Narrow-pore zeolites and zeolite-like adsorbents for CO$_2$ separation
Ocean Cheung
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Faculty opponent:
Professor Paul A. Wright
School of Chemistry, University of St Andrews, United Kingdom

Evaluation committee:
Associate Professor Mattias Grahn
Department of Civil, Environmental and Natural Resources Engineering
Luleå University of Technology, Sweden

Professor Klas Engvall
School of Chemical Science and Engineering,
KTH Royal Institute of Technology, Sweden

Dr. Feifei Gao
Department of Materials and Environmental Chemistry,
Stockholm University, Sweden

Substitute
Associate Professor Sergey Dvinskikh
School of Chemical Science and Engineering,
KTH Royal Institute of Technology, Sweden
Abstract

A range of potential porous solid adsorbents were synthesised and their abilities to separate and capture carbon dioxide (CO₂) from gas mixtures were examined. CO₂ separation from flue gas – a type of exhaust gas from fossil fuel combustion that consists of CO₂ mixed with mainly nitrogen (N₂) - and biogas (consists of CO₂ mixed with mainly methane - CH₄) were considered. The adsorbents tested in this study included the mixed cation zeolite A, zeolite ZK-4, a range of aluminophosphates (AIPOs) and silicoaluminophosphates (SAPOs), as well as two types of titanium silicates (ETS-4, CTS-1). The selected adsorbents were chosen partly due to their narrow pore sizes. Narrow pore can differentiate gas molecule of different sizes via a kinetic mechanism. A large gas molecule should find it more difficult to enter a narrow pore. CO₂ has the smallest kinetic diameter in zeolites when compared with the other two gases in this study. Therefore, narrow pore adsorbents, show enhanced kinetic selectivity to adsorb CO₂ from a gas mixture.

These adsorbents were compared with respect to several characteristics including CO₂ capacity, CO₂ selectivity, cyclic performance, working capacity and cost of synthesis. Each of the tested adsorbents has advantages and disadvantages. Some phosphates were identified as potentially good CO₂ adsorbents, but the high cost of their synthesis must be addressed in order to develop these adsorbents further.

Keywords: CO₂ separation, zeolites, phosphates, titanium silicates, ion exchange, flue gas CO₂ capture, biogas upgrading
論文摘要

二氧化碳分離與捕集: 微孔沸石和類沸石吸附劑

煙道氣及沼氣都是混有二氧化碳的混合氣體, 煙道氣是二氧化碳和氮氣的混合氣, 而沼氣主要則是二氧化碳和甲烷的混合氣。本論文的內容是利用吸附劑從這兩種混合氣體中分離與捕集二氧化碳。為了尋找合適的吸附劑, 我們測試了多種固體多孔材料, 包括各類微孔沸石和類沸石吸附劑, 這種多孔固體一般擁有較窄的孔道。理論上窄小的孔能夠把不同尺寸的氣體分子分離, 這是因為較小的分子其擴散速度高於大分子。由於二氧化碳分子的動力學直徑 (0.33nm) 比氮氣 (0.364nm) 和甲烷 (0.38nm) 小, 因此, 窄小的孔能夠分離不同尺寸的氣體分子。

所選的吸附劑包括混合陽離子沸石 A, ZK-4, 磷鋁分子篩和矽磷鋁分子篩, 以及兩種鈦硅分子篩 (ETS-4, CTS-1)。我們比較研究了它們的二氧化碳的吸附量, 選擇性, 循環再用的性能, 工業過程實際吸附量以及生產成本等。各種被測試的吸附劑都各具有缺點, 其中磷鋁分子篩被認為最富潛力的二氧化碳吸附劑, 但磷鋁分子篩的生產成本較高, 如果要發展成為吸附二氧化碳的固體吸附劑, 需要首先降低其生產成本。
二氧化碳分离与捕集: 微孔沸石和类沸石吸附剂

烟道气及沼气都是混有二氧化碳的混合气体, 烟道气是二氧化碳和氮气的混合气, 而沼气主要则是二氧化碳和甲烷的混合气。本论文的内容是利用吸附剂从这两种混合气体中分离与捕集二氧化碳。为了寻找合适的吸附剂, 我们测试了多种固体多孔材料, 包括各类微孔沸石和类沸石吸附剂, 这种多孔固体一般拥有较窄的孔道。理论上窄小的孔能够把不同尺寸的气体分子分离, 这是因为较小的分子其扩散速度高大于大分子。由于二氧化碳分子的动力学直径 (0.33nm) 比氮气(0.364nm)和甲烷(0.38nm)小, 因此, 窄小的孔能够分离不同尺寸的气体分子。

所选的吸附剂包括混合阳离子沸石A, ZK-4, 磷铝分子筛和硅磷铝分子筛, 以及两种钛硅分子筛 (ETS-4, CTS-1)。我们比较研究了它们的二氧化碳的吸附量, 选择性, 循环再用的性能, 工业过程实际吸附量以及生产成本等。各种被测试的吸附剂都各具有缺点, 其中磷铝分子筛被认为最富潜力的二氧化碳吸附剂, 但磷铝分子筛的生产成本较高, 如果要发展成为吸附二氧化碳的固体吸附剂, 需要首先降低其生产成本。
List of publications/manuscripts:

Paper I:
**Aluminophosphates for CO\textsubscript{2} separation***

*Specific contributions: synthesis and characterisation of ALPOs, adsorption measurements and analysis, contributed to the writing*

Paper II:
**Silicoaluminophosphates as CO\textsubscript{2} sorbents***

*Specific contributions: lead role in this project, synthesis and characterisation of SAPOs, adsorption measurements and analysis, lead role in writing*

Paper III:
**Adsorption kinetics for CO\textsubscript{2} on highly selective zeolites NaKA and nano-NaKA***

*Specific contributions: lead role in this project, synthesis and characterisation of zeolites, adsorption measurements and analysis, lead role in writing*

Paper IV:
**K\textsuperscript{+} exchanged zeolite ZK-4 as a highly selective sorbent for CO\textsubscript{2}***
O. Cheung, Z. Bacsik, P. Krokidas, A. Mace, A. Laaksonen, and N. Hedin, *under revision*

*Specific contributions: lead role in this project, synthesis and characterisation of zeolites, adsorption measurements and analysis, lead role in the writing*
Paper V:
**CO₂ separation properties of high silicon zeolite NaK-ZK-4 with Si:Al up to 2.8:1**
O. Cheung, Z. Bacsik, P. Krokidasand N. Hedin, *in manuscript*

*Specific contributions: lead role in this project, synthesis and characterisation of zeolites, adsorption measurements and analysis, lead role in writing*

Paper VI:
**CO₂ selective NaMg-CTS-1 and its structural formation from the titanium silicate based molecule sieve NaMg-ETS-4 upon dehydration**

*Specific contributions: lead role in this project, synthesis and characterisation of ETS-4 and CTS-1, adsorption measurements and analysis, lead role in writing*

Paper VII:
**Carbon dioxide separation from methane on highly selective ion exchanged zeolite NaKCsA – a possible sorbent for biogas upgrading**
O. Cheung, Z. Bacsik, P. Vasiliev and N. Hedin, *in manuscript*

*Specific contributions: lead role in this project, synthesis and characterisation of NaKCsA, adsorption measurements and analysis, lead role in writing*

Paper VIII:
**Spherical aggregates of microporous aluminum phosphates and silicoaluminophosphates and effects of non-traditional mechanism of crystallization**
T. Rashainbunyawat, O. Cheung, N. Hedin, *submitted*

*Specific contribution: synthesis and characterisation of AlPOs, adsorption measurements and analysis, contributed to the writing*

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Publications not included in the thesis:

Paper IX:
**Interpenetrated metal–organic frameworks and their uptake of CO₂ at relatively low pressures**

*Specific contribution: adsorption measurements and analysis, contributed to the writing*

Paper X:
**Narrow pore zeolite and zeolite-like inorganic porous sorbent for CO₂ separation**

*Specific contribution: lead role in writing*

Paper XI:
**Aluminophosphate monoliths with high CO₂-over-N₂ selectivity and CO₂ capture capacity**
F. Akhtar, N. Keshavarzi, D. Shakarova, O. Cheung, N. Hedin, and L. Bergström, *submitted*

*Specific contribution: synthesis and characterisation of AlPOs, analysis of adsorption data, contributed to the writing*
Note to readers

The content of the thesis acts as a summary and a review of the research work. It consists of two major parts; the main text serves as an introduction and a concise review of the research work, the reprinted papers/manuscripts provide the details of the research findings. The scientific discussions in the papers are not repeated in the main text of the thesis. Research findings that are not included in the listed papers are overviewed in Chapter 2. Readers are strongly encouraged to read the thesis in conjunction with the papers.
# Table of Contents

Abstract..............................................................................................................................................5  
List of publications/manuscripts: ........................................................................................................11  
Note to readers .....................................................................................................................................15  
Table of Contents .................................................................................................................................17  

1. Introduction ...................................................................................................................................19  
   Carbon capture – why? .....................................................................................................................19  
   Fossil fuel combustion .....................................................................................................................20  
   Biogas upgrading .............................................................................................................................22  
   General principle of adsorption ........................................................................................................23  
   Swing adsorption processes .............................................................................................................25  
   The ideal adsorbent ..........................................................................................................................27  
   Existing/potential solid adsorbents ...................................................................................................29  
   CO₂ separation using zeolites ...........................................................................................................33  
   Aim of this study .............................................................................................................................37  

2. Zeolites, phosphates and silicates as CO₂ adsorbents .................................................................39  
   Zeolites A (Paper III, IV, V, and VII) .............................................................................................39  
   Zeolite NaA and nano-zeolite NaA ....................................................................................................43  
   Zeolite NaKA, NaCsA and NaKCsa (paper III and VII) .................................................................45  
   Zeolite ZK-4 and NaK-ZK-4 (paper IV and V) ..............................................................................46  
   Aluminophosphates as CO₂ sorbent (Paper I and VIII) ...............................................................48  
   Silicoaluminophosphate as CO₂ sorbents (Paper II and VIII) ......................................................57  
   Titanium silicate (ETS-4, CTS-1) as CO₂ sorbents (Paper VI) ......................................................61  

3. CO₂ sorbent for flue gas - CO₂ capture ..........................................................................................65  
   CO₂ sorbent showdown: zeolites, phosphates and silicates .......................................................65  
   CO₂ uptake and selectivity ................................................................................................................66  
   Hydrophilicity ..................................................................................................................................75  
   Cyclic capacity .................................................................................................................................76  
   Working capacity ..............................................................................................................................79  
   Cost of production/synthesis ..........................................................................................................81  

4. Highly selective CO₂ adsorbent for biogas upgrading .................................................................83  
   CO₂ Selectivity ...............................................................................................................................83  
   CO₂ Capacity ...................................................................................................................................85  

5. Conclusions .....................................................................................................................................87  

References ............................................................................................................................................89  
Acknowledgement ..............................................................................................................................94  

1. Introduction

Carbon capture – why?

Global warming has now become a familiar phrase to the general public. Scientists use the term to describe many of the recently observable changes to our planet. Governments and politicians use this term to get us to change the way we consume fossil fuel. Vehicle manufacturers invest hugely into what they call “green vehicles”. The major aerospace companies; Boeing and Airbus, both put emphasis on fuel efficiency on their newest models, the 787 and A350, respectively. According to the information on Boeing’s website, the 787 is said to have “unmatched fuel efficiency” and Airbus’s website states that the A350 can “provide a 25 percent step-change in fuel efficiency compared to its current long-range competitor.” Why is global warming linked to fuel efficiency? The answer lies in one simple chemical equation – carbon dioxide, the combustion product of burning fossil fuel. The combustion of methane at a high temperature is given as an example in equation (1)

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad (1)$$

Carbon dioxide (CO$_2$), together with other gases, such as water vapour (H$_2$O), methane (CH$_4$), nitrous oxide (N$_2$O), chlorofluorocarbons (CFCs) and ozone (O$_3$) are considered as greenhouse gases (GHGs). Some of these greenhouse gases (CO$_2$, CH$_4$, N$_2$O and CFCs) are released in large quantities by human activities. The increased concentration of these gases in the atmosphere is generally believed to intensify global warming. Svante Arrhenius published his findings over 100 years ago on how the level of one particular greenhouse gas, carbon dioxide (CO$_2$), can increase the temperature of the earth as its atmospheric concentration increases.\(^1\)

CO$_2$ is a greenhouse gas produced directly from the combustion of fossil fuel. Reducing the amount of CO$_2$ released into the earth’s atmosphere is one possible way to address of global warming. In order to control the release of CO$_2$ effectively, the source of its production needs to be targeted. The production of waste CO$_2$, can be reduced by an efficient combustion process. Engine manufacturers are now putting a lot of effort on developing engines that employ the most efficient combustion process. Efficient combustion saves fuel, and will also decrease the overall amount of CO$_2$ released. Another approach to be considered is in the creation of methodologies to capture CO$_2$ and remove it.
The main focus of this thesis is on post-combustion \( \text{CO}_2 \) capture. The thesis will consider solid adsorbents (solids that can capture \( \text{CO}_2 \)) that can be used in adsorption based \( \text{CO}_2 \) removal processes. The post combustion capture processes in question can be implemented for the removal of \( \text{CO}_2 \) where it is produced as a (waste-) product.

**Fossil fuel combustion**

One of the major reasons for burning fossil fuel is for energy production. As an example, a hypothetical 300 MW coal burning power plant releases around 1500-1600 tons of exhaust gas every hour, of which around 290 tons of the exhaust gas is \( \text{CO}_2 \). This large amount of \( \text{CO}_2 \) is released in a mixture with around 90 tons of oxygen (\( \text{O}_2 \)), 1100 tons of nitrogen (\( \text{N}_2 \)), 6 tons sulphur dioxide (\( \text{SO}_2 \)) and 70 tons water vapour (\( \text{H}_2\text{O} \)). \( \text{CO}_2 \) as a greenhouse gas would need to be removed from the exhaust gas before it is released in order to reduce the effect of global warming. The other components in the exhaust gas - nitrogen and oxygen, are rather inert. Releasing these gases into the atmosphere is not a major problem. Note that sulphur dioxide is a pollutant, but its effect will not be considered in this thesis.

There are established procedures that can capture \( \text{CO}_2 \) at different stages of energy production. The three main possible ways are: pre-combustion capture, oxy-fuel combustion and post-combustion capture.

**Pre-combustion capture**

![A simple schematic representation of the pre-combustion carbon capture process.](image)

**Figure 1.1** A simple schematic representation of the pre-combustion carbon capture process.\(^4,5\)

As the name suggests, this is when \( \text{CO}_2 \) is captured before the energy production process (**Figure 1.1**). Typically, fossil fuel (coal, oil, or natural gas) is heated in oxygen to produce what is called synthesis gas, or syngas (car-
bon monoxide - CO and hydrogen -H₂). These two gases are then passed over a catalyst where CO is oxidised to CO₂ and is captured. The remaining gas, H₂, is combusted in air and energy is produced without producing CO₂. However, this technology can be difficult to implement into older power plants.⁵

**Oxy-fuel combustion**

![Figure 1.2 A simple schematic representation of the oxy-fuel combustion process](#)

When fossil fuel is burnt in air, the exhaust gas contains mainly of N₂. This is because air consist of 78% N₂, which does not participate in the combustion process. The idea of oxy-fuel combustion is to burn fuel in a process where only CO₂ and water is produced (Figure 1.2). The advantage of oxy-fuel combustion is that the exhaust gas is CO₂ rich and suitable for sequestration; however, the production of pure oxygen from air is expensive.⁵
Post-combustion capture

![Diagram of post-combustion carbon capture process]

**Figure 1.3** A simple schematic representation of the post-combustion carbon capture process \(^4,5\)

Of the three different approaches to carbon capture, post combustion capture (Figure 1.3) is perhaps the easiest to understand. Post-combustion capture depends on fuel combustion in air. In this case, the exhaust gas will contain CO\(_2\) and H\(_2\)O in a mixture with N\(_2\), amongst other gases. The exhaust gas is termed “flue gas”. Several different processes can then be used to remove the CO\(_2\) content from flue gas, before it is released into the atmosphere. If the process is efficient, the gas released into the atmosphere will be free from CO\(_2\).

**Biogas upgrading**

Engine manufactures are constantly endeavouring to make their engines more efficient. One of the most common ways to do so is to increase the air-to-fuel ratio by turbocharging (lean burning). For any engine (especially a turbocharged engine) to burn fuel efficiently and have a low emission level, the fuel must be of high quality. This means the fuel must not have any significant amounts of impurities. When biogas is produced from animal or household wastes, it is typically rich in methane (CH\(_4\)), but can also contain as much as up to 50 vol.% of CO\(_2\).\(^6\) CO\(_2\) is energetically inert in the combustion process. High level of CO\(_2\) can reduce the energy per-unit-volume of the fuel. Should a biogas containing a large amount of CO\(_2\) be fed into an internal combustion engine, the air/fuel mixture will have to be adjusted to compensate for the low energy content. This will cause the engine to work with low efficiency, reduce the power output and produce an increased amount of harmful combustion products. If the CO\(_2\) content of the biogas can be reduced or totally removed, the energy content of the fuel can be increased,
making the transport and burning of the fuel more cost effective. For a motor vehicle that runs on methane (or biogas), the fuel typically has a methane content of over 95% to ensure the efficient and smooth running of the engine.

**General principles of adsorption**

**Hosting a guest molecule (CO₂) in a “host”**

The previous section highlighted some examples of where CO₂ removal is necessary and gave some existing solutions to those examples. The scope of this thesis will focus on the “adsorption based” processes. Any kind of sorption (meaning adsorption or absorption) based processes require a “sorbent” and “sorbate”. The sorbent is the object that acts as a host to the sorbate. The relationship is similar to how a hotel (sorbent) has the capacity to host people (sorbate). In this thesis, adsorption processes are considered specifically. Adsorption refers to the enrichment of one or more types of molecules on a surface. A range of different inorganic porous materials are tested as “adsorbents” in processes where the adsorbent is exposed to a gas mixture. The goal is to removed/separate CO₂ (the sorbate) gas from the mixture and capture it (using the adsorbent).

Adsorption processes, including Pressure/Vacuum or Temperature Swing Adsorption (PSA, VSA or TSA), all require an adsorbent. In the upcoming sections, aspects of adsorption and the desirable properties of a solid adsorbent will be discussed.

Take a hypothetical system where there is an excess of gas molecules and a solid object in a box. The gas molecules can be in gas phase or attached to the surface of the solid. When the gas molecules are close to a surface, they are attracted to the surface by electronic interactions. If these gas molecules spend more time close to the surface of the solid than in bulk gas phase, they can be seen as attached to the surface of the solid. A gas molecule that is attached to the surface is described as “adsorbed” on to the solid. “Adsorption” is not to be confused with gas molecules that are “absorbed” to the inside of the solid. In the case of porous solids (macroporous and mesoporous specifically), a gas molecule can “disappear” into the solid but still be adsorbed on the internal surface of the solid, this molecule is still considered as “adsorbed” on to the surface of the solid. The difference between “adsorption” and “absorption” has been clarified by many, such as Brunauer. Brunauer stated that if the gas molecule does not penetrate into the electrical field that exists between the atoms, ions or molecules of the sorbent, it is considered to be “outside” even if the location of the gas molecule is inside the solid. Therefore, the gas molecules are adsorbed and not absorbed. It is im-
portant to note that for microporous solids (micropores are defined by IUPAC- International Union of Pure and Applied Chemistry) as pores up to 2 nm, mesopores are between 2 and 50 nm, and macropores are larger than 50 nm), the narrow pores often mean that “adsorbed” molecules are located very close to the framework atoms of the porous solid. The short distance between the adsorbed molecules and the framework atoms means that adsorbed molecules can disturb the electrical field between the atoms of the porous solid. As a result of this disturbance, these molecules can also be considered as “absorbed”. For microporous solids, the differences between “adsorption” and “absorption” cannot be clearly defined.

Adsorption of a gas molecule on a solid can occur by physisorption or chemisorption. Physisorption (or physical adsorption) is when gas molecules are brought to a surface in excess by physical interactions (i.e. dispersion forces, dipole-dipole interaction, multipolar interactions etc.). At high loadings, the effect of physisorption is somewhat similar to the condensation of a gas to a liquid. The disturbance to the electronic states of the adsorbent (the material that adsorbs the gas molecules) and the sorbate (the adsorbed gas molecules) should be minimal. The process of physisorption is reversible. Physisorbed molecules can be removed from the sorbent by overcoming the forces of interaction between the two bodies.

Chemisorption is where there is strong electronic or chemical interaction between the solid and the gas molecule. It occurs with the formation of valance bonds. Chemisorption involves chemical reactions with the transfer of electrons and in most cases, irreversible. One example of chemisorption is when CO$_2$ interacts with an amine on the surface of a substrate (an example is an amine modified mesoporous silica material). Here, CO$_2$ forms different types of ammonium carbamates on the surface of this mesoporous material.

In general, physisorption of a sorbate on an adsorbent is weaker than chemisorption. Physisorption is mainly based on the strength of intermolecular interaction between the sorbent and the sorbate (intermolecular interactions refer to the attractive/repulsive interactions that involve permanent dipole, quadrupole, induced dipoles, and mixtures thereof). Physisorption usually has a lower enthalpy change than chemisorption, due to the weaker adsorbent-sorbate interaction in physisorption. Chemisorption involves the formation of valence bonds, transfer of electrons and changes in the electronic state of the adsorbent and the sorbate. The activation energy of chemisorption is also higher than that of physisorption. The high activation energy and enthalpy change of chemisorption is due to the disturbance of the electronic state and electron transfer.
The strength of physisorption can, however, vary depending on the physical properties of the adsorbent and the sorbate. Polar sorbates interact more with the adsorbents than non-polar sorbates. Sorbent with high electrical field gradients or high polarising ability will strengthen the molecular interaction (physisorption interaction). Note that in physisorption, the electronic state of the adsorbent and the sorbate does not change. There is negligible electronic interaction. When a gas molecule is brought to a surface, it saturates the unbalanced forces on the surface and decreases the free energy of the system.

Adsorption processes are typically reversible although some examples of chemisorption are irreversible. Both physisorption and chemisorption are exothermic. When a gas molecule goes from a being a in gas phase to the physisorbed phase, the entropy of the system reduces. Physisorption is a spontaneous process. The physisorption process must therefore be exothermic according to the second law of thermodynamics ($\Delta G = \Delta H - T\Delta S$). Chemisorption is also exothermic because it involves the formation of valence bonds.

An adsorption isotherm describes the specific quantity of the adsorbed sorbate on a sorbent under specific conditions (specific equilibrium temperature and pressure) at a varying pressure and a constant temperature. A fast adsorption rate is related to the sorbates being able to reach and percolate through the adsorbent’s internal surface rapidly. A reduced rate can be related to sorbate not being able to reach the adsorptive surface for physisorption, or the occurrence of chemisorption. The slow occurrence of chemisorption is partly due to the high activation energy or the slow rate of the chemical reactions. In short, physisorption typically occurs more quickly than chemisorption.

Swing adsorption processes

“Swing adsorption processes”, as the name implies, concerns processes which use at least one operational variable. In terms of gas sorption, the variable(s) can be pressure (of a gas) or temperature. When pressure is the variable, the process relies on the sorbent being able to adsorb at a relatively high pressure, and to desorb when the pressure is lowered. Depending on the exact range of gas pressure, the process is called pressure swing adsorption (PSA) or vacuum swing adsorption (VSA). Figure 1.4 is a simple flow chart that shows the general principles of CO$_2$ capture and removal in PSA/VSA processes.

The temperature of the process can also be the controlling variable. In this case, the process typically relies on adsorption to take place at a low temper-
ature, and desorption to take place when the temperature of the system is raised. This process is named temperature swing adsorption (TSA).

In this thesis, adsorbents are tested for their CO$_2$ separation and sorption properties towards application in PSA/VSA processes. However, the focus on this thesis will not be on the process, but mainly on adsorbent development.

**Figure 1.4** A simple schematic of the adsorption and desorption steps in PSA/VSA
The ideal adsorbent

Does an “ideal” adsorbent exist? The answer to this question depends greatly on what is required from the adsorbent. When choosing an adsorbent, there are several aspects to be considered. In this section, some most common prerequisites of a “good” adsorbent will be explored.

**CO₂ capacity**

In terms of CO₂ removal, the adsorbent acts as a “host” for the CO₂; therefore, the CO₂ capacity is extremely important. If the CO₂ capacity of an adsorbent is low, the whole process will become inefficient as the adsorbent will need to be “emptied” frequently. The process which removes adsorbed CO₂ from the adsorbent is called “regeneration”. Adsorbents with high CO₂ capacity are desirable as they can increase the efficiency and hence reduce the cost of CO₂ capture.

On the other hand, in some processes, having the highest maximum CO₂ capacity (CO₂ capacity at saturation) may not be relevant. Often the “working capacity” of the material is of higher importance than the maximum capacity. Working capacity can be defined as the amount of CO₂ that the adsorbent can adsorb and desorb under the exact process working conditions. For example, in biogas upgrading, the gas source feed has a pressure a times higher than atmospheric pressure. The adsorbent must adsorb CO₂ at these high pressures, and desorb when the pressure is lowered to around 1 atmosphere. In this case, the maximum CO₂ capacity of the adsorbent is not important, but rather the uptake capacity between the adsorption/desorption pressures.

**Cyclic capacity**

The cyclic capacity of an adsorbent is the CO₂ capacity that can be retained and reused after the adsorption/desorption process. Ideally, the CO₂ capacity of the adsorbent should remain the same throughout its lifetime. Unfortunately, this is not always the case. If the adsorbent is not perfectly stable under the operation conditions, it may begin to lose its CO₂ capacity with the increasing number of cycles. The lost CO₂ capacity reduces the efficiency of the CO₂ removal process, shortens the lifetime of the adsorbent and can add to the cost of CO₂ capture. The shortened life time means that the adsorbent will need to be replaced more frequently. Another way in which the CO₂ capacity gets reduced with the number of cycles is through the formation of strongly adsorbed (chemisorpted) CO₂, or CO₂ trapped inside the material. These CO₂ molecules are then unable to be desorbed. Both of these kinds of
CO₂ are difficult to remove and they can also increase the cost of CO₂ capture.

Selectivity

CO₂ capture at point sources almost always has the CO₂ in a mixture with other gases. Flue gas from a coal power plant can contain around 15 vol% CO₂ in a mixture with mainly N₂. The values are different for a gas-fired power plant. Biogas (from fermentation) can contain up to 50% CO₂ in a mixture with CH₄ and traces of N₂ and hydrogen sulphide (H₂S). If adsorption processes are used to remove CO₂ from flue gas, it is important that the adsorbent can separate CO₂ from these other gases. Adsorption of the other gas will compromise the CO₂ uptake, decreasing the CO₂ removal efficiency. Furthermore, the desorbed gas will not be pure CO₂.

The adsorption of other gases is a particular problem for biogas upgrading by CO₂ adsorption. If the CO₂ selectivity of the adsorbent is low, CH₄ will also be adsorbed and later on released. This should be kept to a minimum as it causes the release of a greenhouse gas and will waste useful combustible fuel (called methane slip). Ideally, the adsorbent should exclusively adsorb CO₂ and adsorb no other sorbates. This means that the adsorbent should also be hydrophobic, as the adsorption of water will also lower the CO₂ uptake.

Cost of adsorbent

The cost of any industrial related process should always be kept as low as possible. Should CO₂ capture using swing adsorption be implemented, the process cost needs to be kept low as well. Ho et al. gives a good summary of the cost associated with PSA and VSA processes for CO₂ removal. The cost of CO₂ capture via adsorption incurs two major types of expense; capital expense and operational expense. The cost of CO₂ capture can be calculated as a function of the capital and operational expenses. Therefore, these expenses should be kept to a minimum. Capital expenses include the cost of setting up the PSA/VSA apparatus, for example flue gas desulphurisation unit (FGD), heat exchanger, dehydration unit, compressors and adsorption units. Operational costs are associated with the running and maintenance of the system. The largest capital expense in a VSA system is the compressor. The energy cost for running the compressor is the largest operational cost, followed by the adsorption unit and the cost of adsorbents. The cost of the adsorbent contributes significantly towards the cost of CO₂ capture, as a very large amount of adsorbent is usually required to fill the adsorbers (where adsorption takes place, in enclosed columns, also called “adsorption beds”). The total volume of the adsorbers may be greater than 600 m³. As a result, the efficiency of the adsorbent for CO₂ capture, and more specifically the
cost of the adsorbents is directly related to the cost of CO₂ capture. The lifetime of an adsorbent must also be accounted for. The adsorbent must be replaced after a certain period/number of adsorption/desorption cycles. Consequently, the production cost of the adsorbent should also not be high. A low-cost adsorbent requires that the raw material for its synthesis is inexpensive and the crystallisation time should be short with high yield of high purity. It is important to note that the relationship between the cost of CO₂ capture and the cost of the adsorbent is also dependent on the properties of the adsorbent itself. For example, if a hypothetical adsorbent has significantly higher CO₂ removal efficiency and longer lifetime than zeolite 13X, a higher production cost may still make it more cost effective for low cost CO₂ capture than zeolite 13X. In short, the cost of the adsorbent should be low, regardless of its properties.

**Others**

Should a particular material be used in any process, some generic properties must also be considered. In terms of an adsorbent, the thermal and mechanical stability of the material is important. An adsorbent for CO₂ capture must be able to withstand the conditions it is exposed to. For a coal burning power plant, flue gas is typically cooled by heat exchangers before it reaches the adsorption unit. Commercially available flue gas heat exchange setups are able to cool the flue gas to around 323 K. An adsorbent must therefore be able to remain structurally sound at this temperature. As mentioned earlier, defected materials will lower the uptake of CO₂, making the process less efficient. The adsorbent should also be able to selectively adsorb and desorb the desired gas quickly. In order to achieve high uptake/removal rate, the diffusivity of the gas molecules in the adsorbent must be high. Fast uptake/removal rate will shorten the time required for each adsorption cycle. The efficiency of the whole process will increase as CO₂ can be captured and removed quickly.

**Existing/potential solid adsorbents**

**Carbon**

Carbon based sorbents are well-known. There are many different types of carbon materials available as sorbents, such as activated carbons, carbon molecular sieves (CMS), carbon nanotubes, and graphenes. They are interesting CO₂ adsorbents because of the low cost. Carbon based adsorbent can be produced with very low costs from bio-mass and other types of waste products. Carbon molecular sieves (CMS-3A, CMS-5A) with narrow pores have demonstrated good properties in separation of different size molecules. The study of Cavenati et al. is a good example of gas separation
using CMS. Activated carbons are some of the most widely studied carbon based materials.

The CO\(_2\) adsorption capacity of activated carbons can be high at high pressures (8.5 mmol/g at 2 MPa, 298 K).\(^{18}\) However, at low pressures activated carbons typically have lower CO\(_2\) uptake than zeolites. The reason for this may be that unmodified (post synthetically) carbons are relatively inert materials with low electrical field gradients. Siriwardane et al.\(^{18}\) studied CO\(_2\) adsorption on activated carbon and compared it with zeolite 13X. The CO\(_2\) uptake at low pressures was found to be lower on activated carbon than zeolite 13X. CO\(_2\) uptake of activated carbon was high at high pressure, and the capacity surpassed zeolite 13X. Although activated carbons are hydrophobic, the presences of water can significant still reduce its CO\(_2\) capacity.\(^{19}\) Wang et al.\(^{27}\) showed that under a gas pressure of 2.5 MPa, CO\(_2\) uptake decreased if the gas stream was wet. At high pressures, the CO\(_2\) capacity was restored, possibly due to chemical fixation, condensation or the formation of hydrates.

Activated carbons tend to weakly physisorb CO\(_2\) with no chemisorption. The enthalpy of CO\(_2\) adsorption (~28 kJ/mol at low loading) was found to be about half of that for zeolite 13X (~55 kJ/mol at low loading).\(^{18}\) Although the low enthalpy of CO\(_2\) adsorption means very little of the CO\(_2\) capacity is lost between adsorption cycles, the CO\(_2\) capacity will decrease dramatically with increasing temperature (due to the exothermic nature of adsorption).\(^{28}\) Furthermore, activated carbons do not offer very high CO\(_2\) selectivity over N\(_2\). Siriwardane et al.\(^{18}\) found that the CO\(_2\)/N\(_2\) uptake ratio was around 2 – 3.

**Metal organic frameworks**

Metal organic frameworks, also known as MOFs, are a class of inorganic-organic hybrid material that can be highly porous. Highly porous MOFs were initially report by Li et al.\(^{29}\) These materials are made by linking organic molecules to metal ions via a mostly dative-covalent bond, forming an interconnected 3D network. There is some ionic character between the metal centres and the linkers because of the difference in electronegativity.\(^{30}\) The organic linkers often govern the topologies and the structure of the material. MOFs can in theory exist in many different variants due to the flexibility of linking different organic molecules with different metal ions.\(^{31}\) Their highly porous framework means that they have gas adsorption capability.

MOFs typically offer pores that are larger than the sorbates considered in this study. MOFs are also relatively inert, they have a neutral framework with low electrical field gradients compared with zeolites, but not as low as silicas. This is because of the inherent ionic character of MOF materials.\(^{32, 33}\)
Hence in terms of CO$_2$ adsorption, the CO$_2$-framework interaction is typically lower than that in zeolites.

As a CO$_2$ adsorbent, MOFs offer very high capacity at high pressures. MOF-177 was reported to have the highest CO$_2$ uptake of all porous materials at saturation (6.4 MPa), the uptake of CO$_2$ reached 33.5 mmol/g at 298 K.$^{34}$ The high CO$_2$ capacity was due to the high pore volume and high surface area offered by this material. However, at low pressures, zeolite 13X outperformed MOF-177 in terms of CO$_2$ uptake. Mg-MOF-74 (a variant of MOF-74) was also found to have significantly higher CO$_2$ capacity (11.3 mmol/g at saturation -3.5 MPa, 273 K) than other well-known adsorbents such as zeolite 13X$^{35}$ and some zeolite imidazolate frameworks (ZIFs).$^{36}$ It also had higher CO$_2$ uptake (7.2 mmol/g) than zeolite 13X (4.2 mmol/g) at low pressure (15 kPa of CO$_2$ at 298 K).$^{37}$ Other MOFs also offer very high CO$_2$ capacity at higher pressures. Millward and Yaghi studied a Zn$_4$O(O$_2$C)$_6$ type framework (namely IRMOF-11, -3, -6 and -1) and found that these materials offer substantially higher capacities (between 10 and 25 mmol/g at saturation) for CO$_2$ than other MOFs tested.$^{34}$

Many MOFs contain pores that are significantly bigger than the kinetic diameters of CO$_2$, N$_2$ or CH$_4$ (kinetic diameters of these gases are discussed later). As a result, the preferential uptake of CO$_2$ observed on MOFs generally comes from the greater interaction CO$_2$ has with the framework, rather than a size selective mechanism (these mechanisms are discussed later). A range of zinc based interpenetrated MOFs also showed high CO$_2$ selectivity. The high selectivity observed was due to the interpenetrating framework reducing the effective pore size of the material, which gave enhanced CO$_2$ selectivity.$^{38}$

**Zeolites**

Zeolites are crystalline inorganic structures with multidimensional channel systems. They can be found naturally as minerals or be synthesised. Their frameworks are constructed of tetrahedrally coordinated atoms (T-atoms), typically aluminium or silicon. These T-atoms are linked by covalently bonded oxygen atoms to form a framework. Aluminium introduces a negative charge to the framework and the zeolite requires the presence of charge balancing cations. Zeolites have high porosity and can be good CO$_2$ adsorbents. The pore window size of zeolites can vary depending on the structure. Some zeolites contain pores windows surrounded by 8, 10, 12 (or more) T-atoms. A pore window surrounded by 8 T-atoms is called an 8-ring (or sometimes referred to as an 8 membered-ring) window.$^{39}$
Zeolites are the most studied class of porous materials. Some zeolites have been commercialised as adsorbents, for example, zeolite 13X. Generally, zeolites offer high CO₂ uptake due to the high electrical field gradients, which is induced by the negatively charged framework and the charge balancing cations. The high uptake capacity is perhaps the most attractive aspect of zeolite adsorbents. Two of the most commonly studied zeolites, zeolite 13X and NaY, have been reported to have around 4.0 mmol/g of CO₂ uptake at atmospheric pressure (303 K). At a lower temperature (273 K), the CO₂ uptake of zeolite 13X can reach over 5 mmol/g at 101 kPa. The exothermic nature of adsorption means that CO₂ adsorption on adsorbents would decrease with increasing temperature. This effect has been observed previously on zeolite-β, zeolite 13X and zeolite NaY.

Zeolites have a high preferential CO₂ uptake, this is due to the high quadrupole moment of CO₂ (4.30 × 10⁻²⁶ esu cm²) when compared with other gases, such as N₂ (1.52 × 10⁻²⁶ esu cm²) and CH₄ (which has no quadrupole moment). The quadrupole moment of CO₂ enhances interaction with the electrical field gradients of zeolite frameworks. This type of interaction is significantly higher between CO₂ and zeolites than for other more “inert” gases. Li and Tezel confirmed this observation on zeolite-β by evaluating the Henry’s Law constants presented in their study. Harlick and Tezel compared the heat of adsorption of CO₂ and N₂ for 13 different zeolites, and drew the same conclusion. External conditions, such as temperature and pressure also play a role in the preferential uptake of CO₂. Shao et al. showed that for zeolite NaY, the CO₂/N₂ uptake at apparent equilibrium (348 K) can vary from 105 to 26 when the pressure increases from 6.7 kPa to 26 kPa.

From the properties discussed above, it seems that zeolites are close to ideal as CO₂ sorbents. However, zeolites are not without their drawbacks. Zeolites tend to be highly hydrophilic due to the aluminium content and the presence of exchangeable metal cations. Water molecules can adsorb around the metal cations, or on aluminium sites. The uptake of water reduces the CO₂ capacity of zeolites as demonstrated by Siriwardane et al. This can hinder efficient CO₂ removal from wet gas streams. If hydrophilic zeolites are to be used in CO₂ removal from wet gas streams, the gas will need to be dried first. The extra drying step is without doubt a drawback of zeolites and will add to the cost of the whole process. The presence of metal cations also means that CO₂ can chemisorb on zeolites at the high energy sites first. The chemisorption of CO₂ is strong and not easily reversible unless the adsorbent is fully regenerated. One way to fully regenerate the zeolite adsorbent is by heating the adsorbent (around 623 K) in high vacuum. This will be too energy demanding to apply in practice. The chemisorbed CO₂, if left not removed, will reduce the CO₂ capacity of the adsorbent in subsequent adsorption cycles.
This thesis deals with zeolite and zeolite-like materials as CO$_2$ adsorbents. CO$_2$ capacity of zeolitic materials is generally quite high. Some zeolites offer high selectivity as well. In order to study or develop zeolites as effective CO$_2$ adsorbents, the mechanism of which CO$_2$ can be separated from other gases must be understood.

**CO$_2$ separation using zeolites**

How do zeolites separate CO$_2$ from a gas mixture?

**Equilibrium selectivity**

Equilibrium selectivity of one gas over another arises from the differences in the level of electrostatic interaction between the adsorbent and the sorbates and to some extent the sorbate-sorbate interactions. In order to consider the different types adsorbent-sorbate interaction related to this study, some of the properties of CO$_2$, N$_2$ and CH$_4$ need to be considered. Gas molecules in gas phase have larger diameters than gas molecules that are inside a zeolite (solid). For this study, only the size of the gas molecules inside a zeolite (the effective kinetic diameter in solids) will be considered, this is referred to as “kinetic diameter” or “effective kinetic diameter” from here on.

**Table 1.1. Physical parameters of CO$_2$, N$_2$ and CH$_4^{50, 51}$**

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Gas phase molecular diameter (nm)</th>
<th>Effective kinetic diameter in solids (nm)</th>
<th>Polarisability ($\times 10^{25}$/cm$^3$)</th>
<th>Dipole moment ($\times 10^{18}$/esu cm$^2$)</th>
<th>Quadrupole moment ($\times 10^{26}$/esu cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.51</td>
<td>0.33</td>
<td>29.11</td>
<td>0</td>
<td>4.30</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.43</td>
<td>0.36</td>
<td>17.40</td>
<td>0</td>
<td>1.52</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.41</td>
<td>0.38</td>
<td>25.93</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

A gas molecule with characteristic dipole moment ($\mu$) can have dipole interaction with the electrical fields ($\vec{E}$) of the zeolite. The interaction energy ($U_\mu$) is given as $U_\mu = -\vec{E}\mu$. Table 1.1 shows that none of the sorbate gases considered in this study has characteristic dipole moments.

Two of the three sorbate gases, CO$_2$ and N$_2$, have characteristic quadrupole moments ($\theta$). The effect of the quadrupole moment of these gas molecules
means that these molecules can have quadrupole interaction with the electrical field gradients \((dE/dr)\) of the zeolite adsorbent. The interaction energy \((U_q)\) from this type of interaction is given as \(U_q=0.5 \theta dE/dr\) can contributes significantly towards the total interaction energy between the zeolite and the gas molecule. CO\(_2\) has an appreciably higher quadrupole moment than N\(_2\). Thus, quadrupole interaction energy \((U_q)\) between N\(_2\) and the electrical field gradient \((dE/dr)\) of the zeolite is lower than that for CO\(_2\). CH\(_4\) has no quadrupole interaction with the electrical field gradients of the zeolite.

With three gases (CO\(_2\), N\(_2\) and CH\(_4\)), as well as other non-polar gases, there are also electrostatic interactions between the gas molecules and the electrical fields of the zeolite. This type of interaction is based on the fact that the electrical fields \((\vec{E})\) on the surface of the adsorbent are able to polarise the gas molecules, regardless of their polarity. Therefore, this type of interaction is enhanced by the polarisability \((\alpha)\) of the gas molecule and the electrical fields \((\vec{E})\) of the zeolite. The interaction energy \((U_n)\) is given as \(U_n=-0.5\alpha |E|^2\). As well as the different types of electrostatic interactions mentioned above, dispersion forces between zeolites and any gas molecules also contribute slightly towards the overall interaction energy between the zeolite and the gas molecule.

CO\(_2\) has the highest polarisability and quadrupole moment out of the three sorbates considered in this study. As a result of that, CO\(_2\) typically interacts more strongly with the electrical fields and the electrical field gradients of zeolites than N\(_2\) and CH\(_4\). The strong interaction leads to a preference for zeolites to adsorb CO\(_2\) over N\(_2\) or CH\(_4\).

**Kinetic selectivity**

Kinetic effect is also a selection mechanism that is able to separate molecules of different sizes. Kinetic selectivity is commonly seen as the product of the equilibrium selectivity and the square root of the involved diffusivities. The selectivity arises partly on the higher diffusivity of one component over another. Kinetically enhanced selective adsorption of one gas component can work well if the adsorption rate of the slowly diffusing gas component is slow with respect of the time scale of the separation process. However, there are few processes that have been commercialised using this as a basis for the effect. One example of this is N\(_2\) purification using CMS, in which PSA units are commercially available for purchase (some manufacturers include: Brechbuehler AG, Air Liquide, Parker Hannifin Corp.). The effect can be based on the ease of molecular diffusion in a confined space. The relationship between diffusivity and the adsorption of a particular gas has been demonstrated by Reid et al. for both linear and spherical gas molecules.\(^{52, 53}\) For example, if there are two molecules of different sizes in a
uniformly shaped porous channel, the smaller molecule will diffuse more freely than the larger one within the channel (given that the all the molecules and the framework are do not interact significantly with each other). The kinetic effect is built on this concept. For the separation of CO$_2$ from N$_2$ and CH$_4$, the kinetic effect can in theory be observed if the adsorbent has porous channels (or pores windows) of molecular dimensions. This is because porous channel or pore window with similar dimensions as CO$_2$, N$_2$ and CH$_4$ allows CO$_2$ to diffuse more quickly through into and through the adsorbent than the other two molecules. A graphical representation of the kinetic effect is shown in Figure 1.5.

The “molecular sieve effect” is the extreme case of kinetic selectivity, where the diffusion of the larger one of two gas molecules has essentially been reduced to zero. Molecular sieving can also be seen as a size exclusion mechanism. CO$_2$, N$_2$ and CH$_4$ all have different kinetic diameters inside a solid (zeolite) as shown in Table 1.1. CO$_2$ has the smallest kinetic diameter of 0.33 nm, followed by N$_2$ with 0.36 nm and CH$_4$ at 0.38 nm. Assuming that porous adsorbents have channels or pore windows that are circular, and that the gas molecule exist in a spherical shape (due to molecular vibration and rotation), the dimension of the windows can govern if a sorbate can enter or not. If the porous adsorbent, such as a zeolite, has channels or pore

![Figure 1.5](image_url)

Figure 1.5 The kinetic separation effect, CO$_2$ with a smaller kinetic diameter can be separated from N$_2$ with a larger kinetic diameter as CO$_2$ diffuses more quickly in narrow pores than N$_2$. 
windows apertures that are smaller than the kinetic diameter of N\textsubscript{2} (0.36 nm) and CH\textsubscript{4} (0.38 nm) but bigger than the kinetic diameter of CO\textsubscript{2} (0.33 nm), then CO\textsubscript{2} should still be able to enter the material freely, but N\textsubscript{2} and CH\textsubscript{4} will be blocked. In this case, the adsorbent is essentially non-porous toward N\textsubscript{2} and CH\textsubscript{4}. It will exclusively adsorb CO\textsubscript{2}, even from a mixture of these gases. A graphical explanation of the molecular sieving effect is shown in Figure 1.6.

The biggest difference between CO\textsubscript{2} separation using “molecular sieving” and “kinetic separation” is the way which N\textsubscript{2} and CH\textsubscript{4} are dealt with. The molecule sieving effect totally eliminates the bigger molecules of a mixture of different molecules from entering the adsorbent. Kinetic separation still allows other sorbates to diffuse within the adsorbent. In theory, kinetic separation seem less effective than molecular sieving for obtaining pure CO\textsubscript{2}, as the adsorption of other gases is allowed. On the other hand, if the adsorbent contains channels/windows small enough to eliminate N\textsubscript{2} and CH\textsubscript{4} adsorption, it must be smaller than 0.36 nm in diameter. These small channels or pore windows do indeed allow CO\textsubscript{2} to enter and be adsorbed on the adsorbent, but they will also restrict the self-diffusivity of CO\textsubscript{2} due to the confined space. Hayhurst, and Paravar demonstrated using silicalite and light hydrocarbons that the diffusivity is related to the relative size between the mole-

Figure 1.6 The molecular sieving effect, CO\textsubscript{2} with a smaller kinetic diameter can be separated from N\textsubscript{2} with a larger kinetic diameter than CO\textsubscript{2}.
cule and the pore opening. The CO$_2$ uptake rate can become extremely slow and significantly decrease the usable CO$_2$ capacity of the sorbent. Adsorbed CO$_2$ can also be “trapped” inside the material, which would further reduce the usable/working CO$_2$ capacity on subsequent cycles. This would make the process less efficient and increase the cost of CO$_2$ removal. Molecular sieving can be the choice for CO$_2$ separation processes where the cycle time is slow, and high purity CO$_2$ is required.

Ideally, to separate CO$_2$ using kinetic separation, the adsorbent should have pores small enough to retard the self-diffusivity of N$_2$ and CH$_4$ excessively without slowing down CO$_2$ diffusion. Kinetic separation can be good for high throughput processes with short cycle time.

**Aim of this study**

In this thesis, a range of inorganic zeolite-like microporous adsorbents will be examined. The selected range of adsorbents is capable of separating CO$_2$ from N$_2$ and/or CH$_4$. Some of these adsorbents separate CO$_2$ by kinetic effect, whereas others separate CO$_2$ using only equilibrium effect. The next chapter will give an overview of these adsorbents and their CO$_2$ adsorption properties. Chapter 3 will then give a direct comparison of all the tested adsorbents from different aspects.
2. Zeolites, phosphates and silicates as CO₂ adsorbents

Zeolites A (Paper III, IV, V, and VII)

Zeolite A (Figure 2.1) is one of the most widely used zeolites in the world. It has the structure type of LTA (Linde Type A) zeolites as defined by the international zeolite association (IZA). Zeolite A is commonly used in its sodium form. This zeolite is used as a water softening agent in washing powder, as well as in other applications. The general chemical formula for dehydrated zeolite A with Na⁺ cations is \([\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8\). Zeolite A is widely used because it possesses great ion exchange properties, and it is also easy and inexpensive to synthesise.

![Figure 2.1 Structural representation of zeolite A. The black lines represent the connections between the metal atoms of the TO₄ tetrahedra (Where T is a metal atom Si or Al) Oxygen atoms are omitted.](image)

Zeolite A has a three dimensional (3D) network structure. It is a giant covalent oxide containing aluminium and silicon. The structure of zeolite A contains sodalite cages linked by a double 4-ring at 6 different locations. The connection of the sodalite cages creates a porous network. The porous network has pore windows that are encircled by 8 T-atoms and 8 oxygen atoms.
These 8-rings are on the faces of cages which are interconnected in two different directions, making the 3D porous network of zeolite A.

In the structure of zeolite A, each intra-framework metal centre (Si or Al) of these giant covalent oxides (like in zeolites) are covalently bonded to four oxygen atoms. The oxygen atoms are bridging two metal centres. As a result, each oxygen atom contributes an oxidation state of -1 towards each metal centre. The zeolite A framework has a Si:Al ratio of 1:1. The Si and Al are strictly alternating in the framework due to the Lowenstein’s rule. The formal oxidation state of Si and Al are +4 and +3 respectively. This means that every Al centre in zeolite A contributes toward the overall negative charges. The negative charges are spread across the framework and extra-framework cations are located at certain crystallographic sites to balance out these charges.

Zeolite A can exist in many forms, the major difference between them are the charge balancing cations present. The most common types of zeolite A are zeolite NaA (4A), KA (3A), and CaA (5A). Zeolite NaA refers to when Na\(^+\) is the only type of cation present in zeolite A. If the cations present are K\(^+\) or Ca\(^{2+}\), then the zeolite is known as KA or CaA. Zeolites can also be named after the size of their pore openings. For example, zeolite KA can be referred to as zeolite 3A (or molecular sieve 3A), while NaA and CaA are referred to as 4A and 5A, respectively. These historical numbers in the names are the approximate pore window diameters of the different zeolites in Å. As suggested by the different names, the pore size of zeolite A can be different depending on the cations present.

Zeolite A containing monovalent cations (for example: Na\(^+\), K\(^+\), Cs\(^+\)) has 12 cations per α-cavity. These cations sites can be divided into three types. Site I refers to the cation sites that are located in the middle of the 8-ring windows. Site II and III both refer to the sites close to the 6-ring of the cavity. Site II cations are located slightly towards the α-cavity and site III cations are located inside the β cage. The occupancies of Na\(^+\) and K\(^+\) respectively in NaA and KA for the three different cations sites are: eight cations in site I, three cations in site II and one cation in site III. For CsA, three Cs\(^+\) cations are located in site I, seven in site II and two in site III (there is a site IV in zeolite CsA, located in the 4-ring and the site can be occupied by 0.5 or 1 cation in some cases). The cations located in site I and site II partially obstruct the 8-ring windows. The size of the 8-ring windows can therefore, be adjusted by having cations of different sizes. A big cation will occupy more space than a small cation, hence reducing the accessible dimension of the pore windows.
The presence of divalent cations has a different effect on the size of the 8-ring windows. In the case of zeolite 5A (or CaA), the divalent Ca\(^{2+}\) cation can also replace Na\(^{+}\). Zeolite 5A usually contains 4 Ca\(^{2+}\) and 4 Na\(^{+}\) per \(\alpha\)-cavity. In zeolite 5A, all cations are located close to the 6-ring of the \(\alpha\)-cavity. The Ca\(^{2+}\) cations are located on the plane of the 6-ring, the Na\(^{+}\) are slight shifted towards the centre of the \(\alpha\)-cavity.\(^{62,63}\) Depending on the level of Ca\(^{2+}\) exchange, the 8-ring window size can also vary.\(^{63}\)

**Synthesis and characterisation of zeolite A**

Zeolite A can be synthesised at a low cost and in large quantities. A typical laboratory scale synthesis can be carried out in many ways. During this work, nano-sized zeolite A was synthesised as detailed in paper III. A generic synthesis procedure is described here. Two plastic Nalagen PE bottles are required. In the first bottle, 72 g of sodium hydroxide (NaOH) is mixed with 30 g of aluminium hydroxide (Al(OH)\(_3\)) in 182 cm\(^3\) of deionised water. In the second bottle, 108 g of sodium hydroxide (NaOH) is mixed with 60 g of fumed silica (SiO\(_2\)) in 310 cm\(^3\) of deionised water. The two mixtures are stirred until homogenised, then mixed together and left to crystallise at 333 K for 2 hours. These procedures yield pure cubic crystals of zeolite NaA with an average dimension of around 200 x 200 nm. The purity of synthetic zeolite A crystals can be determined using powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM); these are shown in Figure 2.2 and Figure 2.3.
Figure 2.2 Powder X-ray diffractogram of zeolite A synthesised using the stated procedures. Data reproduced from Paper III.

Figure 2.3 Scanning electron micrograph of zeolite A synthesised using the stated procedures.
Zeolite NaA and nano-zeolite NaA

Zeolite NaA (4A) has Na$^+$ cations in all 3 of the crystallographic sites. This configuration gives the material 8-ring pores that are approximately 4.1 x 4.1 Å in size. These pores have dimensions very close to the kinetic diameters of CO$_2$ and N$_2$. Zeolite A, in theory, should be able to separate CO$_2$ from N$_2$ via a kinetic separation mechanism, as the smaller CO$_2$ molecule should find it easier to enter pores of these dimensions.

Zeolite A, similar to other aluminium rich zeolites, has relatively high electrical field gradients. The overall electrical field gradients of the zeolite arise from the framework negative charges and the presence of many charge balancing cations close to the framework atoms. As highlighted in Chapter 1, the quadruple moment of CO$_2$ can interact intensely with the electrical field gradients, which enhances the CO$_2$ adsorption on zeolites. Liu et al. are amongst some others who have found that the CO$_2$ uptake of zeolite NaA and NaKA can be relatively high with reasonable CO$_2$ selectivity over N$_2$, based on single component gas adsorption isotherms (Figure 2.4).

A potential drawback for zeolite NaA and NaKA is that the pore windows may be too small even for CO$_2$ to enter easily. After all, fast diffusion of CO$_2$ into the adsorbent is a prerequisite for effective kinetic separation. It is important to note that sorbate diffusion in zeolite A is heavily affected by many factors, such as the origin of the crystals, the crystallinity etc. The diffusivity of a sorbate can be affected by some order of magnitude in zeolite A crystals of different origins. Ruthven recently examined this topic in detail. In general, diffusion of sorbates, such as CO$_2$ in zeolite A is governed by intercrystalline diffusion. The diffusivity can, however, vary significantly between two different samples of zeolite A.

Intercrystalline diffusion states that diffusion rate is inversely proportional to the square root of the crystal diameter (dimension). This means that small crystals should ideally have a fast sorbate uptake rate. Paper III shows an attempt to synthesise and test nano-sized zeolite A as a CO$_2$ sorbent with enhanced uptake kinetics. Unfortunately, the overall uptake rate is not noticeably enhanced on these smaller crystals. The CO$_2$ uptake kinetics shows a skin layer restricted response. The presence of what seems to be a skin layer of very small, perhaps amorphous material (Figure 2.5) can be found on the surface of the material using high resolution scanning electron microscopy (HRSEM).
Figure 2.4 CO₂ and N₂ adsorption isotherms of NaA and NaKA (with 17 at.% of the exchangable cations being K⁺) at 273 K, reproduced using data from Liu et al.⁶⁶

Figure 2.5 Scanning electron micrograph of as synthesized nano-sized zeolite A (NaA), redrawn from Paper III.
Zeolite NaKA, NaCsA and NaKCsA (paper III and VII)

During this work, the highly tuneable property of zeolite A has been thoroughly explored. Paper III and VII show in detail how the gas sorption properties of zeolite A can be modified by ion exchange of NaA. It is important to clarify at this point that the term “M+ at.%” or similar throughout the thesis refers exclusively to the atomic percentage of the number of exchangeable cations in zeolite A. This term is not to be confused with the elemental composition (in atomic percentage) of the zeolite.

Liu et al.\textsuperscript{66} has previously established that zeolite NaKA, with 17 at.% of the exchangeable cations being K\textsuperscript{+}, can restrict the adsorption of N\textsubscript{2} but allow CO\textsubscript{2} to freely adsorb. The reason behind this selective adsorption effect is due to the bigger K\textsuperscript{+} cation replacing the smaller Na\textsuperscript{+} cation at site II and III at this level of exchange. With 17 at.% of the cations being K\textsuperscript{+}, zeolite NaKA has an effective pore windows diameter that is too small for N\textsubscript{2} to freely enter into the porous channels of the zeolite. Hence the adsorption of N\textsubscript{2} is highly restricted. When the number of K\textsuperscript{+} cations has been increased, the pore size of the zeolite continues to become smaller. If the pore windows become too small, the CO\textsubscript{2} uptake rate will become too slow for effective CO\textsubscript{2} capture. On this basis, the zeolite with the largest effective pore windows (lowest K\textsuperscript{+} content) that offer high preferential CO\textsubscript{2} uptake (meaning that it can eliminate N\textsubscript{2} adsorption), is of most interest.

At low levels of exchange (up to 17 K\textsuperscript{+} at. %), the K\textsuperscript{+} cations do not replace Na\textsuperscript{+} at site I. Liu et al.\textsuperscript{66} established using PXRD that the site III Na\textsuperscript{+} is replaced first upon ion exchange (at around 8 at.% K\textsuperscript{+} occupancy). At this level of exchange, the 8-ring is not affected; hence the adsorption of N\textsubscript{2} and CH\textsubscript{4} on zeolite NaKA is not very restricted. At higher levels of exchange than 17 at.\%, the effective pore window size continues to decrease. The smaller window size means that even CO\textsubscript{2} adsorption is becoming more restricted. The uptake of CO\textsubscript{2} will begin to drop simply because CO\textsubscript{2} fails to go through the 8-ring windows easily. Paper III and VII show that zeolite NaKA containing 17 at.% K\textsuperscript{+} is an effective CO\textsubscript{2} adsorbent which can separate CO\textsubscript{2} from N\textsubscript{2} and CH\textsubscript{4} with very high selectivity. In theory, CO\textsubscript{2} adsorption should be heavily restricted at high K\textsuperscript{+} content. Liu et al.\textsuperscript{66}, as well as paper III show the CO\textsubscript{2} can still be adsorbed with significant uptake at high K\textsuperscript{+} content. The reason for this observation is not totally clear but others have proposed many explanations for the unexpectedly high CO\textsubscript{2} uptake. Larin et al.\textsuperscript{70} suggested that chemisorbed CO\textsubscript{2} forms a “carbonate door” with K\textsuperscript{+}, which can shift the K\textsuperscript{+} position and opens up the pore window for CO\textsubscript{2} to enter. Mace et al.\textsuperscript{71,72} suggested that CO\textsubscript{2} can interact with K\textsuperscript{+} (at non-full K\textsuperscript{+} exchange) in a manner that other, more inert gases (N\textsubscript{2}, CH\textsubscript{4}) cannot. The interaction between CO\textsubscript{2} and K\textsuperscript{+} cations induces cation “hopping”, opening
up the channel for CO$_2$ to enter subsequently. Shang et al.$^{73, 74}$ proposed a “molecular trap door” mechanism for K$^+$ exchanged zeolite. Similar to Mace et al.$^{71, 72}$ CO$_2$ can interact with the cations in a way that other gases cannot. They also suggested the “trap door” could also be found on other small pore zeolites, such as zeolite A.

As discussed, NaKA with 17 at. % K$^+$ can separate CO$_2$ from CH$_4$ with high selectivity. However, the high selectivity for CO$_2$ over CH$_4$ can also be achieved with Cs$^+$ ion exchange. Paper VII shows the CO$_2$ separation properties over CH$_4$ of NaCsA. NaCsA with 17 at. % Cs$^+$ shows restricted CH$_4$ uptake, but the CO$_2$ capacity is also lowered. The CO$_2$ selectivity over CH$_4$ can be further enhanced by having “mixed” ion exchange. Zeolite NaA that has been both K$^+$ and Cs$^+$ exchanged (creating NaKCsA) shows that cation replacement at low occupancies can result in a zeolite with high CO$_2$ selectivity over CH$_4$. CO$_2$ is exclusively adsorbed on NaKCsA when the zeolite contains around 8 at.% K$^+$ and around 7 at.% of Cs$^+$ (85 at.% Na$^+$). Furthermore, the high CO$_2$ capacity is preserved, unlike in the case of NaCsA (17 at.% Cs$^+$).

**Zeolite ZK-4 and NaK-ZK-4 (paper IV and V)**

Zeolite ZK-4 is structurally very similar to zeolite A. Both of these zeolites are of the LTA framework type. In zeolite A, the Si:Al ratio is strictly 1:1. This is the highest Al content allowed for zeolites according to the Loewenstein’s rule.$^{57}$ In zeolite ZK-4, the Si:Al ratio is higher than 1. The zeolite is silicon rich. The Loewenstein’s rule is still followed, and the Si and Al atoms are no longer strictly alternating between oxygen atoms. Zeolite ZK-4 can be synthesised very easily under reflux or via hydrothermal routes. A typical synthesis for zeolite ZK-4 involves two reaction mixtures: the first mixture contains sodium aluminate and sodium hydroxide in deionised water. The second mixture contained colloidal silica (HS-40) and TMAOH (tetrabutylammonium hydroxide - 20% in H$_2$O) solution. The two mixtures are agitated for 30 minutes and then combined together. The final mixture is agitated for a further 120 minutes before aging for 24 h at room temperature. The aged reaction gel is transferred to a Teflon lined stainless steel autoclave and to be heated up to 373 K between 20 and 72 h. The as-synthesised zeolite NaZK-4 needs to be calcined at 773 K for 24 h to remove the organic template. Reaction gel compositions are given in paper IV and V for zeolite NaZK-4 with a Si:Al ratio up to 2.8:1.

The higher Si content in zeolite ZK-4 will have some profound effects on its properties, first of which is the lowered number of charge balancing cations. This is because as the number of Al atoms decrease, the net framework negative charges decrease. The reduced number of cations on zeolite ZK-4
also means that the overall electrical field gradients of the zeolite will decrease. On first glance this may suggest that the material might have a lower CO$_2$ uptake than zeolite A (Si:Al =1:1), as the CO$_2$ – cation and CO$_2$ – framework (electrical field gradients) interaction should decrease. However, the reduced number of cations gives the material more available space for CO$_2$ adsorption. In zeolite ZK-4, Na$^+$ and K$^+$ can mainly occupy three different cation sites, the location of these sites are equivalent to those in zeolite A. A fourth site has been identified for K$^+$ in K-ZK-4 by Ikeda et al. The occupancy of the fourth size (which is situated in the 4-ring) become zero once the Si:Al ratio is higher than 1.5:1. Generally speaking, in ZK-4, the location of Na$^+$ cation sites are close to the centre of the 8-ring, and in the centre of the 6-ring. For K$^+$ cations in ZK-4, Ikeda et al. have shown that the 8-ring sites for K$^+$ is crystallographically more to the centre of the 8-ring than in the case of Na$^+$.

Paper IV shows that the CO$_2$ uptake of zeolite ZK-4 with Si:Al ~ 1.3 has very high uptake of CO$_2$. Paper V demonstrates that even at a Si:Al ratio of ~2.8 :1, the CO$_2$ capacity of zeolite ZK-4 is not compromised by the reduced number of cations. These two papers also demonstrate that high quality crystals can further maximise the available volume for CO$_2$ sorption. The very high CO$_2$ uptake is possible due to the presence of many cations that can interact relatively strongly with CO$_2$, in a similar manner as in zeolite A. At Si:Al ratios of up to 2.8:1, there is little difference in the heat of CO$_2$ sorption. Even for zeolite ZK-4 with a Si:Al ratio of 2.8:1 (51 cations per unit cell vs 96 cations per unit cell in zeolite A), the heat of CO$_2$ adsorption is still around 40-45 kJ/mol at non-zero loading.

The presence of cations in a zeolite ZK-4 means that it has cations that can be exchanged. Similar to zeolite A, different cations on zeolite ZK-4 will result in the zeolite having different pore window sizes. Partially K$^+$ exchanged NaK-ZK-4 shows very similar response to NaKA. For NaK-ZK-4 with Si:Al ~ 1.3:1, the adsorption of N$_2$ is significantly restricted when the K$^+$ content reaches 26 at. %. When compared with zeolite NaKA (17 at.% K$^+$ required for selective CO$_2$ adsorption), the higher percentage of K$^+$ on ZK-4 is due to the lower number of the total cations in the Si rich zeolite. The CO$_2$ uptake of this NaK-ZK-4 is still very high. Similar to NaKA (17 at.% K$^+$), NaK-ZK-4 is highly selective for CO$_2$ adsorption over N$_2$.

When the Si content is further increased, the amount of K$^+$ required to create a highly selective CO$_2$ adsorbent also increased. At Si:Al ~2.3 and 2.8:1, around half (50 at. %) of the cations need to be K$^+$ before the window size of the material can be homogenously tuned to restrict N$_2$ adsorption. The CO$_2$ uptake on the highly selective zeolite ZK-4s is still high. At 101 kPa (273 K), the CO$_2$ uptake on these selective zeolite ZK-4s are over 3.5 mmol/g.
N₂ adsorption is very restricted on the aforementioned “highly selective” materials. At even higher K⁺ content than 50 at.%, N₂ adsorption should remain close to zero. This is because the K⁺ cation should further decrease the effective pore window size, disallowing N₂ molecules to enter. Interestingly, at high Si:Al ratio and at high K⁺ content, N₂ adsorption can take place on zeolite NaK-ZK-4 and K-ZK-4 with noticeable uptake. This interesting phenomenon may be due to the repositioning of the cation sites with high K⁺ content at high Si:Al ratios. In this case, K⁺ cations may no longer block the 8-ring windows, allowing N₂ to enter.

**Aluminophosphates as CO₂ sorbent (Paper I and VIII)**

Aluminophosphates (AlPOs), are microporous materials similar to microporous silicas. AlPOs are constructed by covalently linking oxides of aluminium and silicon together, forming multi-dimensional structures. AlPOs have neutral frameworks due to the alternating Al and P atoms. AlPOs in dehydrated forms are isoelectronic with silica. There is no charge balancing cation like the ones found in zeolites. As a results, these materials are generally considered to be relatively neutral, similar to microporous silicas, and very homogenous. There is a wide range of different AlPOs with many different structures, some of them are structurally equivalent to some zeolites. The nomenclature of AlPOs usually contains a number after the notation “AlPO”; this number is assigned according to the relevant structure. Similar nomenclature is used for naming other kinds of porous phosphate materials. For example, AlPO-34 and SAPO-34 (silicoaluminophosphate – 34) have the same basic structure – chabazite (CHA). AlPO-17 and H-SAPO-17 have the same basic structure as the zeolite erionite (ERI).

3 dimensional AlPOs can adopt structures that contain porous channels. These channels can be of different sizes and can be 1, 2 or 3 dimensions. AlPOs have relatively low electrical field gradients compared to zeolites. The low electrical field gradients are due to the lack of framework negative charges and hence the presence of charge balancing cations. As a result, AlPOs tend to weakly adsorb CO₂ and are not very water sensitive.

The syntheses of the AlPOs in this work all require hydrothermal synthesis. An organic structure directing agent (SDA) is required in each case. Generally speaking, the synthesis of AlPOs requires a suitable aluminium source and a phosphorus source. At least one organic structure directing (SDA) agent is required to synthesise a pure AlPO compound. The detailed synthesis procedures for narrow pore (8-ring) AlPOs are presented in paper I. The synthesis of other AlPOs (10-, 12- and 14- rings) is discussed in paper VIII.
Some AlPOs have been previously studied for their CO$_2$ adsorption capability. AlPO-18 has been synthesised into a membrane by Carreon et al. They found that the membrane offers a high CO$_2$ permanence of $\sim 6.4 \times 10^{-8}$ mol s Pa/m$^2$ (295 K). They also observed high CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity (19 and 59, respectively). Deroche et al. studied AlPO-18 using experimental and computational approaches. They found that the CO$_2$ adsorption isotherm of AlPO-18 showed a very gentle slope (the shape of the CO$_2$ isotherms for the different materials will be discussed in section 3). Overall, their findings showed that AlPOs have very high homogeneity and that the interaction between the AlPO framework and CO$_2$ is not as strong as that between zeolites and CO$_2$.

AlPOs with different pore sizes and channel dimensions have been included in this study. Larger pores should mean that diffusion of sorbate is less restricted and should be faster. On the other hand, larger pores openings do not allow sieving of the larger N$_2$ molecules. Here, AlPOs containing 8-ring, 10-ring, 12-ring and 14-ring have been studied. Within this thesis, 8-ring AlPOs are defined as “narrow pore”, 10-ring AlPOs are defined as “medium pore”, and the 12- and 14-ring are defined as “large pore” AlPOs.

**Large pore AlPOs: AlPO-5 and AlPO-8 (Paper VIII)**

AlPO-5 (structure code AFI) is one of the most studied AlPOs. It is a channel type AlPO which has a one dimensional porous channel with 12-ring windows. One interesting feature of AlPO-5 is that the porous channels are very smooth and circular (Figure 2.6). The circular shape means that electrical field gradients inside the channel system are rather low (for example, when compared to a zig-zag shaped channel), especially on this neutral AlPO framework. The comparatively large, smooth channel, together with the low electrical field gradients can result in mediocre uptake of CO$_2$. The diffusion of N$_2$ in these smooth, circular and comparatively large channels should be very unrestricted. This would in theory give AlPO-5 a low CO$_2$ selectivity over N$_2$. 


The CO$_2$ adsorption isotherm of AlPO-5 at 273 K shows that the CO$_2$ uptake only reached around 1.0 mmol/g at 101 kPa. The level of CO$_2$ uptake is low compared with other AlPOs. Surprisingly, even with the large channel dimension, N$_2$ uptake on AlPO-5 is unexpectedly low under the same conditions (101 kPa, 273 K). As a result, the CO$_2$/N$_2$ uptake ratio is higher than expected. The low N$_2$ uptake is not due to any restricted diffusion of N$_2$, as the porous channels are large and smooth. The low CO$_2$ and N$_2$ uptake may be due to the low electrical field gradients of the material, especially around the smooth pores. Consequently, the low electrical field gradients mean that there is very little interaction between the concerned sorbates (CO$_2$ and N$_2$) and the framework.
AlPO-8 (structure code AET)\textsuperscript{56} is another channel type AlPO with large, one dimensional porous channels (Figure 2.7). The pore windows on AlPO-8 are the largest in this work. The 14-ring channel should mean very unrestricted CO\textsubscript{2} and N\textsubscript{2} sorption. The gas sorption properties cannot be determined for AlPO-8, as this material becomes unstable and collapses upon calcination. The large pores may mean that the structure becomes too weak upon the removal of the organic SDA.

**Figure 2.7** Structural representation of AlPO-8 (AET). Black lines represent the connections between the metal atoms of the TO\textsubscript{4} tetrahedra (where T is a metal atom – Al or P in the case of AlPOs). Oxygen atoms are omitted.
Medium pore AlPOs: AlPO-11 and AlPO-41 (Paper VIII)

AlPO-11 (AEL, shown in Figure 2.8)\textsuperscript{56} and AlPO-41 (AFO, shown in Figure 2.9)\textsuperscript{56} are actually built from the same composite building units:\textit{afi},\textit{bog}, and\textit{ns}c chains. Both AlPOs have 1 dimensional 10-ring porous channels with similar dimensions. The syntheses of AlPO-11 and AlPO-41 typically use dipropylamine (DPA) as the organic SDA. Obtaining pure samples of these phases can be difficult as the two structures are very similar and hydrothermal synthesis attempts often yield a mixture of the two AlPOs. The work in paper VIII deals with the synthesis of pure AlPO-11 and pure AlPO-41. The choice of phosphorus source and the organic SDA is important. Impurity free AlPO-11 can be synthesised using di-iso-propylamine (DiPA) instead of di-propylamine (DPA) as an organic template. Pure AlPO-41 can be obtained by using phosphorous acid (H\textsubscript{3}PO\textsubscript{3}) as the phosphorous source instead of the typical orthophosphoric acid (H\textsubscript{3}PO\textsubscript{4}) usually used in AlPO synthesis.

Figure 2.8 Structural representation of AlPO-11 (AEL). Black lines represent the connections between the metal atoms of the TO\textsubscript{4} tetrahedra (where T is a metal atom – Al or P in the case of AlPO). Oxygen atoms are omitted.
The porous channel dimensions of AlPO-11 and AlPO-41 are both larger than the effective kinetic diameter of CO$_2$ and N$_2$. This means that the selectivity of the materials will not be as high as the narrow pore materials, as N$_2$ diffusion into the pores is not kinetically restricted. However, CO$_2$ is preferably adsorbed over N$_2$ on both AlPOs. Similar to that observed for AlPO-5, the preferential CO$_2$ uptake is related to how CO$_2$ interacts more with the framework than N$_2$. The CO$_2$/N$_2$ uptake ratio at 101 kPa (273 K) is around 10 for both AlPO-11 and AlPO-41. This number is lower than that of AlPO-5 and can be due to the less “smooth” channels on these medium pore AlPOs than AlPO-5. The CO$_2$ adsorption isotherms of AlPO-11 and AlPO-41 are of different shapes when compared with AlPO-5 as shown in Figure 2.10. The higher uptake on AlPO-11 and AlPO-41 at low pressures is an indication of the enhanced CO$_2$ framework interaction when compared with AlPO-5. This is related to the strength of framework-CO$_2$ interactions. The isotherms shown in Figure 2.10 may suggest that AlPO-5 has a lower number of high energy sites than AlPO-11 and AlPO-41. The channels on AlPO-5 are also larger and more circular in size than those of AlPO-11 and AlPO-41. It is important to clarify at this point that AlPOs (even AlPO-11 and AlPO-41) are still considered to be very homogenous with very little number of high energy adsorption sites. The framework interaction with CO$_2$ may be higher on AlPO-11 and AlPO-41 than AlPO-5 because of their narrower channels. The narrow channels allow CO$_2$ to be at closer proximity to a higher number

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**Figure 2.9** Structural representation of AlPO-41 (AFO). Black lines represent the connections between the metal atoms of the TO$_4$ tetrahedra (where T is a metal atom – Al or P in the case of AlPO). Oxygen atoms are omitted
of framework atoms than in large channels. Therefore, CO$_2$ may interact with more framework atoms in the medium pore AlPOs than AlPO-5.

**Figure 2.10** CO$_2$ adsorption isotherms of AlPO-5, AlPO-11 and AlPO-41
Narrow pore AlPOs: AlPO-17, AlPO-18, AlPO-21, AlPO-25 and AlPO-53 (Paper I)

Narrow pore AlPOs refer to AlPOs with 8-ring pore windows. These 8-ring AlPOs all have different structures. The pore dimensions on these materials are smaller than the large and medium pore AlPOs. The 8-ring pores windows are rather similar in size to the kinetic diameters of CO₂ in N₂. The similar dimensions between the pore windows and kinetic diameter of CO₂ should, in theory, mean that CO₂ and N₂ can be easily separated by a kinetic effect. CO₂ with its smaller effective kinetic diameter should find it easier to enter the porous channels, whereas the larger N₂ would be more hindered from entering the channels. Paper I exclusively discusses these AlPOs as CO₂ adsorbents. Therefore, only a brief summary of the findings will be described here.

These narrow pore AlPOs have similar pore sizes. One of the main differences between them is the number of dimensions that the channels have. AlPO-17 and AlPO-18 both have 3 dimensional channels. AlPO-53 has two dimensional channels and AlPO-21/25 has 1 dimensional channels (note that AlPO-25 is obtained by calcination of AlPO-21 – detailed in Paper I, the structural projection of the two are identical). There is correlation between the dimensionality of the channels and the equilibrium CO₂ uptake at 101 kPa (273 K). AlPO-17 and AlPO-18 shows the highest CO₂ uptake with their 3 dimensional channels. The high uptake is due to the more optimised and effective use of the space within the framework. Although the actual proportion of the “void volume” is not strictly dependent on the dimensionality of the channels, but more on the construction of the framework. For a porous material with 1 or 2 dimensional channels, the framework typically has a higher “void volume” than one with 3 dimensional channels. All of these AlPOs show high preference to take up CO₂ over N₂, but the sieving effect observed for zeolite A is not observed here. The pore sizes on these AlPOs are still too large to effectively eliminate N₂ adsorption.
Figure 2.11 Structural representations of narrow pore 8-ring AlPOs discussed in Paper I, the black lines represent the connections between the metal atoms of the TO₄ tetrahedra (where T is a metal atom – Al or P in the case of AlPOs). Oxygen atoms are omitted.
Silicoaluminophosphate as CO₂ sorbents (Paper II and VIII)

Silicoaluminophosphates (SAPOs) are the second class of phosphates in this study. Here, only SAPOs with H⁺ as charge balancing cations are considered. SAPOs are somewhat similar to zeolites and can adopt zeolite structures. As the name suggests, SAPOs contain covalently connected oxides of aluminium, phosphorus and silicon. The formation of SAPOs is believed to proceed via an AlPO intermediate in which SAPOs form by the replacement of phosphorus atoms on the framework of AlPOs with silicon atom. As a result, SAPOs can also form as 3 dimensional porous structures. The pore sizes can also vary depending on the particular structure type (large, medium and narrow pores). Unlike AlPOs, SAPOs have negatively charged frameworks. The negative charges come from the fact that silicon (IV) atoms are of lower oxidation states than phosphorus (V), hence the oxidation states of the oxygen atoms (-2 net) are not balanced out. The presence of exchangeable cations contribute +1 oxidation state to balance out the unequal framework oxidation (not that this discussion can also be made in terms of charges) and means that SAPOs have higher electrical field gradients than AlPOs and silicas. SAPOs are generally considered to be more similar to zeolites than AlPOs. However, SAPO frameworks are less negatively charged than zeolites.

As explained earlier, the nomenclature for SAPOs (a phosphate type material) is similar to AlPOs. Some structures also exist in both AlPO and SAPO forms. Two notable examples are the ERI (AlPO-17 and H-SAPO-17) and CHA (AlPO-34, and SAPO-34) structures. SAPO-34 can be very easily synthesised and has been extensively studied due to it highly accessible channel system. The presence of exchangeable cations also allows SAPOs to be tested as catalysts. Deroche et al. studied CO₂ adsorption on SAPO-STA (which was first synthesised by Castro et al.). They found that when compared with AlPOs, SAPOs are much more heterogeneous and have higher heat of CO₂ adsorption at low loading.

In this work, one large pore SAPO (H-SAPO-5) and one medium pore SAPO (H-SAPO-11), together with 4 narrow pore SAPOs (H-SAPO-17, H-SAPO-35, H-SAPO-56 and H-SAPO-RHO) have been studied. SAPOs in this study all have H⁺ as the charge balancing cations.

Large pore SAPO: H-SAPO-5 (Paper VIII)

H-SAPO-5, similar to its AlPO counterpart, is one of the most studied of the known SAPO materials. The two materials (AlPO-5 and H-SAPO-5) share the same basic structure (structure code: AFI). H-SAPO-5 has almost iden-
tical pore size as AlPO-5 due to their structural similarity. H-SAPO-5 can be synthesised in many ways with different organic SDAs.

H-SAPO-5 also has large, smooth one dimensional porous channels. The negatively charged framework means that the electrical field gradients of H-SAPO-5 is higher than AlPO-5. These increased electrical field gradients are also reflected by H-SAPO-5’s comparatively higher CO$_2$ uptake (~1.75 mmol/g at 273 K, 101 kPa) than AlPO-5 (1.0 mmol/g under the same conditions) as shown in Figure 2.12. The increased electrical field gradients on H-SAPO-5 are due to the negatively charged framework and the presence of charge balancing cations. The electrical field gradients also have an effect on the shape of the CO$_2$ adsorption isotherm. The CO$_2$ uptake increases more steeply at low pressures of CO$_2$ on H-SAPO-5 than on AlPO-5. At low pressures, CO$_2$ adsorbs close to the cations or where the electrical field gradients are the greatest. These adsorption sites are more energetically favourable. In the case of H-SAPO-5, more of these are available for CO$_2$ sorption, hence increasing the CO$_2$ uptake at low pressures.

![Figure 2.12 CO$_2$ adsorption isotherms of H-SAPO-5 and AlPO-5 at 273 K](image-url)
Medium pore SAPOs: H-SAPO-11 (Paper VIII)

H-SAPO-11 is the SAPO counterpart of AlPO-11. H-SAPO-11 has 10-ring windows with one dimensional channels. As expected, the uptake of CO$_2$ on H-SAPO-11 is slightly higher than that on AlPO-11.

Narrow pore SAPOs: H-SAPO-17, H-SAPO-35, H-SAPO-56 and H-SAPO-RHO (Paper II)

These four SAPO materials all have narrow pore 8-ring windows. H-SAPO-17 is the SAPO version of AlPO-17 (ERI). H-SAPO-17, H-SAPO-35 (Figure 2.13), H-SAPO-56 (Figure 2.13) and H-SAPO-RHO (Figure 2.14) all have 8-rings of very similar dimensions to the kinetic diameters of CO$_2$ and N$_2$. H-SAPO-17, H-SAPO-56 and H-SAPO-RHO all have three dimensional channels, but H-SAPO-35 only has two dimensional channels. As discussed in the AlPO section earlier, CO$_2$ capacity can be enhanced by high channel dimensionality due to the high accessibility and low void volume (space). Out of these four materials, H-SAPO-35 should in theory, have the lowest CO$_2$ uptake. The CO$_2$ adsorption properties of these SAPOs have been discussed in great detail in paper II. Therefore, only a summary of the most important findings will be explored here.

All narrow pore SAPOs included in this study have high CO$_2$ uptake and high CO$_2$/N$_2$ uptake ratios. In particular, H-SAPO-56’s CO$_2$ capacity at 273 K, 101 kPa surpasses that of zeolite 13X (5.5 mmol/g for H-SAPO-56, 5.2 mmol/g for zeolite 13X). The high uptake of CO$_2$ on H-SAPO-56 is partly due to the AFX structure, which has very little void volume (Figure 2.13) and highly interconnected porous channels. The channels in H-SAPO-56 are comparatively more connected than those in other. H-SAPO-RHO (which can also been seen as a cage type SAPO) offers the highest CO$_2$/N$_2$ uptake out of the tested narrow pore SAPOs. The pore sizes of H-SAPO-RHO (0.36 x 0.36 nm) seems to be small enough to hamper N$_2$ adsorption. The details on CO$_2$ adsorption on SAPOs will be discussed in Chapter 4.
Figure 2.13 Structural representation of SAPO-35 and SAPO-56. Black lines represent the connections between the metal atoms of the TO$_4$ tetrahedra (where T is a metal atom – Al, Si or P in the case of SAPO). Oxygen atoms are omitted.

Figure 2.14 Structural representation of SAPO-RHO. Black lines represent the connections between the metal atoms of the TO$_4$ tetrahedra (where T is a metal atom – Al, Si or P in the case of SAPO). Oxygen atoms are omitted.
Titanium silicate (ETS-4, CTS-1) as CO$_2$ sorbents (Paper VI)

Engelhard titanium silicates (ETS), are a class of materials first reported by Engelhard corporation in the early 1990s.$^{82}$ Since then, two major variants have been studied. They are ETS-4 and ETS-10. These titanium silicates are built from covalently connected oxides of titanium and silicon. The connection leads to three dimensional framework structures with porous channels. Although they are similar to zeolites in the sense that they are porous oxide structures, it should be noted that these materials are not zeolites due to the presence of octahedrally coordinated titanium atoms.

ETS-10 is perhaps more studied than ETS-4, which may be due to its higher thermal stability. The two structures are somewhat related. The stacking sequence of the two materials is different. ETS-10 offers 12-ring porous channels in one direction. For ETS-4, stacking faults provide the material with 8-ring porous channel in one direction ($b$-axis) and 12-ring channels perpendicular to the 8-ring channels ($c$-axis).$^{83}$

ETS-10 has been extensively studied for its ion exchange properties and is deemed to be a candidate for heavy metal waste removal in water treatment processes.$^{84, 85}$ As a CO$_2$ adsorbent, ETS-4 can be of greater interest. ETS-4 offers both 12-rings and 8-rings in two different directions, which means it has less void space than ETS-10. Furthermore, many previous studies have shown that the pore sizes can be tuned by ion exchange$^{82, 86, 87}$, dehydration of the framework$^{83, 88, 89}$ or incorporating halogen atoms on to the framework.$^{90}$

Alkaline earth metal exchanged ETS-4 (Paper VI)

The synthesis of ETS-4 is detailed in paper VI. Hydrothermal synthesis yields pure ETS-4 in its Na$^+$ form. Partially Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ exchanged forms of ETS-4 can be easily obtained by ion exchange. All of these titanium silicates are structurally unstable upon dehydration (under heat and/or vacuum) and some can transform to a structure known as contracted titanium silicate (CTS-1). Under the adopted preparation (dehydration) procedures for volumetric adsorption measurements in this study, only NaBa-ETS-4 remains structurally stable. Even under less intense preparation steps, NaMg-, NaCa- and NaSr-ETS-4 are still unstable.

NaBa-ETS-4’s performance as an adsorbent is discussed in paper VI, and only a summary will be given here. NaBa-ETS-4 offers highest CO$_2$ uptake at 273 K, 101 kPa out of all the tested titanium silicates. Unfortunately, the
uptake of N₂ is also the highest and comparable to zeolite NaA. There is also significant amount of chemisorption on NaBa-ETS-4, which lowers the cyclic performance of this material.

![Diagram of titanium silicate ETS-4](image)

**Figure 2.15** Structural representation of titanium silicate ETS-4. The lines represent the connections between the framework atoms, Si-O bonds are represented in black and Ti-O bonds in grey.

Under the experimental procedures adopted in this study, the other titanium silicates cannot be tested as CO₂ adsorbents in the ETS-4 form. NaMg-, NaCa- and NaSr-ETS-4 transformed into NaMg-, NaCa- and NaSr-CTS-1 during the sample preparation steps. These various forms of CTS-1 are still porous. They are essentially slightly contracted versions of the ETS-4 materials. The CO₂ uptake of all three forms of CTS-1 is reasonably high, with NaMg-CTS-1 being the highest (around 2 mmol/g) at 101 kPa (273 K). NaMg-CTS-1 also has very low N₂ uptake. The high CO₂/N₂ uptake is due to
the smaller Mg$^{2+}$ cation, which has less ability to stabilise the framework. The low framework thermal stability allows the easy fine tuning of the pore size by heating and dehydration. There is a relationship between the heating temperature and the final effective pore size. The other cations can stabilise the framework more than Mg$^{2+}$ at moderate dehydration temperature. Therefore, it is harder to tune the pore size of NaCa- and NaSr-ETS-4 than NaMg-ETS-4 at these temperatures (up to 473 K). To further reduce/tune to pores for effective CO$_2$ separation, the dehydration temperature needs to be increased, however, the crystallinity of the material is significantly reduced at higher temperatures. This would unavoidably reduce the CO$_2$ uptake.
3. CO₂ sorbent for flue gas - CO₂ capture

CO₂ sorbent showdown: zeolites, phosphates and silicates

In Chapter 1, some properties of an “ideal adsorbent” have been highlighted. A perfectly ideal adsorbent should at least show that it has high CO₂ capacity, high CO₂ selectivity, be easy to regenerate, have a long lifetime, a high thermal and mechanical stability, low cost of production and is hydrophobic. In an efficient CO₂ capture process that uses adsorbents, these properties are all of great importance. Many different kinds of microporous adsorbents have been tested here. Chapter 2 has given a short summary of how the different adsorbents perform as CO₂ adsorbents. A list of all the tested sorbents can be found in Table 3.1 below.

This chapter will examine the performance of these adsorbent and make comparisons between them. Different properties of these adsorbents will be compared. The comparisons will hopefully give an overall picture of the advantages and drawbacks of the adsorbents considered here. In this chapter, only the separation of CO₂ from a hypothetical flue gas (which consists mainly of N₂) will be considered.

Table 3.1. List of all of the sorbents tested in this study, the detail can be found in: a) Paper III, b) Paper IV and V, c) Paper VIII, d) Paper I, e) Paper II, f) Paper VI

<table>
<thead>
<tr>
<th>Sorbent type</th>
<th>Zeolite</th>
<th>Alumino-phosphate</th>
<th>Silico-aluminophosphate</th>
<th>Titanium silicates</th>
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<td>Sorbent</td>
<td>NaA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>AlPO-5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>H-SAPO-5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>NaBa-ETS-4</td>
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<td></td>
<td>NaKA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>AlPO-8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>H-SAPO-11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>NaMg-CTS-1</td>
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<tr>
<td></td>
<td>Na-ZK-4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AlPO-11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>H-SAPO-17&lt;sup&gt;e&lt;/sup&gt;</td>
<td>NaCa-CTS-1</td>
</tr>
<tr>
<td></td>
<td>NaK-ZK-4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AlPO-17&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>NaSr-CTS-1</td>
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<tr>
<td></td>
<td>AlPO-18&lt;sup&gt;d&lt;/sup&gt;</td>
<td>AlPO-21/25&lt;sup&gt;d&lt;/sup&gt;</td>
<td>H-SAPO-56&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>AlPO-41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>AlPO-53&lt;sup&gt;d&lt;/sup&gt;</td>
<td>H-SAPO-RHO&lt;sup&gt;e&lt;/sup&gt;</td>
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</table>
CO₂ uptake and selectivity

CO₂ uptake is most probably the first thing to be considered when choosing an adsorbent. An adsorbent with high uptake of CO₂ will be able to remove more CO₂ per adsorption cycle than an adsorbent with low CO₂ uptake. A high CO₂ capacity would speed up the process and reduce the cost of CO₂ removal. The CO₂ adsorption isotherms of the two adsorbents with the highest CO₂ capacity (from each type of adsorbent) at 101 kPa (273 K) are presented in Figure 3.1. All CO₂ isotherms have been recorded under the same conditions for a fair comparison.

Figure 3.1. CO₂ adsorption isotherms (273 K) of the materials that showed the highest CO₂ uptake under each adsorbent type: a) zeolites: NaA and Na-ZK-4 (Si:Al = 2.8:1), b) aluminophosphates: AlPO-17 and AlPO-53, c) silicoaluminophosphates: H-SAPO-56 and H-SAPO-35, d) Titanium silicates: NaBa-ETS-4 and NaMg-CTS-1, data reproduced from Paper I, II, III, IV, VI
H-SAPO-56 has the highest CO\textsubscript{2} uptake out of all the adsorbents tested in this entire study. If an adsorbent is to be chosen because of its CO\textsubscript{2} capacity at 101 kPa (273 K), H-SAPO-56 will no doubt be the best option. The uptake of CO\textsubscript{2} reaches 5.5 mmol/g at 273 K, 101 kPa. This level of CO\textsubscript{2} uptake is higher than that of the commercially available zeolite 13X material. Zeolite 13X has a CO\textsubscript{2} uptake of 5.3 mmol/g under the same conditions (Paper II). Of the LTA type zeolite adsorbents, Na-ZK-4 and NaA have the highest CO\textsubscript{2} uptake. The CO\textsubscript{2} uptakes of these two zeolites are 4.8 and 4.5 mmol/g, respectively. These two adsorbents are the runner-ups behind H-SAPO-56. The top two AlPOs and the titanium silicates have significant CO\textsubscript{2} adsorption capacity (around 2.0 mmol/g), but still noticeably lower than H-SAPO-56 and the LTA type zeolites.

The high uptake of CO\textsubscript{2} on H-SAPO-56 is due to the way the channels are laid out. As discussed in Chapter 2, the channel system in H-SAPO-56 gives the material very little void volume, the channels are also very well interconnected. The porosity towards CO\textsubscript{2} is therefore very high, giving this material very high CO\textsubscript{2} uptake. In the case of zeolite A, porous channels are built on connecting cages. The cages have windows of molecular dimensions and are well connected in 3 directions. The high channel dimensionality means CO\textsubscript{2} can diffuse easily into and inside the framework of zeolite A. Furthermore, the framework negative charges and the presence of a large number of cations (96 in NaA, ~50 in Na-ZK-4 with Si:Al = 2.8:1, per unit cell) gives zeolite A a high electrical field gradients. The cations themselves have high polarisation strength. The high polarisation strength of the cations can increase the polarity of CO\textsubscript{2}. The induced polarity means that CO\textsubscript{2} interaction with the electric field of the zeolite is increased. The electrical field gradients also interact strongly CO\textsubscript{2} due to the presence of a quadrupole moment. Both of these types of interactions give the zeolite A enhanced CO\textsubscript{2} uptake. The lower CO\textsubscript{2} uptake observed on AlPOs may be due to the nature of a neutral framework. The difference between a charged and a neutral framework can be observed from the CO\textsubscript{2} adsorption isotherms of AlPO-17 and H-SAPO-17. The two materials have the same basic structure and should have very similar porosity. This has been confirmed by nitrogen surface area measurements (Figure 3.2). Figure 3.3 shows these CO\textsubscript{2} adsorption isotherms which were recorded at 273 K. The single site Langmuir isotherm model describes the isotherms well (R\textsuperscript{2}>0.999) and the modelled theoretical maximum CO\textsubscript{2} uptake on AlPO-17 and H-SAPO-17 are 4.00 mmol/g and 4.27 mmol/g, respectively. The higher theoretical maximum uptake on H-SAPO-17 can be related to the higher electrical field gradients of H-SAPO-17 and the presence of charge balancing cations. Similar observations have been noted between AlPO-5 and H-SAPO-5, AlPO-11 and H-SAPO-11 (Table 3.2). It is important to note than the SAPOs tested here all have H\textsuperscript{+} as charge balancing cation. The polarisation strength of H\textsuperscript{+} is much lower than
metal cations (for example, Na$^+$) as indicated by their respective charge densities.

![Graph](image)

**Figure 3.2.** Nitrogen adsorption (77 K) of AlPO-17 (top) and H-SAPO-17 (bottom), the calculated Langmuir surface areas of AlPO-17 is ~ 645 m$^2$/g and ~ 601 m$^2$/g for H-SAPO-17
Figure 3.3. CO₂ adsorption isotherm of AlPO-17 (red) and H-SAPO-17 (black) at 273 K, data reproduced from Paper I and Paper II.

The CO₂ adsorption isotherms show that the CO₂ capacity of H-SAPO-17 is around 1.0 mmol/g higher than AlPO-17 at 101 kPa (273 K). The higher CO₂ uptake on H-SAPO-17 can also be related to the higher electrical field gradients of the charged framework. This effect can be especially profound at low relative pressures of CO₂ (p/p₀ = 0.02 at 101 kPa, 273 K) as CO₂ adsorbs first on high energy sites⁴⁹, which are more available than the other sites on SAPOs. Deroche et al.⁷⁸ have found that the heterogeneity of SAPOs is much higher than AlPOs. CO₂ essentially sees AlPOs as highly homogenous. The heat of CO₂ adsorption on SAPOs is also high due to the heterogeneity and the presence of high energy sites. Paper II shows the heats of CO₂ physisorption of H-SAPO-56 and H-SAPO-RHO are around ~30-35 kJ/mol (from close to zero and up to 0.8 mmol/g loading). The heat of CO₂ physisorption on AlPO-17 is around 21 kJ/mol (calculated with CO₂ isotherms presented Paper I using the Clausius–Clapeyron equation – calculation and data not shown). In short, AlPOs have lower CO₂ uptake than SAPOs, this is mainly due to the neutral AlPO framework. The neutral framework gives AlPOs a homogenous surface. The lack of charge balancing cations also reduces the electrical field gradients of AlPOs and eliminates the presence of high energy CO₂ adsorption sites.
The CO₂ uptake on titanium silicates included in this study is not as high as the zeolite A and SAPOs. Out of the tested titanium silicates, NaBa-ETS-4 has the highest CO₂ uptake. The comparatively lower CO₂ uptake on NaBa-ETS-4 than zeolites and SAPOs is partly due to the porous channels that are interconnected with less number of dimensions than those found in zeolite A and some of the phosphates. The channels in NaBa-ETS-4 and the tested CTS-1 adsorbents are maximum two dimensional only, the highly common stacking faults also means that some of the 12-ring channels can be blocked. As a result, the CO₂ uptake of the material decreases. Paper VI discusses the structural aspects of the titanium silicate CTS-1 and how they transform from ETS-4s. The transformation can induce significant structure defects. The defects can reduce the porosity of these adsorbents and hence reducing their CO₂ uptake.

**CO₂ selectivity**

The CO₂ selectivity of the adsorbents must also be considered. High CO₂ selectivity means that the captured CO₂ would be pure and that the CO₂ capacity will not be compromised by the adsorption of other gases. The selectivity of CO₂ can usually be estimated using the ideal adsorbed solution theory (IAST). However, the ideal adsorbed solution theory is a thermodynamic model. The theory assumes that the thermodynamics of the adsorption is ideal. The separation of CO₂ on the adsorbents tested is partly because of kinetic separation. The adsorption rate of N₂ can be very slow on the adsorbents tested here. The slow rate of adsorption is not accounted for by IAST and hence may overestimate the CO₂ selectivity in application. The IAST model is not developed for out-of-equilibrium situations, it can only be used qualitatively if the uptake rate of a gas is slower than the time needed to operationally obtain an adsorption isotherm.

Throughout this study, the adsorption points (quantity of gas /vapour adsorbed at a specific pressure) CO₂ and N₂ adsorption isotherms were recorded when the change in pressure of the experimental setup fell below 0.01% per 10 seconds (equilibration time), with a minimum 100 second delay. These isotherms, especially the N₂ adsorption isotherms for adsorbents with low apparent N₂ uptake, may show slightly higher N₂ uptake equilibration time is increased extensively (due to the slow adsorption rate of N₂). The N₂ uptakes of the adsorbent in presented Table 3.2 are operationally defined for the experimental procedures adopted. As VSA/PSA process are dynamic with relatively short cycle times, these N₂ uptake can still give a good idea of how selective the adsorbents are under real application, although the true selectivity may different from the values in Table 3.2. The comparison of CO₂ selective in this study is qualitative and not quantitative.
CO₂ selectivity of an adsorbent can be conservatively defined as the simple ratio between the uptake of CO₂ and the uptake of N₂ at 101 kPa (1 atmosphere). This definition has been adopted in some of the papers include in this thesis. For the comparison of the sorbents in this study, a more common definition of CO₂ selectivity will be used in this section. The CO₂ selectivity is defined as \( s = \frac{q_{\text{CO}_2}}{q_{\text{N}_2}} \frac{p_{\text{N}_2}}{p_{\text{CO}_2}} \), \( s \) is referred to as the separation factor (referred to as “selectivity” here) \( p_x \) represents the partial pressure of component \( x \) in the mixed gas stream, \( q_x \) is the amount of uptake of component \( x \) at pressure \( p_x \), using the data from pure gas adsorption isotherms. \(^{92, 93}\) This definition of selectivity is operationally defined. The hypothetical flue gas mixture is assumed to have a CO₂ partial pressure \( (p_{\text{CO}_2}) \) of 15 kPa and N₂ partial pressure \( (p_{\text{N}_2}) \) of 85 kPa. To calculate the separation factor \( (s) \), the uptake of CO₂ at 15 kPa is used as \( q_{\text{CO}_2} \), and the uptake of N₂ at 85 kPa is used as \( q_{\text{N}_2} \).

Table 3.2 lists the CO₂ uptake, N₂ uptake and the selectivity is defined as \( s = \frac{q_{\text{CO}_2}}{q_{\text{N}_2}} \frac{p_{\text{N}_2}}{p_{\text{CO}_2}} \) for the adsorbents include in this study. It is important to note that the data presented are for adsorption at 273 K, the adsorption temperature of flue gas is typically around 323 K. \(^{94}\) Therefore, the comparison only serves to give an idea of the true CO₂ selectivity under real application.
Table 3.2 CO₂, N₂ uptake and CO₂/N₂ selectivity of adsorbents in this study at 273 K, selectivities are calculated using $p_{\text{CO}_2}=15$ kPa and $p_{\text{N}_2}=85$ kPa, $q_{\text{CO}_2} = (\text{CO}_2 \text{ uptake at 15 kPa})$, $q_{\text{N}_2} = (\text{N}_2 \text{ uptake at 85 kPa})$ data shown with 2 significant figures, data reproduced from Liu et al. 66, Paper I, II, IV, V, VI

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>CO₂ uptake mmol/g (101 kPa)</th>
<th>N₂ uptake mmol/g (101 kPa)</th>
<th>CO₂ uptake mmol/g (15 kPa)</th>
<th>N₂ uptake mmol/g (85 kPa)</th>
<th>CO₂/N₂ selectivity (s)</th>
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<tr>
<td>Zeolite A</td>
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*data not recorded
Table 3.2 (continued) CO$_2$, N$_2$ uptake and CO$_2$/N$_2$ selectivity of adsorbents in this study at 273 K, selectivities are calculated using $p_{co2}=15$ kPa and $p_{N2}=85$ kPa, $q_{co2} =$ (CO$_2$ uptake at 15 kPa), $q_{N2} =$ (N$_2$ uptake at 85 kPa) data shown with 2 significant figures, data reproduced from Liu et al. 66, Paper I, II, IV, V, VI

<table>
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<th>Adsorbent</th>
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<tr>
<td>NaMg-CTS-1</td>
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<td>2.1</td>
<td>0.57</td>
<td>21</td>
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</tbody>
</table>
Table 3.2 shows that some of the zeolite A and zeolite ZK-4 offer the highest CO\textsubscript{2} selectivities out of the range of adsorbents tested here (up to \( s \approx 2000 \) for NaK-ZK-4 with Si/Al = 2.8 and K\(^+\) = 36 at.% of the cations). These adsorbents separate CO\textsubscript{2} from N\textsubscript{2} using the molecular sieving (kinetic) effect. The very low N\textsubscript{2} uptake indicates that N\textsubscript{2} is excluded from entering the pores of these adsorbent. The ion exchanged zeolite NaKA and NaK-ZK-4 with different Si:Al ratios and different K\(^+\) contents can very effectively adsorb CO\textsubscript{2} over N\textsubscript{2}. Even though these highly selective sorbents also have pores that are very similar in size to the kinetic diameter of CO\textsubscript{2}, Paper III, IV and V show that the CO\textsubscript{2} physisorption kinetics on these highly selective adsorbents can still be considered for swing adsorption processes. For NaKA with 17 at.% K\(^+\) cations, up to 80\% of the equilibrium physisorption CO\textsubscript{2} capacity can be reached in around 130s (Paper III). Furthermore, all of these highly selective zeolites offer very high CO\textsubscript{2} uptake at 101 kPa. These ion exchanged zeolites are the probably the best if an adsorbent is to be chosen based on CO\textsubscript{2} adsorption capacity and selectivity.

After the zeolites, AlPO-53 offered the highest CO\textsubscript{2} selectivity out of the other tested sorbents (\( s \approx 170 \)). N\textsubscript{2} uptake on AIPO-5, AIPO-11, AIPO-25 and AIPO-53 is very low. The low N\textsubscript{2} uptake on AIPO-25 and AIPO-53 can perhaps be the result of molecular sieving. In the case of AIPO-5 and AIPO-11, the low N\textsubscript{2} uptake can be due to the large and smooth pores. A large pore means that the sorbate molecules do not adsorb at low relative pressures. The sorbate molecules are also less “surrounded” by the framework atoms, resulting in a low adsorbent-sorbate interaction. This same explanation may also be used for the low CO\textsubscript{2} uptake on AIPO-5 and AIPO-11. In general, the CO\textsubscript{2} uptake on AIPOs is also comparatively lower than the other types of adsorbents tested.

SAPOs offer high CO\textsubscript{2} capacity and significant CO\textsubscript{2} selectivity, but N\textsubscript{2} uptake is clearly detectable on H-SAPO-17, H-SAPO-35 and H-SAPO-56. N\textsubscript{2} is not blocked from entering the pores of these SAPOs. The detectable uptake of N\textsubscript{2} but high preferential CO\textsubscript{2} uptake is an example of kinetic separation of CO\textsubscript{2} from N\textsubscript{2}. In this case, the CO\textsubscript{2} physisorption should be very fast, perhaps similar to the rapid CO\textsubscript{2} uptake observed on non K\(^+\) exchanged zeolite NaA or Na-ZK-4 (Paper III, IV and V). H-SAPO-5 and H-SAPO-11 both have very low N\textsubscript{2} uptake. The same explanation that is used for AIPO-5 and AIPO-11 is also applicable here. H-SAPO-5 and H-SAPO-11 have higher CO\textsubscript{2} uptake than their AIPO equivalents. The higher uptake on SAPOs than AlPOs with the same structure has already been discussed in this section.

Titanium silicate NaMg-CTS-1 also seems to selectively adsorb CO\textsubscript{2} with reasonably high selectivity (\( s \approx 70 \)). The CO\textsubscript{2} uptake on NaMg-CTS-1 is not
spectacularly high and N\textsubscript{2} uptake is clearly detectable. Overall, in the case of CO\textsubscript{2} separation where high CO\textsubscript{2} capacity and high selectivity are the main requirements, it seems that zeolites and SAPOs showed superior properties over the other adsorbent tested.

**Hydrophilicity**

The hydrophilicity of the sorbents is also of great importance, as discussed in Chapter 1, adsorption of water will compromise the CO\textsubscript{2} capacity of the adsorbent. In this study, the water sensitivity of the adsorbents has been investigated by the means of water vapour adsorption at 293 K. **Figure 3.4** shows the water adsorption isotherm of some zeolites and phosphates.

![Water vapour adsorption isotherm of zeolite NaA, AlPO-53 and H-SAPO-56 at 293 K, the saturation pressure (p/p\textsubscript{0} = 1) of water at this temperature is 2.3 kPa, data reproduced from Paper I, II and V](image)

When a water adsorption isotherm shows that the uptake of water does not rise sharply at very low relative pressure, the adsorbent can be consider as mildly hydrophilic. AlPO-53, as well as other AlPOs, are less hydrophilic than zeolites (Paper I). Under moist conditions, AlPOs will be the least affected out of all tested adsorbents. H-SAPO-56 is clearly less hydrophilic than zeolite NaA, judging by the shape of the isotherms in the Henry’s law
region (low relative pressures), the Henry’s law constant (gradient of the slope) for the uptake of water on H-SAPO-56 is smaller than that of zeolite NaA. The total water uptake is the highest of the three on H-SAPO-56, but this high water uptake is related to the material’s porosity and not directly related to the material’s hydrophilicity. Zeolite NaA and titanium silicates are generally known to be extremely hydrophilic, due to the highly negatively charged frameworks and the large number of charge balancing cations. The hydrophilicity of a zeolite adsorbent is related to the number of Al atoms (or metal charge balancing cations). The CO₂ capacity of these adsorbents will be negatively affected by the adsorption of water. Out of all of the tested sorbents, AlPOs will be the least affected by the presence of moisture.

**Cyclic capacity**

Cyclic capacity (at 101 kPa) is defined here as the CO₂ uptake of the adsorbent after a number of adsorption-desorption cycles without the full regeneration of the sorbent. Full regeneration of the adsorbent requires heat to be applied during the desorption step. In this case, vacuum regeneration is adopted at room temperature. High cyclic capacity is important for adsorption based CO₂ removal process. If the adsorbent is able to retain its CO₂ capacity even after many cycles, it will have a long lifetime.

Adsorbents can lose their CO₂ capacity due to the formation of chemisorbed CO₂, CO₂ entrapment or the loss of porosity/crystallinity. On zeolites, chemisorption of CO₂ usually form coordinated carbonates around the cations of the material. They are energetically favourable if the temperature is not high. It is difficult to remove CO₂ at room temperature, high energy (heat) is required to break the carbonate/framework bonds. CO₂ entrapment can be caused by very narrow pore windows. These narrow windows can hinder the diffusion of CO₂ out from the pores. The entrapped CO₂ can typically be removed by applying low heat to the material.

If the CO₂ capacity of the adsorbent reduces with the increased number of cycles, the lifetime of the adsorbent will be shortened. The full CO₂ capacity may be restored by full regeneration in some cases. Full regeneration will no doubt be energy demanding and expensive. Therefore, an adsorbent that has very little loss in CO₂ capacity under cyclic conditions is desirable. Figure 3.5 shows how the different adsorbents perform under cyclic conditions. The first cycle CO₂ uptake represents the full capacity of the freshly prepared (heat and vacuum) sample.
Figure 3.5 Cyclic CO₂ adsorption capacity of the different types of sorbents, one example of each sorbent is given in this figure. The adsorbents were regenerated only by dynamic vacuum (1 × 10⁻⁴ Pa) at room temperature for 90 minutes between cycles, no heat was applied. Data reproduced from Liu et al., Paper I, II, III, IV, VI.

The neutral framework AlPOs have almost no loss in CO₂ adsorption capacity under these conditions even after 5 cycles (Figure 3.5 and Paper I). This means that neither the chemisorption of CO₂ nor the entrapment of CO₂ occur on AlPOs. CO₂ is not strongly adsorbed on AlPOs. There is also no loss in the porosity of the material, as the CO₂ uptake remained very much unchanged. These adsorbents can potentially have very long lifetime in practice.

SAPOs lose a small portion of the CO₂ sorption capacity after 5 cycles. The loss in CO₂ capacity is related to the small amount of chemisorption of CO₂ as identified by infrared (IR) spectroscopy (Paper II). The SAPOs in this study can retain around 95% of their original capacity after 5 cycles. In the case of H-SAPO-56, 95% of the original CO₂ capacity corresponds to over 5 mmol/g (101 kPa 273 K). When compared to AlPO-53 (given as the exam-
ple in Figure 3.5), the uptake of H-SAPO-56 after 5 adsorption cycles is still more than twice that of AlPO-53 (uptake after 5 cycles = 1.9 mmol/g).

The other adsorbents all show a drop in the CO$_2$ capacity after the first adsorption cycle. Zeolite NaA shows a drop in the CO$_2$ capacity of over 35% after the first cycle. The highly selective NaKA (17 at.% K$^+$) responds similarly. The drop is mainly due to the formation of chemisorbed CO$_2$, which has been identified by some previous literature$^{49,99}$ as well as the work of Paper III. It is important to note that CO$_2$ entrapment is also possible in these narrow pore adsorbents, as shown by Shang et al. on chabazite.$^{73,74}$ The chemisorbed CO$_2$ cannot be removed by vacuum at room temperature and has reduced the CO$_2$ uptake in subsequent adsorption cycles. After 5 cycles, the uptake of CO$_2$ on NaA has gone down to 2.3 mmol/g. On zeolite Na-ZK-4 (Si:Al=1.3:1), the CO$_2$ uptake after 5 cycles is only around 8% less than the original CO$_2$ uptake. Chemisorption of CO$_2$ does not occur to the same extend on this high silicon zeolite. This is because of the high Si content, which reduces the number of cations on the framework. When the number of cations on a zeolite adsorbent is lowered, CO$_2$ can diffuse more easily into and within the porous channels (fewer large metal cations close to the pore windows). As a result, CO$_2$ entrapment is less likely to occur. Chemisorption is still detectable on zeolite ZK-4 with a Si:Al ratio up to 2.8:1 (Paper IV and V) due to the presence of some cations. However, the amount of chemisorbed CO$_2$ that forms on ZK-4 with high Si:Al ratios is minute. The small amount of chemisorption is shown by the high cyclic capacity as well as the differential IR spectra of these zeolites upon CO$_2$ adsorption (Paper IV and V). The partially K$^+$ exchanged NaK-ZK-4 shows a decreased cyclic CO$_2$ capacity, especially the highly selective forms (Paper IV). The decrease is due to the reduced pore size limiting the diffusion of CO$_2$ out of the pores during desorption. The problem can be overcome by heating the sorbent to 343 K under vacuum.

Titanium silicate NaMg-CTS-1 loses part of its CO$_2$ capacity after each adsorption-desorption cycle. The loss can be related to the largely defected nature of the NaMg-CTS-1. A significant amount of chemisorption can also be detected on NaMg-CTS-1 (Paper VI). Some of the chemisorbed CO$_2$ forms very slowly and may still be forming after the first cycle, which further decreases the CO$_2$ capacity of the material. After 5 cycles, around 30% of the CO$_2$ has been lost. More importantly, even after full regeneration, the original CO$_2$ capacity of NaMg-CTS-1 cannot be recovered. The permanent loss of CO$_2$ capacity is probably related to how CO$_2$ may “heal” the defects of NaMg-CTS-1 (Paper VI), which in turn may block the pores of the material.
The phosphates (AlPOs and SAPOs) show the lowest capacity lost under cyclic conditions out of the tested adsorbents. These adsorbents should in theory, have the longest sorbent life time. H-SAPO-56 also offers very high CO₂ uptake even after 5 cycles, as well as reasonable CO₂ selectivity.

**Working capacity**

![Graphs](https://via.placeholder.com/150)

**Figure 3.6** CO₂ adsorption isotherms between 0 and 20 kPa (273 K) of a selected range of sorbents, a) NaKA and NaK-ZK-4, b) AlPO-53 and H-SAPO-56, c) NaMg-CTS-1, the adsorption isotherms are recorded after 1 cycle of CO₂ adsorption-desorption with a maximum CO₂ pressure of 101 kPa (273 K), data reproduced from Liu et al.⁶⁶, Paper I, II, IV, VI

When choosing an adsorbent, it is not sufficient to only consider the uptake of CO₂ at one pressure point. This is because under pressure/vacuum swing adsorption processes, the pressure of the system changes continuously. Adsorption should occur at a high pressure, and desorption should take place spontaneously when the pressure is lowered. It is important that the sorbent can offer a high “swing adsorption capacity”. In fact, swing adsorption capacity can perhaps be more important than the equilibrium CO₂ capacity considered before.
Table 3.3 Working capacity (defined as the equilibrium CO\(_2\) uptake at 15 kPa minus that at 1 kPa) of the sorbents. The precise CO\(_2\) uptake at 1 kPa and 15 kPa is calculated by modelling the CO\(_2\) adsorption isotherms using the two-site Langmuir isotherm model. Working capacities between 10 and 100 kPa are also listed for comparison.

<table>
<thead>
<tr>
<th>Sorbent type</th>
<th>Sorbent name</th>
<th>“Working capacity” (between 1-15 kPa, mmol/g)</th>
<th>“Working capacity” (between 10-100 kPa, mmol/g)</th>
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<tbody>
<tr>
<td>Zeolite</td>
<td>NaKA</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>NaK-ZK-4 Si/Al=1.3 (28 at. % K(^+))</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>A IPO</td>
<td>AlPO-53</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>SAPO</td>
<td>H-SAPO-56</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Titanium silicate</td>
<td>NaMg-CTS-1</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

To judge an adsorbent’s potential working capacity, the shape of the CO\(_2\) isotherms must be considered. For flue gas CO\(_2\) removal, the benchmark experiment considers that the source gas has a feed pressure of 130 kPa, with a blow down (desorption/regeneration pressure of 10 kPa). With ~15% CO\(_2\) content, the partial pressure of CO\(_2\) will be around 15-20 kPa at the gas feed and around 1 kPa during desorption. For the purpose of comparison, the CO\(_2\) uptake at a low partial pressure, 15 kPa, will be considered. It is important to note that this comparison is done one data recorded at 273 K. CO\(_2\) removal from flue gas power plants will usually operate at a higher temperature. Nevertheless, this comparison is able to give an idea of which of the adsorbents may have high working capacity under real application. Figure 3.6 shows the CO\(_2\) adsorption isotherm between 0 – 20 kPa (273 K) for a selected range of adsorbents (selected based on their performance as discussed so far). Note that the isotherms only show physisorption of CO\(_2\) (recorded after the first adsorption cycle and without regeneration by heat).

Regardless of the pressure range considered, H-SAPO-56 offers the highest CO\(_2\) working capacity up to 101 kPa (Table 3.3). The high CO\(_2\) capacity is reflected by the gentle CO\(_2\) adsorption isotherm on H-SAPO-56 (Figure 3.1). When the flue gas pressure (where CO\(_2\) partial pressure goes in between 1 – 15 kPa) is considered, then zeolite NaKA and NaK-ZK-4 also provide high working capacity (Table 3.3). When the pressure range is expanded to between 10 and 100 kPa, AlPO-53’s working capacity becomes higher than that of the zeolites. The low working capacity of AlPO-53 at low
pressure range is due to the low electrical field gradients of AlPOs. CO₂ adsorption at these low pressures is energetically favoured in materials with high electrical field gradients, such as NaKA, NaK-ZK-4 and H-SAPO-56. It is important to note that the electrical field gradients on H-SAPO-56 are lower than the zeolites. The high electrical field gradients on zeolites are reflected by the low working capacity when the pressure range considered is changed to 10-100 kPa. Zeolites with their high electrical field gradients favour the adsorption of CO₂ even at low pressures. As a result, the adsorption sites are crowded even at low pressures. The early occupation of the adsorption sites means that the working capacities of zeolite A and ZK-4 becomes lower when compared with H-SAPO-56. On H-SAPO-56, the occupancy of the adsorption sites increase steadily with increasing CO₂ pressure. The high electrical field gradients of an adsorbent, such as that observed on zeolite A, can also be used to explained the low working capacity of NaMg-CTS-1. The highly negatively charged framework of NaMg-CTS-1 and the large number of metal cations mean that the CO₂ adsorption saturates the material and a relatively low pressure, lowering the working capacity of the this sorbent in the pressure difference range of typical PSA/VSA application.

Out of the tested adsorbents, NaK-ZK-4 and H-SAPO-56 offer the two highest CO₂ working capacities at the pressure range relevant for CO₂ removal from a flue gas stream. Should another process require a larger pressure range (e.g. biogas upgrading), H-SAPO-56 or even AlPO-53 are likely to perform better than NaK-ZK-4 in terms of CO₂ working capacity.

**Cost of production/synthesis**

Should an adsorbent be used to removal CO₂ from point sources, a large quantity of it is required. The production of a large quantity of sorbent is associated with a cost. The cost of the sorbent is directly related to the cost of CO₂ removal as highlighted in Chapter 1. Of course, a detailed cost effective analysis is required should an adsorbent be chosen based on the cost of the material. Detailed economic analysis should account for the efficiency (which is related to the adsorbent’s CO₂ capacity, CO₂ selectivity, cyclic capacity, rate of CO₂ adsorption etc) of the adsorbent as well as its production cost. Such analysis is outside the scope of this thesis. The cost of a typical CO₂ capture system that works on VSA process can be divided into capital cost and operational cost. The cost of adsorbent is the second largest operational cost in a typical VSA CO₂ removal system.¹⁵

One simple idea is that for a cost effective process, the adsorbent should have a low cost. The comparison in this section is aimed only to give an idea
of the cost of the sorbents. The actual cost of synthesis on a large scale is not considered.

Zeolite A has the lowest cost out of the adsorbents tested in this study, it can be purchased in large quantities from commercial suppliers at very low costs (~2 USD/kg from Xi'an Lvneng Purification Technology Co., Ltd. China). Zeolite A can also be synthesised without the use of expensive chemical or organic SDAs. The cost of production is much higher for the other adsorbents. The synthesis of ETS-4 requires a titanium source, which can be expensive when compared with an Al source needed for zeolite A synthesis. Zeolite ZK-4, all AlPOs and SAPOs require organic SDAs for their syntheses. The cost of the organic template can be as high as 2000 USD/L. In the case of H-SAPO-56, the cost of its organic template, \(N,N,N',N'\)-tetramethyl-1,6-hexanediamine (TMHD), costs around 2000 USD/L (SigmaAldrich, Sweden). This quantity (1L) would provide around 290 g of H-SAPO-56 according to the synthesis procedures listed in Paper II. The cost of synthesising 1 kg of H-SAPO-56 will therefore be over 6900 USD. When compared to zeolite A (~2 USD/kg), H-SAPO-56 is much more expensive as a CO\(_2\) adsorbent. A typical VSA system for CO\(_2\) removal can have adsorbers with total internal volume of over 600 m\(^3\). In order to fill these adsorbers once, over 600 tons of the adsorbent is required (density of packed zeolite A is around 1g/cm\(^3\), the density of H-SAPO-56 is assumed be similar). The difference in the cost of the adsorbents becomes extremely large. H-SAPO-56 and many other adsorbents tested in this study have shown great potentials to be CO\(_2\) adsorbents. In order to implement their use as adsorbent in practice, a cheaper way to obtain them must be developed in order to make their use cost effective. From a scientific point of view, there is no doubt that these adsorbents are good candidates for CO\(_2\) removal from point sources \textit{via} adsorption processes.
4. Highly selective CO₂ adsorbent for biogas upgrading

A specific group of zeolites have also been tested as CO₂ adsorbents in biogas upgrading PSA processes. This section will examine their potentials for CO₂ removal from biogas where CO₂ is in a mixture with mainly CH₄. The zeolite adsorbents tested are NaA, NaKA, NaCsA and NaKCsA (Paper VII).

CO₂ Selectivity

One of the most important features of a good CO₂ sorbent for biogas upgrading is high selectivity. As discussed in Chapter 1, co-adsorption of methane contributes towards the methane slip and should be kept to a minimum. If CH₄ is co-adsorbed with CO₂, there will be CH₄ (a greenhouse gas) being released into the atmosphere. This also wastes combustible fuel. For the purpose of this comparison, biogas is assumed to have a feed pressure of 100 kPa, the temperature of the gas is close to room temperature and that the gas contains a 50:50 volume mixture of CO₂ and CH₄. The CO₂ and CH₄ adsorption capacity and the CO₂ selectivity of the different zeolite A adsorbents tested are listed in Table 4.1, the data shown is for CO₂ and CH₄ adsorption at 293 K. The calculated selectivity therefore only serves to give an idea of the true selectivity in real application, where the feed gas temperature and pressure may be different. Selectivity of the sorbents are calculated using $s = (q_{CO₂}/q_{CH₄})/(p_{CO₂}/p_{CH₄})$, where $p_{CO₂}=50$ kPa, $p_{CH₄}=50$ kPa, $q_{CO₂}$ = CO₂ uptake at 50 kPa and $q_{CH₄}$ = CH₄ uptake at 50 kPa.

Zeolite A containing some bigger cations (instead of Na⁺) shows enhanced CO₂ selectivity. The presence of cations larger than Na⁺ (for example: K⁺ or Cs⁺) effectively reduces the pore size of the zeolite, hence increasing the selectivity for the smaller CO₂ (3.3 Å) molecule (when compared with CH₄-3.8 Å). During ion exchange, the large cations first replace Na⁺ that are situated in the 6-ring.⁶⁶ Having large cations in the 6-ring would reduce the effective pore size of the zeolite due to its close proximity to the 8-ring window. Note that in this study, the number of the large cations has been kept low in order not to reduce the pore size of the zeolites too much. In the case of the dual-cation zeolite A (NaKA, NaCsA), NaKA with approximately 17 at.% the cations being K⁺ (83 at.% being sodium) shows the highest CO₂/CH₄ selectivity of ~230. NaCsA also shows the ability to exclusively adsorb CO₂ with negligible CH₄ uptake, but the CO₂ uptake has also significantly decreased when compared with NaA.

The relatively high selectivity of NaKA with 17 at.% K⁺ can be improved. The improvement comes from further fine tuning of the pore size. This can
be carried out by having some of the K\textsuperscript{+} cation as the larger Cs\textsuperscript{+} cation. The resulting material, NaKCsA having approximate 8 at.% of cations being K\textsuperscript{+} and 7 at.% being Cs\textsuperscript{+}, shows even higher CO\textsubscript{2}/CH\textsubscript{4} selectivity (~1200). The negligible uptake of CH\textsubscript{4} suggests that CH\textsubscript{4} is blocked from adsorption on to the zeolite via molecular sieving.

Table 4.1 CO\textsubscript{2}, CH\textsubscript{4} uptake and CO\textsubscript{2}/CH\textsubscript{4} selectivity of adsorbents in this study at 293 K, selectivity of the sorbents are calculated using $p_{CO_2}=50$ kPa and $p_{CH_4}=50$ kPa, $q_{CO_2}$ = CO\textsubscript{2} uptake at 50 kPa and $q_{CH_4}$ = CH\textsubscript{4} uptake at 50 kPa, data shown with 2 significant figures, data reproduced from Paper VIII

<table>
<thead>
<tr>
<th>Na\textsuperscript{+} at.%</th>
<th>K\textsuperscript{+} at.%</th>
<th>Cs\textsuperscript{+} at.%</th>
<th>CO\textsubscript{2} uptake mmol/g (101 kPa)</th>
<th>CH\textsubscript{4} uptake mmol/g (101 kPa)</th>
<th>CO\textsubscript{2} uptake mmol/g (50 kPa)</th>
<th>CH\textsubscript{4} uptake mmol/g (50 kPa)</th>
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<td>0.59</td>
<td>3.4</td>
<td>0.31</td>
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</tr>
</tbody>
</table>
CO₂ Capacity

The presence of the large cations (K⁺ and Cs⁺) reduces the uptake of CO₂. The large cations reduce the effective pore size of the zeolite, making it increasingly difficult for CO₂ to enter, lowering the apparent equilibrium CO₂ uptake under the experiment conditions adopted. In this work, adsorption equilibrium is defined when the pressure change in the system falls below 0.01% in a 20 second interval (with a 200s delay). Another explanation for the reduced CO₂ uptake is that the large cations occupy more space and reduce the volume available for CO₂ sorption, though the effect of this should be insignificant.

Figure 4.1 CO₂ adsorption isotherms of NaA, NaKA (17 at.% K⁺), NaCsA (17 at.% Cs⁺) and NaKCsA (8 at.% K⁺, 7 at.% Cs⁺, 85 at.% Na⁺) at 293 K, data reproduced from Paper VII

Out of the zeolites considered in this section, the CO₂ capacity at 101 kPa, 293 K is the highest for zeolite NaA (Paper VII). NaA only has the comparatively small Na⁺ cations as charge balance cations. The pore size of NaA is larger than NaKA, NaCsA and NaKCsA. The absence of the large cations also means that it has the most available volume for CO₂ adsorption. The CO₂ uptake of dual-cation zeolites containing a low atomic percentage of large cations generally shows good levels of CO₂ uptake (NaKA with up to
17 at. % K\(^+\), NaCsA with up to 8 at.% Cs\(^+\)). At 8 at.% Cs\(^+\) exchange, around 1 Na\(^+\) per \(\alpha\)-cavity has been changed to Cs\(^+\). It is so far not proven as to which exact Na\(^+\) has been replaced at this level of Cs\(^+\) exchange. However, one can speculate that one Na\(^+\) cation in site III (by the 6-ring towards the inside of the \(\alpha\) –cavity) has been exchanged according to Liu et al.\(^{66}\) Their study identified that K\(^+\) exchange on zeolite NaA first occur on site III. In a study on zeolite NaCsA (up to 58 at.% Cs\(^+\) exchanged), the location of the Cs\(^+\) cations in site III was found to be more towards the centre of the \(\alpha\) – cavity by 0.188 nm than an equivalent Na\(^+\).\(^{101}\) The highly selectivity tri-cation NaKCsA (~7 at.% K\(^+\), ~8 at.% Cs\(^+\) and ~85 at.% Na\(^+\)) zeolite also has a reasonably high CO\(_2\) uptake of 3.31 mmol/g (101 kPa, 293 K).

The tri-cation NaKCsA (~7 at.% K\(^+\), ~8 at.% Cs\(^+\) and ~85 at.% Na\(^+\)) offers highest CO\(_2\)/CH\(_4\) selectivity and good CO\(_2\) capacity. NaKCsA also shows reasonable CO\(_2\) uptake rate (Paper VIII). Out of the zeolites tested, NaKCsA seems to be an efficient, low cost adsorbent for CO\(_2\) removal from biogas (biogas upgrading).
5. Conclusions

A range of different types of potential CO₂ adsorbents have been tested in this study. In order to find a good potential adsorbent for CO₂ removal processes, different aspects have been examined.

Many of the tested adsorbents have very good properties. For CO₂ separation from flue gas which consist mainly of N₂. All of the tested adsorbents have the ability to preferentially adsorb CO₂ over N₂. Adsorbents with smaller porous windows and lower void volumes can take up greater quantities of CO₂. Out of the adsorbents considered in this study, H-SAPO-56, zeolite NaKA and NaK-ZK-4 all offer very high CO₂ uptake at atmospheric pressure (273 K). In particular, mix-cation zeolite NaKA and zeolite NaK-ZK-4 have very high CO₂ selectivity. The uptake kinetics of the highly selectivity zeolite NaKA is not slow, although can be problematic in rapid swing adsorption processes. The working capacity of zeolites is not as high as some phosphates (in particular H-SAPO-56). However, the cost of the zeolites (zeolite A) is significantly lower than any other adsorbents tested here. Zeolite A can be very easily synthesised or commercially available at a very low cost. As it also offers very high CO₂ selectivity, it seems to have good potential as a CO₂ adsorbent for CO₂ removal from flue gas. H-SAPO-56 has the highest CO₂ uptake, highest cyclic and working capacity of all tested adsorbents. It also has lower water sensitivity than zeolite A and offers adequate selectivity. Although not experimentally confirmed to date, the CO₂ adsorption rate on H-SAPO-56 is predicted to be much faster than on zeolite NaKA due to H-SAPO-56’s larger pore opening. If high purity CO₂ is not required, H-SAPO-56 can be argued as the best overall CO₂ adsorbent tested for separation of CO₂ from N₂, in terms of its properties. In order to use H-SAPO-56 or any of the other phosphates in a large scale industrial process, the cost of H-SAPO-56 must first be reduced by some orders of magnitude.

Zeolite A containing different kinds of exchangeable cations have also been tested for CO₂ separation from CH₄ for application in biogas upgrading. The tri-cation NaKCsA zeolite with (~7 at.% K⁺, ~8 at.% Cs⁺ and ~85 at.% Na⁺) is the zeolite that offers high CO₂/CH₄ selectivity, high CO₂ capacity and has a very low cost of production. This material can be produced in a large scale. Although the cost of production is still higher than zeolite A, it is still comparatively lower than some of the adsorbents in this study (for example: Al-POs and SAPOs)
This study has shown that a range of different small pore inorganic solid adsorbents can separate CO₂ from N₂ and some that can separate CO₂ from CH₄. Although all of these adsorbents have pore sizes of similar dimensions, their CO₂ adsorption properties and CO₂ selectivity are markedly different. The CO₂ uptake rates also varied significantly even across the same type of materials with very similar pore sizes.

Future research should focus on the phosphates. The phosphates are perhaps the most interesting of all the adsorbents tested. Paper I and II shows that AlPO₅s and SAPOs have properties that can potentially make some of them (for example, H-SAPO-56, AlPO-53) good CO₂ adsorbents for swing adsorption processes. Although paper I and II did not include testing these adsorbents in practice, they have for the first time, identified clearly which particular 8-ring phosphates are potential candidates for CO₂ removal processes. The next steps in developing these adsorbents further should include simplifying the synthetic procedures, processing and the shaping the adsorbents into usable shapes, and testing them in some kind of PSA/VSA systems.

Some of the ion exchanged zeolites offer very impressive properties when tested using the techniques used in this thesis. The CO₂ adsorption kinetics of these zeolites are still the biggest concerns within the experts in the field of adsorbent development. Paper III, IV, V and VII are all able to demonstrate that the highly CO₂ selective zeolites (for example: NaKA, NaKCsA and NaK-ZK-4) all have significant CO₂ uptake within the time scale preferred by swing adsorption processes. However, without testing these zeolites in a PSA/VSA system, convincing arguments cannot be put forward. Furthermore, the true potentials of these zeolites cannot be determined accurately.

The advantages and disadvantages of adsorbents tested here have been identified. Many of them are already suitable CO₂ adsorbents. For these materials to become the “best available” adsorbents, other properties must be further optimised.
References


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