Computer Simulation of Carbon Dioxide Adsorption and Transport in Zeolites

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Computer Simulation of Carbon Dioxide Adsorption and Transport in Zeolites

Jennifer Clare Crabtree

A thesis submitted for the degree of Doctor of Philosophy

University of Bath
Department of Chemistry

January 2014

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# Contents

1 Introduction ................................................. 8  
1.1 Why Capture Carbon Dioxide? .............................. 8  
1.1.1 Carbon Capture Technologies .......................... 9  
1.1.2 Solid Sorbent Materials ............................... 11  
1.2 Literature Review ......................................... 14  
1.2.1 CO$_2$ Adsorption in Zeolites ......................... 14  
1.2.2 CO$_2$ Diffusion in Zeolites ......................... 17  
1.2.3 Gas Mixtures in Zeolites ............................. 22  
1.2.4 The Effect of Water .................................. 24  
1.2.5 Zeolite Surfaces ..................................... 25  
1.3 Aims of the Thesis ...................................... 27  

2 Potential Models ........................................... 28  
2.1 Long range interactions ................................ 29  
2.1.1 Ewald Summation ................................... 29  
2.1.2 Parry Summation ................................... 32  
2.2 Short range interactions ................................. 32  
2.2.1 Lennard-Jones Potential .............................. 32  
2.2.2 Buckingham Potential ................................. 33  
2.2.3 Morse Potential .................................... 33  
2.2.4 Harmonic Potential ................................ 34  
2.2.5 Three body potential ................................ 34  
2.3 Our Potential Model ................................... 34  
2.3.1 Mixing Rules ....................................... 36  
2.4 Summary ............................................... 36
3 Computational Methods

3.1 Energy Minimisation

3.1.1 Steepest Descent and Conjugate Gradients Methods

3.1.2 Newton-Raphson Method

3.1.3 Surface Simulation

3.2 Molecular Dynamics

3.2.1 Integration Algorithms

3.2.2 Time Steps and Equilibration

3.2.3 Ensembles

3.2.4 Properties from Molecular Dynamics

3.3 Grand Canonical Monte Carlo

3.3.1 Trial moves

3.3.2 Properties from Grand Canonical Monte Carlo

3.4 Summary

4 Development of Models

4.1 Siliceous Zeolites

4.1.1 Structures

4.1.2 Cell Parameters

4.2 Siliceous Zeolite Surfaces

4.2.1 Faujasite

4.2.2 Zeolite A

4.2.3 Mordenite

4.2.4 Silicalite

4.2.5 Trends in Surface Energy

4.3 Development of Zeolite-CO$_2$ Potential Model

4.4 Extension of the Potential Model to Aluminosilicates

4.4.1 Effect of Potential Parameters on Zeolite Structure

4.4.2 Effect of Potential Parameters on CO$_2$ Adsorption

4.5 Summary

5 How Surfaces Affect Transport Properties in Faujasite

5.1 Effect of Surface Composition

5.1.1 Density in {111} slabs
5.1.2 Diffusion in \{111\} slabs ........................................ 86
5.2 Effect of Surface Structure .................................. 90
5.3 Summary ..................................................... 94

6 The Effect of Water on CO\textsubscript{2} Adsorption Sites 96
6.1 Adsorption of Single CO\textsubscript{2} Molecules ................. 96
  6.1.1 Sensitivity of the Model .................................. 97
  6.1.2 CO\textsubscript{2} Adsorption Sites ............................. 98
6.2 Densities and Adsorption Sites ............................... 100
  6.2.1 Siliceous Faujasite ...................................... 101
  6.2.2 Sodium Faujasite ....................................... 104
  6.2.3 Siliceous Zeolite A ...................................... 108
  6.2.4 Sodium LTA ............................................. 111
  6.2.5 Siliceous Zeolite L ...................................... 116
  6.2.6 Sodium LTL ............................................. 119
  6.2.7 Silicalite .............................................. 123
  6.2.8 Siliceous Mordenite .................................... 126
  6.2.9 Sodium MOR ........................................... 129
  6.2.10 Radial Distribution Functions .......................... 132
6.3 Summary ..................................................... 133

7 The Effect of Water on CO\textsubscript{2} Adsorption and Transport at MFI Surfaces 135
7.1 Comparing pure CO\textsubscript{2} and pure H\textsubscript{2}O in MFI slabs ................. 136
  7.1.1 Density Profiles of CO\textsubscript{2} and H\textsubscript{2}O ......................... 136
  7.1.2 Residence Times ........................................ 141
7.2 Mixtures of CO\textsubscript{2} and H\textsubscript{2}O in MFI ...................... 142
7.3 Effect of Water on CO\textsubscript{2} Transport through MFI Surfaces .................. 147
  7.3.1 Rate of Travel through the Zeolite ....................... 149
  7.3.2 Single Component Simulations ........................... 150
  7.3.3 50:50 Mixture Simulations .............................. 153
7.4 Summary ..................................................... 156

8 Conclusions and Future Work ................................. 158
Abstract

The aim of this work is to investigate the adsorption and transport of CO$_2$ in a range of zeolites and how these processes are affected by surfaces and by the presence of water.

The background to the project and a review of the literature are presented in chapter 1. Chapters 2 and 3 introduce the methodology used. Firstly the description of potential models is given in chapter 2, and an overview of the computational techniques, including energy minimisation, molecular dynamics (MD) and grand canonical Monte Carlo (GCMC), is given in chapter 3.

Chapter 4 describes the structures and surface of FAU, LTA, LTL, MFI and MOR, and the development and testing of the potential model using GCMC simulations to reproduce experimental isotherms and heats of adsorption.

Surface effects are very important as sorbents will often have large surface area to volume ratios, therefore chapter 5 is an analysis of the effect that surfaces have on the adsorption and transport of CO$_2$. The work uses MD simulations and focusses on faujasite, comparing the siliceous, sodium and potassium forms and the \{100\}, \{011\} and \{111\} surfaces.

Water will usually be present in industrial waste gas streams and is likely to have an effect on the efficacy of CO$_2$ adsorption. The final two chapters therefore present results on the effect of water on CO$_2$ adsorption. Chapter 6 investigates the CO$_2$ adsorption sites in a range of bulk zeolite structures and how the presence of water changes the adsorption. Chapter 7 investigates the effect of water on CO$_2$ transport through zeolite surfaces, comparing the \{100\}, \{010\} and \{001\} surfaces of siliceous MFI.

Finally, chapter 8 draws together the conclusions of the thesis and suggests areas for future work.
Acknowledgements

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Publications and Presentations

Publications:


Presentations:

*Molecular Modelling of Carbon Dioxide Adsorption in Zeolites*

**Poster**, Chemistry Postgraduate Symposium, Internal, May 2011

*Molecular Modelling of Carbon Dioxide Adsorption in Zeolites*

**Poster**, 21st Goldschmidt Conference, Prague, Czech Republic, August 2011

*Molecular Modelling of Carbon Dioxide Adsorption in Zeolites*

**Talk**, DTC Summer Showcase, University of Bath, July 2011

*Molecular Modelling of Carbon Dioxide Adsorption in Zeolites*

**Poster**, South West Computational Chemistry Meeting, Cardiff University, UK, September 2011

*Computer Modelling of Molecular Adsorption at Mineral Interfaces*

**Poster**, RSC Solid State Chemistry Group Christmas Meeting, University of Liverpool, December 2011

*Molecular Modelling of CO$_2$ Adsorption in Zeolites and ZIFs*

**Talk**, Second Year Talks, Internal, April 2012

*Molecular Modelling of Carbon Dioxide Adsorption in Zeolites*

**Poster**, DTC Summer Showcase, University of Bath, July 2012
Zeolites for CO₂ Sequestration: a Computational Study

Talk, 35th British Zeolite Association Meeting, University of Chester, July 2012

Modelling Zeolites for CO₂ Adsorption

Talk, CCP5 Annual Meeting, University of Huddersfield, September 2012

Molecular Modeling of Zeolites for Carbon Dioxide Sequestration

Talk, MRS Fall Meeting, Boston, USA, November 2012

Adsorption and Transport of CO₂ at Faujasite Surfaces

Poster, CCP5-MDNet meeting, University of Warwick, April 2013

Molecular modelling of the Adsorption and Transport of CO₂ in Zeolites

Talk (prize), Chemistry Postgraduate Symposium, Internal, May 2013

Adsorption and Transport of CO₂ at Faujasite Surfaces

Poster, 9th European Conference on Computational Chemistry, Sopron, Hungary, September 2013

Adsorption and Transport of CO₂ at Faujasite Surfaces

Poster, DTC Summer Showcase, University of Bath, September 2013
Chapter 1

Introduction

1.1 Why Capture Carbon Dioxide?

Carbon dioxide is a greenhouse gas and its increasing levels in the atmosphere are contributing to global warming and climate change [1]. In the 1700s the mean global atmospheric concentration of CO$_2$ was 280 ppm [2] but recently CO$_2$ levels in the atmosphere at Mauna Loa, Hawaii were recorded above 400 ppm for the first time since measurements began in 1958 [3]. CO$_2$ levels are predicted to reach 550 ppm by 2050, even if the emission levels stay stable over the next 30 years [2]. An increased level of greenhouse gases in the atmosphere leads to the greenhouse effect, which causes more of the heat from the sun to be captured by the Earth’s surface and atmosphere than would otherwise be the case. This is believed to be the cause of global warming, a gradual increase in the Earth’s surface temperature over the past century. An increase in the temperature also affects the Earth’s weather systems, ocean currents and ice/water balances, so global warming also leads to climate change. Climate change is likely to cause serious problems across the world, particularly affecting developing countries that cannot afford to adapt as easily to changes. Likely effects of climate change include arid areas becoming deserts and low-lying areas flooding.

The UK and the EU are parties to the United Nations Framework Convention on Climate Change (UNFCCC) and the subsequent Kyoto protocol [4], which aim to fight global warming by reducing the emissions of six greenhouse gases: carbon dioxide, methane, nitrous oxide, sulphur hexafluoride, hydrofluorocarbons and perfluorocarbons. The countries that signed and ratified the treaty committed to reducing their emission levels by specified amounts to a series of deadlines, for example the UK committed to reducing emissions to 12.5% below 1990 baseline levels in the commitment period 2008 to 2012 [5]. The UK ex-
ceeded the target, by reducing 2012 emissions to 26.7% below the baseline levels, or 24.9% below if emissions trading is included in the calculation [5]. The Intergovernmental Panel on Climate Change (IPCC) produces regular reports on the progress towards the targets of the UNFCCC and assesses the scientific information relevant to the goals. The most recent report is the IPCC Fourth Assessment Report: Climate Change 2007 [6] and the Fifth Assessment report is now under way, estimated to be completed in 2014. The 2008 Climate Change Act [7] voluntarily commits the UK to reduce greenhouse gas emissions by 80% compared to 1990 levels by 2050. As intermediate steps, commitments to a 22% reduction by 2012, 28% by 2017, 34% by 2022 and 50% by 2027 have also been made [5].

Most of the world’s energy needs are supplied by the use of fossil fuels and hence this is the major source of anthropogenic CO$_2$ emissions, in fact more than 75% come from fossil fuel combustion [8]. Therefore, to reduce the emissions of CO$_2$ to the environment, either the use of fossil fuels must be reduced or stopped or alternatively the CO$_2$ must be captured and dealt with before it is released, in a process known as carbon capture and sequestration (CCS). Amine scrubbing is the traditional method for capturing CO$_2$ but it has several disadvantages such as the high energy costs [9]. An alternative is the use of solid sorbents and the following sections will describe the technologies (section 1.1.1) and sorbents (section 1.1.2) that are available for this purpose.

Once the carbon dioxide has been captured using one of these techniques, there is a problem of what to do with it long-term. Possibilities include storage in oil wells or deep saline aquifers, but there are also newly emerging ideas such as the use of carbon dioxide as a C$_1$ building block for conversion into other chemicals [10].

### 1.1.1 Carbon Capture Technologies

There are three main ways in which CO$_2$ can be captured from source at a power plant: post-combustion, pre-combustion and oxy-combustion, as shown in figure 1.1. Each has its own advantages and disadvantages and therefore the method chosen must depend on the individual situation.

#### 1.1.1.1 Post-combustion Capture

Post-combustion capture is a technique that involves the separation of CO$_2$ from the flue gases produced by the fuel combustion. The CO$_2$ is at a concentration of less than 15% and must be separated from a stream that mainly consists of nitrogen [12]. The low concentra-
tion of CO₂ in the stream means that there is a low partial pressure of CO₂ and therefore the driving force for capture is low. However, this technology is the easiest to implement, as it can be retrofitted to an existing power plant. There are several options for post-combustion capture. The most widely studied and used method is a wet-scrubbing technique, usually an amine-based system. The amines react with the CO₂ to form water-soluble compounds, thereby separating CO₂ from the gas stream. The regeneration of this stream requires high temperatures. Although there are opportunities for heat exchange systems, there still needs to be an energy input, reducing the efficiency of the energy production plant [13]. Other technologies include carbonate-based systems, membranes, solid sorbents, metal organic frameworks (MOFs), enzyme-based systems and ionic liquids. The solid sorbents will be discussed later in this report in section 1.1.2.

It is projected that the other methods for carbon capture (pre-combustion and oxy-combustion) will produce higher efficiencies and therefore compensate the capital investment that will be required for their construction [14].

Figure 1.1: (a) Post-, (b) pre- and (c) oxy-combustion processes (adapted from [11]).
1.1.1.2 Pre-combustion Capture

In pre-combustion technologies, CO\textsubscript{2} is removed before the fuel is burned. This is achieved by the gasification of fossils fuels to give syngas (mainly CO and H\textsubscript{2}), which is then fed, with steam, to a water gas shift reactor, where the CO and water are converted to CO\textsubscript{2} and H\textsubscript{2}. The carbon is separated from this stream, before the H\textsubscript{2} is fed to the combustion engine to produce the energy. In this method, the stream to be separated can be modified to have a higher CO\textsubscript{2} partial pressure, leading to a greater driving force for separation than in post-combustion techniques. The size and cost of the capturing facilities can therefore be reduced [12].

1.1.1.3 Oxy-combustion Capture

Oxy-combustion is an alternative technique that burns the fossil fuels in oxygen mixed with recycled flue gas, so that the flue gas exiting the system contains a high concentration of CO\textsubscript{2}, thereby easing the separation process. The flue gas is in fact predominantly CO\textsubscript{2} and water, which are easily separable, as the water can be condensed out leaving CO\textsubscript{2} with low concentrations of impurities that must then be removed in a purification process. [12]

1.1.2 Solid Sorbent Materials

There are many different materials that have been suggested as potential sorbents for CO\textsubscript{2} [15]. One of the crucial properties for an adsorbent is the adsorption energy. It must be strong enough that the CO\textsubscript{2} will be adsorbed into the material, but not so strong that the regeneration of the material will require conditions that are too extreme, i.e. very high temperatures, which would require additional energy to be put into the system, thereby reducing the efficiency of the power production plant. Some potential CO\textsubscript{2} adsorbents are discussed in the following.

1.1.2.1 Zeolites

Zeolites are a promising class of material for the adsorption of CO\textsubscript{2} [15, 16]. As well as for this application, they have been suggested to be beneficial to other applications such as the removal of CO\textsubscript{2} from spacecraft cabins [17].

Zeolites are microporous aluminosilicate materials, made up of tetrahedral TO\textsubscript{4} units, where T is Si or Al, linked by shared oxygen atoms. The negative charge introduced by each
aluminium atom is counteracted by an extra-framework cation such as Na\(^+\) or K\(^+\). The TO\(_4\) units (or primary building units, PBU\(\))s can be arranged in a variety of configurations, to form structures such as 6-rings, 8-rings or 12-rings. These secondary building units (SBU\(\))s can then be arranged into cages and cylinders which form a network of pores within the material, as shown in figure 1.2.

Figure 1.2: The construction of a zeolite framework from SiO\(_4\) tetrahedra (PBU\(\))s via secondary building units (SBU\(\))s.

There are over 200 different zeolite structures that have been synthesised to date, with a variety of applications including adsorption, catalysis and ion exchange, depending on the Si:Al ratio and the pore structure [18]. As well as the zeolite structures that have already been synthesised, many new zeolite frameworks have been predicted, which can be useful to direct design strategies for the synthesis of new zeolites. Simulated x-ray diffraction patterns of predicted zeolites can also be used to help with the identification of newly synthesised materials. Initial predictive studies [19–21] relied on linking together existing structural subunits in different ways, or using computer search algorithms. A new approach for the systematic enumeration of new structures [22] is based on mathematical tiling theory [23, 24]. When predicting new framework structures it is important to account for the chemical stability of the framework. This is addressed in the work of Foster et al. [25, 26] who modelled the structural parameters such as the lattice energy and framework density in order to identify theoretical frameworks that are likely to be feasible as zeolites. The concept of natural tiling can also be used as a tool to identify structural motifs that are common to zeolites with a particular desirable characteristic, such as selective gas separation [27]. Predictions of other zeolites that may share these properties can then be made.

There are a variety of different systems that are used in the naming of zeolites. When there are natural analogues, the synthetic zeolites are often named after the minerals (e.g. faujasite, mordenite). There are zeolites that are named after Latin and Greek letters, such as zeolites beta and rho and the Linde type zeolites A, L, X and Y. Some zeolites are named
with acronyms that relate to where they were first synthesised, such as the ZSM (Zeolite Socony Mobil) and ITQ (Instituto de Tecnologia Quimica) zeolites. In an attempt to create some order, a classification system was introduced in the Atlas of Zeolite Structure Types [28], which assigns each structural type a three letter code, such as LTA for zeolite A and FAU for zeolites X and Y. In the literature there can, therefore, be a whole range of different names that all relate to the same structure, although usually with a different composition. Table 1.1 lists the names that can be used to describe the same zeolite structures for the zeolites that are mentioned in this thesis.

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Other names</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFI</td>
<td>Beta polymorph A</td>
<td></td>
</tr>
<tr>
<td>BEA</td>
<td>Beta polymorph B</td>
<td></td>
</tr>
<tr>
<td>BEB</td>
<td>Beta polymorph C</td>
<td>ITQ-17, ITQ-14 (overgrowth)</td>
</tr>
<tr>
<td>BEC</td>
<td>Chabazite</td>
<td>SSZ-13, SSZ-62</td>
</tr>
<tr>
<td>DDR</td>
<td>Zeolite A</td>
<td></td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite</td>
<td>Zeolite X, Zeolite Y</td>
</tr>
<tr>
<td>FER</td>
<td>Ferrierite</td>
<td>ZSM-35</td>
</tr>
<tr>
<td>GME</td>
<td>Gmelinite</td>
<td></td>
</tr>
<tr>
<td>HEU</td>
<td>Heulandite</td>
<td></td>
</tr>
<tr>
<td>IFR</td>
<td>ITQ-4, MCM-58</td>
<td></td>
</tr>
<tr>
<td>ISV</td>
<td>ITQ-7</td>
<td></td>
</tr>
<tr>
<td>ITE</td>
<td>ITQ-3</td>
<td></td>
</tr>
<tr>
<td>IWR</td>
<td>ITQ-24</td>
<td></td>
</tr>
<tr>
<td>LTA</td>
<td>Linde Type A</td>
<td>Zeolite A, ITQ-29 (siliceous)</td>
</tr>
<tr>
<td>LTL</td>
<td>Linde Type L</td>
<td>Zeolite L</td>
</tr>
<tr>
<td>MEL</td>
<td>ZSM-11</td>
<td></td>
</tr>
<tr>
<td>MFI</td>
<td>Silicalite</td>
<td>ZSM-5</td>
</tr>
<tr>
<td>MOR</td>
<td>Mordenite</td>
<td></td>
</tr>
<tr>
<td>MTW</td>
<td>ZSM-12</td>
<td></td>
</tr>
<tr>
<td>MWW</td>
<td>ITQ-1, MCM-22 (siliceous)</td>
<td></td>
</tr>
<tr>
<td>SOD</td>
<td>Sodalite</td>
<td></td>
</tr>
<tr>
<td>STI</td>
<td>Stilbite</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Zeolite nomenclature

1.1.2.2 Other Materials

Metal organic frameworks, or MOFs, consist of metal ions or clusters connected together by rigid organic molecules to form one-, two- or three-dimensional networks. These materials are therefore usually porous and the pore size and structure can be easily tailored by altering the metal ions and the organic linkers. This makes them good candidates for gas separators and stores. Their potential as a material for hydrogen storage is particularly notable [29].
Chapter 1. Introduction

There have been a fair number of studies of CO\textsubscript{2} in MOFs, which will not be covered here, but a review by Keskin et al. [30] gives a good overview of the topic.

A subset of MOFs is ZIFs (zeolitic imidazolate frameworks) [31, 32] which have topologies similar to zeolites, but constructed from metals with imidazolate linkers. ZIFs have been shown to have good affinity to CO\textsubscript{2}, and could be a potential rival to zeolites as sorbents [33, 34].

Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon and they can be functionalised with amines to make them a suitable adsorbent for CO\textsubscript{2} [35]. Activated carbon is a form of carbon that has been modified to make it very porous, thereby having a large surface area for adsorption. Siriwardane et al. [36] have shown it to be a good adsorbent for CO\textsubscript{2} including the separation of CO\textsubscript{2} from gas mixtures. Przepiorski et al. [37] found that treating the activated carbon with ammonia enhanced the adsorption properties further.

1.2 Literature Review

There has been extensive research on the adsorption and transport of carbon dioxide in zeolites. It can be difficult to assign articles to single topics, but I have roughly split the work into adsorption studies (section 1.2.1), diffusion studies (section 1.2.2), separation of gas mixtures (section 1.2.3), the effect of water (section 1.2.4) and the effect of surfaces (section 1.2.5).

1.2.1 CO\textsubscript{2} Adsorption in Zeolites

1.2.1.1 Effect of Structure

The effect of pore shape and size on the adsorption of CO\textsubscript{2} and N\textsubscript{2} in siliceous zeolites was investigated by Goj et al. [38]. They chose three structures which had identical chemical compositions but different pore structures: silicalite, ITQ-3 and ITQ-7. All three materials preferentially adsorbed CO\textsubscript{2} over N\textsubscript{2} as both single component and mixture adsorption; however the selectivities varied depending on the structure. For example, at room temperature, the selectivity for CO\textsubscript{2} over N\textsubscript{2} was 10 for ITQ-7, 30 for silicalite, and 100 for ITQ-3. The overall adsorption capacity was determined by the available pore volume of the zeolite.

In aluminosilicate zeolites the location of the cations is important for adsorption as it affects the available volume in the zeolite as well as the adsorption sites. When the Si:Al
ratio of a zeolite changes the number of cations in the structure also changes. The following studies investigate the locations of the cations in various zeolite structures. The locations of the cations in sodium mordenite was investigated by Maurin et al. [39] using Monte Carlo (MC) simulations and $^{29}$Si NMR spectroscopy. The Si:Al ratio was varied from 5.5 to 12 and the cation positions were found for all of these ratios, with good agreement between experiment and simulation. Maurin et al. [40] then investigated how hydration of the zeolite affected the sodium ion positions in mordenite. They used energy minimisation techniques to determine the positions of the cations and the water molecules as a function of the level of hydration. It was found that in the main channels the positions of the cations was altered greatly by the introduction of water, however in the smaller side channels the cations were not disturbed much due to them being trapped in their locations. Molecular dynamics (MD) simulations were used to predict the low-frequency vibrations of the sodium cations in mordenite [41] and then the static and dynamic properties of the cations were explored when changing the Si:Al ratio and the water content [42]. Again, there was found to be a difference in behaviour between the cations in the main channels and those in the smaller side channels. The effect of water on the distribution of cations in sodium faujasites with several Si:Al ratios was studied by Abrioux et al. [43,44] using MC and MD simulations. Water adsorption was found to affect the cation redistributions in Na$_{56}$Y much more than in Na$_{96}$X. The displacement distance of cations is further at higher loadings of water. The cation motion on adsorption of CO$_2$ in NaX and NaY faujasites was investigated with MD simulations [45]. NaX and NaY have the same faujasite structure, but differ in the ratio of Si:Al atoms. The ratios are 1.1 and 2.4 for NaX and NaY respectively. In NaY, at low and intermediate concentrations some of the cations migrate to the centre of the supercages, due to strong interactions with the adsorbates. In NaX some of the cations are also moved significantly by the adsorption of CO$_2$. A comprehensive review of cation distributions in faujasites was published by Frising and Leflaive [46]. The cation sites in FAU frameworks are shown in Figure 1.3.

1.2.1.2 Effect of composition

The presence of cations and the type of cations that are present in a zeolite structure can have a significant impact on gas adsorption. A comparison of the adsorption of CO$_2$ in silicalite and NaZSM-5 (aluminosilicate form of silicalite with Na$^+$ counter ions) was carried out by Hirotani et al. [48]. Their grand canonical Monte Carlo (GCMC) simulations
allowed the movement of the sodium cations within a rigid zeolite framework, as well as the creation, removal and movement of the CO$_2$ molecules. By comparing the energy distributions of CO$_2$ over silicalite and NaZSM-5, it was possible to distinguish between molecules adsorbed in the pores and on cation sites. As the number of Na$^+$ cations increases, all of the CO$_2$ molecules become adsorbed on cation sites. The influence that the cations have on the adsorption properties of X-faujasite was studied using GCMC simulations by Maurin et al. [47,49]. The enthalpies of adsorption of N$_2$ at low coverage increased in the orders LiX > NaX > KX and MnX > CaX > SrX > BaX, which was confirmed by experimental results. The adsorption of CO$_2$ in a similar set of faujasites had also been studied by Barrer and Gibbons [50], who also found that the heat of adsorption decreased with CO$_2$ loading, and at low loadings the heats decreased in the order LiX > NaX > KX > (Rb,Na)X > (Cs,Na)X. Similar trends have also been observed in zeolite beta [51] and RHO [52].

The differences between LiY and NaY faujasites have been extensively studied, both the adsorption behaviour at different temperatures [53] and the diffusivity in the two materials [54,55] using GCMC and MD simulation techniques. It was found that the enthalpy of adsorption is governed by the nature of the cations and deviation of the SII cation position (see figure 1.3) out of the plane of the six-membered ring. Regardless of the faujasite system, the adsorption mechanism is significantly different at high temperature, due to this shift in the cation location.

The effect of the Si:Al ratio on CO$_2$ adsorption in faujasite was investigated by Maurin et al. [56] using GCMC simulations. They used three faujasite zeolites with differing Si:Al ratios: DAY (de-alumiated) with Si:Al ratio of 100, and NaY and NaX with ratios of 2.4 and 1, respectively, and determined the volume of CO$_2$ that was adsorbed at different pressures.
NaX and NaY both adsorbed a greater volume of CO$_2$ than DAY, but similar amounts to each other. The enthalpy of adsorption of CO$_2$ as a function of coverage was also investigated; the highest affinity for adsorption was in NaX, followed by NaY, then DAY. The effect of Si:Al ratio has also been investigated in experimental studies of various zeolites including FER [57, 58], STI [59] and CHA [60]. Overall conclusions are that the isosteric heats of adsorption depend significantly on the cation size, the number of cations, and the amount of adsorbed CO$_2$. Highest energies are observed for systems where CO$_2$ can bridge two cation sites (usually where there are higher numbers of cations, therefore lower Si:Al ratios).

1.2.2 CO$_2$ Diffusion in Zeolites

Beerdsen et al. [61] explain that there are three different ways to describe diffusion behaviour using diffusion coefficients. The first is the transport diffusion coefficient, $D_T$, which is given by Fick’s law (equation 1.1) and can be found by macroscopic methods such as measurements of the uptake of gases and the permeation rates:

$$J = D_T \nabla c$$  \hspace{1cm} (1.1)

where $J$ is the sorbate flux when a concentration gradient $\nabla c$ is applied. However, $D_T$ is often converted to the corrected diffusivity $D_C$ (equation 1.2), which is less loading dependent. $D_C$ is also often known as the Maxwell-Stefan (MS) or Darken diffusivity:

$$D_C = D_T \frac{\delta \ln c}{\delta \ln f}$$  \hspace{1cm} (1.2)

where $c$ is the sorbent concentration and $f$ is the fugacity. The final diffusion coefficient is $D_S$, the self- or tracer-diffusion coefficient. Microscopic methods such as pulsed field gradient NMR can be used to obtain this value experimentally, but it can be thought of as the diffusion of a single particle making its way through the pores and the other molecules. When a system is infinitely dilute the three coefficients can be thought of as equivalent.

1.2.2.1 Effect of Structure

Extensive work has been carried out on the effect of pore shape and size on the diffusion of molecules in zeolites. The first example of intensive studies of the self and transport diffusivities in zeolites other than silicalite was carried out by Skoulidas and Sholl [62], who
investigated the diffusion of CH$_4$, CF$_4$, SF$_6$, Ar, Ne and H$_2$ in silicalite, ITQ-3, ITQ-7 and ZSM-12. They chose these zeolites to include a range of structures with one, two and three dimensional pore structures, and pore volumes with different shapes. The investigation covered the effect of pore loading on the self and corrected diffusivities using equilibrium molecular dynamics (EMD) simulations and adsorption isotherms were generated using GCMC simulations, which were used in conjunction with the EMD results to determine the transport diffusivities. There were only relatively small differences in the adsorption loading for the different zeolites, and these were attributed purely to the differences in available pore volume within the zeolites. The same general trends in self-diffusivity were observed for diffusion in silicalite and ITQ-7, where the diffusion decreases steadily as the loading increases. This trend is due to the increasing steric hindrance as more molecules are added to the same pore volume and has been seen in other work [63, 64]. In ITQ-3, however, a very different trend was observed. At low loading of CH$_4$ and Ar, the diffusion increases before reaching a maximum and then decreases as in the other zeolites. This phenomenon had previously been attributed [65] to adsorbed molecules acting together to lower the energy barrier for a molecule to hop through a window into an adjacent cage. However, once the loading increases further, the steric hindrance comes into play and reduces the diffusivity again. The self-diffusivity in ZSM-12 is different again; this zeolite has a one-dimensional pore structure, and the pores are wide enough for two molecules to pass each other within the pore. This means that there is no restriction to single-file diffusion; however the difficulty encountered when two molecules do pass each other means that the effect of steric hindrance on the diffusion is much greater than in the three-dimensional networks, so the diffusion decreases rapidly with loading.

Selassie et al. [66] carried out MD and GCMC studies on some of the same zeolites: silicalite, ITQ-3 and ITQ-7, to investigate the diffusion of CO$_2$ and N$_2$. In all three of the materials the CO$_2$ was found to diffuse slower than the N$_2$. In addition a noticeable difference in the diffusion in ITQ-3, which has a cage-type structure, compared to the other two materials, which have intersecting channel-type structures was highlighted. In all three materials the diffusion decreases monotonically with loading, in contrast to some of the results with spherical molecules by Skoulidas and Sholl [62]; however, in ITQ-3 the trend is different, the CO$_2$ diffusion decreases much more rapidly than the N$_2$ diffusion. The diffusion of these gases in silicalite in another MD simulation study [67] again found the corrected diffusivity of CO$_2$ decreased with loading, while for N$_2$ there was a weak maximum point.
before it eventually stayed constant. This was due to the fact that CO$_2$ exhibited stronger sorbate-sorbate interactions than N$_2$.

The dependence of loading on diffusion in zeolites was also investigated by van den Bergh et al. [68, 69]. They developed a relevant site model (RSM) that works on the idea that a molecule is located either in a zeolite cage or in its window site. A molecule can only jump to another cage if it is situated in a window site (the relevant site, RS). The materials that they simulated in the development of the model were DDR-type zeolites, which are cage-type zeolites with windows between the cages. Using this technique gave results which reproduced experimental diffusivity data for CO$_2$ and N$_2$ very well. The RSM was extended to include mixtures of light gases in a variety of zeolites [70], including CH$_4$, CO$_2$, Ar, Ne, N$_2$ and O$_2$ in DDR, CHA, MFI and FAU. The work shows that the RSM can successfully be used to model the diffusion of an extended range of light gases in all four of the zeolite structures.

Beerdsen et al. [61] approached the task of understanding the diffusion characteristics by developing a new model to represent the zeolite structures. They simplified all zeolite structures into three main types: ‘cage-type’, ‘channel-type’ and ‘intersecting channel-type’ zeolites and they found that all three give different diffusion behaviour. Some zeolites have structures that cannot easily be classified, as the structure has features of two types, but the majority of zeolites can be clearly classified with this method. By considering the pore structures to be represented by a series of interconnected ellipsoids, the group worked out theoretically what the free energy profiles should be like along the three pore types, and these were verified using computer simulations, as shown in figure 1.4.
Figure 1.4: (Left) Three ways to connect ellipsoids, (top) aligned in a direction perpendicular to the long axis $a$, (middle) aligned along $a$, (bottom) aligned alternatingly. Below each ellipsoidal model on the left, a schematic representation is given of the associated free-energy profile. (Right) Examples of molecular sieves that correspond to each of the ellipsoidal models: SAS (top), AFI (middle), and MFI (bottom), each with their calculated free-energy profile (zero loading); the true free-energy profiles are very similar to the schematic ones. [Reproduced from [61]].

The same group carried out a study into these properties with a wide range of zeolite structures [71]. The adsorbate was methane and 12 zeolites were simulated, from the three structural groups of cage, channel, and intersecting channel zeolites and with as widely differing structures from each other as possible. Therefore, it could be verified whether the trends that were observed for one zeolite could also be seen for other zeolites with a similar structural type. On carrying out extensive work probing the diffusivity, both self and corrected, and the free energy profiles, they [71] decided that in fact there was a fourth zeolite structural group, which they have called ‘weak-confinement-type’ zeolites. The zeolite they have found to be in this section in faujasite (FAU), which falls in between the two classes of cage-type and intersecting channel-type zeolites. The results are in accordance with previous findings by other researchers. For cage-type zeolites, there is a maximum in the self and corrected diffusion caused by reduction in the free-energy barriers, before the diffusivity then decreases to zero. For zeolites with one-dimensional channels, the self- and corrected-diffusivity both depend hugely on the ratio of the narrowest and widest parts
of the channel, \( R_{ctw} \). In channels that have a large \( R_{ctw} \) (almost cage-like) the behaviour resembles that of cage-type zeolites, however for smooth channels, with a low \( R_{ctw} \), the diffusion decreases rapidly with increased loading. In intersecting channel type zeolites, the self-diffusivity resembles that of channel type zeolites with intermediate \( R_{ctw} \). The corrected diffusion has two sequential diffusion regimes. Firstly the diffusion decreases slowly, until one of the channels has reached its maximum loading, then the diffusion decreases rapidly to zero when the zeolite has reached saturation loading. These findings were also verified by the work of Krishna et al. [72] who carried out MD simulations to investigate the loading dependence on MS diffusivity (corrected diffusivity) of CH\(_4\) and CO\(_2\) across zeolite membranes.

### 1.2.2.2 Diffusion in Aluminosilicates

There has been much less research into diffusion in aluminosilicate zeolites. The self-diffusion of CH\(_4\) and a CH\(_4\)/CO\(_2\) mixture in NaY was investigated using MD simulations by Deroche et al. [73]. The group used two different models in their simulations, reproducing experimental results either for the magnitude or the profile of the self-diffusivity, depending on the model used. An interesting experimental result showed that the CH\(_4\) diffusion reached a maximum at 32 molecules per unit cell. Without any inter-framework cations, the diffusivity would be expected to decrease steadily with increased loading, which suggests that there is significant interaction between the methane and the extra-framework Na\(^+\) ions within the supercages. This was hard to reproduce computationally, indicating that the Na\(^+\)/CH\(_4\) interaction must be accurately represented to get a real demonstration of the diffusional behaviour. In the presence of increasing loading of CO\(_2\), the self-diffusivity of methane is only slightly altered, i.e. the gases can be treated separately.

The Si:Al ratio has an impact on CO\(_2\) diffusion in faujasite [55]; there is a greater activation energy for diffusion in NaX than NaY due to the stronger interaction between the CO\(_2\) molecules and the cations. The activation energies were calculated both by molecular dynamics and quasi-elastic neutron scattering with good agreement and the same techniques were used to investigate the effect of the type of cation (Li\(^+\) and Na\(^+\)) on CO\(_2\) diffusion [54]. In both LiY and NaY the transport diffusivity increases with loading, while the self-diffusivity decreases. The self-diffusion in NaY is greater than LiY, as the interaction between Na\(^+\) and CO\(_2\) is less strong; however LiY has a greater transport diffusivity coefficient.
1.2.3 Gas Mixtures in Zeolites

As well as studying the adsorption of CO\textsubscript{2} on its own, it is obviously also important to find out about the effect of other molecules on CO\textsubscript{2} adsorption and diffusion. Several research groups have undertaken modelling studies on gas mixtures including CO\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}O. The characteristics that have been investigated are the adsorption isotherms to see which molecules are preferentially adsorbed by a particular zeolite as a function of pressure and the diffusion characteristics of the molecules within the pores of the zeolite, particularly with respect to the level of loading of the zeolite.

Several pieces of research have found CO\textsubscript{2} to be preferentially adsorbed over other adsorbate molecules in siliceous zeolites. For example, the adsorption of a few small gas molecules (CO\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4}) in siliceous zeolites was studied by Garcia-Perez et al. [74]. They found that in all the zeolites CO\textsubscript{2} was selectively adsorbed over N\textsubscript{2} and CH\textsubscript{4}, although this varied with the zeolite structure and the gas mixture composition. It was also noted that there were very specific sites of adsorption that were different for each of the different systems. Monte Carlo simulations were also used by Babarao et al. [75] to study the storage and separation of CO\textsubscript{2} and CH\textsubscript{4} in silicalite, C\textsubscript{168} schwarzite and IRMOF-1. In these simulations CH\textsubscript{4} was represented as a spherical Lennard-Jones molecule, while CO\textsubscript{2} was a rigid linear molecule with a quadrupole moment. Similarly, they found that CO\textsubscript{2} was preferentially adsorbed over CH\textsubscript{4} in all of the materials, apart from in schwarzite at high pressure. IRMOF-1 was found to have a much greater adsorption capacity than the other two materials, marking it out as a potential storage medium. Dunne et al. [76] carried out MC simulations of methane/CO\textsubscript{2} and ethane/CO\textsubscript{2} mixtures in silicalite to generate adsorption isotherms. It was again found that CO\textsubscript{2} is always preferentially adsorbed over CH\textsubscript{4}. However, in ethane/CO\textsubscript{2} adsorption, ethane is the preferred adsorbate at lower pressures, and CO\textsubscript{2} only becomes preferred at higher pressures.

Carbon dioxide is also found to be selectively adsorbed in aluminosilicate zeolites. Ghoufi et al. [77] used GCMC simulations to show that CO\textsubscript{2} is preferentially adsorbed over CH\textsubscript{4} in NaY for a range of pressures, Pham er al. [60] found from experimental isotherms that cation exchanged SSZ-13 (CHA) had much higher affinity for CO\textsubscript{2} than N\textsubscript{2} and NaKA sorbents have a high CO\textsubscript{2} selectivity over N\textsubscript{2} [78]. In a study of a range of zeolites [79] CO\textsubscript{2} was generally preferentially adsorbed over N\textsubscript{2}, while the best materials were those with near-linear CO\textsubscript{2} isotherms and low Si:Al ratios, therefore more cations.

GCMC simulations were used to investigate the adsorption of mixtures of CO\textsubscript{2}, N\textsubscript{2} and
H$_2$ in zeolite NaA by Akten et al. [80]. The zeolite was highly selective for CO$_2$ over the other two gases at room temperature; however this selectivity decreased slightly as the pressure of the gas was increased. ITQ-1 is a zeolite that contains two independent pore networks that are not connected to each other. The sorption of a CO$_2$/CH$_4$ gas mixture into this material was analysed with GCMC simulations by Leyssale et al. [81] and with MD simulations by Sant et al. [82]. Again, CO$_2$ was preferentially adsorbed over CH$_4$ over all pressures, temperatures and compositions investigated. The CO$_2$ had a monotonic decrease in self-diffusivity with increasing loading, but CH$_4$ showed a more complex dependence. There is a maximum in the self-diffusivity of the methane in the larger cavity network, due to a preferential adsorption site which hinders the diffusion at low occupancy, but as the occupancy increases, there are additional molecules that cannot absorb onto these sites so diffusion is possible. At higher occupancies the diffusion decreases again due to steric effects. In a mixture this trend disappears and the diffusivity again shows a decreasing trend.

The diffusion of a mixture of CO$_2$ and N$_2$ in silicalite, ITQ-3 and ITQ-7 was studied by Selassie et al. [66]. It is clear from their results that the molecules each hinder the other’s diffusion. In ITQ-7 and silicalite the diffusion of N$_2$ in the mixture is slightly lower than the pure component, while CO$_2$ stays about the same. This suggests that CO$_2$ hinders N$_2$ diffusion more. In ITQ-3, however, the N$_2$ diffuses much more slowly in the mixture than it does as a pure component, while again the CO$_2$ is unchanged. This can be explained when looking at the adsorption sites. The preferential adsorption sites are the same for the two molecules within silicalite and ITQ-7, but different for ITQ-3. In ITQ-3 the CO$_2$ molecules prefer to sit within the window region, which hinders the diffusion of N$_2$ from one cage to another. It is suggested that this is a common trait for adsorbates that interact strongly with the window regions, where there are narrow windows between cages.

The diffusion of gas mixtures in DDR zeolite was studied by Krishna and van Baten [72]. GCMC simulations were used to study the adsorption of CO$_2$/CH$_4$, CH$_4$/N$_2$ and CO$_2$/Ar mixtures. The adsorption sites differ between different molecules, for example CH$_4$ and Ar adsorb almost exclusively within the cages, while CO$_2$ and N$_2$ can be found in the window regions as well as in the cages. CO$_2$ molecules that adsorb strongly in the window regions can hinder the diffusion of other molecules within the zeolite. This work improved on much previous work that had used the ideal adsorbed solution theory (IAST) of Myers and Prausnitz [83], which depends on the assumption that the molecules are uniformly adsorbed throughout the zeolite, as that is not always the case. Krishna and
van Baten’s study has shown that segregation effects are important and that some molecules are preferentially located at certain sites within the structure.

1.2.4 The Effect of Water

Many of the studies of CO$_2$ adsorption in zeolites neglect the impact of water. Zeolites are well known to be good adsorbents for water, as they are used as desiccants [84, 85]. As flue gas streams usually contain moisture, this can be a significant problem. Indeed Liu et al. [78] acknowledge that while they have found NaKA sorbents to have excellent CO$_2$-over-N$_2$ selectivity and high adsorption capacity, this is only valid for water-free flue gases. It has been shown that the presence water can significantly reduce the adsorption of CO$_2$ in zeolites 5A and 13X, with the effect increasing with the amount of water that is present [86]. The presence of water lowers the adsorption of CO$_2$ and C$_3$H$_8$ in zeolite X [87] and also lowers the adsorption of CO$_2$ and H$_2$ in MFI membranes (siliceous and Si:Al ratio of 80) but it does not change the selectivity of CO$_2$ over H$_2$ [88].

In a study of a vacuum swing adsorption (VSA) unit with zeolite 13X as the sorbent, Li et al. [89] found that although a humid flue-gas stream negatively impacted on CO$_2$ capture, long term recovery of CO$_2$ was still possible as the water migrated a quarter of the way into the column to form a “water-zone” leaving the rest of the column available for CO$_2$ adsorption. The recovery of CO$_2$ therefore dropped form 78.5% to 60%. Further work by Li et al. [90] used a multi-layered VSA unit with a superior desiccant guard-bed layer to remove water followed by a main layer of zeolite 13X to capture the CO$_2$. The water was successfully retained in the pre-layer meaning that CO$_2$ could be adsorbed by the main adsorbent layer.

A theoretical and experimental study by Galhotra et al. [91] on the adsorption of CO$_2$ in zeolite Y under dry and wet conditions showed that in some cases carbonate and bicarbonate species were formed, although this depended on the experimental conditions, the cation species and also the size of the zeolite particles. Much of the carbonate/bicarbonate formation was at external surface sites, suggesting that nanocrystalline zeolites could be efficient for the conversion of CO$_2$ to other products.
1.2.5 Zeolite Surfaces

All of the literature that has been presented so far has focussed on adsorption and diffusion of CO$_2$ and other gases in bulk zeolites, however much less work has been done on the effect of surfaces on these processes. Surface effects are very important as in industrial applications it can be beneficial to use membranes made up of nanosized microporous crystals i.e. not exceeding 100 nm [92]. In these cases, the diffusion through the surface region may have a great effect on the overall transport in the system as the external surface area to volume ratio is high.

There are several computational studies of the surfaces of LTA including Slater et al. [93] calculating the stable surfaces of siliceous LTA and Greò et al. [94] investigating the structuring of water at the LTA surfaces for both the siliceous and sodium aluminosilicate forms. Combariza and Sastre [95] studied the influence of the siliceous {100} LTA surface on the adsorption of methane using molecular dynamics (MD) simulations. Increasing the methane loading decreases the adsorption free energy barrier while the surface permeability increases. Thompho et al. [96] explored the effect of silanol groups at the zeolite surface on the permeation of methane through the {010} silicalite-1 surface. The surface permeation was lower in the presence of silanol groups. The adsorption mechanism of $n$-butane and isobutane at the surface of silicalite was probed using MD and Monte Carlo (MC) simulations by Chandross et al. [97]. The molecules first adsorb in a layer at the surface, where they hop between preferred adsorption sites before entering a pore mouth. The time spent in this adsorption layer is usually around 10 ps. The interfacial region of silicalite was also found to be important for the adsorption of hexadecane in a study by Webb et al. [98], particularly when adsorbed molecules blocked the surface adsorption sites. The sorption of molecules to a zeolite surface has also been investigated experimentally. Jentys et al. [99] used fast time-resolved IR spectroscopy to study the sorption and transport of aromatics such as benzene from the gas phase onto hydroxyl groups on the surface and in the pores of H-ZSM-5. The surface permeability of nanoporous particles was determined experimentally using pulsed field gradient NMR [100, 101].

Newsome and Sholl [102] compared two methods (dual control volume grand canonical molecular dynamics, DCV-GCMD, and Local Equilibrium Flux Method, LEFM) for estimating the resistance to mass transfer as molecules diffuse through the gas-zeolite interfaces of membranes. Their new LEFM method is a good approximate technique to determine the importance of the interface resistance before using the computationally expensive DCV-
Chapter 1. Introduction

GCMD simulations. Zimmermann et al. [103, 104] investigated the effect of surfaces on the transport of methane and ethane in zeolite AFI. They calculated the surface barriers to diffusion and their implication for the overall flux across a membrane using a variety of molecular simulation techniques (MD, Monte Carlo and Reactive Flux) and tracer molecules. The molecules follow paths close to the pore walls both in the zeolite interior and at the surface. They accurately predicted the surface permeability and found that it does not follow the behaviour of the diffusion coefficients and can be very low, particularly at low temperatures and loading. The work was extended to cover zeolites with different structures, comparing AFI, LTL and MFI [105]. The impact of the surface barriers for gases is important for thin zeolite layers only (up to around 100 unit cells deep) and after that can be assumed to be insignificant. The barriers were also found to depend strongly on the nanopore type, in particular the surface barriers increase in significance with smoother nanopores. There are a number of experimental studies on the permeability of small molecules such as H₂, CO₂, N₂ and CH₄ through zeolite membranes and the selectivity to specific molecules [106–114], many of which focus on silicalite-1 membranes and their modifications.

The surface structure of zeolites has been shown to be important for the selectivity of binary gas mixtures. Mizukami et al. [115] modelled the diffusion of a binary mixture of CO₂/N₂ through thin (30 Å) membranes of NaY and NaA. The surfaces were hydroxylated and the zeolite structures were fixed throughout the MD simulations. The simulations monitored the diffusion of a 1:1 CO₂/N₂ mixture permeating NaY and NaA {111} membranes and a NaA {100} membrane and the separation ratios across the three membranes. The CO₂ selectivity decreased in the order NaA {100} > NaY {111} > NaA {111} and the difference in selectivity between membranes was attributed to the difference in pore diameters at the surface. Jee et al. [116] took the investigation into the impact of surface structure one step further by actively modifying the structure of a silicalite surface with a thin layer of amorphous silica. This improved the H₂/CH₄ selectivity without an unacceptable drop in H₂ flux through the membrane.
1.3 Aims of the Thesis

Having reviewed the research that has been published in the area of CO$_2$ adsorption in zeolites, we have identified a number of key areas that are less well studied, so will form the focus of our work. The first is the effect of surfaces on CO$_2$ transport at surfaces, and the second is the effect of water on CO$_2$ adsorption. Therefore the aims for this thesis are as follows:

- Development of a potential model that can be used for the simulation of CO$_2$ and H$_2$O in siliceous and aluminosilicate zeolites and at their surfaces. The zeolite potential needs to be transferable between frameworks and compositions, and compatible with CO$_2$ and H$_2$O, as well as including terms for hydroxyl groups that will be present at the zeolite surfaces. The suitability of the model can be ascertained by calculating structural parameters such as the unit cell dimensions, adsorption isotherms, heats of adsorption and diffusion coefficients, all of which can be compared to experimental values.

- Investigation into the effect of surface structure and composition on the adsorption and transport of CO$_2$ at zeolite surfaces. Molecular dynamics simulations can be used to model CO$_2$ in slabs of zeolites to find the preferred adsorption sites, the structuring of the molecules at the surfaces, and the density and diffusion of the molecules at surface compared to in the bulk zeolites. Both the composition of the zeolite and the surface type can be varied in order to carry out a comprehensive study.

- Investigation into the effect of water on the adsorption and transport of CO$_2$ in zeolites and at zeolite surfaces. Firstly concentrating on the bulk zeolite structures, CO$_2$ adsorption sites will be identified and how they change when water is also present will be investigated. Secondly focusing on zeolite slabs, the structuring at the surface and the rates of diffusion through the surfaces can be analysed.
Chapter 2

Potential Models

To model a system of particles, we must evaluate the interaction energies and forces between all of the atoms. The techniques for modelling the interaction energies can be separated into two main groups: quantum mechanical and classical methods. Quantum methods model the electron wave functions, in effect solving the many-bodied Schrödinger equation directly. The techniques are therefore very expensive computationally, which limits the size of system and/or length of real time that can be modelled. The less computationally expensive classical methods use potential-based models, which are parameterised analytical equations used to represent the attractive and repulsive forces between the atoms.

The simulation techniques we have used are all potential-based techniques and are detailed in chapter 3. We base our methods on the Born model of solids [117], which assumes that the sum of all pairwise interactions between atoms \( i \) and \( j \) in a simulation cell gives the lattice energy, \( U_{ij} \). If the system requires many-body interactions additional terms can be added, as in equation 2.1.

\[
U_{ij} = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} E_{ij}(r_{ij}) + \sum_{ijk} E_{ijk}(r_{ijk}) + \cdots \tag{2.1}
\]

\( q \) is the charge, \( \varepsilon_0 \) is the permittivity of free space and \( r \) is the distance between atoms \( i \) and \( j \). The first term describes the long range Coulombic interactions and the second and third terms describe the short-range two-body and many-body interactions. In the remainder of this chapter the equations and parameters for the short- and long-range interactions will be defined and the potential parameters we have used will be listed.
2.1 Long range interactions

The long range interactions within a lattice are Coulombic or electrostatic interactions between ions and for inorganic solids often account for 80% of the energy of the system. The Coulombic contribution takes the form of equation 2.2:

\[ U_C = \frac{1}{2} \sum_{i=1}^{N} q_i \phi(r_i) \]  

(2.2)

where \( \phi(r_i) \) is the electrostatic potential at the position of ion \( i \):

\[ \phi(r_i) = \sum_{j} \frac{q_j}{r_{ij}} \]  

(2.3)

When subjected to periodic boundary conditions (see chapter 3), described by three repeat vectors \( c_1, c_2, c_3 \), the interaction of the simulation cell with the rest of the system can be calculated. This means that for an ion \( q_i \) at location \( r_i \), there are also ions with charge \( q_i \) at \( r_i + n_1 c_1 + n_2 c_2 + n_3 c_3 \) where \( n_1, n_2, n_3 \) are arbitrary integers. This notation is simplified to \( r_i + nL \), where \( L \) is the characteristic length of the supercell. Therefore the total Coulombic interaction energy including the periodic images can be written as:

\[ U_C = \frac{1}{2} \sum_{n} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{|r_{ij} + nL|} \]  

(2.4)

A factor of a half is introduced to cancel out the double counting of ions and the \( ' \) symbol serves to exclude the term \( i = j \) when \( n = 0 \). In these (equations 2.2, 2.3 and 2.4) and the following equations we have omitted the factors of \( 4\pi\varepsilon_0 \) for simplicity, which corresponds to adopting a non-SI unit of charge.

For modelling purposes the summation has problems as it converges slowly with \( r \) due to the \( r^{-1} \) term. Therefore, alternative summation techniques must be used, such as those by Ewald [118] and Parry [119, 120].

2.1.1 Ewald Summation

In the Ewald summation technique the point charges are neutralised with a symmetrical charge distribution of the opposite charge, usually a Gaussian distribution with a width of \( \sqrt{2/\alpha} \) (equation 2.5).

\[ \rho_{Gauss}(r) = -q_i (\alpha/\pi)^{3/2} \exp\left(-\alpha r^2\right) \]  

(2.5)
\( \alpha \) is chosen to maximise computational efficiency. The Gaussian distribution of the opposite charge can easily be summed by a direct summation in real space. However, as the full interaction between point charges is not represented, a second summation is carried out representing a charge distribution of the same shape but with the opposite charge (the same charge as \( q_i \)), which converges in reciprocal space through a Fourier series. This is shown schematically in figure 2.1.

\[
\text{Original} = \sum_{j=1}^{N} q_i \left(\frac{\alpha}{\pi}\right) \exp \left[-\alpha \left| r - (r_j + n\mathbf{L}) \right|^2 \right]
\]

Figure 2.1: Ewald summation technique where a divergent summation is split into two convergent summations, one in real space and one in reciprocal space.

First we shall concentrate on the Fourier part. The charge distribution, \( \rho_1 (r) \), of a periodic sum of Gaussians is:

\[
\rho_1 (r) = \sum_{j=1}^{N} q_i \left(\frac{\alpha}{\pi}\right) \exp \left[-\alpha \left| r - (r_j + n\mathbf{L}) \right|^2 \right]
\]  

(2.6)

To calculate the electrostatic potential, \( \phi_1 (r) \), due to this charge distribution we use Poisson’s equation:

\[
-\nabla^2 \phi_1 (r) = 4\pi \rho_1 (r)
\]  

(2.7)

which in its Fourier form is:

\[
k^2 \phi_1 (k) = 4\pi \rho_1 (k)
\]  

(2.8)

Fourier transforming the charge density \( \rho_1 \) gives:

\[
\rho_1 (k) = \frac{1}{V} \sum_{j=1}^{N} q_j \exp (-i\mathbf{k} \cdot \mathbf{r}_j) \exp \left(-k^2/4\alpha \right)
\]  

(2.9)

which inserted into Poisson’s equation gives:

\[
\phi_1 (k) = \frac{4\pi}{k^2} \frac{1}{V} \sum_{j=1}^{N} q_j \exp (-i\mathbf{k} \cdot \mathbf{r}_j) \exp \left(-k^2/4\alpha \right)
\]  

(2.10)

for \( k \neq 0 \).
Chapter 2. Potential Models

We next compute $\phi_1 (r)$:

$$
\phi_1 (r) = \sum_{k \neq 0} \phi (k) \exp (i k \cdot r)
$$

(2.11)

$$
= \frac{1}{V} \sum_{k \neq 0} \sum_{j=1}^{N} \frac{4 \pi q_j}{k^2} \exp [i k \cdot (r - r_j)] \exp \left( -\frac{k^2}{4a} \right)
$$

(2.12)

and therefore, from equation 2.2:

$$
U_1 = \frac{1}{2} \sum_i q_i \phi_i (r_i)
$$

(2.13)

$$
= \frac{1}{2} \sum_{k \neq 0} \sum_{j=1}^{N} \frac{4 \pi q_i q_j}{V k^2} \exp [i k \cdot (r_i - r_j)] \exp \left( -\frac{k^2}{4a} \right)
$$

(2.14)

We must now include a self-interaction term to compensate for the inclusion of a charge cloud of charge $q_i$ as well as a point charge $q_i$.

$$
U_{\text{self}} = \left( \frac{\alpha}{\pi} \right) \frac{1}{2} \sum_{i=1}^{N} q_i^2
$$

(2.15)

As $U_{\text{self}}$ does not depend on the particle positions the term is constant throughout each simulation.

Finally, the real-space sum is calculated as follows. The short-range electrostatic potential due to a point charge $q_i$ surrounded by a Gaussian with net charge $-q_i$ is:

$$
\phi_2 (r) = \frac{q_i}{r} \text{erfc} \left( \sqrt{\alpha} r \right)
$$

(2.16)

where erfc is the complementary error function, defined as:

$$
\text{erfc} (x) = 1 - \text{erf} (x)
$$

(2.17)

$$
= 1 - \left[ \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp (-u^2) \, du \right]
$$

(2.18)

$$
= \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} \exp (-u^2) \, du
$$

(2.19)

The total contribution of the screened Coulomb interactions to the potential energy is then given by:

$$
U_2 = \frac{1}{2} \sum_{i \neq j}^{N} q_i q_j \text{erfc} \left( \sqrt{\alpha} r_{ij} \right) / r_{ij}
$$

(2.20)
Chapter 2. Potential Models

The total electrostatic contribution of the screened Coulombic interactions to the potential energy is therefore:

\[ U_C = U_1 - U_{\text{self}} + U_2 \]  \hspace{1cm} (2.21)

2.1.2 Parry Summation

The Parry summation method [119, 120] is an adaptation of the Ewald method to deal with systems with two-dimensional periodicity such as surfaces. Rather than considering an infinite lattice, the Parry method considers the crystal as a series of infinite charged planes. The vectors are therefore now split into vectors that are in-plane and those perpendicular to the plane. For each plane the sum of charges can no longer be assumed to be zero, so a key component is that the \( k=0 \) term, neglected in the Ewald sum (equation 2.14) is included.

2.2 Short range interactions

Short range interactions can be split into repulsive forces between electron clouds at very short distances and attractive van der Waals forces as the distance increases. In covalent systems many-body terms also need to be included, such as angle and torsion terms. There are many potential forms that can be used to describe the short-range interactions, and in the following section the ones used in this work are detailed.

2.2.1 Lennard-Jones Potential

The Lennard-Jones 12-6 potential is described by equation 2.22.

\[ E_{\text{LJ}} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \]  \hspace{1cm} (2.22)

The first term represents the repulsive interaction between electron clouds, which are dominant at short distances due to the \( r^{-12} \) term. For slightly longer distances the second term, representing the attractive dispersion forces, becomes more dominant due to its dependence on the \( r^{-6} \) term. \( A \) and \( B \) are chosen to fit the properties of the material, and can be defined as follows:

\[ A_{ij} = \epsilon_{ij} r_{mij}^{12} \]  \hspace{1cm} (2.23)
where $\varepsilon_{ij}$ is the depth of the potential well and $r_{mij}$ is the separation between ions at the minimum of the energy well, as shown in figure 2.2.

\[ B_{ij} = 2\varepsilon_{ij}r_{mij}^{6} \]  

(2.24)

Figure 2.2: Schematic of the Lennard-Jones potential

### 2.2.2 Buckingham Potential

The Buckingham potential is similar to the Lennard-Jones potential, but it uses a different functional form for the repulsive term.

\[ E_{B} = A_{ij}\exp \left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^{6}} \]

(2.25)

$A_{ij}$ relates to the ion size and $\rho_{ij}$ relates to the ion hardness. Due to the added flexibility of the repulsive term, the Buckingham potential is often used for the simulation of polar solids where the repulsive terms are more significant.

### 2.2.3 Morse Potential

The Morse potential is usually used to model covalently bonded interactions where the separations vary significantly from the equilibrium distance:

\[ E_{M} = D \left[ 1 - \exp \left(-B_{ij} \{r_{ij} - r_{mij}\} \right) \right]^{2} - D \]

(2.26)

where $D$ is the well depth (relative to the dissociated atoms), $r_{m}$ is the equilibrium bond distance and $B_{ij}$ relates to the curvature of the potential well curve.
2.2.4 Harmonic Potential

The harmonic bond potential adds an energy penalty if a bond length deviates from its equilibrium distance:

\[ E_H = \frac{1}{2} k_{ij} (r_{ij} - r_0)^2 \quad (2.27) \]

where \( k \) is the harmonic force constant and \( r_{ij} \) and \( r_0 \) are the bond distance and equilibrium bond distance.

2.2.5 Three body potential

The three body potential takes into account energy changes that occur when the bond angle, \( \theta \), between a central ion, \( i \), and two neighbouring ions, \( j \) and \( k \), in a molecule or framework fluctuates from the equilibrium bond angle, \( \theta_0 \). The potential depends on the square of the fluctuation, and is therefore zero at the equilibrium angle:

\[ E_{ib} = \frac{1}{2} k_{ijk} (\theta - \theta_0)^2 \quad (2.28) \]

2.3 Our Potential Model

The CO\(_2\) potential that we chose to use in this work was the EPM2 potential model by Harris and Yung [121]. The EPM2 model has been widely used for the simulation of CO\(_2\) and accurately reproduces the liquid-vapour coexistence curve and the critical properties. For the zeolites we needed a model that could be used to model zeolite slabs, with a variety of different framework structures, Si:Al ratios and extra-framework cations. The model also needed to include hydroxyl potentials so that we could model zeolite surfaces. We chose the CLAYFF force field [122], originally parameterised for the simulation of clay minerals, which can be thought of as chemically similar to zeolites because of their aluminosilicate composition. It specifies parameters for a range of metals including Li, Na and Ca. The CLAYFF model is designed to be used with the SPC/E water model [123], indeed the hydroxyl and oxygen-oxygen interactions of CLAYFF are based on the SPC model. Therefore the SPC/E is the water model that we used. The CLAYFF force field has been used successfully for the simulation of zeolites by Bushuev and Sastre [124]. They used the CLAYFF parameters for the zeolite and added O-Si-O and Si-O-Si bend terms to accurately reproduce the zeolite structures. Kerisit et al. [125] successfully used the EPM2 and SPC/E models.
with the CLAYFF model in simulations of scCO₂/H₂O mixtures above a forsterite surface. The zeolite, CO₂ and water potential parameters that we used are listed in table 2.1. A full description of their derivation can be found in chapter 4.

Table 2.1: Lennard-Jones potential parameters and partial charges. Subscript Z refers to zeolite, H refers to hydroxyl, s refers to siliceous zeolite and a refers to aluminosilicate zeolite. Three body terms apply to the following bonds: O-Si-O, O_H-Si-O, O_H-Si-O_H, Si-O_H-H, O-Al-O, O_H-Al-O, O_H-Al-O_H, Al-O_H-H.

<table>
<thead>
<tr>
<th>Charge</th>
<th>$\varepsilon$ (eV)</th>
<th>$r$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
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<td>7.98817x10$^{-8}$</td>
</tr>
<tr>
<td>Al</td>
<td>1.575</td>
<td>7.98817x10$^{-8}$</td>
</tr>
<tr>
<td>O$_{Zs}$</td>
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<td>0.006739</td>
</tr>
<tr>
<td>O$_{Za}$</td>
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<tr>
<td>O$_{Hs}$</td>
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</tr>
<tr>
<td>O$_{Ha}$</td>
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<tr>
<td>H$_W$</td>
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<td>-</td>
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</table>

CO₂ - CO₂

<table>
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<th>$\theta_{ijk}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.1</td>
<td>109.47</td>
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CO₂ - zeolite and water

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<th>$\theta_{ijk}$ (°)</th>
</tr>
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<tr>
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<table>
<thead>
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<th>$j$</th>
<th>$k_{ij}$ (eVÅ$^{-2}$)</th>
<th>$r_{ij}$ (Å)</th>
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<tbody>
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<td>O$_H$</td>
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<td>30.0</td>
<td>1.0</td>
</tr>
<tr>
<td>O$_W$</td>
<td>H$_W$</td>
<td>48.0591</td>
<td>1.0</td>
</tr>
</tbody>
</table>
2.3.1 Mixing Rules

To mix together Lennard-Jones potential parameters, we use the Lorentz-Berthelot rules (equations 2.29 and 2.30) to generate all of the parameters that are needed for the calculations.

\[
e_{ij} = \sqrt{e_{ii} e_{jj}} \quad (2.29)
\]

\[
r_{ij} = \frac{r_{ii} + r_{jj}}{2} \quad (2.30)
\]

The Lorentz-Berthelot rules are widely used, however it has been shown that the rules do not always accurately represent interactions leading to deviation from experiment [126, 127]. The forcefield used in this work (CLAYFF) was parameterised to use the Lorentz-Berthelot mixing rules, and we show in sections 4.3 and 4.4 that we can accurately reproduce experimental data.

2.4 Summary

This chapter introduced the potential models used to calculate the interaction energies and forces between species in potential-based techniques. The next step is to apply them in simulations to calculate the desired properties of a system. The methods used in this thesis are described in chapter 3.
Chapter 3

Computational Methods

In this chapter the three main computational methods are described: energy minimisation (section 3.1), molecular dynamics (section 3.2) and grand canonical Monte Carlo (section 3.3), each of which depends for its accuracy on the potential models described in chapter 2.

All of our atomistic simulations use periodic boundary conditions, which replicate the simulation cell through space to form an infinite lattice. This has the advantage of allowing the number of atoms treated to be relatively small, as each experiences the interaction of an infinite set of images. If a molecule leaves the cell through one face, it simultaneously enters the cell through the opposite face. A two dimensional representation is shown in figure 3.1.

![Figure 3.1: Two-dimensional representation of periodic boundary conditions.](image)
3.1 Energy Minimisation

Energy minimisation (EM) is used to find the lowest energy structure of a material. An initial structure is altered by iteratively moving the atom positions in order to lower the energy of the system. The technique relies on the use of potential models to describe the attractive and repulsive forces between all of the atoms in the structure. We used EM to minimise the zeolite crystal lattice and to find the most stable surfaces using the METADISE code (Minimum Energy Techniques Applied to Dislocation, Interface and Surface Energies) [128].

There are a few disadvantages to EM; firstly the technique requires an initial structure for the process to be run on. Secondly if the energy surface is complex there is the possibility that when an energy minimum has been reached, it could be a local minimum not the global minimum. Finally, the technique does not take into account any of the crystal vibrations and hence neglects temperature, i.e. it is equivalent to the simulations being run at zero Kelvin and ignoring the zero point vibrations. However, although we do not take account of the vibrations in the minimisation, when minimising a crystal structure we do routinely calculate the vibrational frequencies to ensure that there are no instabilities, identified by imaginary modes.

There are two approaches that can be used for EM simulations: constant volume and constant pressure. In constant volume simulations the dimensions of the cell are kept constant, while the ions are allowed to move. For constant pressure, the unit cell dimensions and the positions of the ions are allowed to relax. The ions are considered to have reached the minimum position when all of the net forces are equal to zero:

\[
\frac{dU}{dr} = 0
\]  

(3.1)

where \( U \) is the lattice energy and \( r \) is the atom positions. There are several iterative algorithms that can be used to carry out the energy minimisations, which are described in the following sections.

3.1.1 Steepest Descent and Conjugate Gradients Methods

The steepest descent method searches for an energy minimum by following the slope of the energy surface. The direction of the steepest descent is opposite to the energy gradient, \( g \).
Chapter 3. Computational Methods

During the iterative process, the position of the atoms at iteration \( n+1 \) is calculated using:

\[

\mathbf{r}_{n+1} = \mathbf{r}_n - \alpha_n \mathbf{g}_n
\]

(3.2)

where \( \alpha \) is a constant related to the step size. The direction of each step does not take into account the direction of the previous step, which usually makes the iteration process inefficient. This can be overcome by using the conjugate gradients method [129], which calculates the displacement at step \( n \), \( \mathbf{S}_n \), using the gradient in step \( n \) and the displacement from the previous step:

\[

\mathbf{S}_n = -\mathbf{g}_n + \gamma_n \mathbf{S}_{n-1}
\]

(3.3)

where

\[

\gamma_n = \frac{\mathbf{g}_n \cdot \mathbf{g}_n}{\mathbf{g}_{n-1} \cdot \mathbf{g}_{n-1}}
\]

(3.4)

The conjugate gradients method is more efficient than the steepest descent method, particularly for systems where the energy surface has long narrow valleys. It also has the advantage of only requiring the first derivative of the energy, which is rapid to calculate. However usually a large number of steps are required to reach an accurate result.

### 3.1.2 Newton-Raphson Method

The Newton-Raphson method [130] is a second derivative method, making it more efficient than the conjugate gradients method, as it requires fewer iteration steps to reach a minimum. The energy is expressed as a Taylor expansion to the second derivative:

\[

U(\mathbf{r} + \delta \mathbf{r}) = U(\mathbf{r}) + \frac{dU(\mathbf{r})}{d\mathbf{r}} \delta \mathbf{r} + \frac{1}{2} \frac{d^2U(\mathbf{r})}{d\mathbf{r}^2} (\delta \mathbf{r})^2 + \vartheta (\delta \mathbf{r})^3
\]

(3.5)

where \( \delta \mathbf{r} \) is the displacement of ions between iterations \( n \) and \( n+1 \) and \( \vartheta \) is an accuracy parameter. The gradient at step \( n+1 \) can then be defined as:

\[

\mathbf{g}_{n+1} = \frac{dU(\mathbf{r})}{d\mathbf{r}} + \frac{d^2U(\mathbf{r})}{d\mathbf{r}^2} \delta \mathbf{r}
\]

(3.6)

\[

\therefore \mathbf{g}_{n+1} = \mathbf{g}_n + \mathbf{H}_n \cdot \delta \mathbf{r}
\]

(3.7)

where \( \mathbf{H}_n \) is a Hessian matrix. At the energy minimum, \( \mathbf{g}_{n+1} \) is equal to zero, so the atom displacement is given by:

\[

\delta \mathbf{r} = -\mathbf{g}_n \cdot \mathbf{W}_n
\]

(3.8)
where $W_n$ is the inverse of the Hessian matrix, or $H^{-1}$. Therefore the equation for calculating new atomic positions can be written as:

$$r_{n+1} = r_n - g_n \cdot W_n$$ \hspace{1cm} (3.9)

The Newton-Raphson method requires fewer iterations than the conjugate-gradients method to reach the energy minimum, however for each iteration both the first and second derivatives of the energy must be calculated as well as the inverse of the second derivative matrix, making it very time consuming computationally. There are a number of methods, called quasi-Newton methods, that use approximations of the inverse Hessian to speed up the minimisation. One such method is the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [131]. Instead of calculating the inverse Hessian at each step, it is approximated and only recalculated at fixed intervals or when the energy changes are too large for the approximation to be valid. The approximation depends on the strains, forces, and the previous inverse Hessian matrix.

A strategy that can be used to find the energy minimum is first to use conjugate gradient for a quick scan, followed by BFGS, then finally use Newton-Raphson to pinpoint the exact minimum. The iterative algorithms are used to speed up the energy minimisation technique, but they do not necessarily overcome the problem of finding local rather than global minima. Therefore a series of energy minimisations could be carried out using different initial structures; alternatively molecular dynamics can be used (section 3.2), which gives the atoms velocity allowing them to overcome energy barriers and therefore find the global minimum.

### 3.1.3 Surface Simulation

Surfaces of a crystal are generated by cleaving the bulk structure along a specified Miller index. The indices $(hkl)$ denote a plane that is orthogonal to the $(h,k,l)$ direction, and the low index Miller indices are shown in figure 3.2.

As well as the direction of the cut, the location is also important, as it can lead to a range of different surface terminations for the same Miller index, which will also have different stabilities. Bertaut [132] showed that when the crystal is built by unit cells which have a dipole moment perpendicular to the surface then the surface energy will diverge as the crystal gets thicker and eventually will become infinite. Tasker [133] then defined three
possible types of surface that can be created by changing the location of the cut (shown schematically in figure 3.3):

- Type I surfaces are constructed from repeat units which each have an overall charge of zero. There is a stoichiometric ratio of cations to anions, so there is no net dipole moment.

- Type II surfaces consist of charged sheets with a symmetric stacking sequence, again leading to repeat units with no net dipole moment.

- Type III surfaces are also made up from charged sheets but they are stacked asymmetrically, leaving repeat units with a net dipole moment perpendicular to the surface.

Type I and II surfaces are stable, but the net dipole in type III surfaces results in the surface energies being divergent, i.e. dependent on system size. However, these are also normally unstable. In order to generate stable and converged type III surfaces, they can be reconstructed, for example by removing half of the surface atoms and relocating them to the bottom of the cell (figure 3.3) [134].
3.1.3.1 Generation of Surfaces

Tasker’s initial approach to modelling surfaces produces a crystal that consists of many charged planes stacked on top of each other, which is very computationally expensive to model. This is overcome in the METADISE code by using the two-region approach that was also developed by Tasker [133]. This method considers the system to be comprised of two blocks, each containing two regions, which are periodic in two-dimensions. A schematic representation of this approach is shown in figure 3.4.

The atoms of region I are allowed to relax, while those in region II are held fixed at their bulk equilibrium positions. A bulk system is made up of two blocks, with the region I atoms adjacent to the interface. Surface simulations only contain one block, with the surface located at the top of region I. The energy of a block is made up of the energy of the ions in each of the two regions. The energy in each region can then be subdivided into the interaction energy between the ions in that region, and the interaction energy between that region and the other region. As the ions in region II are held fixed throughout the simulation the energy of interaction between ions in region II is unchanged and therefore is neglected. The total energy is therefore calculated by:

$$E_{tot} = \sum_{i}^{N} U(r_{ij}) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} U(r_{ij}) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} U(r_{ij})$$

$$= \sum_{i}^{N} U(r_{ij}) + \sum_{i}^{N} U(r_{ij})$$

(3.10)

where $i_I$ and $j_I$ are atoms in region I and $i_{II}$ and $j_{II}$ are atoms in region II.
The stability of a surface can be determined by calculating the surface energy, $\gamma$, which is defined as the energy required to cleave the surface and is equivalent to the excess energy of a surface compared to a bulk system with the same number of atoms:

$$\gamma_{\text{dry}} = \frac{U_S - U_B}{A}$$  \hspace{1cm} (3.11)

where $U_S$ and $U_B$ are the energy of the surface block and the energy of the bulk with the same number of atoms and $A$ is the surface area. The surfaces of some materials, such as zeolites, are not stable unless they are hydroxylated because cutting the surface exposes 3-fold coordinated silicon atoms, which are very reactive and hence will spontaneously recover their 4-fold coordination. This is generally modelled by the dissociative adsorption of water onto the surface, adding hydroxyl groups ($\text{OH}^-$) to Si atoms and protons to surface O atoms to maintain surface neutrality. The surface energy is now calculated by:

$$\gamma_{\text{wet}} = \frac{U_H - U_B - nE_{\text{H}_2\text{O}}}{A}$$  \hspace{1cm} (3.12)
where $U_H^*$ is the energy of the hydroxylated surface, $n$ is the number of water molecules adsorbed to the surface and $E_{H_2O}$ is the energy to transfer a proton from water to a lattice oxygen attached to a Si atom. The calculation of this energy will be described in section 4.2.

### 3.2 Molecular Dynamics

Molecular dynamics (MD) simulations use the same interatomic potentials as EM to compute the forces on the molecules. Newton’s equations of motion are then solved to find the velocity, acceleration and position of particles in a defined space at given time intervals. Therefore the particles are effectively in time dependent motion. The computational code we have used to carry out MD simulations is DL_POLY 2.0 [135].

The force, $f_i$, acting on an atom $i$ of mass $m_i$, can be used to determine its acceleration, $a_i$:

$$f_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2}$$  \hspace{1cm} (3.13)

where $r_i$ is the position of the atom $i$. If there is no force acting on the system, the atom positions after a change in time, $\Delta t$, change by $v_i(t) \Delta t$, where $v_i$ is the velocity. When the force is not zero, but remains constant then the new velocities and positions after a change in time can be calculated by:

$$v_i(t + \Delta t) = v_i(t) + a_i(t) \Delta t$$  \hspace{1cm} (3.14)

$$r_i(t + \Delta t) = r_i(t) + v_i(t) \Delta t + \frac{a_i(t) \Delta t^2}{2}$$  \hspace{1cm} (3.15)

However, these equations are only true if the time step is infinitely small. In practice a computer code requires a finite length of time step, therefore integration algorithms are employed.
3.2.1 Integration Algorithms

Integration algorithms are used to determine the coordinates of the atoms at a finite time step. The positions, velocities and accelerations are estimated using a Taylor expansion:

\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{a}_i(t)\Delta t^2}{2} + \frac{\mathbf{b}_i(t)\Delta t^3}{6} + \cdots
\] (3.16)

\[
\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \mathbf{a}_i(t)\Delta t + \frac{\mathbf{b}_i(t)\Delta t^2}{2} + \cdots
\] (3.17)

\[
\mathbf{a}_i(t + \Delta t) = \mathbf{a}_i(t) + \mathbf{b}_i(t)\Delta t + \cdots
\] (3.18)

\[
\mathbf{b}_i(t + \Delta t) = \mathbf{b}_i(t) + \cdots
\] (3.19)

where \(\mathbf{b}_i\) is the third derivative of the position with respect to time. The simplest and most widely used integration algorithm is the Verlet algorithm [136], which uses the positions and accelerations at time \(t\) and the positions at the previous step, \(t - \Delta t\) to calculate the new positions at \(t + \Delta t\). The positions at these steps can be defined by the following third-order Taylor expansions:

\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{a}_i(t)\Delta t^2}{2} + \frac{\mathbf{b}_i(t)\Delta t^3}{6} + \vartheta\Delta t^4
\] (3.20)

\[
\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \mathbf{v}_i(t)\Delta t + \frac{\mathbf{a}_i(t)\Delta t^2}{2} - \frac{\mathbf{b}_i(t)\Delta t^3}{6} + \vartheta\Delta t^4
\] (3.21)

Equations 3.20 and 3.21 can be summed and rearranged, to give an expression for the position at time \(t + \Delta t\):

\[
\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \mathbf{a}_i(t)\Delta t^2 + \vartheta\Delta t^4
\] (3.22)

or

\[
\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\Delta t^2}{m} \mathbf{f}(t) + \vartheta\Delta t^4
\] (3.23)

The velocity is not explicitly calculated, however it can be calculated by dividing the difference in positions at time \(t + \Delta t\) and \(t - \Delta t\) by \(2\Delta t\). It can therefore only be calculated once the positions are known.
An alternative form of the algorithm is the Verlet leapfrog algorithm [137], which evaluates the velocities at half-integer time steps (equations 3.24 and 3.25) and uses them to calculate the new positions.

\[
v_i\left(t - \frac{1}{2}\Delta t\right) = \frac{r_i(t) - r_i(t - \Delta t)}{\Delta t}
\]

\[
v_i\left(t + \frac{1}{2}\Delta t\right) = \frac{r_i(t + \Delta t) - r_i(t)}{\Delta t}
\]

Equation 3.23 can be rearranged to give:

\[
\frac{r_i(t + \Delta t) - r_i(t)}{\Delta t} = \frac{r_i(t) - r_i(t - \Delta t)}{\Delta t} + \frac{\Delta t}{m} f(t) + \vartheta \Delta t^3
\]

and combining this with equations 3.24 and 3.25 we get:

\[
v_i\left(t + \frac{1}{2}\Delta t\right) = v_i\left(t - \frac{1}{2}\Delta t\right) + \frac{\Delta t}{m} f(t) + \vartheta \Delta t^3
\]

and from equation 3.25:

\[
r_i(t + \Delta t) = r_i(t) + v_i\left(t + \frac{1}{2}\Delta t\right) \Delta t + \vartheta \Delta t^4
\]

Therefore the velocities at time \( t + \frac{1}{2}\Delta t \) are calculated from the positions at \( t \) and \( t - \Delta t \) and the forces; the positions at time \( t + \Delta t \) are calculated from the positions at time \( t \) and the new velocities. The current velocities can be calculated as follows:

\[
v_i(t) = \frac{1}{2} \left[ v_i\left(t + \frac{1}{2}\Delta t\right) + v_i\left(t - \frac{1}{2}\Delta t\right) \right]
\]

and can be used to calculate any properties that depend on the positions and the velocities at the same time. At the start of the simulation initial velocities are required, which are randomly assigned ensuring that the system starts at the required temperature and the simulation cell has no translational momentum.

### 3.2.2 Time Steps and Equilibration

The time step, \( \Delta t \), that is chosen for a simulation is very important - too long and the atoms will move unphysical distances causing the simulation to fail, too short and it will take much longer to simulate the same length of real-time. We therefore try to use a time step that is
as long as possible while still giving accurate results; in this work we use a time step of 1 fs
\((10^{-15} \text{ seconds})\) and run simulations for several million steps to obtain a simulation real-
time length of several ns, long enough to ensure convergence of the desired properties. The
first few tens of thousands of steps of a simulation are the equilibration period, during which
the particles’ velocities are scaled to meet the desired temperature and pressure before data
are collected.

3.2.3 Ensembles

Ensembles describe the conditions that are used in a molecular dynamics simulation.

The microcanonical (NVE) ensemble uses a constant number of particles, system volume
and total energy. The conserved quantity in the NVE ensemble, derived from the Hamilto-
nian, \(H\), is:

\[
H_{\text{NVE}} = U + K.E. \tag{3.30}
\]

where \(U\) is the potential energy and \(K.E.\) is the kinetic energy.

The canonical (NVT) ensemble maintains the number of particles, the volume and the
temperature. A heat reservoir is used to keep the temperature constant; we use the Nosé-
Hoover thermostat [138], and this is the primary ensemble that was used to collect data in
this thesis. In the canonical ensemble Newton’s equations of motion are modified to include
a friction coefficient, \(\chi\):

\[
\frac{dv_i(t)}{dt} = a_i(t) - \chi(t)v_i(t) \tag{3.31}
\]

where the friction coefficient is defined by:

\[
\frac{d\chi(t)}{dt} = \frac{N_fk_B}{Q}(T(t) - T_{\text{ext}}) \tag{3.32}
\]

in which \(N_f\) is the number of degrees of freedom, \(T(t)\) is the system temperature at time \(t\),
\(T_{\text{ext}}\) is the temperature of the heat reservoir and \(Q\) is the effective mass of the thermostat,
described by:

\[
Q = N_fk_BT_{\text{ext}}\tau_T^2 \tag{3.33}
\]

where \(\tau_T\) is a specified time constant, often referred to as the relaxation constant. In the
Verlet-leapfrog algorithm the calculation of the velocity at the half-integer time step (equa-
tion 3.27) is therefore modified to:

\[ v_i\left(t + \frac{1}{2} \Delta t\right) = v_i\left(t - \frac{1}{2} \Delta t\right) + \left[ \frac{f(t)}{m} - \chi(t)v_i(t) \right] \Delta t + \vartheta \Delta t^3 \]  

(3.34)

and the friction coefficient at both the half-integer time step and at time \( t \) can be represented by:

\[ \chi\left(t + \frac{1}{2} \Delta t\right) = \chi\left(t - \frac{1}{2} \Delta t\right) + \left[ \frac{N_f k_B}{Q} (T(t) - T_{ext}) \right] \Delta t \]  

(3.35)

and

\[ \chi(t) = \frac{1}{2} \left[ \chi\left(t - \frac{1}{2} \Delta t\right) + \chi\left(t + \frac{1}{2} \Delta t\right) \right] \]  

(3.36)

However, as \( v_i(t) \) is required to be able to calculate \( T(t) \) and therefore itself, several iterations are required to ensure self-consistency. In the canonical ensemble the conserved quantity, derived from the extended Hamiltonian for the system, is:

\[ H_{NVT} = H_{NVE} + \frac{1}{2} Q \chi(t)^2 + \frac{Q}{\tau_f} \int_s \chi(s) ds \]  

(3.37)

The isobaric-isothermal ensemble (NPT) uses a constant number of particles, pressure and temperature and the \( N\sigma T \) ensemble keeps the number of molecules, the strain and the pressure constant. These ensembles can be run either under isotropic or anisotropic conditions, depending on whether the shape of the simulation cell is allowed to change.

### 3.2.4 Properties from Molecular Dynamics

There are a number of different properties that can be calculated from MD simulations and the ones that are reported in this thesis are described here.

The radial distribution function (RDF) describes how particles are distributed around each other. The RDF gives information on how far away from a particular atom type, \( A \), other atoms, \( B \), are and how many \( B \) there are within a given radius of \( A \). The RDF between atoms \( A \) and \( B \) is calculated from:

\[ g_{A-B}(r) = \frac{\langle n_B(r, \delta r) \rangle}{4\pi \frac{N_B}{V} r^2 \delta r} \]  

(3.38)

where \( r \) is the diameter of the shell, \( n_B(r, \delta r) \) is the number of particle \( B \) between shells at \( r - \delta r/2 \) and \( r + \delta r/2 \), \( N_B \) is the total number of particles \( B \), and \( V \) is the volume of the
system, shown schematically in figure 3.5.

![Schematic of the radial distribution function](image)

**Figure 3.5:** Schematic of the radial distribution function

The transport properties of a system can be calculated from the mean-square displacement (MSD):

\[ D = \left( r_i(t) - r_i(0) \right)^2 / 6t \]  

(3.39)

where \( D \) is the diffusion coefficient. The diffusion coefficient can also be calculated in a specific direction, for example \( D_z \) which is diffusion in the \( z \) direction:

\[ D_z = \lim_{t \to \infty} \left( z(t) - z(0) \right)^2 / 2t \]  

(3.40)

The simulation cell can also be divided into slices along the \( z \)-direction and \( D_z \) calculated in each slice, therefore the \( z \)-diffusion can be plotted as a function of the \( z \)-coordinate. Further detail is given in section 5.1.2.

The residence time, \( \tau_r \), gives the average length of time that a particle, \( B \), spends within a specified radius of another particle, \( A \). The \( \tau_r \) is calculated from the residence time correlations function, which is defined as [139]:

\[ R(t) = \frac{1}{N_0} \sum_{i=1}^{N} \Theta_i(0) \Theta_i(t) \]  

(3.41)

where \( N \) is the number of \( B \) within the specified radius and \( \Theta_i \) is the Heaviside function, which is 1 if the \( i^{th} \) \( B \) molecule is within the radius at time \( t \) and 0 otherwise. A molecule is only judged to have left the radius if it does so for at least 2 ps, which allows molecules that temporarily leave then re-enter to be included in \( \tau_r \). Equation 3.41 is integrated to calculate
\[ \tau_r : \]
\[ \tau_r = \int_0^\infty R(t) dt \]  
(3.42)

### 3.3 Grand Canonical Monte Carlo

Monte Carlo methods use random sampling to obtain data. The Metropolis algorithm [140] is used to determine the probability of acceptance of a trial move:

\[ P = \min \left( 1, \exp \left\{ -\beta \Delta E \right\} \right) \]  
(3.43)

where \( \beta = \frac{1}{k_B T} \). If the move is energetically favourable it will be accepted, as the Boltzmann factor will be greater than 1. If the move is not energetically favourable it will only be accepted with the probability of the Boltzmann factor.

We use the grand canonical ensemble (\( \mu VT \) ensemble), where the chemical potential, volume and temperature are kept constant. An important difference between grand canonical Monte Carlo (GCMC) and the other techniques that have been described thus far is that the number of molecules is allowed to change throughout the simulation. Molecules are inserted and deleted in order to obtain the required density at a specified pressure. Therefore to simulate the adsorption of a gas into a material we do not have to run an MD simulation of a material in contact with a gas and monitor the uptake of the gas, which may take a significant amount of time to reach equilibrium, and wastes a lot of computational time modelling the gas phase, which we are not interested in. In such situations a very large system would need to be simulated in order for the effects of the surface to be minimised so that the bulk properties could be investigated. In GCMC simulations we can imagine that the system is in contact with a reservoir of gas with the required temperature and chemical potential and the number of adsorbed particles is allowed to fluctuate during the simulation. Although we cannot, therefore, explicitly specify the pressure of the gas, the pressure is related to the chemical potential via an equation of state so it is possible to calculate the pressure corresponding to a given chemical potential, assuming an ideal gas.

The trial moves that are used in GCMC are insertion, deletion and translation/rotation. First, the type of move that will be trialled is randomly selected, with a pre-determined probability. The move is then attempted, and will be accepted or rejected depending on the change in energy of carrying out the move, as detailed in the following section. All of the
GCMC simulations in this thesis were carried out using the DL_MONTE code [141].

### 3.3.1 Trial moves

During a GCMC simulation there are two main classes of moves that can be attempted.

1. **Displacement of particles**: A particle is selected at random and given a new conformation (i.e. for a rigid molecule a random translation or rotation) and the move is accepted according to a probability factor:

   \[
   P_m = \min \left( 1, \exp \left\{ -\beta \left[ E(s^N) - E(s^N) \right] \right\} \right)
   \]

   where \( E(s^N) \) is the energy of the system at coordinates \( s^N \).

2. **Insertion and removal of particles**: A particle is inserted at a random position, or a randomly selected particle is removed. The probability of acceptance of insertion is governed by equation 3.45 and deletion by equation 3.46.

   \[
   P_i = \min \left( 1, \frac{V}{\Lambda^3(N+1)} \exp \left\{ \beta \left[ \mu - E(N+1) + E(N) \right] \right\} \right)
   \]

   \[
   P_d = \min \left( 1, \frac{\Lambda^3N}{V} \exp \left\{ -\beta \left[ \mu + E(N-1) - E(N) \right] \right\} \right)
   \]

   where \( V \) is the system volume, \( N \) is the number of particles in the system \( \Lambda \) is the thermal de Broglie wavelength (the average de Broglie wavelength of the gas particles in an ideal gas at a specified temperature), \( \mu \) is the chemical potential and \( E(N) \) is the energy of the system containing \( N \) particles. The thermal de Broglie wavelength is defined by:

   \[
   \Lambda = \frac{h}{\sqrt{(2\pi \hbar T m)}}
   \]

   where \( h \) is Planck’s constant and \( m \) is the mass of a particle.

The selection procedure for the insertion/deletion of molecules within the DL_MONTE code uses the partial pressure as a simulation parameter. The insertion of a molecule is governed by the selection procedure:

\[
P_i = \min \left( 1, \frac{V \beta \rho}{(N+1)} \exp \left\{ -\beta \left[ E(N+1) - E(N) \right] \right\} \right)
\]
whilst the selection procedure for deletion is:

\[
P_d = \min \left[ 1, \frac{N}{V\beta P_g} \exp\left\{ -\beta \left[ E(N-1) - E(N) \right] \right\} \right]
\]

(3.49)

where \( P_g \) is the gas partial pressure.

### 3.3.2 Properties from Grand Canonical Monte Carlo

We have used GCMC to generate adsorption isotherms, which plot the amount of adsorbed gas as a function of pressure. A series of GCMC simulations are carried out on the same system over a range of pressures, and once they have reached equilibrium the total number of molecules adsorbed at each pressure is recorded. The isotherms are used to calculate the isosteric heat of adsorption using the Clausius-Clapeyron relationship:

\[
q = -R \left[ \frac{d \ln P}{d \left( \frac{1}{T} \right)} \right]
\]

(3.50)

First, a series of adsorption isotherms are generated over a narrow range of temperature; we typically used 263, 268, 273, 278 and 283 K (figure 3.6a). The data from these isotherms is used to generate adsorption isosteres, which are graphs of \( \log p \) vs. \( 1/T \) at constant coverage (figure 3.6b). The heat of adsorption is then calculated from the gradient by equation 3.50 (figure 3.6c).
Chapter 3. Computational Methods

Figure 3.6: Adsorption of CO\textsubscript{2} in Na-FAU (a) adsorption isotherms, (b) adsorption isosteres, (c) heats of adsorption. [N: the number of CO\textsubscript{2} molecules per unit cell].

3.4 Summary

Having described the key simulation techniques: EM, MD and GCMC, in the following chapters I will demonstrate their application to modelling CO\textsubscript{2} adsorption and transport in siliceous and aluminosilicate zeolites and at their surfaces.
Chapter 4

Development of Models

This chapter gives a brief overview of some zeolite structures in their siliceous forms and the nomenclature used to describe features of the framework structures (section 4.1). We also present the surface structures and stabilities of faujasite, zeolite A, mordenite and silicalite (section 4.2) before moving on to the development of our siliceous zeolite-CO$_2$ potential model (section 4.3), and its extension to aluminosilicates.

4.1 Siliceous Zeolites

As described in section 1.2.2.1, it has become common practice to classify zeolite structures into three broad types: cage-, channel- and intersecting channel-type; the zeolites that have been modelled in this work are shown in table 4.1, split into these categories.

Table 4.1: Zeolite structure classifications

<table>
<thead>
<tr>
<th>Cage-type</th>
<th>Channel-type</th>
<th>Intersecting channel-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITE, LTA, SOD</td>
<td>AFI, IFR, LTL, MOR, MTW</td>
<td>BEA, BEB, BEC, FAU, GME, HEU, ISV, IWR, MEL, MFI</td>
</tr>
</tbody>
</table>

Some zeolites, such as LTL, could be considered to be in two categories. In table 4.1 LTL has been classified as a channel-type zeolite, however it could also be considered to be a cage-type zeolite as the structure consists of one dimensional channels, but with wider and narrower sections which could be considered as cages. The classification of FAU is also debated; some people consider it to be intersecting-channel type, while others consider it to be cage-type. In fact, Beerdsen et al. [61] treat FAU as a class of its own, because a lot of its adsorption characteristics do not match the other classifications.
Chapter 4. Development of Models

4.1 Structures

The structures of some common zeolites were generated by energy minimisation in the METADISE code and are shown in this section alongside descriptions of their structural features.

4.1.1 Faujasite

Faujasite (FAU) is a rare naturally occurring zeolite, which is also synthesised industrially. It is found in sodium, magnesium and calcium forms. As mentioned previously, FAU sits in between the categories of cage-type and intersecting channel-type zeolites. It consists of sodalite cages linked together by 6-ring windows. This framework links together in a way as to give large 12-ring channels and pores and the siliceous form is shown in figure 4.1.

Figure 4.1: Structure of FAU, left: viewed along [110], right: viewed along [111]. [Si: grey, O: red].

4.1.2 Zeolite A

Zeolite A (Linde Type A or LTA) is a cage-type zeolite that is widely used in ion exchange, with applications such as washing detergents. Its structure is made up of sodalite cages linked via their 4-ring windows to produce double 4 rings (D4R), leaving alpha cages in between, which are linked by 8-ring windows (figure 4.2).

4.1.3 Zeolite L

Zeolite L (Linde type L or LTL) is a synthetic zeolite containing one dimensional 12-ring channels, which oscillate between wider and narrower sections (figure 4.3). It is used as a
highly selective catalyst for the aromatisation of hexane to benzene [142].

4.1.1.4 Mordenite

Mordenite (MOR) is one of the most abundant naturally occurring zeolites, and can be found in volcanic rocks such as rhyolite, andesite and basalt and in marine sediments [143]. It is used commercially as a catalyst in the petrochemical industry. MOR has a one-dimensional channel network, with smooth walled 12-ring channels and smaller 8-ring side channels (figure 4.4).
4.1.1.5 MEL and MFI

MEL and MFI (silicalite) have a three-dimensional pore network. MEL has smooth walled 10-ring channels in the [100] and [010] directions. MFI has these channels in the [010] direction, but in the [100] direction the 10-ring channels are staggered (figure 4.5). MFI is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerisation reactions [144].
Chapter 4. Development of Models

4.1.2 Cell Parameters

The calculation of unit cell parameters is a simple way to begin to assess the reliability of a potential model, as the parameters can be compared to experimental values. We have calculated cell dimensions two ways: energy minimisation (EM) and molecular dynamics (MD).

Table 4.2 shows our calculated lattice parameters compared to experimental values. Overall the comparison with experiment is very good, although there is a slight contraction in some of the dimensions. In general the MD dimensions are longer than the EM dimensions, which could be due to the increase in energy of the system by simulating it at temperature, although we acknowledge that it is well known that some zeolites undergo negative thermal expansion [145].

Table 4.2: Simulated zeolite lattice parameters (EM and MD in the N\(\sigma\)T ensemble at 300 K) compared to experiment. Experimental data from \(^a\)Artoli et al. [146] (siliceous), \(^b\)Hriljac et al. [147] (siliceous), \(^c\)Meier [148] (Si:Al = 5), \(^d\)Baerlocher and McCusker [149] (siliceous).

<table>
<thead>
<tr>
<th></th>
<th>EM</th>
<th>MD</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>MOR(^c)</td>
<td>17.987</td>
<td>20.080</td>
<td>7.411</td>
</tr>
<tr>
<td>LTA(^d)</td>
<td>23.534</td>
<td>23.534</td>
<td>23.534</td>
</tr>
</tbody>
</table>

4.2 Siliceous Zeolite Surfaces

Modelling zeolite surfaces is very important; the relative surface energies can be used to predict crystal morphology [94] and if we consider zeolite membranes or very fine powders/nano-sized grains the surface effects will be important. We can simulate the effect of surfaces on the adsorption and diffusion of molecules through materials.

The method for generating surfaces was described in section 3.1.3. Here more detail is given on the hydroxylation and the calculation of the water correction energy. As a reminder, the surface energy is calculated by:

\[
\gamma = \frac{U_H - U_B - nE_{H,O}}{A} \tag{4.1}
\]

where \(U_H\) is the energy of the hydroxylated surface, \(U_B\) is the energy of the bulk with the same number of atoms, \(A\) is the surface area, \(n\) is the number of water molecules adsorbed.
Chapter 4. Development of Models

to the surface and \( E_{H_2O} \) is the energy required to transfer a proton from water to a lattice oxygen attached to a surface silicon atom (for siliceous zeolites):

\[
O_2^{2-} + H_2O(g) \rightarrow 2OH^-(g)
\]  
(4.2)

It is difficult to calculate \( E_{H_2O} \) directly using potential-based methods due to the different charges on the oxygen atoms in \( O_2^{2-} \), \( OH^- \) and \( H_2O \). To overcome this problem we can construct an energy cycle as shown in figure 4.6. The values for reactions (2) and (3) are calculated from the lattice energy of \( SiO_2 \) and \( Si(OH)_4 \) by energy minimisation. The energy for reaction (1) is taken from DFT calculations; we used the value obtained by Greń et al. [94], and corrected it to include the water condensation energy of 43.4 kJ/mol to calculate the energy of cleaving the surface in liquid water. We calculate \( E_{H_2O} \) to be -243.8 kJ/mol per water molecule. All of the values we used in the energy cycle are listed in table 4.3.

![Energy cycle for the dissociative adsorption of water on silica.](image)

Table 4.3: Energies used in the energy cycle to calculate \( E_{H_2O} \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) ( \Delta E_r )</td>
<td>139.88</td>
</tr>
<tr>
<td>(2) ( SiO_2 )</td>
<td>-3974.4</td>
</tr>
<tr>
<td>(3) ( Si(OH)_4 )</td>
<td>-3260.2</td>
</tr>
<tr>
<td>(4) ( E_{H_2O} )</td>
<td>-487.6</td>
</tr>
</tbody>
</table>

In the following sections we focus on the surfaces of siliceous FAU, LTA, MOR and MFI, analysing the surfaces structures and the relative stability of the surfaces. The surface stabilities are important because they are likely to dictate which surfaces form during crystal growth as the crystal will attempt to lower its surface free energy, thereby affecting
the crystal morphology. For each surface a number of different terminations are possible depending on the location of the cut, so the energies of all of these were calculated, to find the most stable.

**4.2.1 Faujasite**

We calculated the surface energies for different surface terminations of the hydroxylated \{111\}, \{011\} and \{100\} surfaces of Si-FAU and these energies are shown in figure 4.7. The experimental crystal morphology is octahedral with the \{111\} surface expressed [150] and we correctly identified the \{111\} surface as the most stable with a surface energy of 0.17 J/m$^2$.

![Surface energies of Si-FAU](image)

Figure 4.7: Surface energies of Si-FAU for the lowest energy terminations of the \{100\}, \{011\} and \{111\} surfaces (coloured blue, red and green, respectively). Black outlines: the terminations that were used in this work; black dashed outlines: the other symmetrical slab terminations.

For our further work on the effect of surfaces on CO$_2$ adsorption and transport (chapter 5) we needed to use slabs of the zeolite and were only interested in surfaces that would give symmetrical slabs (which are indicated by dashed/solid borders in figure 4.7). The structures that we chose to use in our simulations have black borders; these surfaces are not always the most stable, however they are the most stable surfaces that will give a symmetrical zeolite slab. In the case of the \{100\} surface the two terminations that would give symmetrical slabs have the same surface energy (0.32 J/m$^2$). Greñ et al. [94] found with the shell model that singly hydroxylated Si atoms gave the most stable surfaces. As our model
had very similar energies we chose to consider the \{100\} surface that had only one hydroxyl
group per Si atom at the surface. The symmetrical \{100\}, \{011\} and \{111\} surfaces of FAU
that we used in further simulations are shown in figure 4.8.

![Figure 4.8: Hydroxylated surface structures of siliceous faujasite, a: \{100\}, b: \{011\}, c:
\{111\}. [Si: grey, O: red, H: white].](image)

From figure 4.7 we can see that there are two \{100\} surface terminations that are lower
in energy than the symmetrical surface that we chose to use in our simulations. Their struc-
tures are shown in figure 4.9 and in fact they are opposite surfaces, meaning that if a slab
were generated they would form the top and bottom surfaces of the slab. Although these
surfaces are lower in energy, they both have silicon atoms coordinated to two hydroxyl
groups. As mentioned before, we chose to focus on surfaces with only one hydroxyl group
per Si atom, so chose not to use this system. In future work we could, however, try running
some simulations using this slab structure to compare with the symmetrical slabs. For the
Chapter 4. Development of Models

{110} surface there is one surface termination that is slightly more stable than the symmetrical termination that we chose to use. However, its opposite termination is very unstable, so the average surface energy of a slab with these terminations would be 0.28 J/m$^2$, which is higher in energy than the termination we are using.

![Figure 4.9: Structures of the most stable {100} surfaces of Si-FAU with surface energies of (a) 0.27 J/m$^2$, (b) 0.28 J/m$^2$. [Si: grey, O: red, H: white].](image)

4.2.2 Zeolite A

We generated structures and energies for the {100}, {110} and {111} surfaces of Si-LTA. The three most stable surfaces have energies of 0.27 J/m$^2$ for {100}, 0.29 J/m$^2$ for {110} and 0.28 J/m$^2$ for {111} (figure 4.10).

![Figure 4.10: Surface energies of Si-LTA for the lowest energy terminations of the {100}, {110} and {111} surfaces (coloured blue, red and green, respectively).](image)

The structures of these surfaces are shown in figure 4.11. The surfaces of LTA were
simulated by Slater et al. [93] and by Greñ et al. [94], with both sets of simulations finding three stable \{100\} surfaces with similar surface energies. These three terminations are also our most stable three, however ours are not as close in energy to each other. Our most stable surface is the termination that they termed the single 4-ring (S4R) surface, and this was also found to be the most stable by Greñ et al. We also identified the same stable termination for the \{111\} surface as Greñ.

The surface energies of Si-LTA are generally slightly higher than those for Si-FAU. This is because the framework density of LTA is slightly higher than FAU (14.2 Si/1000Å² compared to 13.3 Si/1000Å² [149]) meaning that more bonds need to be broken per unit area in order to create the surface.

Figure 4.11: Hydroxylated surface structures of Si-LTA, a: \{100\}, b: \{110\}, c: \{111\}. [Si: grey, O: red, H: white].
Chapter 4. Development of Models

4.2.3 Mordenite

The surface energies of the \{001\}, \{010\} and \{100\} surfaces of MOR are presented in figure 4.12. The most stable surfaces are the \{100\} and \{010\}, both with energies of 0.27 J/m². The \{001\} surface (exposing the cross-section of the one-dimensional channels) is slightly less stable, with a surface energy of 0.39 J/m². The structures of these surfaces are shown in figure 4.13. A correlation is seen between the number of hydroxyl groups at the surface and the stability of the surface, relating to the number of bonds that need to be broken to generate the surface. The two most stable surfaces (\{100\} and \{010\}) have 0.013 H₂O/Å² and 0.015 H₂O/Å² respectively, while the \{001\} surface has 0.022 H₂O/Å².

Figure 4.12: Surface energies of Si-MOR for the lowest energy terminations of the \{001\}, \{010\} and \{100\} surfaces (coloured blue, red and green, respectively).
Figure 4.13: Hydroxylated surface structures of Si-MOR. a,b: \{001\}; c,d: \{010\}; e,f: \{100\}. [Si: grey, O: red, H: white].
4.2.4 Silicalite

The energies of the \{001\}, \{010\} and \{100\} surfaces of MFI are shown in figure 4.14. The most stable surfaces are the \{010\} and \{100\}, which both have energies of 0.28 J/m\(^2\) and 0.015 H\(_2\)O/Å\(^2\). These surfaces were also determined to be the most stable by Greñ [151]. The \{001\} surface has an energy of 0.39 J/m\(^2\) and has 0.020 H\(_2\)O/Å\(^2\). The structures of these three surfaces are shown in figure 4.15.

Figure 4.14: Surface energies of Si-MFI for the lowest energy terminations of the \{001\}, \{010\} and \{100\} surfaces (coloured blue, red and green, respectively).
Figure 4.15: Hydroxylated surface structures of Si-MFI. a,b: {001}, c,d: {010}, e,f: {100}. [Si: grey, O: red, H: white].
4.2.5 Trends in Surface Energy

Across all of the surfaces that we have investigated there is a correlation between the stability of the surface and the number of bonds that needed to be broken in order to generate the surface. A measure of this is the number of hydroxyl groups on the surface. Figure 4.16 plots the number of water molecules dissociatively adsorbed per unit area against the surface energy for all of the surfaces and terminations that we have modelled, and a strong correlation can be seen.

![Graph showing the correlation between surface energy and number of water molecules adsorbed.](image)

Figure 4.16: Correlation between the surface energy and the number of water molecules dissociatively adsorbed on the surface.

The surface energy increases with increasing numbers of hydroxyl groups. The points on the graph in figure 4.16 are coloured according to the maximum number of hydroxyl groups that are coordinated to each Si atom at the surface. This is a crude measure because many of the surfaces have a range of coordinations at the surface, for example in some cases most of the Si atoms are coordinated to just one OH\(^-\) but one has three OH\(^-\) groups and therefore the surface would be categorised as 3 OH\(^-\) per Si. However, in general the surfaces with higher numbers of OH\(^-\) groups per Si have a higher surface energy, which is a trend that was also seen by Gref\ñ [151].
4.3 Development of Zeolite-CO\textsubscript{2} Potential Model

There are many different potential models that have been used in the literature for modelling CO\textsubscript{2} in zeolites. Some have been developed for very specific systems, and some have been designed to be transferable to different zeolite frameworks. The CO\textsubscript{2} potential that we chose to use in this work was the EPM2 model by Harris and Yung [121]. The EPM2 model has been widely used for the simulation of CO\textsubscript{2}; it accurately reproduces the liquid-vapour coexistence curve and the critical properties. Kerisit et al. [125] successfully used the EPM2 model with the CLAYFF model in simulations of scCO\textsubscript{2}/H\textsubscript{2}O mixtures above a forsterite surface.

To test the accuracy of the model we generated adsorption isotherms using GCMC simulations in the DL-MONTE code [141], as there are many experimental isotherms that could be compared to. For the GCMC simulations the zeolite framework was held rigid, while CO\textsubscript{2} was translated, rotated and inserted/deleted with a probability of 0.2, 0.2 and 0.6, respectively. The simulations were run for a period of equilibration followed by at least $4 \times 10^6$ steps and the potential cut off was 12 Å.

Initially we directly mixed the Lennard-Jones 12-6 CLAYFF zeolite parameters with the EPM2 CO\textsubscript{2} potentials using the Lorentz-Berthelot mixing rules but we found this to overestimate the isotherm at low pressure and underestimate at high pressure. To correct this inaccuracy we altered the parameters for the CO\textsubscript{2}-zeolite interaction, while keeping the CO\textsubscript{2}-CO\textsubscript{2} interactions purely as EPM2. The new CO\textsubscript{2}-zeolite interaction mixed the CLAYFF zeolite with CLAYFF parameters for the oxygen of CO\textsubscript{2} and EPM2 with a slightly modified $r$ value (Lennard-Jones size parameter) for C. Figures 4.17 and 4.18 show the good fit that we have with experimental data.
Chapter 4. Development of Models

Figure 4.17: Isotherm of CO\textsubscript{2} in siliceous MFI at 303K comparing our simulation (red circles) with experimental data (blue triangles) [152].

Figure 4.18: Adsorption isotherms of CO\textsubscript{2} in siliceous MFI, coloured according to temperature. Data points are our simulations, lines are experimental data from Yamazaki et al [153].
We also calculated heats of adsorption for CO$_2$ in Si-FAU and these agree very well with those calculated by Maurin et al. [56] (figure 4.19). Although the values that we are comparing to are simulated results, rather than experimental results, Maurin et al. compared their results with experiment at higher loadings of CO$_2$ and found the results to be in agreement, so we can assume that if our results continue to follow the trend of the simulated results we will also compare favourably with the experimental data.

![Figure 4.19: Isosteric heats of adsorption as a function of CO$_2$ loading in Si-FAU. Blue: our data, red: simulated data from [56].](image)

We found our calculated diffusion coefficients to be comparable with published values, for example at low levels of loading our diffusion coefficient for CO$_2$ in Si-FAU at 300 K is $25 \times 10^{-9}$ m$^2$s$^{-1}$ and this decreases with increased loading. This is in broad agreement with published values of approximately $20 \times 10^{-9}$ m$^2$s$^{-1}$ with a decreasing gradient [70]. We decided not to explore diffusion coefficients and the impact of loading and structure any further due to the large amount of published material in this area.

### 4.4 Extension of the Potential Model to Aluminosilicates

Aluminosilicate zeolites contain inter-framework cations to balance the negative charge introduced by the substitution of silicon for aluminium. The potential model that we are using is a partial charge model, meaning that simulating aluminosilicates introduces a net positive charge into the system, as the charge on the cation is +1, while the difference in charge
between Si and Al is 0.525. This excess charge can be neutralised by spreading the excess charge over the other zeolite atoms. We tested two different methods, firstly altering the partial charge on \(O_z\) (oxygen of zeolite) and secondly altering the partial charge on Al. We found that altering the partial charge of Al gave very poor results for the cell dimensions, therefore altering the charge on \(O_z\) was decided to be the better option. The \(O_z\) partial charge was therefore changed from -1.05 to -1.16875 for a Si:Al ratio of 1. Next we ran a series of tests to see the effect that this change in partial charge had on the reliability of the potential model, and to trial some alterations of the model to improve the comparison with experiment. The experimental parameters that we compared our simulations to were the crystal structure, primarily the unit cell lattice parameters (section 4.4.1) and the adsorption isotherms (section 4.4.2).

### 4.4.1 Effect of Potential Parameters on Zeolite Structure

As a first indicator of the suitability of the model we focussed on potassium LTA (K-LTA) with a Si:Al ratio of 1, and calculated the whole structure i.e. cell dimensions and atomic coordinates and we report the cell dimensions compared to experimental data from Ikeda et al. [154]. We calculated the cell dimensions and angles through energy minimisation of the bulk K-LTA structure using METADISE. As we had changed the charge on \(O_z\) our first test was to change the \(O_z\) \(\epsilon\) value (\(\epsilon_{O_z}\)). Decreasing \(\epsilon_{O_z}\) took the cell parameters further from the experimental values (table 4.4 test 2) while increasing \(\epsilon_{O_z}\) improved the cell parameters (test 3). We then tried increasing \(r_{Al}\) (L-J size parameter) because in the CLAYFF model Si and Al have the same potential parameters, the only difference being the partial charges. Al\(^{3+}\) is a larger ion than Si\(^{4+}\) so increasing \(r_{Al}\) would help to account for this. As we increased \(r_{Al}\) the cell dimensions decreased to bring them closer to the experimental values (tests 4-6). Increasing \(\epsilon_{O_z}\) further worsened the cell parameters slightly (test 8), but with an increased \(r_{Al}\) the parameters were better (test 7). Tests 6 and 7 were determined to be the best structurally, so next we ran a series of grand canonical Monte Carlo (GCMC) simulations with similar potential tests to attempt to reproduce experimental isotherms.

### 4.4.2 Effect of Potential Parameters on CO\(_2\) Adsorption

To further test the potential model we carried out GCMC simulations simulations using the DL_MONTE code [141] and compared our adsorption isotherms to experimental data. Initially we just compared the number of CO\(_2\) molecules that were adsorbed in Na-FAU at
Table 4.4: The effect of changing CLAYFF potential parameters on the cell dimensions and angles of K-LTA when an oxygen charge of -1.16875 is used instead of -1.05. The experimental sample had a Si:Al ratio of 1.02 and the structure was determined at 39.5 K.

<table>
<thead>
<tr>
<th>Test</th>
<th>Change in parameters</th>
<th>% difference from experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td>Expt. unit cell data [154]</td>
<td>24.634</td>
<td>24.634</td>
</tr>
<tr>
<td>1</td>
<td>No change</td>
<td>-3.61</td>
</tr>
<tr>
<td>2</td>
<td>ε₀z, -2.5%</td>
<td>-4.69</td>
</tr>
<tr>
<td>3</td>
<td>ε₀z, +2.5%</td>
<td>-3.52</td>
</tr>
<tr>
<td>4</td>
<td>ε₀z, +2.5%, rAl +0.05Å</td>
<td>-3.24</td>
</tr>
<tr>
<td>5</td>
<td>ε₀z, +2.5%, rAl +0.10Å</td>
<td>-3.02</td>
</tr>
<tr>
<td>6</td>
<td>ε₀z, +2.5%, rAl +0.15Å</td>
<td>-2.10</td>
</tr>
<tr>
<td>7</td>
<td>ε₀z, +11.3%, rAl +0.15Å</td>
<td>-2.21</td>
</tr>
<tr>
<td>8</td>
<td>O ε, +11.3%</td>
<td>-2.97</td>
</tr>
</tbody>
</table>

5 bar and 25 bar at 300 K to experimental values by Maurin et al. [56] of N = 93 and 107 molecules CO₂/u.c. respectively. This gave us a rough idea of the suitability of the potential parameters, then full isotherms and heats of adsorption were generated in order to select the most effective model. The zeolite framework was held rigid in the GCMC simulations but the cations were allowed to move. All of the simulations included a period of equilibration followed by at least 4 x 10⁶ steps. The potential cut off was 12 Å. CO₂ molecules could be inserted, deleted, rotated and translated and the cations could be translated. These moves were undertaken with a probability of 0.05 for cation translation, 0.25 for CO₂ translation, 0.2 for CO₂ rotation and 0.5 for CO₂ insertion/deletion. We inserted dummy atoms into the sodalite cages so that CO₂ could not be inserted into these regions, as it would normally not be able to diffuse there due to the narrow windows.

With the original CLAYFF-EPM2 parameters that had been used for the siliceous zeolites the levels of adsorption differed by -5% at 5 bar and -10% at 25 bar from the experimental values. To improve the fit to experimental data the first test was to increase ε₀z (O₂ ε value) by a series of percentages: 5, 11, 20, 25% (table 4.5 tests 1-4). A higher ε₀z increased the loading at low pressure more than at high pressure, to give a loading that was still too low at higher pressure. The next test used the same percentage increases in ε₀z, whilst also increasing rAl (Al r value) by 0.15 Å (table 4.5 tests 5-8), which had given good results for the cell parameters. The best result with an increased rAl was when ε₀z increased by 11% (the same percentage that the charge had changed by), although the adsorption was still too low at high pressure. We therefore kept these parameters and tried reducing rO₂ (O₂ r value) by 0.05, 0.1 and 0.15 Å (1.4, 2.8 and 4.2%) and found that the loading increased, but at
high pressure it was still not as high as we needed (table 4.5 tests 9-12). Finally we tried altering the Na parameters: reducing r (table 4.5 tests 13-15), reducing ε and increasing ε, all of which seemed to increase the loading at high pressure without increasing the low pressure loading too much. However, the subtleties of the effect of these changes was hard to discern from two data points so we generated whole isotherms and calculated the heats of adsorption for each of them.

The isotherms were all similar and it was hard to choose the best, so the final decision on the parameters that we chose to use was based on being able to reproduce the heat of adsorption, providing the isotherm was satisfactory. The full potential set for the aluminosilicate zeolites is listed in table 2.1.

<table>
<thead>
<tr>
<th>Test</th>
<th>r_{Al} (Å)</th>
<th>ε_{O_{2}}</th>
<th>r_{O_{2}} (Å)</th>
<th>r_{Na} (Å)</th>
<th>p = 5 bar</th>
<th>p = 25 bar</th>
</tr>
</thead>
<tbody>
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<td>base</td>
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<td>3.5532</td>
<td>2.6378</td>
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<td></td>
</tr>
<tr>
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<td>-4.7</td>
<td>-14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>+11</td>
<td></td>
<td>-11.3</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>+20</td>
<td></td>
<td>-12.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>+25</td>
<td></td>
<td>-12.4</td>
<td></td>
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<td></td>
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<td>+4</td>
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<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>9</td>
<td>+4</td>
<td>+11</td>
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<td>+11</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>+4</td>
<td>+20</td>
<td>-14.0</td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>+4</td>
<td>+25</td>
<td>-14.0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>13</td>
<td>+4</td>
<td>+11</td>
<td>-14.0</td>
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<td></td>
</tr>
<tr>
<td>14</td>
<td>+4</td>
<td>+11</td>
<td>-14.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>+4</td>
<td>+11</td>
<td>-14.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The isotherms were all similar and it was hard to choose the best, so the final decision on the parameters that we chose to use was based on being able to reproduce the heat of adsorption, providing the isotherm was satisfactory. The full potential set for the aluminosilicate zeolites is listed in table 2.1.
Figure 4.20 shows the experimental and simulated heats of adsorption by Maurin et al. [56] (red, green) compared with our best simulation results (blue), using potential parameters of $\varepsilon_{Oz}$ increased by 11%, $r_{Al}$ increased by 0.15 Å and $r_{Na}$ decreased by 15%. The orange line in figure 4.20 was generated using the CLAYFF parameters with no modifications other than the $O_z$ charge and $\varepsilon_{Oz}$ increased by 11.3%; clearly the gradient of the slope is positive instead of negative, so our modifications were necessary and successful. The gradient of the heat of adsorption graphs is known to be related to the homogeneity of the adsorbent for adsorbent-adsorbate interactions [56]. An increasing trend indicates a homogeneous environment, such as might be found in a siliceous zeolite, because the increase is due to the interaction between CO$_2$ molecules. The decreasing trend that we see in Na-FAU is due to the heterogeneous environment within the adsorbate.

![Figure 4.20: Heat of adsorption of CO$_2$ in Na-FAU, Si:Al ratio = 1. Red: Maurin et al. experiment, green: Maurin et al. simulation [56], blue: our simulations with chosen potential parameters, orange: our simulation with original CLAYFF parameters and $\varepsilon_{Oz}$ increased by 11.3%](image)

The isotherm with our improved parameters is shown in figure 4.21; it has good fit to experiment at low pressure, but is slightly too low at high pressure, however this is similar to Maurin et al.’s simulated isotherm, which also underestimated the adsorption capacity [56]. This underestimation at higher pressures could be due to the deviation of gases from ideality as the pressure increases. The GCMC method assumes an ideal gas, which is a fair assumption under ambient conditions, but at higher pressures the deviation from ideality could be enough to account for the difference we see between our results and experimental
The final potential parameters that we used can accurately represent a range of zeolite structures. The lattice parameters of some of these are listed in table 4.6 with our simulated parameters compared to experiment. There are some discrepancies between the values, but this could be due to the systems not being exactly comparable, for example our Na-FAU simulations have a Si:Al ratio of 1 and only Na\(^+\) as a cation, whereas the experimental composition is Ca\(_{0.95}\)Mg\(_{0.22}\)Na\(_{1.04}\)K\(_{0.02}\)[Al\(_{3.40}\)Si\(_{8.60}\)O\(_{24}\)] \(-\) 6H\(_2\)O. As well as a different composition, there is also water present in this structure which will affect the lattice parameters. Also energy minimisation calculations do not take into account any crystal vibrations and hence neglect temperature effects.

Table 4.6: Simulated lattice parameters compared to experiment. Experimental data from \(a\) Wise [155], \(b\) Lim et al. [156], \(c\) Ikeda et al. [154].

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated lattice parameters, Å</th>
<th>Experimental lattice parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
</tbody>
</table>
4.4.2.1 Changing Si:Al ratio

When changing the Si:Al ratio, the partial charges must be altered to maintain a charge neutral cell, so again the potentials need to be adjusted to match. The technique that we have found to work well is to adjust the O\(_{z}\) charges to make the cell neutral then adjust the ε\(_{O_z}\) by the same percentage from the original CLAYFF parameters; all other potential parameters are unchanged from those in table 3.3. An isotherm for Na-FAU with a Si:Al ratio of 1.18 is shown in figure 4.22, with excellent agreement with an experimental isotherm [157]. The potential parameters have an O\(_{z}\) charge of -1.15885 and ε\(_{O_z}\) of 0.007437 eV.

![Figure 4.22: Adsorption isotherm of CO\(_2\) in Na-FAU with Si:Al ratio = 1 (green) and Si:Al ratio = 1.18 (red, blue) at 303.2 K. Data points are our simulations, blue line is experimental data from Pillai et al. [157].](image)

Now that we have a reliable model we can use it as a predictive tool to probe the effect of parameters such as composition on adsorption. Figure 4.22 shows the effect on CO\(_2\) adsorption of changing the Si:Al ratio from 1 to 1.18 in Na-FAU, thereby having 96 and 88 Na\(^+\)/unit cell respectively. This small change in composition has a significant effect on the CO\(_2\) uptake, and our model is sensitive enough to be able to discern these differences. The effect that this change of composition has on the CO\(_2\) uptake also highlights how difficult it can be to compare simulated to experimental data as experimentally the samples may not be ideal. For example, if ion exchange is used to change the cation species in a zeolite, it may not be possible to get complete exchange, thus leaving residual amounts of the other cation species which would change the adsorption characteristics.
4.5 Summary

Another possible cause of differences between simulations and experiment may be due to surface effects, as zeolite powders can be comprised of very small crystals with high surface areas. In the next chapter we investigate the effect of the zeolite surfaces on CO₂ transport.
Chapter 5

How Surfaces Affect Transport Properties in Faujasite

The effect of surfaces on the adsorption and transport of CO$_2$ in zeolites is important for applications using membranes or nano-sized crystals. The studies that have been carried out on zeolite surfaces were described in section 1.2.5, however many of them focus purely on siliceous zeolites, and none of them compare silicates and aluminosilicates of the same framework structure.

Here we investigate the effect of the composition and surface structure of faujasite (FAU) on CO$_2$ adsorption and transport, comparing structural features such as the most favourable CO$_2$ adsorption sites and the CO$_2$ structure at the surface, and dynamical properties like the diffusion coefficient of CO$_2$ through the surface region. To compare these properties with different FAU compositions we used a \{111\} slab of the siliceous, sodium and potassium forms (Si-FAU, Na-FAU and K-FAU, respectively). We chose the \{111\} surface as it is the dominant surface in the crystal morphology [150]. To investigate the effect of surface structure we focussed on Si-FAU and modelled the low index \{111\}, \{011\} and \{100\} surfaces. The simulations used slabs of the zeolites with symmetrical surfaces submerged in CO$_2$. The generation of these slabs was described in section 4.2, including the procedure for hydroxylation and a comparison of the stability and structure of the surfaces.

The simulation cells are periodic in all three dimensions and comprise slabs of approximately 50 Å thickness and a gap of at least 40 Å filled with CO$_2$. MD simulations were carried out in the DL_POLY code, with a potential cut off of 8.6 Å and Ewald precision of $10^{-5}$. All atoms were allowed to move during the simulations including the cations. All
simulations were run for a total of 5 ns at 300 K with a 1 fs time step and with the Nosé-Hoover thermostat/barostat. Equilibration was performed for 1 ns in the NVT ensemble and 1 ns was then run in the NσT ensemble allowing relaxation of the cell dimensions but keeping the angles fixed, to ensure that the CO$_2$ reached its required density. The surface dimensions after this equilibration are listed in table 5.1. A final 3 ns run in the NVT ensemble was performed, but data were collected only for the final 2 ns.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-FAU  {111}</td>
<td>34.22</td>
<td>29.59</td>
</tr>
<tr>
<td>Si-FAU  {011}</td>
<td>24.19</td>
<td>34.21</td>
</tr>
<tr>
<td>Si-FAU  {100}</td>
<td>24.17</td>
<td>24.24</td>
</tr>
<tr>
<td>Na-FAU  {111}</td>
<td>34.18</td>
<td>29.76</td>
</tr>
<tr>
<td>Na-FAU  {011}</td>
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<td>29.97</td>
</tr>
<tr>
<td>K-FAU   {011}</td>
<td>24.52</td>
<td>34.70</td>
</tr>
<tr>
<td>K-FAU   {100}</td>
<td>24.48</td>
<td>24.53</td>
</tr>
</tbody>
</table>

In this chapter we discuss the effect of surfaces on CO$_2$ adsorption and diffusion. We report the calculated diffusion coefficients, density, residence time and coordination number of CO$_2$ to build up a comprehensive picture of how the density and diffusion of CO$_2$ vary between the zeolite, the surface and the region above the surface (specified regions are defined in section 5.1.1, figure 5.2) and how it is affected by different compositions and surface structures. First we assess the effect of composition by focusing on CO$_2$ diffusion and transport at the {111} surface of Si-FAU, Na-FAU and K-FAU (section 5.1). Next, we consider the effect of surface structure by comparing the {111}, {011} and {100} surfaces of Si-FAU in section 5.2.

### 5.1 Effect of Surface Composition

The {111} surface is the most stable surface of faujasite and therefore dominates the morphology of the crystal [150]. To determine the effect of the surface composition on the adsorption of CO$_2$ we therefore studied the same hydroxylated termination (4.7 OH groups per nm$^2$) of the {111} surface of Si-FAU, Na-FAU and K-FAU as illustrated for Si-FAU in figure 5.1. The most stable termination of the siliceous {111} surface was determined in section 4.2.1 to be the one that cuts through the double six rings (d6R) between sodalite cages (β-cages) meaning no sodalite cages are broken and accessible to CO$_2$. Although
this may not be the most stable termination for Na-FAU and K-FAU, in order to directly compare the effect of composition we elected to use identical surface terminations for the three compositions.

![Structure of the {111} surface of siliceous faujasite (Si-FAU)](image)

**Figure 5.1: Structure of the {111} surface of siliceous faujasite (Si-FAU)**

### 5.1.1 Density in {111} slabs

The density of CO$_2$ in the zeolite structure can be shown using the z-density. The simulation cell is divided into slices of 0.3 Å along the z-direction, the slices are therefore parallel to the zeolite surface. In each slice the average density of CO$_2$ is calculated and plotted, including both the C and the O$_{C}$ atoms. The z-density of CO$_2$ in {111} slabs of Si-FAU, Na-FAU and K-FAU are presented in figure 5.2. Region 1 (figure 5.2a) is the zeolite bulk and exhibits a periodic pattern of maxima and minima due to the regular structure of channels and cages in the zeolite that are accessible to CO$_2$. Zero is defined as the left hand edge of this region. Region 3 is the interlayer space, which corresponds to bulk CO$_2$ and region 2 is the surface region which is defined in a similar way to that used by Webb and Grest [98]. The surface region is 9 Å thick for all of the slabs, with the upper limit as the first minimum in CO$_2$ density above the surface. In all cases it also covers the minimum below the surface. The density values in figure 5.2 are normalized values with respect to the CO$_2$ density in the interlayer space.
Si-FAU has three main oscillations in the zeolite region (region 1, figure 5.2a) while Na-FAU and K-FAU have four (figure 5.2b,c). This is due to the thickness of the slabs; the aluminosilicate slabs are greater in depth than the siliceous one but the thickness of the slab does not affect the behaviour of CO$_2$ at the surface, which is the focus of this study. Disregarding the number of oscillations there is a clear difference between the CO$_2$ density peaks in the zeolite region of Si-FAU compared to Na- and K-FAU. In Si-FAU each
maximum is a single peak with a shoulder on each side while in the aluminosilicate zeolites it splits into two peaks of equal (or similar) magnitude indicating that the presence of the cations disrupts the redistribution of the CO\textsubscript{2} within the pores. There is on average a higher relative density of CO\textsubscript{2} in the aluminosilicates than in Si-FAU and the density in Na-FAU is greater than K-FAU. This is due to the enhanced attraction between CO\textsubscript{2} and the cations with greater attraction for Na\textsuperscript{+}-CO\textsubscript{2} than for K\textsuperscript{+}-CO\textsubscript{2} [50]. The density of CO\textsubscript{2} in the interlayer space (region 3) is 0.01 CO\textsubscript{2}/Å\textsuperscript{3} in all three systems. This is equivalent to working at elevated pressures such as those experienced in pre-combustion carbon capture [11]. Kerisit et al., working under supercritical conditions, recorded values of CO\textsubscript{2} density in the order of 0.05 CO\textsubscript{2}/Å\textsuperscript{3} above a forsterite surface [125].

For clarity figure 5.3 depicts an enlargement of the surface region (region 2) of the z-density plots (figure 5.2), with the density of the zeolite oxygen and hydrogen atoms shown to mark the location of the zeolite surface. The densities have been scaled for clarity, so comparison can only been made between the positions of the different peaks but not their heights. For all systems, in the surface region there are two peaks of enhanced CO\textsubscript{2} adsorption, one just below and one just above the terminating hydroxyl groups at the surface. The ratio of these two peaks varies between the three zeolites. For Si-FAU the peak above the surface is higher than the one below, as above the surface there is a greater available volume for the CO\textsubscript{2} to adsorb. In Na-FAU the two peaks are approximately of equal magnitude due to two competing phenomena. As in Si-FAU, above the surface there is greater available volume for adsorption but in this case below the surface the interaction between CO\textsubscript{2} and Na\textsuperscript{+} ions increases the level of adsorption giving rise to two peaks of similar magnitude. In K-FAU the situation is different again as the peak below the surface is higher than the one above the surface. Some of the K\textsuperscript{+} ions have diffused out of the zeolite bulk as can be seen from the density of K\textsuperscript{+} in figure 5.3c, leaving a greater volume available for CO\textsubscript{2} adsorption just below the surface compared to the case of Na-FAU.
Figure 5.3: z-density plots of surface region of (a) Si-FAU, (b) Na-FAU and (c) K-FAU \{111\} slabs. Densities have been scaled for clarity, so peak heights should not be compared, just their positions. \( C_{\text{CO}_2} \): blue, \( K^+/Na^+ \): purple dashed, \( H_2 \): green dashed, \( O_2 \): red dashed.

In general, the \( \text{CO}_2 \) z-density plots indicate areas of high and low density due to available volume in the zeolite, but does not give how closely packed the \( \text{CO}_2 \) is without accurately knowing the available volume as a function of the z direction, which is not easy to calculate. An alternative way of viewing the density of \( \text{CO}_2 \) in the slabs is the time averaged density plots shown in figure 5.4.
Chapter 5. How Surfaces Affect Transport Properties in Faujasite

Figure 5.4: Time averaged density plots of (a) Si-FAU {111} slab, (b) Na-FAU {111} slab and (c) K-FAU {111} slab.

These pictures give qualitative information not just about how dense the CO$_2$ is within different regions of the simulation cell but also the favoured CO$_2$ adsorption sites. We do not use these plots to get numerical values for the density of CO$_2$, but use them to compare densities between different systems. The interlayer spaces contain a uniform bulk density of CO$_2$, while in the zeolite region there are white areas of zero CO$_2$ density corresponding to the overlap between the d6Rs and the sodalite cages where CO$_2$ is unable to access (figure 5.5).

Figure 5.5: Faujasite structure, with red denoting the cross-section of the ‘channels’ of zero CO$_2$ density running through the zeolite.

Inspection of figure 5.4 shows that the adsorption in Na-FAU is stronger than Si-FAU, which is likely to be due to the attraction between CO$_2$ and Na$^+$ ions and increased enthalpy of adsorption that is observed in Na-FAU than Si-FAU [56]. In Si-FAU the adsorption sites within the zeolite region are ordered as the CO$_2$ is free to fill the whole of the pores whereas in Na-FAU the location of these sites is more disordered due to the Na$^+$ ions in the pores.
which vary the available volume for CO\textsubscript{2} adsorption and the CO\textsubscript{2} molecules clustering around the cations. While Si-FAU has many regions of intermediate density suggesting that the CO\textsubscript{2} is moving relatively freely throughout the structure, Na-FAU only has regions of high and low density, which indicates that the CO\textsubscript{2} is anchored more firmly into adsorption sites. K-FAU has a similar profile to Na-FAU but with slightly weaker adsorption sites compared to Na-FAU.

The time averaged density plots (figure 5.4) also confirm the argument we presented on the ratio of adsorption peaks at the \{111\} surfaces for the different FAU compositions in figure 5.3. The strength of the CO\textsubscript{2} adsorption sites above and below the surface of Si-FAU (figure 5.4a) is similar but above the surface there are a greater number of adsorption sites available due to the greater available volume. This explains why the adsorption peak above the surface of Si-FAU (figure 5.3a) is higher than the peak below the surface. In Na-FAU (figure 5.4b) the density at each adsorption site below the surface is greater than the density above the surface, but due to less available volume for adsorption below the surface, the result is two adsorption peaks of equal magnitude. K-FAU has a similar time averaged density profile to Na-FAU, however K\textsuperscript{+} diffuses out of the zeolite bulk as shown by the z-density (figure 5.3c), resulting in the CO\textsubscript{2} adsorption peak below the surface having higher intensity compared to the one above (figure 5.3c).

5.1.2 Diffusion in \{111\} slabs

By analysing radial distribution functions (RDF) in the 3 different regions we are able to determine how the average distance between carbon atoms of CO\textsubscript{2} molecules varies, as listed in table 5.2. In all cases the distance between CO\textsubscript{2} molecules is shorter in the zeolite region than in the interlayer space (a contraction of 1.7 - 4.4%), with the value in the surface region in between. The contraction in distance is greater for the aluminosilicates than for the siliceous zeolite. In general shorter C-C distances give lower diffusion, as molecules that are more closely packed diffuse more slowly. The diffusion coefficients in the zeolite region of Si-FAU, Na-FAU and K-FAU are 61\%, 95\% and 93\% lower than the interlayer space, respectively (table 5.2). To explain the higher diffusion coefficient in the K-FAU zeolite region than in Na-FAU despite the shorter C-C distance, we suggest that the interaction between CO\textsubscript{2} and Na\textsuperscript{+} is stronger than between CO\textsubscript{2} and K\textsuperscript{+}, and this is likely to dominate over the fact that the bulkier K\textsuperscript{+} ions are able to coordinate to more CO\textsubscript{2} molecules (4.7 compared to 4.1 for Na\textsuperscript{+}), holding them closer together to sterically hinder their diffusion.
Table 5.2: Average C-C distances between CO$_2$ molecules and average $D_{xyz}$ diffusion coefficients in the zeolite, surface and interlayer space. The errors were calculated at 95% confidence level.

<table>
<thead>
<tr>
<th></th>
<th>Average C-C distance (Å)</th>
<th>Average $D_{xyz}$ ($10^{-9}$ m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zeolite</td>
<td>Surface</td>
</tr>
<tr>
<td>Si-FAU</td>
<td>4.05 ±0.01</td>
<td>4.07 ±0.03</td>
</tr>
<tr>
<td>Na-FAU</td>
<td>4.02 ±0.03</td>
<td>4.09 ±0.06</td>
</tr>
<tr>
<td>K-FAU</td>
<td>3.95 ±0.04</td>
<td>4.03 ±0.06</td>
</tr>
</tbody>
</table>

The diffusion coefficients were calculated from the mean-square displacement (MSD, described in section 3.2.4) of the CO$_2$ molecules in the directions perpendicular to and parallel to the surface as a function of distance. The diffusion coefficient was evaluated as for the $z$-density, dividing the simulation cell along the $z$ direction into slices and calculating the three components ($D_x$, $D_y$ and $D_z$) of the diffusion coefficient of CO$_2$ in each slice [158,159]. For our purpose only $D_z$ (equation 5.1) is reported as it represents the diffusion in the direction perpendicular to the surface. CO$_2$ molecules have to move along this direction to cross the surface and enter the zeolite.

$$D_z = \lim_{t \to \infty} \left[ \frac{(z(t) - z(0))^2}{2t} \right] / 2t$$

(5.1)

We consider the trajectory of a particle, correlating its first position $z(0)$ with its final position $z(t)$ and assign the trajectory to the slice in which the particle resides at $z(0)$. There are therefore two critical parameters in the calculation of the diffusion profiles, the correlation time and the width of the slice. We tested a range of correlation times from 0.5 to 25 ps and found that the shape of the diffusion profiles remains unaffected, however the magnitude of the diffusion coefficients did show some variation. We therefore tested the same correlation times on a box of pure CO$_2$ with a density similar to that above the slab (0.01 CO$_2$\(\text{Å}^3\)) and found that correlation times between 2.5 and 5 ps gave the same magnitude for the $x$, $y$ and $z$ components of the diffusion coefficient in each slice as the global coefficient for the system. We have also tested changing the width of the slices between 0.2 and 1 Å for these correlation times and found that the magnitude of the diffusion coefficient was unaffected. Thus we chose slices of width 0.5 Å and a correlation time of 5 ps as they resulted in smooth profiles [160].

Figure 5.6 shows the change in $D_z$ as a function of the $z$ coordinate in Si-FAU \{111\}. The $D_x$ and $D_y$ (diffusion in the plane of the surface) are similar and do not show any particular features and therefore are not shown. The $z$-density of CO$_2$ of Si-FAU \{111\} is plotted
for comparison. The profiles for Na-FAU and K-FAU are similar to Si-FAU, although with much lower diffusion rates in the zeolite region, and are therefore not displayed. Generally, as the density of CO$_2$ increases the diffusion coefficient decreases. In the surface region the dense layers of adsorbed CO$_2$ reduce the $z$ component of the diffusion, impeding the diffusion of CO$_2$ through the surface into the zeolite bulk. However, at no point is the diffusion in the surface region lower than in the zeolite itself and in the surface region the diffusion increases in between the adsorption peaks to give an average that is higher than in the zeolite (see also table 5.2).

![Figure 5.6: D$_z$ (red) and CO$_2$ density (blue) as a function of distance along z in Si-FAU (111).](image)

We use the residence time ($\tau_r$, described in section 3.2.4) to determine the average length of time that a CO$_2$ molecule spends in contact with each T-site atom (Si and Al atoms of the zeolite). Figure 5.7 illustrates the residence time of O$_C$ atoms (oxygen of CO$_2$) around the T-site, and the average coordination number (CN), which is the average number of O$_C$ atoms within the 5 Å radius. The images display all of the T-site atoms, coloured according to their $\tau_r$ and CN. Red and blue correspond to smaller and larger $\tau_r$ and CN respectively. The side and top views are both shown. The dashed line in the side view defines the boundary between the zeolite bulk and the surface region.

Si-FAU has a homogeneous environment within the zeolite as can be seen from the uniform CN of O$_C$ around Si atoms (figure 5.7b). The CN is greater at the surface, 4.8 compared to 3.0 in the zeolite, as the surface atoms are more accessible to CO$_2$. In the
Figure 5.7: T-sites (Si and Al atoms) in Si-FAU \( \{111\} \) slab (a,b), Na-FAU \( \{111\} \) slab (c,d) and K-FAU \( \{111\} \) slab (e,f), coloured according to average residence time in ps (a,c,e) and average coordination number (b,d,f) of O\(_\text{C}\) within a 5 Å radius of Si. Yellow dashed lines represent the boundary between the zeolite and surface regions. White vertical lines on the graphs represent the range of the scale; anything above this line is in blue.
zeolite and surface regions $\tau_r$ only varies from 5.2 to 7.5 ps in a 2 ns simulation, indicating that the diffusion is rapid and the CO$_2$ molecules diffuse freely without any obstruction. $\tau_r$ is shorter at the surface (top layer of red atoms in the side view and top view for figure 5.7a) suggesting more rapid diffusion occurring at the surface. Just below the surface there is a region with longer $\tau_r$, which agrees with the data from the diffusion profile in figure 5.6 where at the surface there are two minima above and below the surface, with a diffusion maximum in between.

The $\tau_r$ profiles of CO$_2$ in Na-FAU and K-FAU (figure 5.7c,e) are different from Si-FAU (figure 5.7a); $\tau_r$ values are much longer (up to 0.5 ns) as the diffusion of CO$_2$ in Na- and K-FAU is very slow due to the strong adsorption. Again we see a lower $\tau_r$ at the surface suggesting faster diffusion in this region. Na-FAU and K-FAU have similar CO$_2$ $\tau_r$, although the times are shorter in K-FAU. The majority of the CO$_2$ molecules have a $\tau_r$ of 50 ps in K-FAU and 90 ps in Na-FAU as is highlighted by the peaks in the graphs (figure 5.7). The CN profiles of CO$_2$ around the T-site atoms of Na-FAU and K-FAU (figure 5.7d,f) are similar to Si-FAU, and the CNs are on average slightly higher in Na-FAU than K-FAU (4.3 compared to 3.6), suggesting that the CO$_2$ molecules are more closely packed. Again we see a higher CN at the surface, 7.0 O$_C$ atoms per Si atom in Na-FAU and 6.5 in K-FAU.

5.2 Effect of Surface Structure

This section will explore the differences in CO$_2$ behaviour in the surface regions with a change of surface structure. For this purpose we chose the {111}, {011} and {100} slabs of Si-FAU, considering only the most stable hydroxylated symmetrical surface termination in each case, as described in section 4.2.1. The structures of the surfaces are presented in figure 5.8; the {111} surface was also shown previously in figure 5.1, but is presented here with the sodalite cage highlighted. The coverage of hydroxyl groups is 4.7, 5.8 and 8.2 OH/nm$^2$ for the {111}, {011} and {100} surfaces respectively.
Figure 5.8: Hydroxylated surface structures and time averaged density plots of CO$_2$ in siliceous faujasite, a: {111}, b: {011}, c: {100}. O: red, Si: grey, H: white. Blue dashed rings indicate the sodalite cages at the surface. (d): how these surfaces cut through a sodalite cage.

The most striking difference between the three surface structures is whether any sodalite cages are broken by the surface cut. Figure 9d indicates how the sodalite cages are cut by the three surfaces. The most stable termination of the {111} surface does not cut through any sodalite cages so they remain inaccessible to CO$_2$. The {011} surfaces cut the sodalite cages in half across the middle of the six-ring window (s6R) (figure 5.8d), to give a zigzag channel along the surface plane, where CO$_2$ adsorbs strongly. In the case of the {100} surface, the sodalite cage is cut parallel to and just below the s4R face (figure 5.8d), meaning that the cage is accessible to CO$_2$ and acts as a strong adsorption site. The strong adsorption sites in the sodalite cages can be seen in the time averaged density plots in figure 5.8a-c. In the image of the {011} surface (figure 5.8b), two adsorption sites are visible at the surface, which correspond to the sodalite cages to the left and the right of the zigzag channel. At the {100} surface (figure 5.8c), the CO$_2$ is also allowed into the sodalite cages, but in this
case a larger volume of the cage is accessible so the CO\textsubscript{2} penetrates deeper. For the \{111\} surface, the most favourable adsorption sites are above the surface, as all of the sodalite cages are intact. The adsorption sites at the \{011\} and \{100\} surfaces can also be observed in the $\tau_r$ distributions in figure 5.9 as areas with longer $\tau_r$, and the zigzag channels on the \{011\} surface can also be more clearly seen. The longest $\tau_r$ observed at the Si-FAU \{111\} surface is 7.5 ps (figure 5.7a), while we see $\tau_r$ values at the \{011\} and \{100\} surfaces of 8.3 ps and 8.5 ps, respectively, confirming that CO\textsubscript{2} binds more strongly at these surfaces in the sodalite cage adsorption sites.

Figure 5.9: Si atoms in (a) Si-FAU \{011\} slab and (b) Si-FAU \{100\} slab, coloured according to average residence time (ps) of O\textsubscript{C} within a 5 Å radius of Si, shown from the side and from the top (looking down on the surface). Open sodalite cages on the surface are indicated by dashed yellow circles.
Figure 5.10: z-density profiles of CO$_2$ in Si-FAU slabs (a) {111} slab, (b) {011} slab, (c) {100} slab. Densities have been scaled for clarity therefore only the positions of the peaks can be compared, not the heights. Black rings indicate regions of enhanced CO$_2$ density, as described in the text. Black dashed lines indicate the surface region. [O: red, H: green, C$_{CO_2}$: blue].

Figure 5.10 compares the z-density profiles of CO$_2$ at the three zeolite surfaces. All three surfaces show one pronounced adsorption peak above the surface hydroxyl groups. As discussed previously, the {111} surface has a CO$_2$ adsorption peak just below the surface. This peak follows the periodic pattern of the CO$_2$ density profile in the zeolite, but is slightly enhanced. Below the {011} surface the CO$_2$ density is enhanced compared with the profile in the rest of the zeolite region at approximately the same level as the surface hydroxyl groups (highlighted by dashed ring in figure 5.10b), which corresponds to the adsorption
sites in the open sodalite cages as in figures 5.8 and 5.9. Comparing the CO₂ density profile in the \{100\} zeolite slab and at the \{100\} surface (figure 5.10c) there is enhanced adsorption in the region enclosed by the dashed ring due to adsorption in the sodalite cages. The region of enhanced adsorption is deeper into the zeolite for the \{100\} slab than the \{011\} slab because of the difference in volume of the open sodalite cage adsorption sites (as seen in figure 5.8).

Table 5.3 lists density, diffusion and C-C distance data for the 10 Å above the surface hydrogen atoms of the three surfaces. We see a small increase in the density of CO₂ and decrease in the C-C distance above the \{100\} surface, but the significant difference that we see between the three surfaces is a decrease in the CO₂ diffusion coefficient above the \{100\} surface. Therefore although the CO₂ density may not be significantly greater, the \{100\} surface is having an impact on the CO₂ transport compared to the other surfaces.

The change in CO₂ behaviour above the \{100\} surface was also observed for the Na-FAU and K-FAU slabs. We conclude therefore that the \{100\} surface slows the transport of CO₂, and as such would improve the adsorption in zeolite micropores. The experimental morphology of faujasite is octahedral with expression of the \{111\} surfaces. Spherical particles have been synthesized [161], but this is still not a common morphology. However, if a synthetic route could be found to enhance expression of the \{100\} surfaces in the nanocrystals, we predict that CO₂ uptake could be improved.

### 5.3 Summary

We have presented a comprehensive study on the effect of the composition and surface structure of FAU on the adsorption and transport of CO₂. The first was achieved by comparing the CO₂ adsorption on the \{111\} surface of three different FAU (Si-FAU, Na-FAU and K-FAU) and the second by comparing the CO₂ behaviour on the \{100\}, \{011\} and \{111\} surfaces of Si-FAU.

Three regions were identified: bulk zeolite, surface and interlayer regions. We found
that there is always structuring of CO$_2$ at the surfaces. When comparing the same surface for different FAU compositions we found that all three surfaces have two large CO$_2$ adsorption peaks, just above and just below the surface, but the ratio in the height of these peaks varies between the three FAU compositions, depending on the balance between the strength of the CO$_2$-zeolite interaction and the volume available for CO$_2$ to adsorb.

When comparing the three different surfaces for the same composition we found that the adsorption sites at the surface were governed by the surface structure, in particular whether or not any sodalite cages were cut by the surface. The $\{011\}$ and $\{100\}$ surfaces both have broken sodalite cages, which act as strong adsorption sites for CO$_2$ compared to the $\{111\}$ surface. Above the $\{100\}$ surface CO$_2$ diffused more slowly than above the other surfaces. This gives the potential of improved CO$_2$ adsorption by hindering CO$_2$ flow through zeolite micropores.

Overall we have seen that CO$_2$ behaviour at the surface is affected more by the surface structure than the zeolite composition. In keeping with other published work [115, 116] the surface structure is seen to be an important factor for adsorption. Furthermore, as we predict the enhanced adsorption on surfaces with incomplete sodalite units, which are most stable when $\{111\}$ surfaces are not present, we suggest that best adsorption properties will be achieved with spherical particles rather than annealed and facetted crystals expressing a preponderance of $\{111\}$ surfaces.

So far we have concentrated on systems containing pure CO$_2$. The application of this work is the separation of CO$_2$ from gas streams, which will usually contain water. Therefore we now move on to consider the effect that water has on CO$_2$ adsorption sites in zeolites.
Chapter 6

The Effect of Water on CO$_2$ Adsorption Sites

6.1 Adsorption of Single CO$_2$ Molecules

As a measure of the effect of structure on CO$_2$ adsorption, we calculated the adsorption energy of single CO$_2$ molecules in a range of siliceous zeolite structures. Adsorption energies ($E_{ads}$) were calculated for a single molecule of CO$_2$ per unit cell by:

$$E_{ads} = E_{z+CO_2} - (E_z + E_{CO_2})$$

(6.1)

where $E_{z+CO_2}$ is the energy of the zeolite with a CO$_2$ molecule adsorbed, $E_z$ is the energy of the zeolite before adsorption and $E_{CO_2}$ is the energy of a single CO$_2$ molecule before adsorption.

The energies were calculated using energy minimisation to constant pressure in the METADISE code. In zeolites where the internal environment is not very symmetrical it was possible that the adsorption energy would change at different sites within the structure. Therefore wherever possible the structure was minimised with CO$_2$ in several different locations and the lowest energy site was chosen. The adsorption energies are plotted in figure 6.1.
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

Some of the adsorption energies can be compared to published values of the isosteric heats of adsorption by Fischer and Bell [162]. For LTA, we calculated an adsorption energy of 18.7 kJ/mol, while Fischer reports an experimental value of 21 kJ/mol and simulated value of 20.2 kJ/mol. In MFI our calculated adsorption energy is 29 kJ/mol, while Fischer’s values are 25.0 kJ/mol from experiment and 26.2 kJ/mol from simulations. Our values are therefore similar but not exactly the same. The disparity could be due to the calculation methods; Fischer uses the isosteric heats of adsorption calculated from adsorption isotherms, whilst our values are from energy minimisation calculations.

6.1.1 Sensitivity of the Model

Calculation of the adsorption energies gave a good opportunity to test the sensitivity of the potential model to the results. We ran the same energy minimisation calculations with a different potential model to compare the results. The potential model that we compared to was that of Ramsahye and Bell [163] for the zeolites and Garcia-Sanchez et al. [152] for CO$_2$. A comparison of the results is shown in figure 6.2. Although the values for the adsorption energies differ slightly between the two models (the values from our model are consistently slightly lower), the trends are retained for the most part. We can therefore be confident that our model will predict the correct trends and produce reliable results even if the data values are not exactly correct, as a change in parameters to a completely different model did not change the results significantly.
6.1.2 CO$_2$ Adsorption Sites

The CO$_2$ adsorption energies are greatest in HEU, ITE and MFI. ITE and MFI have previously been identified as having high selectivity for CO$_2$ over N$_2$ [38], so this may be due to their high CO$_2$ adsorption energies. The CO$_2$ adsorption sites in these three zeolites are all towards the edges of channels or cages. The highest adsorption energy was observed in MFI. The position of the adsorbed CO$_2$ is shown in figure 6.3, it is located towards the edge of the smooth walled 10-ring channel. Each O$_C$ (oxygen of CO$_2$) is within 4.5 Å of at least five Si atoms and the closest Si-O$_C$ distances are 3.57 and 3.62 Å.

Figure 6.2: Comparison of adsorption energy of CO$_2$ molecule in siliceous zeolites using two different potential models. Blue: CLAYFF-EMP2, red: Ramsahye-Garcia [152,163].

Figure 6.3: Location of adsorbed CO$_2$ molecule in Si-MFI. [Distances are in Å. Si: grey, O: red, C: dark grey].
In ITE the CO$_2$ molecule also orientates itself so that the O$_{C}$ atoms coordinate to as many Si atoms as possible (figure 6.4). In this case the Si-O$_{C}$ distances are shorter than in MFI (closest four are under 4 Å, closest distance is 3.44 Å).

The O$_{C}$ atoms of CO$_2$ in HEU also coordinate to five Si atoms each (figure 6.5) and the closest Si-O$_{C}$ distances are 3.57 and 3.60 Å.

Figure 6.4: Location of adsorbed CO$_2$ molecule in Si-ITE. [Distances are in Å. Si: grey, O: red, C: dark grey].

Figure 6.5: Location of adsorbed CO$_2$ molecule in Si-HEU. [Distances are in Å. Si: grey, O: red, C: dark grey].
Chapter 6. The Effect of Water on CO₂ Adsorption Sites

6.2 Densities and Adsorption Sites

The time averaged density of CO₂ and H₂O in a range of zeolites is shown in the following section. The images depict the average position of the molecules and are generated from MD simulations in the NVT ensemble. The simulations were at least 2 ns in length and were run at 500 K in order to speed up the diffusion and allow adequate sampling of the zeolite framework in a shorter time. Depending on the size of the unit cell, the systems have between 10 and 20 molecules per unit cell. The first type of density profile (e.g. figure 6.6a) presents the density data on a colour-coded scale from low to high density. The red colour denotes areas where the molecules are more likely to be adsorbed and therefore more densely packed, while the blue colour denotes areas where the molecules prefer not to adsorb and thus are rarer. The other type of density profile comprises an isosurface of a particular density level in a single colour per atom/molecule (e.g. C and O in figure 6.6b).

We cannot use the time averaged density plots to get numerical values for the density, but they can be used to compare densities between systems. We use these density profiles to give structural data and as such identify adsorption sites.

For each zeolite we first analyse the adsorption of pure CO₂, then pure H₂O, and finally a 50:50 mixture of CO₂ and H₂O to see how the presence of water affects the CO₂ adsorption sites and vice versa.
6.2.1 Siliceous Faujasite

Adsorption of CO$_2$

Si-FAU has a relatively even CO$_2$ density distribution, but with regular denser spots around the edges of the alpha cages (figure 6.6a). The CO$_2$ molecules cannot enter the sodalite cages, which results in the white areas in the time averaged density. The image in figure 6.6b shows the location of these adsorption sites in relation to the framework and that the sites are within the $\alpha$-cages above the S4R faces of the sodalite cages. The favoured adsorption sites are shown in more detail in figure 6.6c. The molecule adsorbs with one O$_C$ pointing towards the centre of the 4-ring (circled in figure 6.6b) and the rest of the molecule directed towards the centre of the alpha cage.

Figure 6.6: (a) Time averaged density of CO$_2$ in Si-FAU, (b) highest density sites of C (yellow) and O$_C$ (pink) in Si-FAU, (c) detail of preferred adsorption site. [Distances in Å. Si: grey, O: red, C: dark grey].
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

**Adsorption of H$_2$O**

The time averaged density of H$_2$O in Si-FAU is shown in figure 6.7a. In general the density is uniform throughout the pore network (blue areas in figure 6.7a) but there are regular sites of higher density, indicating stronger adsorption. The density of O$_W$ (oxygen of water) and H$_W$ (hydrogen of water) is shown separately in figure 6.7b, showing that the water is orientated with O$_W$ pointing towards the framework. The location is depicted in more detail in figure 6.7c, with the distances between the atoms in the H$_2$O molecule and the framework atoms shown. The H$_2$O molecule sits symmetrically above the S4R with O$_W$ pointing towards the centre of the ring. The H$_W$ atoms are directed into the α-cage and are approximately equidistant between the framework atoms on either side. In a system with eight H$_2$O molecules per unit cell the residence time of H$_2$O molecules in a 5 Å radius of each Si atom varies between 4.4 and 8.5 ps in a 3 ns simulation, with the longest residence times seen around the adsorption sites we have identified. This shows that the water molecules are fairly free-moving and even at the preferred adsorption sites do not adsorb very strongly.

Figure 6.7: (a) Time averaged density of H$_2$O in Si-FAU, (b) highest density sites of O$_W$ (blue) and H$_W$ (green) in Si-FAU overlayed on the zeolite structure, (c) favoured adsorption site of H$_2$O in Si-FAU. [Distances in Å. Si: grey, O: red, H: white].

102
Chapter 6. The Effect of Water on CO₂ Adsorption Sites

Adsorption of CO₂/H₂O mixture

The CO₂ adsorption sites for a mixture of CO₂ and water in Si-FAU are shown in figure 6.8a,b. These sites are the same as in a system of pure CO₂ without any water, and the location is also the same as the water sites that were described earlier (figure 6.7). Indeed, figure 6.8c shows the high density O₆ and O₆ sites and they are in the same areas as each other. As they are competing for the same sites, the two molecules occupy different regions of the pore network, shown by the average density of each molecule over the simulation duration, shown in figure 6.8d.

Figure 6.8: (a) Highest density sites of C (yellow) and O₆ (pink) in Si-FAU, (b) detail of favoured CO₂ adsorption site in Si-FAU, (c) highest density sites of O₆ (pink) and O₆ (yellow) in Si-FAU, (d) time averaged density of CO₂ (yellow) and H₂O (blue) in Si-FAU. [Distances in Å, Si: grey, O: red, C: dark grey]
6.2.2 Sodium Faujasite

Adsorption of CO$_2$

The structure of Na-FAU (Si:Al ratio = 1) is shown in figure 6.9a. Although many of the cations sit within the denser areas of the framework, there are also a significant number that reside within the pores and will therefore have an impact on the adsorption of CO$_2$. The CO$_2$ density in Na-FAU (figure 6.9b,c) shows that CO$_2$ preferentially adsorbs towards the edges of the pores. The adsorption sites do not appear to be very ordered, but due to the strong adsorption giving long residence times we would need longer simulations to gain better statistics and for CO$_2$ to better sample the whole pore network. Figure 6.9d shows one of the preferred adsorption sites, where the CO$_2$ molecule bridges two Na$^+$ cations. The O$_C$-Na$^+$ distances compare very favourably with those identified by Maurin et al. [56].

Figure 6.9: (a) structure of Na-FAU with Si:Al ratio of 1, (b) time averaged density of CO$_2$ in Na-FAU, (c) highest density sites of C (yellow) and O$_C$ (pink) in Na-FAU, (d) detail of favoured adsorption site. [Distances in Å. Si: grey, Al: blue, O: red, Na: purple, C: dark grey].

Figure 6.10 shows the location of the cations averaged over the length of a simulation, and while the cations in the sodalite cages remain relatively stationary, those that are around the edges of the alpha cages move during the course of the simulation. When CO$_2$ is present
the movement of cations within the pores is greater, while the cations within the framework are not greatly affected. Cation motion in Na-FAU in the presence of CO$_2$ was investigated by Plant et al. [45] who observed significant movement of the cations, in particular they found that the SIII’ cations, which are located in the 12-ring windows of the supercages, migrated to nearby vacant SIII’ sites, which could account for the motion that we see.

Figure 6.10: Na-FAU structure overlayed with time averaged density of Na$^+$ ions. (a) in vacuum, (b) in the presence of CO$_2$. [Si: grey, Al: blue, O: red].

**Adsorption of H$_2$O**

The adsorption of H$_2$O in Na-FAU results in very different time averaged density profiles (figure 6.11a). Here we do not see an even spread of H$_2$O throughout the zeolite pores, instead the water remains clustered around the Na$^+$ ions. Indeed, the residence time of H$_2$O molecules around the framework atoms and Na$^+$ ions varies greatly across the unit cell from
a few picoseconds right up to a nanosecond or more around some cations where the water is strongly adsorbed. Figure 6.11b shows the locations with the highest density of H$_2$O, which therefore correspond to the strongest adsorption sites. The adsorption sites are different to those in Si-FAU; instead of a site above the centre of the S4R with O$_W$ pointing towards the centre of the ring, the molecule is above the edge of the S4R with H$_W$ pointing towards an O$_Z$ (oxygen of zeolite) with a distance of 1.61 Å. The O$_W$ is orientated towards a Na$^+$ ion with a separation of 2.16 Å (figure 6.11c). In order to fully analyse the adsorption sites and residence time the simulations should be run for longer with more water molecules in order to get better statistics.

Figure 6.11: (a) Time averaged density of H$_2$O in Na-FAU, (b) highest density sites of O$_W$ (blue) and H$_W$ (green) in Na-FAU, (c) detail of favoured H$_2$O adsorption site in Na-FAU. [Si: grey, O: red, Al: blue, Na: purple, H: white].
Adsorption of CO$_2$/H$_2$O mixture

When a mixture of CO$_2$ and H$_2$O is adsorbed in Na-FAU the preferred adsorption sites for water do not change significantly, but the CO$_2$ sites are disordered and it is difficult to discern preferred adsorption sites (figure 6.12).

Figure 6.12: Highest density sites of (a) O$_W$ (blue) and H$_W$ (green) and (b) C (yellow) and O$_C$ (pink) in Na-FAU, [Si: grey, Al: blue, O: red, Na: purple].
6.2.3 Siliceous Zeolite A

Adsorption of CO$_2$

In Si-LTA the density of CO$_2$ is uniform within the alpha cages, but denser in the 8-ring windows between the cages, suggesting a longer residence time in these locations (figure 6.13a,b). We can see this when viewing the outputs of MD simulations, where CO$_2$ molecules diffuse within the alpha cages for much of the simulations, but when a molecule enters a window region it adsorbs there for a relatively long time before either returning to the cage it was in or moving on to the cage on the other side of the window. The preferred adsorption site within the window is shown in figure 6.13c. The molecule is in the centre of the 8-ring, with O$_C$ atoms pointing out into the alpha-cages on either side.

Figure 6.13: (a) Time averaged density of CO$_2$ in Si-LTA, (b) highest density sites of C (yellow) and O$_C$ (pink) in Si-LTA, (c) detail of preferred CO$_2$ adsorption site. [Distances in Å. Si: grey, O: red, C: dark grey].
Adsorption of H$_2$O

We ran an MD simulation of a unit cell of Si-LTA starting with one H$_2$O molecule per $\alpha$-cage (8 molecules in total per simulation). At the end of a 4 ns simulation we found that the molecules did not sample the whole of the zeolite pore network, instead congregating together in a couple of $\alpha$-cages before finally clustering together in one cage, which can be seen from the difference in density levels between the cages in figure 6.14a. Looking closer at the density profile of the filled cage indicates that there are no preferred adsorption sites, the density is consistent throughout the cage (figure 6.14b). However we do see that the water clusters together to allow the formation of a hydrogen bonding network. In figure 6.14c the H-bonds are shown in green. All of the H-bond distances are between 1.66 and 1.70 Å, indicating strong H-bonds.

Figure 6.14: (a) time averaged density of H$_2$O in Si-LTA, (b) H$_2$O density (blue) in a single $\alpha$-cage of Si-LTA, (c) H-bonding network within $\alpha$-cage of Si-LTA. [Si: grey, O: red, H: white].
Adsorption of CO\textsubscript{2}/H\textsubscript{2}O mixture

With a mixture of CO\textsubscript{2} and H\textsubscript{2}O in Si-LTA the water again clusters together in one alpha-cage, while CO\textsubscript{2} spreads throughout the rest of the system (figure 6.15a). In the same way as when there is no CO\textsubscript{2} in the system the water clusters in the alpha cage to maximise the number of hydrogen bonds (6.15b). The H-bonds have distances of 1.6 to 1.9 Å. The favoured adsorption sites for CO\textsubscript{2} are within the 8-ring windows, as shown in figure 6.15c, which are the same sites as for systems of pure CO\textsubscript{2} without water. At the edge of the alpha-cage containing water the CO\textsubscript{2} molecules are able to coordinate into the H-bonding network (figure 6.15b).

![Figure 6.15](image.png)

Figure 6.15: (a) Time averaged density of H\textsubscript{2}O (blue) and CO\textsubscript{2} (yellow) in Si-LTA, (b) H-bonding network of H\textsubscript{2}O and CO\textsubscript{2} in Si-LTA, (c) Favoured adsorption site of CO\textsubscript{2} in Si-LTA. [Distances in Å, Si: grey, O: red, H: white, C: dark grey].
Chapter 6. The Effect of Water on CO\textsubscript{2} Adsorption Sites

6.2.4 Sodium LTA

Adsorption of CO\textsubscript{2}

The minimised structure of Na-LTA with a Si:Al ratio of 1 is shown in figure 6.16. During MD simulations, with and without CO\textsubscript{2} present, we find that the cations around the edges of the \(\alpha\)-cages are mobile (labelled in figure 6.16) and move between these positions and the 8-ring windows.

![Figure 6.16: Left: structure of Na-LTA with Si:Al ratio of 1. Right: time averaged density of Na\textsuperscript{+} in Na-LTA. [Si: grey, Al: blue, O: red, Na: purple].](image)

From figure 6.17a we can see that the Na\textsuperscript{+} cations move around the outside of the window region that is accessible to CO\textsubscript{2} but do not restrict this accessible volume (compared to the volume that CO\textsubscript{2} can access in Si-LTA in figure 6.13). The CO\textsubscript{2} time averaged density plot in figure 6.17b reveals that the strongest adsorption sites are around the edges of the \(\alpha\)-cages, particularly just inside the 8-ring windows, and less time is spent actually in the windows. The strongest adsorption site is depicted in figure 6.17c. The CO\textsubscript{2} molecule bridges two Na\textsuperscript{+} cations. One O\textsubscript{C} atom points towards the centre of the 8-ring window and the other towards the cation in the 6-ring.
Figure 6.17: (a) Time averaged density of CO$_2$ (yellow) and Na$^+$ (purple) in Na-LTA, (b) time averaged density of CO$_2$ in Na-LTA, (c) detail of preferred adsorption site shown from two perspectives. [Distances in Å. Si: grey, Al: blue, O: red, Na: purple, C: dark grey].
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

**Adsorption of H$_2$O**

Water in Na-LTA behaves in a similar manner to in Na-FAU, clustering around the cations (figure 6.18a,b). In Na-LTA the cations do not move much during the simulation, leading to a more ordered density profile compared to Na-FAU where the cations do move. We were able to identify preferred adsorption sites for water, shown in figure 6.18c,d. The water molecule adsorbs towards the edge of the $\alpha$-cage with 2.24 Å between O$_W$ and a Na$^+$ ion and a strong H-bond to the oxygen of the framework.

![Figure 6.18: Time averaged density of H$_2$O (blue) and Na$^+$ (purple) in Na-LTA viewed along (a) [100], (b) [101] direction. (c) Highest density sites of O$_W$ (blue) and H$_W$ (green) in Na-LTA, (d) favoured H$_2$O adsorption site in Na-LTA. [Distances in Å, Si: grey, Al: blue, O: red, Na: purple, H: white].](image-url)
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

**Adsorption of CO$_2$/H$_2$O mixture**

When CO$_2$ and H$_2$O are adsorbed as a mixture in Na-LTA, water behaves in a similar manner to as a single component. Water molecules cluster around the Na$^+$ ions with the O$_W$ atoms towards the cation (figure 6.19b,d). CO$_2$ spreads more evenly throughout the structure but with strong adsorption sites in the 8-ring windows between the cages (figure 6.19a,c).

![Figure 6.19: Time averaged density of (a) CO$_2$ and (b) H$_2$O in Na-LTA, (c,d) Highest density sites of C (yellow), O$_C$ (pink), O$_W$ (blue) and H$_W$ (green) in Na-LTA, [Si: grey, Al: blue, O: red, Na: purple.]](image)
Chapter 6. The Effect of Water on CO\textsubscript{2} Adsorption Sites

The CO\textsubscript{2} adsorption sites in Na-LTA when mixed with water are different compared to the pure CO\textsubscript{2} systems. The time averaged densities of the two systems are reproduced in figure 6.20 for comparison. When no water was present CO\textsubscript{2} preferentially adsorbed in the alpha-cages above the 8-ring windows. However water also prefers these sites so they are unavailable when water is present. CO\textsubscript{2} therefore changes adsorption sites and adsorbs within the 8-ring windows instead, which is the same location as the adsorption sites in Si-FAU. The CO\textsubscript{2} and water were competing for the same sites to adsorb to Na\textsuperscript{+} cations; because the water retained these sites and the CO\textsubscript{2} moved elsewhere we can conclude that the water-Na\textsuperscript{+} interactions are stronger than the CO\textsubscript{2}-Na\textsuperscript{+} interactions.

Figure 6.20: Time averaged density of CO\textsubscript{2} in Na-LTA, (a) with no water in the system, (b) when water is present.
6.2.5 Siliceous Zeolite L

Adsorption of CO₂

LTL has channels in only one direction, and they oscillate between wider and narrower sections. The highest level of CO₂ adsorption is seen around the edges of the wider sections of the channels, with lowest density within the centre of the channel (figure 6.21a,b). The preferred adsorption site for CO₂ is shown in figure 6.21c; the CO₂ molecule is located equidistant between the top and bottom of the 8-ring, with the OC atoms directed towards the centre of the 4-rings either side.

Figure 6.21: (a) Time averaged density of CO₂ in Si-LTL, (b) highest density sites of C (yellow) and Oₐ (pink) in Si-LTL, (c) detail of preferred adsorption site. [Distances in Å. Si: grey, O: red, C: dark grey].

Chapter 6. The Effect of Water on CO\textsubscript{2} Adsorption Sites

**Adsorption of H\textsubscript{2}O**

In Si-LTL water behaves in a similar way to in Si-FAU, with an overall even distribution but with favoured adsorption sites, which are shown in figure 6.22. The water molecules are consistently orientated with O\textsubscript{W} pointing towards the pore walls. Looking more closely at these adsorption sites we see that they are very similar structurally to the adsorption sites in Si-FAU, a chain of three S4R units, as is shown in figure 6.23.

![Figure 6.22: (a) Highest density sites of O\textsubscript{W} (blue) and H\textsubscript{W} (green) in Si-LTL, (b) favoured adsorption site of H\textsubscript{2}O in Si-LTL. [Distances in Å. O: red, Si: grey, H: white].](image)

![Figure 6.23: Comparison of favoured H\textsubscript{2}O adsorption sites in (a) Si-FAU and (b) Si-LTL. [Distances in Å, angles in °. O: red, Si: grey].](image)
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

**Adsorption of CO$_2$/H$_2$O mixture**

Figure 6.24a shows the high density O$_W$ and O$_C$ adsorption sites of a mixture of CO$_2$ and H$_2$O in Si-LTL. The CO$_2$ molecule straddles two H$_2$O adsorption sites so that the O$_C$ atoms are approximately in the same adsorption location as O$_W$ atoms. The sites of CO$_2$ and H$_2$O adsorption are the same as the sites when adsorbed as single components, but the density profile in figure 6.24b shows that the two molecules tend to separate into different regions of the framework. In general H$_2$O is closer to the framework than CO$_2$, and in the wider sections of the channels many sites are dominated by CO$_2$ and some by H$_2$O.

![Figure 6.24: (a) Highest density sites of O$_C$ (pink) and O$_W$ (blue) in Si-LTL, (b) time averaged density of CO$_2$ (yellow) and H$_2$O (blue) in Si-LTL. [Si: grey, O: red].](image)
6.2.6 Sodium LTL

Adsorption of CO$_2$

The structure of Na-LTL with a Si:Al ratio of 2.72 is shown in figure 6.25a. As there are no Na$^+$ cations situated within the large pores, the density of CO$_2$ is relatively uniform within the bulk of the channels (figure 6.25b). Where the channels widen the CO$_2$ comes into close contact with Na$^+$ ions and therefore it adsorbs more strongly around the edges of the widest sections of the channels (red areas in figure 6.25b). The cations are located within the 8-rings, so the CO$_2$ straddles two of these cation sites. These adsorption sites and the orientation of the CO$_2$ molecules are shown in figure 6.25c,d.

Figure 6.25: (a) Structure of Na-LTL with Si:Al ratio of 2.72, (b) time averaged density of CO$_2$ in Na-LTL, (c) highest density sites of C (yellow) and O$_C$ (pink) in Na-LTL without cations shown, (d) detail of preferred adsorption site. [Distances in Å. Si: grey, Al: blue, O: red, Na: purple, C: dark grey].
### Adsorption of H₂O

In Na-LTL water also has very well defined adsorption sites around the edges of the pores, however in this case the water molecules are adsorbed in front of the 8-ring as this is where they can coordinate to the Na⁺ ions (figure 6.26).

![Figure 6.26: (a) density of H₂O (blue) and Na⁺ (purple) in Na-LTL, (b) highest density O₁ (blue) and H₁ (green) sites in Na-LTL, (c) close-up of favoured adsorption site of H₂O in Na-LTL viewed from 2 perspectives. [Distances in Å: O: red, Si: grey, Al: blue, Na: purple, H: white].](image)
Adsorption of CO₂/H₂O mixture

The same behaviour is observed in Na-LTL as in Si-LTL, the high density adsorption sites of Oᶜ and Oʷ are in the same location as each other (figure 6.27a,b,d) and CO₂ straddles two of the water adsorption sites (figure 6.27c).

Figure 6.27: (a,b,d) Highest density sites of C (yellow), Oᶜ (pink), Oʷ (blue) and Hʷ (green) in Na-LTL. (c) Detail of preferred CO₂ adsorption site in Na-LTL. [Distances in Å, Si: grey, Al: blue, O: red, Na: purple, C: dark grey].


In summary, there are two main adsorption sites in LTL, A in front of the 8-ring window and B in front of the 4-ring window (figure 6.28). Water occupies site B in Si-LTL and site A in Na-LTL. The CO$_2$ molecules adsorb in between the water sites so that the two O\textsubscript{C} atoms can be as close as possible to the O\textsubscript{W} sites meaning that the CO$_2$ adsorbs in site A in Si-LTL and B in Na-LTL, the opposite way to H$_2$O.

Figure 6.28: Locations of the two H$_2$O and CO$_2$ adsorption sites in LTL and Na-LTL.
6.2.7 Silicalite

Adsorption of CO₂

Silicalite (siliceous MFI) has a different channel structure in each direction, which can be clearly seen from the three time averaged density images in figure 6.29. In figure 6.29a the MFI structure is viewed down the staggered channels, so the straight channels that run perpendicular can be seen. Figure 6.29b does not look down any channels, so the two channel systems can be seen running perpendicular to each other to form a grid. The structure of the staggered channels can be seen in figure 6.29c, which looks down the straight channels. The preferred CO₂ adsorption sites are shown in figure 6.29d,e. They are located in the centre of the 10-ring pores (both the straight and staggered ones) but not at the pore intersections.

Figure 6.29: (a-c) Time averaged density of CO₂ in Si-MFI viewed along [100], [001], [010]. (d) Highest density sites of C (yellow) and O in Si-MFI, (e) detail of preferred adsorption site. [Distances in Å. Si: grey, O: red, C: dark grey].
Chapter 6. The Effect of Water on CO$_2$ Adsorption Sites

**Adsorption of H$_2$O**

There are no particular features to the water density in Si-MFI (figure 6.30) except that in each channel the density is greater in the centre of the channel, getting less dense towards the pore walls (figure 6.30b).

![Figure 6.30: Time averaged density of H$_2$O (a) blue, (b) coloured scale] in Si-MFI viewed in the (a) [001] and (b) [010] directions. [O: red, Si: grey].
Chapter 6. The Effect of Water on \( \text{CO}_2 \) Adsorption Sites

**Adsorption of \( \text{CO}_2/\text{H}_2\text{O} \) mixture**

When we adsorb a mixture of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) in silicalite we see that the water does not spread to fill the system but stays clustered in one channel with no adsorption sites preferred ahead of any other (figure 6.31a). The \( \text{CO}_2 \) fills the remainder of the pore system and specific favoured adsorption sites can be identified (figure 6.31b), which are the same sites as in a system of pure \( \text{CO}_2 \). There are two different adsorption sites, one is in the centre of the straight 10-ring pore, the other is in the staggered pore and is shown in more detail in figure 6.31c. The distances between the \( \text{CO}_2 \) molecule and the framework are similar to those that we have seen in other siliceous zeolites, approximately 3-4 Å.

![Figure 6.31: (a,b) Highest density sites of \( \text{O}_\text{W} \) (blue), \( \text{O}_\text{C} \) (pink) and \( \text{C} \) (yellow) in Si-MFI. (c) Detail of preferred \( \text{CO}_2 \) adsorption site in Si-MFI. [Distances in Å, Si: grey, O: red, C: dark grey].](image-url)
6.2.8 Siliceous Mordenite

Adsorption of CO₂

There are two different types of pore in mordenite (MOR), the main 12-ring channels and the smaller side-channels. In the main pore the CO₂ is densest in the centre of the channel, but the highest density overall is found just inside the side-channels. Half way along each side channel is a region of lower density where the channel expands (figure 6.32a).

![Figure 6.32: (a) Time averaged density of CO₂ in Si-MOR, (b) highest density sites of C (yellow) and Oₓ (pink) in Si-MFI, (c) detail of preferred CO₂ adsorption site. [Distances in Å. Si: grey, O: red, C: dark grey].](image)

The preferred CO₂ adsorption sites are within the side channels (figure 6.32b). The CO₂ adsorbs in the centre of the 8-ring channel, orientated in the direction of the channel. There are two favoured sites, one in the intersection between the 12- and 8-ring channels, and one further up the 8-ring channel, where it narrows again after the wider section. The second of
these is shown in figure 6.32c. There is also a third adsorption site that is less favoured in between and perpendicular to the first two sites, in the widest part of the 8-ring side-channel. These adsorption sites are the same as were observed by Fischer and Bell [162].

**Adsorption of H$_2$O**

In Si-MOR water spreads relatively evenly through the 12-ring pore and the 8-ring side channels. The water is denser towards the centre of the channels and more sparse at the edges (figure 6.33a). Within the 8-ring channels there is a favoured adsorption site above a 4-ring with $O_W$ directed into the centre of the ring (figure 6.33b,c), which is similar to the adsorption sites in Si-FAU and Si-LTL. From there the water molecule forms a hydrogen bonding network with other water molecules in the 12-ring pore (figure 6.33c).

![Figure 6.33: (a) Time averaged density of H$_2$O in Si-MOR (b) highest density sites of $O_W$ (blue) and $H_W$ (green) in Si-MOR, (c) location of favoured adsorption site with hydrogen bonds to other water molecules shown with green lines (H-bond distances between 1.64 and 1.86 Å). [Distances in Å, Si: grey, O: red, H: white].](image)
Chapter 6. The Effect of Water on CO₂ Adsorption Sites

**Adsorption of CO₂/H₂O mixture**

In Si-MOR water and CO₂ share similar adsorption sites (figure 6.34a-c). The favoured CO₂ adsorption sites are the same as the sites for pure CO₂, and the H₂O sites are the same as those for pure water. In the main 12-ring pore we generally see CO₂ and H₂O sharing the same volume, but with H₂O getting closer to the pore walls than CO₂ does. In the side-channels there is a region where the channel expands where CO₂ adsorbs more readily than H₂O. This is the same site that was found to be preferred in work by García-Pérez et al. [74] in a study of the adsorption of mixtures of CO₂, N₂ and CH₄.

Figure 6.34: (a) Time averaged density of CO₂ (yellow) and H₂O (blue) in Si-MOR, (b,c) highest density sites of Oₓ (blue), Hₓ (green), C (yellow) and Oₓ (pink) in Si-MOR. [Si: grey, O: red].
6.2.9 Sodium MOR

Adsorption of CO$_2$

In Na-MOR (Si:Al ratio = 11) the cations are located in the 8-ring side channels (figure 6.35a). CO$_2$ is able to access both the 12-ring pores and the smaller 8-ring side channels, as shown by the time averaged CO$_2$ density plots in figure 6.35b,c.

Figure 6.35: (a) Structure of Na-MOR with Si:Al ratio of 11, (b) time averaged density of CO$_2$ (yellow) and Na$^+$ (purple) in Na-MOR, (c) time averaged density of CO$_2$ in Na-MOR, (d-e) detail of preferred CO$_2$ adsorption sites. [Distances in Å. Si: grey, Al: blue, O: red, Na: purple, C: dark grey].

In general there is a uniform low density in the 12-ring channel, with the exception of one area of very high density. This anomaly is due to the movement of the, Na$^+$ cations during the simulation. Figure 6.35b shows that one of the cations moved out from its original location in the side channel to the edge of the 12-ring channel during the course of the simulation, leading to enhanced CO$_2$ density in that area, due to the strength of attraction between CO$_2$ and the cation. This is clearly a low frequency movement, so the simulations should be run for considerably longer to cover other such infrequent occurrences. Figure 6.35d shows the location of the favoured adsorption site within the 8-ring side-channel is in
the same location as in Si-MOR. One O\textsubscript{C} atom coordinates to two cations, while the other is within the wider section of the channel between two 4-rings. Another adsorption site within the side-channels is shown in figure 6.35e, for the case where a cation has moved into the 12-ring pore. In this case the CO\textsubscript{2} molecule can bridge two cations.

**Adsorption of H\textsubscript{2}O**

The cations in Na-MOR are located in the 8-ring side channels so with low levels of water (2 molecules per unit cell) the water exclusively adsorbs there, with very little water in the main 12-ring pore (figure 6.36a). The water only spends time in the 12-ring pore when there is a higher level of water, as shown in figure 6.36b. There are two sites where the water preferentially adsorbs (figure 6.36c,d). One is coordinated to a single Na\textsuperscript{+} cation and located within the side-channel in front of the 4-ring window (similar to the adsorption site in Si-MOR) and the other is located in the plane of the 8-ring coordinated to two Na\textsuperscript{+} cations.

![Figure 6.36: Time averaged density of H\textsubscript{2}O (blue) and Na\textsuperscript{+} (purple) in Na-MOR (a) 2 molecules per unit cell, (b) 10 molecules per unit cell. (c) Highest density sites of O\textsubscript{W} (blue) and H\textsubscript{W} (green) Na-MOR (d) location of two of the favoured H\textsubscript{2}O adsorption sites. [Distances in Å, Si: grey, O: red, Al: blue, Na: purple, H: white].](image)
Chapter 6. The Effect of Water on CO\textsubscript{2} Adsorption Sites

**Adsorption of CO\textsubscript{2}/H\textsubscript{2}O mixture**

The density of CO\textsubscript{2} and H\textsubscript{2}O in Na-MOR is shown in figure 6.37a. Within the 12-ring pore both CO\textsubscript{2} and H\textsubscript{2}O are found, with more CO\textsubscript{2} towards the centre of the pore. Within the 8-ring side channel CO\textsubscript{2} and H\textsubscript{2}O occupy different regions. There is only one strong CO\textsubscript{2} adsorption site within the side channel which is at the intersection between the main pore and the side channel, we no longer see adsorption between 4-rings (figure 6.37d) as we did in Si-MOR meaning that the CO\textsubscript{2} molecule can only coordinate to one Na\textsuperscript{+} cation at a time. The adsorption site between the 4-rings is now dominated by water adsorption as the water prefers to coordinate with the cations that are located there (figure 6.37c). The relationship between the molecules at the two adsorption sites is shown in figure 6.37b. Both molecules are able to coordinate to the Na\textsuperscript{+} cation via an O atom.

![Figure 6.37](image)

Figure 6.37: (a) Time averaged density of CO\textsubscript{2} (yellow) and H\textsubscript{2}O (blue) in Na-MOR, (b) favoured adsorption sites of CO\textsubscript{2} and H\textsubscript{2}O in Na-MOR, (c,d) highest density sites of O\textsubscript{W} (blue), H\textsubscript{W} (green), C (yellow) and O\textsubscript{C} (pink) in Na-MOR. [Distances in Å, Si: grey, Al: blue, O: red, Na: purple, C: dark grey, H: white].
6.2.10 Radial Distribution Functions

The radial distribution functions (RDFs, described in section 3.2.4) can be used to give the distance between the Na\(^+\) cations and CO\(_2\) or H\(_2\)O, and their coordination numbers. Figure 6.38 presents the RDFs of O\(_C\) and O\(_W\) around Na\(^+\) in Na-FAU and Na-MOR.

![Figure 6.38: Radial distribution functions of O\(_C\) and O\(_W\) around Na\(^+\) in Na-FAU and Na-MOR.](image)

In both Na-FAU and Na-MOR the Na\(^+\)-O\(_C\) distance is 2.3 Å and the Na\(^+\)-O\(_W\) distance is 2.1 to 2.2 Å. RDFs are presented for the simulations of single components and the simulation of mixtures. The profiles for the CO\(_2\)/H\(_2\)O mixture in Na-FAU (figure 6.38c) are the same as for the separate components (figure 6.38a,b). This confirms that although the two molecules have the same or similar adsorption sites, they do not disrupt each other’s
Chapter 6. The Effect of Water on CO\textsubscript{2} Adsorption Sites

when adsorbed as a mixture. We could investigate this further by running simulations with a higher number of molecules, to see whether at higher concentrations one species becomes dominant. The RDF profiles for both Na-LTA and Na-LTL are similar to Na-FAU so they are not shown here.

The RDFs for Na-MOR are different from the other zeolites, there is now a difference between the profiles for the mixture (figure 6.38f) compared to the separate components (figure 6.38d,e). The O\textsubscript{H} profile is similar for the single component and as part of a mixture, but the O\textsubscript{C} profile disappears when it is adsorbed as a mixture. This confirms that water displaces CO\textsubscript{2} from its preferred adsorption sites, as we saw in figure 6.37c,d. When water is present CO\textsubscript{2} is no longer able to coordinate to the cations.

6.3 Summary

There are a few notable differences between the adsorption of CO\textsubscript{2} in siliceous zeolites and aluminosilicate zeolites. In general in the aluminosilicates there is greater difference in density between the areas of high and low density of CO\textsubscript{2} than there is in the siliceous zeolites. This is because the CO\textsubscript{2} molecules bind strongly to the cations therefore move less. In the siliceous zeolites, although there are favoured sites for adsorption, the molecules are in general able to diffuse more freely. This is seen particularly in LTL; the adsorption sites are in the same places for Si-LTL and Na-LTL but the contrast is much starker (compare figures 6.21a and 6.25b). The adsorption sites are often more regularly distributed in the siliceous zeolites because in the aluminosilicates the cations move during the simulations, which changes the environment within the pores. Also the long residence times mean that longer simulations need to be run to gain enough statistics to see all of the adsorption sites. There are also differences in preferred adsorption sites between some of the aluminosilicates and silicates. For example in Si-LTA the strongest adsorption sites are within the narrow windows between the α-cages while in Na-LTA these are the least favoured sites, with preference given to the edges of the α-cages. In general we see that the preferred adsorption sites in siliceous zeolites allow coordination of CO\textsubscript{2} to as much of the framework as possible, in particular O\textsubscript{C} atoms pointing towards the centre of 4-ring windows; in aluminosilicate the CO\textsubscript{2} molecules prefer to be able to bridge two cations.

We see two distinct patterns of behaviour for water in siliceous zeolites. The first is seen in Si-LTA, Si-MOR and Si-MFI where the water density is reasonably uniform throughout
the zeolite pore network, but generally denser towards the centre of the pores and more diffuse closer to the pore walls. We expect to see this due to the hydrophobic environment within siliceous zeolites. In Si-FAU and Si-LTL however, we observe specific adsorption sites near to the walls of the zeolite pores and we have identified the same framework structure at the adsorption sites in both zeolites, namely a chain of three connected 4-rings.

In sodium aluminosilicate zeolites we observe similar behaviour in all of the zeolites that we have simulated. The water is seen to cluster around the cations and at low water concentrations no density of water is seen in other areas of the pores. We only see a spread of the water when there is a higher concentration, in which case it has a similar behaviour in the rest of the zeolite as in the siliceous zeolites, generally with a higher density at the centre of the pores.

With mixtures of water and CO\textsubscript{2} the adsorption sites are not disrupted in siliceous zeolites. If there is competition for adsorption sites the two molecules tend to occupy different regions of the zeolite so that each of the molecules takes advantage of the adsorption sites in the region it is in. This suggests that the strength of interaction for the two molecules is similar as if one molecule had a significantly stronger adsorption energy it would displace the other from the adsorption sites throughout the whole system. In aluminosilicates we generally see that water displaces CO\textsubscript{2} from its preferred adsorption sites, showing that the interaction between water and the cations is stronger than between CO\textsubscript{2} and the cations. This was confirmed by the RDFs of O\textsubscript{C} and O\textsubscript{W} around Na\textsuperscript{+} in Na-MOR, when adsorbed as a mixture there was no coordination between O\textsubscript{C} and Na\textsuperscript{+}. However, in Na-FAU, Na-LTA and Na-LTL the RDF profiles for O\textsubscript{C}-Na\textsuperscript{+} in a mixture were unchanged compared to the single component simulation. This may be because at low concentrations of the molecules there are enough adsorption sites for both water and CO\textsubscript{2}. We could therefore run some simulations with a greater concentration of CO\textsubscript{2} and H\textsubscript{2}O to see whether there is a change in the RDFs.

Now that we have investigated the effect of water on CO\textsubscript{2} in bulk zeolites, the next chapter will consider the effect that water has on CO\textsubscript{2} transport at zeolite surfaces.
Chapter 7

The Effect of Water on CO₂ Adsorption and Transport at MFI Surfaces

Many of the applications where adsorbents will be used to separate and capture CO₂, such as flue gases from industry, will have water present. Zeolites are well known to be good adsorbents of water and as such have been used as desiccants for many years. This sorption of water is likely to have an effect on the efficiency of CO₂ adsorption. This chapter aims to investigate whether water has an effect on the adsorption and transport of CO₂ at zeolite surfaces.

We chose to study the {100}, {010} and {001} surfaces of MFI. MFI was chosen not only because it is often associated with zeolite membranes, but it also showed the least selectivity for water in the bulk systems, thus other zeolites are likely to have greater effects. Due to the anisotropic nature of MFI these three surfaces expose different pore structures. MFI has straight channels in the y-direction and staggered channels in the x-direction therefore the {100} surface exposes the cross section of the staggered channels, the {010} surface exposes the straight channels and the {001} does not expose any channels. First we present the diffusion at equilibrium of pure CO₂ and pure water in these slabs. Next we simulate the individual species and their mixtures under non-equilibrium conditions, and the effect that each have on the other’s transport.

The most stable terminations of the {100}, {010} and {001} surfaces of MFI are shown in figure 7.1. The {010} surface is predominant in the crystal morphology, the {100} and
{001} surfaces are also present in the morphology but to a lesser extent.

Figure 7.1: Structure of the (a) {100}, (b) {010}, and (c) {001} surfaces of siliceous MFI. [Si: grey, O: red].

7.1 Comparing pure CO$_2$ and pure H$_2$O in MFI slabs

We generated {100}, {010} and {001} slabs of MFI approximately 40-50 Å thick, with a gap above the surface of 50 Å which we filled with either water or CO$_2$ and ran MD simulations to generate density profiles of the systems. Each simulation was run for 1 ns in the NVT ensemble followed by 1 ns in the NσT ensemble, to allow the water or CO$_2$ to reach its preferred density above the surface. Data were collected for a final 2 ns run in the NVT ensemble.

7.1.1 Density Profiles of CO$_2$ and H$_2$O

The time averaged density plots of CO$_2$ in the MFI slabs (figure 7.2) show clearly the difference between the three surfaces in terms of the pore structure. The {100} surface (figure 7.2a) exposes the staggered channels and the {010} surface (figure 7.2b) exposes the straight channels. Both of these surfaces create a direct route for the molecules to travel into and through the zeolite. Because no channels run in the [001] direction the {001} surface (figure 7.2c) does not expose any channels, hence the molecules have a much longer route through the zeolite, having to zigzag through the network of pores.
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

Figure 7.2: Time averaged density plots of CO$_2$ in siliceous MFI slabs (a) {100} slab looking down [010] and [001], (b) {010} slab looking down [100] and [001], (c) {001} slab looking down [100] and [010].

Comparing the CO$_2$ density plots with water density (figure 7.3) illustrates a difference between the behaviour of the two species in contact with the zeolite. While CO$_2$ explores the whole of the channels of the zeolite, leading to very well defined images of the internal structure of the pores, the hydrophobic environment of the zeolite leads to H$_2$O profiles that appear more diffuse. This can also be seen in the z-density profiles (figure 7.4) as the CO$_2$ peaks are sharper and have more defined features than the water peaks.

Figure 7.3: Time averaged density plots of H$_2$O in siliceous MFI slabs (a) {100} slab looking down [010] and [001], (b) {010} slab looking down [100] and [001], (c) {001} slab looking down [100] and [010].
Chapter 7. The Effect of Water on CO\textsubscript{2} Adsorption and Transport at MFI Surfaces

The z-density profiles of CO\textsubscript{2} and H\textsubscript{2}O (figure 7.4) show a difference in the structuring of the molecules at the zeolite surfaces. There are two peaks in the H\textsubscript{2}O z-density profiles just above the surface of approximately equal magnitude, while the CO\textsubscript{2} profiles have a peak below the surface, and above the surface have two peaks, the first one larger than the second. The relative levels of CO\textsubscript{2} and H\textsubscript{2}O in the zeolite compared to the bulk above the surface are similar (oscillating between 20\% and 60\% of the bulk density).

Figure 7.4: z-density plots of (a,b,c) CO\textsubscript{2} and (d,e,f) H\textsubscript{2}O on siliceous MFI slabs (a,d) \{100\} slab, (b,e) \{010\} slab, (c,f) \{001\} slab. z-density is normalised against the bulk CO\textsubscript{2} or H\textsubscript{2}O density above the surface, distance is zeroed to the position of the surface hydroxyl groups.
Figure 7.5 shows the high density sites that water and CO$_2$ occupy at the $\{100\}$ surface. There is a clear difference between the adsorption sites of the two species; water adsorbs close to the hydroxyl groups, in a position enabling coordination to two hydroxyl groups. The CO$_2$ molecules occupy different sites, adsorbing in regions where there are fewer or no hydroxyl groups.

Figure 7.5: Highest density sites of $O_W$ (blue), $H_W$ (green), C (yellow) and $O_C$ (pink) in Si-MFI $\{100\}$ slab when adsorbed as single components, viewed both from the side and from above. [Si: grey, O: red, H: white].
Chapter 7. The Effect of Water on CO₂ Adsorption and Transport at MFI Surfaces

The favoured adsorption sites at the {010} surface (figure 7.6) are similar to those at the {100} surface. This is because they have very similar surface structures. The {010} surface exposes the cross-section of the straight 10-ring channels, while the {100} surface exposes the staggered channels, however the pore openings are the same for the two cases. This also explains why the z-density plots were very similar for the two surfaces.

Figure 7.6: Highest density sites of O₆W (blue), H₆W (green), C (yellow) and O₆C (pink) in Si-MFI {010} slab when adsorbed as single components, viewed both from the side and from above. [Si: grey, O: red, H: white].
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

The {001} slab has a different surface structure as no 10-ring pores are directly exposed so the CO$_2$ and H$_2$O adsorption sites are also different (figure 7.7). The water molecules adsorb near to the hydroxyl groups, generally bridging two groups, in a similar manner to the {100} and {010} surfaces. CO$_2$ adsorbs above 4-rings in line with the top hydroxyl groups and above 5-rings in line with the lower hydroxyl groups.

![Side view:](image)

![Top view:](image)

Figure 7.7: Highest density sites of O$_W$ (blue), H$_W$ (green), C (yellow) and O$_C$ (pink) in Si-MFI {001} slab when adsorbed as single components, viewed both from the side and from above. [Si: grey, O: red, H: white].

### 7.1.2 Residence Times

We calculated the residence time ($\tau_r$), described in section 3.2.4, of CO$_2$ and H$_2$O in contact with each silicon atom for the three systems. We found that the residence times within the zeolite bulk were similar for both species, varying between 4-20 ps for H$_2$O and 6-20 ps for CO$_2$. The shortest $\tau_r$ was seen for water suggesting slightly faster diffusion, but on average the diffusion rates of the two species were similar. At the surfaces however, we see different behaviour for CO$_2$ compared to H$_2$O. The $\tau_r$ of CO$_2$ is always shorter at the surface than in the bulk zeolite, with times ranging from 5.6-10 ps, while H$_2$O has longer residence times at the surface (from 22-85 ps). This shows the strength of attraction that water has for the hydroxyl groups at the surface, especially compared to the hydrophobic nature of the
Chapter 7. The Effect of Water on CO₂ Adsorption and Transport at MFI Surfaces

inside of the zeolite. Although there was some variation, we found no significant differences between the residence times at the three different surfaces for either species.

7.2 Mixtures of CO₂ and H₂O in MFI

The same three siliceous MFI slabs were simulated with 50:50 mixtures of CO₂:H₂O inside. At the beginning of the simulation the two species were inserted separately into the two halves of the simulation cell. Initially the water forms an impenetrable layer over one of the surfaces meaning that the CO₂ molecules cannot get through. Water then gradually fills the slabs and in the gap between the two surfaces there is only CO₂ with no H₂O density, showing that the two species do not mix. After 30 ns of MD simulation the systems are starting to come towards equilibrium, but some of the systems are still not there. Snapshots of the {100} slab system at 0, 15 and 30 ns are shown in figure 7.8.

Figure 7.8: Snapshots of the simulation of CO₂ and H₂O in the {100} Si-MFI slab at (a) 0 ns, (b) 15 ns, (c) 30 ns. [Si: grey, O: red, H: white, O₆W: blue, C: dark grey].

142
We were surprised to find that water forces CO$_2$ out of the zeolites and fills the pores itself. Figure 7.9 shows the z-density profiles of CO$_2$ and H$_2$O in the three MFI slabs after 20, 25 and 30 ns of simulation.

In all three systems at 20 ns the water is still mainly in a thick layer above the surface although some has begun to travel through the zeolite and a small amount has reached the opposite surface of the slab. By 30 ns the layers on either side of the slab are beginning to reach similar levels although the rate of reaching equilibrium is different in the three slabs. The \{010\} slab, where the straight channels run perpendicular to the surface, appears to be the closest to equilibrium while the \{001\} surface where neither channel type runs perpendicular to the surface is furthest from equilibrium. The \{001\} slab is slightly thicker than the other two slabs (55 Å compared to 50 Å) but in addition to this the water molecules have to travel further to penetrate the same depth into the slab as there is no direct route along a pore.

We did not expect to find that water was preferentially adsorbed over CO$_2$. One explanation for this behaviour is that under these conditions CO$_2$ is not soluble in water and they will tend to separate (see also Kerisit et al. [125]). However, the surface region is dominated by hydroxyl groups, which H-bond to water and hence that region will be dominated
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

by water. Once both surfaces are saturated with water the smallest surface area of contact will be if CO$_2$ is expelled. Another explanation is that our potential model for adsorption of H$_2$O into the zeolite is too strong, so further work should be carried out to confirm this result. A starting point would be to run the same simulations with a few different potential models to see whether the same results are observed.

To analyse the adsorption behaviour at the surfaces, figure 7.10 shows an enlargement of the surface region of the z-density profiles at 20 ns and 30 ns. After 20 ns there is only a small amount of water at the surface rather than a thick layer so we can see where it prefers to adsorb.

![Figure 7.10: The z-density profiles of CO$_2$/H$_2$O mixtures in the surface region of {100}, {010} and {001} slabs of Si-MFI after 20 and 30 ns of MD simulation. The x-axis shows distance in Å and is zeroed to the position of the surface hydroxyl groups. [O$_2$: green, H$_2$: red, CO$_2$: orange and H$_2$O: blue].](image)

We see two different types of behaviour, where the {001} surface is different from the other two. At the {100} and {010} surfaces the surface hydrogen atoms are all on one level (zero on the x-axis) and the strong water layer is approximately 1 Å above with a shoulder
on the edge of the peak at approximately 2 Å. There is a slight peak visible in the CO$_2$ density at 1 Å, but the main peaks are 1 Å below the surface and 3 Å above the surface. At the {001} surface there are two levels of surface hydrogen atoms (as shown in the structure in figure 7.1c) with the main H$_2$O peak at approximately the same level as the highest H atoms (2-3 Å above the lower H atoms). The CO$_2$ profile has a peak 2 Å below the surface at around the same height as the lower H atoms, one just above the higher H atoms and one 3 Å above the surface. The CO$_2$ profiles are similar to those that were seen at the surface when no water was present (figure 7.4), showing that at low levels of water adsorption the adsorption sites of CO$_2$ are not disrupted.

After 30 ns the density profiles at the surface are very different (figure 7.10). At the {100} and {010} surfaces there is a small peak of CO$_2$ density 1 Å below the surface and the density gets steadily greater with increasing distance above the surface. The water now has a large density peak centred around 1 Å above the surface but spanning a region from 2 Å below the surface to 5 Å above. At the {001} surface the large water peak is centred at the same height as the upper H atoms and spans from 2 Å below the surface to 5 Å above the surface. The CO$_2$ density no longer has defined peaks but small peaks are still visible at 2 Å below the surface, 1 Å above the surface and 3 Å above the surface, as was seen after 20 ns.
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

The highest density adsorption sites of CO$_2$ and H$_2$O in a 50:50 mixture at the three Si-MFI surfaces are shown in figure 7.11. The adsorption sites for the two molecules are the same as for the single component simulations (figures 7.5, 7.6 and 7.7). Therefore although the relative amounts of the two species change as the systems come to equilibrium, they are not actually competing for the same adsorption sites.

Figure 7.11: Highest density sites of O$_W$ (blue), H$_W$ (green), C (yellow) and O$_C$ (pink) in Si-MFI (a) {100}, (b) {010} and (c) {001} slabs when adsorbed as a 50:50 mixture, viewed both from the side and from above. [Si: grey, O: red, H: white].
7.3 Effect of Water on CO$_2$ Transport through MFI Surfaces

Having analysed the adsorption sites of CO$_2$ and H$_2$O at MFI surfaces and seeing that water tends to dominate adsorption at the surfaces, the effect that water has on the diffusion of CO$_2$ through the surface was investigated. A series of NVT simulations were run containing various compositions of CO$_2$:H$_2$O for each of the three Si-MFI slabs used previously. The simulations were run at 400 K to speed up the rate of diffusion and lower the length of time that the simulations needed to be run for. The simulation cell set-up is shown in figure 7.12. Firstly the mixture of CO$_2$ and H$_2$O was enclosed between two walls and 50 ps of MD simulations were run (50 000 MD steps) to allow the species to mix. Then one of the walls was removed to allow the mixture to diffuse across a vacuum gap and into the zeolite slab. The walls were constructed from a grid of generic atoms with no charge. The interaction of the wall atoms with H$_2$O and CO$_2$ was related to the interaction between the molecules. The wall-O$_W$ interaction was the same as the O$_W$-O$_W$ interaction, the wall-O$_C$ interaction was the same as the O$_C$-O$_C$ interaction, and the wall-C interaction was the same as the O$_C$-C interaction.

![Figure 7.12: Schematic of the simulations systems](image)

Data on the position of the CO$_2$ and H$_2$O molecules with respect to time were collected to allow analysis of the relative rates of diffusion of the two species and how they changed with composition. For each of the three MFI slabs, simulations were run with seven CO$_2$:H$_2$O compositions: 0, 10, 30, 50, 70, 90 and 100 % CO$_2$ with a constant total number of molecules per slab system. The {001} slab system contained a total of 190 molecules and the {010} and {100} systems contained 260 molecules each. Each simulation was run
Chapter 7. The Effect of Water on CO\textsubscript{2} Adsorption and Transport at MFI Surfaces

for 0.5 ns as this was generally long enough for some of the molecules to reach the other side of the slab.

Figures 7.13, 7.14 and 7.15 show overall time-averaged density plots of all of the simulated systems. The pictures are orientated so that the direction of travel of the molecules is from the bottom to the top of the images. When water is present it forms a layer at the surface, which is the same as we have observed previously. The presence of water also appears to slow the rate of travel through the slabs compared to the 100% CO\textsubscript{2} system i.e. CO\textsubscript{2} generally reaches further through the slab over the course of the simulation with less water present, and with 0% CO\textsubscript{2} the distance travelled by the water molecules is the shortest. The next observation is that in the 0.5 ns simulation water and CO\textsubscript{2} reach the far side of the \{100\} and \{010\} slabs but they only travel around halfway through the \{001\} slab. Although we acknowledge that the \{001\} slab is slightly thicker, this difference in rate can mainly be attributed to the greater distance the molecules have to travel through the zigzagging network of channels.

Figure 7.13: Time-averaged density profile of CO\textsubscript{2} (yellow) and H\textsubscript{2}O (blue) in Si-MFI \{100\} slabs over the first 0.5 ns after release of CO\textsubscript{2}/H\textsubscript{2}O gas mixtures with different CO\textsubscript{2} concentrations. [Si: grey, O: red, H: white].
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

Figure 7.14: Time-averaged density profile of CO$_2$ (yellow) and H$_2$O (blue) in Si-MFI {010} slabs over the first 0.5 ns after release of CO$_2$/H$_2$O gas mixtures with different CO$_2$ concentrations. [Si: grey, O: red, H: white].

Figure 7.15: Time-averaged density profile of CO$_2$ (yellow) and H$_2$O (blue) in Si-MFI {001} slabs over the first 0.5 ns after release of CO$_2$/H$_2$O gas mixtures with different CO$_2$ concentrations. [Si: grey, O: red, H: white].

7.3.1 Rate of Travel through the Zeolite

Table 7.1 lists the average time that it takes for CO$_2$ and H$_2$O to travel through 10 nm of zeolite. This has been calculated by extrapolating the time that it takes for the first molecule of each species to travel all the way through the slab. Some numbers are therefore quoted as “greater than”, which applies to the cases where none of the molecules travel all of the way through the slab in the duration of the simulation. In all cases H$_2$O travels more slowly than CO$_2$. We have already seen (section 7.1.2) that the residence time at the surface is greater for H$_2$O than for CO$_2$, so this is likely to be a contributing factor in the overall slower travel.
Chapter 7. The Effect of Water on $\text{CO}_2$ Adsorption and Transport at MFI Surfaces

Average transport through the slabs is fastest for the \{010\} slab, followed by the \{100\} slab, and finally the \{001\} slab. This is due to the shape of the pores; the molecules have a more direct route through the \{010\} slab as they can travel directly along the straight 10-ring pores. Travel through the \{100\} slab is only slightly slower than the \{010\} slab for $\text{CO}_2$ (on average 0.45 ns compared to 0.35 ns) as the molecules must travel down the staggered channels.

Table 7.1: Average time to travel 10 nm (ns) [based on the time taken for the first molecule to travel through the slab].

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7.3.2 Single Component Simulations

One way that we can present the considerable data from these simulations is to consider a series of distances through the slab, illustrated in figure 7.16, and calculate the number of molecules of each species that have travelled beyond these distances in a specified length of time.

![Figure 7.16: Schematic of the simulation systems showing the positions used to calculate the distance travelled by molecules.](image-url)
Figure 7.17 presents data on the percentage of molecules that have travelled beyond these distances in two sets of simulations, those with 100% CO\textsubscript{2} and 0% CO\textsubscript{2} in the system. We are therefore dealing only with the single components without the added complication of mixtures of the species. The blue lines on the graphs represent the simulations of pure water and the red lines represent the pure CO\textsubscript{2} simulations.

![Figure 7.17: The percentage of each species in single component simulations that have travelled through a specified distance (0, 10, 20, 30 Å) in a given period of time (100, 200, 300, 400 ps), where 0 Å is the edge of the slab, and increasing the distance travelled through the slab. [H\textsubscript{2}O: blue, CO\textsubscript{2}: red, {100}: circle, {010}: square, {001}: triangle].](image)

Let us deal first with graph (a), which illustrates the number of molecules that have travelled beyond 0 Å, in other words the number that have entered the zeolite slab. At all of the times analysed (100-400 ps) more molecules have entered the slab in the simulation of water than in the simulation of CO\textsubscript{2}, e.g. after 100 ps 20-25% of the water has entered the slabs but only 10-15% of the CO\textsubscript{2} (the simulations contain the same total number of molecules). This is probably due to the attraction between water and the hydroxyl groups pulling water towards the surface at the beginning of the simulation so that it is easier for it to enter the zeolite. As the simulations continue, the difference between the amount of water and CO\textsubscript{2} in the slabs increases. By 400 ps between 30 and 50% of the water has entered the slabs (depending on the surface type), while the amount of CO\textsubscript{2} in the slabs is still only 10-20%, so very little extra CO\textsubscript{2} has travelled into the slabs. For both water and
Chapter 7. The Effect of Water on CO2 Adsorption and Transport at MFI Surfaces

CO2 we see that the most molecules enter the \{010\} slab and the least enter the \{001\} slab. Graph (b) gives data for the number of molecules that have travelled 10 Å into the slab. At this distance there is not always more water than CO2, it now depends on the surface type. At all times through the simulations there is a greater percentage of CO2 and H2O beyond 10 Å in the \{100\} and \{010\} slabs than either species in the \{001\} slab. For each species the greatest percentage beyond 10 Å is for the \{010\} slab and the lowest is for the \{001\} slab. For each surface type there is approximately twice as much water than CO2 beyond 10 Å.

At 20 Å through the zeolite (graph (c)) there is more CO2 than water in the \{100\} slab towards the beginning of the simulations, it is only by 400 ps that the amount of water overtakes the amount of CO2. There is still much more water than CO2 in the \{010\} slab, and the amounts are approximately equal in the \{001\} slab.

Finally, graph (d) plots the amount of CO2 and water that has travelled beyond 30 Å. As would be expected, early on in the simulations very little has travelled beyond 30 Å, at 100 ps there is less than 2% of the molecules in all of the zeolite slabs. Later in the simulations no water and very little CO2 has passed 30 Å in the \{001\} slab. The systems with the greatest percentage of gas that has reached 30 Å by 400 ps are H2O in \{010\} followed by CO2 in \{100\} and then CO2 in \{010\}. The amounts of CO2 are similar in the \{100\} and \{010\} slabs, but there is still significantly more water beyond 30 Å in the \{010\} slab than in any other system.

Looking at all of the data, it appears that a certain amount of CO2 enters the slabs at the beginning of the simulations and this amount does not increase significantly over the duration of the simulations, shown by the relatively flat profiles of the CO2 lines on graph (a). Water enters the slabs more consistently throughout the simulations, shown by the relatively constant gradient in the lines of graph (a). The surface type appears to have more of an effect on the water transport than on CO2; generally the range between percentages of water in the different slabs is wider than the range of CO2. For example at 400 ps 30 Å through the slabs there is a range in water percentages between 0 and 15%, while the range in CO2 percentages is only from 2 to 10%.
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

### 7.3.3 50:50 Mixture Simulations

The following section considers the simulations with 50:50 compositions of CO$_2$:H$_2$O. Figure 7.18 illustrates the percentage of CO$_2$ and H$_2$O that has travelled certain distances through the slabs.

![Figure 7.18: The percentage of each species in a 50:50 mix of CO$_2$ and H$_2$O that has travelled through a specified distance (0, 10, 20, 30 Å) in a given period of time (100, 200, 300, 400 ps), where 0 Å is the edge of the slab, and increasing the distance travelled through the slab. [H$_2$O: blue, CO$_2$: red, {100}: circle, {010}: square, {001}: triangle].](image)

Concentrating first on the {100} slab (circles on graphs in figure 7.18), at 100 ps approximately the same amount of CO$_2$ and H$_2$O has entered the slab (14% of CO$_2$ and 17% of H$_2$O) however throughout the remainder of the simulation the amount of CO$_2$ in the slab does not increase, while the amount of H$_2$O increases to 38% of the total H$_2$O molecules in the system (figure 7.18a). This may be because once 14% of the CO$_2$ has travelled beyond 0 Å and therefore entered the slab the water layer at the surface becomes too thick and dense for any more CO$_2$ to be able to reach the surface so no more enters the slab. The H$_2$O level increases over time because the molecules that are in the layer above the surface are able to move into the slab.

The CO$_2$ molecules move more rapidly through the slab than the H$_2$O molecules, 10% of CO$_2$ molecules have travelled beyond 10 Å by 100 ps and only around 1% of the H$_2$O.
Again, the amount of CO$_2$ beyond 10 Å plateaus at 13-14% as all of the CO$_2$ that entered the slab moves beyond this point. It is only by 400 ps that the amount of H$_2$O beyond 10 Å overtakes the amount of CO$_2$.

The amount of CO$_2$ beyond 20 Å (graph (c)) steadily increases to 12% by 400 ps, but at this time there is only 4% of H$_2$O. In a similar way, at 30 Å the amount of CO$_2$ increases to 10% and the water only to 3%. All of this data tells us something about the different way that the two species travel through the slab; the CO$_2$ moves rapidly through the slab (most of the CO$_2$ that entered the slab has passed 30 Å after 400 ps) and H$_2$O fills the gap behind it. Having seen in section 7.2 that water forced CO$_2$ out of the MFI slabs, another way of thinking about that is that the water wants to fill the slab, so “pushes” the CO$_2$ out, meaning that CO$_2$ travels through the slab ahead of the water.

We see very similar behaviour of CO$_2$ and H$_2$O in the {010} slab as in the {100} slab, although H$_2$O travels further through the slab; 15% has travelled 20 Å in 400 ps compared to 4% in the {100} slab. This is as we would expect because the molecules travel down the straight pores rather than the staggered pores. The behaviour in the {001} slab is very different, however. In this case only 6% of the CO$_2$ molecules enter the slab (this corresponds to only 6 molecules). Over the course of the simulations these molecules do not travel very far through the slab, 5 reach beyond 10 Å and only 1 gets beyond 20 Å. More water enters the slab (44% by 400 ps) but this also does not travel far through the slab, the majority stays within the first 10 Å with only 8% going further. It is unclear why 30 % of the water molecules have entered the {001} slab after 100 ps compared to less than 20% in the other two slabs.
Chapter 7. The Effect of Water on CO$_2$ Adsorption and Transport at MFI Surfaces

In order to clarify the effect that the zeolite has on the diffusion through the simulation cell we ran an identical system but with the zeolite removed and analysed the data in the same manner (figure 7.19).

![Graphs showing the percentage of each species in a 50:50 mix of CO$_2$ and H$_2$O that has travelled through a specified distance (0, 10, 20, 30 Å) in a given period of time (100, 200, 300, 400 ps), without any zeolite in the system, where 0 Å is the same position as in simulations with zeolite present.][H$_2$O: blue, CO$_2$: red]

Figure 7.19: The percentage of each species in a 50:50 mix of CO$_2$ and H$_2$O that has travelled through a specified distance (0, 10, 20, 30 Å) in a given period of time (100, 200, 300, 400 ps), without any zeolite in the system, where 0 Å is the same position as in simulations with zeolite present. [H$_2$O: blue, CO$_2$: red].

Focussing first on the CO$_2$, (red lines on graph) we can see that it spreads through the system more rapidly when there is no zeolite present. After 100 ps 55% of the CO$_2$ is beyond 0 Å, rising to a maximum of 66% after 300 ps. This shows that the CO$_2$ is evenly spread through the system after 300 ps, because the 0 Å point has 66% of the simulation cell beyond it, so we would expect 66% of the CO$_2$ to be beyond this point. When this is compared to the systems when the zeolite was present (figure 7.18) and only 6-14% of the CO$_2$ travelled beyond 10 Å, we can see that the presence of the zeolite greatly slows the transport of CO$_2$.

Water behaves in a very different manner when the zeolite is not present. The water clusters together as a droplet and moves back and forth through the system, which explains the shape of the graphs (blue lines in figure 7.18). We see that after 200 ps 100% of the water has passed 0 Å and after 300 ps it has passed 20 Å, before travelling back again. A
snapshot of the system after 500 ps is shown in figure 7.20. When the zeolite is present any water that does not adsorb in the zeolite or at the layer at the surface tends to remain in a small droplet. However, as the majority of the water that is not in the zeolite is in an adsorption layer at the surface we suggest that the surface condenses the droplet.

Figure 7.20: Snapshot of the 50:50 simulation of CO\textsubscript{2} and water without a zeolite. [C: grey, O\textsubscript{C}: red, O\textsubscript{W}: blue, H\textsubscript{W}: white, wall: green].

### 7.4 Summary

The structuring at MFI surfaces is different for CO\textsubscript{2} and water. Water is strongly attracted to the surface hydroxyl groups, while CO\textsubscript{2} adsorbs away from the hydroxyl groups. This means that in a mixture of the two molecules they are not likely to disrupt each other’s adsorption sites. The $\tau_r$ of the two molecules is similar within the zeolite, suggesting that they diffuse at similar rates. At the surface the $\tau_r$ of water is greater than in the bulk zeolite, while the $\tau_r$ of CO\textsubscript{2} is lower than in the zeolite. This supports the idea that the adsorption energies of the two molecules in the zeolite is similar, but the adsorption energy of water at the surface is greater, which causes the longer $\tau_r$.

Simulations were carried out of a mixture of CO\textsubscript{2} and water in MFI slabs and we found that the two species did not mix. Initially water formed thick layers at the surfaces, again showing the preference of adsorption to the hydroxyl groups. After a much longer simulation of 30 ns the water had filled the zeolites and excluded the CO\textsubscript{2}, which is a surprising result that needs further investigation, including testing with other potential models to confirm and explain the results.

When travelling through MFI slabs, water forms layers at the surface and slows the transport of CO\textsubscript{2}. The rate of travel of the two species is different through the three slabs. The fastest transport is observed in the \{010\} slab, closely followed by the \{100\} slab. Both of these slabs expose the 10-ring pores meaning that diffusion in the direction through the slab is rapid, and it is slightly faster through the \{010\} slab as the molecules travel along the straight channels, compared to the staggered channels in the \{100\} slab. Transport through the \{001\} slab is slower as the molecules have to take a longer route through the network.
of channels that run parallel to the surface - there are no channels that run perpendicular to the surface.

In single component simulations water enters the slab more quickly than CO\textsubscript{2} does, and through the first 20 Å of the slab there is always more water in the slab than CO\textsubscript{2}. It is only when looking 30 Å through the slab that the amount of CO\textsubscript{2} overtakes the amount of water for the \{100\} and \{001\} slabs, while there is still more water than CO\textsubscript{2} 30 Å through the \{010\} slab. We again see that travel is fastest through the \{010\} slab and slowest through the \{001\} slab for both species. The only exception is that slightly more CO\textsubscript{2} has travelled beyond 30 Å after 400 ps in the \{100\} slab than the \{010\} slab, although the difference is small. Overall the surface type has more effect on the transport of water than CO\textsubscript{2}, which may be due to the stronger attraction that water feels towards the surface hydroxyl groups.

With mixtures of CO\textsubscript{2} and water the water generally enters the slabs first, but in the \{010\} and \{100\} slabs CO\textsubscript{2} penetrates deeper into the slab more quickly than water. Very little CO\textsubscript{2} manages to enter the \{001\} slab, and it does not travel very far into the slab. The presence of CO\textsubscript{2} slows the transport of water through the slab, only 4.3% of the water reaches 30 Å in 400 ps when in a 50:50 mixture with CO\textsubscript{2}, compared to 14.9% when CO\textsubscript{2} is not present. The amount of CO\textsubscript{2} in the same positions is 8.0% in a single component simulation and 8.9% in a mixture with water, so CO\textsubscript{2} is not slowed as much by the water as water is by CO\textsubscript{2}.

In general we can therefore conclude that the difference in rate of travel through the slabs is affected by the orientation of the channels, but at the surface as long as there is a pore entrance the rate of transport through the surface is not affected by surface type. The presence of water in the system leads to the formation of water layers at the surface, which hinder CO\textsubscript{2} transport into the zeolite. However, once CO\textsubscript{2} enters the slab it is not significantly affected by the water presence, and travels through the slab at a similar rate to without water.
Chapter 8

Conclusions and Future Work

The main focus of this thesis is to improve our capability and understanding of the adsorption of CO$_2$ in zeolites and the work has been grouped into several areas. Chapter 4 describes the development of the potential models that were used in the calculations, both for siliceous and aluminosilicate zeolites, and gives a comparison of the results to experimental data. The focus of chapter 5 is the effect of surfaces on the adsorption and transport of CO$_2$ at faujasite surfaces. Chapter 6 identifies the preferred adsorption sites for CO$_2$ in a range of zeolite structures and investigates the effect that adding water has on these sites. Chapter 7 concentrates on the effect that water has on CO$_2$ behaviour at MFI surfaces. The aim of this chapter is to draw together the conclusions from each of these areas and suggest future work that could be carried out, before drawing some general conclusions for the whole thesis.

Potential Model

We have successfully developed a new potential model, which can be used for the simulation of CO$_2$ in siliceous and aluminosilicate zeolites and at their surfaces, including parameters for hydroxyl groups and water (see chapter 4). The model was verified by the reproduction of experimental structures using energy minimisation and molecular dynamics (MD), and the calculation of CO$_2$ isotherms and heats of adsorption using grand canonical Monte Carlo (GCMC), and in each case they compare favourably with experiment. The models are also able to give reliable CO$_2$ diffusion coefficients and correctly predict the order of surface stabilities for a range of siliceous zeolites.
CO₂ at Zeolite Surfaces

Initially we limited the work to systems of pure CO₂ in zeolites, and explored the effect that surfaces had on the adsorption and transport of CO₂, choosing to focus the work on faujasite zeolites. The effect of zeolite composition on CO₂ at surfaces was analysed by simulating CO₂ at the {111} surface of Si-, Na- and K-FAU (section 5.1). The structuring of CO₂ was different at the three surfaces, particularly relating to the ratio of the adsorption peaks above and below the surface in the z-density plots. We found that the level of adsorption was a balance between the volume available for adsorption and the strength of the zeolite/cation-CO₂ interaction. The diffusion of CO₂ is much slower in the aluminosilicates than in Si-FAU, but the difference is less pronounced in the surface region. This also leads to longer CO₂ residence times within the aluminosilicates compared to the siliceous, but in all cases the residence time at the surface is shorter than in the bulk zeolite, indicating faster diffusion. The surface regions also had a greater coordination number of CO₂ around the T-site atoms (Si and Al) than in the zeolite bulk due to the greater available volume around the T-sites at the surface.

The effect of surface structure on CO₂ transport was analysed by simulating CO₂ at the {100}, {011} and {111} surfaces of Si-FAU (section 5.2). The biggest change in behaviour was related to whether or not the sodalite cages at the surface were broken by the surface cut. The {100} and {011} surfaces have broken sodalite cages, which are usually inaccessible to CO₂ in the bulk zeolite but are now available for adsorption and form strong adsorption sites. The diffusion coefficient of CO₂ above the {100} surface is lower than above the other two surfaces (6.6x10⁻⁹ m²s⁻¹ compared to 10.2 and 9.3x10⁻⁹ m²s⁻¹, which suggests that crystals with enhanced expression of the {100} surface may provide greater CO₂ uptake in microporous zeolites.

The work on the effect of surfaces on CO₂ transport could be extended by considering other surface terminations. For example, when comparing the effect of composition we used the surface termination that was most stable for Si-FAU, but this may not be the most stable Na- or K-FAU termination, so the surface stabilities of these zeolites could be investigated and the slab simulations could then be repeated to see the effect that other terminations have on the results. When modelling the {011} and {100} surfaces of Si-FAU we considered only surfaces that would generate symmetrical slabs and those with singly hydroxylated Si atoms, but there were other possible terminations that could be investigated.
Another extension of the work would be to investigate CO\textsubscript{2} transport at the surfaces of other zeolites. In this way we could see if the specific results are applicable for other zeolite systems and would allow the drawing of general conclusions. In our work we hydroxylated both the Si and Al atoms at the surface, but it can be argued that it is not necessary to hydroxylate the Al atoms as they may be able to stay 3-coordinate, and hence this is another area that could be investigated.

### CO\textsubscript{2} Adsorption Sites and the Effect of Water

The adsorption energy of CO\textsubscript{2} in a range of siliceous zeolites was calculated using energy minimisation techniques and the highest energies were seen for HEU, AFI and MFI. The favoured sites were found to straddle two 4- or 5-membered rings, except from in Si-LTA, where CO\textsubscript{2} adsorbs in the centre of the 8-ring windows between alpha-cages. The sites in other siliceous zeolites and in aluminosilicates were probed using MD and viewing the CO\textsubscript{2} density profiles from the simulations. Most of the favoured sites in the siliceous zeolites involved the coordination to at least one 4- or 5-membered ring, with O\textsubscript{C} pointing towards the centre of the ring. In aluminosilicates the adsorption sites are different, with the CO\textsubscript{2} molecules coordinating to the Na\textsuperscript{+} cations, particularly when CO\textsubscript{2} can coordinate to two cations.

The water adsorption sites are similar to those favoured by CO\textsubscript{2}, generally above 4-membered rings, although in Si-LTA water clusters together to form a droplet in one alpha-cage where the number of H-bonds between the water molecules can be maximised. In aluminosilicates water coordinates to the Na\textsuperscript{+} cations as is well recognised. When mixtures of CO\textsubscript{2} and H\textsubscript{2}O are adsorbed in the zeolites we see different behaviour in siliceous zeolites compared to aluminosilicates. In the siliceous zeolites, although CO\textsubscript{2} and H\textsubscript{2}O had similar adsorption sites when modelled as single components neither dominates those sites when they are adsorbed as a mixture, the two species just occupy different parts of the structure. This suggests that neither has an adsorption energy that is significantly higher than the other. In aluminosilicates CO\textsubscript{2} is generally displaced from its adsorption sites by water, which suggests that the H\textsubscript{2}O-Na\textsuperscript{+} interaction is stronger than CO\textsubscript{2}-Na\textsuperscript{+}. We can also hypothesise that with water dominating the adsorption sites around the cations, CO\textsubscript{2} retention in the aluminosilicates would be reduced in the presence of water as it would not be able to adsorb into its favoured sites.
Chapter 8. Conclusions and Future Work

Due to the very long residence times of CO$_2$ and water in the sodium zeolites longer simulations are needed in order to gain enough statistics to fully analyse the CO$_2$ and H$_2$O adsorption sites. At least 10 ns of simulation is likely to be needed, but dependent on the results it could be longer. Another extension of the work would be to calculate adsorption energies for CO$_2$ in aluminosilicate zeolites and H$_2$O adsorption in siliceous and aluminosilicate zeolite in order to see whether there are any cases where the CO$_2$ adsorption energy is greater than water and so might be preferentially adsorbed.

The Effect of Water at MFI Surfaces

We modelled CO$_2$ and water at the \{001\}, \{010\} and \{100\} surfaces of Si-MFI. The rate of diffusion through the MFI surfaces for CO$_2$ and H$_2$O decreases in the order \{010\} > \{100\} > \{001\} due to the structure of the pore network. Water enters the slabs more rapidly than CO$_2$, probably due to the attraction to the surface hydroxyl groups, but CO$_2$ travels more rapidly through the zeolites.

We found that water is able to displace CO$_2$ from siliceous MFI slabs, which was unexpected because of the hydrophobic nature of siliceous zeolites. As this might be because the potential model gives too strong an attraction between H$_2$O and the zeolite compared to CO$_2$-zeolite, this needs further research. One course of action would be to test a series of other potential models for the system to see whether or not the same results are observed. If we see that CO$_2$ is excluded from siliceous zeolites, we can assume that the same will be true for aluminosilicates, and that zeolites are therefore unsuitable for CO$_2$ capture technologies unless water is first removed from the gas streams, perhaps by the introduction of a desiccant before the CO$_2$ adsorption medium.

We have only considered the effect of water at siliceous surfaces, not aluminosilicates and only for one zeolite. As we have seen that the behaviour of CO$_2$/H$_2$O mixtures in aluminosilicates is different to in siliceous zeolites, this should be investigated further with a range of zeolite structures and compositions.

Overall Conclusions

Some general conclusions can be drawn from this work. Firstly, we see that surfaces can have a great effect on the adsorption and transport of CO$_2$ and therefore the modification of the zeolite crystal morphologies could lead to enhanced adsorption. Secondly we find that
the adsorption of CO$_2$ is affected by water, both in the disruption of adsorption sites within the zeolite bulk and by blocking the surface region to prevent CO$_2$ from travelling into the zeolites.

This work has only considered simulations of specific zeolite systems and therefore the results are not necessarily generally applicable, however they show the effects that can be introduced by surfaces and by water, and therefore can direct future work towards these important areas for research. It is worth noting that the approaches outlined here are applicable to all microporous materials, so can also be used to investigate CO$_2$ and H$_2$O adsorption and transport in other materials such as MOFs and microporous organic solids.
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176


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