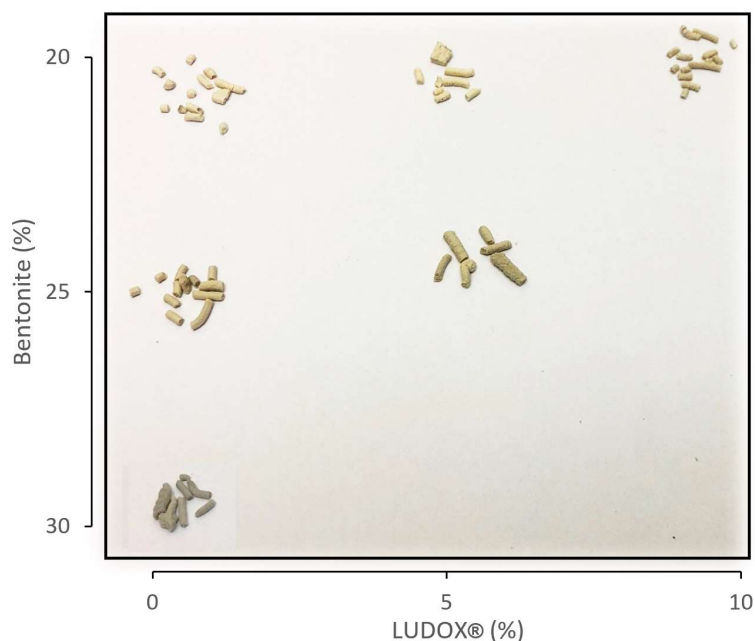


Figure 5.2 Categorisation of the pellets formed by the quantity of bentonite and LUDOX® added per SBA-15.

5.3 Results and Discussion

5.3.1 structural morphology

Figure 5.1 and **Table 5-1** present the compositional and structural characteristics of the pelletised SBA-15 materials. The nitrogen adsorption isotherms of the pelletised samples are of type IV, in-line with the SBA-15 powder, and signify that the internal pore structure was unaltered by the addition of bentonite or colloidal silica. The type H1 hysteresis is another indication that the uniform mesopores in SBA-15 remain intact.

Referring to the **Figure 5.2**, at least 20% bentonite is needed for a solid enough post calcination pellet to be formed. The addition of 20% bentonite decreased S_{BET} by 20% from 490 to 395 m^2/g and V_p by 15% from 1.2 to 1.01 cm^3/g . However, any additional increase in bentonite did not decrease the effective surface area any further. At fractions of 25% and 30% bentonite, the pore volume decreased by 22% and 23%, respectively. It seems that a large effect on porosity

occurs from the initial binder addition which becomes less pronounced as binder composition increases.

No pellet was formed when using only LUDOX® at a concentration of 20%. Consequently, it was added in 5% quantities to provide a contribution in pellet strength and investigate if any benefits result. As seen by the addition of bentonite, no additional change in the surface area was observed when the a 5% quantity of LUDOX was added to 20-25% bentonite binders, and a negligible change in specific surface area from 394 to 385 m²/g at 10% LUDOX®.

From a morphology aspect, bentonite has a smaller effect on the adsorbent's porosity compared to LUDOX®. This is further confirmed by comparing the PSD of the pellets prepared, with 20BE10LU demonstrating the largest volume of blocked pores below 8 nm (**Figure 5.3**).

The SEM images presented in **Figure 5.4** compare powdered SBA-15 with 20BE0LU and 20BE10L, and confirm that LUDOX® does not alter the structural morphology in a different manner compared to bentonite, and therefore the larger effect on PSD is a result of its migration into the pores rather agglomeration along the adsorbent's surface.

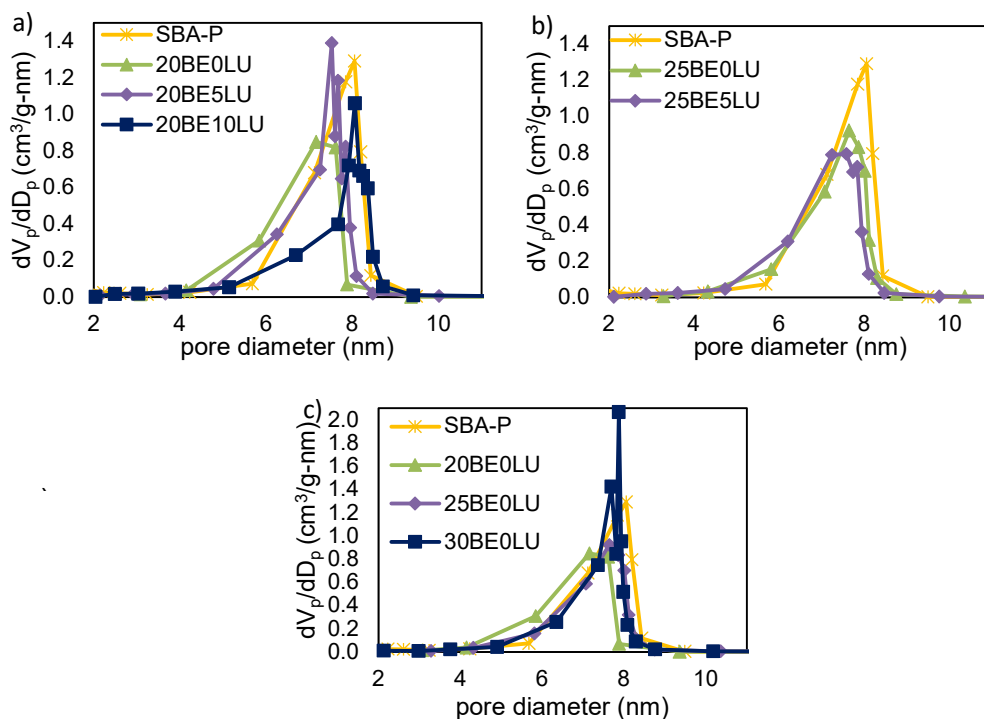


Figure 5.3 PSD calculated from nitrogen adsorption isotherms of pelletised SBA-15 as a function of (a) increasing LUDOX® quantity at 20% bentonite, (b) increasing LUDOX® quantity at 25% bentonite, (c) increasing bentonite quantity at 0% LUDOX®.

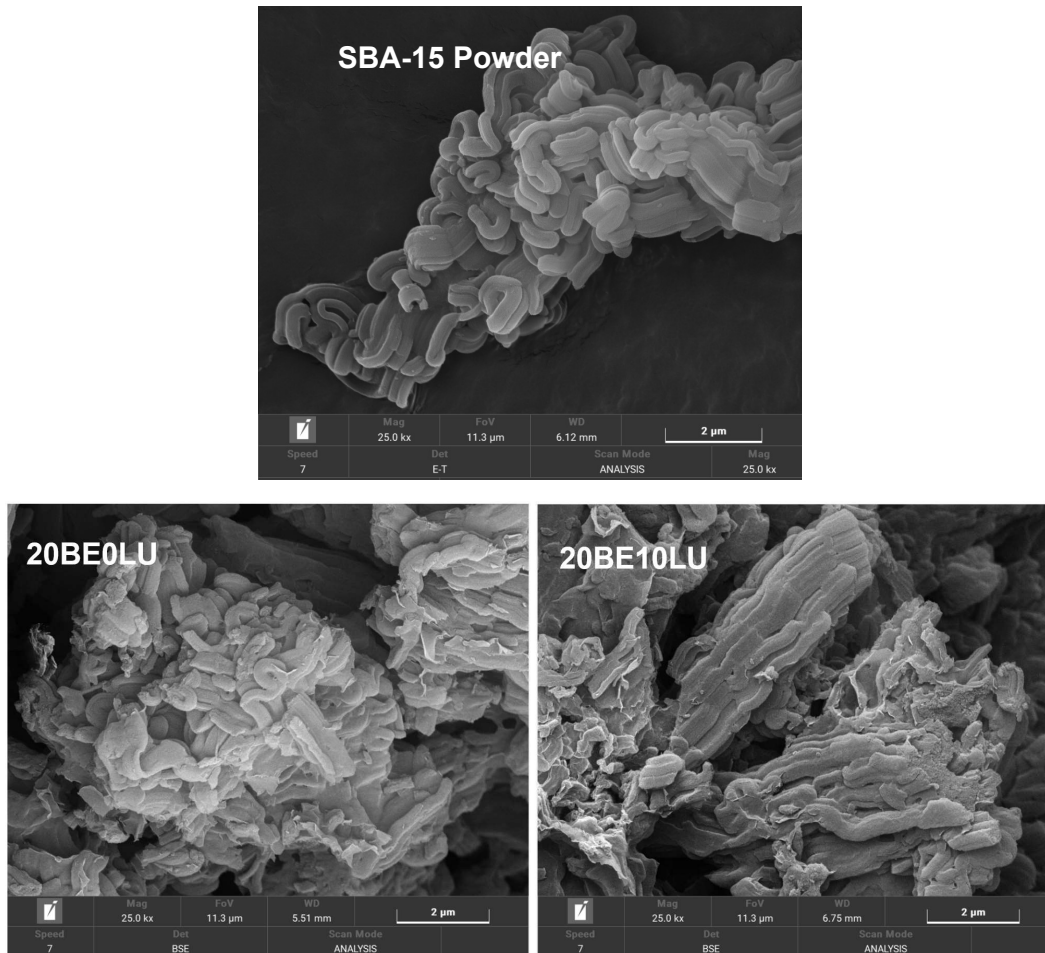


Figure 5.4 SEM image of raw SBA-15, 20BE0LU, and 20BE10LU material.

5.3.2 Compressive strength

Figure 5.5 presents the mean compressive strength of the prepared pellets. The detailed measured parameters, including the compressive displacement, is provided in **Table B.1**, with the standard deviations included to illustrate the variation. The large deviation is caused by the small pellet sizes as well as differences in the extruded shapes prepared. From a comparison of the mean

compressive strength, it is clear that LUDOX provides a much lower contribution to mechanical strength compared to bentonite. This is specifically seen in 25BE5LU, and 20BE10LU, which withstood 1.15 and 0.86 MPa compared to 1.5 and 2 MPa for 25BE0LU and 30BE0LU, respectively.

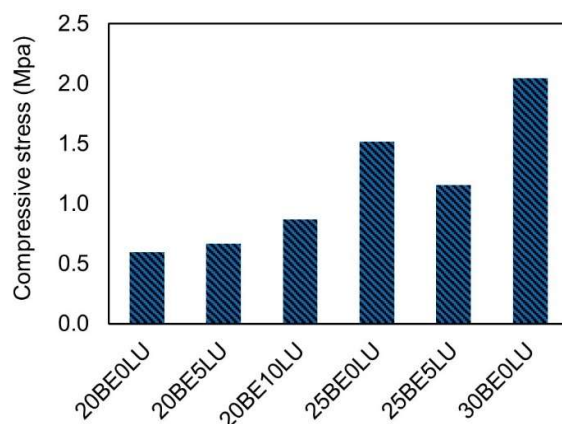


Figure 5.5 Mean compressive strength of the prepared pellets with standard deviation bars overlaid.

5.3.3 Amine grafting of SBA-15 pellets

Triamine was grafted on selected materials to study the effect of the binder material on the efficiency of amine grafting, and the measured loading of amine is presented in **Figure 5.6** and **Table 5-2**. One of the principle factors of amine grafting is the availability of accessible surface silanol hydroxyl groups, and the effect of the binder must be shown to have a minimal effect on this ^{71,72,208}. The organic content of amine was measured by the weight change after 200°C, as any vaporisation below that temperature is attributed to water or toluene solvent. The change in weight with temperature of 20BE0LU and 20BE5LU showed a profile identical to triamine grafted SBA-15 powder. 25BE0LU and 20BE10LU both showed a slightly different profile, with a commencement of triamine removal at ~300°C instead of 400°C. The reason for the faster removal of triamine in these samples is unclear, but since the triamine reagent used has a boiling point of

118°C, it is likely resulting from the degradation of triamines bonded to the surface of the pellets rather than the internal pores. Since 25BE0LU demonstrates a higher grafted amine loading than 20BE5LU and 20BE10LU, it can be concluded that colloidal silica does not offer any added benefits, such as additional surface sites, but rather hinders the organ silane reagent's interaction with surface silanols.

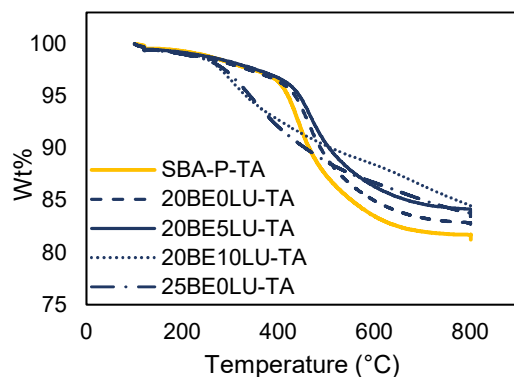


Figure 5.6 The TGA change in weight representative of the quantity of amine grafted on SBA-15 powder and pellets with increasing temperature.

Table 5-2 Amine loading of triamine grafted pellets

Sample	N mmol/g	Uptake (mmol/g)	%Diff*	Amine efficiency (CO ₂ mmol/mmol amine)
SBA-P-TA	3.32	1.46		0.43
20BE0LU-TA	3.05	1.25	-14.3	0.41
20BE5LU-TA	2.76	1.15	-21.2	0.41
25BE0LU-TA	2.94	1.15	-20.8	0.39
20BE10LU-TA	2.83	1.09	-25.1	0.38

*The percent difference of each material compared to the powder SBA-15 functionalised by triamine

5.3.4 CO₂ adsorption performance

The CO₂ adsorption isotherms of the unfunctionalised powder and pelletised SBA-15 is presented in **Figure 5.7** and **Table 5-3**. 20BE0LU had the smallest decrease in adsorption uptake from powdered SBA-15, a 16% drop down to 0.38

mmol/g. The second set of materials using 25% total binder fractions are 25BE0LU and 20BE5L, and a greater decrease in capacity of 28% is seen in 25BE0LU compared to 23% in the latter. At these lower quantities of binder composition, LUDOX® does not affect pore access in the same manner that is seen binder compositions above 25%. For instance, 25BE5LU shows the largest drop in uptake at 100 kPa, decreasing to 0.30 mmol/g from 0.45 mmol/g in powder SBA-15, a 34% drop. A similar decrease in performance has been demonstrated in bentonite containing zeolites, and can be attributed to the decrease in surface area in the pellets formed²⁶².

Compared to bentonite, the addition of LUDOX® at quantities past 25% binder formulations causes a greater decrease to the adsorption capacity, and referring to **Figure 5.5**, creates mechanically weaker pellets. Additionally, the brittleness resulting from high LUDOX® compositions is clearly seen by the particle fractures in the 20BE10LU sample, presented in **Figure 5-2**. The highest addition of bentonite at 30% resulted in only a slight decrease in capacity compared to 25BE0LU, but the highest compressive strength of 2.15 MPa. Out of the compositions studied, the pellets 20BE0LU, 20BE5LU, and 25BE0LU had the highest uptake, pore volume, and reasonable mechanical strength, and were chosen to be functionalised by triamine. Additionally, the 20BE10LU sample was functionalised to clarify the effect of LUDOX® incorporation on the adsorption of CO₂ post grafting.

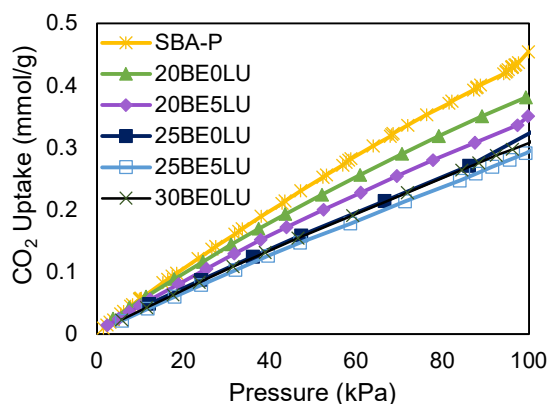


Figure 5.7 CO₂ adsorption isotherms of the unfunctionalized powder and pelletised materials.

Table 5-3 CO₂ adsorption of pelletised SBA-15 compared to the powder SBA-15.

	CO ₂ loading (mmol/g)	%Diff*
SBA-P	0.45	-
20BE0LU	0.38	-16
20BE5LU	0.35	-23
25BE0LU	0.33	-28
25BE5LU	0.30	-34
30BE0LU	0.32	-30

*The percent difference of each material compared to the powder SBA-15 functionalised by triamine

Figure 5.8 presents the CO₂ adsorption isotherms of the pelletised and powdered SBA-15 post functionalisation, while the recorded capacities and amine efficiency at 100 kPa are listed in **Table 5-2**. Amine efficiency is an effective method of comparing the different samples while accounting for any variations in total amine loading, it is defined as the moles of CO₂ adsorbed per gram of amine grafted. Samples 20BE0LU and 20BE5LU showed no real change in amine efficiency compared to the SBA-15 powder, adsorbing ~0.41 mmol CO₂/mmol amine. It seems that in these two samples, the employed binder had no effect on the accessibility of amine moieties by CO₂ compared to the powder.

25BE0LU and 20BE10LU both demonstrated a slightly lower efficiency, ~0.39 mmol CO₂ /mmol N. However, the variation is small and allows us to conclude that at the grafted loadings, all the binder formulations have a very small effect on the amine promoted adsorption of CO₂. Even more, the addition of 10% Ludox® did not provide any discernible benefit, and may be considered to hinder adsorption rather than provide additional sites for adsorbate-adsorbent interactions. Out of all the pellets, the 20BE0LU material showed the highest uptake of CO₂ at an amine efficiency equal to the powder but was mechanically weakest. Taking pellet strength and adsorption capacity into account, 25BE0LU pellets would be the ideal pellet formulations to use for further studies in higher pressure dynamic fixed bed flow schemes.

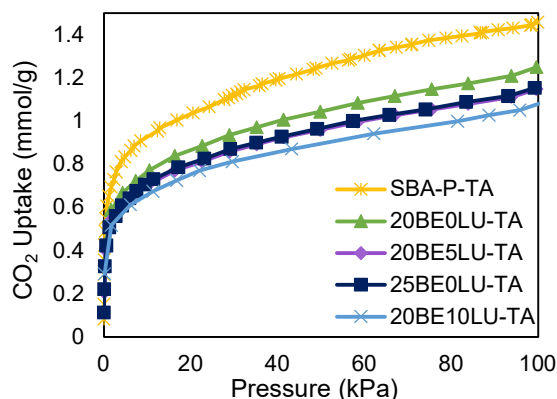


Figure 5.8 Experimental CO₂ adsorption isotherms of triamine functionalized powder and pelletised materials.

5.4 Conclusion

Within a laboratory environment, the adsorption performance of adsorbents is often studied in powder form, but resulting data is often non representative of industrial applications. This is because these processes require the minimisation of the pressure drop across the bed, and the limitation of the carryover of fines; they therefore often utilise spherical or extruded pellets. In this work, pellets using different binder formulations of SBA-15 have been prepared and grafted by triamine, to investigate the ideal binder composition that can maximise mechanical strength, while minimising any deteriorating effect on the adsorption performance. This formulation can then be used for fixed-bed adsorption studies, and produce more representative results of the adsorption behaviour of amine grafted silicas for CO₂ adsorption in real-world applications. The formation of SBA-15 pellets using a minimum of 20% bentonite binder showed good structural strength but decreased CO₂ adsorption by up to 30% compared to powder SBA-15. However, the triamine grafted pellets showed no change in the adsorption behaviour, with amine efficiency remaining almost equivalent to the powder sample. LUDOX® was tested as a co-binder that provides pellet strength and as a source of replacement silanol/hydroxyls for amine grafting, however, there was no enhancement in adsorption performance or the quantity of amine grafted

compared to non-LUDOX® containing pellets. Out of all the compositions, 25BE0LU showed high mechanical strength combined with no change in the amine's efficiency to capture CO₂ after triamine functionalization. However, as was demonstrated here, adjustments to the quantity of bentonite can be made without much effect on the total CO₂ adsorbed, and so 25-30% of SBA-15 as bentonite binder would be good pellet formulations for further fixed bed studies.

Nomenclature

Parameter	Description	Unit
S_{BET}	BET surface area	m ² /g
V_p	Pore volume	cm ³ /g
D_p	Pore diameter	nm
P	Pressure	kPa
q	Molar uptake	mmol/g

6 AMINE GRAFTING FOR DAC: BALANCING KINETICS AND CAPACITY

Direct Air Capture by Amine Grafted SBA-15: Balancing Kinetics and Capacity

ABSTRACT

Successful deployment of direct air capture (DAC) to mitigate severe consequence of climate change, depends on many factors, one of which is the development of kinetically efficient CO₂ sorbents with a high sorption capacity, at ultra-low CO₂ concentrations. This work evaluated the performance of different amine groups at varying loadings, grafted on silica support for DAC applications. The CO₂ adsorption performance of primary, diamine, and triamine grafted SBA-15 and at pressures below 5 kPa was measured through volumetric sorption, followed by humid air (23% RH) adsorption through gravimetric analysis. Under humid air flow, triamines grafted at an amine loading of 4.6 mmol/g, showed the highest enhancement in adsorption, with an uptake of 26 mg/g, but with the lowest adsorption time of 200 minutes. In comparison, primary amine grafted at a loading of 2.6 mmol/g reached an equilibrium uptake of 22 mg/g at an adsorption time of 131 minutes. Nonetheless, the adsorption rate of primary amine for lower CO₂ loadings was superior, reaching 20 mg/g in 86 mins, 30 minutes faster than triamine grafted at 4.6 mmol/g. However, it was found that triamine grafted at a loading of 3.5 mmol/g has the fastest kinetics of all samples. The results indicated that primary amines and moderate-to-high loading triamine reagents incorporated into mesoporous mediums can offer a balance of uptake and adsorption rate, a quality that should be considered when designing for continuous DAC processes.

6.1 Introduction

The intergovernmental panel on climate change (IPCC) recently reported that even if immediate action is taken to decrease CO₂ emissions down to zero, additional negative emission technologies (NETs) are necessary to limit global

warming to 1.5°C by 2100. As a result, Direct Air Capture (DAC) has become a promising technology for atmospheric CO₂ capture, targeting distributed sources, such as transport or agricultural or commercial businesses, that make up about 50% of emissions^{1,180,263}.

One the most promising DAC approaches is to utilise cyclic adsorption processes such as pressure (PSA) and temperature swing adsorption (TSA). However, ambient air conditions have significant implications on the use of current benchmark adsorbents. For example, Kumar et al.¹⁸¹ investigated a number of physisorbents and one chemisorbent under DAC conditions. They found that Zeolite 13x and Mg-MOF-74, which in a variety of applications provide exceptional performance, led to low CO₂ uptakes of 1.5 and 6.3 mg/g, respectively, under ambient air conditions. This was a direct result of a low selectivity of CO₂ to H₂O. Moreover, Mg-MOF-74 also showed structural degradation at the presence of moisture. In comparison, the chemisorbent tetraethylenepentaamine (TEPA) impregnated SBA-15 preformed significantly better, achieving a CO₂ uptake of 158 mg/g when exposed to an air stream at 49% relative humidity (RH) and 23°C for 12 hours. This is in agreement with a number of studies that incorporated PEI in sorbents for DAC conditions, reporting similar CO₂ adsorption and selectivity^{264–267}. Sayari et al.²⁶⁸ showed that under certain adsorbent synthesis conditions, an amine efficiency of ~308 mg of CO₂/g_{PEI} can be achieved for an air stream at 49% RH.

These studies show that high amine loadings, commonly a quality of impregnated materials, provide exceptional adsorption capacity. However, the superior adsorption awarded often results in slow adsorption kinetics and significantly high regeneration energy demands^{20,188}. Brillman et al.¹⁸⁹ illustrated this in a study by the impregnation of TEPA from 26 to 45% on silica and measuring the CO₂ uptake of a dry N₂ stream with 400 ppm of CO₂. They showed a large variation in kinetics, with the adsorption rates varying from 300 minutes up to 900 minutes to achieve CO₂ loadings of 60 to 110 mg/g. For amine grafted materials under similar conditions, Belmabkhout et al.¹⁸⁶ investigated the feasibility of using triamine grafted silica for CO₂ capture in simulated air. An uptake of 40 mg/g was

achievable at an adsorption time of 328 minutes, comparable to low loading of TEPA materials by Brillman et al. In both cases, only dry conditions were studied, and RH was not accounted for. In a study that accounted for humidity, Gebald et al.²⁶⁹ prepared a novel adsorbent by freeze-drying amines on nanofibrillated cellulose. Diamine functionalised materials achieved an adsorption capacity of 30mg/g of CO₂ after 2 hours under air flow at 40% RH, a superior adsorption rate compared to the PEI impregnated silicas.

There are several studies on performance of amines for DAC application. However, they either investigated the isolated performance of one amine type, densely impregnate silicas, or focused on synthesis methods that make it difficult to attribute amine specific capture efficiencies. This work aims to compare the adsorption efficiency of different amine types for DAC applications, to elucidate which amines and what loadings can provide the optimal balance of adsorption capacity and kinetics. Consequently, primary, diamine, and triamine were grafted on SBA-15 to provide a range of surface loadings to evaluate their CO₂ adsorption from ambient air. This includes a comparison of the effects of humidity in ambient air on CO₂ uptake, adsorption rates, and the associated implied desorption demands resulting from each amine at the grafted density. Additionally, the selectivity of CO₂/N₂ is quantified for a comparison of the separation efficiency of each amine type.

6.2 Materials and methods

6.2.1 Materials and synthesis

(3-aminopropyl)triethoxysilane (APTES), 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPT), 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (TAEPT), toluene (99.8%), and methanol (HPLC grade) were supplied by Sigma-Aldrich, UK. SBA-15 mesoporous silica adsorbent was purchased from XFNANO. Nitrogen and carbon dioxide were supplied by BOC, UK with a purity above 99.99%. Air was supplied from the outside atmosphere via a compressor supply line at a dew point of 3°C.

The grafting of SBA-15 followed an inert reflux procedure that is described in detail elsewhere²⁴⁴. In short, the desired quantity of amine was added to 1 g of SBA-15 and placed under inert reflux with toluene as a solvent for 18 hours at 70°C. The samples were denoted as S-x-y, with x referring to the amine type (P-primary, D-diamine, T-triamine) and y the amine loading grafted.

6.2.2 Material Characterisation

The amine loading was estimated by thermogravimetric analysis (TGA 8000, PerkinElmer) and elemental analysis (EA, vario EL III, Elementar). For TGA, an 8-10 mg sample was placed under a nitrogen flow of 60 ml/min and the temperature incrementally increased at a rate of 20°C /min from 30°C to 800°C. This was followed by a five-minute hold at 800°C under air flow. EA measurements utilized combustion analysis to provide the nitrogen content present in each sample.

The functionalised materials' structural morphology was determined based on nitrogen physisorption analysis at -196°C by a 3P Meso 222 sorption analyser (3P instruments). A sample weight of 0.2-0.3 g was used for each measurement and degassed for 2 hours at 90°C under vacuum suction. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to calculate surface area (p/p^0 of 0.05 to 0.2) and pore volume ($p/p^0=0.95$), respectively^{87,154}. The reported pore size distribution (PSD) was calculated by the Broekhoff-de Boer (BdB) method simplified by the Frenkel-Halsey-Hill (FHH) approximation²⁰¹.

6.2.3 Adsorption measurements

CO₂ and N₂ equilibrium adsorption were measured using the 3P meso analyser mentioned previously. Each measurement used 0.25-0.3 g of sample, degassed under the same conditions described for nitrogen physisorption, and measured at a temperature of 25°C, which was maintained by an antifreeze bath (3P Instruments). The CO₂ isotherms were fitted using a modified form of the Toth equation^{209,244} and the N₂ data by the Henry isotherm, details of which can be

found elsewhere⁸⁷. Selectivity ($\hat{S}$) from adsorption isotherms was calculated by Eq (6-1):

$$\hat{S} = \frac{q_i/P_i}{q_j/P_j} \quad (6-1)$$

In which q (mmol/g) is each component's adsorption capacity and P (kPa) is each Ambient air adsorption measurements were conducted by TGA (TGA 8000, Perkin Elmer). A 7.5 mg sample was used for the moderately grafted primary, diamine, and triamine SBA-15, while a 10 mg sample was used for the heavily loaded triamine sample(S-T-4.5); this was chosen since at this weight, an approximately equal amount of adsorbent occupies the same volume within the sample pan. The sample was degassed for 30 minutes at 110 °C under a nitrogen flow of 60 ml/min. The sample temperature was then stabilised at 25 °C and exposed to a flow of 60 ml/min of air at 100 kPa for a period of 150 to 250 minutes, depending on the material. The uptake measured by TGA was considered representative of equilibrium when the rate of change of the sample weight was lower than 10⁻⁴ mg/min.

6.3 Results and Discussion

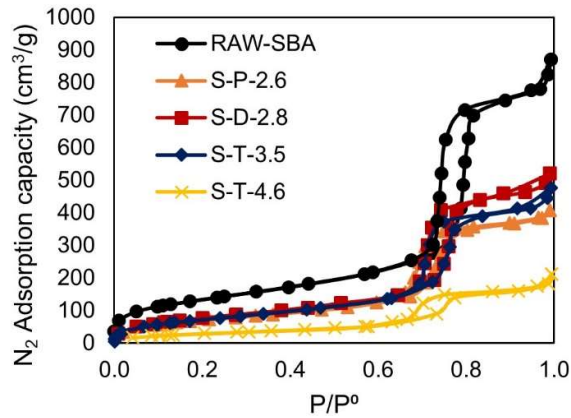


Figure 6.1 N₂ isotherms at -196°C for primary, secondary, and triamine functionalized SBA-15

Table 6-1 Structural properties of raw SBA-15 and functionalized materials.

Sample	Amine type	Amine Added (mmol/g)	Amine loading (mmol/g)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)
RAW-SBA	-	-	-	490	1.2	7.0
S-P-2.6	Primary	8	2.60	267	0.63	5.7
S-D-2.8	Diamine	2	2.78	288	0.74	6.2
S-T-3.5	Triamine	2	3.52	274	0.66	6.3
S-T-4.6	Triamine	8	4.66	115	0.26	5.8

6.3.1 Material Characterization

The structural characteristics of functionalized material samples are provided in **Table 6-1** and **Figure 6.1**. The nitrogen isotherms of S-P-2.6, S-D-2.8, and S-T-3.5 are type IV with a hysteresis loop typical of the mesoporous pores of SBA-15⁸⁷. S-T-4.6 was grafted with the highest loading of amine, and the measured effective surface area decreased to 115 m^2/g , a 76% change from the unfunctionalized SBA-15. This degree of pore filling is more often seen in impregnated mesoporous silicas^{67,70,270}. However, the change in surface area and pore volume does align with literature when a high enough loading of triamine is grafted on SBA-15 of similar structural characteristic⁷⁶. The molecular length and level of grafted loading of triamine leads to excessive pore filling, and this is reflected in the nitrogen isotherm for this specific sample.

6.3.2 CO₂ and N₂ volumetric adsorption

The adsorption isotherms for CO₂ and N₂ at 25°C are presented in **Figure 6.2**. Up to 20 kPa, the CO₂ adsorption capacity is identical for S-P-2.6 and S-D-2.8, reaching ~0.95 mmol/g. Compared to S-P-2.6, S-D-2.8 has a lower loss of pore volume and surface area post functionalization, and an overall smaller degree of chemisorption as shown by us in a previous study^{92,244}. Both of these characteristics contribute to the increase in adsorption uptake above 20 kPa, with physisorption facilitated by the chemisorbed species becoming the principal

adsorption mechanism. Distinguishing this is important as the larger contribution from physisorption plays an important part in the low-pressure adsorption of CO₂ from air of the diamine sample. S-T-3.5 showed a larger CO₂ uptake compared to other samples for CO₂ partial pressure > 0.17 kPa. At 2 kPa, S-T-3.5 adsorbs 32 mg/g compared to 26 mg/g in both S-P-2.6 and S-D-2.8, indicating the presence of more sterically accessible sites for chemisorption. S-T-4.6 has an amine loading of 4.66 mmol/g, the highest out of all functionalities, yet achieves the lowest capacity as pressure increases. This is likely caused by pore plugging from high amine loading, as previously discussed. The saturation of the pores with long TAEPT chains leads to diffusion limitations that hinder access to active sites, for both chemisorption and physisorption. Consequently, there is an initially high degree of CO₂ chemisorption, measured by the 14.5 mg/g at 0.04 kPa that sharply increases up to 32 mg/g at 2.5 kPa before levelling off (**Figure 6.2**), and comprising 61% of the total uptake measured at 100 kPa. Once these sites are occupied there is little pore space left for further adsorption and the capacity increases at a much slower rate. This means that the distribution of TAEPT in this sample becomes significant at much lower pressures, a necessary quality for CO₂ capture from air.

All the materials exhibited an almost negligible N₂ uptake compared to CO₂. The highest uptake of N₂ was ~0.75 mg/g by S-T-3.4 at 100 kPa N₂ partial pressure, followed by S-P-2.6 at 0.5 mg/g, and lowest for S-T-4.6 at 0.2 mg/g. The CO₂/N₂ selectivity calculated from the fitted isotherms is presented in **Table 6-2**. In a 50:50 binary mixture of CO₂:N₂ at a total pressure of 100 kPa, the selectivity of S-T-4.6 reaches 392 followed by 197 in S-P-2.6 and 159 in S-D-2.8. These values are in-line with other works of triamine grafted MCM-41 and exceed zeolite, carbons, and MOF selectivity under similar conditions^{271–273}. Although presenting a high selectivity, a more representative mixture of CO₂ and N₂ for DAC would comprise a ratio of 0.04:99.96 and is presented in **Table 6-2**. This selectivity might not consider the presence of O₂ in air, but it has been shown in literature that the trend of selectivity for CO₂/N₂ and CO₂/O₂ in a variety of ZIF materials and BPL carbon is similar²⁷³. Additionally, Belmabkhout et al.⁶³

investigated the breakthrough of a gas mixture representative of air (0.03:79.98:19.99 for CO₂:N₂:O₂) in triamine grafted MCM-41 at 25°C and 100 kPa. The breakthrough curves of O₂ and N₂ were almost identical. At a CO₂ partial pressure of 0.04 kPa the selectivity of S-P-2.6 and S-D-2.8 approach infinity, exceeding 25,000 with the highly grafted S-T-4.6 reaching over 140,000. This is expected due to the nature of CO₂ adsorption by amines (selective chemisorption), but also by the very low uptake of N₂ by the studied materials.

Table 6-2 Selectivity of functionalised materials in a mixture of CO₂ and N₂ at a total pressure of 101.3 kPa and 25°C

Sample	$\hat{S}$ (50:50 binary mixture)	$\hat{S}$ (0.04:99.96 mixture)
S-P-2.6	206	72552
S-D-2.8	167	51000
S-T-3.5	131	24963
S-T-4.6	399	174453

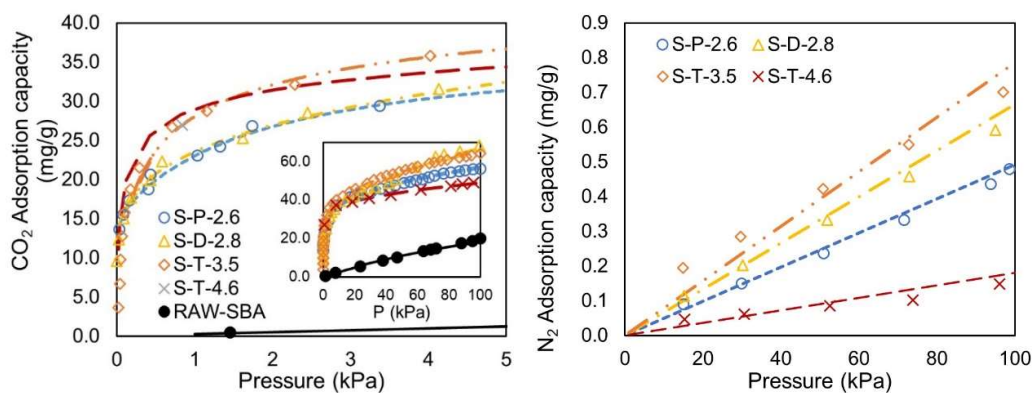


Figure 6.2 Equilibrium adsorption isotherms of functionalized materials at 25°C of (a) CO₂, and (b) N₂. The markers represent the experimental data, while the following lines represent the respective isotherm model: (—)RAW-SBA, (---) S-P-2.6, (···) S-D-2.8, (-.-) S-T-3.5, (- - -) S-T-4.6

Table 6-3 Comparison of the Gravimetric uptake under humid air flow and equilibrium volumetric adsorption of pure CO₂ at P_{CO2} of 0.04kPa. The ambient air flow is at 23% RH.

Sample	ambient air (mg/g)	Pure CO ₂ (mg/g)
S-P-2.6	22.3	14.2
S-D-2.8	13.5	13.6
S-T-3.5	21.9	8.0
S-T-4.6	26.3	14.5

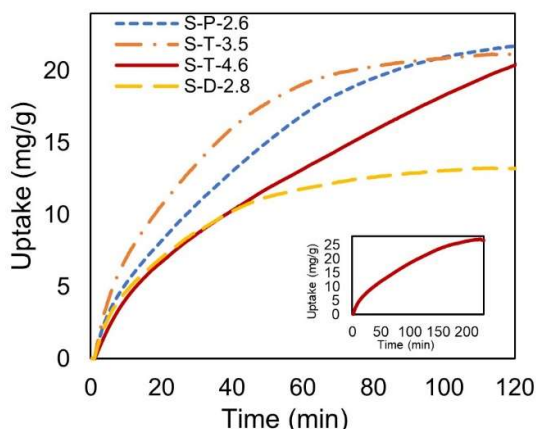


Figure 6.3 Gravimetric uptake of functionalized materials under ambient air flow at 23% RH up to 130 minutes. The full adsorption uptake of S-T-4.6 up to 230 minutes is presented in the lower right.

6.3.3 Ambient air gravimetric measurements

The gravimetric CO₂ adsorption of the functionalized materials under air flow with 23% RH is presented in **Figure 6.3** and **Table 6-3**. Considering the purpose of this paper is to assess the differences in capacity and kinetics by different amine types and the negligible quantity of CO₂ adsorbed by the raw SBA-15 material at CO₂ partial pressures of 0.04 kPa presented in **Figure 6.2**, only the functionalised materials were studied under air adsorption conditions. The highest adsorption was achieved for S-T-4.6 (26.3 mg/g) followed by S-P-2.6 (22.9 mg/g), S-T-3.5 (21.9 mg/g), and S-D-2.8(13.5 mg/g). A comparison of the differences between the dry gas volumetric adsorption and humid dynamic adsorption uptake at P_{CO2} of 0.04 kPa can provide insight on the changes in the observed performance

(**Table 6-3**). The equilibrium adsorption capacity at 0.04 kPa in dry conditions is highest for primary amine and decreases in the order of primary>diamine>triamine. Comparatively, for ambient air adsorption, there is a considerable enhancement in triamine grafted materials, followed by primary amines, and close to none for diamine.

It has been previously shown that the differences observed may be caused by a combination of total RH, adsorbent pore structure, and the measurement method¹⁸. Although the overall uptake is mainly associated with CO₂ chemisorption, H₂O can also be physically adsorbed on the surface or react with amines to facilitate CO₂ adsorption, and therefore contributes to the increased weight observed. However, from a recent study by Jung et al.²⁷⁴ on the competitive adsorption of H₂O and CO₂ on PEI impregnated silica (6.7 N mmol/g), an uptake of ~2 mg/g of H₂O is seen at a P_{H₂O} of 0.73 kPa with a molar fraction of CO₂ (y_{CO₂}) of 0.05 at 40°C²⁷⁵. Although the partial pressure of CO₂ and overall temperature in this study is lower, Jung et al.²⁷⁴ showed that within the limits of 0<y_{CO₂}>0.05 and up to P_{H₂O} of 4 kPa, amine sites tend to favour CO₂ adsorption over H₂O, a behaviour similarly seen by TEPA impregnated adsorption of CO₂ in ambient air studies by Kumar et al.¹⁸¹. Considering this and referring to breakthrough experiments by Belmabkhout et al.^{33,186} on competitive adsorption of CO₂ and H₂O in triamine grafted silicas, it can be inferred that the adsorbed quantity of H₂O contributing to the calculated uptake is relatively low under the conditions studied

With primary amine (S-P-2.6), the minor enhancement from 14.2 mg/g to 22.3 mg/g in capacity from dry to humid conditions agrees with previous studies under similar conditions²⁷⁶. The enhancement observed is likely a combination of RH and pore accessibility. It has been proposed that the presence of water may enhance amine adsorption by the formation of surface bound carbamate species, but at this level of amine loading there is a small number of available surface silanols, making it a low contributor^{246,277}. The most prominent species formed are likely ammonium carbamate ion pairs, shown to readily form on primary amine functionalised silicas at similar surface coverage, in both dry and wet

conditions^{91,277,278}. Additionally, it has been suggested by Mebane et al.⁸² that the presence of water vapour can enhance the total formation of ammonium carbamate through the formation of diffusive intermediates that support the diffusion of CO₂ into internal pores. Under this study's conditions, the observed enhancement in uptake at the rate of adsorption measured is likely a result of a higher quantity of ammonium carbamate formation facilitated by the diffusion of CO₂^{278–280}. This agrees with previous studies showing that the slow forming bicarbonate through CO₂ chemisorption does not occur on primary amines^{277–279,281}.

The diamine sample (S-D-2.8) under ambient air flow had the lowest uptake, with no discernible enhancement from water vapour. The secondary amine moiety in diamine has been shown to form hydrogen bonds with surface silanols, leaving only primary amine moieties to interact with CO₂⁸⁹. Furthermore, Li et al.¹⁹¹ showed that secondary amines in PEI can form hydronium carbamate in humid conditions, but that ammonium carbamate is more energetically favourable. In contrast, Didas et al.²⁸² showed that secondary amines in single amine reagents are more hydrophobic compared to primary amines. The uptake in S-D-2.8 may be a result of the initial formation of carbamate by easily accessible primary amines, aided by water vapour. In the next period, and considering that this material contains 1.4 mmol/g of each primary amine and diamine, it can be surmised that any further chemisorption is sterically limited due to a combination of chemisorbed species and amine clustering, or unavailable amine moieties forming surface hydrogen bond.

The largest difference in uptake was seen specifically in the triamine samples, and may be due to a combination of adsorption mechanisms previously discussed, with an additional possibility of the formation of bicarbonate through CO₂ adsorption in humid conditions²³³. In agreement with pure CO₂ studies on amine impregnated silica by Hahn et al.²⁴⁶, the triamine grafted samples seem to have a propensity to adsorb H₂O, either to form bicarbonate or to act as a base for the deprotonation of a carbamate zwitterion in place of an amine. The densely grafted S-T-4.6 adsorbs CO₂ in humid conditions in a mechanism like

impregnated amines such as diethylenetriamine (DETA), evidenced by the difference between dry and humid adsorption and the slower adsorption time in this specific material. In comparison, S-T-3.5 resulted in a fast-initial adsorption rate, signifying a large quantity of fast forming chemisorbed species, such as ammonium carbamate likely promoted by the water vapour present.

The adsorption time of S-T-3.5 and S-T-4.6 for 16 mg/g was 40 and 81 minutes, respectively. The faster adsorption rate in S-T-3.5 can be a result of facilitated pore diffusion by the adsorbed H₂O film and larger pore volume. In S-T-4.6, the pore filling causes an accumulation of triamine closer to the surface of adsorbent pores and along the pore surface, slowing internal diffusion. Unlike diamine, triamine contains two secondary amines that adsorb in a manner similar to impregnated amine reagents such as DETA; that is, even if one secondary amine forms hydrogen bonds with the surface such as seen in diamines, the second one when accessible, can provide a site for ammonium carbamate, hydronium carbamate, or even bicarbonate formation.

Table 6-4 Comparison of the rate of adsorption of different amines grafted on SBA-15

Sample	Amine loading	Time (min)	Ads (mg/g)
S-P-2.6	2.6	40	13
		55	16
		86	20
		131	22
S-D-2.8	2.8	97	13
S-T-3.5	3.52	28	13
		40	16
		73	20
		200	22
S-T-4.6	4.66	59	13
		81	16
		116	20
		136	22

Comparing the adsorption rates of the different amines, S-T-4.6 reached 26 mg/g after 200 minutes of air exposure, a significant trade-off in adsorption time for a ~4mg/g increase from 22 mg/g. Consequently, the adsorption times for 13, 16,

20 and 22 mg/g uptake are considered optimal targets and have been compared amongst the different amines, presented in **Table 6-4**. As S-P-2.6 approaches equilibrium, the adsorption rate is equivalent to S-T-4.6, taking >130 minutes to reach 22 mg/g, but at lower loadings such as 16 mg/g, it only takes 55 minutes (26 minutes faster), and for 20 mg/g only 86 minutes (30 minutes faster). Although S-P-2.6 demonstrates good rates of adsorption, S-T-3.5 outperforms them all, achieving uptakes of 16 mg/g and 20 mg/g at 40 and 73 minutes, respectively.

From the variations seen in adsorption by the different amines studied, primary and triamines grafted at loadings seen in S-P-2.6 and S-T-3.5, that provide plenty of pore volume, can be the most efficient for ambient air adsorption. In this case, targeting an uptake ahead of the slower rates seen near equilibrium, such as 20 mg/g at an adsorption half time of 37 and 42 minutes for S-T-3.5 and S-P-2.6, would be an optimal usage of these types of amine grafted materials.

6.3.4 Feasibility for DAC

The majority of DAC processes are still in the initial stages of development, but an important factor to consider for continuous operation is the balanced performance of an adsorbent, specifically in terms of the adsorption kinetics and corresponding uptake in humid air adsorption¹⁸⁰. Table 5 summarises selected works reporting the adsorption performance of amine functionalised adsorbents relevant to DAC applications, by tabulating the average adsorption times based on the adsorption half time, defined as the time to reach 50% of the maximum CO₂ adsorption. The impregnation of an adsorbent with TEPA has shown to achieve high CO₂ loading at low partial pressures; In work by Brilman et al.¹⁸⁹, an impregnated silica with 38% TEPA reached an uptake of 110 mg/g after 16 h exposure to dry N₂ at 400 ppm CO₂. Although this is superior to many adsorbents, this work did not account for the effects of humidity on adsorption and desorption rates. In their study, the total time for adsorption was quite long, but did show an approximate adsorption half time of 250 min, which averages to an adsorption rate of 202 µg/g/min. Nonetheless, Azarabadi et al.²⁸³ demonstrated that the cyclability and low cycle times of an adsorbent is crucial in

minimising DAC costs, with respect to these two parameters, the CO₂ capacity of amine impregnated silicas have been shown to deteriorate faster than amine grafted silicas, making them less suitable for long-term DAC processes.

Table 6-5 Reported adsorption performance in DAC conditions of various amine functionalised adsorbents from literature.

Sorbent	Feed gas composition	Max CO ₂ uptake (mg/g)	Adsorption half time (min)	Average Adsorption Rate* (µg/g/min)	Ref
38% TEPA impregnated silica	400 ppm CO ₂ in dry N ₂ stream	101	~250	202	189
Triamine grafted MCM-41 (7 N mmol/g)	0.03% CO ₂ and 99.97% Carbon Free dry Air	43	Adsorption breakthrough time - 167 min	257	186
Hyperbranched amino silica (9.9 N mmol/g)	Humid, 400 ppm CO ₂	76	167	228	284
Hyperbranched amino silica (2.3 N mmol/g)	Humid, 400 ppm CO ₂	7	110	32	284
Stabilized PEI impregnated on Silica T-PEI/CARiACT G10 HPV (10.5 N mmol/g)	Dry CO ₂ 400 ppm balanced by Argon	96	200	240	188
AEAPDMS-NFC-FD	Synthetic Air (506 ppm CO ₂) 49% RH (25°C)	61	92	334	269
Triamine grafted MCM-41 (7.9 N mmol/g)	Synthetic Air (400 ppm CO ₂) 90-110% RH (0°C)	50	Left Overnight	-	190
AEAPTMS grafted Silica Gel (2.48 N mmol/g)	Synthetic Air (400 ppm CO ₂) 20%RH, 25C,		90	38.8	285
S-P-2.6 (2.6 N mmol/g)	Ambient air 24% RH	22	31	354	This work
	Dry 400 ppm CO ₂ equilibrium adsorption	14		-	This work
S-T-3.5 (3.5 N mmol/g)	Ambient air 24% RH	21	20	525	This work
	Dry 400 ppm CO ₂ equilibrium adsorption	8		-	This work
S-D-2.8	Ambient air 24% RH	~13	22	295	This work
S-T-4.6	Ambient air 24% RH	26	59	216	This work

*Average adsorption rate has been calculated based on the maximum capacity and adsorption half-time, assuming two consecutive cycles targeting 50% of the maximum CO₂ adsorbed

Densely grafted triamine (>5 mmol/g) on pore-expanded MCM-41 has also been studied under DAC conditions, reaching 43 mg/g after 167 min through breakthrough experiments and averaging an adsorption rate of 257 µg/g/min, a slightly better performance compared to the 38% TEPA silica¹⁸⁶. Hyperbranched amino silica (HAS) adsorbents developed by Choi et al.²⁸⁴ have also shown high uptake at amine loadings >8 mmol/g under DAC conditions, reaching 75 mg/g, but at a slower rate, with an averaged adsorption rate of 228 µg/g/min. All these studies show that elevated amine loadings result in high uptake, but also cause a decreasing trend in the rates of adsorption, due to diffusion limitations from pore filling.

Despite the low equilibrium uptake of primary amines and triamines in this study, the adsorption rate to reach 75% of equilibrium uptake in ambient air was superior to densely grafted triamine- and diamine-functionalised SBA-15. The average adsorption rate of S-P-2.6 was 354 µg/g/min, while S-T-3.5 reached a value of 525 µg/g/min. Both are indicative of superior kinetic performance and potential for cyclic DAC applications; however, to account for mass transfer diffusion effects, the pelletisation and fixed-bed investigation of their performance should be employed to further understand industrial scale performance. Additionally, S-T-3.5 shows no indication of bicarbonate formation due to the fast adsorption rate, but material S-T-4.6 may have. Bicarbonate formation can heavily affect performance as it has been shown to limit desorption efficiency or incur additional regeneration energy requirements in ethylmonoethanolamine (EMEA) solution²⁸⁶.

Other factors affecting regeneration were demonstrated in a study by Wagner et al.¹⁹⁰ on DAC by densely grafted triamine (7.3 mmol/g) on MCM-41, there was a rapid deterioration in uptake due to the presence of moisture in the desorption gas, which was maintained at 75°C for 2 h. The reason for such behaviour was unclear, but it was suggested that it can potentially be due to the extended two-hour desorption period used in wet conditions. Under ideal conditions, benchmark low

temperature solid-sorbent applications of DAC have already been shown to require higher regeneration energy demands compared to liquid-based applications, but the costs are comparable if low grade heat is used to meet a sorbent's regeneration energy requirements²⁸⁷. In a study by Kulkarni et al.²⁸⁸, they use low-grade steam for desorption and showed that the energy required for a TSA CO₂ capture process of dry air, employing triamine grafted pore expanded MCM-41, is ~5962 MJ/t CO₂ and is dominated by parasitic losses from the heating step. They suggested that the energy could be reduced by up to ~20% if higher capacity adsorbents are employed. However, there was no investigation into the energy implications of maximising the number of adsorption-desorption cycles per 24-hour period. For this reason, further work should be carried out concentrating on the desorption demands of different amines, and the effect of cycle times on the overall process energy requirements to better understand the benefit of fast cycle times in DAC initiatives.

6.4 Conclusion

In this work, a comparison of the adsorption of CO₂ under DAC conditions for primary, diamine and triamine grafted SBA-15 has been carried out. Under equilibrium volumetric sorption of dry CO₂, adsorption at a CO₂ partial pressure of 0.04 kPa was highest for primary amine followed by diamine and last triamines. In comparison, for CO₂ adsorption under air flow at 24% RH, the order is altered, CO₂ loading is enhanced more so for triamine, followed by primary amine and finally diamine. The change in CO₂ loading in DAC conditions indicate that triamine is subject to the largest enhancement from moisture, affecting both the total uptake and adsorption rate, in a manner dependent on the amount of loaded amine. Triamine grafted sample at a loading of 3.5 mmol/g under airflow adsorbed the highest quantity in the shortest time, ~20 mg/g after 73 minutes, and ~16 mg/g in only 40 minutes. This sample was followed by primary amine at a loading of 2.6 mmol/g, presenting a balanced uptake and adsorption rate of ~16 mg/g in 55 minutes and ~20 mg/g in 86 minutes. In comparison to both samples, triamine grafted at 4.6 mmol/g took 116 minutes to reach 20 mg/g. In conclusion, under DAC conditions, densely incorporated amines such as the one studied here

at 4.6 mmol/g of triamine achieve superior equilibrium capacity but are often subject to kinetic limitations and slow adsorption rates. In comparison, primary amines, and moderate-to-high loadings of triamine result in a balance of capacity and kinetics that can potentially be better utilised for continuous DAC processes.

Nomenclature

Parameter	Description	Unit
S_{BET}	BET surface area	m^2/g
V_p	Pore volume	cm^3/g
D_p	Pore diameter	nm
$\hat{S}$	Selectivity	-
P	Pressure	kPa
q	Molar uptake	mmol/g

7 GENERAL DISCUSSION

The purpose of this work was to investigate the role of amine functionalities in CO₂ separations, while focusing on their suitability for low CO₂ partial pressure gases for biogas upgrading, or at ultra-low CO₂ pressures present in air. This has been accomplished by categorising the adsorption behaviour of CO₂ and CH₄ as a factor of amine type and loading, separating the effects of single amine and combined amines to isolate individual contributions.

When grafting primary, secondary, and tertiary amines on SBA-15, primary (APTES) and secondary (BAPT) amines at equal loadings result in small variations in selectivity at CO₂ partial pressures above 40 kPa. One of the contributing reasons identified is the apparent higher degree of interactions between CH₄ and the APTES organ silane. This higher degree of interaction in APTES was seen even when the pore volume and specific surface area of BAPT and tertiary amine (DMAPT) at similar loadings was lower.

However, assessing the selectivity of CO₂ below partial pressures of 40 kPa demonstrated that APTES provides the highest selectivity and CO₂ adsorption capacity when grafted loadings are equivalent to BAPT. Although that indicates that primary amines are the ideal amine type for CO₂/CH₄ separations, under isothermal adsorption-desorption conditions at 25°C, moderately grafted primary and secondary amines (1.7 mmol/g) demonstrate an almost equal working capacity for CO₂ adsorption.

This finding is in-line with behaviour of SBA-15 grafted with diamine (AEAPT) and triamine (TAEPT) organ silanes. Results assessing the influence of amine type show that AEAPT materials can minimise the isosteric heat of adsorption at a CO₂ capacity and selectivity equivalent to APTES, likely a contribution of the secondary amine moiety present in the organ silane branch. Consequently, In combined amines such as diamine at moderate loadings, the lower basicity of the secondary amine combined with its accessibility to adsorbates aids in the formation of chemisorbed species that are more readily desorbed, making the working capacity in isothermal adsorption at 25°C of moderately surface

coverage of AEAPT (2.5 N mmol/g or 1.23 silane mmol/g) equivalent to densely grafted APTES(2.6 N mmol/g or 2.6 silane mmol/g).

In both SA and CA grafted SBA-15, there is a clear correlation of amine loading to regeneration energy, highlighted when comparing isothermal adsorption-desorption at 25°C versus 40°C. Densely grafted materials show working capacities almost equivalent at both operational temperatures, only moderately grafted materials demonstrate an increase in adsorption at 25°C compared to 40°C. Lower amine loadings maintain an overall enhancement in adsorption capacity that is not confined to the low pressures (<5 kPa), employing physisorption and chemisorption distributed across a wide pressure range. This is an essential feature in adsorbent development for biogas upgrading, since state-of-the-art processes employ pressure modulation for CO₂/CH₄ separations, and the adsorbent must maintain a competitive working capacity at desorption conditions of 10-100 kPa¹⁷.

In all cases, the presence of one secondary amine moiety minimises energy demands while primary amines maximize uptake. Since a superior selectivity of CO₂/CH₄ was observed in all the materials up to 100 kPa, the next step is the investigation of the high pressure adsorption behaviour of selected samples, and based on their capacity and energy efficiency include moderately grafted AEAPT, BAPT, and low to moderately grafted APTES.

To employ the SBA-15 powder in higher pressure fixed bed pilot plant studies, an optimal pelletisation procedure for high throughput operation needs to be prepared. To form SBA-15 pellets, an optimal binder composition was identified by preparing a range of samples using varying quantities of bentonite, with LUDOX® as a co-binder. The optimisation criteria were to provide a minimal drop in uptake while displaying mechanical integrity; a 25% fraction of bentonite met these specifications, with no LUDOX® necessary. The triamine grafted pellets of this formulation led to a negligible decrease in the adsorption efficiency of the amine compared to the powder, and an almost equivalent quantity of grafted amines under similar synthesis conditions. The addition of 5% LUDOX® at 20%

bentonite fractions did result in a better pre-functionalisation CO₂ adsorption compared to 25% bentonite only binders, but no benefit was seen post-functionalisation.

The superior capacity at ultra-low CO₂ partial pressures (5 kPa) of densely grafted amines on SBA-15 was the motivation for a separate study comparing their performance in DAC conditions. APTES, AEAPT, and TAEPT were chosen at high grafting loadings as they demonstrated the highest level of chemisorption. From adsorption data, APTES and TAEPT showed the best balance between adsorption capacity and kinetics for CO₂ adsorption from ambient air. In both, the total CO₂ uptake did not exceed 22 mg/g, which is lower than amine impregnated silicas, but demonstrated faster kinetics, with an average adsorption rate (based on half-time of adsorption) of 8 and 12 $\mu\text{mol/g/min}$, respectively. Their adsorption capacity and rate highlight the advantages drawn from moderately grafted amine loadings. These are better adsorption rates compared to what is reported for amine functionalised materials, which have average adsorption rates of 4.5-7.5 $\mu\text{g/g/min}$. In addition, amine functionalised adsorbents outperform zeolites, carbons, and MOFs; due to the effectiveness of chemisorption at ultra-low pressures, and its resistance to water vapour or possible enhancement.

Future studies should concentrate on packed-bed experiments, to further elucidate real-world adsorption kinetics. Furthermore, the capital and operational costs of maximising adsorption rate over capacity need to be the subject of a detailed analysis. Higher CO₂ capacity can minimise the operational cost of DAC units, since it is estimated that in triamine functionalised MCM-41, the heating step for regeneration reaches $\sim 5962 \text{ MJ/t CO}_2$, which can be decreased by up to 20% if higher capacity adsorbents, with a theoretical value of $\sim 4.5 \text{ mmol/g}$, are used. Comparatively, Higher adsorption rates can minimise the capital costs, but incur further operational costs due to the increase in the quantity of regenerations. To the best of the author's knowledge, there has been no study that scrutinises the advantages and disadvantages of faster adsorption-desorption cycles in comparison to higher capacity in DAC applications, especially when considering heat integration from an established plant, or the utilization of low-grade steam

for regenerations, thus minimising energy demands. Overall, DAC remains in the budding stages of applicability, but this preliminary study indicates that the two amine types identified should be considered for future investigations assessing the energy implications and utilisation methods of sorbents in DAC process configurations.

With respect to overall adsorption performance, the sorbents presented here have advantages when used, but this depends on the specific process configuration and product specification. Zeolites and activated carbons have been shown to reach higher capacities >1.45 mmol/g, while incurring lower costs for synthesis, and lower regeneration energy demands. Nonetheless, amine functionalised silicas adsorb much less CH_4 and enhance CO_2 selectivity, allowing for better CH_4 recovery in biogas processes. They also show effectiveness in the presence of common biogas contaminants, such as water vapour and H_2S . In studies on triamine grafted MCM-41, it had an exceptional H_2S adsorption capacity, with uptakes >2.5 mmol/g. However, H_2S does become favoured over CO_2 at pressures above 50 kPa. Regardless, this is not detrimental to performance as H_2S quantities in biogas are typically $<2\%$, making the amine grafted materials prepared here suitable to simultaneously tackle CO_2 and H_2S removal from biogas sources^{209,289,290}. With respect to the economic implications, fast kinetics and high CO_2 adsorption capacities can aid in lowering capital costs, permitting smaller overall units to be designed for a specific biomethane production rate^{271,291}.

8 CONCLUSION

This work focused on assessing the suitability of amine functionalities for carbon capture from gas mixtures containing low CO₂ partial pressures, primarily for biogas upgrading and CO₂ capture in DAC conditions, which represent applications that still require further research, development or optimisation for large-scale implementation. This was accomplished by classifying the adsorption performance of each amine type and loading as a factor of capacity, selectivity, and regeneration energy. For isothermal conditions in CO₂/CH₄ separations, low to moderate amine loadings balance the CO₂ capacity and regeneration energy; This is due to the availability of plenty of physisorption sites, indicating that the enhancement in capacity by chemisorbed species may be sustained up to higher pressures compared to densely grafted amines. This agrees regardless of the type of amine used, whether by combining different amines or when only single amine types are incorporated, however, diamine and secondary amines can both minimise the heat of adsorption (~45 kJ/mol at 1.0 mmol/g capacity) better than other amine types, and better than liquid amine methods using 30% MEA or DEA. In terms of selectivity, All amines showed exceptionally low CH₄ adsorption, under 0.06 mmol/g, but the accessibility of primary amine moieties led to slightly higher CH₄ adsorption capacities at equivalent surface coverage, diamine showed an IAST selectivity of 34-374 while primary amine was capped at 240, this should be further investigated at higher pressures to confirm if this trend continues, and if secondary amine moieties are more effective at repelling CH₄ compared to primary amine moieties. Fixed-bed studies will be facilitated by the pellet formulation presented in this work, a binder that only uses 25-30% bentonite and is extruded. The binder caused a minimal change to the structural morphology of the adsorbents prepared and will allow for representative pilot scale studies up to 10 bar pressures. In DAC conditions, primary and triamine grafted at loadings <3.5 mmol/g and allow plenty of pore volume were found to balance CO₂ uptake and kinetics competitively with materials that employ much higher amine loadings, often impeding adsorption rates to attain higher adsorption capacities. The materials here showed adsorption rates of 5-12

$\mu\text{mol/g/min}$, which can be considered superior to TEPA impregnated silicas. In addition to the conclusions made here, the presented results provide key information that may be used for future adsorbent development, highlighting advantages of amine grafting for DAC, and the CO_2 adsorption mechanisms and CH_4 interactions that develop with each amine type across a range of loadings.

8.1 Future studies

Based on the conclusions made from this work, the following are suggested future studies:

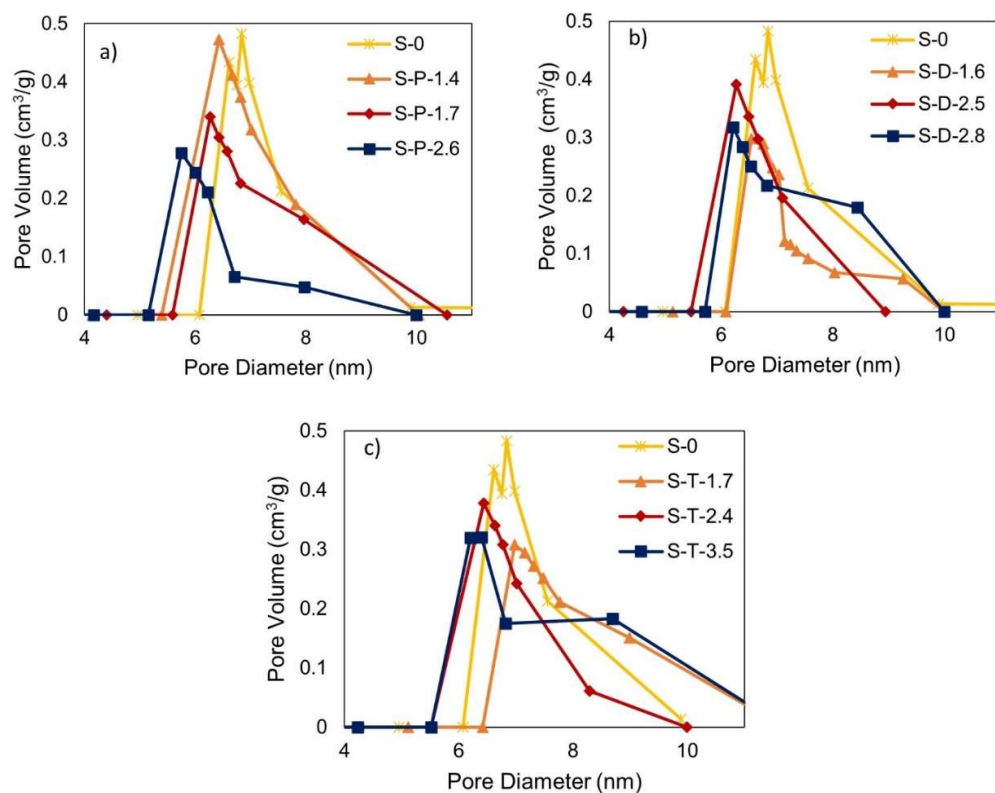
- High pressure CO_2 and CH_4 equilibrium adsorption studies up to 10 bar of low to moderately grafted primary, secondary, and di amine on pelletised mesoporous silica. This is in response to the findings that indicate that: (1) amine- CH_4 interactions seem to lead to higher adsorption in primary amines compared to secondary and tertiary amines, and should be further confirmed up to 10 bar pressures, and (2) the CO_2 capacity of moderately grafted amines may sustain a principally physisorption adsorption mechanism at much higher pressures, if this trend continues, specific loadings of amines may lead to energy efficient adsorption processes that rely on pressure modulation for adsorption-desorption steps.
- Mixed gas adsorption studies of CO_2 and CH_4 from 1 to 6 bar using the Cranfield dynamic and static volumetric gas adsorption fixed bed units capable of holding up to 10 grams of material, and loaded by the functionalised pellets prepared by the optimal binder identified in this work. This step is necessary to determine the equilibrium and kinetics of the selected adsorbents, and to build on the lower pressure studies on the selective adsorption of amine grafted mesoporous silicas. The addition of a binder leads to the formation of macropores, which can have a significant effect on the dynamic efficiency, while also affecting the saturation adsorption of CO_2 , CH_4 , and N_2 . These studies will better reflect the expected adsorption kinetics for real-world applications. The kinetic and equilibrium data will be utilised in Cranfield's existing numerical model to

design cyclic PSA processes and assess capital and operational costs when utilising the selected amine functionalised adsorbents.

- The investigation of the separation efficiency of cage-like adsorbents with structural morphology that adsorbs CO₂ by kinetic diameter tailored pores, but with an absolute minimal level of amine functionalisation. The goal is to exploit the advantages of amines in selectively adsorbing CO₂ without creating pore blockage or excessive chemisorption, thus enhancing their selectivity while maintaining the pre-functionalised capacity.
- The investigation of selected amine grafted SBA-15 in different process arrangements for cyclic DAC application to approximate CAPEX and OPEX implications of this class of materials. This is key information to understand the implied energy demands for adsorbent regeneration, adsorbent life, and thus identify the principal processes that could most economically utilise amine functionalised adsorbents for CO₂ capture from air.

APPENDICES

Appendix A Chapter 3 Supporting Information



FigureA.1 Pore size distribution (PSD) of functionalized samples from the nitrogen desorption branch of (a) APTES, (b) AEAPT, and (c) TAEPT

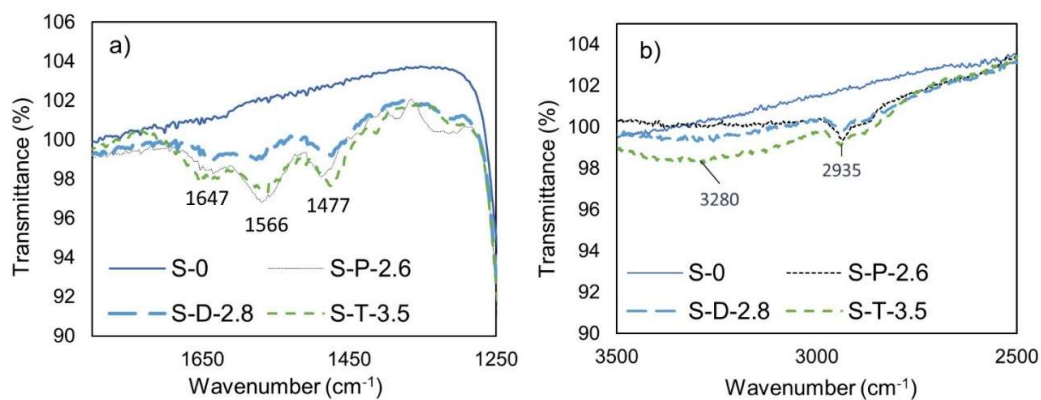


Figure A.2 Magnification of specific IR regions of selected functionalised samples. IR bands at 1477, 1566, and 1641 cm^{-1} correspond to C-H bending in $-\text{CH}_2-$, N-H bending in $\text{Si-CH}_x\text{-NH}_2$ and $-\text{NH}_2$, respectively. However, it is important to note that due to the small differences in the nature of bonds, overlapping may occur, making absolute conclusions difficult to formulate. In all samples, the peak at 2935 cm^{-1} is associated with C-H stretching of the alkanes in the organic chains of each amino-silane. The peak at 1045 cm^{-1} is assigned to the Si-O stretching vibrations in Si-O-Si. Specific to the presence of secondary amines, the band at 3280 cm^{-1} corresponds to N-H stretching in $\text{Si-CH}_x\text{-NH-R}$, but may be a result of OH stretching vibrations from H_2O adsorbed or even the $-\text{NH}_2$ present in diamine/triamine. Like the bands within the 1450-1650 cm^{-1} region, the dilute nature of the functionalised materials may give rise to overlapping and ambiguity in the strict assignment of vibrational modes.

Table A-1. Tabulated data of adsorption performance of the functionalised materials prepared in this work

Sample	25°C			40°C			ΔH_{ads} (kJ/mol)
	CO_2 at 100 kPa (mmol/g)	CH_4 at 100 kPa (mmol/g)	IAST $\hat{S}$ (40:60 $\text{CO}_2:\text{CH}_4$ at 100 kPa)	CO_2 at 100 kPa (mmol/g)	CH_4 at 100 kPa (mmol/g)	IAST $\hat{S}$ (40:60 $\text{CO}_2:\text{CH}_4$ at 100 kPa)	
S-0	0.45	0.070	8	0.33	0.0539	6	8 - 23
S-P-1.4	0.74	0.055	51	0.56	0.048	37	35 - 51
S-P-1.7	0.94	0.054	106	0.69	0.04	124	44 - 121
S-P-2.6	1.28	0.044	240	1.09	0.03	265	27 - 146
S-D-1.6	0.66	0.060	34	0.48	0.036	41.8	22 - 48
S-D-2.5	1.11	0.047	136	0.937	0.042	123	28 - 47
S-D-2.8	1.55	0.040	374	1.146	0.031	324	40 - 84
S-T-1.7	0.68	0.060	41	0.502	0.037	31	22 - 44
S-T-2.4	0.77	0.060	67	0.598	0.036	76	28 - 60
S-T-3.5	1.45	0.045	276	1.22	0.032	303	30 - 80

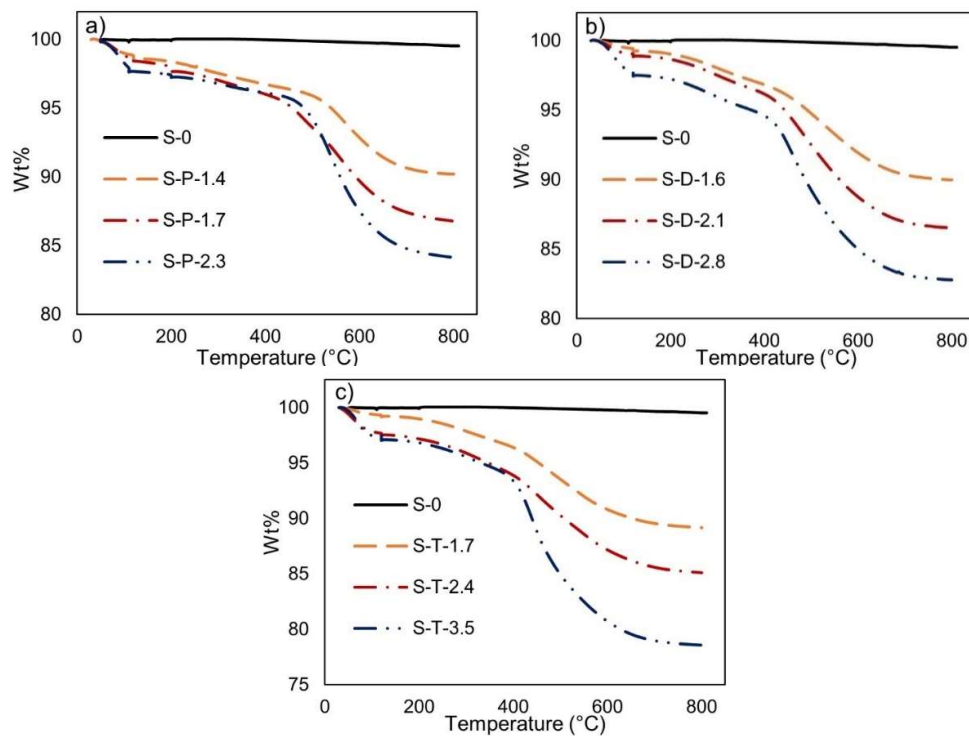


Figure A.3 TGA percent weight change from 30 to 800 °C for all samples.

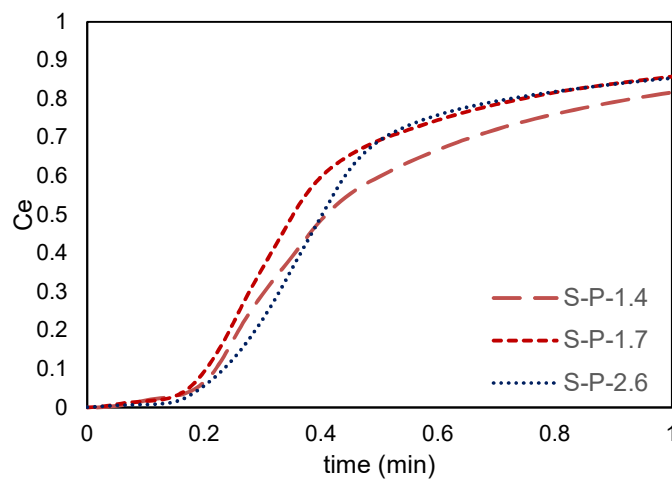


Figure A.4 TGA measurements of CO₂ adsorption at 25 °C of APTES grafted SBA-15 at varying loadings. Q_e represents the fraction of adsorbed CO₂ out of the total equilibrium adsorption at 25 °C and 100 kPa.

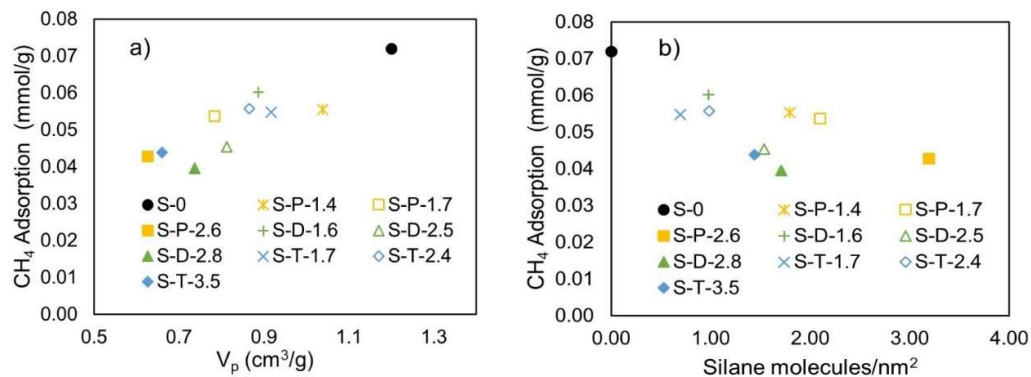


Figure A.5 CH₄ loading at 100 kPa and 25 °C as a function of (a) pore volume, and (b) silane molecule per surface area.

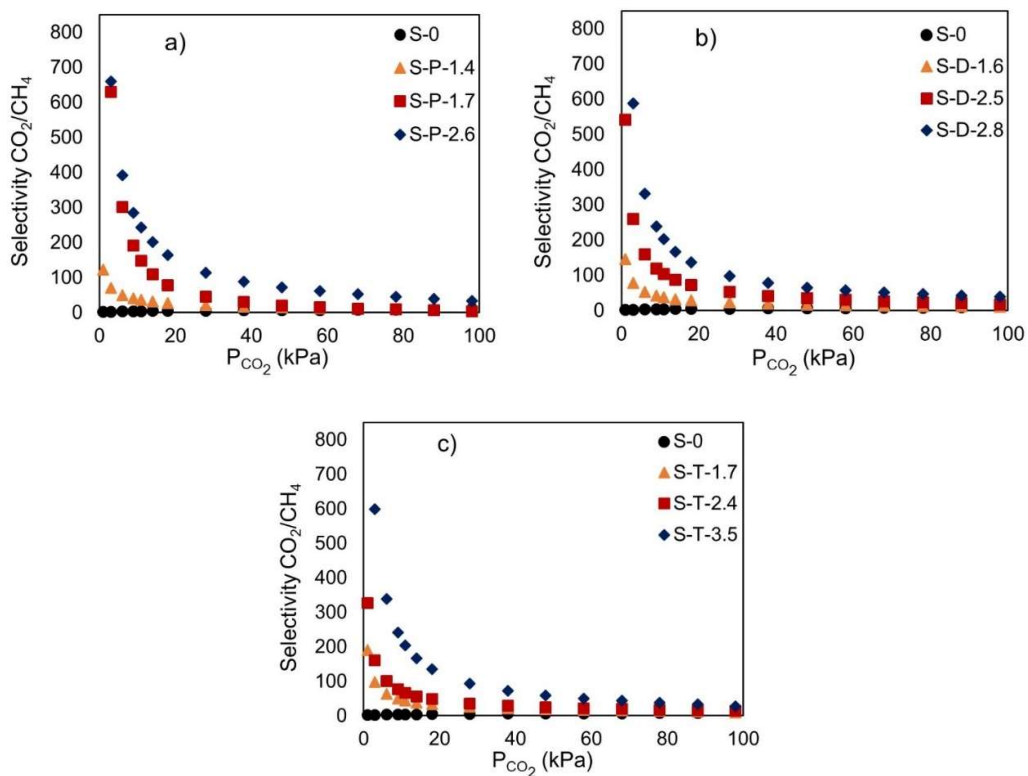


Figure A.6 CO₂:CH₄ selectivity at 40°C up to 100 kPa CO₂ partial pressure for (a) APTES, (b) AEAPT, and (c) TAEPT.

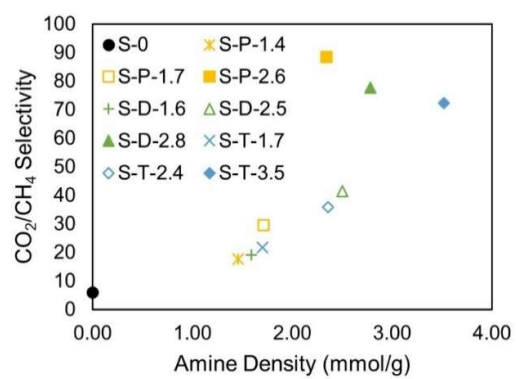


Figure A.7 CO₂/CH₄ Selectivity as a function of amine loading of samples at CO₂ partial pressure of 40 kPa and 40°C

Table A-2. CO₂ and CH₄ adsorption data and associated selectivity of various adsorbents studied within the literature.

Adsorbent	Adsorption Conditions	CO ₂ Adsorption capacity (mmol/g)	CH ₄ Adsorption Capacity (mmol/g)	Reported Selectivity	Ref
Calgon BPL	25C, 120 kPa - multicomponent breakthrough experiments, 50:50 mixture	1.47	0.46	3	219
Norit C	25C, 120 kPa - multicomponent breakthrough experiments, 50:50 mixture	1.50	0.45	3	219
²¹⁹ Pine SawDust	25C, 120 kPa - multicomponent breakthrough experiments, 50:50 mixture	2.00	0.37	5	290
Activated Carbon	30C, 150 kPa - multicomponent breakthrough experiments, 60:40 CH ₄ :CO ₂ mixture	2.14	0.43	7	292
PINPEL20 - AC Carbon from wood pellets					
Zeolite ZSM-5	25C, 100 kPa - pure gas adsorption isotherms	1.78	0.83	4 (Equimolar mixture at 100 kPa)	293
PPB adsorbent	25C, 100 kPa - pure gas adsorption isotherms	~0.60	~0.12	~6 (Equimolar mixture at 100 kPa)	17
Zeolite-13x	20C, 101 kPa - Pure gas adsorption isotherms	~5.00	0.50	15 (Equimolar mixture at 100 kPa)	221
MIL-53(Cr) MOF	30C 2bar - breakthrough measurements, 50:50 mixture	1.20	0.35	3	222
Zeolite-13x	25C, 101 kPa - pure gas adsorption isotherms	4.50	0.50	13 (Equimolar mixture at 100 kPa)	220
MOF-508b	30C, 101 kPa - multicomponent breakthrough experiments, 50:50 mixture	~1.60	~0.40	3	223
APTES-SBA-15	25C 100 kPa - pure gas adsorption isotherms	1.36	0.10	~26	95
APTES-SBA-15	25C 100 kPa - pure gas adsorption isotherms	~0.73	<0.10	25 (Equimolar mixture at 200 kPa)	29
AEAPT-SBA-15	25C 100 kPa - pure gas adsorption isotherms	~1.05	<0.10	1114(Equimolar mixture at 200 kPa)	29
N-3-SBA-15	25C 100 kPa - pure gas adsorption isotherms	~1.35	<0.10	15,000(Equimolar mixture at 200 kPa)	29
S-P-1.4	25C 100 kPa - pure gas adsorption isotherms	0.74	0.05	51	This Work
S-P-1.7	25C 100 kPa - pure gas adsorption isotherms	0.94	0.05	106	This Work
S-P-2.6	25C 100 kPa - pure gas adsorption isotherms	1.28	0.04	240	This Work
S-D-1.6	25C 100 kPa - pure gas adsorption isotherms	0.66	0.06	34	This Work
S-D-2.5	25C 100 kPa - pure gas adsorption isotherms	1.11	0.04	136	This Work
S-D-2.8	25C 100 kPa - pure gas adsorption isotherms	1.55	0.04	374	This Work
S-T-1.7	25C 100 kPa - pure gas adsorption isotherms	0.68	0.06	41	This Work
S-T-2.4	25C 100 kPa - pure gas adsorption isotherms	0.77	0.06	67	This Work
S-T-3.5	25C 100 kPa - pure gas adsorption isotherms	1.45	0.04	276	This Work

Appendix B Chapter 5 Supporting Information

Table B-1 Full compression test results, including the total compressive displacement of synthesised samples.

Sample	Test#	Force (N)	Compressive displacement (mm)	Compressive strain (%displacement)	Compressive stress (MPa)	Standard Deviation
20BE0LU	1	2.3241	0.0742	8.1711	1.3100	0.515
	2	0.5915	0.0376	4.2945	0.3300	
	3	0.3404	0.0257	1.7160	0.1300	
20BE5LU	1	2.1057	0.0628	5.4505	1.1897	0.393
	2	0.5099	0.0307	2.5064	0.2881	
	3	2.7129	0.1039	7.9021	0.9043	
	4	1.5953	0.065	4.0295	0.2849	
20BE10LU	1	0.1480	0.0181	2.5810	0.1873	0.865
	2	0.1466	0.0223	5.6188	0.1856	
	3	0.7589	0.0448	10.1545	0.7988	
	4	4.0775	0.1082	8.8901	2.3037	
25BE0LU	1	3.2609	0.0607	7.9627	3.4325	1.143
	2	1.5081	0.0372	4.3214	1.3346	
	3	0.6963	0.0422	4.6871	0.7330	
	4	1.7638	0.1137	6.3998	0.5617	
25BE5LU	1	6.8763	0.2244	13.0103	2.1899	0.746
	2	1.4587	0.0766	5.0555	0.4645	
	3	2.5264	0.0798	4.3788	0.8046	
30BE0LU	1	3.7007	0.1036	14.901	4.6844	1.348
	2	0.8594	0.0757	6.0291	0.4856	
	3	0.6722	0.0630	5.7245	0.2241	

Appendix C

Table C-1 Isotherm model parameters and regression coefficients

CO ₂	<u>Toth</u>	<u>S-0</u>	<u>S-P-1.4</u>	<u>S-P-1.7</u>	<u>S-P-2.6</u>	<u>S-D-1.6</u>	<u>S-D-2.5</u>	<u>S-D-2.8</u>	<u>S-T-1.7</u>	<u>S-T-2.4</u>	<u>S-T-3.5</u>	<u>S-Sec-1.3</u>	<u>S-Sec-1.6</u>	<u>S-Tert-1.7</u>
	b_{1o}	1.53E-03	4.78E-03	5.00E-03	5.00E-08	2.19E-02	5.30E-03	5.40E-03	5.05E-03	4.98E-03	5.03E-03	4.57E-03	8.60E-07	1.07E-06
	B₁	5.02E-02	1.99E+03	3.45E+03	5.88E+03	1.70E+03	2.29E+03	2.85E+03	2.22E+03	2.30E+03	2.54E+03	2.77E+03	4.16E+03	2.20E+03
	qs_{1o}	3.18E+00	4.23E-01	5.38E-01	1.09E+00	4.99E-01	7.45E-01	7.08E-01	3.43E-01	5.21E-01	1.06E+00	5.90E-01	3.52E-01	1.13E+00
	qst₁	1.77E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	b_{2o}	0.00E+00	7.81E-06	7.41E-06	2.79E-06	1.30E-05	1.53E-05	1.45E-05	1.15E-05	1.27E-05	1.44E-05	1.28E-05	4.38E-05	2.82E-05
	B₂	0.00E+00	1.47E+03	1.41E+03	1.69E+03	1.84E+02	1.04E+03	1.24E+03	4.12E+02	4.54E+02	5.05E+02	4.86E+02	0.00E+00	0.00E+00
	qs_{2o}	0.00E+00	9.87E+01	1.01E+02	9.76E+01	2.83E+02	2.72E+02	2.67E+02	1.97E+02	2.03E+02	2.22E+02	1.98E+02	4.81E+02	2.70E+02
	qst₂	0.00E+00	6.85E+03	6.85E+03	0.00E+00	6.85E+03	6.85E+03	6.85E+03	6.85E+03	6.85E+03	6.85E+03	6.85E+03	1.53E+03	1.53E+03
	t₁	1.36E+01	2.92E-01	2.81E-01	3.74E-01	2.54E-01	3.48E-01	4.39E-01	3.06E-01	3.18E-01	4.17E-01	2.02E-01	6.75E-01	1.11E+00
	t₂	0.00E+00	1.70E-01	1.78E-01	1.62E-01	2.94E-01	1.51E-01	1.55E-01	2.75E-01	2.37E-01	2.31E-01	2.18E-01	1.80E-01	1.16E-01
	X₁	8.21E+00	8.91E+00	8.59E+00	2.17E+00	6.29E+00	2.73E+00	3.64E+00	5.42E+00	5.94E+00	3.41E+00	7.66E+00	9.97E+00	0.00E+00
	X₂	5.43E-02	1.85E+00	2.24E+00	0.00E+00	4.21E+00	1.48E+00	3.98E+00	3.30E+00	2.63E+00	2.20E+00	2.80E+00	0.00E+00	0.00E+00
	R squared	0.99	1.00	1.00	0.99	0.99	1.00	0.99	0.99	1.00	1.00	0.99	1.00	1.00
	ARE* (%)	4	1.6	1.2	4.2	0.2	0.8	1.9	1.1	0.5	3.3	0.5	0.6	3.1
	<u>Henry</u>													
CH ₄	K - 25°C	0.06887	0.05485	0.05569	0.02634	0.06457	0.04687	0.03955	0.05866	0.05938	0.04377	0.04729	0.03944	0.04206
	R squared	1.00	1.00	1.00	1.03	1.01	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	K - 40°C	0.05117	0.04459	0.03836	0.04743	0.03840	0.04325	0.03024	0.03609	0.03533	0.03452	0.03766	0.02750	0.03242
	R squared	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

*Average relative error

The following equations were used to derive the temperature specific parameters of the Toth isotherm for CO₂ adsorption:

$$n_s = q_{s1o} \exp (X_1(1 - (T/T_{ref})))$$

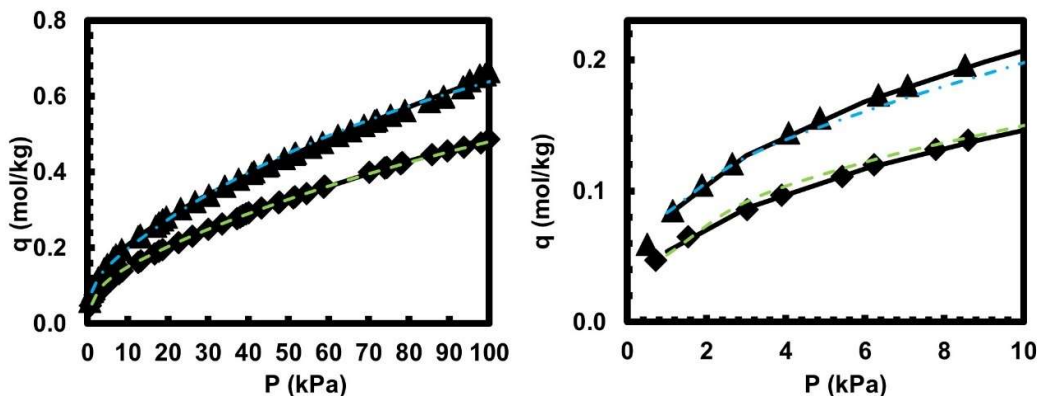
$$n_{s2} = q_{s2o} \exp (X_2(1 - (T/T_{ref})))$$

$$b_1 = b_{1o} \exp (B_1/T)$$

$$b_2 = b_{2o} \exp (B_2/T)$$

Comparison of model fit between the Dual Site Langmuir (DsL) model and modified Toth isotherm used in this work.

S-D-1.6



S-D-2.5

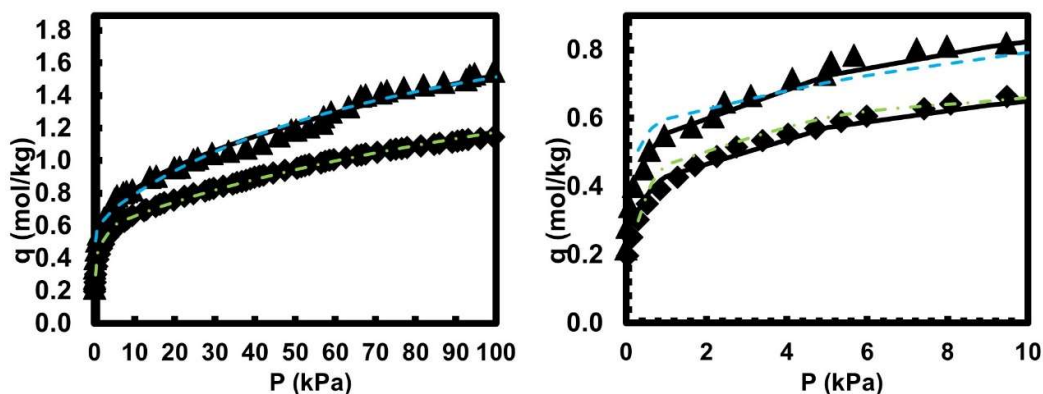


Figure C.1 – experimental CO₂ adsorption data of S-D-1.6 at (▲)25°C and (◆) 40°C. The Toth isotherm model used in this work is represented by (—), while for comparison only, the DsL model at 25°C is represented by (— · —) and at 40°C is represented by (— · —). The Average Relative Error of the DsL method was 2% and 5% for S-D-1.6 and S-D-2.8, respectively. This is in comparison to an ARE of 0.2% and 1.9% using the modified Toth method. This difference is in-line with the available literature, which outline the capability of the Toth model to better describe the low and high pressure region of the commonly used Dual Site Langmuir method for amine functionalised adsorbents, thus providing more accurate fits for experimental data, specifically for high amine loaded materials²¹⁰.

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