The removal of CO$_2$ from gaseous streams using solid sorbents

Thesis presented for award of Doctor of Philosophy (Ph.D.)

By

Emma Daniels (B.Sc.)

University of Limerick

Under the supervision of Dr. T. Curtin

Submitted to College of Science and Engineering
December 2015 Declaration

I hereby declare that the work detailed in this report of the result of my own investigation under the supervision of Dr. Teresa Curtin at the University of Limerick. No part of this thesis has been submitted previously to this or any other university.

__________________________________________________________

Emma Daniels
Abstract

Carbon dioxide (CO₂) is one of a number of gases known as green-house gases which are believed to contribute to global climate change. Anthropogenic sources of CO₂ emissions have increased significantly in the atmosphere. It is believed that the burning of fossil fuels in electric power generation plants is one of the main contributors as in these plants CO₂ is released in the flue gas. This is one of the most serious challenges facing our world.

The current liquid amine scrubber used for CO₂ capture from flue gas stream is inefficient. This work focused on the synthesis of a more efficient solid amine sorbent to remove CO₂ from flue gas streams and also ambient air. Two amines; APTES and TEPA were successfully fixed onto SBA-15, Al-SBA-15 and PE-SBA-15. These solids successfully removed CO₂ from a gas stream from the laboratory test rig. 70%TEPA/SBA-15(I) showed a particularly high capacity and proved stable over 5 CO₂ adsorption/desorption cycles. This solid also successfully captured CO₂ from ambient air with a relative humidity of 89 % and 100 %. This solid is one of the highest capacity solids for CO₂ capture from ambient air.

Two methods of pelletising were investigated. The first method utilised the use of a binder and plasticiser (kaolin and methylcellulose). This method was used to pelletise SBA-15, resulting in cylindrical pellets 1 mm in diameter and 2 mm in length. 70%TEPA/SBA-15(I) was not successfully pelletised using this method, as TEPA was lost during the calcination stage. Therefore the SBA-15 pellets were modified after pellet formation. The second method involved simply pressing 70%TEPA/SBA-15(I) into a circular pellet. The binder based method produced strong, durable pellets, while the self-supported method produced less durable pellets. It is likely that the binder adds strength to the SBA-15 pellets as it bind the SBA-15 particles together into a cohesive unit.

The effect of pressure and temperature were also investigated on 70%APTES/SBA-15(CI) and 70%TEPA/SBA-15(I). Temperature, in particular was found to impact adsorption capacity, while both solids showed high CO₂ uptake at low partial pressures. Overall, the solids showed adsorption characteristics similar to the Dual-
Site Langmuir isotherm model, which is indicative of chemisorption at two adsorption sites. These may be adsorption sites located near the pore moths and further within the solid.
Acknowledgements

Firstly I would like to thank my supervisor Dr. Teresa Curtin for all her support, advice and encouragement during this project.

In particular I would like to thank fellow postgraduate students David Madden and Susan Byrne for their friendship, help, encouragement and support throughout this research. Their friendship and encouragement is particularly valued.

I wish to thank fellow post graduate students and researchers; Jean O’Dwyer, Aideen Dowling, Áine Newell and Michael Ryan, for their empathy, advice and support throughout this project. I would also like to thank my best friends Denise and Quinn for all the chats, pep talks and occasional distractions.

I wish to thank all the laboratory staff in the CES Department and MSSI for their help and support, in particular Bridget Hogan, Wynette Redington and Serguei Belochapkine.

I would like to particularly thank my parents and my sister Sarah for their continued support and encouragement. This would not have been completed without their support.

This project would not have been possible without the funding from the Irish Research Council under the Embark scholarship programme.
Table of Contents

1.0 Introduction................................................................................................................1
1.1 Carbon Dioxide and Global Warming.................................................................1
1.2 Current technologies for CO₂ capture...............................................................6
  1.2.1 Pre-combustion.................................................................................................6
  1.2.2 Oxy-fuel Combustion......................................................................................7
  1.2.3 Post Combustion..............................................................................................7
  1.2.4 Chemical Solvent as CO₂ absorbent...............................................................8
1.3 Porous Solids as Supports.....................................................................................11
1.4 Zeolites as Microporous Solid Supports............................................................11
1.5 Mesoporous Solid Supports.................................................................................13
  1.5.1 Synthesis of SBA-15.......................................................................................13
  1.5.2 Synthesis of SBA-15 with incorporated Al.....................................................15
  1.5.3 Mesocellular foams.......................................................................................17
1.6 Amines....................................................................................................................17
  1.6.1 Amines used in preparing CO₂ adsorbents...................................................18
  1.6.2 CO₂-Amine Interaction...................................................................................19
1.7 Development of amine-modified mesoporous solid supports, as sorbents CO₂ capture...........................................................................................................21
1.8 Characterisation Techniques Theory.................................................................25
  1.8.1 N₂ adsorption/desorption studies.................................................................26
  1.8.2 Thermogravimetric Analysis.......................................................................31
  1.8.3 Atomic Absorption.......................................................................................32
2.0 Aminosilane modified SBA-15, AISBA-15 and Pore expanded SBA-15 as CO$_2$ adsorbents ................................................................. 44
2.1 Introduction ............................................................................. 44
2.2 Experimental ........................................................................ 45
2.2.1 Porous Support Preparation ................................................ 45
2.2.2 Amine Modification .............................................................. 46
2.2.3 Testing of prepared solids for CO$_2$ adsorption/desorption ......... 48
2.2.4 Adsorbent Characterisation ................................................ 50
2.3 Results .................................................................................. 51
2.3.1 CO$_2$ adsorption/desorption analysis of APTES modified-SBA-15 adsorbents ................................................................. 54
2.3.2 CO$_2$ adsorption/desorption analysis of APTES modified-AISBA-15 adsorbents ........................................................................ 62
2.3.3 CO$_2$ adsorption/desorption analysis of APTES modified PESBA-15 adsorbents ................................................................. 66
2.4 Discussion ............................................................................. 68
2.5 Conclusions .......................................................................... 76
2.6 References ............................................................................ 76
3.0 TEPA modified SBA-15 and AlSBA-15 and as CO$_2$
adsorbents.................................................................81

3.1 Introduction.................................................................81

3.2 Experimental.................................................................82

3.2.1 Mesoporous Solid Preparation.................................82

3.2.2 CO$_2$ adsorption/desorption analysis of TEPA modified adsorbents........83

3.2.3 Solid Characterisation................................................84

3.3 Results.................................................................84

3.3.1 CO$_2$ adsorption/desorption analysis of TEPA/SBA-15 adsorbents........84

3.3.2 CO$_2$ adsorption/desorption analysis of TEPA/AlSBA-15 adsorbents.............................91

3.3.3 CO$_2$ adsorption/desorption on 70%TEPA/SBA-15(I).........................................................97

3.4 Discussion...............................................................109

3.5 Conclusion...............................................................115

3.6 References...............................................................115

4.0 TEPA/SBA-15(I) as an adsorbent for removal of CO$_2$ from ambient air.................................................................119

4.1 Introduction...............................................................119

4.2 Experimental...............................................................121

4.2.1 Synthesis of 70%TEPA/SBA-15(I)...........................................121

4.2.2 CO$_2$ adsorption from ambient air.....................................122

4.2.3 Repeated CO$_2$ adsorption/desorption..................................122
4.2.4 Influence of water on CO₂ adsorption/desorption studies .............. 122
4.3 Results .................................................................................................. 123
4.4 Discussion ............................................................................................ 128
4.5 Conclusion ............................................................................................ 131
4.6 References .............................................................................................. 131

5.0 Investigation of CO₂ adsorption by TEPA modified SBA-15 pellets .... 134
5.1 Introduction ............................................................................................. 134
5.2 Experimental .......................................................................................... 137
5.2.1 Pellet Synthesis .................................................................................. 137
5.2.2 Solid Characterisation ......................................................................... 139
5.3 Results ..................................................................................................... 141
5.4 Discussion ............................................................................................... 152
5.5 Conclusion ............................................................................................... 154
5.6 References ............................................................................................... 155

6.0 Investigation of the thermodynamic properties of amine modified SBA-15 CO₂ adsorbents ................................................................. 158
6.1 Introduction .............................................................................................. 158
6.1.1 Adsorption isotherms ......................................................................... 159
6.1.2 Thermodynamics of Adsorption ............................................................ 161
6.1.3 Kinetics of adsorption ......................................................................... 162
6.2 Experimental..............................................................................................162
6.2.1 Adsorbent synthesis................................................................................162
6.2.2 CO₂ Isotherm tests..................................................................................163
6.3 Results.........................................................................................................164
6.3.1 Isotherm studies........................................................................................164
6.3.2 Thermodynamics of CO₂ adsorption on mesoporous amine solids........178
6.3.3 Kinetic parameters....................................................................................179
6.4 Discussion....................................................................................................184
6.5 Conclusion..................................................................................................187
6.6 References..................................................................................................187
7.0 Overall conclusions and recommendations..............................................191

Appendix 1.....................................................................................................195
Appendix 2.....................................................................................................199

List of Figures
Figure 1.1: Atmospheric CO₂ level between 1959 and 2010, at Mauna Lao Observatory.................................................................2
Figure 1.2: CO₂ capture process from a power plant.....................................9
Figure 1.3: Simplified structure of a typical zeolite..........................................12
Figure 1.4: Overall synthesis procedure of SBA-15........................................15
Figure 1.5: Formation of open-cell foams and closed-cell foams..................17
Figure 1.6: Structure of primary, secondary and tertiary amines...................18
Figure 1.7: Structure of APTES .................................................18
Figure 1.8: Structure of TEPA ................................................19
Figure 1.9: Formation of carbamate by reaction of CO$_2$ with primary or secondary amine .........................................................20
Figure 1.10: Surface reaction of amines with CO$_2$ .....................20
Figure 1.11: Mechanism for the reaction between CO$_2$ and tertiary amines .................................................................21
Figure 1.12: IUPAC classification of N$_2$ adsorption/desorption isotherms .................................................................26
Figure 1.13: Hysteresis Loops according to IUPAC classification ....28
Figure 2.1: Testing rig with mass spectrometer ..................................48
Figure 2.2: CO$_2$ profile of a typical run from the test rig using mass spectra detection ............................................................49
Figure 2.3: CO$_2$ calibration plot ..............................................50
Figure 2.4: Nitrogen adsorption/desorption isotherm with pore size distribution, for calcined SBA-15 ........................................52
Figure 2.5: Nitrogen adsorption/desorption isotherms with pore size distribution, for calcined AlSBA ........................................53
Figure 2.6: Nitrogen adsorption/desorption isotherms with pore size distribution, for calcined PESBA-15 ........................................53
Figure 2.7: Typical desorption profile showing CO$_2$ counts detected with temperature .........................................................55
Figure 2.8: CO$_2$ temperature programmed desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min) .........................................................56
Figure 2.9: CO$_2$ adsorption/desorption capacities of APTES/SBA-15(R) sorbents .................................................................57
Figure 2.10: CO$_2$ temperature programmed desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min) .........................................................58
Figure 2.11: CO$_2$ adsorption/desorption capacities of APTES/SBA-15(I) sorbents .................................................................59
Figure 2.12: CO$_2$ temperature programmed desorption profiles of indicated solids
The removal of gaseous streams using solid sorbents (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)…………………………………………………..……..60

Figure 2.13: CO₂ adsorption/desorption capacities of APTES/SBA-15(CI) sorbents…………………………………………………………………………………………………………………………………………………………………………………..61

Figure 2.14: CO₂ desorbed from 70%APTES/SBA-15(CI) during 5 adsorption/desorption cycles (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)……………………………………………..62

Figure 2.15: CO₂ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min)…………………………………………………………………………………………………………………………………………………………………………………..63

Figure 2.16: CO₂ adsorption/desorption capacities of APTES/AlSBA-15(R) sorbents………………………………………………………………………………………………………………………………………………………………………………………………………….64

Figure 2.17: CO₂ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min)……………………………………………………………………………………………………………………………………………………………………………………64

Figure 2.18: CO₂ adsorption/desorption capacities of APTES/AlSBA-15(I) sorbents…………………………………………………………………………………………………………………………………………………………………………………………………………65

Figure 2.19: CO₂ temperature programmed desorption profiles of indicated solids………………………………………………………………………………………………………………………………………………………………………………………………………………………………66

Figure 2.20: CO₂ adsorption/desorption capacities of APTES/AlSBA-15(CI) sorbents………………………………………………………………………………………………………………………………………………………………………………………………………….66

Figure 2.21: CO₂ Adsorption/desorption capacities of APTES/PESBA-15(R) and APTES/PESBA-15(I) adsorbents………………………………………………………………………………………………………………………………………………………………………………………………67

Figure 2.22: Possible silanol arrangements within SBA-15……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..69

Figure 2.23: Siloxane bond formation through dehydration and dehydroxylolation…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………69

Figure 2.24: Simplified structure of AlSBA-15……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..70

Figure 2.25: Possible orientation of APTES molecules attached to Silica/SBA-15…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………71

Figure 2.26: TGA profiles of 70%APTES/SBA-15(CI) and 70%APTES/SBA-15(R), showing weight loss with temperature………………………………………………………………………………………………..72
Figure 2.27: Location of APTES within the pores of SBA-15 for each amine modification method……………………………………………….73
Figure 2.28: TGA profile of 70%APTES/AlSBA-15(CI) and 70%APTES/SBA-15(CI), showing weight loss with temperature…………………74
Figure 2.29: Possible APTES bonding with increased hydroxyl groups in AlSBA-15 adsorbents…………………………………………………….74
Figure 2.30: $T_{\text{max}}$ and adsorption capacities of indicated solids………………75

Figure 3.1: CO$_2$ temperature programed desorption profile of the indicated solids (100 mg adsorbent, 50 ml/ min He flow rate, temperature ramped at 10°C/min).…………………………………………………………………………..85
Figure 3.2: CO$_2$ adsorption/desorption capacities of TEPA/SBA-15(R) sorbents…………………………………………………………………………………..86
Figure 3.3: CO$_2$ temperature desorption profile of the indicated solids (100 mg adsorbent, 50 ml/min He flow rate, temperature ramped at 10°C/min).…………………………………………………………………………..87
Figure 3.4: CO$_2$ adsorption/desorption capacities of TEPA/SBA-15(I) sorbents…………………………………………………………………………………..88
Figure 3.5: CO$_2$ adsorption/desorption capacities following repeated CO$_2$ adsorption/desorption cycles using 70%TEPA/SBA- 15(I)…………………………………………………………………………………..89
Figure 3.6: Weight loss profile of 70%TEPA/SBA-15(I) and unmodified SBA-15 in air……………………………………………………………………………90
Figure 3.7: CO$_2$ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped up to 200°C at 10°C/min).……………………………………………………………………………90
Figure 3.8: CO$_2$ adsorption/desorption capacities of TEPA/SBA-15(CI) sorbents…………………………………………………………………………………..91
Figure 3.9: CO$_2$ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min).……………………………………………………………………………92
Figure 3.10: CO₂ adsorption/desorption capacities of TEPA/AISBA-15(R) sorbents.-----------------------------------------------92
Figure 3.11: CO₂ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min He flow rate, temperature ramped at 10°C/min).-----------------------------------------------93
Figure 3.12: CO₂ adsorption/desorption capacities of TEPA/AISBA-15(I) sorbents.-----------------------------------------------94
Figure 3.13: CO₂ adsorption/desorption capacities of repeated CO₂ adsorption/desorption studies of 40%TEPA/AISBA-15(I).-----95
Figure 3.14: CO₂ adsorption/desorption capacities of TEPA/AISBA-15(CI) sorbents.-----------------------------------------------95
Figure 3.15: CO₂ TPD profiles of 70%TEPA/SBA-15(I) when CO₂ adsorption was conducted at 40, 50, 80 and 100°C, while desorption was conducted up to 150°C.-----------------------------------------------97
Figure 3.16: CO₂ adsorption/desorption capacities of 70%TEPA/SBA-15(I) following repeated CO₂ adsorption/desorption cycles at 200 and 150°C (100 mg sample, adsorption at 50°C).-------------------100
Figure 3.17: Mass spectra taken during CO₂ desorption from the 1st adsorption/desorption cycle at (a) 65°C, (B) 160°C, (C) 200°C and (d) the pre-treatment at 200°C.-----------------------------------------------101
Figure 3.18: Mass spectra taken during CO₂ desorption from the 2nd adsorption/desorption cycle at (a) 65°C, (B) 160°C, and (C) 200°C.-----------------------------------------------102
Figure 3.19: Mass spectra taken during CO₂ desorption from 70%TEPA/SBA-15(I) during the 1st adsorption/desorption cycle at (a) 65°C, (b) 150°C and (c) T_max.-----------------------------------------------103
Figure 3.20: CO₂ desorption from 70%TEPA/SBA-15(I) using the indicated temperature programmed profile. (Initial desorption temperature was 63°C, final desorption temperature was 150°C, 10°C/min).-----104
Figure 3.21: CO₂ desorption from 70%TEPA/SBA-15(I) using the indicated temperature programmed profile. (Initial desorption temperature was 85°C, final desorption temperature was 150°C, 10°C/min).-----105
Figure 3.22: CO₂ desorption from 70%TEPA/SBA-15(I) using the indicated temperature programmed profile. (Initial desorption temperature was 125°C, final desorption temperature was 150°C, 10°C/min)………106

Figure 3.23: CO₂ TPD profiles of 70%TEPA/SBA-15(I), adsorbing the indicated amounts of CO₂ pulses………………………………………………107

Figure 3.24: De-convoluted peaks of 70%TEPA/SBA-15(I) when (a) 1 pulse of CO₂ was adsorbed, (b) 12 pulses of CO₂ were adsorbed, (c) 25 pulses of CO₂ were adsorbed………………………………………108

Figure 3.25: CO₂ adsorption capacities of the indicated tests carried out on 70%TEPA/SBA-15(I) (100 mg solid, adsorption temperature was 50°C, adsorption temperature was 150°C 10°C/min)…………….109

Figure 3.26: TEPA modified solid support……………………………………………………110

Figure 3.27: TEPA modified AlSBA-15…………………………………………………..112

Figure 3.28: Possible location of TEPA molecules in pores at (A) low temperatures and (B) higher temperature …………………………….113

Figure 4.1: CO₂ and H₂O TPD profile from 70%TEPA/SBA-15(I) after 1 hour of ambient air adsorption (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)……………………………………………………124

Figure 4.2: CO₂ and H₂O TPD profile from 70%TEPA/SBA-15(I) after 24 hours of direct air exposure (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)…………………………………….124

Figure 4.3: CO₂ and H₂O TPD profile from 70%TEPA/SBA-15(I) after 1 week of ambient air adsorption (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)………………………………………125

Figure 4.4: De-convoluted peaks from 1 hour, 1 day and 1 week of ambient air exposure………………………………………………………126

Figure 4.5: CO₂ and H₂O TPD profiles after 24 hours direct air exposure at the indicated relative humidities……………………………………..127

Figure 4.6: Repeated ambient air cycles over 2 hours with pump (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)……………………………………………………………128
Figure 5.1: General overview of pelletisation of SBA-15.................................138
Figure 5.2: Pellets cut to 2 mm.................................................................138
Figure 5.3: Nitrogen adsorption/desorption isotherm with pore size distribution
unmodified, calcined binder pellet.........................................................146
Figure 5.4: N$_2$ adsorption/desorption isotherm with pore size distribution, for
calcined SBA-15.......................................................................................146
Figure 5.5: Thermogravimetric analysis profiles of the indicated solids............149
Figure 5.6: Repeated adsorption/desorption studies on pressed pellet of
70%TEPA/SBA-15(I)-P80........................................................................151
Figure 5.7: Thermogravimetric analysis profiles of the indicated solids............153
Figure 6.1: Experimental CO$_2$ adsorption isotherm data on 70%TEPA/SBA-15(I)
at the indicated temperatures (100 mg sample, 50 ml/min He flow
rate, temperature ramped at 10°C/min up to 150°C)...............................165
Figure 6.2: Langmuir CO$_2$ adsorption isotherms and experimental data of
70%TEPA/SBA-15(I) at the indicated temperatures (100 mg sample,
50 ml/min flow rate, temperature ramped at 10°C/min up to
150°C).....................................................................................................166
Figure 6.3: Freundlich CO$_2$ adsorption isotherms and experimental data of
70%TEPA/SBA-15(I) at the indicated temperatures (100 mg sample,
50 ml/min flow rate, temperature ramped at 10°C/min up to
150°C).....................................................................................................167
Figure 6.4: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and
experimental data of 70%TEPA/SBA-15(I) at 30°C (100 mg sample,
50 ml/min flow rate, ramped at 10°C/min up to 150°C).........................169
Figure 6.5: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and
experimental data of 70%TEPA/SBA-15(I) at 40°C (100 mg sample,
50 ml/min flow rate, ramped at 10°C/min up to 150°C).........................169
Figure 6.6: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and
experimental data of 70%TEPA/SBA-15(I) at 50°C (100 mg sample,
50 ml/min flow rate, ramped at 10°C/min up to 150°C).........................170
Figure 6.7: CO$_2$ adsorption isotherm data on 70%APTES/SBA-15(CI) at the
indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped
at 10°C/min up to 200°C)......................................................................172
Figure 6.8: Langmuir modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....173

Figure 6.9: Freundlich modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....174

Figure 6.10: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at 30°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....175

Figure 6.11: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at 35°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 150°C)....176

Figure 6.12: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at 40°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....176

Figure 6.13: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data of 70%APTES/SBA-15(CI) at 50°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....177

Figure 6.14: Isosteric heats of adsorption for 70%TEPA/SBA-15(I) (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 150°C)....179

Figure 6.15: Isosteric heats of adsorption for 70%APTES/SBA-15(CI) (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)....179

Figure 6.16: Breakthrough experimental and Yoon-Nelson modelled data of 70%TEPA/SBA-15(I) at the indicated temperatures...............180

Figure 6.17: CO$_2$ breakthrough and Yoon-Nelson modelled data of 70%TEPA/SBA-15(I) in the indicated mixed gas streams...........181

Figure 6.18: CO$_2$ breakthrough experimental and Yoon-Nelson modelled data of 70%APTES/SBA-15(CI) at the indicated temperatures............182

Figure 6.19: CO$_2$ breakthrough and Yoon-Nelson modelled data of 70%APTES/SBA-15(CI) in the indicated mixed gas streams......184

Figure 6.20: Rate constant ($k_{YN}$) versus temperature for 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI).................................187
List of Tables

Table 1.1: Overview of amine modified mesoporous adsorbents in the literature..............................................................22

Table 2.1: Surface area and pore size characteristics of the parent mesoporous solids..........................................................52

Table 2.2: List of APTES modified SBA-15 sorbents prepared via refluxing..........................................................54

Table 2.3: List of APTES/SBA-15(I) sorbents prepared..............................................57

Table 2.4: Summary of optimum solids..........................................................68

Table 3.1 CO₂ capacities of 70%TEPA/SBA-15(I) when adsorption was conducted at the indicated temperatures..............................96

Table 3.2: CO₂ adsorption/desorption capacities of repeated cycles carried out on 70%TEPA/SBA-15(I) (adsorption temperature 50°C, desorption temperature 150°C).........................................................98

Table 3.3: CO₂ adsorption/desorption capacities of repeated cycles carried out on 70%TEPA/SBA-15(I).................................................99

Table 4.1: Capacities and T_max values of indicated solids.................................126

Table 5.1: Various synthesis conditions of SBA-15 pellets.................................142

Table 5.2: Effect of plasticiser on pellet formation................................................143

Table 5.3: Effect of binder on pellet formation.....................................................144

Table 5.4: Effect of water on pellet formation.....................................................144

Table 5.5: Surface area and pore size characteristics of the indicated solids..145

Table 5.6: Results of binder based amine modified pellets.................................147

Table 5.7: CO₂ adsorption/desorption capacities of the indicated solids............148

Table 5.8: Results of binder-less pressed pellets................................................150

Table 5.9: Mechanical strength of indicated solids.............................................152

Table 6.1: Langmuir constants for CO₂ adsorbed on 70%TEPA/SBA-15(I) ...167

Table 6.2: Freundlich constants for CO₂ adsorbed on 70%TEPA/SBA-15(I).168
Table 6.3: Dual-Site Langmuir constants for CO$_2$ adsorbed on 70%TEPA/SBA-15(I).................................................................171
Table 6.4: Langmuir constants for CO$_2$ adsorbed on 70%APTES/SBA-15(CI)................................................................................173
Table 6.5: Freundlich constants for CO$_2$ adsorbed on 70%APTES/SBA-15(CI)................................................................................174
Table 6.6: Dual-Site Langmuir constants for CO$_2$ adsorbed on 70%APTES/SBA-15(CI).................................................................178
Table 6.7: Yoon-Nelson model parameters for 70%TEPA/SBA-15(I)........181
Table 6.8: Yoon-Nelson parameters for 70%TEPA/SBA-15(I) in indicated gas streams.................................................................182
Table 6.9: Yoon-Nelson parameters for 70%APTES/SBA-15(CI) at indicated temperatures.................................................................183
Table 6.10: Yoon-Nelson parameters for 70%APTES/SBA-15(CI) in indicated gas streams.................................................................184
1 Introduction
1. Introduction

This chapter describes some background information relevant to this research. It will discuss the relevance of CO\textsubscript{2} in the atmosphere, current technologies used to capture CO\textsubscript{2}, porous solids and their characteristics, various amines used in CO\textsubscript{2} capturing technologies and briefly discuss characterisation methods used in this research.

1.1 Carbon Dioxide and Global Warming

Earth is habitable to a vast array of life due to its temperature, which is controlled by the balance between the incoming energy from the sun and the loss of this energy back into space. This balancing act is aided through a phenomenon referred to as the “natural greenhouse effect”, which relies on certain gases such as H\textsubscript{2}O, CO\textsubscript{2}, CH\textsubscript{4}, O\textsubscript{3} and nitrous oxides. These gases are referred to as greenhouse gases (GHG). The energy from the sun is in the form of short-wave radiation such as visible and ultraviolet light. Of the radiation which hits Earth, approximately 30% is reflected back into space. The remaining 70% is mostly absorbed by land and the oceans with a small amount absorbed by the atmosphere. By absorbing this radiation, the Earth’s surface warms up, resulting in the emission of long-wave radiation in the form of infrared radiation. This infrared radiation is absorbed by GHG in the atmosphere, and is then re-radiated back to the lower atmosphere and surface. This process ensures that the Earth’s temperature is around 35°C warmer than it would be if the atmosphere did not exist [1, 2].

Humans exacerbate this natural effect by altering the natural flows of energy through changes in atmospheric composition of GHG [1]. Human activities in the form of burning fossil fuels are believed to be causing an increase in the atmospheric concentration of GHG such as CO\textsubscript{2}. As is illustrated in Figure 1.1, the average CO\textsubscript{2} levels in the atmosphere have continued to rise over the past four decades. The data presented in this figure is recorded as the number of molecules of carbon dioxide divided by the number of all molecules in air; including CO\textsubscript{2} itself, after water vapour has been excluded. The small up and down curve represents seasonal
The removal of gaseous streams using solid sorbents

Emma Daniels

variations. CO₂ levels decrease during spring and summer time in the northern hemisphere as a result of plant growth. However in the winter, plant and leaves die, releasing CO₂ back into the atmosphere causing an increase in CO₂ levels. As most deciduous vegetation is located in the northern hemisphere, the seasonal curve is based on the seasonal data from the northern hemisphere. The overall trend line takes into account these seasonal variations.

Currently the CO₂ content of the atmosphere is rising by 2 ppm per year. Fossil-fuel-fired power generating plants account for 40% of the world’s carbon-derived emissions [3]. With more energy demands expected from developing countries in the near future, this upward trend is likely to continue. Changes in the atmospheric compositions of GHG occur from anthropogenic emissions of these gases, such as CO₂, from the combustion of fossil fuels. Other GHG include methane and nitrous oxide which are produced from numerous human and natural activities. These gases have long atmospheric lifetimes, which results in an accumulation in the atmosphere and a build-up in concentrations of GHG. This can be clearly seen by instrumental

Figure 1.1: Atmospheric CO₂ level between 1959 and 2010, at Mauna Lao Observatory [4]
observations of air samples since 1958 and in bubbles of air trapped in ice cores before then [1]. Besides burning fossil fuels, human induced changes in land use is also known to affect climate and to alter it, for example the large-scale deforestation and desertification in Amazonia and the Sahel where evidence indicates these activities impacted regional climate [1]. Human dependence on fossil fuels for energy most likely will not be met by alternative sources of energy for the foreseeable future, for example, nearly half of the electricity produced in the USA comes from coal combustion [4], and worldwide 85% of our energy is supplied by fossil fuels [3]. Not only are humans dependent on fossil fuels but our demand for oil, coal and gas is steadily increasing.

The United Nations Framework Convention on Climate Change sets a structure for intergovernmental efforts to deal with the climate change threat. Under this convention, governments are encouraged to collaborate and share information on greenhouse gas emissions and policies. Linked to the United Nations Framework Convention on Climate Change is the Kyoto Protocol. This Protocol was the first international agreement between most industrialised countries excluding Australia and the United States of America, to reduce their greenhouse gas emissions. This protocol set binding targets for 37 industrialised countries along with the EU to reduce greenhouse gas emissions [6]. In May 2002, the Kyoto Protocol was ratified in Ireland and all Member States of the EU. Ireland was legally bound to meet the agreed reduction target of greenhouse gas emissions as outlined under the protocol. Under the Kyoto Protocol Ireland's total emissions were limited to 314.18 million tonnes of CO₂ equivalent for the five-year commitment period of 2008-2012. After the first two years of this period Ireland was 1.9 million tonnes above this target. However, Ireland met its Kyoto Protocol target through the use of Kyoto Protocol credits already purchased by the State and use of unused allowances set aside for new developments as outlined in the New Entrant Set Aside scheme under the EU Emissions Trading Scheme. Ireland’s National Allocation Plan (2008-2012) set aside free 8,884,870 allowances to be allocated to new developments due to begin operation before the 31st December 2012 [7].
While it is encouraging that the target was achieved it must be noted that the reduction in emissions can also be partially attributed to the economic crisis which led to a decrease in industrial and commercial activity and therefore a reduction in emissions. The methods for fulfilling the targets from the Kyoto Protocol were implemented through the National Climate Change Strategy [8]. Under the Kyoto Protocol countries agreed to reduce emissions by 2012. After 2012, these countries including Ireland are no longer bound by these commitments and theoretically can start emitting greenhouse gases without regard to their effect on climate change. A legally-binding agreement has not been forthcoming since Kyoto, however the “Bali Action Plan” has been agreed to by over 180 countries. This plan aims to promote “long-term cooperative action” after 2012. More recently at the 2012 UN Climate Change Conference in Doha, Qatar, governments built on previous negotiations and set out a timetable to adopt a universal climate agreement by 2015 which should come into effect by 2020 [9].

The Emissions Trading Scheme (ETS) is a key policy introduced by the European Union in order to reduce emissions of CO$_2$ and other greenhouse gases. The EU ETS commenced in January 2005 and is implemented through distinct phases, also known as “trading periods”. Phase 1 ran between 2005 and 2007 and acted as a learning tool in time for phase 2, which ran between 2008 and 2012. Phase 2 coincided with the first commitment period of Kyoto. Phase 3 will run from 2013 to 2020 and aims to encourage long-term investment in emission reductions [10]. Emissions’ trading is a market-based approach used to limit pollution. Theoretically, this is achieved by creating economic incentives for limiting pollution levels. Typically, a government body sets a limit or cap on the amount of a pollutant that is allowed to be emitted. The relevant limit is allocated or sold to firms in the form of emissions permits. Under the EU Emissions Trading Scheme, GHG from power-generating plants, oil refineries, steel works and production of certain metals, cement, lime, glass, ceramics and some chemicals such as adipic, nitric, glyoxal and glyoxylic acids are limited. Commercial aviation is also subject to the EU ETS. Countries or indeed private investors are also allowed to invest in emission reductions outside their own territory, for which they can gain credits. Take for example Cement Roadstone Holdings’ €210 million investment in its cement plant in Polilsky in the Ukraine.
The kilns in this cement plant were updated, reducing emissions of CO₂. By 2012, a reduction of 3 million tonnes of CO₂ was achieved by this investment [11].

Permits must match the amount of emissions released from a firm, if not, other permits must be purchased from others who did not use all their allowances or heavy fines are imposed. With regards to CO₂, fines are €100 per ton of extra CO₂ released. This transfer of permits is referred to as “a trade”. This essentially means that the buyer is paying a fee for polluting, while the seller is being rewarded for having reduced their emissions. This ensures that pollution reduction is achieved at the lowest cost to society.

The limits for CO₂ in 2013 were set at 2.084 billion allowances, where each allowance is equivalent to one ton of CO₂. Every year after 2013 this limit will decrease by 1.74% of the average total quantity of allowances issued annually in 2005-2012. This will ensure a reduction of emissions so that by 2020 emissions from stationary sources will be 21% lower than in 2005. The aviation allowances have been set at 2.103 billion allowances per year and will remain the same in the trading period between 2013 and 2020. By 2020, emissions from the aviation sector will be 5% below the average annual level of aviation emissions in the 2004-2006 period [12]. Emissions trading schemes can be advantageous as they create incentives in order to achieve targets [13]. Between 2008 and 2012, the number of allowances given out was reduced by 6.5%, however due to the economic downturn emissions were reduced anyway and so demand for allowances decreased further. This led to a surplus of unused allowances, making abatement of emissions less cost-effective [14]. Another potential issue with this trading scheme is “carbon leakage” whereby production processes which are responsible for emitting GHG are moved to other countries with less rigid legislation for GHG emissions reduction. The aim of the trading period between 2013 and 2020 is to resolve these issues and phase out the giving out of free allowances in favour of auctioning allowances.

The penalties associated with emissions have led to more interest in CO₂ capture technologies as a potential way for reducing emissions.
1.2 Current technologies for CO₂ capture

Most power plants utilise pulverised coal as fuel. Firstly, the coal is ground into a fine powder and then burned in the presence of air. The heat produced from this is used to convert water into steam which turns a turbine eventually producing energy. However, newer modern plants employ integrated gasification combined cycle technology which is more efficient than the traditional plants as the coal is not burned but firstly converted into its gaseous components [15]. The CO from this gas stream can be converted to CO₂ through the water-gas shift reaction. Both retro-fit and capital costs for this technology are quite high and so the majority of power plants continue to use the traditional pulverised coal method. This method of producing energy releases vast amounts of CO₂ which is the biggest source of anthropogenic GHG, contributing to global warming.

Carbon Capture and Sequestration (CCS) uses technology to capture, transport and sequester CO₂ from large stationary sources such as power-generating plants. Established scrubbing technology is used to capture CO₂; transport of CO₂ is conducted through a pipeline or by ship and CO₂ is stored in underground structures, such as empty oil wells. It is likely that CCS will play a key role in meeting CO₂ emission reduction targets. There are a number of ways of capturing CO₂ from fossil-fuel-fired power plants. The three main methods of separating CO₂ from the flue gas are: pre-combustion, post-combustion and oxy-fuel combustion [16].

1.2.1 Pre-combustion

Pre-combustion CO₂ capture is the process of removing carbon from the fuel before the combustion process. Typically the hydrocarbon fuel is partially oxidized in steam and oxygen or air under high temperature and pressure to form synthesis gas, which is composed of a mixture of H₂, CO, and some other gaseous species, such as methane [15]. The syngas then undergoes the water-gas shift reaction which converts CO and H₂O to CO₂ and H₂. This results in a H₂ and CO₂-rich gas mixture with a concentration of CO₂ of 15-50%. The CO₂ can then be captured, separated, transported, and re-used or sequestered, while the H₂-rich fuel is combusted [16].
Currently pre-combustion is the most efficient method of separating CO\textsubscript{2} and therefore is also the cheapest. The CO\textsubscript{2} can then be subsequently captured using conventional techniques such as liquid amine scrubbers. Compared to post-combustion; pre-combustion allows a more concentrated stream of CO\textsubscript{2} to be produced at a higher partial pressure, making it much easier to separate from H\textsubscript{2}. However, in the case of coal-fired power plants, pre-combustion capture can only be applied when integrated gasification combined cycle is employed in the power plant [16].

### 1.2.2 Oxy-fuel Combustion

In relation to carbon capture, oxycombustion is a process where the fuel is burned in a mixture of pure oxygen and flue gas, rather than air. Combustion in a N\textsubscript{2}-free gas produces a flue gas mainly composed of water vapour and CO\textsubscript{2} with some low levels of impurities such as SO\textsubscript{x} and NO\textsubscript{x}. The water can be condensed, leaving a highly concentrated CO\textsubscript{2} gas stream which can be further purified and then compressed for transportation or sequestration [17]. There are some disadvantages however, namely; the high cost associated with oxygen production through cryogenic air separation and also energy loss due to large quantities of CO\textsubscript{2} exhaust recycle, which is required to control combustion temperatures [18]. Even though it is possible to retro-fit existing power plants with oxycombustion technology, it requires large capital and operational costs [17].

### 1.2.3 Post Combustion

Post combustion CO\textsubscript{2} capture technology is designed to separate CO\textsubscript{2} from conventional pulverised coal-fired power plants. CO\textsubscript{2} is removed from the flue gas after combustion of the fuel. Pulverised flue gas streams are typically composed of 10-15% CO\textsubscript{2} with the remainder a mixture of N\textsubscript{2}, steam and impurities such as SO\textsubscript{x} and NO\textsubscript{x} [16].

Currently the best CO\textsubscript{2} capture method is absorption using a chemical solvent such as monoethanolamine (MEA). MEA forms a chemical bond with the acidic CO\textsubscript{2} and
thus it is separated from the flue gas. The MEA solvent containing CO$_2$ can be
regenerated by heating. This step is very energy intensive, and can reduce a power
plant’s overall efficiency by up to 30% [19]. This method of CO$_2$ capture is
discussed in more detail below.

1.2.4 Chemical Solvent as CO$_2$ absorbent

Figure 1.2 illustrates a typical system designed to capture CO$_2$ from the flue gas after
combustion of the fossil fuel. Flue gas from the power plant first enters the cooler
(C1). Then the flue gas and lean amine solution, typically around 40 wt %
monoethanolamine in water, contact each other in the absorber (C2). This is where
the amine solution chemically reacts with CO$_2$ from the flue gas. This occurs through
the formation of ammonium carbamate through the following equation:

\[
\text{CO}_2 + 2(\text{R-NH}_2) \rightleftharpoons \text{R-NH-COO}^- + \text{R-NH}_3^+
\]

Equation 1.1

The flue gas is now CO$_2$-free. This CO$_2$-free gas enters a washer where
monoethanolamine droplets are recovered and recycled back into the absorber. The
amine solution carrying CO$_2$–rich amine is sent to the stripper (C4), where the amine
solvent is regenerated by heating the solvent at 110°C-140°C. Heat is required in the
reboiler to heat the solvent to the required temperature; this provides the heat to
desorb the CO$_2$ and to produce steam as steam is used to maintain the regeneration
stage, and is reclaimed in the condenser (C5). Thus CO$_2$ is desorbed from the amine
solvent. Most of the lean amine solution passes through the lean amine cooler, where
it is cooled and then recycled for further carbon dioxide absorption. The separated
CO$_2$ can then be passed to a reflux condenser; where it is passed through a dryer and
purification unit to produce good quality CO$_2$ feed [20].
Physical solvents such as methanol, propylene carbonate, polyethylene glycol, dimethyl ether and dimethyl carbonate can also be used to strip CO$_2$ from the flue gas. Physical absorption relies on the solubility of CO$_2$ in the solvent rather than a chemical reaction between CO$_2$ and the solvent. The solubility of CO$_2$ is dependent on its partial pressure and so physical absorption works on the principle of Henry’s Law. Henry’s Law states that the solubility of a gas is proportional to its partial pressure, so an increase in pressure results in an increase in the rate at which gas molecules interact with the solvent [21]. As absorptive capacity of physical solvents increases with external pressure and decreases with temperature, these solvents are regenerated by increasing temperature or lowering the external pressure [19]. Physical absorption is more suited to Integrated Gasification Combined Cycle (IGCC) based plants and in plants utilising pre-combustion capture technology, where the CO$_2$ can be desorbed mainly by depressurisation. This would avoid the high energy requirements needed to heat amine solvents during the regeneration stage. However, depressurisation of the solvent still results in a significant energy penalty.

Once the CO$_2$ is separated and captured from the flue gas it must be compressed before it can be either re-used as a feedstock or stored. There are a number of
potential storage options: geological storage, storage in the oceans and above-ground storage. Geological storage is the most promising option and is already carried out in the oil industry in a process known as “enhanced oil recovery” where CO$_2$ is injected into depleted oil and gas wells. CO$_2$ can also be stored in saline-filled formations and un-minable coal sites. This is quite possible as Statoil has been injecting the CO$_2$ separated from its production of natural gas into a saline aquifer since 1996 in the North Sea [22]. An innovative way to deal with captured CO$_2$ is currently being applied in the Netherlands involving the horticultural industry. The supply of CO$_2$ captured from a gas-fired cogeneration plant is used to increase crop yield in greenhouses [23]. It has been found that, depending on the crop, production can be increased by 25% by increasing the CO$_2$ concentration to 500 ppm inside the greenhouse. CO$_2$ is also an important raw material in the production of many important chemicals such as methanol, formic acid, dimethyl carbonate, methyl formate and higher hydrocarbons, and also polymeric materials and pharmaceutical chemicals [24].

One of the issues with CCS technology is the expense of capturing CO$_2$, as the liquid amine scrubbing system is still the only commercial technology available at present. Typically MEA is used as the CO$_2$ scrubbing liquid; however it was developed over 70 years ago as a general solvent for removing acid gases from natural gas streams. The major disadvantages associated with this technology are amine degradation and cost of capture and compression. Amine degradation leads to amine loss, foaming, corrosion and the formation of environmentally hazardous compounds. When a CO$_2$ capture system is added to a power plant, its overall thermal efficiency drops from 38.55 to 29.3%. This is caused by the parasitic energy load from the CO$_2$ capture system. This comes from the extraction of steam from the turbine to the stripper during amine regeneration, this steam also raises the temperature of the amine solution to the operating temperature of the stripper, and electricity is also needed to drive the compression of CO$_2$ and also to push the flue gas through the absorber. The drop in thermal efficiency also affects the operational costs of the plant, as 30% more coal must be burned to produce the same amount of electricity, thus increasing the consumption of coal/kWh and an increase in capital investment. These problems could be addressed by using an amine solid sorbent. Amine solid sorbents would
require less energy to regenerate as heating of dilute aqueous amine is no longer required, there would be no corrosion to plant infrastructure and the system could be retrofitted to existing plants [25].

1.3 Porous Solids as Supports

Any material containing cavities, channels or apertures can be regarded as porous materials. These pores can become filled with liquids or gases, and thus have become quite important in the areas of catalysis and adsorption. According to IUPAC porous materials are categorised into three different types of materials based on their pore size; (1) microporous solids containing pores less than 2 nm in diameter, (2) mesoporous materials containing pores with diameters between 2-50 nm, and (3) macroporous materials containing pores bigger than 50 nm in diameter. There are many different types of pore structures and shapes, for example they can be classified as open or closed and be cylindrical, funnel, ink bottle or slit shaped. Porous materials have certain advantages compared to non-porous materials such as their large specific surface areas and high pore volume [26]. These types of materials have been widely investigated as supports and catalysts.

1.4 Zeolites as Microporous Solid Supports

Microporous solids are advantageous for CO$_2$ adsorption as they have high surface areas and exhibit size selectivity of molecules. Zeolites are aluminosilicate crystalline solids with microporous cavities, channels and pores. They occur naturally, usually in basaltic and volcanic rock and in sedimentary deposits. Zeolites were first discovered by a Swedish mineralogist named Axel F. Cronstedt in 1750. The material he first worked on is thought to be stilbite, which is now known to be a class of zeolite [27]. The term zeolite was formed from two Latinised Greek words “zeo” and “lithos” which means “to boil a stone” as Cronstedt noticed that this mineral swelled when heated. From this discovery many studies were conducted on zeolites and their ability for adsorption and cation exchange has been thoroughly investigated. The first definite synthesis of a zeolite material was recorded in 1948 by Richard M. Barrer. This led to the discovery of a number of commercially
The removal of gaseous streams using solid sorbents

significant zeolite types in the 1950s such as zeolite A, X and Y by Robert M. Mitten and Donald W. Breck. This culminated in 1962 when Mobil Oil introduced the use of synthetic zeolite X as a hydrocarbon cracking catalyst. Since then, the use of zeolites has continued to grow in industry, with approximately 367,000 tonnes of zeolite material used as an industrial catalyst by 2008 [28].

Structurally, zeolites are complex crystalline structures with an infinitely extending three or four dimensional framework of AlO$_4$ and SiO$_4$ tetrahedra linked together through oxygen ions. The ways in which these tetrahedral are arranged are virtually limitless and thus, hundreds of zeolite structures are known [28]. When some of the Si$_4^+$ is replaced by Al$_3^+$ ions, an excess negative charge is created; this negative charge must be balanced by a cation as presented in Figure 1.3. These non-framework cations can be carefully selected and are central to a zeolite’s catalytic nature.

Zeolites can be specifically tailored for CO$_2$ adsorption by cation exchange or modification by loading an amine into the pores. However, the small pore sizes may limit the amount of amine which can be loaded onto zeolites and thus limit CO$_2$ adsorption abilities. A major disadvantage of zeolites is the preferential adsorption of water over CO$_2$ in flue gas streams containing moisture. This can limit a zeolite’s ability to adsorb CO$_2$ [29].
1.5 Mesoporous Solid Supports

Mesoporous solids are advantageous for CO$_2$ adsorption as they have larger pore sizes, allowing amine modification for CO$_2$ capture. The larger pores compared to zeolites may facilitate the loading of larger amine molecules and/or higher amounts of amine onto the solid, thus increasing CO$_2$ adsorption capacity.

The discovery of silicate/aluminosilicate mesoporous materials by Mobil Oil in 1992 was the first time a high surface area mesoporous solid, containing a regular array of pore arrangement with a narrow pore size distribution, was synthesized. Mobil Composition of Matter No.41 (MCM-41) is perhaps the most famous member of the family of mesoporous solids known as M41S. MCM-41 was created using quaternary ammonium surfactants [30]. In more recent times, Santa Barbara Amphorous (SBA) mesoporous materials were prepared using polyethylene-polypropylene oxide as surfactant under acidic conditions.

1.5.1 Synthesis of SBA-15

1996 saw the discovery of mesoporous silicates with pore sizes of 4 nm to 30 nm. These were first produced in the University of California, Santa Barbara. This material was subsequently called SBA, and has proven popular as a molecular sieve in medicinal applications, catalysis and biosensor technology.

The most popular method of producing SBA-15 and silica has been the template-directed sol-gel route. This was the approach also utilised in this research. This process results in the condensation of Si(OH)$_4$ molecules, forming siloxane bonds. Typically, alkoxy silanes such as tetraethylorthosilicate (TEOS) have been used as the silica precursor. Poly (ethylene oxide) poly (propylene oxide) poly (ethylene oxide), also known as P123, is the most commonly used surfactant in SBA-15 synthesis. P123 is composed of hydrophobic (polypropylene) and hydrophilic parts (polyethylene), thus creating micelles with the hydrophobic part in the centre with the hydrophilic ends outwards facing the solution. It is around these templated micelles that the silica network is formed [31].
Silica synthesis is centred on the measured condensation of Si(OH)$_4$ species. In reality, hydrolysis and condensation processes occur at the same time. In order to get a rapid hydrolysis, acidic or basic conditions are required. Acid catalysed hydrolysis, as was undertaken in this research, proceeds by an $S_N$2 type of reaction. The leaving alkoxy group is quickly protonated while a water molecule performs a nucleophilic attack on the silicon atom. Condensation also occurs by the reaction of the alkoxy silanes with a silanol group, releasing an alcohol as illustrated in Equation 1.2.

$$=\text{Si-OH} + \text{RO-Si}= \rightarrow =\text{Si-O-Si}= + \text{ROH} \quad \text{Equation 1.2}$$

As hydrolysis and condensation occur simultaneously, the rate of both processes determines the structure. Under acidic conditions, condensation is slower than hydrolysis. The rate of condensation slows with increasing number of siloxane linkages around a central silicon atom. This results in weakly branched polymeric networks. However, in basic conditions, condensation is faster compared to hydrolysis and so highly branched networks with ring structures are formed.

The next stage is referred to as gelation, whereby the solution thickens to a gel-like substance as the polymeric network extends throughout the solution. The rate of this process determines the initial pore structure. During the ageing process, when the gel is kept in contact with the liquid, with the liquid filling the pores, its structures and properties continue to change with time. Different processes occur during this stage, such as; polycondensation, syneresis, coarsening and phase transformation, these affect the resulting pore structure and surface area of the silicate. Polycondensation is the further reaction of silanols and alkoxy groups to form siloxane bonds, hardening the siloxane network. Syneresis is the expulsion of the pore liquid, caused by the condensation of surface groups inside the pores and thus the pores narrow. Coarsening occurs as small particles are deposited and then brought back into solution and re-deposited on larger particles, causing the links between particles to elongate and causing small pores to be filled in; this can increase the average pore size and decrease specific surface area.
The next stage in the synthesis is the drying stage, in which the pores are emptied of liquid during which pore shrinkage occurs. The final changes in pore size, pore size distribution and surface area occur during this stage. The final heat treatment is the calcination stage in which the surfactant is removed [31], thus forming pore channels.

Figure 1.4 illustrates the overall procedure of SBA-15 synthesis. Firstly the surfactant lines up with the hydrophobic end located in the centre. This results in rod-like structures which aggregate hexagonally. It is around these hexagonal structures that the silica network condenses. Calcination removes the surfactant leaving pore channels.

![Figure 1.4: Overall synthesis procedure of SBA-15 [32]](image)

1.5.2 Synthesis of SBA-15 with incorporated Al

While SBA-15 has larger pore sizes compared to zeolites, it also has low acidic strength and is non-active catalytically. Acid sites, such as aluminium, can be introduced into SBA-15 [33]. There are a number of ways of introducing Al into mesoporous materials. One of the first methods reported, was the introduction of zeolite structure-building units into the mesoporous synthesis. This is typically how AlMCM-41 materials were initially synthesized.

However, this method needs to be controlled quite carefully, as MCM-41 materials are synthesized under alkaline conditions, which favours the formation of zeolite structure rather than mesoporous structure. As a result, a mixture of zeolite and
MCM-41 properties can be formed [34]. SBA-15 has thicker walls, larger pores and higher stability than MCM-41, so it was decided to incorporate Al into SBA-15 rather than MCM-41 in this work. It was also decided to use an aluminium salt as an Al precursor rather than zeolite-starting material in this research to ensure the formation of a mesoporous solid.

A high acidic medium is required when synthesizing SBA-15, however this can limit the amount of Al incorporated, so strict controls regarding pH is necessary when synthesizing Al-SBA-15 [35]. Zukal et al proposed that the formation of the hexagonal mesophase occurs under acidic conditions through following the $S^0\mathrm{H}^+\mathrm{X}^-\mathrm{I}^+$ mechanism where S is the non-ionic surfactant, $\mathrm{X}^-$ denotes halogen anions and $\mathrm{I}^+$ the protonated SiO$_2$ species. At acidic pH, the alkylene oxide groups of the surfactant are solubilized and the hydronium ions are associated with the alkylene oxygen atoms. As the point of zero net charge of silica is at pH 2, the silica species are positively charged by proton abstraction at low pH. The charged alkylene oxide units and the cationic silica species interact together by electrostatic, hydrogen bonding, and van der Waals interactions, this can be designated as $(S^0\mathrm{H}^+)(\mathrm{X}\mathrm{I}^+)$ [34]. When the surfactant and silica species are protonated, the positively charged silica species undergo partial condensation and form the associated mesostructure through the counter anion ($\mathrm{X}^-$) with the cationic surfactant species. When the pH of the synthesis medium rises above the zero net charge of silica, the silica species are subsequently negatively charged, thus enhancing the interaction with the Al(OH)$_2^+$ species, as the concentration of H$^+$ decreases in the synthesis gel, the concentration of aluminium hydroxyl species increases, allowing the partially condensed silica species to form Al-O-Si bond with Al(OH)$_2^+$ species when the pH is equal to 2 or more [36].

All silicon atoms in SBA-15 usually exist in an oxidation state of +4; however aluminium typically exists in an oxidation state of +3. When Al is incorporated into the SBA-15 framework the aluminium-oxygen tetrahedra form centres with a negative charge. To balance this negative charge an OH group is used to balance the charge using the H$^+$ atom. The OH groups located near the AlO$_4$ tetrahedra are considered strong Brønsted acids [29].
1.5.3 Mesocellular foams

A relatively new material known as mesocellular foams (MCFs) are mesoporous siliceous materials with ultra large pores, usually around 30 nm. They contain a continuous 3-D pore system which is interconnected through windows [37]. They are typically formed in a similar synthesis procedure as SBA-15, with the addition of a pore-swelling agent such as mestylene. The pore-swelling agent and the PEO amphipilic block copolymer form a micro-emulsion, from which the MCF is templated. The swelling agent enlarges the hydrophobic PPO blocks of the template, increasing pore size while maintaining the overall cylindrical structure of the mesophase. The spherical cell diameter is controlled by the pore-swelling agent: block copolymer ratio. The nature of the foams can be controlled by the synthesis conditions, for example using basic conditions “closed-cell” pore systems are formed whereas in acidic conditions “open-cell” pore systems are formed as depicted in Figure 1.5 [26]. Open-celled foams are much more useful for amine modification and subsequent CO₂ adsorption as gas flow through the pores is uninhibited.

![Diagram of foam formation](image)

**Figure 1.5:** Formation of open-cell foams and closed-cell foams [38]

1.6 Amines

Amines are organic compounds which contain nitrogen. This nitrogen atom is the key atom in the amine functional group. Amines resemble ammonia (NH₃), where one or more hydrogen atoms have been replaced by alkyl or other hydrocarbon
groups. The number of alkyl groups attached to the nitrogen atom in an amine determines the classification of the amine. Primary amines have one alkyl group attached to the nitrogen, a secondary amine has two alkyl groups and tertiary amines have 3 alkyl groups as shown in Figure 1.6. The nitrogen atoms in amines are sp³ hybridised and also contain a lone pair of electrons. Due to the lone pair of electrons, amines are both basic and nucleophilic [39].

![Figure 1.6: Structure of primary, secondary and tertiary amines](image)

### 1.6.1 Amines used in preparing CO₂ adsorbents

Two amines were used in this study; 3-aminopropyltriethoxysilane (APTES) and tetraethylenepentamine (TEPA) for the adsorption of CO₂. There are a number of differences between these amine groups. APTES is a primary amine with ethoxy silane groups while TEPA is considered to have 2 primary amine groups and three secondary amines. TEPA also lacks any ethoxy silane groups.

The molecular structure of APTES is presented in Figure 1.7. The presence of the silanol anchoring group makes APTES quite stable as the form siloxane bonds with the mesoporous support. This is especially useful when attaching APTES molecules onto solid supports. It’s molecular weight is 221 g/mol while its overall molecular length is 0.8 nm.

![Figure 1.7: Structure of APTES](image)
Tetraethylenepentamine (TEPA) is a low molecular amine with a molecular weight of 77.09 g/mol. TEPA possesses 5 amine functional groups: 2 primary amine entities and 3 secondary amines as shown in the molecular structure in Figure 1.8. The size of a TEPA molecule is 0.12 nm.

![Figure 1.8: Structure of TEPA](image)

TEPA lacks the anchoring ethoxy groups as seen in APTES, this inhibits the covalent attachment of TEPA to silica surfaces and so TEPA is held to the surface through weaker hydrogen bonds between surface OH groups and an amine group.

### 1.6.2 CO₂-Amine Interaction

CO₂ is considered an inorganic carbonyl. The reactivity of carbonyl compounds is due to the polarity of the carbonyl group which results from oxygen being more electronegative than carbon. The carbonyl carbon is an electrophile and so reacts more readily with nucleophiles, such as amines [39].

The CO₂-amine chemistry in the liquid phase has been established. It is believed that the interaction between CO₂ and amine results in the formation of ammonium carbamates, ammonium bicarbonates and carbamic acid [40]. This is the same for both primary and secondary amines. Caplow’s zwitterionic method is the most widely accepted as the most accurate mechanism. This mechanism consists of two steps (1) formation of the zwitterion and (2) the base-catalysed deprotonation of the zwitterion [41]. Figure 1.9 presents a schematic of carbamate formation via a zwitterion intermediate. The initial step begins when the lone pair on the amine attacks the carbon of CO₂, resulting in the formation of a zwitterion. The second step is achieved when a free base deprotonates the zwitterion thus forming the carbamate as illustrated in Figure 1.9 [42]. In an aqueous system the base can be another amine, H₂O or OH⁻.
It is widely believed that the above mechanism is also applicable to amines immobilised onto solid supports with a free amine as the base needed to deprotonate the zwitterion, again it is the same process for both primary and secondary amines. This implies that in a dry gaseous system, the amount of CO$_2$ adsorbed is limited to 1 mole of CO$_2$ for every 2 moles of amine, forming ammonium carbamate while this is increased to 2 moles of CO$_2$ for every 2 moles of amine in the presence of water as depicted in Figure 1.10, resulting in the formation of ammonium bicarbonate.

![Figure 1.9: Formation of carbamate by reaction of CO$_2$ with primary or secondary amine](image)

![Figure 1.10: Surface reaction of amines with CO$_2$](image)

When tertiary amines are involved it is thought that a different mechanism is undertaken involving the hydration of CO$_2$ by a base acting as a catalyst. The tertiary amine dissociates H$_2$O forming a cationic species and OH$^-$. A hydroxide ion then
attacks CO$_2$ forming a bicarbonate anion concluding with the ionic association of the protonated amine and bicarbonate as shown in Figure 1.11 [42].

![Reaction Mechanism](image)

**Figure 1.11**: Mechanism for the reaction between CO$_2$ and tertiary amines [42]

### 1.7 Development of sorbents for CO$_2$ capture

A review of previous work was carried out to identify potential composite materials, methods and mechanisms of CO$_2$ adsorption. The focus of this section is to highlight the development of mesoporous solids as supports for amine solid sorbents for CO$_2$ capture. Table 1.1 presents a brief summary of some of the amine-modified mesoporous adsorbents found in the literature.

Silica gels modified with amines for CO$_2$ adsorption were first used by Tsuda and Fujiwara in 1992. They discovered that incorporating APTES onto silica resulted in a sorbent capable of adsorbing CO$_2$. APTES was introduced onto the silica by refluxing in xylene for a number of hours. These sorbents were used for CO$_2$ capture under anhydrous conditions [41].

Leal reported the use of amine functionalised mesoporous silicas for CO$_2$ adsorption in 1995. Silane chemistry was employed to immobilise propyl amine groups onto
The removal of gaseous streams using solid sorbents

Emma Daniels

mesoporous silica gel [43]. Xu et al first reported the use of amine-impregnated silica for CO$_2$ capture in 2002. The branched polymer polyethylenimine (PEI), which contains branched chains with numerous amino groups, was impregnated onto MCM-41 at various wt % loadings. Adsorption studies were conducted at 75°C and it was found that 75 wt % loading of PEI onto MCM material resulted in the best CO$_2$ capacity sorbent, with an adsorption capacity of 133 mg/g adsorbent [44]. Since then many studies and developments into these sorbents have been undertaken. Hiyoshi also investigated the potential of APTES modified SBA-15 sorbents for CO$_2$ capture. This sorbent adsorbed between 18-80 mgCO$_2$/g of sorbent [45]. David and co-workers also investigated APTES/SBA-15 as CO$_2$ adsorbents and found similar CO$_2$ adsorption capacities [46].

Table 1.1: Overview of amine modified mesoporous adsorbents in the literature

<table>
<thead>
<tr>
<th>Support</th>
<th>Amine</th>
<th>CO$_2$ capacity mg/g adsorbent</th>
<th>Desorption Temperature °C</th>
<th>Cycles</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>PEI</td>
<td>13-79</td>
<td>120</td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td>Silica</td>
<td>APTES</td>
<td>20</td>
<td>100</td>
<td></td>
<td>[42]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>PEI</td>
<td>107</td>
<td>100</td>
<td></td>
<td>[44]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>TEPA</td>
<td>173</td>
<td>100</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>MSPs</td>
<td>EDA</td>
<td>102</td>
<td>120</td>
<td>16</td>
<td>[48]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>TEPA</td>
<td>221</td>
<td>100</td>
<td>6</td>
<td>[50]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>APTES</td>
<td>50</td>
<td>25-120</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>AISBA-15</td>
<td></td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>[34]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>APTES</td>
<td>18-80</td>
<td>100</td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>HMS</td>
<td>PEI</td>
<td>128-184</td>
<td>75</td>
<td>4</td>
<td>[51]</td>
</tr>
</tbody>
</table>
Huang and colleagues carried out a study developing selective solid sorbents for CO$_2$ removal from natural gas mixtures. MCM-48 was functionalised with APTES. At room temperature it was found that the sample adsorbed 50 mg CO$_2$/g of sorbent. CO$_2$ adsorption on unmodified MCM-48 was also undertaken and this sorbent adsorbed much less (14 mg/g of sorbent). These results indicate that amine-modified MCM-48 has a strong affinity to CO$_2$ due to weak chemical interactions between the basic amine groups and CO$_2$ molecules. Desorption tests were carried out by heating the sorbents from 25°C-120°C. It was found that when the sample reached 75°C, CO$_2$ desorbed completely [47].

Amines without the anchoring silanol groups, such as EDA, TEPA and PEI were also investigated as it was thought that their linear shape would allow deeper penetration into the pores of mesoporous supports. Diamines have been investigated as potential amines for CO$_2$ capture. Ethylenediamine is the most commonly used diamine. In a study by Lu et al, ethylenediamine was loaded onto mesoporous spherical silica. Adsorption was undertaken at 60°C and desorption occurred at 120°C, with a maximum CO$_2$ adsorption of 102 mg/g. This sorbent also underwent 16 adsorption/desorption cycles with CO$_2$ adsorption remaining constant, suggesting this particular amine solid is reasonably stable [48]. An interesting discovery from this study was the identification of increased CO$_2$ adsorption with increasing influent CO$_2$ concentration, meaning that CO$_2$ adsorption becomes more efficient with higher CO$_2$ concentrations. Yue and co-workers investigated TEPA modified SBA-15 as potential sorbents. This sorbent adsorbed 173 mg/g, which was much more than APTES modified sorbents. This may be explained by the increased number of potential CO$_2$ binding sites in TEPA [49]. Yue et al also carried out research on efficient CO$_2$ adsorbents using TEPA supported on MCM-41. A number of advantages were identified for this amine solid, chiefly an increased CO$_2$ adsorption capacity compared to aminosilane modified solids. In this study impregnation was used to fix TEPA onto MCM-41. CO$_2$ desorption occurred between 90 and 100°C. Initially adsorption capacity in a pure stream of CO$_2$ was 211 mg/g sorbent, while the initial capacity in a 5% CO$_2$ stream was 200 mg/g. This sorbent underwent 6 adsorption/desorption cycles in the 5% CO$_2$ stream, with CO$_2$ adsorption capacity
decreasing to 183 mg/g in the final cycle [50]. Polyethylenimine is also a commonly studied amine for CO$_2$ capture. It is a polymer with a repeating amine group. PEI can be a linear or branched molecule. Chen and co-workers investigated PEI modified hexagonal mesoporous silicas (HMS). PEI was introduced onto HMS by impregnation methods, using different PEI wt %. A 45 wt% PEI had a CO$_2$ adsorption capacity of 128 mg/g, when the PEI loading was increased up to 60 wt %, the adsorption ability increased to 184 mg CO$_2$/g sorbent. This is one of the highest CO$_2$ adsorption abilities reported in the literature for this type of amine modified solid. Adsorption and desorption occurred at 75°C and was stable over 4 repeated adsorption/desorption cycles with [51]. Other studies have also shown PEI to be a suitable amine for CO$_2$ adsorption, and in general this amine shows good CO$_2$ adsorption ability typically between 82 and 105 mg CO$_2$/g sorbent.

Other materials such as ionic liquids, membranes and activated carbons are showing potential as possible sorbents for CO$_2$ capture. There are a number of advantages of using activated carbons (AC) as adsorbents. These materials are inexpensive in comparison with other solid adsorbents and are also insensitive to moisture. Furthermore, they are heat resistant and radiation resistant, while also being stable in acidic and alkaline solutions. There are however some disadvantages as activated carbons have decreased adsorption capacity at moderately high temperatures, for example its CO$_2$-adsorption capacity drops dramatically at temperatures common in power-plant flue gases which are in the region of 50–120°C [24, 52].

Ionic liquids are salts with melting points below the boiling point of water. They usually consist of an organic cation and inorganic anion. They are highly flexible as different properties can be acquired by using different cations or anions. Ionic liquids have the advantage that desired properties can be created by altering the cations, anion or substituent ions. Another advantage of ionic liquids is the negligible evaporation losses due to their relatively low vapour pressures [53].

Membrane gas absorption uses appropriate absorption liquids in conjunction with porous polypropylene hollow fibre membranes for carbon dioxide removal.
This method has received some attention due to the fact that it combines the advantages of absorption, such as high selectivity with numerous advantages of membranes such as modularity and small size. This is especially advantageous for power plant flue gases [23]. One of the most important requirements in a membrane absorber is a porous, water repellent, polymeric membrane. The gas phase and liquid phases are kept separated by the hydrophobicity of the membrane. The flue gas stream is fed along one side of the membrane. The components to be removed from the gas stream (i.e. CO$_2$) will diffuse through the gas-filled pores of the membrane. Once on the other side of the membrane they will be absorbed into the absorption liquid. There are certain advantages to this membrane absorber system, such as: in packed/tray columns, issues arise such as foaming, flooding and entrainment, however in a membrane absorber set-up the gas and liquid flow are independent resulting in avoidance of such problems. There is no need to have a wash section after the absorber in order to recover absorption liquid which is carried over, as this is no longer a problem. This method results in equipment that will be compact through the use of hollow fibre membrane. Another crucial requirement is a suitable combination of absorption liquid and membrane. It is necessary that the pores remain gas-filled; this is facilitated by the hydrophobicity and pore characteristics of the membrane material. PTFE membranes appear to be the most suitable for this purpose. The most suitable conditions for membrane methods are in small to medium scale separations and also when product purity requirements are not particularly stringent [54]. While there are some advantages with this technology such as a simple flow configuration and low-maintenance operation, membrane systems cannot compete with current amine systems for most carbon dioxide removal applications. This is because of the low selectivity of current membranes [55].

1.8 Characterisation Techniques Theory

Various methods were used to characterise the unmodified porous supports and the amine modified supports. N$_2$ adsorption/desorption results were used to determine surface area, pore size and pore volume. Fourier transform infrared spectrometry was used to detect the presence of silanol and amine functionalities. Thermogravimetric
analysis was used to determine amine loadings on modified supports, while atomic absorption spectrometry was used to calculate the amount of Al incorporated into AlSBA-15.

1.8.1 $N_2$ adsorption/desorption studies

$N_2$ adsorption/desorption analysis can be used to determine a number of key characteristics of solids; such as surface area, pore size, pore size distribution and pore volume. These are obtained from adsorption and desorption results. Adsorption measurements are obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature, while desorption measurements are obtained by measuring gas removed as pressure is reduced. Figure 1.12 illustrates the 6 isotherms classified by IUPAC [56].

![Figure 1.12: IUPAC classification of $N_2$ adsorption/desorption isotherms [57]](image)}
The Type 1 isotherm Reversible Type I isotherms are given by microporous solids having relatively small external surfaces. A Type I isotherm is concave to the \( \frac{p}{p^o} \) axis and the amount adsorbed approaches a limiting value. This limiting uptake is governed by the accessible micropore volume rather than by the internal surface area. A steep uptake at very low \( \frac{p}{p^o} \) is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at very low \( \frac{p}{p^o} \).

Type II isotherms are given by the physisorption of most gases on nonporous or macroporous adsorbents. The shape is the result of unrestricted monolayer-multilayer adsorption up to high \( \frac{p}{p^o} \). Point B, the beginning of the middle near linear section, usually corresponds to the completion of monolayer coverage.

Type III isotherm, there is no Point B and therefore no identifiable monolayer formation; the adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favourable sites on the surface of a nonporous or macroporous solid. In contrast to a Type II isotherm, the amount adsorbed remains finite at the saturation pressure.

Type IV isotherms are given by mesoporous adsorbents (e.g., many oxide gels, industrial adsorbents and mesoporous molecular sieves). The adsorption behaviour in mesopores is determined by the adsorbent-adsorptive interactions and also by the interactions between the molecules in the condensed state. In this case, the initial monolayer-multilayer adsorption on the mesopore walls, which takes the same path as the corresponding part of a Type II isotherm, is followed by pore condensation.

Type V isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent-adsorbate interactions. At higher \( \frac{p}{p^o} \), molecular clustering is followed by pore filling. For instance, Type V isotherms are observed for water adsorption on hydrophobic microporous and mesoporous adsorbents.
- Type VI isotherm is representative of layer-by-layer adsorption on a highly uniform nonporous surface. The step-height now represents the capacity for each adsorbed layer, while the sharpness of the step is dependent on the system and the temperature [57-59].

Hysteresis loops in the multilayer range of physisorption isotherms are associated with capillary condensation in mesoporous adsorbents. From these hysteresis loops, pore shape can be identified. Figure 1.13 presents the four different types of hysteresis loops. These hysteresis loops may display a wide variety of shapes. H1 type is associated with capillary condensation and desorption in open-ended cylindrical mesopores. The width of the hysteresis loop increases with increasing mesopore size. H2 type hysteresis is associated with materials of ill-defined pore size and shape, typically oxide gels and porous glass materials. H3 and H4 hysteresis is associated with porous materials with plate-like particles and slit-shaped pores, respectively [57-59].

![Hysteresis Loops](image)

**Figure 1.13:** Hysteresis Loops according to IUPAC classification [57]
Determining Surface Area:

Irving Langmuir first hypothesised that surface area could be determined by calculating the amount of adsorbate adsorbed on an adsorbent’s surface, as a function of partial pressure or concentration at a given temperature. Kinetics played a key role in the evolution of this theory as it is based on the principle that the rate of adsorption is dependent on the pressure and the amount of adsorption sites, while desorption is dependent on the number of occupied sites and the energy of activation. There are a number of assumptions in this theory; such as; the energy of adsorption for the first layer is usually much larger than for the second or subsequent layers, therefore implying that multilayer formation of adsorbate is only possible at higher pressures, resulting in an irregular isotherm. This occurs in only one isotherm, Type VI, however this model cannot be reconciled with all the known stepwise isotherms, making it a limited method of calculating surface area [56].

Brunauer, Emmett and Teller expanded on Langmuir’s idea to form the BET method of determining surface area. The BET method includes the possibility of multilayer formation with the following assumptions: firstly; gas molecules can adsorb onto a solid in indefinite amount of layers with infinite thickness, secondly; the adsorbed molecules on one layer can act as adsorption sites for other molecules and thirdly the Langmuir equation can be applied to each layer. The BET equation is illustrated in Equation 1.3.

\[
p/v_a (p^o - p) = 1/v_m \cdot C + (C-1)p/v_mC.p^o
\]

Equation 1.3

\(v_a\) is the number of moles adsorbed per gram adsorbate at gas pressure \(p\), \(v_m\) is the monolayer capacity of the surface. It is calculated when Equation 1.3 is applied in the pressure range of 0.05 to 0.30, \(p^o\) is the saturation pressure while \(C\) is the BET constant. Using the monolayer capacity, the specific surface area \(S_{\text{BET}}\) can be calculated from Equation 1.4, where \(n^a\) is Avogadro’s number, \(a_{m}\) is the molecular cross sectional area of adsorbate gas molecule.

\[
S_{\text{BET}} = v_m.a_m.n^a.10^{-20} \text{ (m}^2/\text{g})
\]

Equation 1.4
There are limitations to the BET method as it assumes that all the adsorption sites involved in multilayer formation are energetically identical and that all layers after the first layer possess liquid-like properties and there can be up to a 20% divergence in accuracy of surface area. Despite these limitations it is still the most common method used as it is applicable to most adsorption sites [56-61].

Pore Size and Pore Size Distribution:

Between 1945 and 1970 quite a few different mathematical procedures were proposed for the derivation of pore size and pore size distribution. All of these hypotheses were based on the application of the Kelvin equation, which is depicted in Equation 1.5:

\[ r_K = \frac{-2\gamma V_m}{RT \ln (p/p_0)} \]  

Equation 1.5

Where \( \gamma \) is the surface tension of nitrogen at 77K, \( V_m \) is the molar volume of liquid nitrogen; \( R \) is the gas constant, \( T \) the boiling point of liquid nitrogen and \( P/P_o \) the relative pressure of nitrogen.

The Kelvin radius \( r_K \) does not equal the actual pore radius as multilayer adsorption occurs before capillary condensation, resulting in a pore narrowing. Therefore, it is more accurate to include the thickness of the adsorbed layer, which brought about the BJH method of determining pore size:

\[ r_p = r_K + t \]  

Equation 1.6

Where \( r_p \) is the actual radius of the pore, \( r_K \) is Kelvin radius of the pore and \( t \) is the thickness of adsorbed layer. The thickness of the adsorbed film is calculated from numerous equations including the Halsey equation, the generalised Halsey equation and the deBoer equation.
Barrett, Joyner and Halenda also derived a model for determining pore size distribution. This model is based on two assumptions; (1) the pores are cylindrical and (2) the amount of adsorbate in equilibrium with the gas phase is retained by the adsorbent by either physical adsorption on the walls or by capillary condensation. The model is represented in Equation 1.7:

\[
V_{Pn} = R_n \Delta V_n - R_n \Delta t_n \Delta t_n \sum_{j=1}^{n-1} c_j A_{pj}
\]

Equation 1.7

Where \( V_{Pn} \) is pore volume of the \( n \)th desorption step, \( R_n \) is the radius at the \( n \)th desorption stage, \( \Delta V_n \) the change in volume, \( \Delta t_n \) the change in thickness and \( c_j A_{pj} \) the average area from which the adsorbed gas desorbed [39, 59-62].

**Pore volume**

The pore volume, \( V_p \), is derived from the amount of vapour adsorbed at a relative pressure close to unity (typically \( p/p_0 \) of 0.95), by assuming that the pores are filled with the adsorbate in the bulk liquid state, by applying the Gurvich rule. The calculation for pore volume is illustrated in Equation 1.8:

\[
V_{liq} = P_a V_{ads} V_m / RT
\]

Equation 1.8

\( V_{liq} \) is the volume of liquid nitrogen in the pore, \( P_a \) is the ambient pressure, \( V_{ads} \) is the volume of gas adsorbed, \( V_m \) is the molar volume of the liquid adsorbate and \( RT \) is the gas ideal constant and ambient temperature.

1.8.2 **Thermogravimetric Analysis**

In thermogravimetric analysis (TGA), a substance is heated and its mass is recorded as a function of temperature. Most TGA experiments are conducted in inert atmospheres. This allows for the analysis of pyrolysis. In air, components will be combusted and therefore lost from the sample at different temperatures, thus allowing analysis of % compositions of certain materials. TGA relies on three
measurements; mass change, temperature and temperature change. TGA can also be used to determine the thermal stability of a material.

1.8.3 Atomic Absorption

In atomic spectroscopy, a substance is decomposed into atoms in a flame or furnace. This is achieved by vaporising the sample at 2,000-8,000 K causing the liquid to evaporate and the remaining solid is atomised in the flame. Concentrations of atoms in the vapour are measured by absorption of certain wavelengths of radiation. Atomic absorption is sensitive enough to distinguish one element from another in a complex sample. The relationship between absorbance, concentration and length of the light path is known as Beer-Lambert’s law:

\[
A = \varepsilon cl
\]

Equation 1.8

A is the absorbance of the sample \((\log Io/I)\), c refers to the concentration of the sample in moles/litre and \(\varepsilon\) is the molar absorptivity \((\text{litre mol/L cm}^{-1})\).

The concentration of an absorbing species in a sample is determined by Beer’s Law; which states that absorbance is proportional to the concentration of the absorbing species; however this is usually difficult to measure in atomic absorption so concentration is typically determined by the use of a calibration curve of known standard concentrations [63,64].

1.8.4 Mass Spectrometry

When J.J. Thomson first determined the mass-to-charge ratio in the 1890s, the principles of mass spectrometry were established. Mass spectrometry is a method of studying the masses of atoms, molecules or fragments of molecules. The mass spectrometer is composed of 5 important components (1) the sample inlet, which brings the sample to be analysed to the mass spectrometer, which leads to (2) the ion source where the molecules of the sample are converted into gaseous ions, these are
accelerated by an electromagnetic field, which leads to (3) the mass analyser which separates the ions based on their mass-to-charge ratios, m/z. These ions are counted by (4), the detector and the data is recorded by the (5) data system. The output from the data system is known as the mass spectrum, which is typically a graph of the number of ions detected as a function of their m/z ratio [65].

The most common method for converting sample molecules to ions is electron ionisation (EI) whereby, a beam of high energy electrons is emitted from a filament that is heated to several thousand degrees, emitting electrons which are accelerated at a voltage of 70 V, creating electrons with an energy of 70 eV (electron volts). After an electron is accelerated through an electric field, it gains kinetic energy [59]. The kinetic energy of an accelerated ion is determined as:

\[
\frac{1}{2}mv^2 = zV
\]  

Equation 1.9

Where m is the mass of the ion, v is the velocity of the ion, z is the charge on the ion and V is the potential difference of the ion-accelerating plates [63-67].

These high energy electrons strike the stream of uncharged, neutral molecules (M) that has been admitted from the sample inlet system, removing an electron from the molecule, creating a cation as shown below:

\[
e^- + M \rightarrow M^+ + 2e^- 
\]  

Equation 1.10

This creates a positively charged molecular ion. In a vacuum, at 70 eV, these interactions between electrons and molecules can leave some molecules with so much extra energy that they begin to fragment, giving ions of differing mass.

\[
e^- + M \rightarrow M^+ + 2e^- + A^+ + B^+ 
\]  

Equation 1.11
All molecules have a characteristic fragmentation pattern and can be used to identify compounds. The mass of an electron is quite small compared to the total mass of the molecule; hence the relative molecular mass of a molecule is almost the same as that of the molecular ion. Thus $\text{Mr} = \text{Mr}^+$, and so is known as $\text{M}^+$. An ion of a given mass with a single positive charge ($z = 1$), has a mass to charge ratio of:

$$\frac{m}{z} = \frac{m}{1} = m$$  \hspace{1cm} \text{Equation 1.12}

Therefore, the mass to charge ratio is equal to the mass of the ion [67]. Most elements also have more than one isotope; whereby the nuclei have the same atomic number but different mass numbers due to different numbers of neutrons. Mass spectrometry is a great tool for distinguishing between different isotopes, for example; CO$_2$ comes in three different masses, depending on the isotopic makeup as C has two isotopes ($^{12}\text{C}$ and $^{13}\text{C}$), and O has 3 isotopes ($^{16}\text{O}$, $^{17}\text{O}$ and $^{18}\text{O}$). Most commonly available CO$_2$ has a molecular mass of 44, however CO$_2$ containing a $^{13}\text{C}$ instead of $^{12}\text{C}$ atom and two $^{16}\text{O}$ atoms has mass 45. It is also possible that CO$_2$ can contain an $^{18}\text{O}$ instead of $^{16}\text{O}$ oxygen isotope, resulting in a mass of 46. There are CO$_2$ molecules that contain a $^{13}\text{C}$ and an $^{18}\text{O}$, or even two $^{18}\text{O}$ atoms, however these are extremely rare. The relative abundance of isotopologues (molecules of the same material but with different isotopes in them) helps determine which elements contribute to a particular molecular formula [66, 67].

### 1.9 Aim and Scope of thesis

The first aim of this research is to synthesize a high capacity solid capable of adsorbing CO$_2$ over repeated CO$_2$ adsorption/desorption cycles. CO$_2$ adsorption studies will be done on a test rig with a simulated flue gas stream and also from ambient air. The second aim of this research is to pelletise the solid, as any industrial application will need the solid in pellet form. The final aim of this research is the investigation of the thermodynamic and kinetic characteristics of CO$_2$ adsorption on an amine modified solid.
1.10 References


The removal of gaseous streams using solid sorbents

Emma Daniels


The removal of gaseous streams using solid sorbents

union of pure and applied chemistry, physical chemistry division, commission on colloid and surface chemistry, subcommittee on characterization of porous solids, 66 (8), 1739–1758


The removal of gaseous streams using solid sorbents


2 Aminosilane modified SBA-15, AlSBA-15 and pore expanded SBA-15 as CO$_2$ adsorbents
2 Aminosilane modified SBA-15, AlSBA-15 and Pore expanded SBA-15 as CO$_2$ adsorbents

2.1 Introduction
Mesoporous materials have many potential uses in a wide variety of applications including; environmental remediation, catalysis, electronics and medical applications [1-8]. Mesoporous materials such as SBA-15 have a number of advantages as an adsorbent material, such as; reasonably large pore sizes, allowing the mesoporous materials to interact with bigger molecules, and large surface areas resulting in a great number of potential binding sites dispersed within the pore structure [4, 5]. CO$_2$ adsorbents must possess the capability for fast adsorption and desorption kinetics, large adsorption capacity, selectivity for CO$_2$ over other components in the gas stream and an ability to be regenerated and remain stable over time [7]. Mesoporous materials possess these attributes, making them ideal potential CO$_2$ adsorbents. The substitution of Al into the mesoporous framework of SBA-15 introduces Brønsted acidity into the structure [9-12]. Mesoporous aluminosilicates thus have the advantages of mesoporous silicas and the acidity usually associated with zeolites. Expanding the pores of mesoporous materials increases the pore size which may lead to higher amine uptake during amine modification processes. This may increase CO$_2$ adsorption capacity.

Adsorption is considered the most promising means of stripping CO$_2$ from fossil fuel fired power plants [13]. In its simplest form, adsorption can be described as the attachment of particles to a solid surface. Adsorption and desorption processes are also extremely important in catalysis. The following steps are usually found in these processes; diffusion of sorbate to catalyst surface, diffusion of sorbate into the pores, adsorption of the sorbate on the inner surface of the pores, chemical reaction between sorbate and catalyst surface, desorption of product from the catalyst surface and diffusion of product out of the pores [13-15]. These steps may also be applied to CO$_2$ adsorbents, where the sorbate is CO$_2$, and instead of forming a product; the carbamate is formed between the CO$_2$ and the amine-modified catalyst surface. During regeneration the CO$_2$ is released and the amine is restored.
In this work, SBA-15, SBA-15 incorporated with Al (AlSBA-15) and pore expanded SBA-15 (PESBA-15) were modified with 3-aminopropyltriethoxy silane (APTES). A number of amine modification techniques were utilised; refluxing, impregnation and capillary impregnation. This chapter discusses the influence of the mesoporous support and amine modification technique in the preparation of APTES adsorbents for CO$_2$ adsorption. This work also highlights the influence of APTES loading in the preparation of these CO$_2$ adsorbents. The performance of a high capacity adsorbent was selected for repeated adsorption/desorption studies in order to establish the stability and reusability of the APTES adsorbent.

2.2 Experimental
All materials used in the synthesis of porous supports were obtained from Sigma Aldrich. All materials and chemicals were used as received excluding toluene, which was dried before use.

2.2.1 Porous Support Preparation
Mesoporous silica (SBA-15), mesoporous silica with incorporated Al (AlSBA-15) and pore expanded SBA-15 (PESBA-15) were prepared by hydrothermal means as outlined below.

*Mesoporous silica (SBA-15)*
SBA-15 was prepared by dissolving 12 g of surfactant (P123) in 90 g de-ionised water. To this, 360 g of 2M HCl was added. This was stirred for 2 hours at 40°C. Subsequently, 24 g tetraethylorthosilicate (TEOS) was added as a silica source. This solution was stirred for 24 hours at 40°C. This white solution was then placed into an autoclave at 80°C for 3 days. The resulting mixture was filtered using a Buchner funnel and washed with several volumes of distilled water. The resulting white powder was dried overnight at room temperature. This was then calcined at 550°C in flowing air at 20 ml/min. The temperature ramp rate was 5°C/min and was held for 8 hours [16, 17].
Mesoporous silica with incorporated Al (AlSBA-15)

AlSBA-15 was synthesized according to a procedure reported elsewhere [18-21]. This involved dissolving 4 g of P123 in 30 g of water for 4 hours at room temperature. To this, 1.75 g of 2M HCl and a further 70 g of de-ionised water were added. This was stirred at 40°C for 2 hours. Then 9 g TEOS and 1.26 g aluminium isopropoxide was added. This solution was stirred for 20 hours at 40°C. The resulting mixture was aged for 2 days at 100°C in a Teflon lined steel autoclave. This solution was then filtered and washed with distilled water. The resulting powder was dried overnight at room temperature and then calcined in air at a flow rate of 20 ml/min by heating to 500°C at 5°C/min. The temperature was then held at 550°C for 8 hours.

Pore expanded SBA-15 (PESBA-15)

PESBA-15 was prepared as outlined by Chang et al [17]. Typically 12 g P123 was added to 90 ml de-ionised water, which was stirred at room temperature for a number of hours to allow the surfactant to dissolve. Then 3.6 ml tri-methyl benzene was added at 20°C which acted as a micelle expander. This was allowed to stir for 2 hours after which 25 ml of TEOS was added as the silica precursor. This solution was kept at 20°C for 22 hours. The white solution was then aged at 80°C for 3 days in a steel autoclave with a Teflon liner. It was then filtered and washed with several volumes of water. This was then calcined in flowing air at 20 ml/min and held at 550°C for 8 hours. The temperature ramp rate was 5°C/min.

2.2.2 Amine Modification

Pure silica is not able to adsorb much CO₂ as the hydroxyl groups do not provide strong interactions with CO₂. However, this deficiency is overcome by surface modification with amines which provide specific adsorption sites for CO₂ [22, 23]. There are a number of ways to introduce amines onto mesoporous solids. In this research, various modification methods have been investigated. These include; refluxing, impregnation and capillary impregnation. Each of these is described as follows.
Refluxing

The prepared mesoporous solids were modified with APTES through post synthesis grafting/refluxing. Firstly the calcined support (SBA-15, AISBA-15 or PESBA-15) was dried at 150°C for 16 hours, to remove adsorbed CO\textsubscript{2} and water. Toluene was dried over zeolites for 1 hour prior to sorbent synthesis. An appropriate amount of APTES was dissolved in 25 ml of dried toluene for 30 minutes. This was then added to approximately 1 g of dried support and refluxed at 110°C for 2 hours. This suspension was filtered in a Buchner flask and washed with toluene to remove unreacted silane molecules. A number of wt % loadings of amine on silica samples were prepared by this method. This is illustrated in Scheme 1 in the Appendix.

Impregnation

Before impregnation was carried out, SBA-15, AISBA-15, PESBA-15 and toluene were dried as previously outlined. An appropriate amount of APTES was dissolved in 25 ml dried toluene for 30 minutes. To this, 1 g of the mesoporous solid was added. This suspension was stirred for 2 hours at room temperature. The solvent was then removed using a rotary vacuum evaporator. The resulting powder was dried in the oven at 110°C for 1 hour. As before, various wt % loadings of APTES on the mesoporous support were prepared. This is illustrated in Scheme 2 in the Appendix.

Capillary Impregnation

This method is similar to impregnation; however a much smaller amount of synthesis solution is used; just enough to fill the pores of the solid support. This may allow better distribution within the pores. The required amounts of APTES and toluene are introduced in a volume corresponding to the pore volume of the support which in this study was found to be approximately 1 ml/g. Therefore, appropriate amounts of APTES were dissolved in less than 1 ml of dried toluene. For example 70%APTES/SBA(CI) was synthesised using 0.30 g toluene plus 0.7 g APTES. This amine solution was then added drop wise to 1 g of support and stirred until all the support had been wetted by the amine solution. This sometimes produced a gel like substance which was then dried at 110°C for 16 hours in a vacuum oven. Various concentrations of APTES in toluene solution were utilised where the % of APTES in the solid’s name denotes the wt % of APTES with respect to the amount of solid support. This is illustrated in Scheme 3 in the Appendix.
2.2.3 Testing of prepared solids for CO$_2$ adsorption/desorption

The APTES modified mesoporous solids were analysed for their CO$_2$ adsorption/desorption ability using an on-line testing rig with mass spectroscopy detection. The mass spectrometer was an Agilent Technologies 5975C inert MSD with Triple-Axis Detector. The rig is presented in Figure 2.1 and consists of a gas delivery system, a reactor housed in an oven and a mass spectrometer. The sample to be tested was placed in a quartz reactor; typically 100 mg sample was used. The sample was kept in place by two plugs of quartz wool. The reactor was then inserted into the furnace of the rig and fixed into place by attaching screws on each end of the reactor. Once the reactor was loaded, a flow of helium was sent through the reactor at a rate of 50 ml/min.

Figure 2.1: Testing rig with mass spectrometer

Figure 2.2 presents a typical CO$_2$ profile recorded by the mass spectrometer. Once the reactor was loaded into the furnace, it was heated to 200°C at 10°C per minute with helium flowing at 50 ml/min. The temperature was held at 200°C for 5 minutes. This is known as the “pre-treatment” step and is carried out to remove any adsorbed water and CO$_2$ that may have accumulated on the mesoporous sample while exposed to the atmosphere. The first peak in Figure 2.2 is associated with this “pre-treatment” step and shows the desorption of CO$_2$. The temperature of the furnace was then allowed to cool to 30°C. Once the furnace was cooled, a number of CO$_2$ pulses (15%
CO₂ in He) were sent into the reactor to quickly determine CO₂ adsorption ability. The sample was then saturated with CO₂ to ensure that all adsorption sites were utilized by flowing 15% CO₂ in He over the adsorbent for 5 minutes. Following this CO₂ saturation step the CO₂ stream was stopped and replaced by helium. Once the CO₂ levels had reached zero, the “CO₂ desorption” step could begin. This step was carried out by heating the now CO₂ saturated adsorbent to 200°C at 10°C/min. This resulted in a CO₂ temperature programmed desorption (CO₂ TPD) profile. All subsequent graphs and calculations are derived from this step of the adsorption/desorption cycle tests. Once this CO₂ peak had levelled out, a pulse of CO₂ from the sample loop was passed directly to the mass spectrometer which was necessary for calibration purposes. The peak areas from the desorption and calibration pulses were used to calculate the amount of CO₂ desorbed by the sample which is indicative of the amount which was adsorbed.

![CO₂ profile of a typical run from the test rig using mass spectra detection](image)

**Figure 2.2:** CO₂ profile of a typical run from the test rig using mass spectra detection

To calculate the quantity of CO₂ desorbed from an adsorbent it was necessary to calibrate the test rig. This was done by injecting various quantities of pure CO₂ onto an adsorbent in a similar fashion as previously outlined, typically 0.5 ml up to 2 ml.
The adsorbed CO$_2$ was subsequently desorbed from the adsorbent allowing the peak areas to be measured. A calibration graph of CO$_2$ area counts versus mg CO$_2$ could then be constructed as shown in Figure 2.3. This calibration line allowed the quantification of CO$_2$ desorbed from the various samples.

The gas from the reactor was continuously monitored using the Agilent 5975 MS. A range of ions could be monitored; in particular ions 18, 28, 32 and 44 which correspond with the molecular masses of H$_2$O, N$_2$, O$_2$ and CO$_2$ respectively, were measured constantly. The MS also allowed the detection of other ions throughout the run cycle as well as the option to retrieve complete mass spectra for any ion during a test.

![Figure 2.3: CO$_2$ calibration plot](image)

**2.2.4 Adsorbent Characterisation**

Both unmodified and amine modified solids were characterised by various techniques, which are outlined below.

*Nitrogen adsorption/desorption analysis*

Nitrogen adsorption/desorption analysis was carried out on a Quantachrome Autosorb AS-1. This was done to determine the pore volume, pore size distribution and surface area of the un-functionalised SBA-15, AISBA-15 and PESBA-15 solids. Before analysis, approximately 100 mg of the sample was
outgassed at 150°C for 16 hours. This sample was then analysed for its surface area, pore volume and pore radius. Surface area was calculated using the Brunauer-Emmet-Teller method, pore size was determined using the Barrett, Joyner and Halenda method and the Kelvin equation was used to determine pore radius.

**Atomic Absorption**

Atomic absorption (AA) was carried out on AlSBA-15 to investigate the presence of aluminium. From a 1000 ppm stock solution, 1 ppm, 10 ppm, 25 ppm, 100 ppm and 250 ppm aluminium standards were made. 50 ml potassium nitrate was added to each to suppress ionisation of aluminium. Each of these were analysed to give a standard curve from which the aluminium content of AlSBA-15 could be calculated. In preparation for analysis, 50 mg AlSBA-15 was dissolved in aqua regia and then made up to the mark with deionised water in a 100 ml volumetric flask. This solution was then analysed. Acetylene was used as the fuel with a lamp current of 10 mA.

**Thermogravimetric Analysis**

Thermogravimetric analysis was carried out on a SDT Q600 TGA. A baseline had to be established before analysis; this was done by carrying out a typical run with an empty crucible. This was then subtracted from the sample TGA. A sample of approximately 8 mg was placed into an alumina crucible and weighed in the internal balance of the SDT Q600. The sample was heated up to 700°C in air at a heating rate of 10°C/min with the weight continuously recorded. The data was then imported into Excel to create the temperature-weight loss profiles.

**2.3 Results**

All porous supports were characterised by nitrogen adsorption/desorption analysis to determine surface area, pore volume and pore size. Table 2.1 illustrates these characteristics. Figures 2.4-2.6 illustrate the N₂ adsorption/desorption isotherms and pore size distribution profiles of SBA-15, AlSBA-15 and PESBA-15, respectively. All samples showed type IV isotherms with a hysteresis loop which is indicative of capillary condensation in the pores which is a characteristic of mesoporous solids. The hysteresis loops observed in all solid supports was type H1 indicating the
The removal of gaseous streams using solid sorbents

Emma Daniels

presence of open ended cylindrical shaped pores [23]. SBA-15 was found to have pore sizes averaging 8 nm, AISBA-15 average pore size was 11 nm while PESBA-15 was found to have an average pore size of 32 nm with a wide pore size distribution. The surface areas were 656, 796 and 420 m$^2$/g for SBA-15, AISBA-15 and PESBA-15, respectively. All testing was carried out at standard temperature and pressure.

**Table 2.1:** Surface area and pore size characteristics of the parent mesoporous solids

<table>
<thead>
<tr>
<th>Support</th>
<th>Surface Area, m$^2$/g</th>
<th>Pore size, nm</th>
<th>Pore Volume, cc/g</th>
<th>Al Content, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>656</td>
<td>8</td>
<td>0.991</td>
<td>0</td>
</tr>
<tr>
<td>AISBA-15</td>
<td>796</td>
<td>11</td>
<td>0.998</td>
<td>7</td>
</tr>
<tr>
<td>PESBA-15</td>
<td>420</td>
<td>32</td>
<td>2.709</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 2.4:** Nitrogen adsorption/desorption isotherm (STP) with pore size distribution, for calcined (550°C for 8 hours) SBA-15
Figure 2.5: Nitrogen adsorption/desorption isotherms (STP) with pore size distribution, for calcined AlSBA-15

Figure 2.6: Nitrogen adsorption/desorption isotherms (STP) with pore size distribution, for calcined (550°C for 8 hours) PESBA-15
2.3.1 CO₂ adsorption/desorption analysis of APTES modified-SBA-15 adsorbents

Three modification methods were used to modify SBA-15. The first series of solid adsorbents to be discussed are those prepared via refluxing. Five sorbents were prepared using the refluxing method with APTES as the amine and SBA-15 as the porous support. Table 2.2 lists these sorbents and their corresponding amounts of APTES used during the preparation of each solid. Each sorbent is named to include the wt % APTES, the support used and the method of amine-modification. For example 10%APTES/SBA-15(R) is a sorbent which was prepared by refluxing 1 g of SBA-15 with 0.1 g of APTES and 25 ml dried toluene. The synthesised 10%APTES/SBA-15(R) sample does not necessarily contain 10 wt % APTES as some can be lost during the preparation method.

Table 2.2: List of APTES modified SBA-15 sorbents prepared via refluxing

<table>
<thead>
<tr>
<th>Name</th>
<th>APTES g/Solid g</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%APTES/SBA-15(R)</td>
<td>0.1/1.0</td>
<td>Reflux</td>
</tr>
<tr>
<td>20%APTES/SBA-15(R)</td>
<td>0.2/1.0</td>
<td>Reflux</td>
</tr>
<tr>
<td>40%APTES/SBA-15(R)</td>
<td>0.4/1.0</td>
<td>Reflux</td>
</tr>
<tr>
<td>50%APTES/SBA-15(R)</td>
<td>0.5/1.0</td>
<td>Reflux</td>
</tr>
<tr>
<td>70%APTES/SBA-15(R)</td>
<td>0.7/1.0</td>
<td>Reflux</td>
</tr>
</tbody>
</table>

Each of the solids shown in Table 2.2 was tested for their ability to adsorb and subsequently desorb CO₂. A typical desorption profile is illustrated in Figure 2.7. From this figure it can be seen that CO₂ desorption starts at about 60°C and maximum CO₂ desorption (Tmax) occurs at 110°C and by 150°C most of the CO₂ has been desorbed. There also appears to be a shoulder around 80°C, which may be due to various adsorption sites or different amine-CO₂ interactions. From this CO₂ temperature programmed desorption (TPD) profile, the amount of CO₂ desorbed can be calculated by determining the peak area and using the CO₂ calibration data as shown in Figure 2.3.
Figure 2.8 presents the CO$_2$ TPD profiles of all APTES/SBA-15(R) sorbents, listed in Table 2.2. These are derived from the desorption step of the CO$_2$ adsorption/desorption analysis for each sorbent. For each sorbent, the temperature and associated abundance of desorbed CO$_2$ is illustrated. Desorption typically occurred between 50 and 150°C. As is shown in Figure 2.8, 50%APTES/SBA-15(R) had the highest amount of released CO$_2$ during the desorption step. Increasing the amine level in the synthesis solution above 50%, i.e. 70%APTES/SBA-15(R), resulted in a solid that desorbed less CO$_2$.

![Desorption profile](image)

**Figure 2.7:** Typical desorption profile showing CO$_2$ counts detected with temperature

Figure 2.9 summarises the CO$_2$ adsorption/desorption ability in terms of mgCO$_2$/g of sorbent for each APTES/SBA-15(R) sorbent and is plotted with its associated theoretical wt % loading of APTES. 50%APTES/SBA-15(R) desorbed the highest amount of CO$_2$ during the desorption step (26 mgCO$_2$/g of sorbent), indicating that this is the optimum loading. It is interesting to note that increasing the APTES content from 40% to 50% (a relatively modest increase) resulted in a significant increase (7 fold increase) in CO$_2$ adsorption capacity. This may be due to the lack of adequate amine groups located closely together to interact with CO$_2$ in a 2:1 fashion at the lower amine loadings. 50%APTES/SBA-15(R) desorbed the highest amount of CO$_2$ during the desorption step (26 mgCO$_2$/g of sorbent). It is possible that the increased amine concentration in the synthesis solution used to prepare a solid with a
The removal of gaseous streams using solid sorbents

Emma Daniels

higher amine content than that of 50% i.e. 70%APTES/SBA-15(R) caused APTES agglomerates to form. These agglomerates would not be able to fix onto SBA-15 and thus would be lost during the heat treatment reducing the amine content of the solid and thus lowering CO$_2$ adsorption capacity. It is also possible that the increased APTES concentration in the synthesis solution of 70%APTES/SBA-15(R) results in pore blocking which would inhibit and thus lower CO$_2$ adsorption capacity. There appears to be an increase in desorption temperature with increasing CO$_2$ uptake. This may be attributable to the higher volume of CO$_2$ exiting the pores which may take more time which may appear as a higher $T_{max}$.

**Figure 2.8**: CO$_2$ temperature programmed desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)
Figure 2.9: CO₂ adsorption/desorption capacities of APTES/SBA-15(R) sorbents

APTES was also immobilised onto SBA-15 through impregnation, the method for which has been outlined previously in Section 2.2.2. Sorbents containing between 10 and 80 wt % APTES were prepared and are listed in Table 2.3. Each sorbent is named to include the wt % APTES, the support used and the method of amine-modification. For example 10%APTES/SBA-15(I) is a sorbent which was prepared by impregnating 1.0 g of SBA-15 with 0.1 g APTES in 25 ml toluene.

Table 2.3: List of APTES/SBA-15(I) sorbents prepared

<table>
<thead>
<tr>
<th>Name</th>
<th>APTES g/Solid g</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%APTES/SBA-15(I)</td>
<td>0.1/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>20%APTES/SBA-15(I)</td>
<td>0.2/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>40%APTES/SBA-15(I)</td>
<td>0.4/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>50%APTES/SBA-15(I)</td>
<td>0.5/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>60%APTES/SBA-15(I)</td>
<td>0.6/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>70%APTES/SBA-15(I)</td>
<td>0.7/1.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>80%APTES/SBA-15(I)</td>
<td>0.8/1.0</td>
<td>Impregnation</td>
</tr>
</tbody>
</table>

Figure 2.10 presents the CO₂ TPD profiles of the solids listed in Table 2.3. CO₂ desorption generally begins at 45°C while T_max is observed below 100°C typically around 90°C. As CO₂ capacity increases the T_max is observed closer to 100°C as seen
in the TPD profile of 70%APTES/SBA-15(I). This may be as a result of the increased volume of CO$_2$ exiting the pores compared to the other sorbents in the series. The highest capacity adsorbent from this series was 70%APTES/SBA-15(I) with a modest capacity of 15 mgCO$_2$/g of sorbent.

Figure 2.10: CO$_2$ temperature programmed desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)
Figure 2.11 summarizes the CO$_2$ desorption capacities of the APTES/SBA-15(I) series of adsorbents, with CO$_2$ capacity, in mgCO$_2$/g sorbent, plotted against the corresponding wt % loadings of APTES. Overall these solids showed low CO$_2$ capacity. Maximum capacity was observed for 70%APTES/SBA-15(I) which had a capacity of 15 mgCO$_2$/g of sorbent.

![Figure 2.11: CO$_2$ adsorption/desorption capacities of APTES/SBA-15(I) sorbents](image)

APTES was immobilised onto SBA-15 through capillary impregnation, the method for which has been outlined previously in Section 2.2.2. Various sorbents were prepared in the range of 10%APTES/SBA-15(CI) to 80%APTES/SBA-15(CI). Figure 2.12 presents the CO$_2$ TPD profiles of these APTES/SBA-15(CI) adsorbents. CO$_2$ adsorption increased with increasing amount of APTES up to 70 wt % APTES. Capillary impregnation seems to have slightly higher $T_{\text{max}}$ of 125°C compared to previous sorbents which may be explained by the slower evacuation of relatively larger levels of CO$_2$ from the pores, thus prolonging the desorption step. Figure 2.13 presents the amount of CO$_2$ desorbed from each APTES/SBA -15(CI) sorbent. The lower CO$_2$ capacity observed in 80%APTES/SBA-15(CI) may be due to pore blocking as a result of increased APTES concentration in the synthesis solution. This would cause the pores to become inaccessible preventing APTES and CO$_2$ interacting. Similar to that observed in the previous adsorbents prepared via refluxing, it is also possible that the increased concentration in the synthesis solution
caused APTES agglomerates to form. These agglomerates would not be able to fix onto SBA-15 lowering APTES content on the solid and thus lowering CO$_2$ adsorption capacity.

**Figure 2.12:** CO$_2$ temperature programmed desorption profiles of indicated solids (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)
Figure 2.13: CO₂ adsorption/desorption capacities of APTES/SBA-15(CI) sorbents

70%APTES/SBA-15(CI) underwent continuous CO₂ adsorption/desorption cycles to ascertain its stability with repeated use. CO₂ was adsorbed onto the solid. After 5 mins the CO₂ gas was switched off. This was then desorbed from the sample by heating to 200°C. Once the temperature had cooled to 30°C, another adsorption step was carried out by adsorbing CO₂ onto the solid. This was then desorbed. This exact process was repeated 5 times in total. Figure 2.14 illustrates the results from this experiment. It is clear that the sorbent remains stable as CO₂ capacity remained constant over 5 cycles of repeated CO₂ adsorption/desorption analysis.
2.3.2 CO₂ adsorption/desorption analysis of APTES modified-AlSBA-15 adsorbents

In order to compare the influence of the surface chemistry of the mesoporous support on the capacity for CO₂, AlSBA-15 was modified with APTES. AlSBA-15 was synthesized as outlined in Section 2.2.1. The presence of Al atoms within the SBA-15 framework would increase the surface acidity of the porous solid, producing a more reactive solid.

APTES was immobilised onto AlSBA-15 through refluxing, as outlined previously in Section 2.2.2. Similar to previous methods, sorbents between 10 and 70 wt % were prepared. Figure 2.15 presents the CO₂ TPD profiles of the APTES/AlSBA-15(R) adsorbents. The CO₂ adsorption/desorption level increases with increasing amount of APTES in the synthesis solution. Maximum CO₂ adsorption/desorption occurs with 70%APTES/AlSBA-15(R). Similar to the previous series, desorption begins at about 50°C with $T_{\text{max}}$ around 100°C.

Figure 2.16 presents the amount of CO₂ desorbed from each APTES/AlSBA-15(R) sorbent with its corresponding theoretical wt % loading of APTES. CO₂ adsorption/desorption ability increases with increasing amount of APTES in the synthesis solution. Overall these adsorbents had very low capacities rendering them
unsuitable for further analysis. AISBA-15 sorbents prepared via refluxing showed less CO₂ adsorption capacity than APTES/SBA-15(R) sorbents. Maximum CO₂ adsorption/desorption occurs with 70%APTES/AISBA-15(R) with a capacity of only 5 mgCO₂/g.

APTES was immobilised onto AISBA-15 through the impregnation method outlined in Section 2.2.2. Figure 2.17 presents the CO₂ TPD profiles of the APTES/AISBA-15(I) adsorbents. Very small amounts of CO₂ were observed for 10%APTES/AISBA-15(I), 20%APTES/AISBA-15(I) and 30%APTES/AISBA-15(I). The CO₂ capacity reached a maximum using 40%APTES/AISBA-15(I) which presented a CO₂ adsorption capacity of 40 mgCO₂/g, as shown in Figure 2.18.

![CO₂ TPD profiles](image)

**Figure 2.15:** CO₂ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min)
Figure 2.16: CO₂ adsorption/desorption capacities of APTES/AlSBA-15(R) sorbents

Figure 2.17: CO₂ temperature desorption profiles of the indicated solids
(100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min)
APTES was also immobilised onto AlSBA-15 through capillary impregnation. Adsorbents with theoretical APTES wt % loadings between 10 and 70 were prepared and added drop wise to 1 g of AlSBA-15 as outlined in Section 2.2.2. Figure 2.19 presents the CO$_2$ TPD profiles of these prepared sorbents. CO$_2$ adsorption reached a maximum at 50%APTES/AlSBA-15(CI) with $T_{\text{max}}$ typically occurring before 100°C. A significant drop in CO$_2$ adsorption/desorption ability was observed in 70%APTES/AlSBA-15(CI).

Figure 2.20 shows the calculated CO$_2$ adsorption/desorption capacities of the APTES/AlSBA-15(CI) adsorbents. The 50%APTES/AlSBA-15(CI) solid desorbed 28 mgCO$_2$/g while 70%APTES/AlSBA-15(CI) desorbed only 3 mgCO$_2$/g.
The removal of gaseous streams using solid sorbents  

Emma Daniels

Figure 2.19: CO\textsubscript{2} temperature programmed desorption profiles of indicated solids

Figure 2.20: CO\textsubscript{2} adsorption/desorption capacities of APTES/AlSBA-15(CI) sorbents
2.3.3 CO$_2$ adsorption/desorption analysis of APTES modified PESBA-15 adsorbents

PESBA-15 is a mesoporous solid similar to SBA-15, however its pore diameters are much larger than those in SBA-15 as outlined in Table 2.1. Figure 2.21 presents the CO$_2$ desorption capacities of APTES/PESBA-15(R) and APTES/PESBA-15(I) adsorbents with their respective wt % loading of APTES. Impregnation produced a higher capacity solid, however overall this solid support (PESBA-15) did not produce a high capacity adsorbent; this may be due to the decreased surface area associated with PESBA-15, thus limiting the number of OH groups necessary for binding with APTES.

![Figure 2.21](image)

**Figure 2.21:** CO$_2$ Adsorption/desorption capacities of APTES/PESBA-15(R) and APTES/PESBA-15(I) adsorbents

Table 2.4 summarises the solids with the highest CO$_2$ adsorption/desorption capacities for each support from each amine modification method investigated. The adsorbent name, the optimum APTES loading, maximum CO$_2$ uptake in mgCO$_2$/g and $T_{max}$ are included for comparison.
Table 2.4: Summary of optimum solids

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Optimum APTES amount, wt %</th>
<th>Maximum CO$_2$ uptake, mgCO$_2$/g</th>
<th>$T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%APTES/SBA-15(R)</td>
<td>70</td>
<td>25</td>
<td>110</td>
</tr>
<tr>
<td>70%APTES/SBA-15(I)</td>
<td>70</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>70%APTES/SBA-15(CI)</td>
<td>70</td>
<td>86</td>
<td>120</td>
</tr>
<tr>
<td>70%APTES/AISBA-15(CI)</td>
<td>70</td>
<td>29</td>
<td>95</td>
</tr>
<tr>
<td>40%APTES/AISBA-15(I)</td>
<td>40</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>70%APTES/AISBA-15(R)</td>
<td>70</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>70%APTES/PESBA-15(CI)</td>
<td>70</td>
<td>19</td>
<td>125</td>
</tr>
<tr>
<td>50%APTES/PESBA-15</td>
<td>50</td>
<td>12</td>
<td>95</td>
</tr>
</tbody>
</table>

2.4 Discussion

This study produced a number of CO$_2$ adsorbents composed of APTES on a variety of solid supports (SBA-15, AISBA-15 and PESBA-15). These supports each had differing characteristics and it was shown that these attributes were influential in determining the CO$_2$ adsorption capacities of the resulting adsorbents. Figure 2.22 presents the various possible silanol structures that can be present on the SBA-15 surface: isolated silanols, vicinal silanols and geminal silanols are possible [24-26]. The vicinal silanols are arranged in such a way that two single hydroxyl groups are attached to different silicon atoms and a hydrogen bond is formed between them. The geminal silanols consist of two hydroxyl groups that are attached to one silicon atom. These hydroxyls are too close to form hydrogen bonds between themselves [24, 25].
Figure 2.22: Possible silanol arrangements within SBA-15 [26]

Figure 2.23 presents the formation of stable and inert siloxane bonds. This occurs through two processes: dehydration and dehydroxylation. It is thought that in the temperature range of 200-400°C mainly vicinal hydroxyls condense, whereas in the region above 400°C mainly isolated hydroxyls condense while temperatures greater than 1200°C are required to remove all silanols. All types of silanols illustrated in Figure 2.22 and Figure 2.23 may be found in SBA-15 [26].

Figure 2.23: Siloxane bond formation through dehydration and dehydroxylation [27]

Figure 2.24 presents a simplified overview of the surface structure of AlSBA-15. When some Si$^{4+}$ ions are replaced by Al$^{3+}$ ions, the resulting structure is negatively charged as Al usually exists in an Al$^{3+}$ state. By forcing Al into these silicon tetrahedra frameworks, a negative charge is introduced into the AlSBA-15 structure. This negative charge must be balanced by a positive charge such as H$^+$. These OH groups located near aluminium tetrahedra are considered strong Brønsted acids [27, 28]. In this way AlSBA-15 is quite similar to the structures found in zeolites.
APTES is bonded to SBA-15, AISBA-15 and PESBA-15 through its ethoxy silane groups as shown in Figure 2.25. The attachment of APTES onto silica supports begins with the protonation of NH₂ as the N lone pair attracts an H from the SBA-15 hydroxyl, forming an ammonium salt and leaving behind a negative O. This negatively charged O reacts with the slightly positive Si in APTES, resulting in the exclusion of the -OC₂H₅ section of the amine. Ethanol is then formed from the hydrolysis of the ethoxy groups after the deprotonation of the ammonium salt, leaving APTES bonded to SBA-15 as illustrated in Figure 2.25. These siloxane bonds result in the NH₂ group facing away from the silica surface and so allow them to interact with CO₂ molecules [25]. It is possible that all three ethoxy groups can be removed allowing the amine silanol to form three bonds with the SBA-15 surface. It is also possible that only one or two ethoxy groups leave the APTES molecules, allowing one or two bonds between APTES and support surface. The amount of siloxane bonds formed depends on the heat treatment of the modified solids.

APTES molecules bound to the SBA-15 surface may also interact amongst themselves resulting in many different ways in which APTES arranges itself inside the pores of SBA-15. It is possible for these attached APTES molecules to cross link amongst themselves or for the NH₂ to be weakly attracted to the surface OH group, with no siloxane bonds formed between APTES and SBA-15. These factors can inhibit CO₂ adsorption ability.
In the work presented in this chapter, APTES modified SBA-15 produced higher capacity adsorbents compared to AISBA-15 and PESBA-15 modified solids. The highest capacity solid was found in the solids prepared via capillary impregnation (70%APTES/SBA-15(CI) with a measured capacity of 89 mgCO$_2$/g of sorbent). In order to compare the amine loading generated by refluxing and capillary impregnation, 70%APTES/SBA-15(R) and 70%APTES/SBA-15(CI) were analysed using thermogravimetric analysis. These weight loss profiles are shown in Figure 2.26. Both have weight losses between 30°C and 200°C which may be attributed to water and CO$_2$ which have adsorbed on to the sorbents before thermogravimetric analysis. The weight losses seen after 200°C can be attributed to the decomposition of APTES. APTES is fixed onto SBA-15 through secure siloxane bonds, which have extremely high thermal stability; a number of these bonds are possible as outlined in Figure 2.25. These siloxane bonds will not be liberated during TGA analysis, so the weight losses above 200°C observed in Figure 2.26 correspond to the remaining part of APTES, i.e. the propyl chain with the NH$_2$ segment and any remaining ethoxy groups that have not bonded with a surface hydroxyl through a siloxane bond. The weight loss observed in 70%APTES/SBA-15(R) is 9 % while the weight loss attributable to APTES loss in 70%APTES/SBA-15(CI) is 12%. There is no great difference between these weight losses, however there is a significant difference between these two adsorbent’s ability to adsorb CO$_2$; 70%APTES/SBA-15(R) had a CO$_2$ adsorption/desorption capacity of 26 mgCO$_2$/g, while 70%APTES/SBA-15(CI)
had a CO$_2$ adsorption/desorption ability of 86 mgCO$_2$/g. As the amine contents are relatively similar, this result indicates that the distribution of APTES within the pores may be more important than the amount of amine loaded onto the solid.

![TGA profiles of 70%APTES/SBA-15(CI) and 70%APTES/SBA-15(R), showing weight loss with temperature](image)

**Figure 2.26**: TGA profiles of 70%APTES/SBA-15(CI) and 70%APTES/SBA-15(R), showing weight loss with temperature

Capillary impregnation encourages capillary action of the APTES-containing solution into the pores of SBA-15. This is much quicker than the diffusive process which occurs in impregnation and refluxing due to the larger volume of solvent used in those modification methods [23]. A possible reason for the higher CO$_2$ adsorption/desorption capacities in sorbents prepared via capillary impregnation is that there is a better distribution of APTES within the pores due to capillary action forcing APTES to penetrate within the pores. The APTES molecules are more attracted to the solid surface than to each other; however the APTES molecules can still adhere to each other. This causes each APTES molecule to be pulled along by another APTES molecule thus creating better dispersion of APTES within the pore and full penetration of the pores [24]. Refluxing and impregnation do not encourage this capillary behaviour, it is likely that these methods lead to the deposition of APTES close to the pore mouth, inhibiting dispersion of APTES within the pores and thus limiting CO$_2$ adsorption capacity. Figure 2.27 illustrates the likely location
of APTES within SBA-15 for all three modification methods where the small lines represent APTES molecules.

![Diagram showing the location of APTES within the pores of SBA-15 for each amine modification method](image)

**Figure 2.27:** Location of APTES within the pores of SBA-15 for each amine modification method

Overall AlSBA-15 solids performed poorly as amine supports, with CO$_2$ adsorption capacities ranging from 1 mgCO$_2$/g of sorbent to 45 mgCO$_2$/g of sorbent. Figure 2.28 presents the weight loss profiles from the thermogravimetric analysis of 70%APTES/SBA-15(CI) and 70%APTES/AlSBA-15(CI). The weight loss attributable to APTES loss is 12% in 70%APTES/SBA-15(CI) while APTES loss in 70%APTES/AlSBA-15(CI) was 13%. While there is a slight increase in APTES loading observed in 70%APTES/AlSBA-15(CI), the difference in CO$_2$ adsorption capacity is quite significant. 70%APTES/SBA-15(CI) had a CO$_2$ adsorption capacity of 86 mgCO$_2$/g of sorbent while 70%APTES/AlSBA-15(CI) had a CO$_2$ adsorption capacity of 28 mgCO$_2$/g. This is a threefold decrease in CO$_2$ adsorption ability when Al was incorporated into the siliceous support. This implies that the increased surface hydroxyls in AlSBA-15 led to a slight increase in APTES loading but did not result in increased CO$_2$ adsorption capacity. These results indicate that increasing the surface acidity of SBA-15 by Al incorporation results in a neutralisation effect.
between these highly reactive surface hydroxyls and APTES molecules. The amine group is attracted to the acid site via hydrogen bonds. This results in a bond between the amine and surface hydroxyl which makes this amine molecule unavailable for CO$_2$ adsorption, as depicted in Figure 2.29. This would lead to a drop in the CO$_2$ adsorption capacity of the adsorbent. This would explain the lower CO$_2$ adsorption abilities of APTES modified AISBA-15 solids.

**Figure 2.28:** TGA profile of 70%APTES/AISBA-15(CI) and 70%APTES/SBA-15(CI), showing weight loss with temperature

**Figure 2.29:** Possible APTES bonding with increased hydroxyl groups in AISBA-15 adsorbents
From the CO$_2$ TPD profiles the $T_{\text{max}}$ seems to increase with increasing CO$_2$ adsorption capacity. In an effort to investigate this in more detail the $T_{\text{max}}$ associated with the APTES/SBA-15 solids were compared with their CO$_2$ adsorption capacities and Figure 2.30 summarises these results. From this figure it can be seen that the $T_{\text{max}}$ generally increased with increasing CO$_2$ adsorption capacity. This may be explained by the slower evacuation of larger levels of CO$_2$ from the pores, which would prolong the desorption step accounting for the higher $T_{\text{max}}$ values recorded. It is also possible that as more strongly bound CO$_2$ is found in higher capacity solids, these solids will require a higher temperature to remove these more strongly bound CO$_2$ molecules than those with weaker bound CO$_2$ molecules. This phenomenon will be investigated further in subsequent chapters.

Figure 2.30: $T_{\text{max}}$ and adsorption capacities of indicated solids

PESBA-15 produced low capacity solids. The reduction in surface area may be a contributing factor to the low CO$_2$ adsorption capacity seen in amine-modified PESBA-15 adsorbents. As illustrated in Table 2.1, the surface area reduced from 656 m$^2$/g in SBA-15 to 420 m$^2$/g in PESBA-15. This loss of surface area will likely decrease the available OH groups to which APTES will be bound.
2.5 Conclusions

APTES modification was carried out on a number of mesoporous supports; SBA-15, AISBA-15 and PESBA-15. A number of APTES modification methods were employed; refluxing, impregnation and capillary impregnation. These adsorbents were tested for their CO$_2$ adsorption/desorption characteristics and produced capacities ranging from 1 mgCO$_2$/g to 86 mgCO$_2$/g. From the CO$_2$ adsorption/desorption capabilities, $T_{\text{max}}$ was found to occur between 80 and 125°C for most adsorbents.

The solid support characteristics were found to be highly influential in the subsequent adsorbents CO$_2$ adsorption ability. Modifying SBA-15 with aluminium was expected to lead to higher uptake of the amine, but it was actually found to inhibit amine-CO$_2$ interaction. This was most likely due to a neutralisation effect between the amine functionality of APTES and the surface hydroxyls in AISBA-15.

The amine modification method also proved to be an extremely important consideration as it influenced the CO$_2$ adsorption capacity of the resulting adsorbent. There was a considerable increase in CO$_2$ adsorption capacity when capillary impregnation was used to modify SBA-15 with APTES. Indeed the highest capacity solid from this study was 70%APTES/SBA-15(CI) with a CO$_2$ adsorption capacity of 86 mgCO$_2$/g of adsorbent.

Overall SBA-15 was found to be a suitable mesoporous support for CO$_2$ adsorbents. In the following chapters SBA-15 will be used as the support while a different amine (TEPA) will be used. These adsorbents will be compared to the 70%APTES/SBA-15(CI) in terms of CO$_2$ capacity and stability.

2.6 References


The removal of gaseous streams using solid sorbents

Emma Daniels


The removal of gaseous streams using solid sorbents

Emma Daniels


3  TEPA modified SBA-15 and AlSBA-15 as CO$_2$ adsorbents
3 TEPA modified SBA-15 and AlSBA-15 as CO$_2$ adsorbents

3.1 Introduction

Previously reported studies on TEPA modified mesoporous supports have produced varied results. Yue and co-workers modified SBA-15 with both DEA and TEPA resulting in an adsorbent with a CO$_2$ capacity of 163 mg/g with desorption typically completed by 100°C, when exposed to a pure CO$_2$ stream [1]. In a later study conducted by the same group, MCM-41 was modified with TEPA. 50 wt % TEPA on MCM-41 was found to produce a solid with a CO$_2$ capacity of 237 mg/g, with desorption occurring at 100°C. The stability of the solid was also tested and a drop in capacity to 183 mg/g was noticed after 6 repeated adsorption/desorption cycles [2].

Bhagiyalakshmi modified MCM-41, MCM-48 and SBA-15 with TEPA. Adsorption studies were carried out at 25, 50 and 75°C, while desorption occurred at 105°C. This study found that adsorption at 25°C produced the highest capacity adsorbent with a capacity of 40 mg/g. It was argued that the higher temperatures of 50°C and 75°C led to CO$_2$ molecules with higher kinetic energy which led to a disruption in the usual CO$_2$-amine interaction mechanism [3]. In a study conducted by Linneen et al, silica aerogel was modified with TEPA producing a solid with a capacity of 264 mg/g using a pure CO$_2$ stream while this was reduced to 154 mg/g using a dry 10% CO$_2$/Ar stream. It was found that the optimal loading was 80 wt % TEPA when adsorption was conducted at 75°C while desorption occurred at 100°C [4].

Chapter 2 illustrated the CO$_2$ adsorption/desorption abilities of APTES modified SBA-15, AlSBA-15 and PESBA-15. The aim of this chapter is to discuss the possibility of TEPA modified SBA-15 and AlSBA-15 as adsorbents for CO$_2$ adsorption. TEPA lacks an ethoxy silane anchoring group and thus TEPA modified solids can show low stability over repeated CO$_2$ adsorption/desorption studies. The performance of 2 high capacity adsorbents was selected for repeated adsorption/desorption studies in order to establish the stability and reusability of
TEPA adsorbents. This led to further studies on the optimisation of TEPA modified solids. These results are also presented in this chapter.

3.2 Experimental
Tetraethylenepentamine (TEPA) was the amine chosen for this study and ethanol was the solvent employed. All materials used were obtained from Sigma Aldrich, and were used as received.

3.2.1 Mesoporous Solid Preparation
A number of solid supports were used in this study. These included SBA-15 and AlSBA-15. These were prepared via a hydrothermal route, followed by calcination, as previously outlined in Chapter 2, Section 2.2.1. Before TEPA modification was carried out, SBA-15 and AlSBA-15 were dried in a vacuum oven for 16 hours at 150°C. The synthesis of TEPA modified SBA-15 and AlSBA-15 was carried out using three amine modification methods; refluxing, impregnation and capillary impregnation. These are summarised as follows:

Refluxing
An appropriate amount of TEPA was dissolved in 25 ml of ethanol for 30 minutes. This was then added to approximately 1 g of dried support and refluxed at 80°C for 2 hours. This suspension was filtered in a Buchner flask and washed with ethanol and water. Various concentrations of TEPA in ethanol solution were utilised where the % of TEPA in the solid’s name denotes the wt % of TEPA with respect to the amount of solid support.

Impregnation
Impregnation was carried out by dissolving appropriate amounts of TEPA in 25 ml ethanol for 30 minutes. To this, 1 g of the mesoporous solid was added. This suspension was stirred for 2 hours at room temperature. The solvent was then removed using a rotary vacuum evaporator. The resulting powder was dried in the oven at 80°C for 1 hour. Similarly to refluxing, various concentrations of TEPA in ethanol were utilised where the % of TEPA in the solid’s name denotes the wt % of TEPA with respect to the amount of solid support.
The removal of gaseous streams using solid sorbents

Emma Daniels

Capillary Impregnation

Capillary Impregnation involved dissolving appropriate amounts of TEPA in less than 1 ml of ethanol. For example 70%TEPA/SBA(CI) was synthesised using 0.30 g ethanol plus 0.7 g TEPA. This amine solution was then added drop wise to 1 g of support and stirred until all the support had been wetted by the amine solution. This sometimes produced a gel like substance which was then dried at 80°C for 16 hours in a vacuum oven. Again, various concentrations of TEPA in ethanol solution were utilised where the % of TEPA in the solid’s name denotes the wt % of TEPA with respect to the amount of solid support.

3.2.2 CO₂ adsorption/desorption analysis of TEPA modified adsorbents

The TEPA modified mesoporous solids were analysed for their CO₂ adsorption/desorption ability using an on-line testing rig with mass spectroscopy detection as outlined in Chapter 2, Section 2.2.3. The same procedure was used as reported for the APTES adsorbents; adsorption was conducted at 30°C and desorption was carried out up to 200°C at 10°C/min. Additional tests were then carried out whereby the adsorption and desorption temperatures were changed. A number of adsorption temperatures were chosen (30, 40, 50, 60, 80 and 100°C) and a number of desorption temperatures were investigated: 150 and 200°C. The characteristic shoulders observed in the CO₂ TPD profiles were further investigated by de-convoluting some desorption profiles using Origin® Pro 8 software.

A study was carried out which involved controlling the amount of adsorbed CO₂ during the adsorption step and subsequently studying the desorption characteristics of this adsorbed CO₂. For this experiment, a fresh sample of 70%TEPA/SBA-15(I) was loaded into the reactor. It was pre-treated by heating up to 150°C at 10°C/min. It was then cooled to 50°C. A single pulse of CO₂, which contained 0.39 mg CO₂ was adsorbed onto the solid. This solid was then heated up to 150°C at 10°C/min producing a CO₂ TPD profile. It was then allowed to cool to 50°C once more and 12 pulses were passed over the solid. This solid was then heated to 150°C producing a CO₂ TPD profile. This process was repeated using 25 and 30 pulses. For comparison purposes the solid was then saturated with CO₂ which has been the usual adsorption
practice in previous chapters. This involved passing the 15 % CO₂ stream over the solid for 5 minutes continuously.

### 3.2.3 Solid Characterisation

Both unmodified and TEPA modified solids were characterised by thermogravimetric analysis as outlined in Chapter 2 Section 2.2.4. A known quantity of solid was placed in an alumina crucible and heated up to 700°C in air at a rate of 10°C/min with the weight continuously recorded. The data was then imported into Excel to create the temperature-weight loss profiles.

### 3.3 Results

This section reports on CO₂ adsorption/desorption tests carried out on TEPA modified SBA-15 and TEPA modified AlSBA-15.

#### 3.3.1 CO₂ adsorption/desorption analysis of TEPA/SBA-15 adsorbents

Three modification methods were used to modify SBA-15 with TEPA. The first to be discussed are those prepared via refluxing. Figure 3.1 presents the CO₂ TPD profiles of the TEPA/SBA-15(R) adsorbents. These are derived from the desorption step of the CO₂ adsorption/desorption analysis for each sorbent. The nomenclature used for the synthesised solids includes the amount of TEPA used in the preparation stage, for example 10%TEPA/SBA-15(R) is a sorbent which was prepared by refluxing 1 g of SBA-15 with 0.1 g of TEPA and 25 ml ethanol. For each sorbent, the temperature and associated abundance of desorbed CO₂ is illustrated. CO₂ desorption typically began after 50°C, while $T_{\text{max}}$ was observed around 80°C. 40%TEPA/SBA-15(R) had the highest amount of released CO₂ during the desorption step. Increasing the amine level in the synthesis solution above 40 %, i.e. 50%TEPA/SBA-15(R) and 70%TEPA/SBA-15(R) resulted in a solid that desorbed less CO₂.
Figure 3.1: CO$_2$ temperature programed desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min He flow rate, temperature ramped at 10°C/min)

Figure 3.2 presents the calculated CO$_2$ desorption capacities of the TEPA/SBA-15(R) sorbents. CO$_2$ capacity is shown with the corresponding wt % loading of TEPA with respect to SBA-15 in the synthesis solution. Refluxing of TEPA with SBA-15 did not result in high CO$_2$ adsorption capacity solids, the highest capacity solid was 40%TEPA/SBA-15(R) which only desorbed 11 mgCO$_2$/g sorbent.
TEPA was also immobilised onto SBA-15 via impregnation and 8 sorbents were synthesised which contained loadings between 10 and 100 wt % TEPA with respect to the solid in the synthesis solution. Figure 3.3 presents the CO\textsubscript{2} TPD profiles of these prepared adsorbents. Desorption usually began around 55°C while T\textsubscript{max} generally occurred between 95 and 110°C.
The removal of gaseous streams using solid sorbents

Emma Daniels

Figure 3.3: CO₂ temperature desorption profile of the indicated solids
(100 mg adsorbent, 50 ml/min He flow rate, temperature ramped at 10°C/min)

Figure 3.4 summarizes the CO₂ desorption capacities of the TEPA/SBA-15(I) series
of adsorbents, with CO₂ capacity in mgCO₂/g sorbent plotted against the associated
wt % loadings of TEPA. The highest capacity solid was 70%TEPA/SBA-15(I)

87
which had a capacity of 116 mg/g of adsorbent. This is a high capacity, indeed one of the highest observed from this study.

![Figure 3.4: CO₂ adsorption/desorption capacities of TEPA/SBA-15(I) sorbents](image)

70%TEPA/SBA-15(I) underwent repeated CO₂ adsorption/desorption cycles to ascertain its stability with repeated use. After the first desorption, which involved heating the CO₂ saturated sample in a flow of He up to 200°C, the temperature of the furnace was cooled to 30°C and a second CO₂ adsorption step was carried out. Once the CO₂ levels from this had levelled out, the second desorption was undertaken by heating the CO₂ saturated solid again up to 200°C at a rate of 10°C/min. This was repeated 3 more times, the results of which are presented in Figure 3.5, where the desorption capacity, in mgCO₂/g of adsorbent, is presented with the desorption number. The first adsorption/desorption cycle achieved a high CO₂ adsorption capacity, reaching 116 mgCO₂/g. However this significantly reduced to just 26 mgCO₂/g after the second desorption. Each subsequent desorption showed a lower capacity.
Figure 3.5: CO$_2$ adsorption/desorption capacities following repeated CO$_2$ adsorption/desorption cycles using 70%TEPA/SBA-15(I)

Figure 3.6 presents the weight loss observed for 70%TEPA/SBA-15(I) and unmodified calcined SBA-15 during thermogravimetric analysis. The weight loss observed up to around 100°C in SBA-15, attributed to adsorbed CO$_2$ or H$_2$O, was 4%. Above 100°C only a slight weight loss was observed indicating the stability of SBA-15 at higher temperatures. The profile of 70%TEPA/SBA-15(I) shows three areas of weight loss; the first up to 150°C, the second between 150°C and 200°C and the third between 300°C and 700°C. The losses below 150°C can be attributed to CO$_2$ and water, the losses between 150-200°C can be associated with the evaporation of weakly held TEPA while the loss seen between 200 and 700°C can be attributed to the evaporation/decomposition of more strongly bound TEPA. These results are similar to the literature, as it has been reported that TEPA solids show three areas of weight loss; below 120°C, 120-200°C and 200 to 700°C [5, 2]. Taking all these losses into account, 10% can be attributed to loss of CO$_2$ and water, while the total weight loss observed was 35%, this implies that 25 % of this weight loss can be attributed to TEPA, which is significantly less than the expected 70 weight % loading in the synthesis solution. This indicates that a significant amount of TEPA from the synthesis solution is not adsorbed by the solid. Some weakly held TEPA may be lost through evaporation during the solvent evaporation step of the solid preparation stage.
SBA-15 was also modified with TEPA via capillary impregnation. Figure 3.7 presents the CO$_2$ TPD profiles of these TEPA/SBA-15(CI) sorbents. Desorption began around 55°C while T$_{\text{max}}$ was observed around 80°C.

**Figure 3.6:** Weight loss profile of 70%TEPA/SBA-15(I) and unmodified SBA-15 in air

**Figure 3.7:** CO$_2$ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped up to 200°C at 10°C/min)
Figure 3.8 illustrates the CO$_2$ adsorption/desorption capacity of each TEPA/SBA-15(CI) sorbent. The capacities are very low compared to other TEPA modified sorbents, implying that capillary impregnation of TEPA does not produce a high capacity solid. As discussed in Chapter 2 Section 2.4, capillary impregnation encourages capillary action of the APTES-containing solution into the pores of SBA-15. This is much quicker than the diffusive process which occurs in impregnation. This method may not allow sufficient time for TEPA to diffuse within the porous network.

![Figure 3.8: CO$_2$ adsorption/desorption capacities of TEPA/SBA-15(CI) sorbents](image)

### 3.3.2 CO$_2$ adsorption/desorption analysis of TEPA/AlSBA-15 adsorbents

TEPA was also immobilised onto AlSBA-15 via refluxing, impregnation and capillary impregnation. The first adsorbents to be presented are those prepared via refluxing. Sorbents modified with between 10 and 70 wt % TEPA loadings were prepared and Figure 3.9 presents the CO$_2$ TPD profiles of these adsorbents.

Figure 3.10 presents the capacities of the prepared TEPA/AlSBA-15(R) sorbents. The CO$_2$ desorption capacities were relatively small for all samples and a relatively high temperature (200°C) was required for CO$_2$ removal.
Figure 3.9: CO$_2$ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min flow rate, temperature ramped at 10°C/min)

Figure 3.10: CO$_2$ adsorption/desorption capacities of TEPA/AlSBA-15(R) sorbents
Figure 3.11 presents the CO$_2$ desorption profiles of TEPA/AlSBA-15(I) sorbents. $T_{\text{max}}$ occurs between 125°C and 150°C for all samples. Figure 3.12 presents the calculated CO$_2$ adsorption/desorption abilities of TEPA/AlSBA-15(I) adsorbents. As can be seen from this figure, most of these sorbents had low CO$_2$ adsorption/desorption capacities, except for 40%TEPA/AlSBA-15. Capacity reached a maximum at 40%TEPA/AlSBA-15(I) which had a CO$_2$ adsorption/desorption capacity of 170 mgCO$_2$/g. This is a high capacity solid; indeed it is the highest from this study.

**Figure 3.11:** CO$_2$ temperature desorption profiles of the indicated solids (100 mg adsorbent, 50 ml/min He flow rate, temperature ramped at 10°C/min)
Figure 3.12: CO$_2$ adsorption/desorption capacities of TEPA/AlSBA-15(I) sorbents

40% TEPA/AlSBA-15(I) underwent repeated CO$_2$ adsorption/desorption cycles in order to establish its stability over repeated cycles. Figure 3.13 presents the results of this study. This adsorbent initially had a high CO$_2$ adsorption/desorption capacity of 170 mgCO$_2$/g. However after the second desorption cycle the capacity dropped quite significantly to only 1 mgCO$_2$/g. Subsequent desorption studies similarly demonstrated close to zero CO$_2$ capacities. From the thermogravimetric data presented in Figure 3.6, TEPA begins to evaporate/decompose after 150°C. It is likely that after a pre-treatment and desorption carried out at 200°C, TEPA has been lost from the solid accounting for the decreased CO$_2$ capacity.
Figure 3.13: CO₂ adsorption/desorption capacities of repeated CO₂ adsorption/desorption studies of 40%TEPA/AlSBA-15(I)

Figure 3.14 presents the CO₂ adsorption capacities of TEPA modified AlSBA-15 prepared via capillary impregnation. Overall, the CO₂ adsorption capacities of these solids are low, with the highest capacity observed with 20%TEPA/AlSBA-15(CI) which had a capacity of 26 mgCO₂/g sorbent.

Figure 3.14: CO₂ adsorption/desorption capacities of TEPA/AlSBA-15(CI) sorbents
The CO$_2$ desorption capacities presented in this chapter are related to TEPA modified solids where CO$_2$ adsorption was conducted at 30°C and desorption was carried out up to 200°C at a rate of 10°C/min. A summary of these results are presented in Table 3.1. The highest capacity solids were 40%TEPA/AlSBA-15(I) and 70%TEPA/SBA-15(I). While these solids had high capacities (170 mgCO$_2$/g of adsorbent and 116 mgCO$_2$/g of adsorbent, respectively) both showed poor stability over repeated adsorption/desorption cycles. From the thermogravimetric analysis it is clear that TEPA evaporation begins after 150°C accounting for the poor stability of the TEPA modified adsorbents. Therefore it was decided to investigate different testing conditions which may help improve the stability of TEPA adsorbents. Different desorption temperatures were investigated. Different adsorption temperatures were also investigated. For these studies 70%TEPA/SBA-15(I) was chosen as it showed slightly better stability than 40%TEPA/AlSBA-15(I).

**Table 3.1:** Summary of optimum solids

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Optimum APTES amount, wt %</th>
<th>Maximum CO$_2$ uptake, mgCO$_2$/g</th>
<th>$T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%TEPA/SBA-15(I)</td>
<td>70</td>
<td>116</td>
<td>110</td>
</tr>
<tr>
<td>20%APTES/SBA-15(R)</td>
<td>20</td>
<td>11</td>
<td>95</td>
</tr>
<tr>
<td>70%APTES/SBA-15(CI)</td>
<td>70</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>40%TEPA/AlSBA-15(I)</td>
<td>40</td>
<td>170</td>
<td>115</td>
</tr>
<tr>
<td>50%TEPA/AlSBA-15(R)</td>
<td>50</td>
<td>11</td>
<td>80</td>
</tr>
<tr>
<td>20%TEPA/SBA-15(CI)</td>
<td>20</td>
<td>25</td>
<td>100</td>
</tr>
</tbody>
</table>
3.3.3 CO$_2$ adsorption/desorption on 70%TEPA/SBA-15(I)

A number of studies were carried out using 70%TEPA/SBA-15(I) which investigated the optimum CO$_2$ adsorption and desorption temperatures. A number of CO$_2$ TPD profiles were de-convoluted to investigate the CO$_2$ TPD profiles in greater detail.

The optimum temperature for CO$_2$ adsorption was investigated. CO$_2$ adsorption was carried out at various temperatures; 30, 40, 50, 60, 80 and 100°C, in order to investigate the effect of adsorption temperature on adsorption capacity. The CO$_2$ TPD profiles from some of these experiments are presented in Figure 3.15 while Table 3.2 presents the CO$_2$ adsorption capacities in mgCO$_2$/g and mmolCO$_2$/g for all prepared solids. From Figure 3.15 all profiles are similar in that they have a desorption peak which contain two shoulders. From Table 3.1 adsorption at 50°C resulted in the highest CO$_2$ desorption capacity, above 50°C capacity decreased. Capacity at 50°C is well above the 2 mmol/g necessary to compete with liquid amine absorption systems. As a result of this, all further adsorption studies were conducted at 50°C.

![CO$_2$ TPD profiles](image)

**Figure 3.15:** CO$_2$ TPD profiles of 70%TEPA/SBA-15(I) when CO$_2$ adsorption was conducted at 40, 50, 80 and 100°C, while desorption was conducted up to 150°C.
Table 3.2: CO₂ capacities of 70%TEPA/SBA-15(I) when adsorption was conducted at the indicated temperatures

<table>
<thead>
<tr>
<th>Adsorption Temperature, °C</th>
<th>CO₂ adsorption/desorption capacity, mg/g</th>
<th>CO₂ adsorption/desorption capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>116</td>
<td>2.63</td>
</tr>
<tr>
<td>40</td>
<td>198</td>
<td>4.50</td>
</tr>
<tr>
<td>50</td>
<td>211</td>
<td>4.79</td>
</tr>
<tr>
<td>60</td>
<td>201</td>
<td>4.56</td>
</tr>
<tr>
<td>80</td>
<td>141</td>
<td>3.20</td>
</tr>
<tr>
<td>100</td>
<td>87</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The TPD profiles in the first section of this chapter were conducted at a heating rate of 10°C/min up to 200°C. When these adsorption/desorption cycles were repeated following desorption at temperatures of 200°C, the CO₂ desorption capacity significantly decreased indicating that the stability of these solids were low. This could be due to the loss of TEPA at high temperatures. From the thermogravimetric analysis it is clear that loss of TEPA begins after 150°C. Examination of the TPD profiles illustrated that the Tₘₐₓ was found well below 200°C, typically around 110°C, suggesting that heating up to 200°C is unnecessary. In order to establish if 70%TEPA/SBA-15(I) was more stable at 150°C rather than 200°C, repeated adsorption/desorption cycles were carried out. Adsorption was conducted at 50°C and desorption was conducted up to 150°C at 10°C/min. This was repeated 4 more times. These results are presented in Table 3.3. Included in the table are the adsorption temperatures and CO₂ adsorption/desorption capacity in both mg/g and mmolCO₂/g of sorbent. It has been reported that the benchmark capacity required for industrial applications is 2 mmol CO₂/g of sorbent to provide a capacity comparable to the conventional liquid amine scrubber [6]. All the capacities presented in Table 3.3 have CO₂ adsorption capacities above the 2 mmol benchmark, adsorption at 50°C resulted in an average CO₂ adsorption/desorption capacity of 4.70 mmolCO₂/g. The capacity remains constant over repeated cycles indicating that at 150°C 70%TEPA/SBA-15(I) is stable and re-generable.
Table 3.3: CO₂ adsorption/desorption capacities of repeated cycles carried out on 70%TEPA/SBA-15(I) (adsorption temperature 50°C, desorption temperature 150°C)

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Adsorption Temperature, °C</th>
<th>Desorption Temperature, °C</th>
<th>CO₂ adsorption capacity, mg/g</th>
<th>CO₂ adsorption capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>150</td>
<td>211</td>
<td>4.79</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>150</td>
<td>207</td>
<td>4.70</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>150</td>
<td>207</td>
<td>4.70</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>150</td>
<td>206</td>
<td>4.68</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>150</td>
<td>204</td>
<td>4.63</td>
</tr>
</tbody>
</table>

Repeated adsorption/desorption cycles were conducted on 70%TEPA/SBA-15(I) under two different sets of conditions. Adsorption was carried out at 50°C, while the desorption stage was carried out up to a temperature of 200°C at 10°C/min. These results are compared to those obtained under similar conditions but a desorption temperature of 150°C at 10°C/min. Figure 3.16 presents these results. When the desorption step was conducted up to 200°C the capacity dropped significantly between the first and second desorption, however when repeated cycles were conducted up to 150°C, capacity remained constant suggesting that 70%TEPA/SBA-15(I) is stable at 150°C.
Figure 3.16: CO$_2$ adsorption/desorption capacities of 70%TEPA/SBA-15(I) following repeated CO$_2$ adsorption/desorption cycles at 200 and 150°C (100 mg sample, adsorption at 50°C)

To examine the stability of 70%TEPA/SBA-15(I) in more detail, the mass spectra obtained during the pre-treatment and desorption steps were analysed. Figure 3.17 presents the mass spectra taken during CO$_2$ desorption from the 1st adsorption/desorption cycle at (a) the pre-treatment at 200°C, (b) 65°C, (C) 160°C, (d) 200°C. The ions at 18, 28, 32 and 44 are attributed to water, nitrogen, oxygen and carbon dioxide, respectively. During the pre-treatment stage at 165°C, a variety of ions were detected between 15-20 m/z and 40-45 m/z which may be associated with organic species from the defragmentation of TEPA as the profile is similar to a typical TEPA mass spectra [7].
Figure 3.17: mass spectra taken during CO$_2$ desorption from the 1$^{st}$ adsorption/desorption cycle at (a) pre-treatment at 200°C, (b) 65°C, (c) 160°C and (d) 200°C.

Figure 3.18 presents the mass spectra taken during the CO$_2$ desorption of the 2$^{nd}$ adsorption/desorption cycle at (a) 65°C, (b) 160°C and (c) 200°C. The ions attributable to TEPA fragmentation are no longer observed, implying that TEPA evaporation/decomposition is complete. This may suggest that over the course of the pre-treatment and desorption step from the 1$^{st}$ adsorption/desorption cycle TEPA has evaporated/decomposed. By the desorption step of the 2$^{nd}$ adsorption/desorption cycle, no ions associated with TEPA were observed, indicating that TEPA is no longer evaporating/decomposing. It is likely that there is less TEPA on 70%TEPA/SBA-15(I) during the adsorption step of the 2$^{nd}$ adsorption/desorption cycle. This would lower the CO$_2$ adsorption/desorption capacity.
Figure 3.18: mass spectra taken during CO$_2$ desorption from the 2nd adsorption/desorption cycle at (a) 65°C, (B) 160°C, and (C) 200°C.

Figure 3.19 presents the mass spectra taken during CO$_2$ desorption from the 1st adsorption/desorption cycle at (a) 65°C, (b) $T_{\text{max}}$ at 145°C and (c) 150°C when desorption was conducted up to 150°C at 10°C/min. The only ions detected were those at 18, 28, 32 and 44, which are attributed to water, nitrogen, oxygen and carbon dioxide, respectively. There are no ions present to indicate TEPA fragmentation caused by evaporation/decomposition. This suggests that lowering the desorption temperature to 150°C prevents TEPA loss, accounting for the high CO$_2$ adsorption/desorption capacities over repeated adsorption/desorption cycles.
From the CO₂ TPD profiles presented in this chapter, it appears that they are composed of a desorption peak with two shoulders centred at 115 and 145°C. Further studies were carried out to investigate these shoulders in more detail. This involved adsorbing CO₂ onto the sample at 50°C. Once the CO₂ levels had reached zero the sample was heated to a much lower temperature than 150°C at 10°C/min to investigate whether all the CO₂ could be desorbed at this temperature over a prolonged period of time. The solid was then heated up to 150°C to investigate if any more CO₂ would desorb from the sample. The first temperature investigated was 63°C. The furnace was held at this temperature until CO₂ detected had decreased by 90%. The furnace was then heated up to 150°C from 63°C at a rate of 10°C/min. The result from this study is presented in Figure 3.20. Time, temperature and CO₂ counts are presented. From this figure, it is observed that some of the CO₂ was released at temperatures up to 63°C, however the release of a substantial portion of the CO₂ required temperatures greater than 63°C.
Figure 3.20: CO\textsubscript{2} desorption from 70\%TEPA/SBA-15(I) using the indicated temperature programmed profile. (Initial desorption temperature was 63°C, final desorption temperature was 150°C, 10°C/min)

Figure 3.21 presents a similar desorption profile, but at an initial desorption temperature of 85°C. The temperature was increased up to 85°C at a rate of 10°C/min, and then it was held at 85°C until CO\textsubscript{2} levels had decreased by 90\%. The furnace was then heated up to 150°C from 85°C at a rate of 10°C/min. As can be seen from Figure 3.21 a large CO\textsubscript{2} desorption peak was recorded at a temperature of 85°C where most of the CO\textsubscript{2} was released. A minute CO\textsubscript{2} peak was detected once the temperature was increased from 85°C up to 150°C.
Figure 3.21: CO$_2$ desorption from 70%TEPA/SBA-15(I) using the indicated temperature programmed profile. (Initial desorption temperature was 85°C, final desorption temperature was 150°C, 10°C/min)

Figure 3.22 presents a similar desorption profile, but at an initial desorption temperature of 125°C. Desorption progressed up to 125°C at a rate of 10°C/min, and then it was held at 125°C until CO$_2$ levels had decreased by 90%. The furnace was then heated up to 150°C from 125°C at a rate of 10°C/min. As can be seen from Figure 3.22 a large peak is detected when desorption is held at 125°C, no additional CO$_2$ is detected when the temperature is raised from 125°C to 150°C.
From the results presented in Figures 3.20-3.22, it is clear that all of the CO₂ has been released by 125°C when the CO₂ saturated solid was held at this temperature for 30 mins. When the temperature was held at 85°C for 42 minutes a significant portion of the CO₂ was desorbed from the solid and when the temperature was further increased to 150°C only a very small desorption peak was seen. Interestingly when the temperature was held at 63°C for 30 mins, only a small fraction of the CO₂ was desorbed, once the furnace temperature was increased to 150°C, all the remaining CO₂ was desorbed. As nearly all of the CO₂ can be released at 85°C over 42 minutes, it is likely that only one form of carbamate species is present.

To further analyse these shoulders, CO₂ was adsorbed in a controlled manner onto 70%TEPA/SBA-15(I) via pulsing as outlined in Section 3.3.4. Figure 3.23 presents the CO₂ TPD profiles from this study. One pulse of CO₂ produced a CO₂ TPD profile with a $T_{\text{max}}$ at 105°C. When the number of pulses was increased to 12, the $T_{\text{max}}$ was again found at 105°C. When the number of CO₂ adsorption pulses were increased to 25, a desorption peak with a $T_{\text{max}}$ at 95°C was observed, while two shoulders were observed at 70 and 110°C. A similar trend was observed when the number of pulses was increased to 30. When the solid was saturated with CO₂ which
involved passing CO$_2$ over the solid for 5 minutes continuously, the $T_{\text{max}}$ shifted to 110°C and two shoulders were observed at 70 and 90°C, respectively.

![Figure 3.23: CO$_2$ TPD profiles of 70%TEPA/SBA-15(I), adsorbing the indicated amounts of CO$_2$ pulses](image)

To further investigate these profiles a selection of the CO$_2$ TPD profiles from Figure 3.23 were de-convoluted using Origin8® software. These are presented in Figure 3.24. The CO$_2$ TPD profiles in Figure 3.25 show two peaks, the first has a $T_{\text{max}}$ around 105°C which broadens as the desorption capacity increases and a second one with a $T_{\text{max}}$ around 115°C which increases vertically as CO$_2$ desorption capacity increases. As TEPA likely diffuses fully within the pores these two peaks may be attributed to diffusional limitations. The peak observed at the lower temperature of 95°C may be due to CO$_2$ bound to TEPA closer to the pore mouth while the second peak may be associated with CO$_2$ bound to TEPA further within the pores.
Figure 3.24: De-convoluted peaks of 70%TEPA/SBA-15(I) when (a) 1 pulse of CO\textsubscript{2} was adsorbed, (b) 12 pulses of CO\textsubscript{2} were adsorbed, (c) 25 pulses of CO\textsubscript{2} were adsorbed.

Figure 3.25 presents the desorption capacities of each pulse study. Included in Figure 3.25 are the number of pulses adsorbed onto 70%TEPA/SBA-15(I) and the corresponding CO\textsubscript{2} desorption capacity. It is clear that increasing the number of pulses adsorbed onto the solid increases the CO\textsubscript{2} adsorption uptake.
Figure 3.25: CO$_2$ adsorption capacities of the indicated tests carried out on 70%TEPA/SBA-15(I) (100 mg solid, adsorption temperature was 50°C, adsorption temperature was 150°C 10°C/min)

3.4 Discussion

TEPA is a non-branched linear amine which does not contain ethoxy silane groups. It has 5 potential CO$_2$ adsorption sites; two primary amines and three secondary amines. Compared to APTES there are 5 more adsorption sites in TEPA. TEPA modified solids can therefore have higher CO$_2$ adsorption capacities compared to APTES modified solids. The way these amines are attached to solid supports is also different; as discussed in Chapter 2, APTES forms siloxane bonds between its ethoxy silane groups and surface silanes on the solid support. This is not possible for TEPA modified solids as they do not contain any ethoxy silane groups to form siloxane bonds with the solid support. Instead, TEPA is attached to the solid support by hydrogen bonds between it and surface hydroxyls. It is possible for a number of hydrogen bonds to exist as depicted in Figure 3.26. While there are 5 potential CO$_2$ adsorption sites in the TEPA molecule some of these may not be utilised for CO$_2$ adsorption due to hydrogen bonding between them and surface hydroxyls. These bonds are weaker than the siloxane bonds present in APTES solids. This may affect the stability of TEPA adsorbents. Indeed from the thermogravimetric analysis presented in this chapter in Figure 3.6, TEPA evaporation/decomposition began after 150°C whereas the thermogravimetric analysis of APTES sorbents presented in Chapter 2 indicated that APTES was stable up to at least 200°C.
Figure 3.26: TEPA modified solid support

From the results presented in both Chapter 2 and this chapter, it appears that the molecular structure of the amine determines which sorbent preparation method is most suitable. The highest capacity sorbent from Chapter 2 was 70%APTES/SBA-15(Cl), whereas the highest capacity from the results presented in this chapter was 70%TEPA/SBA-15(I). As TEPA is a non-branched amine it can diffuse through the pores relatively easily allowing the pores within SBA-15 to become full with TEPA. During impregnation the TEPA/ethanol solution is contacted with SBA-15 for 2 hours before the introduction of heat, this allows a better dispersion of TEPA within the pores. The ethanol is then slowly removed by evaporation leaving behind TEPA inside the pores. Distribution of TEPA can be slow, however compared to refluxing and capillary impregnation; impregnation is a slow modification method which allows time for equilibrium and distribution of TEPA solution within the pores to occur [6,8]. As discussed in Chapter 2, impregnation of APTES likely led to deposition of APTES near or on the pore mouth as APTES will likely bind to the first hydroxyl group it encounters, this likely limited APTES uptake as pores became inaccessible to APTES molecules. The capillary impregnation method utilises a lower amount of solvent compared to the other modification methods. Capillary impregnation encourages capillary action of the APTES-containing solution into the pores of SBA-15. This is much quicker than the diffusive process which occurs in impregnation and refluxing due to the larger volume of solvent used in those modification methods. Capillary impregnation may not allow enough time for TEPA to fully diffuse through the porous structure in SBA-15. This may have contributed
to TEPA agglomeration near the pore entrances, thus inhibiting further TEPA uptake, therefore lowering CO$_2$ adsorption capacity. For both amines, refluxing produced sorbents with modest capacities, this may be due to the loss of amine during the filtration step.

Similar to the results presented in Chapter 2, AlSBA-15 solids did not produce a high capacity, stable adsorbent. While 40%TEPA/AlSBA-15(I) had a high capacity of 170 mgCO$_2$/g, the rest of the sorbents in the series had modest capacities between 40 mgCO$_2$/g and 80 mgCO$_2$/g. These results indicate that increasing the surface acidity of SBA-15 by Al incorporation does not increase CO$_2$ adsorption/desorption capacity. As discussed in Chapter 2, it is likely that there is a neutralisation between the basic amine sites and the acid sites in AlSBA-15 resulting in low capacity solids. This is also true for TEPA modified AlSBA-15. When the amine group in the functionalised molecule is attracted to the acid site via a hydrogen bond the acid site protonates the amine, deactivating it as a CO$_2$ adsorption site in the process. This yields a bond between amine and a surface hydroxyl which becomes unavailable for further reactions making the amine unavailable for CO$_2$ adsorption. This would lead to a drop in the CO$_2$ adsorption capacity of the adsorbent. Figure 3.27 illustrates this. Compared to Figure 3.26, there are less amine sites available to interact with CO$_2$, thus limiting CO$_2$ adsorption ability accounting for the modest CO$_2$ adsorption/desorption capacities observed in TEPA/AlSBA-15 solids.
Normally chemisorption is an exothermic process which results in decreased adsorption capacities at higher temperatures. However for materials such as TEPA which are not chemically fixed onto SBA-15, CO$_2$ adsorption can increase with increasing adsorption temperature, as at higher temperatures the amine molecules become more mobile and allow for greater CO$_2$ transport through the sorbent, reaching a greater number of amine adsorption sites. At lower adsorption temperatures TEPA may exist in the pores like nano-sized particles, allowing CO$_2$ to only interact with amine sites on the outside of this nano-sized like particle, however as TEPA becomes more mobile at higher temperatures, more amine sites are opened up as depicted in Figure 3.28 where the amine sites are represented by the spheres [6, 8, 9]. Above a certain maximum temperature of 50°C, however, the adsorption capacity begins to fall. As can be seen from Table 3.1 the CO$_2$ adsorption capacity decreased above 50°C, while more adsorption sites become available at higher temperatures, desorption becomes more preferential, resulting in a decrease in adsorption capacity above 50°C. As can be observed from Table 3.2, the mmolCO$_2$/g capacities of the repeated adsorption/desorption studies are above the 2 mmol/g required, indicating the potential of this sorbent for real life applications when the adsorption temperature was raised to 50°C.
Figure 3.28: Possible location of TEPA molecules in pores at (A) low temperatures and (B) higher temperature [9]

Figure 3.16 illustrated the difference in capacity over repeated CO$_2$ adsorption/desorption cycles over 70%TEPA/SBA-15(I) when the desorption step was conducted up to 200°C and 150°C. From the thermogravimetric analysis, there is a loss of the amine above 150°C up to 700°C. It is clear that the repeated cycles conducted at the lower temperature of 150°C produced a more stable solid as capacity remained constant over 5 cycles. This is in sharp contrast with the repeated cycles at 200°C, where a significant drop was seen between the first cycle (200 mg/g) and the second cycle (30 mg/g). This is likely due to the loss of TEPA through evaporation/decomposition at higher temperatures. Indeed the mass spectra presented in Figure 3.17 indicated the presence of organic materials during the pre-treatment and desorption stage of the 1$^{st}$ adsorption/desorption cycle. Some of these ions, particularly those between 15 and 20 m/z and 40-45 m/z can be attributed to fragmentation of TEPA due to TEPA evaporation/decomposition. These ions were typically seen at around 165°C. These ions were not observed in the mass spectra taken during the cycles conducted at 150°C as illustrated in Figure 3.20, implying
TEPA evaporation/decomposition did not occur when the desorption step was conducted up to 150°C.

There seems to be an increase in $T_{\text{max}}$ with increasing CO$_2$ adsorption/desorption capacity. For example, when CO$_2$ was adsorbed at 30°C, CO$_2$ adsorption/desorption capacity was 116 mgCO$_2$/g with $T_{\text{max}}$ observed at 100°C. When the adsorption temperature was increased to 50°C, CO$_2$ adsorption/desorption capacity increased to 211 mgCO$_2$/g and $T_{\text{max}}$ increased to 145°C. This may suggest that when more CO$_2$ is adsorbed, more time is required to remove this CO$_2$ from the pores of the solid due to diffusional constraints. Another characteristic of the CO$_2$ TPD profiles to date have shown a desorption profile composed of multiple peaks. From the de-convoluted peaks in Figure 3.25, there appears to be two peaks within the CO$_2$ TPD profile, one centred around 115°C and the other around 145°C, both of these peaks increases with increasing capacity. The results presented in Figures 3.20-3.22 indicated that only some CO$_2$ could be desorbed at 63°C, while at 83°C most of the CO$_2$ was desorbed. This may suggest that the 1st peak in the de-convoluted profiles is due to CO$_2$ bound to TEPA just at the pore mouth. While the second peak may be due to CO$_2$ bound to TEPA further within the pore structure. The CO$_2$ bound further within the pores may require more time to desorb compared to the CO$_2$ bound closer to the pore mouth. This may suggest that a CO$_2$ transport mechanism is used to avail of all adsorption sites. This is supported by the CO$_2$ “hopping mechanism” reported by Ostwal et al. This theory suggests that CO$_2$ may be weakly held by amine sites located near the pore mouth of the solid. As more CO$_2$ is introduced, these amine sites may interact with free CO$_2$ molecules to form a stronger bond. The loosely bound CO$_2$ then bonds with neighbouring amine adsorption sites. As more CO$_2$ is introduced this process continues allowing the adsorbed CO$_2$ to permeate deeper into the adsorbent [10, 11].

As CO$_2$ is introduced into 70%TEPA/SBA-15(I), the CO$_2$ occupies adsorption sites just within the pores as more CO$_2$ is introduced, the “hopping mechanism” causes CO$_2$ to travel deeper and deeper into the pore structure until these internal adsorption sites are completely filled.
3.5 Conclusion

It is clear that the type of amine modification is extremely important when synthesizing mesoporous solids suitable for CO₂ adsorption. The type of amine used in the modification step will determine which modification method works best. From the results presented in this chapter it appears that impregnation is the most suitable modification method when TEPA is the amine in question. Overall, refluxing does not seem to produce a high capacity solid when TEPA was the amine used; regardless of which porous support was modified. This may be due to amine loss during the filtration step. Capillary impregnation similarly produced low capacity TEPA solids. This is likely due to the nature of the TEPA molecule which may be more suited to diffusive processes such as impregnation.

Adsorption and desorption temperatures are also important factors for consideration when TEPA solids are used as CO₂ adsorbents. It is important to note that the thermal swing process can be more economical than the pressure-swing process if the temperature range of the thermal swing process is between ambient temperature and the temperature of steam which is typically around 135°C but is often as high as 150°C [9, 10, 11]. Therefore the experimental conditions as outlined in Section 3.3.3 were chosen with these constraints in mind. Adsorption at 50°C and desorption carried out up to 150°C produced a high capacity solid with good stability over 5 CO₂ adsorption/desorption cycles.

The CO₂ TPD profiles show that the desorption profile is composed of two peaks. The 1st peak may be attributed to CO₂ bound to TEPA close to the pore mouths, while the second peak may be due to a diffusional limitation of CO₂ bound to TEPA further within the pore structure.

3.6 References


TEPA/SBA-15(I) as an adsorbent for removal of CO$_2$ from ambient air
4 TEPA/SBA-15(I) as an adsorbent for removal of CO\(_2\) from ambient air

4.1 Introduction

Currently, most carbon capture and sequestration technologies being pursued are focused on capturing CO\(_2\) emissions from large point sources such as power plants and cement factories. While this is admirable work aiming at reducing CO\(_2\) emissions, it, at best will only slow the rate of increasing levels of CO\(_2\) in the atmosphere. About one third of CO\(_2\) emissions come from distributed sources such as transportation vehicles. These vehicles are unsuited for on-board CO\(_2\) capture and thus direct CO\(_2\) capture from ambient air can play a major role in mitigating these emission sources. Capturing CO\(_2\) from ambient air involves the separation of a fairly dilute component from a large volume of gas as CO\(_2\) only comprises approximately 0.039 % of ambient air. Direct air capture provides the possibility to maintain current atmospheric CO\(_2\) levels but also to remediate the anthropogenic impact on climate since the beginning of the industrial revolution. It also has the potential to enable the continuous consumption of powerful and convenient energy sources such as petrol and diesel in a carbon-neutral manner [1]. As the concentration of CO\(_2\) in ambient air is at equilibrium around the world, CO\(_2\) extraction plants could be located anywhere, offering more flexibility compared to source point capture plants. Once the CO\(_2\) is separated and captured from the ambient air it can be either re-used in the carbonated drinks industry or in greenhouses, as a feedstock or stored. To allow for any subsequent chemical recycling to chemical feedstocks, plants should be located near hydrogen production sites; similarly if the CO\(_2\) captured is to be geologically stored, the capture plant should be located near these storage sites [2, 3].

Capturing CO\(_2\) from air is technically feasible and has been employed in air separation in closed circuit environments such as submarines and space ships. Lackner first proposed the use of direct air capture of CO\(_2\) from ambient air as a potential climate change mitigation option in 1999. This air capture method involves the use of a sodium hydroxide (NaOH) solution which absorbs CO\(_2\) from ambient air. Sodium hydroxide is regenerated using the Kraft chemical recovery process.
The CO$_2$ released during this stage can be separated or compressed and then stored or used in manufacturing processes. There are a number of options that can be used for contacting the extracting solution with the air. These include; large convection towers, open stagnant pools and packed scrubbing towers. As CO$_2$ is quite dilute in air, the contactor must have a large cross-sectional area and be able to process large volumes of air with a low pressure-drop compared to typical industrial gas-absorption processes. Alternatively, a fine spray of sodium hydroxide could be generated through an open tower. This would be capable of operating with a small pressure drop in air but would require more energy due to pumping and creating the spray [2, 4, 5, 6]. Another issue with this technology is the high binding energy of CO$_2$ to NaOH which makes regeneration of the sorbent quite expensive. Strong bases such as sodium hydroxide are energy intensive in terms of their re-generation as they require a desorption temperature of up to 450°C. Amines either physically or chemically bound to solid supports require much lower temperatures for their re-generation, typically up to 200°C [3].

There are few amine solids in the literature regarding CO$_2$ capture from ambient air. A notable study was conducted by Wang and co-workers. They studied PEI/SBA-15 for CO$_2$ capture from gas streams with low CO$_2$ concentrations under ambient conditions. Adsorption studies were conducted using a simulated air flow with 200 ppmv CO$_2$ in N$_2$ and various temperatures were investigated (25, 75, 100°C), while desorption was conducted up to 110°C in a He flow. At an adsorption temperature of 25°C a capacity of 0.51 mmolCO$_2$/g was achieved. The study showed that the sorbent could adsorb CO$_2$ from a gas stream containing a low concentration of CO$_2$, the sorbent could be regenerated between 50 and 110°C and was stable for at least 20 cycles [3]. Conventional liquid amine scrubbers can be ruled out for direct air capture due to evaporation of the amine and issues handling large volumes of corrosive liquid. Due to the low CO$_2$ concentration in ambient air (0.039 %), the presence of moisture and the need to operate at room temperature and atmospheric pressure, selective amine adsorbents are ideally suited for capturing CO$_2$ from ambient air.
Research in this area is in its infancy as more work needs to be undertaken to fully explore the key challenges such as the process design for efficient air/adsorbent contact, the regeneration strategy, material durability and cyclic re-generability and economic feasibility as the economic viability will depend on many factors including the technology used as well as the cost of labour, materials and energy [1, 2]. While there is no question that the capture of CO\(_2\) from the air is possible, more research and development is clearly needed to optimize this technology and determine its economic viability.

This chapter aims to investigate 70%TEPA/SBA-15(I) as a suitable adsorbent for CO\(_2\) capture from direct air. This solid was exposed to ambient air for different lengths of time; 1 hour, over 1 day and 1 week. The solids were then desorbed on the test rig outlined previously in Chapter 2, Section 2.2.3, in order to calculate adsorption/desorption capacity under ambient air exposure. The influence of water was also investigated on CO\(_2\) capture. 70%TEPA/SBA-15(I) was also repeatedly exposed to ambient air in order to investigate the re-generability of the adsorbent under ambient air capture conditions.

### 4.2 Experimental

All materials used in the synthesis of 70%TEPA/SBA-15(I) were obtained from Sigma Aldrich. All materials and chemicals were used as received.

#### 4.2.1 Synthesis of 70%TEPA/SBA-15(I)

Impregnation was the amine modification method employed as it produced a high capacity TEPA based adsorbent. Before impregnation was carried out, calcined SBA-15 was dried at 150°C for 16 hours. An appropriate amount of TEPA was dissolved in 25 ml ethanol for 30 minutes. To this, 1 g of the dried mesoporous solid was added. This suspension was stirred for 2 hours at room temperature. The solvent was then removed using a rotary vacuum evaporator. The resulting powder was dried in the oven at 110°C for 1 hour.
4.2.2 CO$_2$ adsorption from ambient air

A given quantity of 70%TEPA/SBA-15(I) was pre-treated in the laboratory test rig as outlined in Chapter 2 Section 2.2.3. This simply involved heating the adsorbent up to 150°C at 10°C/min in a helium flow of 50 ml/min. The temperature was held for 5 minutes. This was then allowed to cool to room temperature (20°C) and then the reactor was taken from the rig and the pre-treated solid was taken from the reactor and weighed. Various amounts were then placed on watch glasses and left on the laboratory bench and exposed to the air for various amounts of time; one hour, 24 hours and 7 days. After the required exposure, the solids were loaded onto the test rig as outlined in Chapter 2 Section 2.2.3. Typically 100 mg of exposed solid was placed into the quartz reactor. Once the reactor was loaded, a flow of helium was sent through the reactor at a rate of 50 ml/min. Then the furnace, housing the reactor was heated up to 150°C at a rate of 10°C/min producing a CO$_2$ TPD profile. The temperature was held at 150°C for 5 minutes. CO$_2$ and H$_2$O were continuously monitored during the desorption step.

4.2.3 Repeated CO$_2$ adsorption/desorption studies

For repeated studies, 100 mg of the solid was pre-treated in the test rig as outlined by heating the furnace housing the solid up to 150°C at 10°C/min in a He flow of 50 ml/min. This was then allowed to cool to room temperature (20°C) and removed from the rig but still housed within the reactor. To help aid air flow, the reactor was attached to an Interpret Airvolution mini pump for 2 hours as contact with the air may be limited by the quartz reactor. Air was drawn through the pump and over the solid at 1.25 L/min. After 2 hours of exposure, the reactor was once again attached to the test rig and heated to 150°C at 10°C/min producing a CO$_2$ TPD profile. This was repeated twice more to investigate the re-generability of the solid for direct air capture.

4.2.4 Influence of water on CO$_2$ adsorption/desorption studies

A given quantity of 70%TEPA/SBA-15(I) was pre-treated in the laboratory test rig by heating the furnace housing the solid up to 150°C at 10°C/min in a He flow of 50 ml/min. This was then allowed to cool to room temperature (20°C) and then the reactor was taken from the rig and the 70%TEPA/SBA-15(I) was taken from the
reactor and weighed. This was then left in a desiccator which contained a small beaker of water, for 24 hours. The relative humidity of the desiccator was taken to be 100%. The lid was taken off the desiccator for a couple of minutes every few hours to ensure adequate air supply in the desiccator. The relative humidity of the ambient air in the laboratory during testing was observed to be 80%. This solid was then attached to the laboratory test rig and heated up to 150°C at a rate of 10°C/min producing a CO$_2$ TPD profile.

4.3 Results
Following the exposure of a pre-treated sample of 70%TEPA/SBA-15(I) in air for various periods of time, the level of CO$_2$ adsorbed was measured by carrying out a TPD study. Particular attention was given to the desorption of both CO$_2$ and H$_2$O.

Figure 4.1 presents both the CO$_2$ and H$_2$O TPD profiles from 70%TEPA/SBA-15(I) after 1 hour of ambient air exposure. The exposed solid was attached to the rig as outlined in Section 4.2.2. Desorption of CO$_2$ was detected between 60 and 150°C with $T_{\text{max}}$ observed at 105°C. Very little water was desorbed, implying the preferential adsorption of CO$_2$ over water in ambient air when the relative humidity was 80%. The CO$_2$ TPD profile was narrow with a shoulder around 100°C.

Figure 4.2 presents the CO$_2$ and H$_2$O TPD profiles of 70%TEPA/SBA-15(I) after 24 hours of ambient air adsorption. Similarly to Figure 4.1, CO$_2$ is preferentially adsorbed over water. The CO$_2$ profile is broader than the one observed in Figure 4.1. The TPD profile appears to be composed of 3 peaks, the 1$^{\text{st}}$ one centred at 60°C, the 2$^{\text{nd}}$ at 85°C and the 3$^{\text{rd}}$ one centred at 110°C.
Figure 4.1: CO$_2$ and H$_2$O TPD profile from 70%TEPA/SBA-15(I) after 1 hour of ambient air adsorption (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)

Figure 4.2: CO$_2$ and H$_2$O TPD profile from 70%TEPA/SBA-15(I) after 24 hours of direct air exposure (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)

Figure 4.3 presents the CO$_2$ and H$_2$O TPD profiles of 70%TEPA/SBA-15(I) after 1 week of ambient air adsorption. Similar to the other profiles there is much more CO$_2$ present than water, suggesting that CO$_2$ is preferentially adsorbed over water. The $T_{\text{max}}$ occurs at 110°C, and there appears to be three shoulders present similar to those in Figure 4.2.
To further investigate the TPD profiles from the ambient air exposure studies, the CO$_2$ TPD profiles from Figures 4.1-4.3 were de-convoluted using Origin8® software. The profile from 1 hour of exposure is similar to those presented in Chapter 3 and is composed of two peaks centred around 95°C and 110°C. The profiles for 1 day and 1 week exposure appear to be composed of three peaks centred at about 65°C, 95°C and 110°C. The two peaks centred at 95°C and 110°C appear to increase with increased exposure to ambient air and CO$_2$ adsorption/desorption capacity. This is similar to the de-convoluted peaks reported in Chapter 3, Section 3.3.3. The large peak centred at 95°C may be attributed to CO$_2$ bound to TEPA just within the pore structure, while the peak centred at 110°C may be attributed to CO$_2$ bound to TEPA further with the porous network. The peak between 60 and 70°C (in the profiles from 1 day and 1 week of exposure) may be physisorbed CO$_2$ as at room temperature, CO$_2$ would be able to utilise adsorption sites suitable for physisorption.
The removal of gaseous streams using solid sorbents

Emma Daniels

Figure 4.4: De-convoluted peaks from 1 hour, 1 day and 1 week of ambient air exposure

Table 4.1 summarises the CO$_2$ adsorption capacities of 70%TEPA/SBA-15(I) when exposed to ambient air for 1 hour, 1 day and 1 week, respectively. Time of exposure, $T_{\text{max}}$ and capacity in mgCO$_2$/g and mmolCO$_2$/g are recorded. As the length of exposure was increased from one hour to one day, capacity increased from 93 mgCO$_2$/g to 210 mgCO$_2$/g. When the length of exposure was further increased from 1 day to 1 week, no further increase in capacity was observed. As the capacity increased a slight increase in $T_{\text{max}}$ was observed.

Table 4.1: CO$_2$ Adsorption/desorption capacities and $T_{\text{max}}$ values of 70%TEPA/SBA-15(I) with exposure

<table>
<thead>
<tr>
<th>Time of Exposure</th>
<th>$T_{\text{max}}$</th>
<th>Capacity, mgCO$_2$/g</th>
<th>CO$_2$ capacity, mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>105</td>
<td>93</td>
<td>2.11</td>
</tr>
<tr>
<td>1 day</td>
<td>110</td>
<td>210</td>
<td>4.77</td>
</tr>
<tr>
<td>7 days</td>
<td>110</td>
<td>200</td>
<td>4.54</td>
</tr>
</tbody>
</table>
As the previous TPD profiles have shown, a larger amount of CO\textsubscript{2} was present in the TPD profiles compared to H\textsubscript{2}O. The H\textsubscript{2}O content was very low, similar to background levels, indicating the preference for CO\textsubscript{2} adsorption in 70\%TEPA/SBA-15(I). The relative humidity in ambient air was observed to be 80 \% with a CO\textsubscript{2} concentration of 0.039\%. In order to fully investigate the role of water a simple experiment was developed as outlined in Section 4.2.3. Figure 4.5 presents the CO\textsubscript{2} and H\textsubscript{2}O TPD profiles of 70\%TEPA/SBA-15(I) at the indicated relative humidities. The profiles are similar with T\textsubscript{max} observed between 115 and 120°C. When 70\%TEPA/SBA-15(I) was exposed to ambient air with a relative humidity of 80\%, CO\textsubscript{2} adsorption capacity was calculated as 210 mgCO\textsubscript{2}/g. When 70\%TEPA/SBA-15(I) was exposed to ambient air with a relative humidity of 100\%, CO\textsubscript{2} adsorption capacity was 213 mgCO\textsubscript{2}/g, further illustrating the negligible impact humidity has on the CO\textsubscript{2} adsorption capacity of 70\%TEPA/SBA-15(I).

![Figure 4.5: CO\textsubscript{2} and H\textsubscript{2}O TPD profiles after 24 hours direct air exposure at the indicated relative humidities (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)](image)

In order to test the re-generability of the solid for direct air capture, an Interpret Airvolution mini air pump was used to circulate air through the solid as outlined in Section 4.2.4. 70\%TEPA/SBA-15(I) was exposed to ambient air for 2 hours over 4 CO\textsubscript{2} adsorption/desorption cycles. Figure 4.6 presents the results from this study.
There is little difference in capacity between each desorption, implying that 70%TEPA/SBA-15(I) is stable over repeated ambient air adsorption cycles as CO$_2$ adsorption capacity ranged from 157 to 150 mgCO$_2$/g.

![Graph showing CO$_2$ adsorption capacity over different desorption cycles](image)

**Figure 4.6:** Repeated ambient air cycles of 70%TEPA/SBA-15(I) (100 mg adsorbent, 50 ml/min flow rate He, temperature ramped at 10°C/min)

### 4.4 Discussion

Capturing CO$_2$ from air is challenging due to its low concentration, the presence of moisture and the need to operate at ambient pressure and temperature. These constraints limit the technologies which can be applied to direct air capture. For example, at atmospheric pressure physical adsorbents such as zeolites and activated carbons can be excluded for their low CO$_2$ selectivity. Liquid amine solvents can also be ruled out due to evaporation issues and the large volumes of liquid to be handled. In this chapter 70%TEPA/SBA-15(I) was investigated for its potential to capture CO$_2$ from ambient air. The first aspect of this study was concerned with CO$_2$ capture from ambient air over different amounts of exposure time. Figure 4.1 to Figure 4.4 illustrates the results of this study. Figure 4.1 presents the CO$_2$ TPD profile of 70%TEPA/SBA-15(I) after 1 hour of exposure to ambient air, which had a CO$_2$ adsorption/desorption capacity of 93 mgCO$_2$/g and $T_{\text{max}}$ was observed at 105°C. When the length of exposure was increased to 1 day, capacity increased to 210
mgCO₂/g, with T_{max} observed at 110°C. When the length of exposure was once again increased from 1 day to 1 week, no increase in capacity was observed implying that 1 day exposure to ambient air is sufficient for all amine sites to adsorb CO₂. As the CO₂ concentration in the atmosphere is 0.039 %, the ability of 70%TEPA/SBA-15 to selectively adsorb 4.77 mmolCO₂/g in ambient air and at a high relative humidity makes it a viable option for direct CO₂ capture from ambient air. The solid reported by Wang et al, achieved a capacity of 0.51 mmolCO₂/g after 30 minutes of exposure [7]. While the solid reported in this chapter (70%TEPA/SBA-15(I)) had a capacity of 2.11 mmolCO₂/g after 1 hour of exposure.

The influence of water vapour on the CO₂ adsorption capacity was also studied. Figure 4.5 presented the CO₂ TPD profiles of 70%TEPA/SBA-15(I) when exposed to two different relative humidities of 80 and 100 %, respectively. From this figure, it is clear that increasing the relative humidity of the ambient air does not negatively affect CO₂ adsorption, in fact a slight increase in capacity was observed. The advantage of amine modified solids lies in their ability to specifically bind to CO₂. As previously outlined in Chapter 1, Section 1.6.2, it is believed that the interaction between CO₂ and amine results in the formation of ammonium carbamates, ammonium bicarbonates and carbamic acid. The initial step begins when the lone pair on the amine attacks the carbon of CO₂, resulting in the formation of a zwitterion. This mechanism is also applicable to amines immobilised onto solid supports with a free amine as the base needed to deprotonate the zwitterion. In a dry gaseous system, the amount of CO₂ adsorbed is limited to 1 mole of CO₂ for every 2 moles of amine, forming ammonium carbamate while this is increased to 2 moles of CO₂ for every 2 moles of amine in the presence of water, resulting in the formation of ammonium bicarbonate [8-10], thus illustrating that the presence of water does not negatively affect the CO₂ adsorption capacity of 70%TEPA/SBA-15.

Figure 4.4 presented the de-convoluted profiles of the CO₂ TPD profiles presented in Figure 4.1-4.3. The profile from 1 hour of exposure is similar to those presented in Chapter 3 and is composed of two peaks centred around 95°C and 110°C. The profiles for 1 day and 1 week exposure appear to be composed of three peaks centred at about 65°C, 95°C and 110°C. The two peaks centred at 95°C and 110°C appear to
increase with increased exposure to ambient air and CO\textsubscript{2} adsorption/desorption capacity. This is similar to the de-convoluted peaks reported in Chapter 3, Section 3.3.3. Compared to the de-convoluted profiles in Chapter 3 however, the 2\textsuperscript{nd} peak centred at 110°C is much bigger. As discussed in Chapter 3, this peak may be attributable to CO\textsubscript{2} bound to TEPA deep within the pore network; explained by the CO\textsubscript{2} transport mechanism discussed in Chapter 3. This theory suggests that CO\textsubscript{2} may be weakly held by amine sites located near the pore mouth of the solid. As more CO\textsubscript{2} is introduced, these amine sites may interact with free CO\textsubscript{2} molecules to form a stronger bond. The loosely bound CO\textsubscript{2} then bonds with neighbouring amine adsorption sites. As more CO\textsubscript{2} is introduced this process continues allowing the adsorbed CO\textsubscript{2} to permeate deeper into the adsorbent [11, 12]. The increase observed with the second peak in the de-convoluted profiles presented in Figure 4.4 compared to those presented in Chapter 3 may be due to more CO\textsubscript{2} adsorbed further within the porous solid, as there was more time for adsorption during the tests carried out in this chapter. This supports the theory that an amine hopping mechanism does exist within 70%TEPA/SBA-15(I). It is possible that the lower temperature in ambient air may encourage physisorption of CO\textsubscript{2} onto the solid, this would account for the smaller peak centred between 60 and 70°C in the profiles from the solid when it was exposed to ambient air for 1 day and 1 week.

Another important factor for the widespread application of CO\textsubscript{2} capture from ambient air is the regeneration of potential direct air capture technologies [8]. Figure 4.6 illustrated the CO\textsubscript{2} TPD profiles of 70%TEPA/SBA-15(I) over 4 adsorption/desorption cycles. There was a small drop in capacity observed over the 4 cycles with capacity ranging from 150 to 157 mgCO\textsubscript{2}/g. This indicates the stability of this solid for ambient air CO\textsubscript{2} capture. All of these attributes make 70%TEPA/SBA-15(I) a very good solid for CO\textsubscript{2} capture from ambient air as it demonstrates that the solid can become saturated with CO\textsubscript{2} and reach equilibrium within 1 day of exposure when the CO\textsubscript{2} concentration is very small and can be quickly regenerated at a modest temperature of up to 150°C. This type of solid and capacity has yet to be reported on for direct air capture technologies.
4.5 Conclusion

From the results presented in this chapter it is clear that 70%TEPA/SBA-15(I) is a strong candidate for CO$_2$ capture from ambient air as it has a high CO$_2$ adsorption/desorption capacity, is stable over repeated CO$_2$ adsorption/desorption studies and has also been shown to preferentially adsorb CO$_2$ in ambient air. When the profiles were de-convoluted they showed two principle peaks similar to those observed in Chapter 3. Interestingly when exposure was increased to 1 day and 1 week, a small peak was observed between 60 and 70°C. This may be attributed to physisorbed CO$_2$.

4.6 References


5 Investigation of CO$_2$ adsorption by TEPA modified SBA-15 pellets
5 Investigation of CO$_2$ adsorption by TEPA modified SBA-15 pellets

5.1 Introduction

As outlined in previous chapters, anthropogenic induced global climate change, caused by increased levels of CO$_2$ in the atmosphere is one of the most serious environmental challenges facing our society. The potential of solid amine adsorbents offsetting CO$_2$ emissions from fossil fuel fired power plants has also been outlined in previous chapters; however these adsorbents in powder form are unsuited to real-life industrial settings due to the large pressure drops in gas phase interactions [1]. Therefore it is necessary to convert these powder adsorbents into pellets or extrudates suited for industrial purposes through a pelletisation process. Pelletisation, as defined by IUPAC, is a “process of agglomeration that converts fine powders or granules of bulk drys and excipients into small, free-flowing, spherical, or semi-spherical units, referred to as pellets” [2]. Pelletisation can be achieved by simply pressing the parent material into a compacted unit or by the addition of binders and plasticisers which creates a paste which can then be extruded through a mesh or die creating a pellet.

It is extremely important to maintain the mesoporous structure and surface hydroxyl sites of the parent material during the pelletising process. It is expected that the addition of binders and plasticisers may reduce surface area and pore diameter. This may be resolved by adding only small amounts of binders and plasticisers to the parent material. Binders are added to encourage mesoporous material particles to stick together, while a plasticiser is added to help add fluidity to the paste, make it malleable and ease the formation of the pellets especially during the extrusion process. Bentonite and alumina are clay-like materials often used as binders in pellets for industrial applications, most notably in catalysts used for the Friedal-Crafts reaction [1]. Other potential binders include; kaolin, graphite, starch, and resin binders such as acacia gum [3-7].
Little work has been done on pelletisation of amine adsorbents. Rezaei and co-workers investigated the effect of pressing pressure on various amine supported solids. PEI and APTES were loaded onto silica, SBA-15, and γ-alumina via wet impregnation. The pellets were formed by loading the amine powders into a 13 mm Carver press die and pressing at either 1000 psig or 5000 psig without the addition of a binder or plasticiser. The pellets were then crushed and sieved through a mesh for further analysis. Based on N₂ physisorption analysis they concluded that the lower pressing pressure of 1000 psig had little effect on surface area or pore volume whereas pressing at 5000 psig resulted in a decrease of 85 % in surface area and pore volume. CO₂ adsorption also decreased in the pellets pressed at 5000 psig with a reduction of between 13 and 44 % observed in the pellets compared to the powder form. No noticeable difference in CO₂ capacity was observed in the pellets that were pressed at 1000 psig. Neither mechanical strength nor durability was tested in this study. A particularly important find from this study indicated that APTES modified pellets were more affected by pressing pressure than PEI modified pellets. It was hypothesized that APTES may preferentially attach near hydroxyl sites located near the pore mouths while PEI is more evenly distributed throughout the pore network perhaps enhancing the stability of these adsorbents. It was also noted that as a result of the pelletising process no loss of PEI occurred. This was confirmed through FTIR analysis [8].

Xu and associates also investigated the effect of pelletisation on PEI modified MCM-41 and alumina. PEI modified MCM-41 and alumina were pelletised through a simple pressing method. Both the parent powder material and pellet were analysed for their CO₂ adsorption ability. They reported a 10 % decrease in CO₂ adsorption capacity for the pellets compared to the parent powder material [9]. Sharma and colleagues investigated a number of properties which could affect the CO₂ adsorption capacity of MCM-41, MCM-48 and SBA-15 based pellets. MCM-41, MCM-48 and SBA-15 were added to various amounts of binders and passed through an extruder to form pellets of 5 mm size. These were then modified with a 50 wt % loading of PEI via impregnation. This study found that the use of methylcellulose in the synthesis of the pellets added stability to the pellets and retained the pore structure of the pellets. In cases where methylcellulose was used in the synthesis of
the pellets, pellets showed higher mechanical strength compared to those without methylcellulose. Mechanical strength was determined using a Mecmesin strength tester whereby the pellet was held between two anvils and then a load was applied along the vertical direction of pellet until it exhibited failure [10]. Klinthong and co-workers pelletised APTES and PEI modified MCM-41. The pellets were synthesised by mixing the powdered adsorbents with an aqueous solution of 3 wt % polyallyamine (PAA) and NaOH and pressing the paste through an extruder. After varying the amounts of each of these components, it was found that the optimal synthesis conditions were 3 wt % PAA and 2 wt % NaOH. PAA was found to be an advantageous binder as it contains primary amino groups which can also bind with CO₂. This was found to help alleviate the decrease in CO₂ adsorption capacities of the pellets compared to their parent powder form. Overall just a 10 % decrease in CO₂ adsorption capacity was noticed compared to the powdered form. These pellets also expressed good mechanical strength and durability. A universal testing machine was used to measure the mechanical strength of the pellets. The pellets were kept between the two anvils of a strength machine and then an increasing load was applied at a constant rate along the direction vertical to the pellet, until cracking or breaking was observed. The applied load at fracture was recorded as the mechanical strength of the tested pellets. The durability of the pellets was determined through drop resistance tests, in which pellets were dropped four times from a height of 1.85 m onto a metal plate. The durability was calculated as the percentage of retained weight after dropping (initial weight minus breakages), relative to the initial weight [11].

To date, the main studies regarding pellets have focused on PEI and APTES modified solids. There is also a lack of data about pellet re-generability which is a crucial characteristic for industrial applications. The aim of this chapter is to produce a high capacity TEPA/SBA-15 pellet which can be regenerated without loss of CO₂ adsorption capacity. Two simple pellet synthesis methods were designed in this research. One method involved the use of a binder and plasticiser. Kaolin was used as a binding agent and methylcellulose was used as a plasticiser. The amounts of these additives were varied to investigate the influence of these components on the CO₂ adsorption capacity, stability, strength and durability of the resulting pellets.
These pellets were modified with TEPA and tested for their CO$_2$ adsorption/desorption capacity. The second method simply involved pressing TEPA modified SBA-15 into self-supporting pellets.

5.2 Experimental

All materials were procured from Sigma Aldrich and used as received. Kaolin and methylcellulose were the binder and plasticiser chosen for this study, respectively.

5.2.1 Pellet Synthesis

Two methods were developed to synthesise SBA-15 pellets; firstly through the addition of a binder and plasticiser and secondly through a binder-less process which involved simply pressing the parent powder material into self-supported circular shaped pellets. Both of these methods are outlined below.

Binder based pellet synthesis

SBA-15 was the mesoporous support used, it was synthesised as outlined in Chapter 2 Section 2.2.1, followed by calcination in air for 8 hours at 550°C, with a ramp rate of 5°C/min. The SBA-15 was then dried in a vacuum oven at 150°C for 16 hours before being pelletised. Various methods of producing pellets have been proposed by several authors [1, 12]. A general overview of the process is outlined in Figure 5.1. In a typical synthesis: 1.5 g of calcined and dried SBA-15 was added to 0.5 g kaolin and 0.5 g methylcellulose. Kaolin acted as a binder while methylcellulose added plasticity to the paste. It was decided to use these particular materials as they are common industrial binders and relatively cheap and easy to obtain. This powder mixture was mixed into a paste with a small volume of H$_2$O (typically 7 ml). This was mixed for 5 minutes. The paste was then put through a Makin’s clay extruder with a series of circular holes 1 mm in diameter, and the resulting paste was dried in air for 10 mins. The pellets were then cut to around 2 mm length as depicted in Figure 5.2. These were then dried in a vacuum oven at 90°C for 5 hours and calcined at 550°C for 5 hours in air. A number of these parameters such as the amount of binder, water and plasticiser were altered to investigate their influence on pellet formation. These will be discussed in more detail in the following sections.
Figure 5.1: General overview of pelletisation of SBA-15 [12]

Figure 5.2: Pellets cut to 2 mm
Amine modification of pellets through capillary impregnation

Typically 1 ml of ethanol plus 1 ml of TEPA was stirred for 30 mins. This solution was then added drop-wise to a small beaker containing 1 g of pellets synthesised through the binder based method, until the pellets began to look wet. The beaker was then allowed to stand overnight and then placed in a vacuum oven at 100°C for 16 hours. In some cases a second or third capillary impregnation was carried out i.e. multiple capillary impregnations.

Self-supported pellet synthesis

70%TEPA/SBA-15(I) was prepared following the procedure outlined in Chapter 3 Section 3.2. The 70%TEPA/SBA-15 powder was placed into a die and then loaded onto a hydraulic arm and pressed at various pressures; 80 psi and 140 psi. This produced a circular disk which was cut into pieces and placed into a reactor which was then loaded onto the gas testing rig for CO₂ adsorption/desorption.

5.2.2 Solid Characterisation

A number of methods were used to characterise the unmodified SBA-15 pellets and TEPA modified SBA-15 pellets. These are discussed in the following section.

Nitrogen adsorption/desorption analysis

Nitrogen adsorption/desorption analysis was carried out on a Quantachrome Autosorb AS-1 as outlined in Chapter 2 Section 2.2.4. This was done to determine the pore volume, pore size distribution and surface area of the unmodified binder based pellets. Surface area was calculated using the Brunauer-Emmett-Teller method, pore size was determined using the Barrett, Joyner and Halenda method and the Kelvin equation was used to determine pore radius.

Thermogravimetric analysis

Thermogravimetric analysis as outlined in Chapter 2 Section 2.2.4, was carried out on a selection of samples to establish their thermal stability and to measure TEPA loading in the TEPA modified SBA-15 pellets. Typically a sample of approximately 8 mg was placed into an alumina crucible and weighed in the internal balance of
the SDT Q600 instrument. The sample was heated up to 700°C in air at a heating rate of 10°C/min with the weight continuously recorded.

**Durability testing**

The durability of the pellets was established using a similar procedure as that reported by Klinthong et al [11]. This was achieved through drop resistance tests which involved dropping the pellets 3 times from a height of 1.85 m onto a metal plate. The durability was then calculated as the percentage of the retained weight (initial weight minus any fragments) after dropping relative to the initial weight. The method was modified by dropping certain samples a further 10 times to test their durability in harsher conditions.

**Mechanical Strength testing**

The strength of the pellets was measured using a vertical compressor rig (Instron-MSI-Instron-1 with a 100 N load cell). The pellets were kept between the two anvils of a vertical compressor rig and then an increasing load was applied at a constant rate of 4 mm/min along the direction vertical to the pellet until cracking or breaking was observed. The applied load at fracture was recorded as the mechanical strength of the pellets.

**CO₂ adsorption/desorption analysis**

All TEPA modified solids were tested for their CO₂ adsorption/desorption ability using an on-line testing rig with mass spectroscopy detection as outlined in Chapter 2 Section 2.2.3. The pellets were left uncrushed and added to a quartz reactor, which was loaded onto the test rig. A flow of helium was continuously sent through the reactor at 50 ml/min. The pre-treatment step was conducted first, which involved heating the furnace, which housed the reactor, up to 150°C at 10°C/min. The temperature was held for 5 mins. This step removed previously adsorbed CO₂. The furnace was then allowed to cool to 50°C. Then the adsorption was conducted by switching the gas flow to a CO₂ containing stream using 15% CO₂ in helium. A number of CO₂ pulses were passed over the solid, and then the solid was saturated with CO₂ by passing the CO₂ stream over the solid for 5 minutes continuously. The
CO$_2$ containing stream was then switched off. The CO$_2$ levels were then allowed to return to background levels before the desorption step was conducted. Desorption was conducted by heating the now CO$_2$ saturated pellet sample up to 150°C at 10°C/min, where it was held for 5 minutes. This step produced a CO$_2$ TPD profile from which CO$_2$ adsorption/desorption capacities were calculated.

5.3 Results

This section will outline the results of different synthesis procedures on pellet formation, TEPA modification of pellets and their CO$_2$ adsorption/desorption capacities.

Two processes were used to produce pellets. The first pellet adsorbents to be discussed are those prepared through the addition of a binder and plasticiser as outlined in Section 5.2.2. These pellets were formed using a simple method based on the use of water and kaolin which acted as a binder and methylcellulose which added plasticity to the SBA-15/kaolin/water mixture. This paste was extruded and calcined to form pellets 2 mm in length. Initially it was necessary to investigate the synthesis of pellets through the use of different amounts of SBA-15, kaolin, water and methylcellulose. These results are presented in Table 5.1. Included in the table is the amount of SBA-15, methylcellulose, kaolin and water used. Also included is an indicator of pellet formation whereby “✓✓” indicates very good pellets formed, i.e. the paste passed through the extruder easily and the resulting pellets held their shape after extrusion. The pellets labelled “✓” indicated pellet formation with a little more difficulty compared to those labelled with “✓✓”. These pellets may have been more brittle, did not keep their shape or were difficult to extract from the extruder. For samples labelled with the symbol “×” the paste was not very malleable and was difficult to pass through the extruder. From the table, it is clear that the presence of binder and plasticiser is crucial to pellet formation. Another key component is the amount of water used, too little produced very brittle pellets, while too much produced pellets which did not keep their shape.
A number of acceptable pellets were formed from the initial study. Therefore, it was then decided to optimise the procedure by investigating the effect of varying the amounts of binder and plasticiser used in the synthesis of pellets. The role of plasticiser on pellet formation was investigated first in more detail. The amount of SBA-15, kaolin and water were kept constant while the amount of methylcellulose was varied between 0 and 0.5 g. The result of this investigation is presented in Table 5.2. Included in the table are the amounts of SBA-15, plasticiser, binder and water used. The durability of the resulting pellets is also shown. Durability is a measurement of the robustness of the pellets and their ability to withstand wear and damage. It is clear from this table that pellets will not form in the absence of plasticiser as it plays a key role in keeping the SBA-15 and binder particles together, adds flexibility to the paste and eases the formation and shaping of pellets. Too little plasticiser produced good pellets but better quality pellets were produced when the amount of plasticiser was the same as the amount of binder added. The table also shows that the pellets produced with 0.5 g methylcellulose had the highest durability at 99.81 %. A further 10 more drop tests were conducted as the initial durability tests presented similar results. From these 13 drop resistance tests it can be seen that pellets formed with 0.5 g methylcellulose had the highest durability.
Similarly it was decided to investigate the role of the kaolin binder by varying its amount from 0 g to 0.5 g while keeping the SBA-15, methylcellulose and water amounts constant. Table 5.3 presents the results from this investigation. Similar to methylcellulose, the synthesis of pellets was not possible without the presence of a binder as it was the binder that pulls the SBA-15 particles together into a cohesive paste allowing pellets to form and adds mechanical strength to the pellets. The best quality pellets were formed when the amount of binder equalled that of the plasticiser. The highest durability after 13 drop resistance tests was observed in the pellet composed of 1.5 g SBA-15, 0.5 g methylcellulose, 0.5 g kaolin and 7 ml water.

Table 5.2: Effect of plasticiser on pellet formation

<table>
<thead>
<tr>
<th>SBA-15, g</th>
<th>Methylcellulose, g</th>
<th>Kaolin, g</th>
<th>Water, ml</th>
<th>Pellets formed</th>
<th>Durability after 3 drop tests, %</th>
<th>Durability after 13 drop tests, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.0</td>
<td>0.5</td>
<td>7.0</td>
<td>X</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1.5</td>
<td>0.25</td>
<td>0.5</td>
<td>7.0</td>
<td>✓</td>
<td>99.07</td>
<td>90.13</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>7.0</td>
<td>✓ ✓</td>
<td>99.81</td>
<td>96.11</td>
</tr>
</tbody>
</table>
The role of water on pellet formation was also investigated. The amount of SBA-15, kaolin and methylcellulose was kept constant while the amount of water was varied. The results of this study are presented in Table 5.4, the optimum amount of water was found to be 7 ml. From the results presented in the previous tables and Table 5.4, the pellets with the highest durability were those synthesized with 1.5 g SBA-15, 0.5 g methylcellulose, 0.5 g kaolin and 7 ml water. Therefore all subsequent pellets were synthesized using those amounts of support, plasticiser, binder and water.

Table 5.3: Effect of binder on pellet formation

<table>
<thead>
<tr>
<th>SBA-15, g</th>
<th>Methylcellulose, g</th>
<th>Kaolin, g</th>
<th>Water, ml</th>
<th>Pellets formed</th>
<th>Calcined Durability after 3 drop tests, %</th>
<th>Durability after 10 drop tests, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.0</td>
<td>7.0</td>
<td>×</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.25</td>
<td>7.0</td>
<td>✓</td>
<td>Y</td>
<td>96.89  87.33</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>7.0</td>
<td>✓ ✓</td>
<td>Y</td>
<td>99.81  96.11</td>
</tr>
</tbody>
</table>

Table 5.4: Effect of water on pellet formation

<table>
<thead>
<tr>
<th>SBA-15, g</th>
<th>Methylcellulose, g</th>
<th>Kaolin, g</th>
<th>Water, ml</th>
<th>Pellets formed</th>
<th>Calcined Durability after 3 drop tests, %</th>
<th>Durability after 10 drop tests, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>×</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>7.0</td>
<td>✓ ✓</td>
<td>Y</td>
<td>99.81  90.12</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>16.0</td>
<td>✓</td>
<td>Y</td>
<td>70.68  67.33</td>
</tr>
</tbody>
</table>
N₂ adsorption/desorption analysis was undertaken on unmodified calcined PB-SBA-15 (pellet formed using 1.5 g SBA-15, 0.5 g methylcellulose, 0.5 g kaolin, 7 ml water, it was not modified with TEPA) and unmodified, calcined SBA-15 powder. These results are presented in Table 5.5 and Figure 5.3 and Figure 5.4. Both Figures represent a type IV isotherm with a hysteresis loop, indicative of capillary condensation in the pores which is a characteristic of mesoporous solids [13-15]. A reduction in surface area and pore volume was observed for PB-SBA-15. As PB-SBA-15 was composed of 75 wt % SBA-15 and 25 wt % kaolin, when the results presented in Table 5.5 are reviewed, a truer reflection of surface area would be 680 m²/g while pore volume would be 1.01 cc/g would be observed for 1 g of the PB-SBA-15 sample. Therefore it can be concluded that the pelletising process had little effect on the surface area and pore volume of the mesoporous support.

<table>
<thead>
<tr>
<th>Support</th>
<th>Surface Area, m²/g</th>
<th>Pore Size, nm</th>
<th>Pore Volume, cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-SBA-15</td>
<td>516</td>
<td>6</td>
<td>0.77</td>
</tr>
<tr>
<td>SBA-15 powder</td>
<td>656</td>
<td>8</td>
<td>0.99</td>
</tr>
</tbody>
</table>
The removal of gaseous streams using solid sorbents

Emma Daniels

Figure 5.3: Nitrogen adsorption/desorption isotherm with pore size distribution unmodified, calcined binder pellet

Figure 5.4: $N_2$ adsorption/desorption isotherm with pore size distribution, for calcined SBA-15
The pellets prepared using 1.5 g SBA-15, 0.5 g kaolin, 0.5 g methylcellulose and 7 ml water (PB-SBA-15) were modified with TEPA. Pellets were modified via capillary impregnation as outlined in Section 5.2.2. This solid will be referred to as PB-SBA-15/TEPA(CI) where the PB indicates pelletisation with binder before TEPA modification, amine (TEPA), parent material (SBA-15) and amine modification method (CI) are included. For comparison purposes, SBA-15 powder was modified with 70 wt % TEPA via impregnation as outlined in Chapter 2 Section 2.2.2 where 70 % indicates the wt % of TEPA with respect to SBA-15 in the synthesis solution. This 70%TEPA/SBA-15(I) was then pelletised according to the binder based method reported in Section 5.2.1 which included calcining in air at 550°C for 5 hours. This solid will be referred to as 70%TEPA/SBA-15/PB. Table 5.6 presents the CO\textsubscript{2} adsorption/desorption capacities of each of these solids. Included in the table are the solid name, amine modification method, pellet synthesis method and CO\textsubscript{2} adsorption/desorption capacity. 70%TEPA/SBA-15/PB had a low capacity of 4 mgCO\textsubscript{2}/g of sorbent, likely due to loss of TEPA during calcination. Therefore amine modification post pellet synthesis was investigated further.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Amine Modification method</th>
<th>Capacity, mgCO\textsubscript{2}/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-SBA-15/TEPA(CI)</td>
<td>Capillary impregnation after pellet synthesis</td>
<td>47</td>
</tr>
<tr>
<td>70%TEPA/SBA-15-PB</td>
<td>Impregnation of SBA-15 before pellet synthesis</td>
<td>4</td>
</tr>
</tbody>
</table>

In relation to PB-SBA-15/TEPA(CI), after one TEPA modification, the CO\textsubscript{2} capacity was 47 mgCO\textsubscript{2}/g, indicating that the conventional capillary impregnation method of PB-SBA-15 does not produce a high CO\textsubscript{2} capacity solid. When a second capillary impregnation was carried out; this produced a solid with a higher capacity of 68 mgCO\textsubscript{2}/g. A third capillary impregnation was then carried out producing a solid with a capacity of 70 mgCO\textsubscript{2}/g. It is clear that after two capillary impregnations of the pellets, further impregnations do not significantly enhance the CO\textsubscript{2} adsorption/desorption ability.
Table 5.7: CO₂ adsorption/desorption capacities of the indicated solids

<table>
<thead>
<tr>
<th>Solid</th>
<th>CO₂ adsorption capacity, mgCO₂/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-SBA-15/TEPA(CI1)</td>
<td>47</td>
</tr>
<tr>
<td>PB-SBA-15/TEPA(CI2)</td>
<td>68</td>
</tr>
<tr>
<td>PB-SBA-15/TEPA(CI3)</td>
<td>70</td>
</tr>
</tbody>
</table>

Figure 5.5 presents the thermogravimetric profiles of unmodified PB-SBA-15 and PB-SBA-15/TEPA(CI1). The weight loss observed (4 %) for PB-SBA-15 is very small over the entire temperature range (30-700°C) indicating that this solid is quite stable. This weight loss may be due to adsorbed CO₂ at low temperatures (< 200°C). There is little weight loss above 200°C, indicating the solid is stable at high temperatures. There is a much bigger weight loss observed in the profile for PB-SBA-15/TEPA(CI1). The profile shows three areas of weight loss; the first up to 150°C (2 %), the second between 150°C and 200°C and the third between 200°C and 700°C. The losses below 150°C can be attributed to CO₂ and water, the losses between 150-200°C can be associated with the evaporation of weakly held TEPA while the loss seen between 200 and 700°C can be attributed to the evaporation/decomposition of more strongly bound TEPA. Taking these losses into account approximately 12 wt % can be attributed to TEPA.
As the binder based pelletisation process did not produce a high capacity adsorbent, the binder-less self-supported pelletisation process was investigated. This process simply involved pressing a small amount of 70%TEPA/SBA-15(I) into a pellet using a die and hydraulic arm. A number of pellets were produced using this method, the results of which are presented in Table 5.8. Included in the table is the pellet name, pelletising pressure used and CO$_2$ adsorption/desorption capacity of the resulting solid. For example 70%TEPA/SBA-15(I)-P80 is a pellet which is composed of SBA-15 which has been modified with 70 wt % TEPA via impregnation; this has been pelletised, through the binder-less method, at a pressure of 80 psi. 70%TEPA/SBA-15(I)-P80 had a high capacity of 173 mgCO$_2$/g, 70%TEPA/SBA-15(I)-P140 had a lower capacity of 153 mgCO$_2$/g, both of which are lower than 211 mgCO$_2$/g capacity observed in 70%TEPA/SBA-16(I) powder. Both 70%TEPA/SBA-15(I)-P80 and 70%TEPA/SBA-15(I)-P-140 showed similar durability after 3 drop tests. However after 13 drop tests a larger difference in their durability was observed. The pellet pressed at 140 psi was more brittle than the one pressed at 80 psi.

![Figure 5.5: Thermogravimetric analysis profiles of the indicated solids](image-url)
The removal of gaseous streams using solid sorbents

**Table 5.8: Results of binder-less pressed pellets**

<table>
<thead>
<tr>
<th>Solid</th>
<th>Pelletising Pressure, psi</th>
<th>mgCO₂/g</th>
<th>Durability after 3 drop tests, %</th>
<th>Durability after 13 drop tests, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%TEPA/SBA-15(I)-P80</td>
<td>80</td>
<td>173</td>
<td>98.7</td>
<td>75.09</td>
</tr>
<tr>
<td>70%TEPA/SBA-15(I)-P140</td>
<td>140</td>
<td>153</td>
<td>97.4</td>
<td>63.99</td>
</tr>
<tr>
<td>70%TEPA/SBA-15(I)</td>
<td>N/A</td>
<td>211</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

70%TEPA/SBA-15(I)-P80 underwent repeated CO₂ adsorption/desorption studies. Figure 5.6 presents the results of this study and shows desorption number with CO₂ adsorption/desorption capacity in mgCO₂/g of solid. A small decrease in capacity can be seen between the first and second desorption cycles, however after this CO₂ capacity remains stable over the last two adsorption/desorption cycles. This solid is the highest capacity pellet produced in this work. As discussed in Chapter 3, 70%TEPA/SBA-15(I) had a capacity of 211 mgCO₂/g. 70%TEPA/SBA-15(I)-P80 showed an 19% decrease in capacity compared to the parent powder adsorbent, which is comparable to the literature where the solids were PEI modified SBA-15 and PEI modified MCM-41, respectively [8, 9]. This solid also showed reasonable durability of 98.7% after 3 drop resistance tests but this decreased to 75.09 % after 13 drop tests.
Mechanical strength is an important characteristic of pellets. A simple test was conducted to determine the strength of the pellets as outlined in Section 5.2.3. It was not possible to test the self-supported pellets as the instrumentation was not equipped to accommodate the circular shape of the pellets synthesised in this work. Table 5.9 presents the mechanical strength of PB-SBA-15 and PB-SBA-15/TEPA(CI1). Interestingly once amine is added to the binder based pellet its strength increased from 0.15 MPa in PB-SBA-15 to 0.22 MPa in PB-SBA-15/TEPA(CI1). For comparison purposes a reference from Klinthong et al [11] is included.

**Table 5.9:** Mechanical strength of indicated solids

<table>
<thead>
<tr>
<th>Solid</th>
<th>Mechanical Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-SBA-15</td>
<td>0.15</td>
</tr>
<tr>
<td>PB-SBA-15/TEPA(CI1)</td>
<td>0.22</td>
</tr>
<tr>
<td>APTES/MCM-41</td>
<td>0.40</td>
</tr>
</tbody>
</table>
5.4 Discussion

Two pellet synthesis methods were investigated; the first method utilised the addition of binding agents forming cylindrical pellets 1 mm in diameter and 2 mm in length, the second method did not include the addition of binding agents, instead, SBA-15 was pressed into self-supported compacted circular discs approximately 1 cm in diameter and 1 mm in thickness.

Kaolin and methylcellulose were the binder and plasticiser, respectively, chosen for this study. These ingredients plus water and SBA-15 were simply mixed to form a paste. This paste was extruded and calcined to form pellets of 2 mm length. Kaolin is an aluminosilicate clay material; it is a di-octahedral 1:1 layered aluminosilicate. The cohesive energy in kaolin is primarily electrostatic with some van der Waals attractions and contains a degree of hydrogen bonding between the hydroxyl groups of one layer and the oxygen atoms of the adjoining layer. When a clay binder comes into contact with water it begins to expand as the electrostatic attraction between the individual platelets relaxes. This allows the platelets to slip across each other. When a shear force is applied through mixing, the platelets within the clay particles slide to form fibers and sheets over the surface of the SBA-15, bonding the materials together [14, 15]. Varying the amount of binding agent (kaolin) and plasticiser (methylcellulose) was found to significantly affect the formation of pellets. A weight ratio of 1:1 between kaolin and methylcellulose produced the best quality pellets. During calcination the methylcellulose plasticiser is removed producing pellets composed of 75 wt % SBA-15 known as PB-SBA-15. Pellets produced with less than 0.5 g methylcellulose were more brittle than those made with 0.5 g methylcellulose. When kaolin was absent from the pellet synthesis, the paste was difficult to extract from the extruder and pellets could not be formed, as the particles were not joined into a cohesive unit. Durability of the pellets increased with increasing amount of kaolin. The results from Table 5.2 and Table 5.3 show that both plasticiser and binder are needed to produce good quality, durable pellets. PB-SBA-15 showed good durability as after 13 drop tests the durability was 96.11%.

As discussed in Chapter 3, the highest CO$_2$ adsorption/desorption capacity solid was 70%TEPA/SBA-15(I), which had a capacity of 211 mgCO$_2$/g. When PB-SBA-15
was modified with TEPA through capillary impregnation, PB-SBA-15/TEPA(CI1) had a modest capacity of 47 mgCO\(_2\)/g. When a further capillary impregnation was carried out on PB-SBA-15/TEPA(CI1), PB-SBA-15/TEPA(CI2) had a CO\(_2\) adsorption/desorption capacity of 68 mgCO\(_2\)/g. When a third capillary impregnation was carried out, capacity marginally increased to 70 mgCO\(_2\)/g. For comparison purposes the thermogravimetric analysis profiles of 70%TEPA/SBA-15(I) powder and PB-SBA-15/TEPA(CI1) are presented in Figure 5.7. In the PB-SBA-15/TEPA(CI1) profile there is a 12 wt % loss attributable to TEPA, while in 70%TEPA/SBA-15(I) powder there is a 25 wt % loss attributed to TEPA. There is half as much TEPA present in PB-SBA-15/TEPA(CI1) compared to 70%TEPA/SBA-15(I). This may suggest that the pelleting process may inhibit TEPA uptake. As the binder slides over the SBA-15 surface, pulling the SBA-15 particles together, access to surface hydroxyls may be reduced, which would limit the amount of TEPA uptake. This may physically limit TEPA to the external surface of the pellets, accounting for the lower TEPA uptake compared to the powder solid. This ultimately limits the CO\(_2\) adsorption/desorption capacity of the pellet.

![Figure 5.7: Thermogravimetric analysis profiles of the indicated solids](image)

Pellets were also produced by simply pressing the parent powder material into compacted circular units. The capacity of these self-supported pellets was significantly higher than those pellets synthesised through the addition of binding and plasticiser agents. Compared to 70%TEPA/SBA-15(I) powder, there was just a
19% reduction in CO\textsubscript{2} adsorption/desorption capacity. These pellets also proved to retain CO\textsubscript{2} adsorption/desorption capacity over repeated CO\textsubscript{2} adsorption/desorption cycles as presented in Figure 5.6.

The self-supported pellets showed high CO\textsubscript{2} adsorption/desorption capacities however durability was significantly reduced compared to PB-SBA-15 pellets. The addition of a binder and plasticiser improve both the durability and mechanical strength of pellets. They do this by uniting the SBA-15 particles into a cohesive unit. Indeed the mechanical strength recorded for PB-SBA-15/TEPA/(CI1) was 0.22 MPa which is just above the 0.2 MPa requirement for industry [11]. The self-supported pellets were compressed into cohesive circular pellets but were more brittle than the PB-SBA-15 pellets. They showed reasonable durability over 3 drop resistance tests, however after 13 drop resistance tests, the durability was significantly lower than PB-SBA-15.

5.5 Conclusion

Two pellet synthesis methods were investigated; (1) through the addition of binding agents and (2) through simply pressing the parent powder material into a compacted unit. The first method produced pellets which showed good durability and mechanical strength however their CO\textsubscript{2} adsorption/desorption capacities were low. This was likely due to physical restraints limiting TEPA to the external surface of the pellets.

The second method produced high capacity self-supporting circular pellets which demonstrated high CO\textsubscript{2} adsorption/desorption capacities and stability over repeated CO\textsubscript{2} adsorption/desorption cycles. It was not possible to test the mechanical strength of these pellets due to their shape but they showed reasonable durability after three drop resistance tests, however after 13 drop resistance tests their durability was lower than the binder based pellets. To date the standard durability test typically involves 3 or 4 drop resistance tests; in this work it was expanded to 13 to add credibility to the test.
Overall, it has been shown that TEPA modified SBA-15 can be pelletised through two different methods; the binder based approach produced more robust pellets however CO\textsubscript{2} adsorption/desorption capacity was compromised while the self-supported, binder-less method produced the highest capacity solids with lower durability.

5.6 References


6 Investigation of the thermodynamic and kinetic properties of amine modified SBA-15 CO\(_2\) adsorbents
6 Investigation of the thermodynamic properties of amine modified SBA-15 CO₂ adsorbents

6.1 Introduction

As already highlighted in previous chapters, adsorption is considered a key process in tackling CO₂ emissions. Indeed, adsorption is widely applied in many environmental remediation processes. There are two different types of adsorption: physical adsorption also referred to as physisorption and chemical adsorption otherwise known as chemisorption. Physisorption is characterised by the interaction via van der Waals forces between the adsorbate and the substrate. These van der Waals interactions are weak and typical enthalpy of physisorption is usually around 0-20 kJ/mol. This small enthalpy change is insufficient to give rise to bond breaking and results in electrostatic attraction between molecules. Physisorption may occur between CO₂ and unmodified OH groups found in most solid supports or amine molecules tethered to solid supports. Chemisorption is characterised by a chemical reaction between the solid and sorbate resulting in bond breaking. The enthalpy for this type of adsorption is much higher than that of physisorption; it is typically in the region of 20-200 kJ/mol [1-3]. In terms of CO₂ adsorption this type of adsorption is characterised by the formation of ammonium carbamate between amine-modified solids and CO₂ as discussed in Chapter 1.

In order to fully understand the processes occurring in the CO₂ adsorbents previously outlined in this study, it is necessary to look at the thermodynamic properties of the solids and their interactions. It is also necessary to investigate the influence of temperature and pressure on CO₂ adsorption. The evaluation of an adsorptive process is usually based on two properties: the adsorption isotherms and the heat of adsorption. The adsorption isotherm is a measure of the adsorption capacity at various pressures and temperatures. Adsorption isotherms describe how gaseous pollutants, in this case CO₂, interact with adsorbents. These isotherms can also be used to reliably predict adsorption parameters [4, 5]. Post combustion flue gas is released at a temperature in the range of 40-60°C and at a total pressure of approximately 1 bar, within this; CO₂ is present at a low partial pressure of between 0.13-0.16 bar. Therefore it is necessary to investigate the CO₂ adsorption capacities
within these temperature and pressure constraints [8]. For this reason, CO$_2$ adsorption studies at temperatures between 30-50°C and partial pressures of 0.03 to 1 atm were investigated on the test rig as outlined in Section 6.2.3. There are a number of models available for adsorption prediction, such as the Langmuir, Freundlich and Tóth models. This work will focus on the linear form of the Langmuir and Freundlich models and the non-linear Dual-Site Langmuir model. Analysis of adsorption isotherms collected at different temperatures allows an estimation of the coverage-dependent heat of adsorption, known as $Q_{st}$ [4, 5].

### 6.1.1 Adsorption isotherms

An adsorption isotherm is a curve obtained by plotting at constant temperature, the quantity of adsorbate against the concentration of the substance in the equilibrium gas or solution. The concentration is taken as the partial pressure of the gas being adsorbed in the total gas stream. Adsorption isotherms can be used for determining predictions of adsorption parameters. There are a number of models available for adsorption predictions. This study utilised the linear form of the Langmuir and Freundlich isotherm models and the non-linear Dual-Site Langmuir model.

**Langmuir Isotherm**

The Langmuir isotherm was originally developed to describe gas-solid-phase adsorption onto activated carbon and is perhaps the most commonly used isotherm model. This model assumes monolayer adsorption one molecule in thickness. Adsorption can only occur at a fixed amount of localised sites. There is no lateral interaction or hindrance between the adsorbed molecules even on adjacent sites. This isotherm refers to homogenous adsorption where every molecule possesses constant enthalpies and adsorption activation energy [6, 7]. The mathematical expression of the non-linear Langmuir isotherm model is illustrated in Equation 6.1, while the linear expression of Langmuir isotherm model is illustrated in Equation 6.2:

$$Q_e = \frac{Q_m K_L P}{1 + K_L P}$$  \hspace{1cm} \text{Equation 6.1}
The removal of gaseous streams using solid sorbents

Emma Daniels

\[
\frac{P}{Q_e} = \frac{1}{KLQ_m} + \frac{P}{Q_m}
\]

Equation 6.2

Where \( K_L \) is the Langmuir adsorption constant, \( P \) is the partial pressure of the gas adsorbate (\( \text{CO}_2 \)), \( Q_e \) is the amount of gas adsorbate adsorbed at equilibrium and \( Q_m \) is the calculated maximum amount of gas adsorbed at equilibrium. A plot of \( (P/Q_e) \) versus \( (P) \) results in a linear representation of the adsorption data with a slope \( (1/Q_m) \) and intercept \( (1/K_LQ_m) \). The assumption made in the Langmuir isotherm is that the surface of the adsorbent forms a monolayer and the adsorption energy is the same for all adsorption sites on the adsorbent surface [5].

**Freundlich Isotherm**

The Freundlich isotherm is the earliest known relationship describing reversible adsorption which is not restricted to the formation of a monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [6]. This isotherm is mainly applied in heterogeneous systems. The nonlinear and linear expressions of the Freundlich isotherm are illustrated in Equation 6.3 and Equation 6.4, respectively, where \( K_F \) is the Freundlich equilibrium constant and \( (1/n) \) is the heterogeneity factor. The value for \( (1/n) \) ranges between 0 and 1 and is a measure of adsorption intensity, becoming more heterogeneous as its value gets closer to zero, while a value close to 1 implies a chemisorption process. The various parameters can be calculated using a plot of \( (\ln Q_e) \) versus \( (\ln P) \) which gives a straight line with slope \( (1/n) \) and an intercept \( (\ln K_F) \) [5, 6, 7].

\[
Q_e = K_F P^{(1/n)}
\]

Equation 6.3

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln P
\]

Equation 6.4
Dual-Site Langmuir Isotherm

A dual model combines two models creating a model which possesses more flexibility when fitting isotherm models to experimental data. One of the most commonly used dual site models is the Dual-Site Langmuir isotherm model. There is no linear form of the Dual-Site Langmuir model so it requires a computational approach. Equation 6.5 illustrates the non-linear equation of the Dual-Site Langmuir isotherm model. \( Q_m \) and \( K_L \) represent the maximum adsorption capacity and Langmuir constants, respectively, for each adsorption site. \( K_{L1} \) and \( K_{L2} \) are found using the Solver function in Excel based on the best fit to the data; from this the \( Q_m \) values are determined [8, 9, 10].

\[
Q_e = \frac{Q_{m1}K_{L1}P}{1+K_{LP}} + \frac{Q_{m2}K_{L2}P}{1+K_{L2}P}
\]

Equation 6.5

6.1.2 Thermodynamics of Adsorption

In order to investigate the strength of the interaction between CO\(_2\) molecules and amine solids, the isosteric heat of adsorption \( (Q_{st}) \) was calculated using CO\(_2\) isotherms at 30, 35, 40 and 50°C. There are two common ways to acquire experimental data when studying heats of adsorption, firstly the extrapolation of adsorption isotherm data at different temperatures for use in the Clausius-Clapeyron equation and secondly the direct measurement of heats of adsorption using adsorption calorimetry. Molecular simulation can then be carried out using the experimental data from either of these methods [11, 12, 13]. While the use of the Clausius-Clapeyron equation can be invalid at higher pressures it is a useful technique that can be readily applied to many experimental set-ups. On the other hand, the direct measurement of heats of adsorption through adsorption calorimetry requires a purpose built measurement system. For this reason the Clausius-Clapeyron method is the most widely used method for determining heats of adsorption. The isosteric heat of adsorption, \( Q_{st} \), reported in kJ/mol at a given surface loading \( (q_e) \), can be calculated using the Clausius-Clapeyron equation and is illustrated in Equation 6.6. \( Q_{st} \) is the isosteric heat of adsorption, \( T \) is the temperature (K), \( P \) is the
CO₂ partial pressure, \( q_e \) is the given adsorbate loading and \( R \) is the universal gas constant (8.314 JK\(^{-1}\) mol\(^{-1}\)).

\[
\left( \frac{\partial (\ln P)}{\partial (1/T)} \right)_{q e} = \frac{Q st}{R} \tag{Equation 6.6}
\]

### 6.1.3 Kinetics of adsorption

Adsorption kinetics for CO₂ uptake was also investigated using the CO₂ breakthrough data. The CO₂ breakthrough data were fitted to the Yoon-Nelson model to calculate the rate constant for CO₂ uptake for given gas streams [14]. The Yoon-Nelson model assumes that the rate of change in the breakthrough concentration is proportional to the breakthrough concentration and the number of adsorption sites. The mathematical expression of the Yoon-Nelson model is illustrated in Equation 6.7.

\[
\frac{C}{Co} = \frac{1}{1 + \exp[kYN(\tau-t)]} \tag{Equation 6.7}
\]

Where \( kYN \) is the Yoon-Nelson rate constant (seconds\(^{-1}\)), \( t \) is the sampling time (seconds), \( \tau \) is time (seconds) for 50 % CO₂ breakthrough, \( C \) is the exhaust concentration of CO₂ and \( Co \) is the inlet concentration of CO₂. The \( kYN \) value is an index for the overall adsorption rate and depends on the slope of the breakthrough curve [14-17].

### 6.2 Experimental

#### 6.2.1 Adsorbent synthesis

70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI) were synthesised as outlined in Chapter 3 Section 3.2.2 and Chapter 2 Section 2.2.2, respectively.
6.2.2 CO₂ Isotherm tests

Adsorption isotherm studies of amine modified adsorbents were carried out using the gas adsorption rig as described in Chapter 2, Section 2.2.3. Mixtures of pure CO₂, pure He and 15% CO₂ (in He) were used to create a gas flow with CO₂ partial pressures between 0.035 and 1.0 atm (0.035, 0.07, 0.15, 0.5 and 1 atm). Typically 100 mg of the adsorbent was placed in a quartz reactor and attached to the rig illustrated in Figure 2.1 in Chapter 2. The partial pressure of the gas was taken as it % composition in the gas stream. Similar to other CO₂ TPD tests, sample pretreatment was carried out. This involved heating the sample to 150°C for 70%TEPA/SBA-15(I) and 200°C for 70%APTES/SBA-15(CI) at a rate of 10°C/min, to remove any adsorbed water and CO₂ that may have accumulated on the sample while exposed to the atmosphere. This temperature was held for a number of minutes and then the sample was cooled to 30°C. Once the furnace had reached 30°C, CO₂ at a partial pressure of 0.035 atm, was introduced to the sample. This was done in a similar fashion to previous CO₂ adsorption steps as outlined in Chapter 2; however the adsorption time was increased to 1 hour to allow maximum uptake and breakthrough of CO₂ to occur. Once complete saturation had been achieved, after 1 hour, the gas flow was switched from a CO₂ containing mixture to the helium carrier gas. When the CO₂ counts had decreased and levelled out, the adsorbent was heated to 200°C (for 70%APTES/SBA-15(CI)) or 150°C (for 70%TEPA/SBA-15(I)) resulting in a CO₂ desorption peak. This was used to calculate the CO₂ uptake for the adsorbent at the indicated CO₂ partial pressure. When CO₂ desorption was complete, the solid was once again cooled to 30°C and this process was repeated for a number of CO₂ partial pressures between 0.07 and 1.0 atm. This process was repeated again at different adsorption temperatures of 35, 40 and 50°C. The data from these isotherm adsorption/desorption studies was used in a number of adsorption isotherm models to produce CO₂ isotherms. Isosteres were then derived from these isotherms to evaluate the isosteric heat of adsorption for each solid.

The kinetics of CO₂ adsorption was also investigated. In a typical CO₂ adsorption kinetics experiment, 100 mg of the sample was heated to 200°C (for 70%APTES/SBA-15(CI)) and 150°C (for 70%TEPA/SBA-15(I)) at a rate of 10°C/min.
to remove any impurities from the adsorbent. The sample was held at the desired
temperature for 5 minutes, the sample was then cooled to 30°C before being exposed
to the CO₂ containing gas stream. The solid adsorbent was exposed to the gas flow
until CO₂ breakthrough was observed. The CO₂ adsorption breakthrough data was
used to investigate CO₂ adsorption kinetics. This data was then fitted to the Yoon-
Nelson model to calculate the rate constants for CO₂ adsorption. Following
breakthrough the gas flow was switched back to a helium flow (50 ml/min). When
CO₂ levels had returned to background levels, the solid was then heated to 200°C or
150°C and the exiting gases were constantly recorded using the mass spectrometer.
The CO₂ adsorption step was repeated at 35, 40 and 50°C. The adsorption
breakthrough data was then used to determine the rate of CO₂ uptake. In order to
investigate the effect of other gases (such as CH₄) in the gas stream on kinetics, a gas
stream containing 0.15 atm CO₂ and 0.025 atm CH₄ were passed over the solids. A
total gas flow volume of 50 ml/min was maintained at all times. The CO₂
adsorption breakthrough data from these experiments were used to determine the
impact of the presence of CH₄ on the rate of CO₂ adsorption.

6.3 Results

The data from the CO₂ adsorption isotherm experiments were then used to calculate
constants for use in modelling the data in order to fully investigate the
thermodynamic properties of the chosen solids. In Chapter 2, 70%APTES/SBA-
15(CI) was found to be the highest capacity sorbent from all APTES solids, while in
Chapter 3, 70%TEPA/SBA-15(I) was found to have the highest capacity of all TEPA
samples. For this reason, the adsorption characteristics, thermodynamic and kinetics
of CO₂ adsorption on 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI) were
further investigated. This section will present the results from these experiments.

6.3.1 Isotherm studies

Figure 6.1 presents the adsorption isotherms of CO₂ adsorption on 70%TEPA/SBA-
15(I) at the indicated partial pressures and temperatures. There was a steep increase
in CO₂ adsorption capacity in the lower partial pressure range. This increase
becomes less steep towards the higher partial pressure range. This phenomenon can be explained by the high affinity of CO$_2$ for amine adsorbents, facilitating CO$_2$ adsorption at low relative pressure. These isotherms are similar to a Type 1 isotherm as outlined in Chapter 1 Section 1.8. The highest capacity of 205 mgCO$_2$/g was observed at 1 atm at 50°C. This is similar to the results presented in Table 3.1 in Chapter 3, where the adsorption was conducted at various temperatures (30, 40, 50, 60, 80 and 100°C). The highest capacity was found when adsorption was conducted at 50°C.

Figure 6.1: Experimental CO$_2$ adsorption isotherm data on 70%TEPA/SBA-15(I) at the indicated temperatures (100 mg sample, 50 ml/min He flow rate, temperature ramped at 10°C/min up to 150°C)

Figure 6.2 presents the modelled Langmuir CO$_2$ adsorption isotherms of 70%TEPA/SBA-15(I) at the indicated temperatures. All isotherms are similar to each other as they all show an increase in CO$_2$ uptake with increasing pressure. This increase is more steep in the lower pressure range up to 0.15 atm. It is clear that the adsorption temperature affects adsorption capacity, with the highest capacities found at 50°C.
Figure 6.2: Langmuir CO$_2$ adsorption isotherms and experimental data on 70%TEPA/SBA-15(I) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, temperature ramped at 10°C/min up to 150°C)

Table 6.1 presents the Langmuir constants acquired from the data presented in Figure 6.1. The Langmuir constant $K_L$ was calculated from the equation of the line of the linear form of the Langmuir isotherm. The value of $K_L$ is indicative of how sharp the increase in CO$_2$ uptake is with increasing partial pressure and is an indication of the level of affinity between CO$_2$ and the adsorbent. $Q_m$, the calculated maximum adsorption capacity of the adsorbent, increased with increasing temperature which is similar to the experimental data presented in Figure 6.1. $R^2$, the coefficient of determination, is a number that indicates how well data fit a statistical model, typically a linear one. $R^2$ values range between 0 and 1 with 1 being the best fit. The closer the $R^2$ value is to 1, the better the fit. RSME is a measure of error between the experimental data and the modelled data. It is the square root of the variance, known as the standard deviation. The threshold is defined by the experimental data, in this case the range is 0 to 205, therefore the lower the number, the smaller the error. The $R^2$ values are close to 1, indicating a good fit with the data. The RMSE values presented in Table 6.1 are relatively low, indicating a good fit between the experimental data and the modelled data.
Table 6.1: Langmuir constants for CO\textsubscript{2} adsorbed on 70\%TEPA/SBA-15(I)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( K_L )</th>
<th>( Q_m )</th>
<th>( R^2 )</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>24.01</td>
<td>138</td>
<td>0.9989</td>
<td>3.78</td>
</tr>
<tr>
<td>40</td>
<td>24.03</td>
<td>154</td>
<td>0.9969</td>
<td>4.12</td>
</tr>
<tr>
<td>50</td>
<td>32.06</td>
<td>205</td>
<td>0.9989</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Figure 6.3 presents the modelled Freundlich CO\textsubscript{2} adsorption isotherms at the indicated temperatures along with the experimental data, using the 70\%TEPA/SBA-15(I) solid. Compared to the Langmuir model in Figure 6.2, the Freundlich model does not appear to be a good fit with the experimental data.

Table 6.2 presents the Freundlich constants from the results presented in Figure 6.3. \( K_F \) is the Freundlich equilibrium constant and \( 1/n \) is the heterogeneity constant. As the value for \( 1/n \) becomes closer to zero, a more heterogeneous cover is implied while a value near 1 implies a chemisorption process. This model is generally applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over a heterogeneous surface. This model did not fit the experimental data as well as the Langmuir isotherm model; this is supported by the \( R^2 \) and RMSE values in Table 6.2. This suggests that multilayer adsorption does not occur; instead
it is likely that only monolayer adsorption occurs at a fixed number of adsorption sites.

Table 6.2: Freundlich constants for CO₂ adsorbed on 70%TEPA/SBA-15(I)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>1/n</th>
<th>K_F</th>
<th>R²</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.2071</td>
<td>130</td>
<td>0.7331</td>
<td>32.30</td>
</tr>
<tr>
<td>40</td>
<td>0.2094</td>
<td>150</td>
<td>0.7623</td>
<td>39.40</td>
</tr>
<tr>
<td>50</td>
<td>0.1496</td>
<td>205</td>
<td>0.7111</td>
<td>55.01</td>
</tr>
</tbody>
</table>

The Dual-Site Langmuir model was also investigated as the Langmuir was a close fit with the data and the results presented in Chapter 3 indicated the presence of multiple adsorption sites. This model allows for the calculation of CO₂ adsorption in two different adsorption sites, both of Langmuir type. This allows more flexibility for fitting isotherm models to experimental data. Figure 6.4 presents the Dual-Site Langmuir modelled data and the experimental data at 30°C. This model shows a very good fit for the experimental data as the combined model and experimental data match very well. Surface 1 shows traditional Langmuir characteristics with a plateau in CO₂ uptake as the CO₂ partial pressure approached 1 atm. The second adsorption site, Surface 2, shows a somewhat linear type isotherm with CO₂ uptake increasing proportionally with an increase in CO₂ partial pressure. When these two profiles are combined the experimental data matches it quite well.
Figure 6.4: Dual-Site Langmuir modelled CO\textsubscript{2} adsorption isotherms and experimental data on 70\%TEPA/SBA-15(I) at 30°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 150°C)

Figure 6.5 presents the Dual-Site Langmuir model and experimental data at 40°C. Once again the combination of the two adsorption sites matched the experimental data very well. The amount of CO\textsubscript{2} adsorbed on Surface 2 increased compared to that observed in Figure 6.4. This may be due to the increased mobility of TEPA at higher temperatures, opening up more sites for CO\textsubscript{2} adsorption.

Figure 6.5: Dual-Site Langmuir modelled CO\textsubscript{2} adsorption isotherms and experimental data on 70\%TEPA/SBA-15(I) at 40°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 150°C)
Figure 6.6 presents the Dual-Site Langmuir modelled data and experimental data from 50°C. Similarly to Figure 6.4 and Figure 6.6, the combination of the two Langmuir adsorption sites fits the experimental data quite well. Similarly to the results presented in Figure 6.5, adsorption attributable to Surface 2 has increased. TEPA molecules become more mobile at higher temperatures; this is likely to result in increased adsorption sites at higher temperatures. Surface 2 may be attributed to the increased TEPA adsorption sites available at 50°C.

Table 6.3 presents the Dual-Site Langmuir constants obtained from the fitted models. When the Dual-Site Langmuir model was applied to the experimental data using 70%TEPA/SBA-15(I), it showed a very good fit to the data, especially at 50°C as shown by the RMSE values. Both the $K_{L1}$ and $K_{L2}$ values increased with increasing temperature, highlighting the increased affinity on both adsorption sites with increasing temperature.
Table 6.3: Dual-Site Langmuir constants for CO$_2$ adsorbed on 70%TEPA/SBA-15(I)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$K_{L1}$</th>
<th>$K_{L2}$</th>
<th>$Q_{m1}$</th>
<th>$Q_{m2}$</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>39.20</td>
<td>0.0001</td>
<td>141.24</td>
<td>0.308</td>
<td>1.19</td>
</tr>
<tr>
<td>40</td>
<td>98.15</td>
<td>0.0008</td>
<td>146.96</td>
<td>22.90</td>
<td>1.27</td>
</tr>
<tr>
<td>50</td>
<td>109.07</td>
<td>0.0016</td>
<td>154.50</td>
<td>49.30</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The results presented in Figure 6.4 to Figure 6.6, indicate that the Dual-Site Langmuir model is the best fit with the experimental data. This suggests that there are two adsorption sites within 70%TEPA/SBA-15(I). This is similar to the results of the de-convoluted profiles in Figure 3.25 in Chapter 3, suggesting that the CO$_2$ may be bound to TEPA near the pore mouths and further within the porous network. The adsorption sites are likely accessed via an amine hopping mechanism discussed in Chapter 3.

CO$_2$ adsorption isotherm experiments were also carried out on 70%APTES/SBA-15(CI). Figure 6.7 presents the experimental data obtained at the indicated CO$_2$ partial pressures and temperatures. The isotherms were similar to each other as CO$_2$ capacity increased with increasing pressure. This increase was particularly steep in the lower partial pressure range, however temperature was found to impact capacity. When the temperature was raised from 30°C to 35°C, an increase in capacity was observed. When the temperature was increased from 35°C to 40°C, adsorption/desorption capacity decreased. Similarly, when the temperature was increased from 40°C to 50°C a further decrease in CO$_2$ adsorption/desorption was observed. This suggests that temperature is a significant factor during the adsorption process with the optimum adsorption temperature observed at 35°C.
Figure 6.7: CO$_2$ adsorption isotherm data on 70%APTES/SBA-15(CI) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C).

Figure 6.8 presents the experimental and Langmuir modelled data for 70%APTES/SBA-15(CI). The optimum temperature at which the highest CO$_2$ adsorption/desorption was found to be 35°C, similar to the experimental data. Table 6.4 presents the Langmuir constants acquired from the data presented in Figure 6.8. $Q_m$, the calculated maximum adsorption capacity of the solid, decreased when the temperature exceeded 35°C. Above 35°C, there is a reduction of $Q_m$ as the temperature at which adsorption is carried out approaches the temperature at which CO$_2$ desorption begins. From the RSME values, the Langmuir model was found to be a good fit with the experimental data, indicating monolayer adsorption of CO$_2$ adsorption on 70%APTES/SBA-15(CI).
Figure 6.8: Langmuir modelled CO\textsubscript{2} adsorption isotherms and experimental data on 70\%APTES/SBA-15(CI) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped at 10\(^\circ\)C/min up to 200\(^\circ\)C)

Table 6.4: Langmuir constants for CO\textsubscript{2} adsorbed on 70\%APTES/SBA-15(CI)

<table>
<thead>
<tr>
<th>Temperature, (^\circ)C</th>
<th>(K_L)</th>
<th>(Q_m)</th>
<th>(R^2)</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>11.57</td>
<td>108</td>
<td>0.9998</td>
<td>4.24</td>
</tr>
<tr>
<td>35</td>
<td>27.11</td>
<td>124</td>
<td>0.9998</td>
<td>4.76</td>
</tr>
<tr>
<td>40</td>
<td>25.01</td>
<td>100</td>
<td>0.9998</td>
<td>5.09</td>
</tr>
<tr>
<td>50</td>
<td>14.08</td>
<td>96</td>
<td>0.9997</td>
<td>6.00</td>
</tr>
</tbody>
</table>

Figure 6.9 presents the modelled Freundlich and experimental data obtained from the indicated CO\textsubscript{2} partial pressures and temperatures. Compared to the Langmuir models in Figure 6.8, the Freundlich model appears not to fit the experimental data.
Figure 6.9: Freundlich modelled CO\(_2\) adsorption isotherms and experimental data on 70\%APTES/SBA-15(CI) at the indicated temperatures (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C).

Table 6.5 presents the Freundlich constants for 70\%APTES/SBA-15(CI). The RSME values are bigger compared to those for the Langmuir model, suggesting that the Langmuir isotherm is a better fit for 70\%APTES/SBA-15(CI). Similarly, the R\(^2\) values are lower than those reported for the Langmuir model, supporting the theory that the Freundlich model is not a good fit for the experimental data.

Table 6.5: Freundlich constants for CO\(_2\) adsorbed on 70\%APTES/SBA-15(CI)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>(1/n)</th>
<th>(K_F)</th>
<th>R(^2)</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.337</td>
<td>114</td>
<td>0.677</td>
<td>8.24</td>
</tr>
<tr>
<td>35</td>
<td>0.339</td>
<td>120</td>
<td>0.610</td>
<td>8.12</td>
</tr>
<tr>
<td>40</td>
<td>0.338</td>
<td>106</td>
<td>0.699</td>
<td>8.16</td>
</tr>
<tr>
<td>50</td>
<td>0.331</td>
<td>90</td>
<td>0.669</td>
<td>10.01</td>
</tr>
</tbody>
</table>

Figure 6.10 presents the Dual-Site Langmuir modelled data and the experimental data at 30°C. This model assumes that there are two forms of CO\(_2\) adsorption; Surface 1 shows traditional Langmuir characteristics with a plateau in CO\(_2\) uptake as the CO\(_2\) partial pressure approached 1 atm. The second adsorption site, Surface 2, shows a somewhat linear type isotherm with CO\(_2\) uptake increasing proportionally.
with an increase in CO\textsubscript{2} partial pressure similar to those presented for 70\%TEPA/SBA-15(I). When these two profiles are combined it fits the experimental data quite well.

![Dual-Site Langmuir modelled CO\textsubscript{2} adsorption isotherms and experimental data](image)

**Figure 6.10:** Dual-Site Langmuir modelled CO\textsubscript{2} adsorption isotherms and experimental data on 70\%APTES/SBA-15(CI) at 30\°C (100 mg sample, 50 ml/min flow rate, ramped at 10\°C/min up to 200\°C)

This Dual-Site Langmuir model was also fitted to the experimental data obtained at 35\°C. Figure 6.11 presents the modelled data and the experimental data at 35\°C. Similar to the data presented in Figure 6.10, the modelled data fits the experimental data quite well. The adsorption associated with Surface 2 increased compared to that observed in Figure 6.10.
Figure 6.11: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data on 70%APTES/SBA-15(CI) at 35°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 150°C)

Figure 6.12 presents the Dual-Site Langmuir modelled data and the experimental data at 40°C. The Dual-Site Langmuir is once again a good fit with the experimental data. The adsorption associated with Surface 2 remained the same as that observed in Figure 6.11.

Figure 6.12: Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data on 70%APTES/SBA-15(CI) at 40°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)
Figure 6.13 presents the Dual-Site Langmuir modelled data and the experimental data at 50°C. This Figure is somewhat different to the previous three Figures as the adsorption associated with the second site has decreased compared to Figure 6.12.

![Figure 6.13](image)

**Figure 6.13:** Dual-Site Langmuir modelled CO$_2$ adsorption isotherms and experimental data on 70%APTES/SBA-15(CI) at 50°C (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C)

Table 6.6 presents the Dual-Site Langmuir constants for 70%APTES/SBA-15(CI). Figures 6.10 to Figure 6.13 have shown that the Dual-Site Langmuir model appears to be a good fit with the experimental data, this is supported by the R$^2$ and RSME values in Table 6.6. The adsorption associated with Surface 1 was found to be responsible for more CO$_2$ adsorption than Surface 2. Based on the R$^2$ and RSME values, the Dual-Site Langmuir model is the best fit to the experimental data for both 70%APTES/SBA-15(CI) and 70%TEPA/SBA-15(I).
Table 6.6: Dual-Site Langmuir constants for CO$_2$ adsorbed on 70%APTES/SBA-15(CI)

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>$K_{L1}$</th>
<th>$K_{L2}$</th>
<th>$Q_{m1}$</th>
<th>$Q_{m2}$</th>
<th>$R^2$</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>35.78</td>
<td>0.070</td>
<td>99.41</td>
<td>6.39</td>
<td>0.997</td>
<td>0.124</td>
</tr>
<tr>
<td>35</td>
<td>46.14</td>
<td>0.069</td>
<td>108.55</td>
<td>20.43</td>
<td>0.999</td>
<td>0.131</td>
</tr>
<tr>
<td>40</td>
<td>46.13</td>
<td>0.070</td>
<td>108.48</td>
<td>20.31</td>
<td>0.998</td>
<td>0.158</td>
</tr>
<tr>
<td>50</td>
<td>12.81</td>
<td>0.004</td>
<td>97.30</td>
<td>01.45</td>
<td>0.995</td>
<td>0.101</td>
</tr>
</tbody>
</table>

6.3.2 Thermodynamics of CO$_2$ adsorption on mesoporous amine solids

Isotherms at various temperatures allows for the calculation of the coverage-dependent isosteric heat of adsorption, known as $Q_{st}$. The $Q_{st}$ was calculated using the Clausius-Clapeyron equation as outlined in Equation 6.6. Isosteres were developed using the results of experimental data fitting the Langmuir model for 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI). The partial pressure required for CO$_2$ adsorption at given temperatures at a specific CO$_2$ loading was obtained. When $1/T$ is plotted versus the obtained log $P$, the slope of the resulting isosteres can be used to calculate the $Q_{st}$.

Figure 6.14 presents the isosteres (A) and isosteric heats of adsorption (B) at given temperatures for 70%TEPA/SBA-15(I). The average heat of adsorption is 129 kJ/mol which implies a chemisorption process.
Figure 6.15 presents the Isosteres (A) and isosteric heats of adsorption (B) at given CO\(_2\) loadings for 70\%APTES/SBA-15(CI). The average heat of adsorption is 189 kJ/mol which is indicative of a chemisorption process.

![Figure 6.15: Isosteres (A) and isosteric heats of adsorption (B) for 70\%APTES/SBA-15(CI) (100 mg sample, 50 ml/min flow rate, ramped at 10°C/min up to 200°C) (image)](image)

### 6.3.3 Kinetic parameters

Investigation of the kinetic parameters is necessary when investigating potential solid adsorbents as it is important to know how fast adsorption occurs and the effect the presence of other gases may have on the solid’s adsorption performance. The effect of flue gas properties on the rate of CO\(_2\) uptake were examined, including the selectivity of CO\(_2\) over CH\(_4\). During the adsorption step, CO\(_2\) breakthrough for 70\%TEPA/SBA-15(I) and 70\%APTES/SBA-15(CI) were recorded. The Yoon-Nelson model was then applied to this data to determine the kinetic rate constant for various gas streams.

Figure 6.16 presents the CO\(_2\) experimental and modelled breakthrough curves for 70\%TEPA/SBA-15(I) when exposed to 0.15 atm CO\(_2\) in helium at a flow rate of 50 ml/min at various temperatures. The temperature was found to have an impact on the CO\(_2\) adsorption properties. At 30°C the initial CO\(_2\) breakthrough occurred at 157.5 seconds, when the temperature was increased to 40°C, the time for CO\(_2\) breakthrough to occur increased to 177.8 seconds. When the temperature was
increased to 50°C, the time for CO₂ breakthrough also increased to 212.5 seconds. The CO₂ breakthrough curves illustrate how the time of CO₂ increased with increasing temperature. This is as a result of the increased capacity for CO₂ adsorption at 50°C, as a result it takes longer for CO₂ to pass through the solid and be detected by the mass spectrometer.

![Graph](image)

**Figure 6.16**: CO₂ Breakthrough experimental and Yoon-Nelson modelled data on 70%TEPA/SBA-15(I) at the indicated temperatures

Table 6.7 presents the kinetic parameters for CO₂ breakthrough using the Yoon-Nelson model. The Yoon-Nelson model was found to fit the data with a high level of accuracy as indicated by the RSME values. The Yoon-Nelson rate constant $k_{YN}$ decreased with increasing temperature. The larger this rate constant, the faster the rate of CO₂ adsorption.

**Table 6.7**: Yoon-Nelson model parameters for 70%TEPA/SBA-15(I)

<table>
<thead>
<tr>
<th>Adsorption Temperature, °C</th>
<th>$k_{YN}$ (seconds⁻¹)</th>
<th>$\tau$ (seconds)</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.0089</td>
<td>190.0</td>
<td>1.6</td>
</tr>
<tr>
<td>40</td>
<td>0.0086</td>
<td>212.4</td>
<td>1.0</td>
</tr>
<tr>
<td>50</td>
<td>0.0077</td>
<td>245.1</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Different gases such as CH₄ are found in typical industrial flue gas streams. To investigate the impact the presence of CH₄ may have on CO₂ uptake,
70%TEPA/SBA-15(I) was exposed to a gas stream containing 0.15 atm CO\textsubscript{2} and 0.025 atm CH\textsubscript{4} at a total flow rate of 50 ml/min. Figure 6.17 presents the CO\textsubscript{2} experimental and modelled breakthrough curves for 70%TEPA/SBA-15(I) which was exposed to 0.15 atm CO\textsubscript{2} only, and 0.025 atm CH\textsubscript{4} and 0.15 atm CO\textsubscript{2}, respectively. In the presence of 0.025 atm CH\textsubscript{4}, there was a decrease in the breakthrough time observed for CO\textsubscript{2}.

![Figure 6.17: CO\textsubscript{2} breakthrough and Yoon-Nelson modelled data on 70%TEPA/SBA-15(I) in the indicated mixed gas streams](image)

Table 6.8 presents the Yoon-Nelson kinetic parameters for CO\textsubscript{2} breakthrough in a gaseous stream without CH\textsubscript{4} and with CH\textsubscript{4}, respectively. The \( k_{YN} \) rate constant decreased slightly when CH\textsubscript{4} was introduced to the gas stream suggesting CH\textsubscript{4} may have slowed the uptake of CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>PCH\textsubscript{4}</th>
<th>( k_{YN} ) (seconds(^{-1}))</th>
<th>( \tau ) seconds</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0077</td>
<td>245.1</td>
<td>0.90</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0059</td>
<td>194.6</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Figure 6.18 presents the CO\textsubscript{2} experimental and modelled breakthrough curves for 70%APTES/SBA-15(CI) when exposed to 0.15 atm CO\textsubscript{2} in helium at a flow rate of 50 ml/min at various temperatures. The temperature was found to have an impact on
the CO₂ adsorption properties. At 30°C the initial CO₂ breakthrough occurred at 152.1 seconds, when the temperature was increased to 35°C, the time for CO₂ breakthrough to occur increased to 172.5 seconds. When the temperature was further increased to 40°C, the time for CO₂ breakthrough decreased to 132.7 seconds.

![Figure 6.18: CO₂ breakthrough experimental and Yoon-Nelson modelled data on 70%APTES/SBA-15(CI) at the indicated temperatures](image)

Table 6.9 presents the kinetic parameters for CO₂ breakthrough using the Yoon-Nelson model. The Yoon-Nelson model was found to fit the data with a high level of accuracy as indicated by the RSME values. The Yoon-Nelson rate constant $k_{YN}$ decreased with increasing temperature.

**Table 6.9: Yoon-Nelson parameters for 70%APTES/SBA-15(CI) at indicated temperatures**

<table>
<thead>
<tr>
<th>Adsorption Temperature, °C</th>
<th>$k_{YN}$ (seconds⁻¹)</th>
<th>$\tau$, seconds</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.022</td>
<td>142.9</td>
<td>0.50</td>
</tr>
<tr>
<td>35</td>
<td>0.020</td>
<td>162.2</td>
<td>0.36</td>
</tr>
<tr>
<td>40</td>
<td>0.005</td>
<td>183.0</td>
<td>0.44</td>
</tr>
</tbody>
</table>
70%APTES/SBA-15(CI) was exposed to a gas stream containing 0.15 atm CO$_2$ and 0.025 atm CH$_4$ at a total flow rate of 50 ml/min. Figure 6.19 presents the CO$_2$ experimental and modelled breakthrough curves for 70%APTES/SBA-15(CI) which was exposed to 0.15 atm CO$_2$ only, and 0.025 atm CH$_4$ and 0.15 atm CO$_2$, respectively. In the presence of 0.025 atm CH$_4$, there was a decrease in the breakthrough time observed for CO$_2$.

![Figure 6.19: CO$_2$ breakthrough and Yoon-Nelson modelled data on 70%APTES/SBA-15(CI) in the indicated mixed gas streams](image)

Table 6.10 presents the Yoon-Nelson kinetic parameters for CO$_2$ breakthrough in a gaseous stream without CH$_4$ and with CH$_4$, respectively. The CO$_2$ uptake rate decreased as the partial pressure of CH$_4$ increased from 0.0 to 0.025 atm.

<table>
<thead>
<tr>
<th>PCH$_4$</th>
<th>k$_{YN}$ (seconds$^{-1}$)</th>
<th>$\tau$, seconds</th>
<th>RSME</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.020</td>
<td>162.2</td>
<td>0.36</td>
</tr>
<tr>
<td>0.025</td>
<td>0.013</td>
<td>109.8</td>
<td>0.30</td>
</tr>
</tbody>
</table>
6.4 Discussion

In order to investigate the impact of temperature and pressure on the CO\textsubscript{2} adsorption capacity, experiments were conducted at CO\textsubscript{2} partial pressures of 0-1 atm and temperatures between 30 and 50°C on 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI). For both solids the adsorption capacity increased throughout the pressure range studied. It was observed from the experimental data presented in Figure 6.1 and Figure 6.7 that the adsorption capacity increased sharply at low partial pressures, the increase in CO\textsubscript{2} adsorption then slowed in the upper pressure range. This is similar to Type 1 isotherms outlined in Chapter 1 Section 1.8, indicating that CO\textsubscript{2} adsorption amongst these solids is similar to the Langmuir isotherm, indicating monolayer adsorption whereby adsorption can only occur at a fixed number of adsorption sites, which are similar.

From the experimental data it was observed that temperature has a significant impact on CO\textsubscript{2} adsorption/desorption capacity. With regards to 70%TEPA/SBA-15(I), adsorption/desorption capacity increased with temperature up to 50°C. For materials such as TEPA which are not chemically fixed onto SBA-15, CO\textsubscript{2} adsorption can increase with increasing adsorption temperature, as at higher temperatures the amine molecules become more mobile and allow for greater CO\textsubscript{2} transport through the sorbent, reaching a greater number of amine adsorption sites. At lower adsorption temperatures TEPA may exist in the pores like nano-sized particles, limiting amine sites available to interact with CO\textsubscript{2}, as discussed in Chapter 3. 70%APTES/SBA-15(CI) showed a different trend to the TEPA solid; CO\textsubscript{2} adsorption reached a maximum at 35°C, after which CO\textsubscript{2} adsorption decreased. As APTES is chemically fixed to SBA-15 through a number of siloxane bonds, increasing the temperature will not increase the mobility of APTES and thus not increase CO\textsubscript{2} adsorption. At higher temperatures, desorption will be preferred.

The next stage in this investigation was the fitting of experimental data to isotherm models. Three isotherm models were chosen; Langmuir, Freundlich and Dual-Site Langmuir. Overall, the Dual-Site Langmuir model was the best fit for both 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI). This model assumes that there are two similar adsorption sites at different locations. Surface 1 may be attributed to
the more easily accessed sites close to the pore entrances, while Surface 2 can be assigned to additional adsorption sites further with the porous solid. The adsorption associated with Surface 2 increased with temperature on 70%TEPA/SBA-15(I). This may be due to the increased mobility of TEPA at higher temperatures which may open up more CO₂ adsorption sites, as discussed in Chapter 3. As a result of this, CO₂ may be adsorbed more fully within the porous network binding to sites near the pore mouth and further within the porous network. This would explain the increased CO₂ adsorption seen in Surface 2 with increasing temperature.

The isosteric heats of adsorption $Q_{st}$ were calculated. $Q_{st}$ is a measure of the enthalpy of adsorption as each CO₂ molecule is adsorbed by an adsorbent [4]. $Q_{st}$ is an important characteristic for practical gas separation processes in temperature swing adsorption set ups. Isosteres were developed from the experimental data collected at the various temperatures for each solid. The slopes of the isosteres were used to calculate the $Q_{st}$. A $Q_{st}$ value of 0-20 kJ/mol is indicative of physisorption, while chemisorption occurs at a $Q_{st}$ value between 20-200 kJ/mol [4]. $Q_{st}$ values of 129 kJ/mol and 189 kJ/mol were obtained for 70%TEPA/SBA-15(I) and 70%APTES/SBA-15(CI), respectively. These results show that the dominant interaction between CO₂ and these amine solids is chemisorption. The $Q_{st}$ for 70%TEPA/SBA-15(I) is lower than that calculated for 70%APTES/SBA-15(CI) but still within the chemisorption range, which may indicate that CO₂ is less strongly attached to the TEPA solid. These results indicate that physisorption did not occur on the solids and supports the theory that the shoulders observed in the TPD profiles are due to similar adsorption sites at different locations in the solids.

The CO₂ breakthrough curves were also examined. For 70%TEPA/SBA-15(I) the time for initial CO₂ breakthrough increased with increasing temperature. This is due to the increased CO₂ adsorption capacity with increasing temperature; this would delay the detection of CO₂ on the mass spectrometer. Similarly temperature also impacted the time for CO₂ breakthrough to occur on 70%APTES/SBA-15(CI); the longest time for CO₂ breakthrough occurred at 35°C which was also found to be the optimum CO₂ adsorption temperature. The CO₂ breakthrough data was then used to calculate the Yoon-Nelson rate constant ($k_{YN}$). For both solids, the $k_{YN}$ value decreased with increasing temperature as illustrated in Figure 6.20. A very slight
difference in the $k_{YN}$ values was observed for 70%TEPA/SBA-15(I), while a much bigger difference was observed for 70%APTES/SBA-15(CI). As discussed in Chapter 3, 70%TEPA/SBA-15(I) becomes more mobile at higher temperatures allowing more amine sites to interact with CO$_2$. As CO$_2$ likely makes its way to the additional adsorption sites via an amine hopping mechanism, this may slow down the overall CO$_2$ adsorption rate. The decrease in $k_{YN}$ values recorded for 70%APTES/SBA-15(CI) showed a bigger decrease between 35 and 40°C which may be attributable for the preference for desorption at temperatures above 35°C.

Both solids were then exposed to a gas stream containing CH$_4$. In both instances the presence of CH$_4$ reduced the rate of CO$_2$ uptake. While there was no methane uptake by the amine solids, the presence of CH$_4$ molecules appear to inhibit the interactions between CO$_2$ and amine adsorption sites, increasing the time required to achieve equilibrium during the CO$_2$ adsorption stage.

**6.5 Conclusion**

This chapter investigated the adsorption characteristics of 70%TEP/SBA-15(I) and 70%APTES/SBA-15(CI). Overall, the Dual-Site Langmuir isotherm model was found to be the best fit to the experimental data. This supports the theory of multiple adsorption sites within the amine solids as amine sites may be located close to pore
entrances and further within the porous network. The $Q_{st}$ values for both solids was found to lie in the range for chemisorption processes.

The temperature was found to affect the CO$_2$ breakthrough time; it increased with temperature on 70%TEPA/SBA-15(I) and decreased after 35°C on 70%APTES/SBA-15(Cl). The rate constant was found to decrease with increasing temperature for both solids. The presence of CH$_4$ in the gas stream was also found to affect the CO$_2$ uptake of the sorbents by slowing the CO$_2$ adsorption rate. While no CH$_4$ was detected during the desorption step, implying selectivity for CO$_2$, the presence of CH$_4$ molecules likely inhibited CO$_2$ molecules interacting with adsorption sites.

6.6 References


The removal of gaseous streams using solid sorbents

Emma Daniels


[16] Han, R., Wang, Y., Zhao, Wang, Y., Xie, C., Tang, Mi. (2009) ‘Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column:

188
experiments and prediction of breakthrough curves’, *Desalination*, 245 (1), 284-297.

7 Overall conclusions and recommendations
7 Overall conclusions and recommendations

The overall aim of this research was to find a high capacity solid adsorbent that could be used for post combustion CO\(_2\) capture from fossil fuel fired power plants and also CO\(_2\) capture from ambient air. A number of solid adsorbents were modified with two amines; APTES and TEPA. A range of CO\(_2\) adsorption/desorption tests were carried out on a number of adsorbents and a detailed examination of CO\(_2\) TPD profiles and thermodynamic characteristics was also undertaken. From these results, a number of conclusions can be drawn:

- Chapter 1 provided a detailed review of a range of CO\(_2\) capture technologies. A number of studies had been conducted on a range of mesoporous amine solids. The aim of this project was to optimise the use of mesoporous solids modified with amine as CO\(_2\) adsorbents.

- Chapter 2 focused on modifying SBA-15, AISBA-15 and PESBA-15 with APTES through refluxing, impregnation and capillary impregnation. The AISBA-15 solid produced low capacity solids due to a neutralisation effect between the amine and surface acid sites. \(T_{\text{max}}\) was found to occur below 100°C for most adsorbents. The highest capacity solid from this study was 70%APTES/SBA-15(CI) with a CO\(_2\) adsorption capacity of 86 mgCO\(_2\)/g of adsorbent and showed stability over repeated CO\(_2\) adsorption/desorption studies.

- Chapter 3 focused on TEPA modified SBA-15 and AISBA-15. Two high capacity solids were found, however they showed poor stability over repeated adsorption/desorption cycles. This was likely due to the high desorption temperature of 200°C, which likely contributed to decomposition of TEPA from the solids. Therefore further tests were carried out on 70%TEPA/SBA-15(I) at a lower desorption temperature of 150°C which improved stability over repeated adsorption/desorption cycles. Different adsorption temperatures were also investigated and it was found that 50°C was the optimum adsorption temperature. This study produced a solid with a
capacity of 211 mgCO₂/g of solid, which is double the 2 mmol/g requirement for industrial adsorbents. This solid underwent further analysis and 2 shoulders were identified from the TPD profiles. These shoulders are likely the result of 2 similar adsorption sites, the first located near the pore entrances and the second located further within the porous structure. The sites found further within the solid are likely accessed through a CO₂–amine hopping mechanism.

- Chapter 4 focused on the application of 70%TEPA/SBA-15(I) as an adsorbent for CO₂ capture from ambient air. This solid showed preferential adsorption of CO₂ in moist conditions and stability over repeated cycles. A separate adsorption study was utilised to examine the CO₂ TPD profiles, once more showing two key areas of interest attributable to the CO₂ hopping mechanism. As the time of exposure increased to 1 day and 1 week, a third small peak was detected at about 60°C. This is likely due to physisorbed CO₂. As under ambient conditions appropriate conditions are met to allow CO₂ to be physisorbed.

- Chapter 5 focused on pelletising SBA-15 and modifying it with TEPA. Two methods were used to produce pellets; a binder based approach and a binder-less, self-supported approach. The binder based pellets showed good mechanical strength and durability; however they had low CO₂ adsorption capacity. The self-supported pellets showed good durability and high CO₂ adsorption capacities which were stable over repeated cycles. It was not possible to test the mechanical strength of these pellets due to instrumental limitations, but these results showed the possibility to pelletise 70%TEPA/SBA-15(I).

- Chapter 6 investigated the characteristics of two CO₂ adsorbents; 70%APTES/SBA(CI) and 70%TEPA/SBA-15(I). Overall, the Dual-Site Langmuir isotherm model was found to be the best fit to the experimental data. This is likely due to the presence of CO₂ adsorption sites in different
locations within the porous solids. The temperature was found to affect the CO\textsubscript{2} uptake rate; it decreased with increasing temperature for both solids. The presence of CH\textsubscript{4} in the gas stream was also found to affect the CO\textsubscript{2} uptake of the sorbents by slowing the CO\textsubscript{2} adsorption rate. While no CH\textsubscript{4} was detected during the desorption step, implying selectivity for CO\textsubscript{2}, the presence of CH\textsubscript{4} molecules likely inhibited CO\textsubscript{2} molecules interacting with adsorption sites.

CO\textsubscript{2} adsorption studies and characteristics of amine modified mesoporous solids were studied in this work. The results of which provide a significant contribution in the understanding of CO\textsubscript{2}-amine interactions. It also highlights the ability of a high capacity stable solid to be pelletised for industrial and ambient air applications.

**Recommendations**

The adsorption tests carried out on the test rig were conducted primarily for the single component adsorption isotherm. It is recommended that more extensive adsorption tests for multi-component adsorption isotherm simulating life-like flue gas composition be conducted. In particular the effectiveness of 70\%TEPA/SBA-15(I) in the presence of SO\textsubscript{x} and NO\textsubscript{x} would be an interesting and beneficial study. A more comprehensive study in a wet gaseous stream may also be beneficial.

While chemisorbents are more suited to temperature desorption studies, it would also be worthwhile to tests these solids in pressure-swing adsorption experiments. This could then contribute to a comparison study with solids used in pressure swing studies.

Since the start of this research metal organic frameworks and metal organic materials have gained interest as CO\textsubscript{2} sorbents. A comparison with these solids may be interesting especially in terms of ambient air capture. 70\%TEPA/SBA-15(I) was included in a paper with physisorbents (see Appendix 3). A more detailed and extensive comparison would lead to a clearer understanding of 70\%TEPA/SBA-15(I) high CO\textsubscript{2} adsorption/desorption capacity in ambient air.
Further characterisation of self-supported pellets might highlight the applicability of these pellets for industrial use. This may be achieved with a more sensitive testing instrument than what was available during this study.
Appendix 1
Refluxing

APTES plus 25 ml toluene, stirred for 30 minutes

1 g support

1 g support plus amine solution, refluxed for 2 hours at 110°C

Filtration

Dried in air at room temperature overnight then placed in oven at 110°C for 1 hour

Scheme 1: Refluxing process
Impregnation

APTES plus 25 ml toluene, stirred for 30 minutes

1 g support

Attached to ROTAVAP for 20 mins at 110°C

Placed in oven at 110°C for 1 hour

Scheme 2: Impregnation process
Capillary Impregnation

APTES plus 1 ml toluene, stirred for 30 minutes

Amine solution added drop wise to 1 g support

Placed in oven at 110°C for 1 hour

Scheme 3: Capillary impregnation process
Appendix 2
Non-peer reviewed articles


Table of oral presentations

<table>
<thead>
<tr>
<th>Title</th>
<th>Conference Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stability of amine-modified CO₂ adsorbents for fossil fuel-fired power plants can be highly influenced by preparation of adsorbents”</td>
<td>ENVIRON, Trinity, 26th-28th Feb 2014</td>
</tr>
<tr>
<td>Potential of amine-modified porous solids as CO₂ adsorbents in fossil-fuel fired power plants”</td>
<td>ENVIRON, Trinity, 26th-28th Feb 2014</td>
</tr>
<tr>
<td>Investigation of impregnation methods in amine modification of mesoporous solids</td>
<td>UL-NUI Galway Alliance Annual Research Day, 26th May University of Limerick</td>
</tr>
<tr>
<td>The removal of CO₂ from gaseous streams using solid adsorbents</td>
<td>UL-NUI Galway Alliance Annual Research Day, 26th May University of Limerick</td>
</tr>
</tbody>
</table>

Conferences attended

- ENVIRON 2013-presented a poster entitled: “Effects of water and impregnation methods in amine modification of mesoporous solids

- UL-NUI Galway Alliance Second Annual Research Day-presented a poster “Investigation of impregnation methods in amine modification of mesoporous solids

- Attended XIth European Congress on Catalysis and presented a poster entitled “Influence of preparation method and support on amine based carbon capture solids”

- Attended and gave a brief oral presentation at the MSSI research day 27th June 2013

- ICEC 2012- presented a poster entitled: “Development of amine solids for the capture of CO₂ from gaseous streams”
• ENVIRON 2012-presented a poster entitled: “Amine solids for CO₂ Capture”

• UL-NUI Galway Alliance Second Annual Research Day-presented a poster
Appendix 3
Direct Air Capture of CO2 by Physisorbent Materials
Amrit Kumar, David G. Madden, Matteo Lusi, Kai-Jie Chen, Emma A. Daniels, Teresa Curtin,
John J. Perry IV, and Michael J. Zaworotko

http://dx.doi.org/10.1002/anie.201506952