Doctoral Thesis

Development of amine-functionalized adsorbent for carbon dioxide capture from atmospheric air

Author(s):
Gebald, Christoph

Publication Date:
2014

Permanent Link:
https://doi.org/10.3929/ethz-a-010171623

Rights / License:
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
DEVELOPMENT OF AMINE-FUNCTIONALIZED ADSORBENT FOR CARBON DIOXIDE CAPTURE FROM ATMOSPHERIC AIR

A dissertation submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

presented by

CHRISTOPH GEBALD

MSc ETH ME, ETH Zurich

born on April 03, 1983
citizen of Germany

accepted on the recommendation of

Prof. Dr. Aldo Steinfeld
Dr. Tanja Zimmermann

2014
Abstract

A novel amine-functionalized adsorbent for the direct capture of CO\textsubscript{2} from air (DAC) was developed, which uses biogenic raw materials and an environmentally benign synthesis route without organic solvents. The adsorbent was synthesized through freeze drying an aqueous suspension of nanofibrillated cellulose (NFC) and an aminosilane. A screening of commercial aminosilane moieties revealed that 3-aminopropylmethyldiethoxysilane (APDES) and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS) are feasible to yield high capacity DAC adsorbents. At a CO\textsubscript{2} concentration of 506 ppm in air and a relative humidity of 40 \% at 298 K, AEAPDMS-functionalized NFC adsorbed 1.39 mmol CO\textsubscript{2}/g after 12 h CO\textsubscript{2} adsorption in a packed bed arrangement.

A fundamental analysis of single-component and binary CO\textsubscript{2} and H\textsubscript{2}O adsorption of amine-functionalized NFC was carried out in the temperature range 283-353 K and at CO\textsubscript{2} partial pressures in the range 0.02-105 kPa, where the ultralow partial pressure range is relevant for DAC. Single-component CO\textsubscript{2} and H\textsubscript{2}O adsorption experimental data were fitted to the Toth and Guggenheim-Anderson-de Boer models, respectively. Corresponding heats of adsorption, derived from explicit solutions of the van’t Hoff equation, were -50 kJ/mol CO\textsubscript{2} and -49 kJ/mol H\textsubscript{2}O. Binary CO\textsubscript{2}/H\textsubscript{2}O adsorption measurements for humid air revealed that the presence of H\textsubscript{2}O at 2.55 kPa enhances CO\textsubscript{2} adsorption, while the presence of CO\textsubscript{2} at 0.045 kPa does not influence H\textsubscript{2}O adsorption. Consequently H\textsubscript{2}O adsorption for DAC is solely driven by the relative humidity of the air during CO\textsubscript{2} adsorption. It was found that H\textsubscript{2}O adsorption increased significantly with increasing relative humidity of the air. Therefore the energy demand of the temperature-vacuum-swing (TVS) adsorption/desorption cycle for delivering pure CO\textsubscript{2} from air increases significantly with increasing relative humidity and urges the need to reduce the hygroscopy of the adsorbent.

Finally, the chemical and physical stability of amine-functionalized NFC was investigated during TVS cycling. The presence of O\textsubscript{2} at 363 K degraded the adsorbent, reducing its CO\textsubscript{2} adsorption capacity by 30 \% after 15 h of treatment in moist air with a dew point of 295 K. In contrast, exposure to moist CO\textsubscript{2} at 363 K with a dew point of 295 K did not deteriorate its CO\textsubscript{2} adsorption capacity after 15
h. Performing 100 TVS consecutive cycles, with CO₂ adsorption from ambient air containing 400-530 ppm CO₂ at 303 K and 60 % relative humidity and with CO₂ desorption at 363 K and 30 mbar, resulted in a reduction of the equilibrium CO₂ adsorption capacity by maximum 5 %. The average CO₂ adsorption capacity during TVS cyclic operation was 0.90 mmol CO₂/g.
Zusammenfassung


Es wurde eine fundamentale Analyse von Einkomponenten und Zweikomponenten CO₂ und H₂O Adsorption von aminfunktionalisierter NFC im Temperaturbereich 283-353 K und im CO₂ Partialdruckbereich 0.02-105 kPa durchgeführt, wobei der tiefe CO₂ Partialdruckbereich relevant für DAC ist. Experimentelle Messdaten der Einkomponenten CO₂ und H₂O Adsorption wurden jeweils mit dem Toth und Guggenheim-Anderson-de Boer Modell modelliert. Die entsprechenden Adsorptionswärmen, welche als explizite Lösungen der van’t Hoff Gleichung berechnet wurden, waren -50 kJ/mol CO₂ und -49 kJ/mol H₂O. Zweikomponenten CO₂/H₂O Adsorption von feuchter Luft zeigte, dass Luftfeuchtigkeit mit einem Partialdruck von 2.55 kPa die CO₂ Adsorption verstärkte, wohingegen CO₂ mit einem Partialdruck von 0.045 kPa keinen Einfluss auf die H₂O Adsorption hatte. Damit ist die H₂O Adsorption für DAC einzig von der relativen Luftfeuchtigkeit der Luft während der CO₂ Adsorption bestimmt. Es wurde festgestellt, dass die H₂O Adsorption stark mit steigender relativer Luftfeuchtigkeit der Luft ansteigt. Daraus folgt, dass der Energieverbrauch von Adsorption/Desorption Zyklen basierend auf einem Temperatur-Vakuum-Wechselverfahren (TVS), welches während der Desorption hochreines CO₂ zur
Zusammenfassung

Verfügung stellt, signifikant mit steigender relativer Luftfeuchtigkeit ansteigt und somit die Notwendigkeit von reduzierter Hygroskopie des Adsorbens aufzeigt.

Schließlich wurde die chemische und physikalische Stabilität von aminfunktionalisierter NFC während TVS Zyklen untersucht. Die Präsenz von O₂ bei einer Temperatur von 363 K degradiert den Adsorbens, so dass die CO₂ Kapazität nach 15 h Behandlung in feuchter Luft mit einem Taupunkt von 295 K um 30 % abgenommen hatte. Im Gegensatz dazu führte Kontakt mit feuchtem CO₂ mit einem Taupunkt von 295 K nach 15 h Behandlung bei 363 K zu keinem CO₂ Kapazitätsverlust. Nach 100 TVS Zyklen in Folge, wobei CO₂ Adsorption von Umgebungsluft mit einer CO₂ Konzentration von 400-530 ppm bei 303 K und 60 % Luftfeuchtigkeit und CO₂ Desorption bei 363 K und 30 mbar durchgeführt wurden, war der Verlust der CO₂ Kapazität maximal 5 %. Die durchschnittliche CO₂ Adsorptionskapazität während der TVS Zyklen war 0.90 mmol CO₂/g
Acknowledgements

This work has been conducted in the framework of a joint project of ETH Zurich, the Swiss Federal Laboratories for Materials Science and Technology (Empa) and the ETH Spin-off company Climeworks Ltd. I would like to thank GEBERT-RÜF-FOUNDATION, the Swiss Federal Office for Professional Education and Technology, the European Union, Climeworks Ltd., the Applied Wood Materials Laboratory at Empa and the Professorship of Renewable Energy Carriers at ETH Zurich for financial support. I thank the Professorship of Renewable Energy Carriers at ETH Zurich and the Applied Wood Materials Laboratory at Empa for providing office and laboratory space as well as other technical infrastructure, which was crucial for my work.

Further, I would like to thank Prof. Dr. Aldo Steinfeld, for initiating, supporting and financing the research on CO₂ capture from atmospheric air at ETH Zurich more than ten years ago and for giving me the opportunity to perform research in such an interesting and highly relevant field. Prof. Dr. Aldo Steinfeld always pursued the vision of closing the carbon cycle via capturing CO₂ from atmospheric air and its subsequent solar conversion to hydrocarbon fuels and contributed through his continuity and vision to an overall very successful project. Special thanks go to Dr. Tanja Zimmermann and Dr. Philippe Tingaut for their supervision, advices and critical reviews. I thank Dr. Andreas Borgschulte for assistance with CO₂ adsorption measurements and their interpretation and all bachelor and master students who were involved in that project. Moreover, I would like to thank the staff at the Applied Wood Materials Laboratory and the Professorship of Renewable Energy Carriers for friendly and fruitful meetings and discussions.

Additionally I would like to thank all investors and supporters of Climeworks Ltd. I am thankful for financial support as well as business coaching and for giving me the opportunity to finalize my PhD besides the management of the company.

Finally I would like to thank my family and all friends for walking an incredibly exciting path together throughout the last years. I would like to especially thank my project and business partner and very good friend Jan Andre Wurzbacher for realization of what most people thought is impossible when we started our journey.
# Contents

Abstract ........................................................................................................................................... i
Zusammenfassung ............................................................................................................................ iii
Acknowledgements .......................................................................................................................... v
Contents ........................................................................................................................................... vii
Nomenclature ................................................................................................................................... xi
Acronyms .......................................................................................................................................... 1

1 Introduction ..................................................................................................................................... 1
  1.1 Direct Air Capture ..................................................................................................................... 1
  1.2 Amine-functionalized Adsorbents ............................................................................................ 5
  1.3 Thesis Outline ............................................................................................................................ 10

2 Description of Adsorbent Feedstock and Synthesis ................................................................. 13
  2.1 Experimental Section ................................................................................................................. 14
    2.1.1 Materials ............................................................................................................................. 14
    2.1.2 Adsorbent Synthesis ........................................................................................................... 14
    2.1.3 Adsorbent Characterization ............................................................................................... 15
    2.1.4 CO₂ Adsorption/Desorption Measurements ...................................................................... 16
  2.2 Description of Nanofibrillated Cellulose .................................................................................. 17
  2.3 Description and Screening of Aminosilanes ............................................................................ 19
    2.3.1 Results and Discussion Aminosilane Screening ................................................................. 21
    2.3.2 Aminosilanes used in this Thesis ...................................................................................... 26
  2.4 Adsorbent Synthesis ................................................................................................................. 27
    2.4.1 Adsorbent Synthesis via Air Drying .................................................................................. 28
    2.4.2 Adsorbent Synthesis via Freeze Drying ............................................................................ 28
  2.5 Summary and Conclusions ......................................................................................................... 29

3 CO₂ Adsorption/Desorption Analysis ......................................................................................... 31
  3.1 Experimental Section ............................................................................................................... 31
    3.1.1 Materials ............................................................................................................................. 31
### Contents

3.1.2 Adsorbent Synthesis ................................................................. 31
3.1.3 Adsorbent Characterization ..................................................... 32
3.1.4 CO₂ Adsorption/Desorption Measurements ............................... 32

3.2 Experimental Results and Comparison to State of the Art Adsorbents 33

3.2.1 Adsorbent Characterization ..................................................... 33
3.2.2 CO₂ adsorption measurements ................................................. 36
3.2.3 CO₂ Desorption Measurements ............................................... 41
3.2.4 Cyclic CO₂ Capacity ............................................................... 43

3.3 Summary and Conclusions .......................................................... 44

4 Single-Component and Binary CO₂ and H₂O Adsorption .................... 45

4.1 Experimental Section .................................................................. 45

4.1.1 Materials .................................................................................. 45
4.1.2 Adsorbent Synthesis ................................................................. 45
4.1.3 Adsorbent Characterization ..................................................... 46
4.1.4 Single Component CO₂ Adsorption Analysis .............................. 46
4.1.5 Single Component H₂O Adsorption Analysis ............................. 46
4.1.6 Binary CO₂ and H₂O Adsorption Analysis ................................. 47

4.2 Adsorption Models ...................................................................... 49

4.2.1 CO₂ Adsorption ................................................................. 49
4.2.2 H₂O Adsorption ................................................................. 49
4.2.3 Fitting Accuracy ................................................................. 50
4.2.4 Heat of Adsorption ............................................................... 50

4.3 Results and Discussion .................................................................. 52

4.3.1 Adsorbent Characterization ..................................................... 52
4.3.2 Single Component CO₂ Adsorption Analysis .............................. 52
4.3.3 Heat of CO₂ Adsorption .......................................................... 55
4.3.4 Single-component H₂O adsorption analysis ............................... 57
4.3.5 Heat of H₂O Adsorption .......................................................... 59
4.3.6 Binary CO₂ and H₂O adsorption analysis ................................. 60
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.4 Summary and Conclusions</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Adsorbent Stability Analysis</td>
<td>67</td>
</tr>
<tr>
<td>5.1</td>
<td>Experimental Section</td>
<td>71</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Materials</td>
<td>71</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Adsorbent Synthesis</td>
<td>71</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Adsorbent Characterization</td>
<td>71</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Equilibrium CO₂ Adsorption Analysis</td>
<td>72</td>
</tr>
<tr>
<td>5.1.5</td>
<td>CO₂/O₂ Induced Degradation</td>
<td>73</td>
</tr>
<tr>
<td>5.1.6</td>
<td>TVS Cycles</td>
<td>74</td>
</tr>
<tr>
<td>5.2</td>
<td>Experimental Results</td>
<td>74</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Adsorbent Characterization</td>
<td>74</td>
</tr>
<tr>
<td>5.2.2</td>
<td>CO₂/O₂ Induced Degradation</td>
<td>74</td>
</tr>
<tr>
<td>5.2.3</td>
<td>TVS Cycles</td>
<td>81</td>
</tr>
<tr>
<td>5.3</td>
<td>Summary and Conclusions</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>Summary</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>Outlook</td>
<td>93</td>
</tr>
<tr>
<td>7.1</td>
<td>Adsorbent Synthesis Optimization</td>
<td>93</td>
</tr>
<tr>
<td>7.2</td>
<td>Adsorbent Performance Optimization</td>
<td>94</td>
</tr>
<tr>
<td>7.3</td>
<td>Adsorbent Stability Analyses</td>
<td>94</td>
</tr>
<tr>
<td>7.4</td>
<td>Long-term Fundamental Research Needs</td>
<td>95</td>
</tr>
</tbody>
</table>

List of Figures | 97 |
List of Tables | 101 |
References | 103 |
Nomenclature

\( b \)  
Toth model parameter [1/kPa]

\( b_0 \)  
Toth model parameter at reference temperature [1/kPa]

\( c_0 \)  
CO\(_2\) concentration at the inlet of packed bed [ppm]

\( c_1 \)  
CO\(_2\) concentrations at the outlet of packed bed [ppm]

\( C_G \)  
Guggenheim-Anderson-de Boer model parameter [-]

\( C_m \)  
Guggenheim-Anderson-de Boer model parameter [mmol/g]

\( err \)  
normalized standard deviation [-]

\( \Delta H_C \)  
adsorption enthalpy difference between the H\(_2\)O monolayer and multilayer [kJ/mol]

\( \Delta h_{H_2O} \)  
total heat of H\(_2\)O adsorption [kJ/mol]

\( \Delta h_{iso,CO_2} \)  
isosteric heat of CO\(_2\) adsorption [kJ/mol]

\( \Delta h_{iso,H_2O} \)  
isosteric heat of H\(_2\)O adsorption [kJ/mol]

\( \Delta h_{iso,0} \)  
isosteric heat of adsorption at low adsorbate loading [kJ/mol]

\( \Delta H_K \)  
adsorption enthalpy difference between the H\(_2\)O multilayer and the bulk liquid [kJ/mol]

\( \Delta h_{vap} \)  
heat of H\(_2\)O vaporization [kJ/mol]

\( K_{ads} \)  
Guggenheim-Anderson-de Boer model parameter [-]

\( m_s \)  
mass of the adsorbent material contained in packed bed [g]

\( \dot{n}_{gas} \)  
molar flow rate of gas stream [mmol/s]

\( N \)  
number of data points [-]

\( n_s \)  
Toth model parameter [mmol/g]

\( p_{CO_2} \)  
CO\(_2\) pressure [kPa]

\( p_{H_2O} \)  
H\(_2\)O partial pressure [kPa]

\( p_{H_2O}/p_0 \)  
relative humidity [-]

\( p_0 \)  
saturation pressure of water vapor [kPa]

\( \Delta q \)  
integrated adsorption/desorption CO\(_2\) capacity [mmol CO\(_2\)/g]

\( q_{CO_2} \)  
CO\(_2\) loading [mmol/g]

\( q_{exp} \)  
experimental adsorbate loading [mmol/g]

\( q_{H_2O} \)  
H\(_2\)O loading [mmol/g]

\( q_{mod} \)  
modeled adsorbate loading [mmol/g]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>ideal gas constant [J/mol/K]</td>
</tr>
<tr>
<td>$t$</td>
<td>Toth model parameter [-]</td>
</tr>
<tr>
<td>$t_0$</td>
<td>Toth model parameter at reference temperature [-]</td>
</tr>
<tr>
<td>$t_{ads}$</td>
<td>adsorption time</td>
</tr>
<tr>
<td>$t_{des}$</td>
<td>desorption time</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature [K]</td>
</tr>
<tr>
<td>$T_0$</td>
<td>reference temperature [K]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Toth model parameter [-]</td>
</tr>
<tr>
<td>Acronyms</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------------</td>
<td>------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>ABCR</td>
<td>Supplier of specialty chemicals</td>
</tr>
<tr>
<td>AEAPDMS</td>
<td>N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane</td>
</tr>
<tr>
<td>AEAPDMS-NFC</td>
<td>diaminosilane-functionalized nanofibrillated cellulose adsorbent</td>
</tr>
<tr>
<td>APDES</td>
<td>3-aminopropylmethyldiethoxysilane</td>
</tr>
<tr>
<td>APDES-NFC</td>
<td>monoaminosilane-functionalized nanofibrillated cellulose adsorbent</td>
</tr>
<tr>
<td>A-PEI/silica</td>
<td>aminosilane stabilized polyethylenimine modified porous silica¹</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller method</td>
</tr>
<tr>
<td>DAC</td>
<td>direct air capture</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform-Infrared-Spectroscopy</td>
</tr>
<tr>
<td>GAB</td>
<td>Guggenheim-Andersen-de Boer model for H₂O adsorption</td>
</tr>
<tr>
<td>HAS6</td>
<td>hyperbranched aminosilica²</td>
</tr>
<tr>
<td>MEA</td>
<td>monoethanolamine</td>
</tr>
<tr>
<td>NFC</td>
<td>nanofibrillated cellulose</td>
</tr>
<tr>
<td>NFC-FD</td>
<td>freeze dried nanofibrillated cellulose</td>
</tr>
<tr>
<td>PEI</td>
<td>polyethylenimine</td>
</tr>
<tr>
<td>PEI/silica</td>
<td>polyethylenimine modified porous silica¹</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEPA</td>
<td>tetraethylenepentamine</td>
</tr>
<tr>
<td>TRI-PE-MCM-41</td>
<td>aminosilane modified pore expanded mesoporous silica³</td>
</tr>
<tr>
<td>TVS</td>
<td>temperature-vacuum-swing</td>
</tr>
<tr>
<td>T-PEI/silica</td>
<td>tetrapropyl orthotitanate stabilized polyethylenimine modified porous silica¹</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Direct Air Capture

CO$_2$ capture from atmospheric air – commonly referred to as direct air capture (DAC) – can address CO$_2$ emissions released by the transportation sector, other distributed sources and emissions from the past. It can be coupled with CO$_2$ sequestration in geological formations to reduce the atmosphere’s CO$_2$ content, or with the conversion into CO$_2$-neutral liquid or gaseous hydrocarbon fuels using renewable energy (renewable fuels).$^{4-8}$ On the one hand such renewable fuels are CO$_2$-neutral and on the other hand the concept of hydrocarbon fuel synthesis from CO$_2$ offers the potential to store fluctuating renewable energy in the form of a chemical fuel, which can be stored, transported and used in today’s hydrocarbon energy infrastructure without limitation, schematically illustrated in Figure 1. Upon combustion of renewable fuels CO$_2$ is emitted back to the atmosphere which can be re-captured at an arbitrary location by a DAC plant, thus closing the carbon material cycle. In the short term, DAC in combination with technologies for hydrocarbon fuel synthesis constitutes a scalable, location independent and CO$_2$-neutral possibility to store, transport and use renewable energy which is fully compatible with the existing energy system. In the long term, DAC may become indispensable for stabilizing the global CO$_2$ concentration in the atmosphere in view of continuously increasing emissions above threshold limits.
Generally DAC proceeds via exothermic sorption of atmospheric CO$_2$ by a liquid or solid sorbent followed by its subsequent endothermic regeneration. The most recent literature reports the following different sorbents: calcium oxide/hydroxide,$^9$-$^{12}$ sodium hydroxide,$^{13}$-$^{19}$ basic ion exchange resins$^{20}$-$^{22}$ and amine-functionalized adsorbents.$^1$-$^3$, $^{23}$-$^{33}$ The sorbent choice determines the processes of CO$_2$ sorption and regeneration. Table 1 summarizes sorbent/process pairs which can be found in the literature as well as their advantages and disadvantages.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorption</th>
<th>Regeneration</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO/CaOH&lt;sup&gt;10&lt;/sup&gt;</td>
<td>$T &gt; 623 \text{ K}$</td>
<td>$T &gt; 1073 \text{ K}$</td>
<td>- Largely available, low cost sorbent</td>
<td>- High thermal energy consumption</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Sorbent handling in fluidized bed</td>
<td></td>
</tr>
<tr>
<td>Basic ion exchange resin&lt;sup&gt;21&lt;/sup&gt;</td>
<td>Requires low RH: 20/40 % CO$_2$ capacity loss at 48/62 % RH</td>
<td>Humidity swing (wetting the resin)</td>
<td>- No thermal energy requirement for regeneration</td>
<td>- Low purity of desorbed CO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Works only in very dry climates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Complicated sorbent handling</td>
</tr>
<tr>
<td>NaOH&lt;sup&gt;17&lt;/sup&gt;</td>
<td>No conditioning</td>
<td>1. step: no conditioning (caustization) 2. step: $T &gt; 1073 \text{ K}$ (calcination)</td>
<td>- No conditioning during sorption</td>
<td>- Regeneration at 1073 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Requires O$_2$ fired kiln</td>
</tr>
<tr>
<td>Amine-functionalized adsorbent&lt;sup&gt;31, 34&lt;/sup&gt;</td>
<td>No conditioning</td>
<td>Option 1: $T = 363 \text{ K}$, $p = 100 \text{ mbar}_{\text{abs}}$ (TVS) Option 2: steam stripping at 378 K</td>
<td>- No conditioning during sorption</td>
<td>- Complicated sorbent handling</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. State of the art sorbent/process pairs used for DAC and their advantages and disadvantages
The thermal energy consumption of CaO-carbonation/CaCO$_3$-calcination cycles is high with 2485 kJ/mol CO$_2$ and therefore the process is considered not feasible for DAC.$^{11}$ In contrary CO$_2$ sorption through basic ion exchange resins does not require any thermal energy input for regeneration but is performed via humidity swing (a detailed process description is given by Wang et al.$^{21}$). However, practicability of basic ion exchange resins operated with humidity swing process is questionable as firstly CO$_2$ sorption is limited to low relative humidity (RH), e.g. below 40 %, and secondly regeneration delivers CO$_2$ with low purity in a purge gas which has to be further concentrated.$^{21}$ Sorption of CO$_2$ by NaOH in solution with subsequent caustization and calcination is considered a technically feasible sorbent/process pair because sorption does not require any conditioning of the gas stream, the sorbent and most process equipment are available on industrial scale and the energy consumption is modest with 350 kJ/mol CO$_2$. Clear downsides of the technology are on the one hand that regeneration requires temperatures of 1073 K and on the other hand the necessity to use an O$_2$ fired kiln, which is not yet industrially available and challenging to develop. Generally liquid sorbent processes enable simple sorbent handling through piping, so that e.g. the sorption process requiring large air contacting surface can be separated from the regeneration process working at higher temperatures. Consequently both processes run continuously. In contrary solid sorbents are typically operated in batch processes since adsorbents are brittle and prone to attrition rendering solid handling technically complicated. Thus sorption and regeneration are usually performed in fixed bed systems: Wurzbacher et al.$^{31}$ introduced a DAC system where CO$_2$ adsorption and desorption were performed in the same apparatus and Eisenberger et al.$^{35}$ described the application of monolithic fixed bed CO$_2$ adsorption structures which were moved to a central desorption chamber for regeneration. Advantages of DAC systems featuring amine-functionalized adsorbents are that CO$_2$ sorption does not require any conditioning and that regeneration can be performed with low-grade heat at 363 K, which is commonly available as industrial waste heat, solar heat or geothermal heat. Further regeneration of high purity CO$_2$ above 97.6 % was shown experimentally via temperature-vacuum-swing (TVS) operation.$^{31}$ In conclusion DAC systems featuring NaOH and amine-functionalized adsorbents are generally considered
technically feasible. The economic viability of such systems can only be judged once detail engineering of respective industrial demonstration plants is available.

This thesis focuses on the development of a novel category of amine-functionalized adsorbents feasible for TVS operation. The motivation for application of a DAC system featuring an amine-functionalized adsorbent stems from the vision of efficiently providing atmospheric CO₂ for renewable fuel synthesis: thermochemical or electrolytic technologies for fuel synthesis from CO₂, H₂O and thermal or electrical energy, respectively, generally provide waste heat, e.g. low-temperature electrolysis based fuel synthesis stores roughly 50-55 % incoming electricity in the higher heating value of the produced fuel and the remainder is emitted as waste heat, usually at the temperature level of the synthesis process, which is e.g. performed at 473-573 K for methanol synthesis. Such waste heat can be used to meet the thermal energy demand of a low-grade heat driven DAC technology, reducing the operational cost of DAC as well as the indirect CO₂ emissions associated with the process.

Recent reports of the American Physical Society (APS), House et al. and Mazzotti et al. questioned the economic viability of DAC. Those reports cover the DAC sorbent/process pairs introduced in Table 1 except for amine-functionalized adsorbents, presumably due to a lack of data available during time of writing those reports. The goal of this thesis, as further outlined below, is to provide thorough characterization of a novel amine-functionalized adsorbent suitable for DAC, in order to provide sufficient data for consideration in future reports.

### 1.2 Amine-functionalized Adsorbents

Because of the need to process at least 2600 moles air per mole of CO₂ captured, the feasibility of the chemical DAC system will be strongly dependent on its ability to capture CO₂ in the presence of moisture without heating, cooling or compressing the air stream. Amine-functionalized adsorbents are especially suitable for this purpose, since amines react selectively with atmospheric CO₂ in the presence of moisture at ambient temperature and pressure while it has been experimentally shown that high purity CO₂ can subsequently be released in one step through TVS desorption.
Generally amine-functionalized adsorbents adsorb CO₂ via a 2-step mechanism consisting of the reaction of CO₂ with an amine group to form a zwitterion, followed by its deprotonation by a free base (either another amine group or water) to form carbamate as the final state of adsorbed CO₂. The corresponding reactions are (given for primary amine groups):

Zwitterion formation:

\[
CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^- 
\]  

Zwitterion deprotonation through primary amine group:

\[
RNH_2^+COO^- + RNH_2 \leftrightarrow RNHCOO^- + NH_3^+ 
\]  

Zwitterion deprotonation through water:

\[
RNH_2^+COO^- + H_2O \leftrightarrow RNHCOO^- + H_3O^+ 
\]  

Further amine-functionalized adsorbents adsorb H₂O from humid gas streams either through physisorption or in a protonated form when involved in the zwitterion mechanism.

For the enthalpy change of reaction for CO₂ adsorption, values of -50 to -130 kJ/mole CO₂ were reported, depending on the CO₂ and amine loading of the adsorbent. Usually the enthalpy change of reaction is high for low CO₂ loadings and decreases for increasing CO₂ loadings. In this thesis -73 kJ/mol CO₂ were evaluated for low CO₂ loadings and -50 kJ/mol CO₂ at a CO₂ loading of 1 mmol CO₂/g. For the heat of H₂O adsorption previous studies reported -47 kJ/mol H₂O and -51 kJ/mol H₂O, which is in good agreement to -49 kJ/mol H₂O reported in this thesis.

Amine-functionalized adsorbents generally feature a solid support and one type or a mixture of amines, which are either physically or chemically bonded to the surface of the solid support. Besides, one study introduced an adsorbent where both the support and the amine functionalization consisted of aminosilanes. The literature generally divides amine-functionalized adsorbents into three classes (classification following Li et al.), further described below.

- **Class 1 adsorbents** describe materials, where amine monomers or polyamines are physically adsorbed on solid supports, e.g. PEI on fumed silica.
- **Class 2 adsorbents** feature amine monomers or polyamines, which are covalently bonded to a solid substrate. Most commonly such covalent
bonds are established between materials rich in surface hydroxyl groups, e.g. mesoporous silica, and aminosilanes. Another class 2 amine functionalization used for a DAC adsorbent was the addition of amine monomers to porous carbon via surface chlor functions.\textsuperscript{52, 53}

- Class 3 adsorbents are characterized by polyamines covalently bonded to a solid support, where the polyamine was incorporated through polymerization of amine monomers, e.g. polymerization of aziridine on SAB-15.\textsuperscript{2, 54}

![Figure 2. Schematic of a) class 1, b) class 2 and class 3 adsorbent (source: Li et al.\textsuperscript{34})](image)

Table 2 summarizes amine-functionalized adsorbents used for DAC in the literature. It has been shown that amine-functionalized adsorbents feature high CO\textsubscript{2} capacities well above 1 mmol CO\textsubscript{2}/g at DAC conditions. Although class 1 adsorbents are most commonly studied for DAC, class 2 and class 3 adsorbents are considered especially suitable for CO\textsubscript{2} capture applications as covalent bonding of the amine groups reduces the risk of amine volatilization during the adsorption/desorption cycles, e.g. low molecular weight PEI (800g/mol) modified fumed silica (class 1 adsorbent) suffered from amine losses.\textsuperscript{51, 55, 56} Following the literature and the summary given in Table 2, mesoporous silica is the most frequently applied solid support among all adsorbent classes.\textsuperscript{28, 29, 55, 56} However, such surfactant template, ordered mesoporous silicas are expensive at ~$600/kg.\textsuperscript{57}
Mesoporous disordered commercial silicas and aluminas are available at significant lower cost. Coal-derived activated carbon and carbon black supports are available for $\sim$20/kg.\textsuperscript{57} This study introduces for the first time nanofibrillated cellulose (NFC) as solid support, offering additional cost saving at less than $2/kg.\textsuperscript{58}
<table>
<thead>
<tr>
<th>Author</th>
<th>Solid support</th>
<th>Amine group</th>
<th>CO$_2$ capacity</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goeppert et al.$^{23,51}$</td>
<td>Fumed silica</td>
<td>PEI</td>
<td>1.74 (298 K, 67 % RH)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Wang et al.$^{59}$</td>
<td>SBA-15</td>
<td>PEI</td>
<td>0.51 (348 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Chaikittisilp et al.$^{63}$</td>
<td>MCF</td>
<td>Poly(allylamine), PEI</td>
<td>1.74 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Choi et al.$^1$</td>
<td>Porous silica</td>
<td>Tetraethyl orthotitanate modified PEI</td>
<td>2.19 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Chaikittisilp et al.$^{61}$</td>
<td>Mesoporous $\gamma$-alumina</td>
<td>PEI</td>
<td>1.74 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Gebald et al.$^{62}$</td>
<td>Carbon fiber</td>
<td>Epoxy resin modified PEI</td>
<td>1.30 (298 K, 100 %)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Choi et al.$^{63}$</td>
<td>MOF</td>
<td>Ethylene diamine</td>
<td>1.50 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Kuwahara et al.$^{27}$</td>
<td>Zirconia modified SBA-15</td>
<td>PEI</td>
<td>0.85 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>McDonald et al.$^{26}$</td>
<td>MOF</td>
<td>Dimethylethylenediamine</td>
<td>2.0 (298 K, dry)</td>
<td>Class 1</td>
</tr>
<tr>
<td>Belmabkhout et al.$^3$</td>
<td>PE-MCM-41</td>
<td>TRI</td>
<td>0.98 (298 K, dry)</td>
<td>Class 2</td>
</tr>
<tr>
<td>Stuckert et al.$^{33}$</td>
<td>SBA-15</td>
<td>APTES</td>
<td>0.13 (298 K, humid)</td>
<td>Class 2</td>
</tr>
<tr>
<td>Lu et al.$^{52}$</td>
<td>SBA-15</td>
<td>Diethylenetriamine</td>
<td>1.04 (295 K, dry)</td>
<td>Class 2</td>
</tr>
<tr>
<td>Didas et al.$^{30}$</td>
<td>MCF</td>
<td>APTES</td>
<td>1.13 (298 K, dry)</td>
<td>Class 2</td>
</tr>
<tr>
<td>Chaikittisilp et al.$^{64}$</td>
<td>SBA-15</td>
<td>Poly(L-lysine)</td>
<td>0.60 (298 K, dry)</td>
<td>Class 3</td>
</tr>
<tr>
<td>Choi et al.$^{2}$</td>
<td>SBA-15</td>
<td>Polymerized aziridine</td>
<td>1.72 (298 K, dry)</td>
<td>Class 3</td>
</tr>
<tr>
<td>He et al.$^{32}$</td>
<td>3-aminopropyltriethoxysilane</td>
<td></td>
<td>1.78 (303 K, 0.15 % v/v)</td>
<td>-</td>
</tr>
</tbody>
</table>
1.3 Thesis Outline

This thesis was conducted in the framework of a joint project of ETH Zurich, the Swiss Federal Laboratories for Materials Science and Technology (Empa) and the ETH spinoff company Climeworks Ltd. The overall project goals were on the one hand the development of amine-functionalized NFC as novel adsorbent suitable for DAC and on the other hand the development of a novel apparatus featuring the adsorbent for the efficient capture of CO$_2$ from atmospheric air. This thesis covers part one of the work performed in the field of amine-functionalized adsorbent development, characterization and testing.

Chapter 2 provides a general introduction into NFC and aminosilanes. Further, three different commercial aminosilanes are evaluated for their feasibility to be used in the synthesis of amine-functionalized NFC as high capacity adsorbent for DAC. Finally two different adsorbent synthesis routes are presented.

Chapter 3 introduces detail characterizations of amine-functionalized NFC including specific surface area measurement by N$_2$ adsorption, morphology characterization by scanning electron microscopy (SEM), investigations of chemical composition by Fourier-Transform-Infrared-Spectroscopy (FTIR) and elemental analysis and finally CO$_2$ adsorption/desorption analysis in packed bed experiments. The equilibrium and dynamic CO$_2$ loading are compared to state of the art adsorbents described in the literature.

Chapter 4 investigates single-component and binary CO$_2$/H$_2$O adsorption of amine-functionalized NFC in detail at temperatures and partial pressures pertinent to realistic temperature-vacuum-swing (TVS) operation under DAC conditions. The governing equations for modeling the adsorption isotherms are formulated and the corresponding heats of CO$_2$ and H$_2$O adsorption are determined analytically.

Chapter 5 describes O$_2^-$, H$_2$O-, and CO$_2$-induced degradation of amine-functionalized NFC at a representative desorption temperature of 363 K. The results are compared to those obtained with amine-functionalized silicas in order to elucidate degradation mechanisms. The analysis is limited to O$_2^-$, H$_2$O-, and CO$_2$-induced degradation as these gases are considered to be the air components potentially influencing degradation of amine-functionalized NFC during desorption, where other major components of air such as N$_2$ and Ar are chemically inert. The stability of amine-functionalized NFC is evaluated during 100
subsequent TVS cycles. All test gases in this chapter are humidified so that they can be representative for DAC.

Chapter 6 summarizes this thesis and in Chapter 7 an outlook provides recommendations for future work in the field of adsorbent development for DAC.
2 Description of Adsorbent Feedstock and Synthesis

Starting point for this thesis were the results of Gebald et al.\textsuperscript{62, 65} introducing a class 1 adsorbent featuring physically adsorbed polyamines polyethylenimine (PEI) and tetraethylenepentamine (TEPA) on carbon fiber. Although the adsorbent showed high CO\textsubscript{2} loadings under DAC conditions, its practical feasibility remained questionable, since volatile amine losses were expected during cycling adsorption/desorption experiments. In the framework of this thesis amine-functionalized NFC was developed as novel class 2 adsorbent. The novel aspects are on the one hand that this thesis introduces for the first time NFC as solid adsorbent support and on the other hand the choice of amine functionalization.\textsuperscript{66}

NFC is a promising ecological and economical feasible support for CO\textsubscript{2} adsorbents for several reasons: first, cellulose is a regrowing resource and the most abundant biopolymer on earth.\textsuperscript{67, 68} Second, amine functionalization of NFC is possible in an aqueous suspension not requiring organic solvents.\textsuperscript{69} Third, cellulose is rich in surface hydroxyl groups which are required for covalently bonding amine functionalities to the NFC surface. Finally, to date NFC is the most economical adsorbent support known in the literature with a projected cost (cost of feedstock and energy only) of less than $2/kg.\textsuperscript{58}

In the framework of this thesis amine functionality was introduced on NFC through grafting of aminosilanes, which have been used commonly for class 2 adsorbent synthesis.\textsuperscript{29, 55} Moreover, aminosilanes have been used previously for amine-modification of cellulose fibers and NFC in the context of cellulose fiber/NFC reinforcement of composite materials.\textsuperscript{70-77} Previous studies exclusively focused on the application of aminosilanes featuring three alkoxy groups, however, the hydrolysis and self-condensation of such moieties is fast and leads to the build-up of three-dimensional siloxane networks.\textsuperscript{78} This characteristic is unfavorable for DAC adsorbents, as functional amine sites and pores are likely to be blocked by

\footnotesize
\textsuperscript{1} Material from this chapter has been filed as a patent: Gebald, C.; Zimmermann, T.; Tingaut, P. Porous adsorbent structure, useful for removing carbon dioxide from gas stream, preferably atmospheric air, comprises support matrix of surface modified cellulose nanofibers covered with coupling agent being covalently bound to its surface. WO2012168346-A1; EP2532410-A1, WO2012168346-A1.
siloxane networks. In this thesis NFC was functionalized with aminosilanes having two alkoxy functions instead of three alkoxy functions, as dialkoxy silanes build up only two-dimensional linear structures or ring structures upon self-condensation, hence, avoiding the undesired blocking of functional amine sites.\textsuperscript{79} It is shown in Chapter 4 that this novel approach of amine modification results in the highest CO\textsubscript{2} capacity under representative DAC conditions reported for a class 2 adsorbent to date.

\section*{2.1 Experimental Section}

\subsection*{2.1.1 Materials}

The following aminosilanes were obtained with 97 \% purity from ABCR (Germany) and used as received:

- 3-aminopropyltriethoxysilane (APTES)
- 3-aminopropylmethyldiethoxysilane (APDES)
- N-(2-Aminoethyl)-3-aminopropyl-methyldimethoxysilane (AEAPDMS)

As starting material for the isolation of NFC commercially available refined fibrous beech wood pulp suspension was used (Arbocel P 10111, 13.5\% w/w aqueous suspension with a hemicellulose content of 7.1 \% w/w and a Kappa number of 1, Rettenmeier & Söhne GmbH & Co. KG, Germany).

\subsection*{2.1.2 Adsorbent Synthesis}

NFC was obtained through a two-step mechanical isolation process from the refined fibrous beech wood pulp suspension following a procedure described elsewhere.\textsuperscript{80} In a typical experiment 1.2 kg refined fibrous beech wood pulp suspension having a dry material content of 13.5 \% w/w was placed in a 10 liter thermostatic glass reactor kept at 15 \(^\circ\)C and diluted with 8.8 kg of deionized water. The resulting suspension was stirred at 148 rpm for 21 h to allow for swelling. Thereafter the suspension was homogenized for 170 min through an inline Ultra-Turrax system (Megatron MT 3000, Kinematica AG, Switzerland) at 15'000 rpm, which was connected to the glass reactor. The homogenized suspension was subjected to high shearing-stress generated through a high-shear homogenizer (Microfluidizer Type M-110Y, Microfluidics Corporation, USA). Thereby the
suspension was pumped for 10 passes through a sequence of 400 μm and 200 μm interaction chambers and subsequently for 5 passes through a sequence of 200 μm and 75 μm interaction chambers at a flow rate of 9.75 g/s.

Six aminosilane-NFC suspensions were prepared where APTES/APDES/AEAPDMS was added to a 0.5 % w/w NFC hydrogel until the total silane concentration reached 2/4 % w/w.

After 24 h stirring, the suspensions were centrifuged (Hettich Rotanta/AP) at 3600 rpm for 20 min and the remaining water was removed by freeze-drying. For this last processing step, each retentate was poured in a copper cylinder that was then immersed in liquid N₂ and the frozen sample was dried in a freeze-dryer (Leybold Lyovac GT2). Once dried, the material was removed from the copper cylinders and heated in an inert argon atmosphere to 393 K for 2 hours. The resulting adsorbents are in the following referred to as:

- 2-APTES-NFC
- 4-APTES-NFC
- 2-APDES-NFC
- 4-APDES-NFC
- 2-AEAPDMS-NFC
- 4-AEAPDMS-NFC

Besides freeze drying, air drying was applied to remove the water from the aminosilane-NFC suspension. After 24 h stirring of a 0.5 % w/w NFC suspension containing 4 % w/w APDES, it was poured on a Nutsche filter equipped with filter paper (Whatman No. 3). The suspension was filtered by gravitation for 1 h and the retentate was dried in air at room temperature for 48 h. Once dried, the material was removed from the filter paper and heated in an inert argon atmosphere to 393 K for 2 hours. The resulting adsorbent is in the following referred to as 4-APDES-NFC-AD.

2.1.3 Adsorbent Characterization

The morphology was examined by scanning electron microscopy (FEI Nova NanoSEM 230). Specific surface areas were determined by N₂ adsorption (Micrometritics TriStar) by Brunauer-Emmett-Teller method with samples degassed (Micrometritics FlowPrep 060) at 378 K for 24 h in dry N₂ flow. The N
content was determined via elemental analysis. The density was calculated from weight and volume, which was determined by measuring the diameter and height of the dried cylindrical product.

2.1.4 CO₂ Adsorption/Desorption Measurements

CO₂ adsorption/desorption measurements were performed in a fully-automated system, schematically shown in Figure 3. It consists of a 40 mm-i.d 30 mm-height cylindrical packed bed filled with 1.2 g of adsorbent material. The adsorbent was broken in irregularly shaped pieces of mean size approximately 10 mm. The temperature of the packed bed was measured by a K-type thermocouple. The gas flow was controlled by two electronic mass flow controllers (Bronkhorst ELFLOW®). One of the gas streams was bubbled through a water bath kept at 298 K. The relative humidity before and after the packed bed arrangement was monitored by two electronic humidity sensors (Vaisala HMP110). After passing the off-gas through a filter and a condenser, the CO₂ content was analyzed by an IR analyzer (Siemens Ultramat 23) equipped with two detectors for the CO₂ concentration ranges of 0-1000 ppm and 0-5 %, at 1 Hz sampling rate and 0.2 % range detection limit. Pressurized air with a CO₂ concentration of 500 ppm was used for CO₂ adsorption. Argon was used for CO₂ desorption. All CO₂ adsorption experiments were carried out at an air flow rate of 1 l/min at 298 K and 40 % RH. All CO₂ desorption experiments were performed at an Ar flow rate of 0.8 l/min containing a level of moisture which corresponds to a RH of 40 % at 298 K. In this study Ar was used as a purge gas during desorption to enable precise measurement of the amount of desorbed CO₂ in the off-gas. In an industrial application, concentrated CO₂ is obtained by a temperature-vacuum-swing process.³¹ With the onset of CO₂ desorption, the packed bed arrangement was heated externally by a water bath at 368 K until the packed bed temperature reached 363 K ± 1 K. After CO₂ desorption, the packed bed was cooled by a water bath at 293 K until the packed bed temperature reached 298 K. Prior to all CO₂ adsorption measurements, pre-adsorbed CO₂ was removed through CO₂ desorption at the defined conditions for 1 h. To determine the equilibrium CO₂ capacity of the sample, CO₂ adsorption was performed for 12 h. For all adsorption and desorption experiments, the CO₂ uptake and release, Δq, was calculated by integrating the signal of the IR gas analyzer,
\[
\Delta q = \int_{t=0}^{t=\text{t}_{\text{ads/des}}} \frac{\dot{n}_{\text{gas}} \cdot (c_0 - c_1)}{m_s} dt
\]

where \( t_{\text{ads/des}} \) is the adsorption and desorption time, respectively, \( \dot{n}_{\text{gas}} \) the molar flow rate of the respective gas stream, \( c_0 \) and \( c_1 \) the CO\(_2\) concentrations at the inlet and outlet of the packed bed, respectively, and \( m_s \) the mass of the adsorbent material contained in the packed bed.

![Experimental setup for CO\(_2\) adsorption/desorption measurements at ETH Zurich](image)

**Figure 3.** Experimental setup for CO\(_2\) adsorption/desorption measurements at ETH Zurich

### 2.2 Description of Nanofibrillated Cellulose

NFC denotes a mixture of entangled cellulose microfibril aggregates with diameters in the range of 10-100 nm and several micrometer in length.\(^{67, 68}\) Figure 4 illustrates schematically the hierarchical structure of an isolated cellulose fiber, consisting of macrofibrils with a diameter of 500 nm which itself are aggregates of microfibrils, which again are made up of molecular cellulose chains. As described above, NFC is a promising adsorbent support as it naturally features high surface area and as it is rich in surface hydroxyl groups necessary for covalent bonding of amine functionalities.
Figure 4. Schematic illustrating the hierarchical structure of a cellulose fiber

One possibility to obtain NFC is through two-step mechanical disintegration of cellulosic raw material, where in a first step the cellulosic feedstock is refined and in a second step it is disintegrated through high pressure homogenization.\textsuperscript{58, 81}

Figure 5 shows a SEM image of the refined fibrous beech wood pulp before isolation and Figure 17a shows NFC as obtained after the two-step mechanical isolation process as described above. It can be seen that the isolation process yields entangled cellulose microfibrils with occasionally occurring macrofibrils.
Figure 5. SEM image of refined fibrous beech wood pulp (Arbocel P 10111, Rettenmeier & Söhne GmbH & Co. KG, Germany) used as raw material for the isolation of NFC in this study.

The most common cellulosic raw material is wood pulp, however, agricultural waste and bagasse have also been utilized successfully.\textsuperscript{82, 83} In the literature different designations can be found for NFC, e.g. microfibrillated cellulose (MFC) or cellulose nanofibrils, which all describe the same material. In this thesis the designation NFC is used.

### 2.3 Description and Screening of Aminosilanes

Figure 6 shows schematically the structure of an organofunctional silane, featuring an organofunctional group and three silicon functional groups.

**Figure 6.** Schematic of organofunctional silane featuring an organofunctional group and three silicon functional groups.

Silicon functional and organofunctional groups of typical commercial aminosilanes are:
OR:
- Methyl: CH₃
- Methoxy: OCH₃
- Ethoxy: OC₂H₅

Y:
- 3-aminopropyl: H₂N(CH₂)₃
- N-(2-aminoethyl)-3-aminopropyl: H₂N(CH₂)₂HN(CH₂)₃
- 3-[2-(2-Aminoethylamino)ethylamino]propyl: H₂N(CH₂)₂HN(CH₂)₂HN(CH₂)₃

Aminosilanes are commonly applied in class 2 adsorbent synthesis. Typically, in a first step aminosilanes react exothermically with water to form silanol groups and release alcohol groups. This step is referred to as hydrolysis (Figure 7):

\[
\text{OR} \quad Y - \text{Si} - \text{OR} + 3 \text{H}_2\text{O} \leftrightarrow \text{OH} \quad Y - \text{Si} - \text{OH} + 3 \text{ROH} \\
\text{OR} \quad \text{OH}
\]

**Figure 7.** Schematic of organofunctional silane hydrolysis

Subsequently silanol groups adsorb on surface hydroxyl groups of the solid support and react with the latter upon water removal, referred to as silane condensation and covalent bonding (see Figure 8):

\[
\text{OH} \quad Y - \text{Si} - \text{OH} + \text{HO} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{OH} \quad \text{OH} \quad \text{OH} + 3 \text{H}_2\text{O} \\
\]

**Figure 8.** Schematic of silane condensation and covalent bonding

In literature studies it was concluded that aminosilanes featuring primary amines are the most suitable choice for DAC, since on the one hand they feature the highest ratio of CO₂ loading over amine groups (amine efficiency) and on the other hand they offer the highest stability towards oxidation. Moreover, the linker length between the amine group and the Si backbone was varied and it was found that propyl spacers yield the highest amine efficiency for DAC. Therefore, based on literature studies, 3-aminopropyltriethoxysilane (APTES) is an optimal candidate for synthesizing amine-functionalized adsorbents for DAC.
Coincidentally APTES is a bulk chemical which is produced industrially in large quantities for coatings and as coupling agent, e.g. for the production of composite materials.

In contrary, an aminosilane screening performed in the framework of this thesis showed that aminosilanes featuring three alkoxy functional groups (ethoxy or methoxy functional group), as they were used in literature studies, do not yield high capacity \( \text{CO}_2 \) adsorbents for application of NFC as support. Rather aminosilanes featuring two alkoxy functions and one methyl function are suggested. The detailed analysis is given in the following.

2.3.1 Results and Discussion of Aminosilane Screening

The amount of aminosilane addition to the NFC hydrogel was chosen so that an excess of aminosilane moieties was available for modification of surface hydroxyl groups, which were calculated based on a theoretical procedure outlined by Ho et al.\(^6\) Assuming an average microfibril radius of 5 nm and a glucose monomer radius of 7.95 Å, the accessible hydroxyl density was 4.2 mmol/g. Several factors may affect the accuracy of the aforementioned calculation, as cellulose is a natural product containing impurities and amorphous porous constituents, influencing the amount of available hydroxyl groups. Besides, precise determination of the average microfibril diameter is experimentally complicated.

The adsorbent synthesis employed 2/4 g aminosilane per 0.5 g NFC, translating into the following molar ratios:

- 2-APTES-NFC: 9.0 mmol APTES over 2.1 mmol available hydroxyl groups
- 4-APTES-NFC: 18.1 mmol APTES over 2.1 mmol available hydroxyl groups
- 2-APDES-NFC: 10.5 mmol APDES over 2.1 mmol available hydroxyl groups
- 4-APDES-NFC: 20.9 mmol APDES over 2.1 mmol available hydroxyl groups
- 2-AEAPDMS-NFC: 9.7 mmol AEAPDMS over 2.1 mmol available hydroxyl groups
- 4-AEAPDMS-NFC: 19.4 mmol AEAPDMS over 2.1 mmol available hydroxyl groups
The final amount of aminosilane modification on NFC was on the one hand a result of the amount of adsorbed aminosilanes and on the other hand determined by the amount of aminosilanes remaining in suspension which underwent freeze drying. Table 3 summarizes the amine loading of the investigated adsorbents. For example, 4-APDES-NFC featured an amine loading of 2.8 mmol N/g, translating into 1.1 APDES moieties per available surface hydroxyl group. 4-APTES-NFC in turn features only 0.6 APTES moieties per available surface hydroxyl group, which can be explained as follows: it is known that aminosilanes carrying three alkoxy functions, such as APTES, form three dimensional polysiloxane structures upon hydrolysis (in the literature referred to as T structures). Such polysiloxane networks lead to the formation of comparatively big agglomerates, which firstly yield inhomogeneous surface modification and which secondly were likely to be discarded with the filtrate after centrifugation during adsorbent synthesis reducing the amount of aminosilanes remaining in suspension which underwent freeze drying. The existence of large polysiloxane agglomerates after APTES hydrolysis is further corroborated by Figure 9 showing a SEM image of 4-APTES-NFC. The marked area and the insert, showing the magnification of the marked area, clearly show a region featuring spherical structures attached to the NFC surface, which are likely to be polysiloxane agglomerates. The morphology of the marked area is different from the rest of the SEM image proving inhomogeneity of surface modification.

Table 3 further summarizes the BET surface area of the investigated adsorbents. APTES modification led to the highest BET surface areas. However, if the BET surface area is compared per amine loading, then AEAPDMS modification yields the highest values.
Table 3. BET surface area, amine loading and density of adsorbents investigated in aminosilane screening

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET surface area [m²/g]</th>
<th>Amine loading [mmol N/g]</th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ADPES-NFC</td>
<td>20.1</td>
<td>1.8</td>
<td>44</td>
</tr>
<tr>
<td>4-APDES-NFC</td>
<td>9.6</td>
<td>2.8</td>
<td>53</td>
</tr>
<tr>
<td>2-AEAPDMS-NFC</td>
<td>14.5</td>
<td>3.6</td>
<td>44</td>
</tr>
<tr>
<td>4-AEAPDMS-NFC</td>
<td>7.1</td>
<td>5.1</td>
<td>61</td>
</tr>
<tr>
<td>2-APTES-NFC</td>
<td>29.8</td>
<td>1.0</td>
<td>38</td>
</tr>
<tr>
<td>4-APTES-NFC</td>
<td>15.9</td>
<td>1.8</td>
<td>46</td>
</tr>
</tbody>
</table>

Figure 9. SEM image of 4-APTES-NFC with insert showing magnification of marked area

Figure 10 shows the CO₂ loading of adsorbents investigated in aminosilane screening as a function of time for CO₂ adsorption at 298 K, 40 % RH and 500 ppm CO₂ concentration. The results indicate that APTES modification of NFC leads to unfavorable CO₂ adsorption performance, where 2-APTES-NFC and 4-APTES-NFC adsorbed 0.23 and 0.25 mmol CO₂/g, respectively, after 12 h of CO₂
adsorption. In contrary, APDES and AEAPDMS modification of NFC yield high capacity CO₂ adsorbents, where 4-APDES-NFC and 4-AEAPDMS-NFC adsorbed 1.11 and 1.38 mmol CO₂/g, respectively, after 12 h of CO₂ adsorption. Interestingly 2-APDES-NFC and 4-APTES-NFC feature an identical amine loading of 1.8 mmol N/g, but the CO₂ loading of the latter is more than two times smaller. The favorable CO₂ adsorption performance of APDES/AEAPDMS modified NFC is explained by two effects. Firstly, as outlined above, APTES forms three dimensional polysiloxane agglomerates upon hydrolysis. Presumably such structures contain amine groups in their bulk, which are not accessible to CO₂. In contrary to APTES, APDES and AEAPDMS feature only two alkoxy functions and thus such aminosilane moieties build up two dimensional linear or ring structures upon hydrolysis. Thus amine groups remain accessible to CO₂. Secondly, it is likely that APDES modified NFC features a higher number of unreacted silanol groups, which are known to catalyze CO₂ adsorption.

Figure 10 further illustrates that CO₂ uptake rate is dominated by amine loading rather than BET surface area, e.g. 4-APDES-NFC and 4-AEAPDMS-NFC reach a CO₂ loading of 0.5 mmol CO₂/g after around 1 h of CO₂ adsorption. 2-APDES-NFC and 2-AEAPDMS-NFC, both having higher BET surface area than 4-APDES-NFC and 4-AEAPDMS-NFC, require more than 2 h to reach the same CO₂ loading.
Figure 10. CO$_2$ loading of adsorbent investigated in aminosilane screening as a function of time (packed bed CO$_2$ adsorption at 298 K, 40 % RH and 500 ppm CO$_2$ concentration)

Figure 11 shows that CO$_2$ desorption is fast and Table 4 confirms that CO$_2$ adsorption of all adsorbents is fully reversible, so that the amount of desorbed CO$_2$ is comparable to the amount of adsorbed CO$_2$. Following Table 4 the amount of desorbed CO$_2$ is generally higher than the amount of adsorbed CO$_2$. It can be assumed that CO$_2$ desorption capacity has higher precision than CO$_2$ adsorption capacity, since integration of the signal of the IR sensor is performed over a shorter time period.
Figure 11. Cumulative amount of desorbed CO\textsubscript{2} over time during (packed bed CO\textsubscript{2} desorption at 363 K in Ar carrying a level of moisture corresponding to 40 % RH at 298 K)

Table 4. CO\textsubscript{2} adsorption/desorption mass balance of adsorbents investigated in aminosilane screening

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>CO\textsubscript{2} adsorption capacity [mmol CO\textsubscript{2}/g]</th>
<th>CO\textsubscript{2} desorption capacity [mmol CO\textsubscript{2}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-APDES-NFC</td>
<td>0.57</td>
<td>0.64</td>
</tr>
<tr>
<td>4-APDES-NFC</td>
<td>1.11</td>
<td>1.14</td>
</tr>
<tr>
<td>2-AEAPDMS-NFC</td>
<td>0.77</td>
<td>0.82</td>
</tr>
<tr>
<td>4-AEAPDMS-NFC</td>
<td>1.38</td>
<td>1.41</td>
</tr>
<tr>
<td>2-APTES-NFC</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>4-APTES-NFC</td>
<td>0.25</td>
<td>0.32</td>
</tr>
</tbody>
</table>

2.3.2 Aminosilanes used in this Thesis

Based on the results of the analysis given above, APDES and AEAPDMS were evaluated as promising aminosilane moieties for modification of NFC to yield high capacity CO\textsubscript{2} adsorbents feasible for DAC.

Chapter 3 and chapter 5 focus on the application of AEAPDMS (see Figure 13) carrying both, a primary and a secondary amine group, to achieve high amine
loadings, which is beneficial for DAC.\textsuperscript{2} Moreover, AEAPDMS-functionlized NFC offers the highest ratio of BET surface area over amine groups of the aminosilanes investigated in this thesis. In Chapter 4 APDES (see Figure 12) is chosen as aminosilane moiety, carrying one primary amine group. This choice was made to enable precise determination of heat of CO\textsubscript{2} adsorption for the class of primary amine groups rather than for a mixture of primary and secondary amine groups.

![Figure 12. Structure of APDES](image)

![Figure 13. Structure of AEAPDMS](image)

### 2.4 Adsorbent Synthesis

Figure 14 schematically illustrates adsorbent synthesis, which generally consists of a two-step procedure, where in a first step aminosilanes and NFC were mixed in aqueous suspension and in a second step the suspension was dried.

![Figure 14. Schematic illustrating adsorbent synthesis process via freeze drying and air drying](image)
In the framework of this thesis drying of the aminosilane-NFC suspension was performed on one hand via freezing the suspension and subsequent freeze drying and on the other hand via filtering the suspension and subsequent air drying of the retentate.

2.4.1 Adsorbent Synthesis via Air Drying

Filtering and air drying of aminosilane-NFC suspensions generally led to transparent to yellowish brittle films. Figure 15 shows a SEM image of 4-APDES-NFC-AD, featuring a non-porous morphology. CO$_2$ adsorption/desorption measurements yielded a CO$_2$ capacity of only 0.06 mmol CO$_2$/g.

![SEM image of 4-APDES-NFC-AD](image)

Consequently filtering and subsequent air drying of aminosilane-NFC suspensions is regarded not feasible for the synthesis of high capacity CO$_2$ adsorbents. The motivation for the investigation of such drying method was the goal to identify a low-cost drying method.

2.4.2 Adsorbent Synthesis via Freeze Drying

In contrary to air drying, freezing of aminosilane-NFC suspensions and subsequent freeze drying led to high capacity CO$_2$ adsorbents, e.g. 4-APDES-NFC
yielded a CO$_2$ capacity of 1.11 mmol CO$_2$/g at 298 K, 40 % RH and 500 ppm CO$_2$ concentration. Consequently freezing and freeze drying was applied for adsorbent synthesis performed in the framework of this thesis. Figure 16 shows a photograph of exemplary adsorbent granules produced via freeze drying used throughout this work. The granules feature and average diameter of 5 mm and an average length of 10 mm.

![Figure 16. Photograph of exemplary adsorbent granules used throughout this work](image)

However, freeze drying for large-scale commercial production can become economic unfeasible due to its high energy consumption. For commercial production of amine-functionalized NFC more energy- and cost-efficient processes have to be identified as outlined in Chapter 7, e.g. more energy-efficient atmospheric freeze drying might be applied.

### 2.5 Summary and Conclusions

In summary three different commercial aminosilanes were evaluated for their feasibility to be used in the synthesis of amine-functionalized NFC as high capacity adsorbent for DAC. It was concluded that only aminosilanes featuring two alkoxy functions, such as APDES and AEAPDMS, result in high capacity CO$_2$ adsorbents. In contrary, aminosilanes featuring three alkoxy functions, such as APTES, did not yield high capacity CO$_2$ adsorbents feasible for DAC. This finding differs from previous literature studies, which suggested APTES as most promising aminosilane.
moiety for amine functionalization of mesoporous silica. Further, two different adsorbent synthesis routes were presented. Generally the synthesis of amine-functionalized NFC proceeds via a two-step procedure, where in a first step aminosilanes and NFC are mixed in aqueous suspension and in a second step water is removed. Water removal was performed via filtering and subsequent air drying as well as via freezing and subsequent freeze drying. Only freezing and subsequent freeze drying led to high capacity CO$_2$ adsorbents and is therefore recommended for adsorbent synthesis.
3 CO₂ Adsorption/Desorption Analysis

Amine-functionalized adsorbents proved to reversibly adsorb 0.9 mmol/g ± 0.09 mmol CO₂/g (TRI-PE-MCM-41), 3 1.72 mmol CO₂/g (HAS6), 2 2.36 mmol CO₂/g (PEI/silica), 2.26 mmol CO₂/g (A-PEI/silica) and 2.19 mmol CO₂/g (T-PEI/silica) from air. Previous synthesis of amine-functionalized adsorbent materials employed mainly inorganic materials as support. 29 In the following amine-functionalized NFC is proposed as novel adsorbent suitable for DAC. The novel adsorbent was characterized by BET, SEM, elemental analysis, the CO₂ capture mechanism was analyzed by FTIR and the CO₂ capacity as well as CO₂ uptake rate were evaluated through adsorption of humid air at 40% RH and desorption at 363 K in Ar in a packed bed arrangement and compared to state of the art adsorbents described in the literature.

3.1 Experimental Section

3.1.1 Materials

N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS, 97% purity) was obtained from ABCR (Germany) and used as received. As starting material for the isolation of NFC commercially available refined fibrous beech wood pulp suspension was used (Arbocel P 10111, 13.5% w/w aqueous suspension, Rettenmeier & Söhne GmbH & Co. KG, Germany).

3.1.2 Adsorbent Synthesis

NFC was obtained through a two-step mechanical isolation process from the refined fibrous beech wood pulp suspension as described in detail in Chapter 2. AEAPDMS was added to a 0.5% w/w NFC hydrogel until the total silane concentration reached 4% w/w. After 24 h stirring, the suspension was centrifuged (Hettich Rotanta/AP) at 3600 rpm for 20 min and the remaining water was removed by freeze-drying. For this last processing step, the retentate was poured in a copper cylinder that was then immersed in liquid N₂ and the frozen sample was

---

2 Material from this chapter has been published in: Gebald, C.; Wurzbacher, J. A.; Tingaut, P.; Zimmermann, T.; Steinfeld, A., Amine-Based Nanofibrillated Cellulose As Adsorbent for CO₂ Capture from Air. Environ. Sci. Technol. 2011, 45 (20), 9101-9108; DOI: 10.1021/Es202223p
dried in a freeze-dryer (Leybold Lyovac GT2). Once dried, the material was removed from the copper cylinder and heated in an inert argon atmosphere to 393 K for 2 h. The resulting material is in the following referred to as AEAPDMS-NFC. For comparison, the synthesis procedure above was repeated without silane addition and the produced sample is referred to as NFC-FD.

3.1.3 Adsorbent Characterization

The morphology was examined by scanning electron microscopy (FEI Nova NanoSEM 230). Specific surface areas were determined by N<sub>2</sub> adsorption (Micrometritics TriStar) by Brunauer-Emmett-Teller method with samples degassed (Micrometritics FlowPrep 060) at 378 K for 24 h in dry N<sub>2</sub> flow. The density was calculated from weight and volume, which was determined by measuring the diameter and height of the dried cylindrical product. The composition was determined through elemental analysis and Fourier-Transform-Infrared-Spectroscopy (Digilab BioRad FTS 6000 Spectrometer, ATR mode, 32 scans, 4 cm<sup>-1</sup> resolution).

3.1.4 CO<sub>2</sub> Adsorption/Desorption Measurements

CO<sub>2</sub> adsorption/desorption measurements were performed in the packed bed setup described in Chapter 2. Pressurized air with a CO<sub>2</sub> concentration of 506 ppm was used for CO<sub>2</sub> adsorption. Argon was used for CO<sub>2</sub> desorption. All CO<sub>2</sub> adsorption experiments were carried out at an air flow rate of 1 l/min at 298 K and 40% RH. All CO<sub>2</sub> desorption experiments were performed at an Ar flow rate of 0.8 l/min containing a level of moisture which corresponds to a RH of 40% at 298 K. With the onset of CO<sub>2</sub> desorption, the packed bed arrangement was heated externally by a water bath at 368 K until the packed bed temperature reached 363 K ± 1 K. After CO<sub>2</sub> desorption, the packed bed was cooled by a water bath at 293 K until the packed bed temperature reached 298 K. Prior to all CO<sub>2</sub> adsorption measurements, pre-adsorbed CO<sub>2</sub> was removed through CO<sub>2</sub> desorption at the defined conditions for 1 h. To determine the equilibrium CO<sub>2</sub> capacity of the sample, CO<sub>2</sub> adsorption was performed until the CO<sub>2</sub> outlet concentration was higher than 97% of the CO<sub>2</sub> inlet concentration, which occurred after 12 h of CO<sub>2</sub> adsorption in this study. To determine the cyclic CO<sub>2</sub> capacity of the sample and to examine the stability of the AEAPDMS grafting, consecutive 2 h-adsorption/1 h-desorption cycles were carried out.
FTIR spectra after CO₂ adsorption and desorption were recorded from a sample which was removed from the packed bed arrangement after 12 h of humid CO₂ adsorption and 1 h of CO₂ desorption, respectively.

3.2 Experimental Results and Comparison to State of the Art Adsorbents

3.2.1 Adsorbent Characterization

SEM images of the NFC before and after freeze-drying are shown in Figure 17a and Figure 17b, respectively. Before freeze-drying, the NFC hydrogel morphology was composed of entangled cellulose nanofibrils of submicron diameter. After freeze-drying, the NFC-FD morphology was composed of cellulose sheet structures with single irregularly distributed cellulose nanofibrils attached to the cellulose sheets. Aggregation of cellulose nanofibrils to form sheets upon freezing and drying was previously observed.\(^{88-90}\) The cellulose sheet forming was explained through ice crystal growth during freezing, which squeezed cellulose nanofibrils around the ice crystal in the form of cellulose sheets.\(^{90}\) The presence of AEAPDMS in the NFC suspension further increased the sheet-forming tendency and eliminated single cellulose nanofibrils, as shown in Figure 17c. Ice crystal growth presumably caused cellulose nanofibril aggregation while the hydrolyzed silane molecules in solution are pushed into the spaces between the ice crystals, forming dense cellulose-silane aggregates. Comparing Figure 17a and Figure 17c indicates the potential of AEAPDMS-NFC: by finding ways to keep the nanofibrillar structure intact after amine modification and drying, more amine groups can be accessible for surface reaction with CO₂, which will enhance the CO₂ uptake rate of the adsorbent.
The BET surface area of NFC-FD was 26.8 m$^2$/g and the density was 26 kg/m$^3$ (Table 5). These values are comparable to those of cellulose aerogels prepared
The BET surface area of AEAPDMS-NFC was 7.1 m$^2$/g and the density 61 kg/m$^3$, indicating that the surface modification reduced the available surface area but increased the density of the sample. For comparison, the BET surface area was 367 m$^2$/g for TRI-PE-MCM-41$^3$ and 45 m$^2$/g for HAS6.$^2$

**Table 5.** BET surface area, density, and amine loading of NFC-FD and AEAPDMS-NFC

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area [m$^2$/g]</th>
<th>Density [kg/m$^3$]</th>
<th>Amine loading [mmol N/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFC-FD</td>
<td>26.8</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>AEAPDMS-NFC</td>
<td>7.1</td>
<td>61</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Nevertheless, previous studies indicated that, for CO$_2$ adsorption from gas streams with CO$_2$ partial pressures of less than 0.01 atm, the equilibrium CO$_2$ capacity of the adsorbent is mainly influenced by the amine loading and less dependent on the surface area.$^{91,2}$ The amine loading of AEAPDMS-NFC was obtained through elemental analysis and determined to be 4.9 mmol N/g. For comparison, the amine loading was 7.95 mmol N/g for TRI-PE-MCM-41,$^{92}$ 9.9 mmol N/g for HAS6$^2$ and 10.5 mmol N/g for T-PEI/silica.$^1$

The FTIR spectra of NFC-FD and AEAPDMS-NFC are shown in Figure 18. The spectrum of NFC-FD exhibited typical bands for cellulose, such as OH stretching at 3345 cm$^{-1}$, CH stretching at 2900 cm$^{-1}$, CH$_2$ symmetric bending at 1430 cm$^{-1}$, OH and CH bending as well as C-C and C-O stretching at 1380, 1317 and 1256 cm$^{-1}$, C-O-C skeletal vibrations around 1055 cm$^{-1}$, C$_1$-H deformation with ring vibration contribution and OH bending at 898 cm$^{-1}$, and OH out of plane bending at 666 cm$^{-1}$. The spectrum of AEAPDMS-NFC after thermal treatment showed successful grafting of AEAPDMS on NFC through NH$_2$ bending at 1600 cm$^{-1}$. The band at 1662 cm$^{-1}$, similar to the one for mesoporous silica modified with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,$^{95}$ was assigned to aminosilane employed herein and is associated with asymmetric NH$_3^+$ deformation, formed through the interaction of primary amines with water or silanol groups.$^{95,97-100}$ The bands at 2917 cm$^{-1}$, 2877 cm$^{-1}$ and 2810 cm$^{-1}$ were assigned to CH stretching and the band at 1446 cm$^{-1}$ was assigned to CH$_2$ bending of the silane propyl chain.$^{43,95,98}$ The grafting conditions employed herein were
sufficient for covalent bonding of silane molecules, as corroborated by the appearance of signals associated with vibrations from silicon-based linkages at 1256 cm\(^{-1}\) (\(v_{\text{Si-C}}\)), and between 1180-700 cm\(^{-1}\) (Si-OH, Si-O-C, \(v_{\text{Si-C}}\), \(v_{\text{as Si-C}}\), \(v_{\text{as Si-O-Si}}\), \(v_{\text{s Si-O-Si}}\)).\(^{43, 71, 77}\)

**Figure 18.** FTIR spectra of NFC-FD and AEAPDMS-NFC

### 3.2.2 CO\(_2\) adsorption measurements

The CO\(_2\) outlet concentration as a function of the adsorption time of AEAPDMS-NF is shown in Figure 19. CO\(_2\) adsorption of AEAPDMS-NFC was stopped after 12 h of experiment, when the CO\(_2\) uptake rate became small (0.67 \(\mu\)mol/g/min) and the CO\(_2\) outlet concentration reached 97% of the inlet concentration. By integration, the CO\(_2\) loading of AEAPDMS-NFC was calculated to be 1.39 mmol CO\(_2\)/g. The amine efficiency of AEAPDMS-NFC was calculated to be 28%. The highest CO\(_2\) loading reported to date was 2.36 mmol CO\(_2\)/g obtained by Choi et al.\(^1\) for CO\(_2\) adsorption from dry Ar with 400 ppm CO\(_2\) concentration on PEI/silica having an amine density of 10.5 mmol N/g, resulting in an amine efficiency of 22%. Note that the amine efficiency of Choi et al.\(^1\) is given
for CO₂ adsorption from a dry gas, which usually increases when a wet gas stream is used. Moreover, Choi et al.² achieved 1.72 mmol CO₂/g for CO₂ adsorption from humid air with 400 ppm CO₂ concentration on HAS6 having an amine loading of 9.9 mmol N/g, corresponding to an amine efficiency of 17% in the fully loaded state. Belmabkhout et al.³ reported an equilibrium CO₂ capacity of 0.98 mmol CO₂/g for CO₂ adsorption from dry air with 400 ppm CO₂ concentration on TRI-PE-MCM-41, where the amine efficiency was 12%. Its capacity increased from 1.9 mmol CO₂/g to 2.04 mmol CO₂/g when moisture was introduced in a gas stream with 5% CO₂ concentration. Lackner²⁰ reported that a commercially available strong base ion exchange resin having a charge density of 1.7 mmol/g can theoretically absorb 0.85 mmol CO₂/g. In the patent literature, Olah et al.¹⁰¹ reported a CO₂ loading of 0.61 mmol CO₂/g sorbent on amine modified fumed silica nanoparticles for dry air containing 380 ppm of CO₂, and Gebald et al.⁶² reported a CO₂ loading of 1.87 mmol CO₂/g on amine modified air oxidized carbon fibers for humid CO₂ adsorption from air having a CO₂ concentration of 500 ppm.

To fully characterize amine-functionalized adsorbents, both the CO₂ capacity and CO₂ adsorption rate as a function of time are reported, as shown in Figure 20. Choi et al.¹,² reported the kinetic data in the form of adsorption half time (time to 50% of final CO₂ uptake), but this indicator is only meaningful in combination with the CO₂ capacity as a small adsorption half time does not necessarily correspond to a high CO₂ adsorption rate. Nevertheless, the adsorption half time is also given here for comparison (Figure 21). Note that particle size, residence time, linear velocity of the incoming gas and length over diameter of the packed bed investigated here differ from those used by Choi et al.¹,² The adsorption half time of AEAPDMS-NFC was 92 min, corresponding to an average CO₂ adsorption rate of 7.6 μmol/g/min during the adsorption half time. The adsorption half time and corresponding average CO₂ adsorption rate was 309 min and 3.8 μmol/g/min for PEI/silica, 196 min and 5.8 μmol/g/min for A-PEI/silica, 210 min and 5.2 μmol/g/min for T-PEI/silica and 167 min and 5.2 μmol/g/min for HAS6.¹,² The amine-functionalized solid adsorbent TRI-PE-MCM-41 synthesized by Belmabkhout et al.³ needed 15 min to reach 90% of its equilibrium CO₂ capacity for CO₂ adsorption from a dry gas mixture with 1000 ppm CO₂ concentration. Lackner²⁰ reported that 2500 kg of strong base ion exchange resin are needed to capture 0.25 mol CO₂/s from air, corresponding to an uptake rate of 6 μmol/g/min,
which is comparable to that of AEAPDMS-NFC during the first 120 min (6.7 μmol/g/min). In spite of the relatively small BET surface area and a particle diameter of 10 mm, the CO₂ adsorption rate of AEAPDMS-NFC is comparable to that of HAS6, PEI/silica, A-PEI/silica and T-PEI/silica in powder form, as shown in Figure 22, where the CO₂ adsorption rate of the literature adsorbents was assumed as constant. From this result we conclude that the bulk CO₂ uptake rate of 10 mm AEAPDMS-NFC particles is feasible for air capture. The favorable CO₂ uptake rate can be explained by the highly porous structure of AEAPDMS-NFC, which is composed of cellulose sheets separated by pores in the micrometer range (see Figure 17). For comparison purposes, NFC-FD was also tested for CO₂ adsorption. The CO₂ outlet concentration reached the value of the CO₂ inlet concentration immediately after gas introduction, confirming that no physisorption of CO₂ occurs on the solid support without modification.

![Figure 19. CO₂ outlet concentration during humid CO₂ adsorption on AEAPDMS-NFC (solid line) and fractional uptake of the CO₂ capacity (dashed line).](image)
Figure 20. CO$_2$ adsorption rate of AEAPDMS-NFC (solid line) and adsorbed amount CO$_2$ (dashed line)

Figure 21. Comparison of adsorption capacity and adsorption half time of AEAPDMS-NFC (star), HAS6 (sphere), PEI/silica (rhombus), A-PEI/silica (triangle), T-PEI/silica (square)$^{1,2}$
Figure 22. Comparison of CO₂ capacity as a function of time of AEAPDMS-NFC (dashed line), HAS6 (spheres), PEI/silica (rhombuses), A-PEI/silica (triangles) and T-PEI/silica (squares)$.1,2$

The FTIR spectrum of AEAPDMS-NFC after 12 h of humid CO₂ adsorption is shown in Figure 23. FTIR spectra of CO₂ adsorption on aminosilane modified NFC have not been reported yet. The FTIR spectrum obtained after CO₂ adsorption on AEAPDMS-NFC is tentatively compared to FTIR spectra obtained from CO₂ adsorption on amine-modified silicas. The band at 1568 cm$^{-1}$ was ascribed to (N)COO$^{-}$ asymmetric stretching,$^{43, 95, 97-100, 102}$ the band at 1466 cm$^{-1}$ to symmetric NH$_3^+$ deformation and the bands at 1410 cm$^{-1}$, 1369 cm$^{-1}$ and 1310 cm$^{-1}$ to symmetric stretching of (N)COO$^{-}$.$^{99, 102}$ From CO₂ absorption in amine solutions it is known that CO₂ reacts with primary and secondary amines to form carbamic acid, carbamate and bicarbonate species.$^{99, 103, 104}$ By comparing the FTIR spectra obtained in this work to the FTIR spectra obtained from CO₂ absorption in amine solution, the band at 1369 cm$^{-1}$ could be further assigned to bicarbonate.$^{103}$ However, this assignment remains questionable. First the formation of carbamate species, through deprotonation of carbamic acid, is kinetically and thermodynamically favored over bicarbonate formation for primary and secondary amines.$^{103, 104}$ Second aminosilane modification of NFC rendered the NFC surface less hydrophilic when compared to unmodified NFC,$^{71}$ questioning the feasibility of comparing the FTIR spectra obtained in this work to FTIR spectra obtained from CO₂ scrubbing in amine solutions.
Figure 23. FTIR spectra of AEAPDMS-NFC after humid CO$_2$ adsorption

3.2.3 CO$_2$ Desorption Measurements

 CO$_2$ desorption from AEAPDMS-NFC was fast and completed after 30 min, as shown in Figure 24. By integration, the amount of desorbed CO$_2$ was calculated to be 1.41 mmol CO$_2$/g, which confirmed the amount of adsorbed CO$_2$ within 1.5% error. More than 85% of the CO$_2$ is desorbed within 19 min at a packed bed temperature below 353 K.
Figure 24. Desorbed CO$_2$ from AEAPDMS-NFC (solid line) and packed bed temperature profile during CO$_2$ desorption (dashed line)

The FTIR spectra of AEAPDMS-NFC after CO$_2$ desorption is shown in Figure 25. The peaks that evolved after CO$_2$ adsorption disappeared and the FTIR spectrum of the pristine AEAPDMS-NFC was re-established.
3.2.4 Cyclic CO₂ Capacity

Figure 26 shows 20 consecutive CO₂ adsorption/desorption cycles. No decrease in cyclic capacity was observed, which confirmed the structural stability of AEAPDMS-NFC under the conditions used. During 2 h of CO₂ adsorption at 298 K and 40 % relative humidity and 1 h of CO₂ desorption in Ar at 363 K and 40% RH, the average cyclic CO₂ capacity was 0.695 mmol CO₂/g. During CO₂ desorption, humidity was added to avoid urea formation and a related loss of amine functionality. In an industrial application, the cycle duration might deviate from the one used in this study. Short cycle times maximize the amount of CO₂ captured per mass of adsorbent per time and therefore reduce the capital cost. Long cycle times favor high CO₂ loading, which minimizes the energy requirement for desorption. The optimal duration results from a trade-off between these two aspects.
Figure 26. Multicycle adsorption (squares) and desorption (spheres) experiments with AEAPDMS-NFC

3.3 Summary and Conclusions

In summary, the environmentally benign synthesis of AEAPDMS-NFC, a novel amine-functionalized adsorbent on a renewable cellulose support employed for CO$_2$ capture from ambient air, was described. The pair cellulose-aminosilane is advantageous because cellulose is a natural material rich in surface functional groups needed to anchor aminosilanes covalently through C-O-Si bonds, which can be applied in environmental friendly aqueous systems. The synthesis process is simple and enables the formation of macroscopic structures enabling high CO$_2$ uptake rates. The CO$_2$ loading and CO$_2$ adsorption rate of AEAPDMS-NFC are comparable to those obtained with state of the art amine-functionalized adsorbents. Twenty consecutive 2-hour-adsorption/1-hour-desorption cycles were performed to confirm chemical stability of the aminosilane functionalization as well as the structural stability of the cellulose support. The reaction mechanism between CO$_2$ and AEAPDMS-NFC was investigated through FTIR analysis and carbamate formation, as suggested by literature studies, was confirmed.
4 Single-Component and Binary CO$_2$ and H$_2$O Adsorption$^3$

For the design and costing of DAC systems featuring amine-functionalized adsorbents, detail understanding of single-component and binary CO$_2$ and H$_2$O adsorption is crucial because the CO$_2$ output and energy requirement of the DAC system depend on the temperature and RH of air. CO$_2$ adsorption in the presence of H$_2$O has been examined for concentrated sources$^{29}$ and diluted sources,$^3, 24, 25, 32, 106$ but little is known about co-adsorption of CO$_2$ and H$_2$O in a range of conditions relevant to DAC.

In the following single-component and binary CO$_2$/H$_2$O adsorption of APDES-NFC is investigated in detail at temperatures and partial pressures pertinent to the TVS cycle. The governing equations for modeling the adsorption isotherms are formulated and the corresponding heats of CO$_2$ and H$_2$O adsorption are determined analytically.

4.1 Experimental Section

4.1.1 Materials

3-aminopropylmethyldiethoxysilane (APDES, 97% purity, ABCR, Germany) and refined fibrous beech wood pulp suspension (Arbocel P 10111, 13.5% w/w aqueous suspension with a hemicellulose content of 7.07% w/w and a Kappa number of 1, Rettenmeier & Söhne GmbH & Co. KG, Germany) were used as starting materials.

4.1.2 Adsorbent Synthesis

A 5.6% w/w NFC hydrogel was obtained through a two-step mechanical isolation process from the refined fibrous beech wood pulp suspension and subsequent centrifugation, as described in Chapter 1. APDES was added to this

NFC hydrogel until the total silane concentration reaches 8.9% w/w. The resulting suspension was stirred, then homogenized in an ultrasonic bath for 30 min and finally left at room temperature for 12 h. The suspension was then pressed into liquid N\textsubscript{2} through a perforated metal plate with 5mm-dia openings. The frozen particles were subjected to freeze drying for 48 h and subsequent heating to 393 K in N\textsubscript{2} atmosphere for 2 h. Freeze drying for 48 h for large-scale commercial production can become economic unfeasible due to its high energy consumption. Alternatively, more energy-efficient atmospheric freeze drying might be applied.\textsuperscript{87} The obtained material is in the following referred to as APDES-NFC.

4.1.3 Adsorbent Characterization
The nitrogen content of APDES-NFC was obtained through elemental analysis. The specific surface area was determined by N\textsubscript{2} adsorption (Belsorb) by Brunauer-Emmett-Teller (BET) method with samples pretreated at 363 K under vacuum (<10\textsuperscript{-6} mbar) for 1 h.

4.1.4 Single Component CO\textsubscript{2} Adsorption Analysis
CO\textsubscript{2} adsorption measurements were performed using a volumetric reactor (Belsorp max, Bel, Japan). A sample mass of 7 g of APDES-NFC was loaded. Prior to the runs, the sample was outgassed at 363 K under vacuum (<10\textsuperscript{-6} mbar) for 1 h and then cooled to the desired adsorption temperature. Due to the absence of an inert purge gas, the temperature was set to a maximum of 363 K, so that potential adsorbent degradation during pretreatment was avoided. Experiments were performed at temperatures of 296, 323, and 343 K using dry CO\textsubscript{2} at absolute pressures ranging from 0.02 kPa (ultra-diluted) to 105 kPa (concentrated).

4.1.5 Single Component H\textsubscript{2}O Adsorption Analysis
H\textsubscript{2}O adsorption measurements were performed using a gravimetric reactor (TA Instruments, VTI-SA+ Vapor Sorption Analyzer, USA). A sample mass of 45 mg of APDES-NFC was loaded. Prior to the runs, the sample was heated to 378 K at a rate of 10 K/min in dry N\textsubscript{2} atmosphere, held at 378 K for 1 h, and then cooled to the desired adsorption temperature. Experiments were performed in N\textsubscript{2} at atmospheric pressure, at 283, 296, 303, 343, and 353 K, and at RH ranging from 5 to 80 %. The experimental parameters are listed in Table 6.
Pretreatment conditions for single component H₂O and CO₂ adsorption measurements differ due to different technical infrastructure of the respective devices. In both cases the temperature and pressure were chosen such that pretreatment was carried out above the boiling point of water.

### 4.1.6 Binary CO₂ and H₂O Adsorption Analysis

Binary CO₂ and H₂O adsorption measurements were performed using a packed-bed reactor. The experimental setup and is shown schematically in Figure 27. It comprised a cylindrical 40 mm-i.d. 30 mm-height packed bed. A sample mass of 1 g of APDES-NFC was loaded. The reactor temperature was controlled by a heating/cooling thermostat circulating water through the jacket. The temperature inside the packed bed was measured with a K-type thermocouple. The gas flow was controlled by two electronic mass flow controllers (Bronkhorst EL-FLOW®). One of the gas streams was passed through a bubbler-type humidifier contained in a water bath at constant temperature and mixed with the dry air stream. The RH of the air was thus controlled by adjusting the ratio of the two streams. For runs using CO₂ concentrations above ~0.045%, dried, technical-grade pressurized air was mixed with dried, technical grade pressurized CO₂ for a total gas flow rate of 0.5 l/min. During desorption, CO₂ concentration and RH were measured upstream and downstream of the reactor with electronic sensors (for CO₂: Vaisala GMP343 with ± 3 ppm; for RH: Vaisala HMP110 with ± 1.7%, 1 Hz sampling rate). The sensors were calibrated against each other with flows by-passing the reactor. The experimental parameters, namely: adsorption temperature, CO₂ partial pressure, and RH are listed in Table 7. CO₂ desorption was carried out for 60 min at 363 K.

### Table 6. H₂O adsorption parameters

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Relative humidity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>5, 10, 20, 40, 60, 80</td>
</tr>
<tr>
<td>296</td>
<td>5, 10, 20, 40, 60, 80</td>
</tr>
<tr>
<td>303</td>
<td>5, 10, 20, 40, 60, 80</td>
</tr>
<tr>
<td>343</td>
<td>2.5, 5, 10, 20, 30, 40</td>
</tr>
<tr>
<td>353</td>
<td>2.5, 5, 10, 15, 20, 25</td>
</tr>
</tbody>
</table>
in 1 l/min dried, technical grade N₂. The total amount of adsorbed CO₂ and H₂O was obtained through integration of the signal of the electronic sensors during desorption. Each experiment was started with CO₂ desorption.

Figure 27. Schematic of experimental setup used for binary CO₂/H₂O adsorption analysis

Table 7. Adsorption temperature, CO₂ concentration, and relative humidity for binary CO₂/H₂O adsorption analysis

<table>
<thead>
<tr>
<th></th>
<th>( q_{\text{CO}_2} ) quantification</th>
<th>( q_{\text{H}_2\text{O}} ) quantification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption temperature</td>
<td>296, 323 K</td>
<td>296, 303 K</td>
</tr>
<tr>
<td>CO₂ partial pressure</td>
<td>(~0.045, 1, 10, 100) kPa (~0.045, 1, 10, 100%)</td>
<td>(~0.045) kPa (~0.045%)</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>60% (at 303 K)</td>
<td>42, 50, 71% (at 296 K)</td>
</tr>
<tr>
<td>(at corresponding temperature)</td>
<td></td>
<td>28, 48, 70% (at 303 K)</td>
</tr>
</tbody>
</table>
Selective single-component measurements were also performed using the packed-bed reactor to verify reproducibility vis-à-vis the single-component CO₂ and H₂O measurements performed using the volumetric and gravimetric reactors, respectively. Such runs yielded good agreement. For example, CO₂ adsorption capacity of 1.11 mmol CO₂/g determined in the volumetric reactor compared well versus 1.19 mmol CO₂/g determined in the packed-bed reactor at 296 K and 0.045 kPa CO₂ pressure, and a H₂O adsorption capacity of 5.09 mmol H₂O/g determined in the gravimetric reactor compared well versus 5.05 mmol H₂O/g determined in the packed-bed reactor at 303 K and 70% RH.

4.2 Adsorption Models

4.2.1 CO₂ Adsorption

The CO₂ adsorption isotherms are described by the Toth equation:

\[ q_{CO_2} = n_s \frac{bp_{CO_2}}{\left(1 + \left(bp_{CO_2}\right)^t\right)^{1/t}} \] (5)

where \( q_{CO_2} \) denotes the amount of adsorbed CO₂ in equilibrium at a partial pressure of \( p_{CO_2} \), \( n_s \) is the maximum adsorbate loading at saturation, \( b \) and \( t \) are temperature dependent parameters:

\[ b = b_0 \exp \left[ \frac{\Delta h_{iso,0}}{RT_0} \left(\frac{T_0}{T} - 1\right)\right] \] (6)

\[ t = t_0 + \alpha \left(1 - \frac{T_0}{T}\right) \] (7)

where \( T_0 \) denotes a reference temperature, \( \Delta h_{iso,0} \) the isosteric heat of adsorption at low loading, and \( R \) the ideal gas constant. In this thesis \( T_0 \) was 296 K.

4.2.2 H₂O Adsorption

The H₂O adsorption isotherms are described by the Guggenheim-Anderson-de Boer (GAB) equation:

\[ q_{H_2O} = C_m \frac{C_G K_{ads} p_{H_2O}}{p_0} \left(1 - K_{ads} \frac{p_{H_2O}}{p_0}\right) \left(1 + (C_G - 1)K_{ads} \frac{p_{H_2O}}{p_0}\right) \] (8)

\[ C_G K_{ads} \frac{p_{H_2O}}{p_0} \]
where $q_{H_2O}$ denotes the amount of adsorbed H$_2$O in equilibrium at a partial pressure of $p_{H_2O}$ or a RH of $p_{H_2O}/p_0$, $C_m$ is the H$_2$O capacity in the monolayer, $C_g$ and $K_{ads}$ are temperature dependent parameters:\textsuperscript{109}

$$C_g = C_0 \exp \left[ \frac{\Delta H_C}{RT} \right]$$ (9)

$$K_{ads} = K_0 \exp \left[ \frac{\Delta H_K}{RT} \right]$$ (10)

where $\Delta H_C$ denotes the adsorption enthalpy difference between the H$_2$O monolayer and multilayer, and $\Delta H_K$ the adsorption enthalpy difference between the H$_2$O multilayer and the bulk liquid.\textsuperscript{109}

4.2.3 Fitting Accuracy

The fitting accuracy of both adsorption models is given by the normalized standard deviation:\textsuperscript{49,110}

$$err = \sqrt{\frac{\sum \left( \frac{q_{exp} - q_{mod}}{q_{exp}} \right)^2}{N - 1}}$$ (11)

where $N$ denotes the number of data points, $q_{exp}$ and $q_{mod}$ are the experimental and modeled adsorbate loading, respectively, and $err$ is the normalized standard deviation.

4.2.4 Heat of Adsorption

The isosteric heat of adsorption $\Delta h_{iso}$ is defined by the van’t Hoff equation:\textsuperscript{107}

$$\left( \frac{\partial \ln(p)}{\partial T} \right)_q = -\frac{\Delta h_{iso}}{RT^2}$$ (12)

Inserting Equations (5) – (7) in Equation (12) yields the isosteric heat of CO$_2$ adsorption:\textsuperscript{107}

$$\Delta h_{iso,CO_2} = \Delta h_{iso,0} - \frac{1}{t} \alpha R T_0 \left\{ \ln \left[ \frac{q_{CO_2}}{(n_s^t - q^t)^{1/t}} \right] - \ln \left( \frac{q_{CO_2}}{n_s} \right) \right\}$$ (13)

Taking the total differentiation of Equation (8) results in:
\[ (1 - K_{ads}) dq_{H2O} - \frac{p_{H2O}}{p_0} q_{H2O} dK_{ads} - K_{ads} q_{H2O} d\left(\frac{p_{H2O}}{p_0}\right) \]

\[ = \frac{1}{\left(1 + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0}\right)^2} \left[C_m C_G K_{ads} d\left(\frac{p_{H2O}}{p_0}\right)\right] \]

\[ + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0} \]

\[ - (C_G - 1)K_{ads} C_m C_G K_{ads} \frac{p_{H2O}}{p_0} d\left(\frac{p_{H2O}}{p_0}\right) \]

\[ + C_m C_G \frac{p_{H2O}}{p_0} dK_{ads} \left(1 + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0}\right) \]

\[ - (C_G - 1) \frac{p_{H2O}}{p_0} C_m C_G K_{ads} \frac{p_{H2O}}{p_0} dK_{ads} \]

\[ + C_m K_{ads} \frac{p_{H2O}}{p_0} dC_G \left(1 + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0}\right) \]

\[ - K_{ads} \frac{p_{H2O}}{p_0} C_m C_G K_{ads} \frac{p_{H2O}}{p_0} dC_G \]

Differentiating Equations (9) and (10) yields:

\[ dK_{ads} = -K_{ads} \frac{\Delta H_K}{RT^2} \]

\[ dC_G = -C_G \frac{\Delta H_C}{RT^2} \]

Inserting Equations (14) – (16) in Equation (12) at constant adsorbate loading \( (dq_{H2O} = 0) \), yields the isosteric heat of \( H_2O \) adsorption:

\[ \Delta h_{iso,H2O} = \frac{1}{K_{ads} \frac{p_{H2O}}{p_0} \left(1 - K_{ads} \frac{p_{H2O}}{p_0}\right) \left(1 + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0}\right) + 1} \]

\[ \cdot \left[ \left(1 + (C_G - 1)K_{ads} \frac{p_{H2O}}{p_0}\right) K_{ads} \frac{p_{H2O}}{p_0} + 1 \right] \Delta H_K \]

\[ + \left(1 - K_{ads} \frac{p_{H2O}}{p_0}\right) \Delta H_C \]
Adsorbed H$_2$O undergoes condensation, so that the total heat of H$_2$O adsorption is given as:

$$\Delta h_{H_2O} = \Delta h_{iso,H_2O} + \Delta h_{vap}$$

(18)

where $\Delta h_{vap}$ is the heat of H$_2$O vaporization.

### 4.3 Results and Discussion

#### 4.3.1 Adsorbent Characterization

The BET surface area of APDES-NFC was 7.5 m$^2$/g. The nitrogen content, as determined through elemental analysis, was 4.2 mmol N/g. The amount of accessible hydroxyl groups of NFC was calculated based on a theoretical procedure outlined by Ho et al. and related to the amount of APDES modification. Assuming an average microfibril radius of 5 nm and a glucose monomer radius of 7.95 Å, the accessible hydroxyl density was 4.2 mmol/g. The adsorbent synthesis employed 8.9 g APDES per 5.6 g NFC, translating into 46.6 mmol APDES and 23.5 mmol available hydroxyl groups, so that in average each cellulose hydroxyl group formed a covalent bond with an APDES dimer. Several factors may affect the accuracy of the aforementioned calculation, as cellulose is a natural product containing impurities and amorphous porous constituents, influencing the amount of available hydroxyl groups. Besides, precise determination of the average microfibril diameter is experimentally complicated.

#### 4.3.2 Single Component CO$_2$ Adsorption Analysis

Figure 28 shows the CO$_2$ adsorption isotherms of APDES-NFC, i.e. the specific CO$_2$ adsorption capacity as a function of the partial pressure of CO$_2$ at 296, 323, and 343 K. The curves are steep for pressures below 1 kPa, which particularly qualifies the adsorbent for CO$_2$ removal from ultra-diluted sources such as atmospheric air. At 296 K and 0.04 kPa CO$_2$ pressure – which corresponds to the CO$_2$ concentration in atmospheric air – APDES-NFC adsorbed 1.1 mmol CO$_2$/g. Flattening of the CO$_2$ loading was observed at higher pressures: at $p_{CO_2} = 1.4$, 8.5, and 104 kPa, the CO$_2$ loading increased to 1.7, 2.0, and 2.3 mmol CO$_2$/g, respectively. The latter value corresponded to an amine efficiency, defined as the amount of CO$_2$ over the amount of amine groups, of 0.54. This value is slightly above the theoretical maximum of 0.5 for carbamate formation as described in
Equation (1), which is explained by two effects: Firstly, mesoporous sorbents are likely to adsorb CO\textsubscript{2} via physisorption for \(p_{\text{CO}_2} > 10\) kPa, allowing overstoichiometric CO\textsubscript{2} adsorption.\textsuperscript{49, 112} As it will be shown in the analysis that follows, APDES-NFC adsorbs CO\textsubscript{2} via physisorption to some extent, increasing amine efficiency beyond the limit of carbamate formation. Secondly, CO\textsubscript{2} adsorption might be catalyzed by unreacted silanol groups. Brunelli et al.\textsuperscript{85} compared CO\textsubscript{2} capacities at 400 ppm (dry) of adsorbents with capped surface silanol groups (through reaction with hexamethyldisilazane) and uncapped ones, and reported a strong catalyzing effect of the latter. It was stated that through cooperative amine-silanol interactions, amine efficiencies of 1 are theoretically possible for dry CO\textsubscript{2} adsorption, however, amine-amine interactions are the dominant mode of adsorption.\textsuperscript{85} As aforementioned, APDES-NFC features in average one aminosilane dimer molecule per cellulose surface hydroxyl group, so that some unreacted silanol groups can be expected to catalyze CO\textsubscript{2} interaction with amine groups, possibly enhancing amine efficiency slightly beyond the theoretical limit of carbamate formation. Note the relatively high amine efficiency (0.26) for APDES-NFC at 0.04 kPa dry CO\textsubscript{2}, approaching the highest reported value (0.30) for MCF\textsubscript{-APS}\_hi under similar conditions (Figure 34).\textsuperscript{30} Although the specific surface area of APDES-NFC was almost two orders of magnitude smaller than the one of MCF\textsubscript{-APS}\_hi, amine groups were accessible even under ultradiluted dry conditions. Similarly, Goeppert et al.\textsuperscript{51} found that CO\textsubscript{2} adsorption capacity was not influenced by the surface area of the support between 125 and 344 m\textsuperscript{2}/g; the size of adsorbent particles and their morphology had a greater effect.

The amount of adsorbed CO\textsubscript{2} decreased with increasing temperatures, which is in alignment with thermodynamics, although opposite behavior was observed for some adsorbents of class 1 (classification according to of Li et al.\textsuperscript{34, 51, 57}) The equilibrium CO\textsubscript{2} adsorption capacity of APDES-NFC at 343 K and \(p_{\text{CO}_2} = 99\) kPa was 1.4 mmol CO\textsubscript{2}/g. This value was 40\% lower than the corresponding loading at 296 K, but above the saturation CO\textsubscript{2} loading at \(p_{\text{CO}_2} = 0.04\) kPa, indicating that a temperature increase to 343 K alone was insufficient to regenerate the adsorbent under DAC conditions. Combined pressure reduction and temperature increase are necessary to carry out the desorption explaining the functioning of the TVS cycle. For instance, to regenerate the sorbent at 343 K, the CO\textsubscript{2} pressure has to be below 2.2 kPa.\textsuperscript{31, 113}
The CO\(_2\) adsorption isotherms exhibited a typical Langmuir shape characteristic for chemisorption with a steep rise at low pressures and a plateau at higher pressures.\(^{49, 114}\) The Toth model with three parameters was applied to enable a precise fit, as previously applied to the chemisorption of CO\(_2\) on amine-functionalized mesoporous silica.\(^{49}\) Physisorption of CO\(_2\) is expected to be small as a plateau was observed for pressures above 10 kPa, presumably due to the relatively small BET surface area of APDES-NFC. The model parameters were obtained with a nonlinear least squares algorithm and are listed in Table 8, along with the corresponding normalized standard deviations.

**Table 8.** Toth parameters and normalized standard deviation for different CO\(_2\) adsorption temperatures

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>(n_s) [mmol CO(_2)/g]</th>
<th>(b) [1/kPa]</th>
<th>(t) [-]</th>
<th>(err) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>2.27</td>
<td>339.90</td>
<td>0.40</td>
<td>5.10</td>
</tr>
<tr>
<td>323</td>
<td>2.05</td>
<td>28.75</td>
<td>0.51</td>
<td>8.21</td>
</tr>
<tr>
<td>343</td>
<td>1.48</td>
<td>4.32</td>
<td>0.58</td>
<td>6.03</td>
</tr>
</tbody>
</table>
As shown in Figure 28, the modeled CO₂ adsorption isotherms (solid lines) produced a good fit with err values of 5.1, 8.2, and 6.0% at 296, 323, and 343 K, respectively. Note that the Toth parameters for 323 and 343 K are only valid for \( p_{CO_2} \) above 0.08 kPa and 0.2 kPa, respectively. The experimental data for CO₂ adsorption at 323 and 343 K cannot be modeled with sufficient accuracy in the very low pressure regime between 0.03-0.08 kPa and 0.1-0.2 kPa, respectively. In contrast, the adsorption isotherm at 296 K is fitted to the model with high accuracy starting from the first measurement point at \( p_{CO_2} = 0.016 \) kPa. The CO₂ adsorption isotherms of APDES-NFC at 323 K and 343 K feature a very steep rise at ultra-diluted pressures followed by a plateau, as shown in Figure 29. Such quasi rectangular shape is an extreme form of Type 1 isotherm (classification following Brunauer et al.\(^\text{115}\)). Empirical equations used for modelling of common Type 1 isotherms, e.g. Toth model, fail to predict such behavior with sufficient accuracy in the complete pressure range, so that the validity of the model has to be reduced to a certain pressure range. Future work should explore alternate isotherms.

Figura 29. CO₂ adsorption isotherms of APDES-NFC-FD at 296 K (spheres), 323 K (rectangles) and 343 K (triangles) as a function of CO₂ pressure

### 4.3.3 Heat of CO₂ Adsorption

Figure 30 shows the isosteric heat of CO₂ adsorption as a function of CO₂ loading. By applying Equation (13), the isosteric heat of CO₂ adsorption is \(-73\) kJ/mol CO₂ at low loadings and it decreases to \(~-50\) kJ/mol CO₂ at 1 mmol CO₂/g.
Wang and Yang\textsuperscript{50} reported a heat of adsorption stemming from chemisorption of CO\textsubscript{2} on amine-functionalized adsorbents in the range -48 to -90 kJ/mol CO\textsubscript{2}. They showed that, for adsorbents with low amine loading, the heat of CO\textsubscript{2} adsorption ranged from values typical for chemisorption to those typical for physisorption, e.g. for amine-SBA-15-ext (3.2 mmol N/g) and amine-SBA-15-cal (2.2 mmol N/g), the heat of adsorption ranged from -88 to -70 kJ/mol CO\textsubscript{2} and from -85 to -33 kJ/mol CO\textsubscript{2}, respectively.\textsuperscript{50} The heat of adsorption values determined in this study were largely in the range typical for chemisorption, indicating that CO\textsubscript{2} adsorption on APDES-NFC is dominantly based on interaction with amine groups, however, physisorption occurs to some small extent. Similarly, Zukal et al.\textsuperscript{47} showed heat of adsorption values covering the range typical for both chemisorption and physisorption, e.g. SBA-15-AP2 (2.0 mmol N/g) with a heat of adsorption of -65 kJ/mol at 5 cm\textsuperscript{3} CO\textsubscript{2}/g STP and around -25 kJ/mol CO\textsubscript{2} at loadings exceeding 20 cm\textsuperscript{3} CO\textsubscript{2}/g STP. Other studies analyzing the isosteric heat of CO\textsubscript{2} adsorption from single-component CO\textsubscript{2} adsorption isotherms of amine-functionalized adsorbents reported values of -80 kJ/mol CO\textsubscript{2} at 1 mmol CO\textsubscript{2}/g and -55 kJ/mol at 1.5 mmol CO\textsubscript{2}/g (TRI-PE-MCM-41), -65 kJ/mol CO\textsubscript{2} at zero loading as well as at a loading corresponding to 395 ppm CO\textsubscript{2} (aminopropyl modified SBA-15),\textsuperscript{24} -130 kJ/mol CO\textsubscript{2} at zero coverage and -87.5 kJ/mol CO\textsubscript{2} (extracted from graph) at 1 mmol CO\textsubscript{2}/g (MCF\_APS\_hi),\textsuperscript{30} -71 kJ/mol CO\textsubscript{2} for alkylamine-functionalized metal-organic-framework (mmen-2),\textsuperscript{26} -125 kJ/mol CO\textsubscript{2} at zero coverage and -49 kJ/mol CO\textsubscript{2} at 0.8 mmol CO\textsubscript{2}/g (PCH+APTES).\textsuperscript{45} Microcalorimetric analysis of single-component CO\textsubscript{2} adsorption on 3-aminopropyl modified mesoporous silica (Si-APS) yielded -80 kJ/mol CO\textsubscript{2} at a loading of 0.3 µmol CO\textsubscript{2}/m\textsuperscript{2} and -40 kJ/mol CO\textsubscript{2} at a loading of 1 µmol CO\textsubscript{2}/m\textsuperscript{2}.\textsuperscript{43} Further studies using differential scanning calorimetry measurements reported -94 kJ/mol CO\textsubscript{2} for HSC+ as adsorbent,\textsuperscript{40} and using differential thermal analysis reported -50 to -60 kJ/mol CO\textsubscript{2} for aminopropyl, ethylenediamine and ethylenetriamine modified HMS.\textsuperscript{41}
4.3.4 Single-component H\textsubscript{2}O adsorption analysis

H\textsubscript{2}O adsorption isotherms of APDES-NFC at 283, 296, 303, 343 and 353 K are shown as a function of RH in Figure 31, and as a function of $p_{H_2O}$ in Figure 32. The H\textsubscript{2}O loading was strongly dependent on RH and temperature. At 296 K and 40% RH, the H\textsubscript{2}O capacity was 2.1 mmol H\textsubscript{2}O/g. It almost doubled for every step of 20% in RH, e.g. it reached 4.0 mmol H\textsubscript{2}O/g at 60% RH and 7.4 mmol H\textsubscript{2}O/g at 80% RH. The strong temperature dependency of H\textsubscript{2}O is corroborated in Figure 32: at $p_{H_2O} = 2.5$ kPa and 303 K, 3.7 mmol H\textsubscript{2}O/g were adsorbed, whereas at a similar $p_{H_2O}$ (2.3 kPa) and 353 K, only 0.12 mmol H\textsubscript{2}O/g were adsorbed. Thus, regeneration of loaded amine-functionalized adsorbents requires an additional energy input for the co-desorption of H\textsubscript{2}O and CO\textsubscript{2}.

Previous studies measuring H\textsubscript{2}O adsorption of amine-functionalized adsorbents yielded ~3.75 mmol H\textsubscript{2}O/g (extracted from graph) at 298 K and 40% RH using MONO-PE-MCM-41,\textsuperscript{112} ~4.75 mmol H\textsubscript{2}O/g (extracted from graph) under similar conditions using TRI-PE-MCM-41\textsuperscript{116} and ~0.035 mmol H\textsubscript{2}O/m\textsuperscript{2} (equivalent to 8.05 mmol H\textsubscript{2}O/g at surface area of 230 m\textsuperscript{2}/g) at $p_{H_2O} = 2$ kPa (63% RH) and 298 K using MCF\textsubscript{APS.hi}.\textsuperscript{30} In comparison to APDES-NFC, literature materials adsorbed roughly twice as much H\textsubscript{2}O under comparable conditions, implying a higher energy penalty for adsorbent regeneration.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig30.png}
\caption{Calculated heat of CO\textsubscript{2} adsorption of APDES-NFC-FD as a function of CO\textsubscript{2} loading.}
\end{figure}
Figure 31. H$_2$O loading of APDES-NFC-FD as function of the RH

Figure 32. H$_2$O loading on unmodified NFC and APDES-NFC as function of H$_2$O partial pressure

APDES-NFC showed reduced H$_2$O adsorption compared to the unmodified NFC support. Figure 32 shows the water loading as a function of the water vapor partial pressure for unmodified freeze dried NFC at 303 K and the corresponding values for APDES-NFC at 303, 343, and 353 K. In the low pressure regime the reduction of H$_2$O adsorption of APDES-NFC compared to unmodified NFC is
pronounced, e.g. at 1.7 kPa the water loading is decreased from 3.5 mmol H\textsubscript{2}O/g for unmodified NFC to 2.0 mmol H\textsubscript{2}O/g for APDES-NFC. However, in the high pressure regime this effect becomes minor.

The isotherms are modeled with the GAB equation, which is commonly applied for modeling H\textsubscript{2}O adsorption by cellulose based materials.\textsuperscript{108, 117} The model parameters were obtained with a nonlinear least squares algorithm and are listed in Table 9 along with the normalized standard deviation. As shown in Figure 31, the modeled H\textsubscript{2}O adsorption isotherms (solid lines) produced a good fit. Only the data points at 5\% (283 K) and 2.5\% RH (343 K) did not fit well and lead to higher err values. Excluding these first data points yielded err values of 6.6\% and 5.6\% at 283 K and 343 K, respectively.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>(c_m) [mmol/g]</th>
<th>(c_G) [-]</th>
<th>(K_{ads}) [-]</th>
<th>err [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>4.87</td>
<td>1.06</td>
<td>0.79</td>
<td>18.24</td>
</tr>
<tr>
<td>296</td>
<td>3.72</td>
<td>1.34</td>
<td>0.80</td>
<td>3.92</td>
</tr>
<tr>
<td>303</td>
<td>3.27</td>
<td>1.46</td>
<td>0.82</td>
<td>0.57</td>
</tr>
<tr>
<td>343</td>
<td>1.92</td>
<td>1.56</td>
<td>0.91</td>
<td>12.43</td>
</tr>
<tr>
<td>353</td>
<td>1.65</td>
<td>1.69</td>
<td>0.98</td>
<td>8.64</td>
</tr>
</tbody>
</table>

### 4.3.5 Heat of H\textsubscript{2}O Adsorption

Figure 33 shows the isosteric heat of H\textsubscript{2}O adsorption of APDES-NFC as a function of H\textsubscript{2}O loading at 296 K. Since H\textsubscript{2}O condenses during the adsorption process, the total heat release during H\textsubscript{2}O adsorption comprises the sum of the heat of H\textsubscript{2}O condensation, -44.1 kJ/mol H\textsubscript{2}O at 296 K, and the isosteric heat of H\textsubscript{2}O adsorption, yielding a total of -48.8 kJ/mol H\textsubscript{2}O at 296 K for a H\textsubscript{2}O loading of 2.1 mmol H\textsubscript{2}O/g (corresponding to 40\% RH). Previous reported values for amine-functionalized silica of -47.2 kJ/mol H\textsubscript{2}O\textsuperscript{40} and -51 kJ/mol H\textsubscript{2}O\textsuperscript{41} are comparable.
4.3.6 Binary CO$_2$ and H$_2$O adsorption analysis

Table 10 lists the CO$_2$ adsorption capacities under both dry and humid conditions at 296 K and 323 K, respectively. Addition of humidity resulted generally in an increase of adsorbed CO$_2$, however, this effect was especially pronounced for low CO$_2$ concentrations. For example, at 0.04 kPa, CO$_2$ capacities increased by 92% and 1191% for adsorption at 296 K and 323 K, respectively. Previous studies reporting dry and humid CO$_2$ adsorption from ultra-diluted gases are summarized in Figure 34, which compares amine efficiency and amine loading under dry and humid DAC conditions for literature adsorbents at 298 K and for APDES-NFC at 296 K.

As aforementioned, APDES-NFC performed with a high amine efficiency of 0.26 under dry DAC conditions, which approaches the highest reported value of 0.30 for MCF_APS_hi. Under humid DAC conditions, the amine efficiency increased to 0.34 and 0.51 at 323 K (21% RH) and 296 K (91% RH), respectively. Amine efficiencies of literature adsorbents under similar humid DAC conditions were 0.23 for FS-PEI-33 (298 K, 67% RH), 0.13 for amine grafted SBA-15 (298 K, 80% RH), 0.20 for TRI-PE-MCM-41 (298 K, 64% RH), and 0.21 for RFAS (298 K, 5% RH). Compared to literature studies, APDES-NFC featured the highest amine efficiency under humid DAC and the highest CO$_2$ capacity reported for a class 2 adsorbent. Several promising materials remain to be...
investigated under such conditions, e.g. HAS 6 or MCF_APS_hi. Due to the relatively high cost of aminosilanes, high amine efficiencies are desired for economical feasible adsorbents making use of such moieties.
Table 10. CO₂ capacity under dry and humid conditions ($p_{H_2O} = 2.55$ kPa) at 296 K and 323 K

<table>
<thead>
<tr>
<th>$p_{CO_2}$ [kPa]</th>
<th>T = 296 K</th>
<th></th>
<th>T = 323 K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single-component $q_{CO_2}$ [mmol CO₂/g]</td>
<td>Binary $q_{CO_2}$ [mmol CO₂/g]</td>
<td>Single-component $q_{CO_2}$ [mmol CO₂/g]</td>
<td>Binary $q_{CO_2}$ [mmol CO₂/g]</td>
</tr>
<tr>
<td>0.04</td>
<td>1.11</td>
<td>2.13</td>
<td>0.11</td>
<td>1.42</td>
</tr>
<tr>
<td>1</td>
<td>1.72</td>
<td>2.29</td>
<td>1.51</td>
<td>1.97</td>
</tr>
<tr>
<td>10</td>
<td>2.03</td>
<td>2.37</td>
<td>1.81</td>
<td>2.29</td>
</tr>
<tr>
<td>100</td>
<td>2.26</td>
<td>2.54</td>
<td>2.05</td>
<td>2.37</td>
</tr>
</tbody>
</table>

Table 11. H₂O capacities from single-component adsorption and in presence of ultra-diluted CO₂ ($p_{CO_2} = 0.045$ kPa) at 296 K and 303 K

<table>
<thead>
<tr>
<th>RH [%]</th>
<th>T = 296 K</th>
<th></th>
<th>T = 303 K</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single-component $q_{H_2O}$ [mmol H₂O/g]</td>
<td>Binary $q_{H_2O}$ [mmol H₂O/g]</td>
<td>RH [%]</td>
<td>Single-component $q_{H_2O}$ [mmol H₂O/g]</td>
</tr>
<tr>
<td>42</td>
<td>2.29</td>
<td>2.10</td>
<td>28</td>
<td>1.31</td>
</tr>
<tr>
<td>50</td>
<td>2.99</td>
<td>3.10</td>
<td>48</td>
<td>2.63</td>
</tr>
<tr>
<td>71</td>
<td>5.45</td>
<td>5.06</td>
<td>70</td>
<td>5.09</td>
</tr>
</tbody>
</table>
Figure 34. Amine efficiency and amine loading under dry and humid DAC conditions at 298 K for literature adsorbents and for APDES-NFC (at 296 K). a) amine-grafted SBA-15, b) MCF_APS_hi, c) APDES-NFC, d) FS-PEI-33, e) TRI-PE-MCM-41, f) RFAS, g) PEI/Zr7-SBA-15, h) HAS6, i) T-PEI/silica

APDES-NFC possesses amine sites that are freely accessible and those that are buried inside the bulk of the adsorbent only accessible through diffusion. As shown above, at 100 kPa CO₂ pressure, all amine sites were accessible under dry and humid conditions. However, at ultra-diluted CO₂ pressures, humidity was necessary to achieve high efficiencies, presumably because of the low diffusion rate of CO₂ across the bulk. Mebane et al. showed that diffusive intermediates exist under humid conditions, which enable accessibility to the amine sites and, consequently, enhance CO₂ adsorption.

In contrary to CO₂ adsorption at ultra-diluted conditions, humidity only slightly enhances CO₂ adsorption at high CO₂ concentrations. For example, at 100 kPa CO₂ pressure and 296 K, the amine efficiency increased from 0.54 under dry conditions to 0.60 under humid conditions. Given that the amine efficiency slightly exceeded the theoretical limit of 0.50 for carbamate formation under dry conditions, mass transfer (i.e. accessibility of amine groups) was unlikely the limiting mechanism, but rather the system approaching chemical equilibrium of carbamate formation was the governing mechanism under humid conditions, as suggested previously.
Interestingly, H$_2$O adsorption remains largely unaffected by the presence of ultra-diluted CO$_2$. Table 11 lists H$_2$O adsorption capacities obtained for single-component adsorption in the presence of ultra-diluted CO$_2$ at 296 K and 303 K, respectively. H$_2$O adsorption was neither enhanced nor hindered by the presence of ultra-diluted CO$_2$. Similarly, H$_2$O adsorption on TRI-PE-MCM-41 proceeded unaffected by the presence of CO$_2$, i.e. the H$_2$O loading without co-adsorption of CO$_2$ was 2.96 mmol H$_2$O/g at 298 K and 27% RH and 2.7 mmol H$_2$O/g under similar conditions in the presence of a 50:50 CO$_2$:CH$_4$ gas mixture.

Consequently H$_2$O adsorption during DAC is solely driven by the temperature and RH of the air. For temperatures between 283 and 303 K and RH between 40 and 80%, both ranges typical for DAC, APDES-NFC is expected to have H$_2$O loadings between 2 and 8 mmol H$_2$O/g. The regeneration of the adsorbent and closed mass balance for both H$_2$O and CO$_2$, in which all of the adsorbed H$_2$O and CO$_2$ were desorbed, were demonstrated for ten consecutive TVS cycles. The stability of the adsorbent under humid air conditions was experimentally shown for 100 TVS consecutive cycles. CO$_2$ loadings lied in the range of 1 mmol CO$_2$/g. Therefore, under typical DAC conditions, 2 to 8 mol of H$_2$O are expected to be adsorbed per mol of CO$_2$. Such H$_2$O loadings increase the thermal energy demand during regeneration from 98 up to 390 kJ/mol CO$_2$.

Therefore, although high H$_2$O loadings were shown to be beneficial for achieving high CO$_2$ loadings, especially at ultra-diluted CO$_2$ pressures, reduced H$_2$O adsorption is desirable to improve the overall energy efficiency of the TVS adsorption/desorption process.

In the co-adsorption system, CO$_2$ undergoes adsorption via a 2-step mechanism consisting of the reaction of CO$_2$ with a primary amine group to form a zwitterion, followed by its deprotonation by a free base (either water or another primary amine group) to form a carbamate as the final state of adsorbed CO$_2$. The corresponding reaction mechanisms are given by Equations (1)-(3).

The final state of adsorbed water is either physisorbed at a free silanol group, a free cellulose hydroxyl group, an unreacted amine group or in a protonated form when involved in the zwitterion mechanism.

The adsorption site of CO$_2$ is a primary amine group. The adsorption site of H$_2$O is either a silanol group, a free cellulose hydroxyl group, an unreacted amine group
or in a protonated form at an amine group, when acting as a free base for deprotonation of a zwitterion.

4.4 Summary and Conclusions

In summary single-component and binary CO₂ and H₂O adsorption of amine-functionalized NFC was studied under conditions relevant to the direct capture of CO₂ from air via a TVS cycle. The amine efficiencies achieved under dry and humid conditions were comparably high, and pointed out to an effective exploitation of the aminosilane moieties. The CO₂ capacity achieved under humid DAC conditions is the highest reported to date for a class 2 adsorbent. Single-component CO₂ and H₂O adsorption increased with decreasing temperature and increasing adsorbate concentration. Adsorption isotherms were modeled successfully and the corresponding heats of adsorptions were determined analytically. Binary CO₂ and H₂O adsorption measurements showed that CO₂ adsorption was enhanced by the presence of humidity, especially in the low pressure regime. In contrast, H₂O adsorption remained unaffected by the presence of ultra-diluted CO₂ and was solely driven by temperature and relative humidity. H₂O loadings were generally higher than the corresponding CO₂ loadings. This translated to a substantial energy penalty during adsorbent regeneration, as H₂O desorption requires more than twice the thermal energy needed for CO₂ desorption. Thus, less hygroscopic adsorbents should decrease the energy demand and improve the performance of the TVS process.
5 Adsorbent Stability Analysis

Little is known about the long-term stability of amine-functionalized adsorbents during cyclic CO₂ adsorption/desorption operation, which in turn is crucial for the industrial implementation. Recent studies investigated the thermal, oxidative and CO₂-induced degradation of amine-functionalized sorbents as well as stability during steam stripping. It was found that primary amines exhibit stability in O₂-containing atmospheres at typical desorption temperatures. The amine structures of sorbents from literature are shown in Table 12. For example, the CO₂ adsorption capacity of SBA-15-AP was not affected by exposure to air at 383 K for 24 h, but it decreased by about 10% after prolonging treatment to 72 h. In another study, MCF_APS did not show any significant drop in CO₂ adsorption capacity after treatment for 24 h at 408 K in pure O₂. On the contrary, secondary amines or a mixture of primary and secondary amines degrade significantly in O₂-containing atmospheres at temperatures above about 363 K. For example, the CO₂ capture capacity of TS 25/75 dropped from 1.234 to 0.454 mmol CO₂/g after 12 h in air at 373 K. In other studies, TRI, MCF_DA, and SBA-15PL-600(55) lost 47%, ~30% (extracted from graph), and 22% of their CO₂ adsorption capacity after exposure for 12 h to carbon-free air at 363 K, for 24 h to 100% O₂ at 378 K, and for 30 h to carbon-free air at 363 K respectively. Addition of polyethylene glycol (PEG) proved to increase oxidative stability of silica-supported TEPA sorbents, e.g. the CO₂ capacity of TP200S 10/10/80 dropped from 1.585 to 0.868 mmol CO₂/g after 12 h in air at 373 K. Tertiary amines (MCF_DMAPS) proved to be stable in 100% O₂ up to 408 K, however, their CO₂ adsorption under DAC conditions was negligible.

Prolonged contact to dry CO₂ at temperatures above 328 K led to degradation of primary amines and mixtures of primary and secondary amines; however, isolated secondary amines were stable. In one experiment pMono lost 21% of its CO₂ adsorption capacity after 60 cycles with adsorption at 328 K in pure dry CO₂ and desorption at 393 K in N₂. A decrease of CO₂ uptake capacity was observed

---

upon increasing temperature, e.g. pMono lost 66% CO$_2$ uptake capacity after 30 cycles with adsorption at 323 K and desorption at 403 K, both in dry CO$_2$.\textsuperscript{125} The behavior was similar for Diamine and TRI.\textsuperscript{105, 125} In contrast, sMono did not show any CO$_2$ uptake loss during identical experiments.\textsuperscript{125, 126} PEI 423 MM modified mesoporous silica lost 38% CO$_2$ uptake capacity after exposure to pure dry CO$_2$ at 403 K for 60 min.\textsuperscript{124} Sayari et al.\textsuperscript{105} found that primary amines and mixtures of primary and secondary amines can be stabilized in CO$_2$ atmospheres through H$_2$O addition: TRI-PE-MCM-41 was operated stable over 700 adsorption/desorption cycles, with adsorption at 343 K in humid CO$_2$ and desorption at 343 K in humid N$_2$, where both gases had a dew point of 293 K.

Jones et al.\textsuperscript{61, 127} analyzed the stability of mesoporous silica and aluminia supported amines and found that both showed reduced CO$_2$ capacity after steam exposure, however, less pronounced for the latter: the CO$_2$ capacity of MS25 dropped by 67.1% and the one of SynA30 by only 16.3% after steam treatment at 378 K for 24 h.
**Table 12. Amine structure of sorbents from literature degradation studies**

<table>
<thead>
<tr>
<th>Sorbent name</th>
<th>Support</th>
<th>Amine</th>
<th>Amine structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCF-APS(^{84})</td>
<td>MCF</td>
<td>3-aminopropyltrimethoxysilane</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>MCF-DA(^{84})</td>
<td>MCF</td>
<td>N-(3-(trimethoxysilyl)-propyl)ethylenediamine</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>MCF-DMPAS(^{128})</td>
<td>MCF</td>
<td>(N,N-dimethylaminopropyl)-trimethoxysilane</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>SynA30(^{61})</td>
<td>Mesoporous (\gamma)-alumina</td>
<td>Polyethylenimine</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>PEI 423 MM(^{124})</td>
<td>Mesoporous silica</td>
<td>Polyethylenimine</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>pMono(^{126})</td>
<td>PE-MCM-41</td>
<td>3-aminopropyltrimethoxysilane</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Material</td>
<td>Linkage</td>
<td>Structure</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------------------</td>
<td>------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>TRI-PE-MCM-41</td>
<td>PE-MCM-41</td>
<td>N1-(3-trimethoxysilylpropyl) diethylenetriamine</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>TRI-PE-MCM-41</td>
<td>PE-MCM-41</td>
<td>N1-(3-trimethoxysilylpropyl) diethylenetriamine</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>sMono</td>
<td>PE-MCM-41</td>
<td>N-methylaminopropyl trimethoxysilane</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>SBA-15-AP</td>
<td>SBA-15</td>
<td>3-aminopropyltrimethoxysilane</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>SBA-15PL-600(55)</td>
<td>SBA-15</td>
<td>Polyethylenimine</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>MS25</td>
<td>SBA-15</td>
<td>Polyethylenimine</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>TS 25/75</td>
<td>Silica</td>
<td>tetraethylenepentamine (TEPA)</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>TP200S 10/10/80</td>
<td>Silica</td>
<td>tetraethylenepentamine (TEPA)</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
</tbody>
</table>
In the following $O_2$, $H_2O$, and $CO_2$-induced degradation of amine-functionalized NFC is investigated at a representative desorption temperature of 363 K. The results are compared to those obtained with amine-functionalized silicas in order to elucidate degradation mechanisms. The analysis is limited to $O_2$, $H_2O$, and $CO_2$-induced degradation as these gases are considered to be the air components potentially influencing degradation of amine-functionalized cellulose during desorption, where other major components of air such as $N_2$ and Ar are chemically inert. The stability of amine-functionalized NFC is evaluated during 100 subsequent TVS cycles. All test gases in this study are humidified so that they can be representative for DAC. Moreover, this study focuses on an aminosilane carrying both primary and secondary amines to achieve high amine loadings, which is beneficial for DAC.

5.1 Experimental Section

5.1.1 Materials

N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS, 97 % purity, ABCR, Germany) and fibrillated cellulose suspension (Borregaard SA) were used as starting materials.

5.1.2 Adsorbent Synthesis

AEAPDMS was added to a NFC hydrogel until a w/w concentration of 5% NFC and 5% AEAPDMS was obtained. The resulting suspension was stirred at room temperature for 12 h and then pressed into liquid $N_2$ through a perforated metal plate with round 5 mm-i.d. openings. The frozen particles were subjected to freeze drying for 48 h and subsequent heating to 393 K in $N_2$ atmosphere for 2 h. The obtained material is N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane modified nanofibrillated cellulose, in the following referred to as AEAPDMS-NFC.

5.1.3 Adsorbent Characterization

The nitrogen content of AEAPDMS-NFC was obtained through elemental analysis. Specific surface areas were determined by $N_2$ adsorption (Micrometritics TriStar) using the Brunauer-Emmett-Teller (BET) method with samples degassed (Micrometritics FlowPrep 060) at 378 K for 48 h in dry He flow. IR spectra of
Adsorbent Stability Analysis

Sorbent samples were recorded using a Digilab BioRad FTS 6000 Spectrometer. All spectra were recorded between 4000 and 600 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) and 32 scans. Before every experiment the sample was heated for 2 h at 393 K in N\(_2\). XPS analysis was performed on a Physical Electronics (PHI) Quantum 2000 photoelectron spectrometer with settings previously described.\(^\text{129}\) To compensate for the surface charging, the binding energies of all spectra were shifted so that the O1s signal was at 533.2 eV, the reference position for cellulose. Surface elemental concentrations were calculated from the high resolution spectra, once having identified the contributions of all elements from the survey spectra. Analysis of the XPS spectra was performed using the MultiPak 6.1A software (Physical Electronics). Scanning Electron Microscopy (Jeol 6300F SEM) images were obtained for AEAPDMS-NFC before and after 100 TVS cycles.

5.1.4 Equilibrium CO\(_2\) Adsorption Analysis

CO\(_2\) adsorption measurements were performed in a custom built packed bed arrangement similar to the one used in Chapter 1. A schematic of the setup is shown in Figure 35, featuring a cylindrical 40 mm-i.d. 30 mm-height packed bed, which was loaded with 1 g of sorbent material. The reactor temperature was controlled by a heating/cooling thermostat circulating water through the jacket. The temperature inside the packed bed was measured with a K-type thermocouple. Prior to each experiment, the sample was heated for 2 h at 393 K in N\(_2\). CO\(_2\) adsorption was carried out for 600 min at 303 K and 60% relative humidity (RH) at a flow rate of 0.5 l/min dried, technical-grade, pressurized air with a CO\(_2\) concentration of 444-463 ppm. The air flow was controlled by two electronic mass flow controllers (Bronkhorst EL-FLOW\(^\circledR\)). One of the air streams was passed through a bubbler-type humidifier contained in a water bath at constant temperature and mixed with the dry air stream. The RH of the air was thus controlled by adjusting the ratio of the two streams. To avoid inaccuracies derived from possible CO\(_2\) solution in the water bath, the water in the bubbler was saturated with CO\(_2\) by streaming air through it until the CO\(_2\) concentration in the air flow leaving the bath was equal to the CO\(_2\) concentration in the inlet air flow. This procedure was performed prior to each experimental run. CO\(_2\) content and RH were measured before and after the reactor with electronic sensors (Vaisala GMP343 with \(\pm (3 \text{ ppm} + 1\% \text{ of reading})\) and Vaisala HMP110 with \(\pm 1.7\% \text{ RH,}\)
respectively, 1 Hz sampling rate), accounting for temperature and pressure compensation. The sensors before and after the reactor were calibrated against each other by by-passing the reactor. CO₂ desorption was carried out for 60 min at 363 K in 1 l/min N₂, carrying a level of moisture which corresponds to a RH of 60% at 303 K. Each experiment started with CO₂ desorption.

**Figure 35.** Schematic of experimental setup used for CO₂ adsorption analysis (not including dashed part) and TVS cycles (including dashed part)

### 5.1.5 CO₂/O₂ Induced Degradation

For each experiment, 2 g of AEAPDMS-NFC were placed in a packed bed arrangement of 40 mm-i.d. 30 mm-height and heated to 363 K for 15 h at a flow rate of 200 ml/min CO₂ or 20% O₂/80% N₂. Both gases were passed through a bubbler-type humidifier kept at 296 K and are subsequently referred to as humid 100% CO₂ and humid 20% O₂, respectively. Before and after the experiments, the samples were characterized by FTIR, XPS and equilibrium CO₂ adsorption analysis. The sample treated in humid 20% O₂ is in the following referred to as AEAPDMS-NFC-O₂ and the one treated in humid 100% CO₂ is referred to as AEAPDMS-NFC-CO₂.
TVS Cycles

Long-term TVS cycles were performed in an experimental setup similar to the one introduced previously. A schematic of the setup is shown in Figure 35, featuring a vacuum tight 61 mm x 61 mm rectangular packed bed with a height of 80 mm, which was loaded with 15 g of AEAPDMS-NFC. Control of the reactor temperature as well as control and humidification of the adsorption gas stream were performed as described for the equilibrium CO$_2$ adsorption analysis. CO$_2$ adsorption was carried out for 150 min at 303 K and 60% RH at a flow rate of 10 l/min dried, technical-grade, pressurized air with a CO$_2$ concentration of 400-530 ppm, which was obtained by compressing ambient air. CO$_2$ desorption was carried out for 45 min at 363 K and 30 mbar absolute pressure (KNF Neuberger, N84.3 ANDC). Such desorption parameters are representative for industrial application, featuring minimum desorption pressures of around 50 mbar and similar desorption times. After compression in the vacuum pump, the desorbed CO$_2$ was passed through a mass flow meter (Bronkhorst EL-FLOW®) and integration of the signal gives the amount of desorbed CO$_2$. Each experiment started with CO$_2$ desorption.

5.2 Experimental Results

5.2.1 Adsorbent Characterization

The BET surface area of AEAPDMS-NFC was 8.3 m$^2$/g and the nitrogen content, as determined through elemental analysis, was 8.29% w/w (5.9 mmol N/g).

5.2.2 CO$_2$/O$_2$ Induced Degradation

FTIR spectra of AEAPDMS-NFC before and after exposure to 363 K for 15 h in humid CO$_2$ and humid 20% O$_2$ are shown in Figure 36. The characteristic vibrations of the silylated pristine sample are similar to those reported previously: CH$_2$ bending of the aminosilane propyl chain at 1443 cm$^{-1}$, NH$_2$ bending at 1591 cm$^{-1}$, asymmetric NH$_3^+$ deformation through hydrogen bonding of primary amines with water at 1663 cm$^{-1}$, CH stretching between 2804 cm$^{-1}$ and 2918 cm$^{-1}$ and NH stretching between 3277 cm$^{-1}$ and 3339 cm$^{-1}$. The same peaks can be observed in the spectrum of AEAPDMS-NFC after exposure to humid CO$_2$ (after heating the sample for 2 h in N$_2$ at 393 K), therefore not indicating any chemical change after exposure to humid CO$_2$ at 363 K. This result is further corroborated through
equilibrium CO\textsubscript{2} adsorption analysis showing that the CO\textsubscript{2} capacity of pristine AEAPDMS-NFC (1.28 mmol CO\textsubscript{2}/g at 444 ppm) was comparable to the one after exposure to humid CO\textsubscript{2} at 363 K for 15 h (1.33 mol CO\textsubscript{2}/g at 408 ppm). The results obtained here are similar to those obtained previously for amine-functionalized silicas.\textsuperscript{105, 120} Sayari and Belmabkhout\textsuperscript{105} studied the degradation of PE-MCM-41 modified with MONO, TRI and PEI in the presence of dry and humid (dew point of 293 K) pure CO\textsubscript{2} at temperatures varying from 323 to 378 K during multiple adsorption/desorption cycles, where regeneration of the materials was carried out in N\textsubscript{2} at temperatures varying from 378 to 423 K. They found that all materials degraded in the presence of dry CO\textsubscript{2} but were stabilized when humidity was added. In particular, it was shown that TRI-PE-MCM-41 was stable over 700 subsequent adsorption/desorption cycles, where humid CO\textsubscript{2} adsorption was carried out at 343 K and regeneration at the same temperature in N\textsubscript{2}. Similarly, Heydari-Gorji and Sayari\textsuperscript{120} showed the stability of PEI modified SBA-15 during 66 subsequent CO\textsubscript{2} adsorption/desorption cycles, where CO\textsubscript{2} adsorption was performed in pure humid (dew point of 293 K) CO\textsubscript{2} at 348 K and desorption in N\textsubscript{2} at 378 K and 393 K. Therefore, as a first conclusion, AEAPDMS-NFC proved to be stable in the presence of humid CO\textsubscript{2}, which is important as exposure to humid CO\textsubscript{2} at 363 K is expected during TVS regeneration.\textsuperscript{31, 113}

In contrast, a decrease in peak intensities in the regions 3339-3277 cm\textsuperscript{-1} and 2918-2804 cm\textsuperscript{-1} was observed in the spectrum of AEAPDMS-NFC treated in humid 20\% O\textsubscript{2}, which is associated with a reduction of the intensities related with NH and CH stretching vibrations, respectively. Similarly, TRI-PE-MCM-41,\textsuperscript{121} PEI modified SBA-15\textsuperscript{120} and SiO\textsubscript{2}-supported TEPA\textsuperscript{122} treated for 40 h at 393 K in carbon-free air, 12 h at 373 K in air, and 30 h at 363 K in carbon free air, respectively, showed a reduction in FTIR peak intensities at 3400-3300 cm\textsuperscript{-1} and disappearance of the band at 2826 cm\textsuperscript{-1}. Additionally TRI-PE-MCM-41, PEI modified SBA-15 and SiO\textsubscript{2}-supported TEPA developed a peak at ca. 1670 cm\textsuperscript{-1}, assigned to C=\textit{N} species in oxime/imine/nitrile and C=O in amide/imide.\textsuperscript{120-122} This peak was also observed for AEAPDMS-NFC, however, likely to overlap with asymmetric NH\textsubscript{3}\textsuperscript{+} deformation, as described above.
To further understand O$_2$-induced degradation, the surface chemical composition of pure NFC and AEAPDMS-NFC before and after exposure to humid 20% O$_2$ were assessed using XPS analysis. XPS spectra and deconvolution of the C1s high resolution signal are shown in Figure 37 and Figure 38, respectively. Table 13 gives the atomic concentration of the analyzed samples obtained from the high-resolution spectra while the corresponding deconvolution of the C1s region is presented in Table 14. The O/C ratio for pure cellulose is 0.71 (Table 13). This value is lower than the theoretical ratio of neat cellulose (0.82) and is attributed to the presence of surface contaminants such as adsorbed molecules due to air exposure, wood extractives or lignin, as already observed for nanocellulose films.\textsuperscript{129, 130} After silylation, the detection of nitrogen and silicon contributions, together with a concomitant decrease of the O/C ratio from 0.71 to 0.27, confirmed the addition of AEAPDMS to NFC. These results are further confirmed by the analysis of the deconvoluted C1s spectra of pure and silylated NFC (Table 14), for which an increase in the C1 contribution from 12.98 to 26.42% was observed, respectively. After treatment for 15 h at 363 K in humid 20% O$_2$, a decrease of the C1 contribution at 285.08 eV, \textit{i.e.}, associated with C-C, C-H and C-Si bonds, was observed. Additionally, the C2 contribution at 286.23 eV increased, corresponding to an increase of C-O linkages on the surface of the cellulosic sorbent material (Table 14). Moreover, the Si and N atomic concentrations of the oxidized sample both decrease (Table 13). Therefore, among

\textbf{Figure 36.} FTIR spectra before and after exposure to humid 100% CO$_2$ and a humid 20% O$_2$ for 15 h at 363 K

![FTIR spectra](image-url)
several potential factors contributing to the aforementioned XPS peak intensity changes, the loss of aminosilane moieties partially contributed to a reduction of the peak at 285.08 eV. The corresponding higher cellulose over aminosilane ratio was likely to be one reason for both increases of the peak at 286.23 eV (Table 14) and O/C ratio (Table 13), as pure cellulose is richer in C-O groups than the aminosilane modified one. The C3 and C4 peaks at 287.66 eV and 289.2 eV showed slightly decreasing and increasing contributions, respectively. In the literature, a peak at 288.8 eV (close to the C4 peak in this study) was assigned to a C atom in an acid, amide and/or urea linkage, which was obtained after treating amine-functionalized silicas (MCF_MAPS and MCF_DA) for 24 h at 408 K in 100% O₂. In this study the formation of an acid occurred only to a small extent, if any, as FTIR analysis (Figure 36) showed no characteristic band at 1700 cm⁻¹. Moreover, it is unlikely that urea species form upon exposure to humid 20% O₂, as urea formation was solely reported in the context of CO₂-induced degradation of amine-functionalized sorbents. The occurrence of amide/imide species is possible because, besides the XPS results, FTIR analysis (Figure 36) showed a characteristic band at 1663 cm⁻¹ corresponding to C=O vibrations in such species. This band is likely to overlap with the previous attribution to NH₃⁺ groups and longer degradation period is needed to provide distinct difference. Amide/imide formation as major O₂-induced degradation product was further supported through other literature studies investigating in detail oxidation of SiO₂-supported TEPA through FTIR analysis and ¹³C NMR spectroscopy after exposure for 12 h to air at 373 K. Further, the same study reported the formation of nitrile species as O₂-induced degradation product. Also these species are likely to occur in this study as the N1s peaks before and after exposure to humid 20% O₂ were at 400.32 eV and 400.13 eV, respectively, thus shifting to slightly lower binding energies, indicating the formation of imine or nitrile species. In conclusion, loss of aminosilane moieties and formation of amide/imide and nitrile/imine groups are some of the mechanisms for humid O₂-induced degradation.
Figure 37. XPS low-resolution survey spectra of pure NFC, AEAPDMS-NFC, AEAPDMS-NFC-O₂ and AEAPDMS-NFC-100TVS

Table 13. Atomic concentrations of pure NFC, pristine AEAPDMS-NFC, AEAPDMS-NFC after treatment for 15 h at 363 K in humid 20% O₂ and after 100 TVS cycles, obtained after analysis of the high-resolution XPS spectra

<table>
<thead>
<tr>
<th></th>
<th>C₁s</th>
<th>N₁s</th>
<th>O₁s</th>
<th>Si₂p</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NFC</td>
<td>58.6</td>
<td>0</td>
<td>41.4</td>
<td>0</td>
<td>0.71</td>
</tr>
<tr>
<td>AEAPDMS-NFC</td>
<td>63.21</td>
<td>11.07</td>
<td>17.02</td>
<td>8.7</td>
<td>0.27</td>
</tr>
<tr>
<td>AEAPDMS-NFC-O₂</td>
<td>63.77</td>
<td>9.51</td>
<td>19.54</td>
<td>7.18</td>
<td>0.31</td>
</tr>
<tr>
<td>AEAPDMS-NFC-100TVS</td>
<td>64.14</td>
<td>10.25</td>
<td>16.77</td>
<td>8.84</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Figure 38. Deconvolution of C1s high resolution signal of pure NFC, AEAPDMS-NFC, AEAPDMS-NFC-O₂ and AEAPDMS-NFC-100TVS
Table 14. Deconvolution of the C1s high-resolution region of pure NFC, pristine AEAPDMS-NFC, AEAPDMS-NFC after treatment for 15 h at 363 K in humid 20% O₂ and after 100 TVS cycles.

<table>
<thead>
<tr>
<th></th>
<th>C=C</th>
<th>C-C, C-H, C-Si</th>
<th>C-O</th>
<th>C=O, O-C-O</th>
<th>O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1 (%)</td>
<td>C2 (%)</td>
<td>C3 (%)</td>
<td>C4 (%)</td>
<td></td>
</tr>
<tr>
<td>Pure NFC</td>
<td>285.08 eV</td>
<td>286.23 eV</td>
<td>287.66 eV</td>
<td>289.2 eV</td>
<td></td>
</tr>
<tr>
<td>AEAPDMS-NFC</td>
<td>12.98</td>
<td>56.61</td>
<td>25.55</td>
<td>4.86</td>
<td></td>
</tr>
<tr>
<td>AEAPDMS-NFC-O₂</td>
<td>26.42</td>
<td>43.25</td>
<td>24.49</td>
<td>5.84</td>
<td></td>
</tr>
<tr>
<td>AEAPDMS-NFC-TVS</td>
<td>19.81</td>
<td>51.55</td>
<td>22.3</td>
<td>6.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.5</td>
<td>41.63</td>
<td>25.74</td>
<td>6.13</td>
<td></td>
</tr>
</tbody>
</table>
Adsorbent Stability Analysis

The chemical change observed by FTIR and XPS was further corroborated through equilibrium CO\(_2\) adsorption analysis showing that the CO\(_2\) capacity of the sample exposed to the O\(_2\)-containing atmosphere drops from 1.28 to 0.89 mmol CO\(_2\)/g (at 463 ppm CO\(_2\) concentration), hence, 30\% reduction compared to the pristine sample. In comparison, amine-functionalized silicas, which carry secondary amines or a mixture of primary and secondary amines, showed the following drops in CO\(_2\) capacity after exposure to dry O\(_2\)-containing atmospheres at representative desorption temperatures: PEI modified SBA-15 dropped by 22\% after exposure to carbon free air for 30 h at 363 K;\(^{120}\) SiO\(_2\)-supported TEPA decreased by 63\% after exposure to air at 373 K for 12 h;\(^{122}\) TRI lost 47\% of its equilibrium CO\(_2\) capacity after exposure to carbon free air for 30 h at 363 K;\(^{121}\) and MCF-DA was reduced by ~30\% (extracted from figure) after exposure to pure O\(_2\) at 378 K for 24 h.\(^{84}\) It is evident that these values cannot be compared directly to the CO\(_2\) uptake loss of AEAPDMS-NFC-O\(_2\) as several factors influence a drop in CO\(_2\) capacity, including O\(_2\) concentration, exposure time, and temperature, as well as CO\(_2\) concentration during CO\(_2\) capacity measurement. Nevertheless, it can be concluded that both types of sorbents, amine-functionalized silica and amine-functionalized NFC, showed strong degradation in the presence of O\(_2\). This conclusion is limited to amine functionalities carrying both primary and secondary amines. In contrast, amine-functionalized silicas featuring only primary amines proved to be stable in 100\% O\(_2\) up to 408 K.\(^{84}\) In summary CO\(_2\)/O\(_2\) degradation studies showed that humid 100\% CO\(_2\) at 363 K does not lead to degradation of AEAPDMS-NFC, but humid 20\% O\(_2\) leads to severe loss of functionality and thus contact to O\(_2\) at elevated temperatures should be avoided in the desorption process. In comparison, degradation mechanisms of aqueous amines, where particularly monoethanolamine (MEA) was studied in detail, involve oxidative reactions and CO\(_2\) induced degradation through carbamate polymerization.\(^{28,40}\)

5.2.3 TVS Cycles

The evolution of the amount of adsorbed and desorbed CO\(_2\) over 100 consecutive TVS cycles is presented in Figure 39. A cyclic capacity of around 0.90 mmol CO\(_2\)/g was reached for the silylated sorbent material studied in this work. The fluctuations of the cyclic CO\(_2\) adsorption and desorption capacity were associated with the variations in the incoming CO\(_2\) concentration. Wurzbacher et
al.\textsuperscript{113} reported deviations of +/- 0.025 mmol CO\textsubscript{2}/g for CO\textsubscript{2} concentrations between 408 and 500 ppm and an average CO\textsubscript{2} capacity of 0.4 mmol CO\textsubscript{2}/g under TVS regeneration, hence, fluctuations of around 6\% with respect to CO\textsubscript{2} capacity. In this study, identical deviations were observed for average CO\textsubscript{2} concentrations between 417 ppm and 491 ppm.

Table 15 shows the CO\textsubscript{2} concentration during adsorption as well as the adsorption CO\textsubscript{2} capacity, each averaged over 10 cycles, starting from cycle 5 to avoid initial effects. The average CO\textsubscript{2} adsorption capacity during cycles 5-14 was 0.87 mmol CO\textsubscript{2}/g for an average CO\textsubscript{2} concentration of 426 ppm and 0.87 mmol CO\textsubscript{2}/g during cycles 85-94 for an average CO\textsubscript{2} concentration of 446 ppm. In conclusion, the cyclic CO\textsubscript{2} capacity remained constant for a slightly increased CO\textsubscript{2} concentration, indicating minor loss in cyclic capacity.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Average CO\textsubscript{2} concentration [ppm]</th>
<th>Average CO\textsubscript{2} capacity [mmol CO\textsubscript{2}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-14</td>
<td>426</td>
<td>0.87</td>
</tr>
<tr>
<td>15-24</td>
<td>424</td>
<td>0.87</td>
</tr>
<tr>
<td>25-34</td>
<td>417</td>
<td>0.87</td>
</tr>
<tr>
<td>35-44</td>
<td>467</td>
<td>0.93</td>
</tr>
<tr>
<td>45-54</td>
<td>491</td>
<td>0.93</td>
</tr>
<tr>
<td>55-64</td>
<td>462</td>
<td>0.89</td>
</tr>
<tr>
<td>65-74</td>
<td>467</td>
<td>0.88</td>
</tr>
<tr>
<td>75-84</td>
<td>454</td>
<td>0.88</td>
</tr>
<tr>
<td>85-94</td>
<td>446</td>
<td>0.87</td>
</tr>
</tbody>
</table>

CO\textsubscript{2} adsorption analysis after 100 TVS cycles yielded 1.22 mmol CO\textsubscript{2}/g at 484 ppm CO\textsubscript{2} concentration, indicating a small reduction compared to the pristine sample at 444 ppm CO\textsubscript{2} concentration. Elemental analysis indicates that the N content of the sample was reduced by 2\% after 100 TVS cycles. XPS analysis gave a reduction of 7 at. \% for the corresponding values, as well as a slight reduction of the O/C ratio from 0.27 to 0.26 (see Table 13). The Si content of the sample
remained constant, as corroborated by XPS (see Table 13), indicating that amine loss did not occur through Si-carrying species.

![Figure 39. Amount of adsorbed / desorbed CO\textsubscript{2} over 100 consecutive TVS cycles](image)

Figure 39. Amount of adsorbed / desorbed CO\textsubscript{2} over 100 consecutive TVS cycles

Figure 40 shows the FTIR spectra of pristine AEAPDMS-NFC and after 100 TVS cycles. The same characteristic bands were observed on both spectra, however, the intensity of the 2918-2804 cm\textsuperscript{-1}, 1591 cm\textsuperscript{-1} and 1443 cm\textsuperscript{-1} peaks were reduced after 100 TVS cycles, indicating reductions in CH stretching, NH\textsubscript{2} bending, and CH\textsubscript{2} bending, respectively. Similar reductions in FTIR peaks were observed for O\textsubscript{2}-induced degradation, as shown in Figure 40, but the reductions after TVS cycles seemed to be less pronounced. Moreover, the peak at 1663 cm\textsuperscript{-1} shows a small increase.

XPS analysis of the C1s region indicated a slight increase of the C4 contribution at 289.2 eV after 100 TVS cycles (Table 14), suggesting the formation of amide, acid and/or urea species based on a literature study associating a peak at 288.8 eV with such species.\textsuperscript{84} For this study it can be concluded that acid formation occurred to only a small extent, if any, as FTIR analysis shows no characteristic band at 1700 cm\textsuperscript{-1} (Figure 40). Further, formation of urea is unlikely, as FTIR analysis (Figure 40) showed no characteristic bands: Sayari et al.\textsuperscript{125} reported that AEAPDMS degrades strongly under dry CO\textsubscript{2} through the formation of cyclic urea species with characteristic FTIR bands at 1498-1500 cm\textsuperscript{-1} (C-N stretch) and 1700 – 1705 cm\textsuperscript{-1} (C=O stretch). Amide groups are likely to be formed as further supported through a small increase of the corresponding FTIR band at 1663 cm\textsuperscript{-1} (Figure 40). Amide formation is reported in the context of O\textsubscript{2}-induced degradation.
During TVS cycles, small concentrations of O\(_2\) are likely to either remain in the desorption chamber after evacuation and before the onset of CO\(_2\) and H\(_2\)O desorption, or enter the desorption chamber through leaks. The leak rate of the experimental setup used in this study was 2 ml air per desorption cycle, hence 0.6% of the desorbed CO\(_2\) volume or 0.13% O\(_2\) when mixed with the total volume of desorbed CO\(_2\). It is assumed that the O\(_2\) concentration was further diluted through desorbed H\(_2\)O. The N1s peaks before and after 100 TVS cycles were at 400.32 eV and 400.37 eV, respectively, remaining constant and thus indicating the absence of nitrile/imine formation.

In summary, through FTIR, XPS, and elemental analysis, the loss of amine groups and the formation of amide/imide species are identified as degradation mechanisms during TVS operation. The latter might be reduced through lowering the vacuum pressure during desorption and better sealing of the desorption chamber, as both measures reduce the O\(_2\) concentration during desorption. It is unclear whether loss of amine groups is also related to contact with O\(_2\), e.g. through ammonia emissions, or occurring independent of the presence of O\(_2\) during desorption.

In total, the AEAPDMS-NFC material was operated for 75 h (cumulative) in desorption mode at 363 K (max.) and 30 mbar absolute pressure in a gas atmosphere composed of desorbed CO\(_2\), H\(_2\)O vapor, and air inclusions. 100 TVS cycles resulted in a reduction of the CO\(_2\) adsorption capacity by up to 5%, which is relatively low considering its high reactivity. It remains unclear whether the measured loss will continue at the same rate for higher number of cycles. The relatively high chemical stability of AEAPDMS-NFC during the TVS cyclic operation is due to several factors. Firstly, the desorption at 30 mbar absolute pressure reduces the partial pressure of O\(_2\) by a factor of 33 compared to atmospheric conditions. Secondly, the desorption of CO\(_2\) and H\(_2\)O vapor continuously purges the sample chamber removing remaining O\(_2\). In this study, 15 g of AEAPDMS-NFC were used in a packed bed featuring a volume of 300 ml. 0.90 mmol CO\(_2\)/g were obtained during sorbent regeneration in average, corresponding to 326 ml CO\(_2\) in total at atmospheric pressure, thus purging the chamber 36 times at 30 mbar, further diluting the remaining O\(_2\) in the desorption chamber. Finally, it was shown\(^{113}\) that APDES-NFC-FD – an sorbent modified with 3-aminopropyldimethyldiethoxysilane that contains only primary amine groups
adsorbed and desorbed 3 mmol H$_2$O/g under comparable adsorption/desorption conditions, i.e. more than three times the gas volume of adsorbed and desorbed CO$_2$. Accordingly, the likelihood of dry CO$_2$ atmospheres and corresponding CO$_2$-induced degradation through urea formation during desorption is considered low.

Besides the relatively high chemical stability during 100 TVS cycles, AEAPDMS-NFC further proved to be physical stable. The BET surface area of AEAPDMS-NFC after 100 TVS cycles was 10.3 m$^2$/g, showing that no collapse of pore structure or agglomeration of cellulose fibers occurred. This is further confirmed by the SEM images taken before and after 100 TVS cycles, Figure 41 and Figure 42, respectively. No change in morphology can be observed after 100 consecutive TVS cycles of wetting and vacuum drying. Pristine AEAPDMS-NFC is composed of sheets and bundles of amine-modified fibrillated cellulose fibers forming a highly porous structure. The fibrous cellulose matrix is covered by polysiloxanes, hence, two strong interconnected polymers maintain the morphology throughout TVS cycling. As described above, during every desorption step, the packed bed of AEAPDMS-NFC particles is purged about 36 times with desorbed CO$_2$, and many more times with desorbed water vapor.
Figure 41. SEM of pristine AEAPDMS-NFC

Figure 42. SEM of AEAPDMS-NFC after 100 TVS cycles
5.3 Summary and Conclusions

In summary, the stability of AEAPDMS-NFC as a sorbent for direct air capture was investigated. The TVS cyclic process adsorbs CO₂ from atmospheric air at ambient conditions and desorbs high-purity CO₂ at slight vacuum pressures (~30 mbar) and by supplying low-grade (~363 K) heat. Humid O₂-containing atmospheres at 363 K lead to significant reduction in the CO₂ adsorption capacity, presumably due to the loss of aminosilanes and the formation of amide/imide species. In contrast, exposing amine-functionalized NFC to humid pure CO₂ at 363 K showed no detrimental effect in the CO₂ adsorption capacity. 100 TVS adsorption/desorption cycles under realistic process operating conditions resulted in a reduction of the CO₂ adsorption capacity of up to 5%. Identified degradation mechanisms are the loss of amine groups and formation of amide/imide species through contact with O₂ during desorption. Lowering the desorption pressures and better sealing should further reduce degradation, as both measures reduce the O₂ concentration during the desorption process. H₂O and CO₂ are always co-adsorbed and co-desorbed, hence, avoiding CO₂-induced degradation.
6 Summary

Amine-functionalized nanofibrillated cellulose was introduced as novel adsorbent especially suitable for capturing CO$_2$ from atmospheric air. The adsorbent was synthesized through freeze drying an aqueous nanofibrillated cellulose-aminosilane suspension, which, once dried, forms a highly porous web of nanofibrillated cellulose fibers being surface modified with aminosilanes through C-O-Si bonds. The advantages of using nanofibrillated cellulose as solid support were: first, cellulose is a regrowing resource and the most abundant biopolymer on earth. Second, amine functionalization of nanofibrillated cellulose is possible in an aqueous suspension not requiring organic solvents. Third, cellulose is rich in surface hydroxyl groups which are required for covalently bonding amine functionalities to the nanofibrillated cellulose surface. Finally, to date nanofibrillated cellulose is the most economical adsorbent support known in the literature with a projected cost (includes only the cost of feedstock and energy) of less than $2/kg.

Comparison of amine-functionalized nanofibrillated cellulose with state of the art adsorbent materials synthesized from non-renewable supports showed that their CO$_2$ capacities and CO$_2$ uptake rates were comparable. The amine efficiency of amine-functionalized nanofibrillated cellulose, defined as the ratio of adsorbed CO$_2$ over available amine groups, was the highest reported to date, which is crucial to make efficient use of expensive aminosilane moieties.

Fourier Transform Infrared Spectroscopy analysis revealed that the reaction mechanism between CO$_2$ and amine-functionalized nanofibrillated cellulose was identical to the one of state of the art adsorbents: in a first step CO$_2$ and an amine group form a zwitterion, which is in a second step deprotonated by a free base (amine group or water) to yield carbamate. The heat of CO$_2$ adsorption was obtained analytically through inserting the Toth isotherm model into the van’t Hoff equation and subsequent explicit solution yielding -73 kJ/mol CO$_2$ at low CO$_2$ loadings and -50 kJ/mol CO$_2$ at a loading of 1 mmol CO$_2$/g. Further it was found that amine-functionalized nanofibrillated cellulose adsorbed H$_2$O either through physisorption at an unreacted silanol, hydroxyl or amine group, or through acting as a free base for zwitterion deprotonation. The heat of H$_2$O adsorption was obtained analytically through inserting the Guggenheim-Anderson-de Boer
Summary

isotherm model into the van’t Hoff equation and subsequent explicit solution yielding \(-49 \text{ kJ/mol H}_2\text{O}\). Under typical DAC conditions 2 to 8 mol H\(_2\)O were adsorbed per mol of CO\(_2\), increasing the thermal energy demand during temperature-vacuum-swing regeneration of the adsorbent from 98 up to 390 kJ/mol CO\(_2\). Although H\(_2\)O adsorption is important to achieve high CO\(_2\) loadings, it was concluded that reduced H\(_2\)O loading is desirable to reduce the thermal energy consumption during adsorbent regeneration. Generally H\(_2\)O adsorption of amine-functionalized adsorbents is rarely reported in the literature. However, among the published data amine-functionalized nanofibrillated cellulose features the lowest H\(_2\)O loading and is therefore expected to require the least thermal energy for regeneration. Further it was shown that amine-functionalized nanofibrillated cellulose features the highest CO\(_2\) capacity among all class 2 adsorbents used for CO\(_2\) capture from air under humid conditions.

Binary CO\(_2\) and H\(_2\)O adsorption analysis showed that humidity enhanced CO\(_2\) adsorption strongly at ultra-diluted CO\(_2\) partial pressures, e.g. 0.045 kPa, but led to only a small increase in CO\(_2\) capacity at high CO\(_2\) partial pressures, e.g. 100 kPa. In contrast, the presence of CO\(_2\) at a partial pressure of 0.045 kPa had no effect on H\(_2\)O adsorption, which is consequently determined by the adsorption temperature and relative humidity only.

Finally the chemical and physical stability of amine-functionalized nanofibrillated cellulose was analyzed through exposure to O\(_2\), CO\(_2\) and through temperature-vacuum-swing cycling operation. The presence of O\(_2\) at 363 K degraded the adsorbent, reducing its equilibrium CO\(_2\) capacity by 30% after 15 h treatment in moist air with a dew point of 295 K. In contrast, exposure to moist CO\(_2\) at 363 K with a dew point of 295 K did not deteriorate its CO\(_2\) adsorption capacity after 15 h. Performing 100 consecutive temperature-vacuum-swing cycles, with CO\(_2\) adsorption from ambient air containing 400–530 ppm CO\(_2\) at 303 K and 60% relative humidity and with CO\(_2\) desorption at 363 K and 30 mbar, resulted in a reduction of the equilibrium CO\(_2\) adsorption capacity by maximum 5%. The reduction in equilibrium CO\(_2\) capacity was assigned to the presence of O\(_2\) during temperature-vacuum-swing regeneration, either stemming from remaining air in the desorption chamber or entering through leaks. In general temperature-vacuum-swing proved to be feasible for adsorbent regeneration, as it minimizes the
presence of O$_2$ during desorption and maximizes the presence of humid CO$_2$, which was shown to conserve the functionality of the adsorbent.
7 Outlook

Based on the results and experience gathered in the framework of this thesis, in the following recommendations for future developments are given, which are categorized in adsorbent synthesis optimization, adsorbent performance optimization, adsorbent stability analysis and optimization and finally general fundamental research needs, independent of the adsorbent presented in this study.

7.1 Adsorbent Synthesis Optimization

All adsorbent materials in this thesis are produced by a two-step procedure, where in a first step nanofibrillated cellulose and aminosilanes are mixed in an aqueous suspension and in a second step water is removed from the suspension through freeze drying. However, application of freeze drying for large-scale commercial production can be uneconomical due to its high energy consumption. Future investigations should look at alternatives for dewatering of the feed and keeping its porosity in a more energy efficient and thus more economical way. Rather than optimizing the drying process in an isolated manner, a holistic adsorbent synthesis optimization is recommended: by identifying methods which allow cellulose hydroxyl group substitution in aqueous suspension, collapsing of the porous cellulose backbone is assumed to be avoided during conventional drying procedures, since hydroxyl groups are blocked. Currently, during the first synthesis step silanol groups of hydrolyzed aminosilanes adsorb on hydroxyl groups of cellulose and once water is removed during the second step silanol and hydroxyl groups undergo reaction yielding C-O-Si bonds and water. Since substitution of hydroxyl groups appears only upon complete water removal, collapsing of the porous cellulose backbone was only avoided through freeze drying.

The cost of adsorbent synthesis can be further reduced through identifying alternative amine carriers. This thesis focuses on application of aminosilanes, because of their availability, their ability to be used in aqueous systems and their ability to form covalent C-O-Si bonds with cellulose. However, such moieties are expensive at around $5-10/kg and the production involves energy intensive electrolytic reduction of SiO$_2$ as well as handling and recycling of toxic Cl compounds. To the best of the author’s knowledge, the Si backbone of aminosilane
grafted nanofibrillated cellulose has no functionality for CO₂ capture from air, so that theoretically the Si atom can be omitted. Consequently future research should identify non-aminosilane amine carries for amination of nanofibrillated cellulose. It is important that such amine carriers feature solely primary amines, as such type of amine feature the highest resistance to O₂-induced degradation. Further such amine carriers have to be covalently attached to the cellulose backbone to avoid volatile losses, where such covalent reaction preferably happens in suspension to avoid expensive freeze drying operation. Finally such amine carriers should be applicable in aqueous systems, to avoid the use of solvents.

Finally future research should systemically investigate the effect of the quality of nanofibrillated cellulose on adsorbent performance. This study focused only on high quality nanofibrillated cellulose. It was shown that during drying nanofibers agglomerate to form adsorbent sheets so that some of the initially high quality is lost. It is likely that similar adsorbent performance as obtained in this study can be obtained with lower quality nanofibrillated cellulose. However, the effect on final cost of the adsorbent is less pronounced than for the adsorbent optimization recommendations given above. Where high quality nanofibrillated cellulose has a cost of around $2/kg, low quality nanofibrillated cellulose has a cost of around $1/kg.

7.2 Adsorbent Performance Optimization

To further optimize the performance of the adsorbent it is recommended to reduce its hygroscopy. It was shown above that the H₂O loading of amine-functionalized cellulose is moderate up to a relative humidity of 50 %. For high relative humidities above 80 % the water loading becomes very high with values above 8 mmol H₂O per mmol CO₂. During the relative humidity cycle of a day such high relative humidities cannot be avoided, especially in the evening and morning hours.

7.3 Adsorbent Stability Analyses

In this thesis critical questions regarding the stability of amine-functionalized cellulose towards O₂, CO₂ and H₂O were answered and it was proven that the adsorbent is feasible for cycling temperature-vacuum-swing operation. However,
for industrial application of the adsorbent additional stability analyses have to be performed.

Ambient air carries several pollutants and impurities in trace quantities, e.g. SO\textsubscript{x}/NO\textsubscript{x}/bacteria/fungus/particle matter, which are likely to reduce adsorbent functionality over several thousand adsorption/desorption cycles. Future research should investigate stability of amine-functionalized cellulose towards such trace impurities.

Further, for economic operation adsorbent lifetime has to be on the order of 10’000 cycles. Currently stability data exists for 100 cycles, representing 1 % of the projected lifetime. To allow for adsorbent lifetime extrapolation cycling adsorption/desorption experiments have to be performed on the order of 1000 cycles.

### 7.4 Long-term Fundamental Research Needs

Long-term fundamental research should aim at identifying new reaction mechanisms for chemisorption of atmospheric CO\textsubscript{2} on solid adsorbents, fulfilling the following criteria:

- The heat of CO\textsubscript{2} adsorption is similar to the one achieved with amine-functionalized adsorbents.
- The CO\textsubscript{2} capture mechanism proceeds independent of relative humidity.
- The chemical functionality is resistant to O\textsubscript{2}- and CO\textsubscript{2}-induced degradation in the temperature range 243 to 383 K.
- The chemical functionality is odor free.
List of Figures

Figure 1. Schematic illustrating the closed carbon cycle for transportation fuels, where atmospheric CO$_2$, H$_2$O and renewable energies are stored, transported and used in the form of hydrocarbon fuels (source: Climeworks Ltd) ........................................ 2

Figure 2. Schematic of a) class 1, b) class 2 and class 3 adsorbent (source: Li et al.$^{34}$) ......................................................................................................................................................... 7

Figure 3. Experimental setup for CO$_2$ adsorption/desorption measurements at ETH Zurich .......................................................... 17

Figure 4. Schematic illustrating the hierarchical structure of a cellulose fiber .... 18

Figure 5. SEM image of refined fibrous beech wood pulp (Arbocel P 10111, Rettenmeier & Söhne GmbH & Co. KG, Germany) used as raw material for the isolation of NFC in this study ......................................................... 19

Figure 6. Schematic of organofunctional silane featuring an organofunctional group and three silicon functional groups ........................................ 19

Figure 7. Schematic of organofunctional silane hydrolysis ................................ 20

Figure 8. Schematic of silane condensation and covalent bonding .............. 20

Figure 9. SEM image of 4-APTES-NFC with insert showing magnification of marked area ................................................................. 23

Figure 10. CO$_2$ loading of adsorbent investigated in aminosilane screening as a function of time (packed bed CO$_2$ adsorption at 298 K, 40 % RH and 500 ppm CO$_2$ concentration) .................................................................................................................... 25

Figure 11. Cumulative amount of desorbed CO$_2$ over time during (packed bed CO$_2$ desorption at 363 K in Ar carrying a level of moisture corresponding to 40 % RH at 298 K) .................................................................................................................. 26

Figure 12. Structure of APDES ......................................................... 27

Figure 13. Structure of AEAPDMS .................................................. 27

Figure 14. Schematic illustrating adsorbent synthesis process via freeze drying and air drying ............................................................................ 27

Figure 15. SEM image of 4-APDES-NFC-AD .................................... 28

Figure 16. Photograph of exemplary adsorbent granules used throughout this work ......................................................................................... 29

Figure 17 a) SEM of NFC hydrogel b) NFC-FD c) AEAPDMS-NFC .......... 34

Figure 18. FTIR spectra of NFC-FD and AEAPDMS-NFC ................. 36
Figure 19. CO$_2$ outlet concentration during humid CO$_2$ adsorption on AEAPDMS-NFC (solid line) and fractional uptake of the CO$_2$ capacity (dashed line) ........... 38
Figure 20. CO$_2$ adsorption rate of AEAPDMS-NFC (solid line) and adsorbed amount CO$_2$ (dashed line) .................................................................................................................. 39
Figure 21. Comparison of adsorption capacity and adsorption half time of AEAPDMS-NFC (star), HAS6 (sphere), PEI/silica (rhombus), A-PEI/silica (triangle), T-PEI/silica (square)$^{1,2}$ ........................................................................................................... 39
Figure 22. Comparison of CO$_2$ capacity as a function of time of AEAPDMS-NFC (dashed line), HAS6 (spheres), PEI/silica (rhombuses), A-PEI/silica (triangles) and T-PEI/silica (squares)$^{1,2}$ .......................................................................................................................... 40
Figure 23. FTIR spectra of AEAPDMS-NFC after humid CO$_2$ adsorption .......... 41
Figure 24. Desorbed CO$_2$ from AEAPDMS-NFC (solid line) and packed bed temperature profile during CO$_2$ desorption (dashed line) ................................................................. 42
Figure 25. FTIR spectra of AEAPDMS-NFC after CO$_2$ desorption .................... 43
Figure 26. Multicycle adsorption (squares) and desorption (spheres) experiments with AEAPDMS-NFC ................................................................. 44
Figure 27. Schematic of experimental setup used for binary CO$_2$/H$_2$O adsorption analysis ................................................................................................................................. 48
Figure 28. CO$_2$ adsorption isotherms of APDES-NFC-FD at 296 K (spheres), 323 K (rectangles) and 343 K (triangles) as a function of CO$_2$ pressure, and the numerically fitted Toth model (solid line).............................................................................. 54
Figure 29. CO$_2$ adsorption isotherms of APDES-NFC-FD at 296 K (spheres), 323 K (rectangles) and 343 K (triangles) as a function of CO$_2$ pressure .............. 55
Figure 30. Calculated heat of CO$_2$ adsorption of APDES-NFC-FD as a function of CO$_2$ loading ............................................................................................................................. 57
Figure 31. H$_2$O loading of APDES-NFC-FD as function of the RH .................. 58
Figure 32. H$_2$O loading on unmodified NFC and APDES-NFC as function of H$_2$O partial pressure ................................................................................................. 58
Figure 33. Calculated heat of H$_2$O adsorption of APDES-NFC-FD as a function of water loading ............................................................................................................. 60
Figure 34. Amine efficiency and amine loading under dry and humid DAC conditions at 298 K for literature adsorbents and for APDES-NFC (at 296 K). a) amine-grafted SBA-15,$^{24}$ b) MCF_APS_hi,$^{30}$ c) APDES-NFC, d) FS-PEI-33,$^{25}$ e)
TRI-PE-MCM-41, f) RFAS, g) PEI/Zr7-SBA-15, h) HAS6, i) T-PEI/silica

Figure 35. Schematic of experimental setup used for CO$_2$ adsorption analysis (not including dashed part) and TVS cycles (including dashed part) ............................................................................. 63

Figure 36. FTIR spectra before and after exposure to humid 100% CO$_2$ and a humid 20% O$_2$ for 15 h at 363 K ............................................................................................................. 76

Figure 37. XPS low-resolution survey spectra of pure NFC, AEAPDMS-NFC, AEAPDMS-NFC-O$_2$ and AEAPDMS-NFC-100TVS .......................................................... 78

Figure 38. Deconvolution of C1s high resolution signal of pure NFC, AEAPDMS-NFC, AEAPDMS-NFC-O$_2$ and AEAPDMS-NFC-100TVS ....................................................... 79

Figure 39. Amount of adsorbed / desorbed CO$_2$ over 100 consecutive TVS cycles ................................................................................................................................. 83

Figure 40. FTIR spectra before and after 100 TVS cycles ........................................ 85

Figure 41. SEM of pristine AEAPDMS-NFC ................................................................ 86

Figure 42. SEM of AEAPDMS-NFC after 100 TVS cycles ........................................ 86
List of Tables
Table 1. State of the art sorbent/process pairs used for DAC and their advantages and disadvantages ................................................................. 3
Table 2. Summary of amine-functionalized adsorbents used for DAC ............ 9
Table 3. BET surface area, amine loading and density of adsorbents investigated in aminosilane screening ......................................................... 23
Table 4. CO₂ adsorption/desorption mass balance of adsorbents investigated in aminosilane screening ......................................................... 26
Table 5. BET surface area, density, and amine loading of NFC-FD and AEAPDMS-NFC ................................................................. 35
Table 6. H₂O adsorption parameters ............................................................ 47
Table 7. Adsorption temperature, CO₂ concentration, and relative humidity for binary CO₂/H₂O adsorption analysis ................................................................. 48
Table 8. Toth parameters and normalized standard deviation for different CO₂ adsorption temperatures ................................................................. 54
Table 9. Guggenheim-Anderson-de Boer model parameters for different H₂O adsorption temperatures ................................................................. 59
Table 10. CO₂ capacity under dry and humid conditions (pH₂O = 2.55 kPa) at 296 K and 323 K ......................................................................................... 62
Table 11. H₂O capacities from single-component adsorption and in presence of ultra-diluted CO₂ (pCO₂ = 0.045 kPa) at 296 K and 303 K ................. 62
Table 12. Amine structure of sorbents from literature degradation studies ........ 69
Table 13. Atomic concentrations of pure NFC, pristine AEAPDMS-NFC, AEAPDMS-NFC after treatment for 15 h at 363 K in humid 20 % O₂ and after 100 TVS cycles, obtained after analysis of the high-resolution XPS spectra ............ 78
Table 14. Deconvolution of the C1s high-resolution region of pure NFC, pristine AEAPDMS-NFC, AEAPDMS-NFC after treatment for 15 h at 363 K in humid 20 % O₂ and after 100 TVS cycles ......................................................... 80
Table 15. Average CO₂ concentration during adsorption and average adsorption capacity of CO₂ ................................................................. 82
References

12. Nikulshina, V.; Steinfeld, A., CO2 capture from air via CaO-carbonation using a solar-driven fluidized bed reactor-Effect of temperature and water vapor


26. McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R., Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-


34. Li, W.; Choi, S.; Drese, J. H.; Hornbostel, M.; Krishnan, G.; Eisenberger, P. M.; Jones, C. W., Steam-Stripping for Regeneration of Supported Amine-Based CO2 Adsorbents. Chemsuschem 2010, 3, (8), 899-903; Doi 10.1002/Cssc.201000131


37. **Direct Air Capture of CO**₂ **with Chemicals**; The American Physical Society: College Park, MD, 2011.
48. Belmabkhout, Y.; Sayari, A., Effect of pore expansion and amine functionalization of mesoporous silica on CO2 adsorption over a wide range of


81. Tingaut, P.; Zimmermann, T.; Sebe, G., Cellulose nanocrystals and microfibrillated cellulose as building blocks for the design of hierarchical
87. Claussen, I. C.; Ustad, T. S.; Strommen, I.; Waide, P. M., Atmospheric freeze drying - A review. *Dry Technol* 2007, 25, (4-6), 947-957; Doi 10.1080/07373930701394845


116. Belmabkhout, Y.; De Weireld, G.; Sayari, A., Amine-Bearing Mesoporous Silica for CO(2) and H(2)S Removal from Natural Gas and Biogas. Langmuir 2009, 25, (23), 13275-13278; Doi 10.1021/La903238y


127. Li, W.; Bollini, P.; Didas, S. A.; Choi, S.; Drese, J. H.; Jones, C. W., Structural Changes of Silica Mesocellular Foam Supported Amine-Functionalized CO2 Adsorbents Upon Exposure to Steam. *Acs Appl Mater Inter* 2010, 2, (11), 3363-3372; Doi 10.1021/Am100786z


List of Publications

Journal Papers


Patents
Gebald, C.; Wurzbacher J. A. Distributed building integrated carbon dioxide extraction arrangement, has multiple carbon dioxide extraction units directly
extracting carbon dioxide from air contained in room, where extraction units are connected to small pipes. WO2013075981-A2.

