An Investigation into the Effect of Cation-exchange on the Adsorption Performance of Indium-based Sodalite-ZMOF

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

King Abdullah University of Science and Technology

Thuwal, Kingdom of Saudi Arabia

© April 2016

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ABSTRACT

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Umer Anwar Samin

There is a pressing need for advanced solid-state materials that can be implemented in industrial gas separation processes to achieve separations with a significantly reduced energy input compared to what is typically required from current technologies.

Although certain porous materials like zeolites bear some commercial significance for gas separation; their inherent lack of tunability limits the extent to which these materials may be exploited in industry. Zeolite-like Metal-Organic Frameworks (ZMOFs) are a sub-class of Metal-Organic Framework materials (MOFs) that show a structural semblance to zeolites while possessing the tunability advantages of MOF materials. ZMOFs which are topologically similar to certain zeolites can be functionalised and tuned in numerous ways to improve their gas separation properties.

In this work, indium-based sod-ZMOF was tuned by cation-exchange and then characterised by different experimental tools such as single-crystal x-ray diffraction, elemental analysis and gas adsorption. It was found that various parameters like the choice of cation, the concentration of salt solution and the choice of solvent had a significant bearing on the cation-exchange of sod-ZMOF and its subsequent adsorption properties.
ACKNOWLEDGEMENTS

It has been a great pleasure to be part of the Functional Materials Design, Discovery and Development research group under the supervision of Professor Mohamed Eddaoudi. I would like to thank Professor Eddaoudi for giving me the opportunity to work in such a constructive learning environment.

I am immensely grateful to Dr. Youssef Belmabkhout, Dr. Karim Adil and Dr. Osama Shekhah for their continued support and guidance throughout the duration of my thesis research.

I would also like to thank all my fellow colleagues in the group for their wholehearted support during my master’s. In particular I would like to thank Rasha, Valeriya, Prashant, Towsif, Ayalew, Norah, Ali, Jiangtao, Alex and Mikhail for helping me with my work.

Finally, I would like to thank Professor Mohamed Eddaoudi, Professor Klaus-Viktor Peinemann and Professor Ingo Pinnau for being part of my thesis committee.
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<tr>
<td>EtOH/H₂O</td>
<td>Ethanol/water</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively-coupled plasma optical emission spectroscopy</td>
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<td>ImDC</td>
<td>Imidazole dicarboxylic acid</td>
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<tr>
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Chapter 1: Current Trends in Gas Separation Technology

Section 1.1: Introduction

In recent years, access to energy has become a serious concern for people living all across the World. In the past century, the sole reliance on fossil fuels to produce energy for transportation, electricity generation and domestic heating has seen the rapid decline of these limited non-renewable resources. While the intensive use of fossil fuels has been damaging to the environment, it has also driven the industrialisation and economic growth of the world; contributing to an increase in the GDP per capita of the global population and generally affording the average person a better quality of life.

The ease and current accessibility of extracting fossil fuels does not distract from on-going efforts that are being made to find sustainable and feasible energy alternatives. Fossil fuels can also be harnessed in ways other than to simply produce energy; oil and natural gas for example, are also major sources of petrochemicals. Therefore, the transition for energy dependency onto renewable sources does not only yield environmental benefit, but also conserves a high-value non-renewable resource that can be exploited for other uses.

The unparalleled role that oil has played in supporting the growth of economies and infrastructure in nations across the World could not be realised without the know-how and application of separation technologies. Crude oil can only be exploited for use in various forms, whether it be in the form of petroleum and naphtha for energy needs or for the manufacture of materials like plastics, due to the existence of a process to separate the crude
oil mixture into its various substituents, this process, namely fractional distillation, is at the forefront of industrial processes that have made a ground-breaking contribution to society.

Separation processes play a role in all industries, from biotechnology, where microorganism-derived products are purified using an assortment of membrane and chromatography based separation processes, to the mining industry, where advanced centrifugation techniques are employed to extract valuable metals from their ores. Advancements in separation technologies not only represent scientific progress, but have the potential to surpass limitations on industrial separation processes of a traditional design, yielding not only economic and environmental benefits, but also by making previously impracticable solutions to be the preferred and pragmatic choice.
Section 1.2: Gas Separation

Gas separation is a field that has attracted considerable interest over the past few decades. Industrial-scale gas separation processes have been on-going since the beginning of the 20th century, when Carl Von Linde separated liquefied air into nitrogen and oxygen using distillation techniques. At the time, pure oxygen was needed by the mining industry to improve the performance of iron ore smelting (Kerry 2007), now however, oxygen as well as various other gases are required in large quantities in many industries for applications that include space exploration, freeze-drying and 3D printing (Praxair 2016).

The production of nitrogen gas is achieved by separating air by cryogenic distillation; nitrogen and oxygen, the two predominant components of air, are able to be separated due to the higher vapour pressure of nitrogen. Separation is achieved when the column is cooled sufficiently enough for nitrogen to rise to the top of the column and exit, with oxygen condensing

![Figure 1.2.1: Carl Von Linde’s first attempt at air separation, here the liquefied air (A) is fractionated using a distillation column, a liquid air reflux is also sent to the top of the column (B) to improve the purity of the nitrogen stream.](image-url)
Cryogenic distillation is the standard method adopted by industrial gas producers for air separation, and while it is a well-established and reliable method of producing pure gaseous streams of nitrogen and oxygen, it is an energy-intensive process and only becomes economically feasible to apply when performed on a large scale (Energy 2005).

**Membrane technology**

Up and coming gas separation technologies, from novel adsorbents to rationally-designed polymeric membranes have the potential to surpass cryogenic distillation as the separation method of choice for air separation as well as for the industrial production of other gases. At present, membrane separation systems that produce nitrogen or nitrogen-enriched air are already in place for small-scale applications such as in food and combustible-fuel blanketing (Sanders et al. 2013).

Current commercially available membranes come in forms that are either organic or inorganic in nature. Organic polymeric membranes are generally the material of choice for membrane fabrication due to their low cost and processability, with the inorganic membranes made up of materials like ceramic reserved for separation processes taking place in harsher conditions. Figure 1.2.2 shows a generalised diagram of a membrane separation process and Table 1.2.1 outlines some of the advantages and disadvantages of membrane technology.
The advantage of membrane separation processes lies heavily in their ability to achieve separation with a significantly reduced energy input in comparison to distillation or absorption processes. Energy is introduced into a membrane separation in the form of a driving force such as pressure, resulting in the favourable permeation of one species over another. In the case of gas separations, both porous and non-porous membranes are available for applications, however, most commercial membranes depend on non-porous membranes that separate based on the solubility-diffusivities of the species being separated (Baker 2006).

<table>
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<tr>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>energy efficient</td>
<td>short lifetime</td>
</tr>
<tr>
<td>mild conditions</td>
<td>performance limited by selectivity or flux of membrane</td>
</tr>
<tr>
<td>scalable</td>
<td>membrane fouling</td>
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<tr>
<td>flexible</td>
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Table 1.2.1: Advantages and disadvantages of membrane separation processes (Mulder 1996)
While non-porous polymeric membranes have shown suitability for small-scale applications, upon consideration for large-scale air separation, the technology quickly becomes impracticable due to the low permeation rates and selectivities achieved by current membranes. Typically, a low selectivity membrane requires a multi-stage separation process to achieve and satisfy the demand of high purity 99% N₂, this leads to a reduced overall recovery – and further coupled with the low permeation rates membranes and additional equipment costs, there is a diminished financial gain to be had for industrial air separation plants to adopt membrane technology at present on a large-scale basis (Baker & Low 2014).

Nascent gas separation technologies are breaking ground however in other areas, this is clear for example in the realm of natural gas purification. In regards to the treatment of natural gas, much focus is paid to the removal of acid gases like carbon dioxide and hydrogen sulfide from natural gas reservoirs. While levels of these gases vary between different reservoirs, their amounts often need to be reduced in order to increase the calorific value of the gas and minimise pipeline corrosion. The most widely adopted method for
acid gas removal from natural gas is by using an amine solvent such as monoethanolamine (MEA) as an absorbent for the sour gases. Figure 1.2.4 shows a schematic process diagram for a typical amine absorption process, here, natural gas is made to flow to an absorption contactor where the sour gas contacts the liquid MEA solution, the acid constituents of the sour gas stream then react with the solution to form carbamate salts, with the now ‘sweet’ gas leaving the column at the top and the MEA solution directed to a reboiler step for regeneration (Alireza 2014).

Amine absorption setups such as the one described above are the predominant method to purify natural gas streams of acid gases in order to meet pipeline specifications. However, a significant disadvantage of this method is the cost of the energy required for the reboiler step to strip the solvent of the acid gases. It is for this reason that membranes have undergone much evaluation for implementation in this application, with
particular interest in membranes that show promising CO₂/CH₄ separation capabilities.

Amine absorption setups are not only expensive in their operational costs in terms of energy and chemicals, but also have a large footprint and require significant capital investment. Membranes are superior to conventional amine absorption strategies in all of these regards with their energy-efficiency, flexibility and ease-of-use. Until now however, while numerous membranes have been tested for CO₂/CH₄ separation, few have the potential to displace traditional gas-sweetening processes.

Figure 1.2.5 shows a two-stage membrane setup that utilises cellulose acetate membranes to act as a selective barrier; favouring the permeation of CO₂ over CH₄. While it is the first separation stage that produces the product gas containing minimal levels of CO₂, it is the second stage which limits the economics of the process. The second stage is where methane recovery is maximised by recirculating the retentate back to the first stage, however, with current commercially available membrane materials like cellulose acetate which have CO₂/CH₄ selectivites of 15, the 2-4% of methane that is lost in the process makes the membrane process uneconomical when compared to amine absorption (Baker & Low 2014).
There is a need for robust, low-cost membranes with high permeabilities and selectivities for natural gas purification applications. Better performing membranes can thus be more economically feasible in their application and potentially displace amine absorption as the method of choice for acid gas removal from natural gas. Such an objective is difficult to obtain, because while many exciting membrane materials such as polymers of intrinsic microporosity (PIMS), thermally rearranged polymers, and novel polyimide polymers continue to be developed, they are inevitably hindered by the trade-off between the permeability and selectivity found in polymeric membranes (Adewole et al. 2013). This inverse relationship between the two parameters is best illustrated by the Robeson plot for \( \text{CO}_2/\text{CH}_4 \) shown in Figure 1.2.6. There is a need for a paradigm shift in membrane science, to push for reliable materials that can offer high-permeabilities hand-in-hand with high selectivities which will better suit separation applications compared to conventional means.

![Figure 1.2.6: The Robeson upper-bound plot, this shows the inverse trade-off between the permeability and selectivity of polymeric membranes and the respective properties of such membranes (Adewole et al. 2013).](image)
One way in which such a paradigm-shift can be realised is by encouraging the development of nanocomposite ‘mixed-matrix membranes’ that combine the molecular sieving properties of inorganic materials with the low-costs and processability of polymeric membranes. In this manner, hybrid materials can be created which can leverage the strengths of both classes of materials to create membranes that can surpass the Robeson upper bound and be better suited for potential applications.

Several inorganic materials have been tested for their suitability as fillers in mixed-matrix membranes, these include carbon molecular sieves, zeolite and metal-organic framework nanoparticles. Extensive testing on polymer-based zeolitic MMMs have shown that using zeolites can enhance the permeabilities and selectivites of some polymeric membranes (Adams et al. 2010; Jiang & Chung 2006). However, this comes with the large drawback that defect-free membranes are often difficult and time-consuming prepare due to poor dispersion of the zeolites in the organic phase. It is often the case that MMM studies involving zeolites result in poorly-formed membranes riddled with cracks and defects which are unable to provide a consistent, reliable separation basis.

Figure 1.2.7: A mixed-matrix membrane with dispersed zeolite particles (Baker 2006)
At present, metal-organic fillers show the most promise in their role as fillers for MMMs, this is because of the organic ligands that make up the MOF structure contributes to dispersing the particles amongst the organic polymer phase (Adams et al. 2010). Along with the inherently higher pore volumes and lower densities of MOFs in comparison to traditional zeolites, MOFs can offer improved membrane integrity and performance enhancement in their role as fillers for MMMs (Adatoz et al. 2015).

Some key objectives that need to be achieved in order for MOF MMM to be feasible for applications is to improve the interfacial compatibility between MOFs and the organic phase, optimise filler loading levels, and improve filler dispersion and distribution (Adatoz et al. 2015). Since the bulk of the membrane is made up of the non-porous polymeric phase, gas transport through a MOF MMM relies heavily on the solution-diffusion mechanism. Here, the presence of the MOF filler can potentially enhance the solubility and diffusivity of one species over another in the membrane.

It is also recognised that, in addition to improving fabrication methods for MMMs, any performance improvements that a MOF MMM can yield are ultimately limited by the properties of the type of MOF being used as the filler. Screening promising MOF candidates for use as fillers in MMMs can ultimately result in membrane materials that sufficiently exceed the Robeson upper bound and make them suitable for implementation in large-scale separations. Better performing MOF candidates can be developed if the tunability advantages of MOFs can be leveraged, altering the MOF structure
and introducing suitable functionalities could be the key to discovering state-of-the-art membrane materials.
Section 1.3: References


Chapter 2: Metal-Organic Framework Materials

Section 2.1: Introduction

Metal-organic frameworks are a relatively new class of porous materials that can be constructed by the assembly of metal ions or clusters with organic ligands via coordination bonds. The result is a porous coordination network that can have angstrom-sized pores. MOFs are well-recognised as a class of porous crystalline compounds that are tunable and have exceptionally high surface areas.

MOFs are usually synthesised solvothermally; where a mixture of metal, ligand and solvent are heated at a high temperature over long periods of time; what follows is the slow, self-assembly and growth of MOF crystals. Structure-directing agents (SDAs) and acids can also be added to these reactions, the SDA helps to shape the framework by acting as an intermediate template during the self-assembly process, while the acid slows down the deprotonation of the ligand to form better quality single crystals. Other ways of synthesising MOFs include microwave, and hot-plate heating methods, which

Figure 2.1.1: Metal-organic framework formation via coordination bonds (Dhakshinamoorthy & Garcia 2014)
encourage faster growth of the MOF crystal structure and thus form smaller, nanoparticle crystalline compounds.

Figure 2.1.2 shows the structure of MOF-5, one of early discoveries made in Metal-Organic Framework chemistry (Li 1999). MOF-5 is made up Zn₄O tetrahedra (Figure 1A), connected with 1,4 benzene dicarboxylate organic linkers (Figure 2.1.2 B) to form a framework can be classified as a 3D cubic net, containing pores that have window width of 8 Å and a pore diameter (represented by the yellow sphere) of 12 Å (Figure 2.1.2 C).
Subsequent sorption studies on MOF-5 evaluated its porous characteristics and found that the material exhibited a reversible type I Langmuir isotherm and a high apparent Langmuir surface area of 2,900 m² g⁻¹.

Further investigations into MOF-5 sought to explore and exploit the tunability potential of MOFs to observe their subsequent effect on the properties of the resulting compounds. In 2002, researchers set out to explore the effect of...
modifying MOF-5 by changing the organic linkers linking the metal clusters (Eddaoudi et al. 2002). They were successful in their endeavour and developed a new series of MOFs termed isoreticular MOFs (IRMOFs), which retained their topology and metal cluster identity, but with varying organic linker length and functionality (Figure 2.1.3).

Of these new series of MOFs, the ones which were synthesised with a longer linker showed expected increases in pore sizes, of greater interest though were members of the series that showed improvements in their sorption uptake for particular gases. Such was the case for IRMOF-6, which showed a large increase in its sorption performance for methane.

Figure 2.1.3: An example of an iso-reticular series of MOFs (IR-MOF 1-6) first synthesised In 2002, here, the numbers indicate the numbers in the series, with IR-MOF 1 being the native MOF-5, with subsequent IR-MOFs retaining the metal cluster with varying organic linker identities (Eddaoudi et al. 2002).
It is the example of the IR-series of MOFs that gives confidence to MOF chemists in that they can tune and tailor the structure of MOFs systematically and screen these new structures for promising attributes that could potentially be exploited for some application.
Section 2.2: Zeolite-like Metal-Organic Frameworks

‘Zeolite-like’ metal-organic frameworks, or ZMOFs, are a sub-class of MOF materials that are constructed by design, to show semblance to zeolites in their overall topology. Zeolites are crystalline micro- and meso-porous materials made of aluminasilicate compounds, an example of a common zeolite, sodalite, is shown in Figure 2.2.1 below, here the silicon and aluminium atoms share a tetrahedral bonding geometry with oxygen atoms of a T-O-T form (T=Si/Al), where the T-O-T bond angle is at 145° (Scott M. Auerbach, Kathleen A. Carrado 2003).

![Figure 2.2.1: Construction of the zeolitic sodalite framework from the TO₄ tetrahedra (A). The T-O-T bonds are at an angle of 145° which connect to form the β cage of sodalite (B). The yellow sphere represents the largest sphere that can fit inside the cavity without touching the van der Waals atoms of the framework.](image)

Discovering new ZMOF compounds involves employing the ‘edge expansion’ strategy; where a zeolite-like net is expanded at the oxygen atom bridges of the corner-sharing tetrahedra by substituting the oxygen atoms with an organic linker (Eddaoudi et al. 2014).

Figure 2.2.2 shows the ZMOF-equivalent of sodalite, which has the same overall topology, but instead, indium ions and a 4,5 imidazole dicarboxylic
acid organic linker make up the framework to achieve edge expansion of the structure. Notably, while there is a chemical difference in the building units, the same overall topology is achieved, including the 145° T-O-T bond angle. As a result, the window size of the sodalite net is expanded from 2 Å to 4.1 Å, and the pore size from 4 Å to 5.3 Å.

Figure 2.2.2: Construction of the sod-ZMOF framework from its tetrahedral molecular building block (C). A fragment of the sod-ZMOF framework is shown (D), viewed along the four-member window. The yellow sphere represents the largest sphere that can fit inside the cavities without touching the van-der Waals atoms of the framework.
Employing a metal-organic design strategy to yield this zeolitic topology offers several advantages over the native zeolitic material and intrinsically amongst MOFs, these include (Eddaoudi et al. 2014):

- larger cavities and openings than the native zeolite analogue
- homogeneous openings of fixed size and shape
- no interpenetration in the framework
- choice of additional functionality if desired
- chemical stability in water

In addition to being notable from a synthetic standpoint, ZMOFs are also interesting as adsorbents for gas separation applications, this is mainly due to the fact that the integral framework of ZMOFs, like zeolites, is charged, necessitating the existence of extra-framework cations to balance the overall charge. The benefit of this is twofold:

1. The existence of a charged framework can contribute to the favourable adsorption of some gases over others by introducing electrostatic effects between the gas and framework.
2. The extra-framework cations offer ion-exchange tunability to ZMOFs, the cations in the parent ZMOF can be readily exchanged with others to potentially alter adsorption performance.

In 2006, two ZMOF compounds were discovered; rho- and sod-ZMOF (Liu et al. 2006). Both were synthesised by expanding the original zeolite nets via substitution of the oxygen atom using a 4,5-imidazole carboxylic acid linker (ImDC).
These two new compounds were synthesised with the aforementioned 4,5-imidazoledicarboxylic acid organic linker with In$^{3+}$ as the single metal ion. In the case of sod-ZMOF, the ligand is deprotonated, allowing for coordination with the indium ion. Two ligands are hetero-chelated to the indium ion, while another two coordinate by the ancillary nitrogen-donor, resulting in six-coordinate indium ions that form the desired molecular building blocks (MacGillivray, 2010).

Conditions for the synthesis of both materials are similar, with the main difference between the two compounds being the choice of structure-directing agent (SDA); rho-ZMOF requires HPP (1,3,4,6,7,8-hexahydro-2H-pyrimidol[1,2-a]pyrimidine, while sod-ZMOF requires imidazole for its synthesis. Both of the SDAs in this case ultimately become the extra-framework cations, compensating the charge of the anionic framework.
Section 2.3: Reported Cation-Exchange on rho-ZMOF

The structure of rho-ZMOF has a very open and accessible structure with a window size of 8.1 Å compared to sod-ZMOF which has a window size of 4.1 Å. Both ZMOFs were tested for their ion-exchange capabilities i.e. replacing the original extra-framework cations in the parent structure with other cations. By submerging the ZMOFs in various salt solutions, it was found that the parent organic cations could be fully exchanged with various organic and inorganic cations in less than 24 hours.

Previous studies performed the In-based rho-ZMOF showcase the tunability potential that ZMOFs have to offer. A fragment of the anionic rho-ZMOF framework is shown in Figure 2.3.1.

Due to its ion-exchange tunability and large cavities, Nouar et.al (Nouar et al. 2009) investigated whether rho-ZMOF could be modified by ion-exchange to introduce stronger electrostatic effects between the framework and an adsorbent gas in order to better suit hydrogen storage applications. The
synthetic route was altered to make rho-ZMOF with an alternate charge-balancing cation, dimethylacetamide DMA\(^+\), which could then be readily exchanged with various inorganic cations. The organic DMA\(^+\) cations in rho-ZMOF were then exchanged fully with nitrate solutions of Li\(^+\) and Mg\(^{2+}\), with adsorption experiments showing a marginal increase in hydrogen uptake in the Li- and Mg-rho-ZMOF as compared to the DMA-rho-ZMOF (Figure 2.3.2).

Most notably however, is that while the overall H\(_2\) uptake is not significantly different, the Li- and Mg-rho-ZMOF isotherms display a steeper initial rise as compared to the DMA-rho-ZMOF; this is attributed to increases in their isosteric heats of adsorption of up to 14\%, which were achieved due to the introduction of the more densely charged inorganic cations into the framework. These increases in the interaction energy of the H\(_2\) gas to the adsorbent are significant for MOF materials which tend to have low interaction energies. In this manner it was demonstrated that ion-exchange could be performed with ZMOFs in order to improve their adsorption performance. Following this report in the literature, others attempted to perform similar experiments on sod-ZMOF.
Figure 2.3.2: Comparison of the effects of cation-exchange on the \( \text{H}_2 \) uptake of rho-ZMOF (Nouar et al. 2009).
Section 2.4: Reported Cation-Exchange on sod-ZMOF

In 2010, researchers probed the effect of cation exchange on sod-ZMOF and its effect on H$_2$ adsorption (Calleja et al. 2010). Following various experiments, they successfully achieved partial cation-exchange of sod-ZMOF with Na$^+$, Li$^+$, K$^+$ and Mg$^{2+}$ whilst noting that exchange with the larger K$^+$ and Mg$^{2+}$ cations led to a decrease in the crystallinity of the framework by 50% and 100% respectively. They successfully replaced 15% of the parent imidazolium cation (Im$^+$) with Na$^+$, and managed to achieve a higher cation-exchange of 28% with Na$^+$ in the same timeframe by regularly refreshing the salt solution (Table 2.4.1).

<table>
<thead>
<tr>
<th></th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{mc}}$ (cm$^3$/g)</th>
<th>Sorbed H$_2$ (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sod-ZMOF</td>
<td>361</td>
<td>0.13</td>
<td>1.6</td>
</tr>
<tr>
<td>Na$^+$ 15%</td>
<td>399</td>
<td>0.17</td>
<td>1.2</td>
</tr>
<tr>
<td>Na$^+$ 28%</td>
<td>804</td>
<td>0.33</td>
<td>1.6</td>
</tr>
<tr>
<td>Li$^+$ 16%</td>
<td>334</td>
<td>0.12</td>
<td>1.18</td>
</tr>
<tr>
<td>K$^+$ 81%</td>
<td>181</td>
<td>0.07</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2.4.1: Comparison of BET Surface areas, pore volumes and H$_2$ uptake for cation-exchanged sod-ZMOF exchanged over 24 hours (Calleja et al. 2010)

Between the various cations tested, it was only by exchanging the parent imidazolium cation with Na$^+$ that an increase in the surface area of the material could be realised; while this did not lead to any improvement in the H$_2$ uptake, it was found that a greater extent of exchange led to an increase in the surface area and pore volumes. It was suggested that this was due to the smaller Na$^+$ cations displacing the bulkier imidazolium in the framework, leaving more room for adsorbate-adsorbent interactions. However, the Na$^+$
ions introduced into the framework also interacted more weakly with H₂, such that despite a 125% increase in the BET surface area of the material, the H₂ uptake was unchanged when compared to the unmodified parent material.

Following this work, other researchers (Chen et al. 2011) also carried out cation-exchange experiments on sod-ZMOF and observed its effect on CO₂ adsorption. It was theorised that the increased quadrupole moment of CO₂ compared to that of H₂ would mean that the introduction of strong electrostatic effects into the cavities by ion-exchange would increase CO₂ uptake far more than the marginal increases seen with H₂. Indeed, cation-exchange with Na⁺, Li⁺ improved CO₂ adsorption capacities, with the potassium-exchanged sample prominently resulting in an increase of 15% more than the parent material as shown in Figure 2.4.1.

Figure 2.4.1: CO₂ adsorption isotherm comparison between parent sod-ZMOF and cation-exchanged sod-ZMOF with K⁺ 28%, Na⁺ 22% and Li⁺ 27%. (P₀ = 1bar) (Chen et al. 2011)
Indeed, both sets of reported cation-exchange results (Calleja et al. 2010; Chen et al. 2011), reported only the improved adsorption performance of partially-exchanged sod-ZMOF material. It was suggested that, in principle, if all the parent cations were to be fully exchanged, more significant improvements in adsorption could be achieved. In 2013, another group of researchers studied and compared the effects of partial and full cation-exchange on sod-ZMOF using Monte Carlo and molecular dynamics simulation methods (Ahunbay 2013).

The simulation method involved introducing the charge-compensating imidazolium Im+ cations into the anionic framework in positions where they minimise their free energy by the Monte Carlo method, and then subsequently partially replacing some of the parent cations with Na+, Li+ and K+; in this way cation-exchanges of 26%, 21% and 27% were achieved respectively. These extents of exchange were deliberately chosen as a basis for the simulations in order to correspond to the 27%, 22% and 28% exchanges achieved by Chen et al in order to compare simulated and experimental data (Figure 2.4.2).
As shown in Figure 2.4.2, the simulation method employed by Ahunbay yields strikingly similar adsorption results to those experimentally collected by Chen et al. for partially exchanged material, validating the accuracy of the simulation method up to 1 bar. As mentioned earlier, the enhanced electrical fields present within the framework as a result of cation-exchange, favour the adsorption of molecules with quadrupole moments such as CO$_2$ over those with no quadrupole moment such as methane, CH$_4$. For this reason, further simulations involved testing sod-ZMOF for the adsorption of CO$_2$ and CH$_4$ in unary and binary forms, these tests would also indicate the suitability of using cation-exchanged sod-ZMOF for the purification of CO$_2$ from methane gas streams.

Figure 2.4.2: CO$_2$ adsorption isotherms of cation-exchanged sod-ZMOF determined by experiments (Chen et al. 2011) (black squares) and simulated data (Ahunbay 2013) (red circles) [$P_0$=1bar]
Adsorption simulations on partial- and fully-exchanged sod-ZMOF for CO₂ and CH₄ were subsequently performed at conditions mimicking typical process pressures of 10 bar and at temperatures of 308K (Figure 2.4.3). It is clear to see that while partially exchanging the Im⁺ cations can result in increases of up to 30% for the unary adsorption of CO₂, full cation-exchange can result in increases of more than 200%. It was suggested that this is because while partial exchange replaces some of the imidazolium cations in the framework, the presence of the remaining cations is still sufficient to block pore openings and hinder adsorption; full replacement of the bulky imidazolium however, removes this hindrance, leading to remarkable increases in adsorption capacity.

Simulation of binary mixed-gas adsorption of CO₂ and CH₄, show that CO₂ mostly retains its unary adsorption capacity in spite of competition with CH₄ due to its quadrupole nature and as such its stronger interactions with the material over CH₄. As a result of its weaker interactions however, the diffusivity of CH₄ within the material is several-fold higher than that of CO₂. In
order to compare the effects of adsorption and diffusion within the material, the authors opted to use the resulting adsorption, diffusion and perm selectivities of each of the materials as an indicator of performance. They found that in mixed-gas simulation experiments, only full-exchange of the parent cation yield improvements in the overall permselectivity, while partial-exchanged materials did not show any improvements over the parent. (Table 2.4.2)

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_{\text{adsorption}}$</th>
<th>$\alpha_{\text{diffusion}}$</th>
<th>$\alpha_{\text{overall}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sod-ZMOF</td>
<td>3.99</td>
<td>0.91</td>
<td>3.64</td>
</tr>
<tr>
<td>Li+ 27%</td>
<td>3.21</td>
<td>0.61</td>
<td>1.95</td>
</tr>
<tr>
<td>Na+ 22%</td>
<td>4.44</td>
<td>0.38</td>
<td>1.68</td>
</tr>
<tr>
<td>K+ 28%</td>
<td>3.55</td>
<td>1</td>
<td>3.55</td>
</tr>
<tr>
<td>Li+ 100%</td>
<td>22.76</td>
<td>1.29</td>
<td>29.36</td>
</tr>
<tr>
<td>Na+ 100%</td>
<td>35.1</td>
<td>1.11</td>
<td>39.12</td>
</tr>
<tr>
<td>K+ 100%</td>
<td>66.56</td>
<td>2.6</td>
<td>172.74</td>
</tr>
</tbody>
</table>

Table 2.4.2: Sorption, diffusion and perm selectivities of cation-exchanged sod-ZMOF materials for CO$_2$/CH$_4$ separation

In order to yield a change in the CO$_2$ sorption uptake for sod-ZMOF, partial cation-exchange is sufficiently interesting; however, a sorbent with promising sorption capacities for CO$_2$ must be tested in conditions which best resemble a useful application in industry, Such an application is natural gas purification, where CO$_2$ is removed from CH$_4$ streams. Exchanging the parent Im$^+$ with a more densely charged inorganic cation such as Na$^+$, increases the strength of the electric field within the framework; this in turn preferentially increases the strength of its interactions with CO$_2$ compared to those with CH$_4$. While this increases the adsorption selectivity of CO$_2$/CH$_4$ separation by the material,
there is also a decrease in the diffusion selectivity, and for partially exchanged sod-ZMOF materials; this trade-off acts unfavourably and only sabotages their performance for CO₂/CH₄ separation when compared to the parent material. However, with the full replacement of the parent imidazolium cation, the pores become more accessible and can potentially result in enhanced permselectivities of up to 170.
Conclusion
All studies that have yet been published on the cation-exchange of sod-ZMOF, point to the conclusion that achieving partial cation-exchange does not yield any significant benefits in the adsorption capacities of sod-ZMOF, and in the case of mixed gas mixtures, only impedes the separation performance. Possibly, the only way that ion-exchange can be used method to constructively tune sod-ZMOF for the aforementioned mixed-gas separation, is by attempting to achieve full exchange of the parent imidazolium cation.
Section 2.5: References


Chapter 3: Cation-exchange of sodalite-ZMOF

Section 3.1: Introduction

Past work has proven that ion-exchange is an effective method to tune the properties of ZMOFs, leading in some cases, to significant improvements in gas adsorption performance. The indium-based sod-ZMOF is one such material that, upon cation-exchange, has shown increases in its adsorption capacity of up to 15% (Chen et al. 2011), with simulated models predicting that even greater improvements in adsorption capacities can be achieved upon achieving high ion-exchange degrees (Ahunbay 2013). To date, the properties of sod-ZMOF have been enhanced only by partial-exchange of the parent cation; experimental work detailing the effect of full-exchange of the parent cation has not yet been reported.

As sod-ZMOF has been previously reported to showcase interesting properties as a membrane (Al-Maythalony et al. 2015). It is expected that ground-breaking improvements in its properties by ion-exchange can pave the way for the development of a novel class of materials; ion-exchanged ZMOF membranes. Such membranes could yield interesting insights into the properties of ZMOF membranes and can potentially be tailored to suit particular gas separation applications (Figure 3.1.1).

Cation-exchange of the bulk sod-ZMOF material will be attempted in this study with inorganic cations such as sodium, lithium, potassium and magnesium. It is hypothesised that once sod-ZMOF is submerged in highly concentrated salt solutions containing these cations; the inorganic cations will enter the sod-ZMOF framework via its windows and displace the organic
imidazolium cations from within the framework over time. This mechanism of displacement relies on two factors to achieve an overall increase in the degree of exchange over time: a large concentration gradient favouring the displacement of the imidazolium cations with the inorganic cations, and potentially higher interaction energies between the more densely charged inorganic cations and the framework.

Figure 3.1.1: A scheme illustrating the potential translation of successful cation-exchange experiments on the bulk material being incorporated into membrane form.
Figure 3.1.2 shows a diagram of the sod-ZMOF framework viewed along its six-member window; the largest sized window granting access to the pores of the framework. The ionic diameter of the cations desired to be introduced into the framework are listed in Table 3.1.1. It is important to note, that while the diameter of the cations is smaller than the size of the sod-ZMOF six-member window; the cations can coordinate with surrounding H₂O molecules, increasing their effective diameter.

![Sod-ZMOF Framework Diagram](image)

**Figure 3.1.2:** The sod-ZMOF framework viewed along its six-member window

![Sodium Cation Hydration](image)

**Figure 3.1.3:** A representation of the hydration of a sodium cation with H₂O molecules
It is hypothesised that while the size of the hydrated cations might be larger than the size of the sod-ZMOF window; the inorganic cation may temporarily exist with a partial state of hydration during which the cation may be able to enter the framework and displace the parent cation.

The aim of this work is to investigate whether the adsorption properties of sod-ZMOF can be modified by completely exchanging the parent imidazolium cation with various, smaller inorganic cations. What follows is a fundamental study of the bulk adsorbent material of sod-ZMOF, the ion-exchange procedure, and its effect on the material’s adsorption performance.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic Diameter (Å) (No Hydration)</th>
<th>Ionic Diameter (Å) (Hydrated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>1.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.9</td>
<td>7.2</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.4</td>
<td>6.6</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 3.1.1: Comparison of the non-hydrated and hydrated ionic diameters of some inorganic cations (Dove & Nix 1997)
Section 3.2: Experimental Method

Synthesis

*sod*-ZMOF was synthesised following the procedure published by Eddaoudi et al. (Liu et al. 2006). Table 3.2.1 lists the reagents that were added to a 20-mL glass scintillation vial:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Chemical formula</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium nitrate hydrate</td>
<td>In(NO$_3$)$_3$.xH$_2$O</td>
<td>0.0435 mmol</td>
</tr>
<tr>
<td>4,5 imidazole dicarboxylic acid</td>
<td>C$_5$H$_4$N$_2$O$_4$</td>
<td>0.1305 mmol</td>
</tr>
<tr>
<td>Imidazole</td>
<td>C$_3$H$_4$N$_2$</td>
<td>0.3 mmol</td>
</tr>
<tr>
<td>N,N dimethylformamide (DMF)</td>
<td>C$_2$H$_7$NO</td>
<td>0.3 mL</td>
</tr>
<tr>
<td>3.5M nitric acid in DMF</td>
<td>HNO$_3$ in DMF</td>
<td>1.5 mL</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH$_3$CN</td>
<td>0.5 mL</td>
</tr>
</tbody>
</table>

Table 3.2.1: Reagents added to a 20-mL vial for the synthesis of *sod*-ZMOF

The vial is then sonicated in a sonication bath for 15 minutes to ensure a homogenous reaction mixture and then heated at 85°C for 12 hours and at 105°C for 23 hours in an oven. Following synthesis, the reaction mixture is allowed to cool at room temperature prior to characterisation.
The reaction yields approximately 5 mg of the colourless polyhedral crystals shown in Figure 3.2.1. The chemical formula of sod-ZMOF is reported to be \( \text{In}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)\_2(\text{C}_3\text{N}_2\text{H}_5)(\text{DMF})_4(\text{CH}_3\text{CN})(\text{H}_2\text{O})_4 \)

**Post-synthesis characterisation**

Following synthesis of sod-ZMOF, crystals with similar morphologies are gathered and tested by powder x-ray diffraction (PXRD) using an X’Pert Pro Powder X-Ray Diffractometer. The x-ray diffraction pattern is then compared to one calculated by single-crystal x-ray diffraction in order to verify the material’s identity and phase purity as shown in Figure 3.2.2. The crystals are then washed with ethanol/water and methanol/acetonitrile solvent mixtures for three days and checked again using PXRD in order to verify the stability of sod-ZMOF in those solvent mixtures.

![Figure 3.2.2: PXRD pattern comparison of sod-ZMOF as-synthesised, in methanol/acetonitrile and in ethanol/water with the calculated pattern](image)

Figure 3.2.2: PXRD pattern comparison of sod-ZMOF as-synthesised, in methanol/acetonitrile and in ethanol/water with the calculated pattern
Ion-exchange

The parent cation (imidazolium in the case of sod-ZMOF) was exchanged with various metal cations such as sodium, lithium and magnesium. Solutions of the respective metal nitrates were prepared in either a mixture of ethanol (EtOH) and water (0.75: 0.25) (Nouar et al. 2009) or a mixture of methanol (MeOH) and acetonitrile (CH$_3$CN) (0.7:0.3) in keeping with past cation-exchange experiments in our research group. All the metal nitrate solutions that were prepared are summarised in Table 3.2.2; two different forms of solutions were prepared in order to compare the effect of the presence, and absence of water on cation-exchange.

<table>
<thead>
<tr>
<th>Metal nitrate</th>
<th>Solvent mixture</th>
<th>Concentrations prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>EtOH/H$_2$O</td>
<td>0.2M, 0.6M, 1M</td>
</tr>
<tr>
<td>Lithium nitrate</td>
<td>EtOH/H$_2$O</td>
<td>0.2M, 1M</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>EtOH/H$_2$O</td>
<td>0.1M</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>EtOH/H$_2$O</td>
<td>0.2M, 1M</td>
</tr>
<tr>
<td>Sodium nitrate</td>
<td>MeOH/CH$_3$CN</td>
<td>0.2M</td>
</tr>
</tbody>
</table>

Table 3.2.2: A summary of the metal nitrate solutions prepared for the purpose of cation-exchange

The parent sod-ZMOF is prepared for cation-exchange by first washing the as-synthesised sample twice for 24 hours with DMF to remove any unreacted material, ‘washing’ here refers to submerging the sample in a particular solvent, and refreshing the solution two times in 24 hours. This is then followed by washing the sample six times for 72 hours with the solvent mixture to be used for cation-exchange; an illustration of this approach is shown in Figure 3.2.3.
After the sample is sufficiently washed, it is gathered, air-dried and then distributed into separate vials, with each vial containing 40 mg of sod-ZMOF. The metal nitrate solution is then added to the sample, ensuring that the sample forms a uniform layer across the base of the vial. For highly concentrated solutions (0.6 – 1 M), 5 mL of the metal nitrate solution was added, while for the lower concentrations (0.1 - 0.2 M), 15 mL was added. Once the allotted time for cation-exchange is complete, the solution in the vial is removed and the sample is washed three times with 5 mL of the solvent mixture to remove any excess salt.

Post-ion-exchange characterisation
Following cation-exchange, the sample is characterised by PXRD and compared to the non-exchanged parent sodalite to observe the effect of cation-exchange on its crystallinity.

In order to determine the ion-exchange degree for the sample, the amount of metal cations in the sample are analysed by inductively-coupled plasma
optical emission spectroscopy (ICP-OES). This technique quantitatively detects the amount of an element in a solution by first ionising the atoms in a sample with high energy plasma and measuring the characteristic wavelengths of visible light emitted upon combination of the atom with a high-energy free electron. The wavelength and intensity of the emitted light respectively correspond to the identity and quantity of a particular element.

The sample is prepared for ICP-OES analysis by digesting 5 mg of cation-exchanged sod-ZMOF with 5 mL of concentrated nitric acid. The resulting solution is then diluted to 20 mL with distilled water and analysed. The results from such an analysis are shown in Table 3.2.3, these indicate the mass of each element present in the sample. Each of the masses is divided by its respective atomic mass, and the molar ratios of the elements are compared.

<table>
<thead>
<tr>
<th>sod-Sample_4h Na⁺ Exchange</th>
<th>In (λ=451.131 nm)</th>
<th>Na (λ=588.995 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detected mass (mg/kg sample)</td>
<td>16.03</td>
<td>0.984</td>
</tr>
<tr>
<td>Atomic mass (mg/mol)</td>
<td>115000</td>
<td>23000</td>
</tr>
<tr>
<td>Molar amount (mol/kg sample)</td>
<td>1.40x10⁻⁴</td>
<td>4.30x10⁻⁵</td>
</tr>
<tr>
<td>Molar ratio</td>
<td>0.770</td>
<td>0.230</td>
</tr>
<tr>
<td>Degree of exchange</td>
<td>31%</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2.3: An example of how results from the ICP-OES are processed to determine the degree of cation-exchange achieved. The degree of exchange signifies the percentage of the parent imidazolium cation that has been replaced by the metal cation.

According to the chemical formula of the parent sod-ZMOF, there is one indium atom to each imidazolium cation in the framework. As such, the degree of exchange is determined by calculating the ratio of the molar amount
of the metal desired to be exchanged to the molar amount of indium i.e. Me/In.

**Adsorption**

Nitrogen and carbon dioxide adsorption experiments are performed on the parent sod-ZMOF and the various cation-exchanged samples to determine the adsorption uptake, BET surface area and pore volume of the material. Prior to activation, the sample is washed with its respective solvent six times over three days. The choice of activation solvent varies depending on the solvent mixture being used for the cation-exchange of the sample, Table 3.2.4 summarises these differences in the choice of solvent below.

<table>
<thead>
<tr>
<th>Solvent mixture for cation-exchange</th>
<th>Activation solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH/H₂O</td>
<td>EtOH*</td>
</tr>
<tr>
<td>EtOH/H₂O</td>
<td>EtOH/H₂O</td>
</tr>
<tr>
<td>MeOH/CH₃CN</td>
<td>MeOH/CH₃CN</td>
</tr>
</tbody>
</table>

Table 3.2.4: The choice of activation solvent for cation-exchanged sod-ZMOF used in this study. *EtOH was later abandoned as an activation solvent following stability tests.

The sample is then activated under vacuum at room temperature (22 °C) using a Quantachrome Instruments Autosorb Degasser for eight hours, nitrogen and carbon dioxide adsorption experiments are then carried out using a Quantachrome Instruments Quadrasorb Surface Area Analyser. Nitrogen adsorption is performed at 77 K up to a relative pressure of P/P₀= 1 while carbon dioxide adsorption is performed at 298 K up to a relative pressure of 0.016 (1 bar). The adsorption experiments are then repeated, with re-activation being performed at 55 °C, 85 °C, 105 °C etc. until the activation
solvent is fully removed and a pore volume is attained that matches the theoretical one.
Section 3.3: References


Chapter 4: Results and Discussion

Section 4.1: Preliminary Trial I - Cation-Exchange with Ethanol/Water and activation with Ethanol

Initial cation-exchange experiments focused on studying the time taken to achieve 100% exchange of the parent cation by submerging the material in 0.2 M solutions of metal nitrate prepared with EtOH/H₂O. These exchanges were carried out over a 1, 4 and 12 day period, and the metal nitrate solution in each vial was refreshed every 24 hours. X-ray diffraction diagrams (Figure 4.1.2) indicate that the cation-exchanged sod-ZMOF materials generally maintain their crystallinity after exposure to the metal nitrate solutions.

<table>
<thead>
<tr>
<th></th>
<th>Na⁺</th>
<th>Li⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-day exchange</td>
<td>35%</td>
<td>49%</td>
<td>9%</td>
<td>55%</td>
</tr>
<tr>
<td>4-day exchange</td>
<td>85%</td>
<td>113%</td>
<td>55%</td>
<td>86%</td>
</tr>
<tr>
<td>12-day exchange</td>
<td>200%</td>
<td>-</td>
<td>136%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1.1: ICP-OES results of the degree of cation-exchange achieved over a 1, 4 and 12-day period on sod-ZMOF. The percentages indicated in bold were tested for their N₂ adsorption performance.

It is worth noting that the degree of cation-exchange of the samples detailed in Table 4.1.1 may exceed 100% exchange, i.e. apparently over-compensating for the anionic charge on the framework. It is presumed that this occurs due to a change in the integral structure of sod-ZMOF; where the cation can situate itself between the carboxylate groups on the ligand, thus allowing a cation to bind to the framework and permitting the ratio of In to...
metal cation to be 1:2, where one cation becomes an extra-framework cation, while the other becomes part of the framework.

Figure 4.1.1: The imidazole dicarboxylic acid ligand

Figure 4.1.2: X-ray diffraction patterns comparing cation-exchanged sod-ZMOF to the parent sod-ZMOF
The nitrogen adsorption performance of the parent sod-ZMOF is shown in Figure 4.1.3; an optimal pore volume of 0.16 cm$^3$ g$^{-1}$ with a BET surface of 355 m$^2$g$^{-1}$ obtained upon activation at 85 °C with ethanol.

![Figure 4.1.3: Nitrogen adsorption isotherm of the parent sod-ZMOF activated at 85 °C with ethanol](image)

![Figure 4.1.4: Carbon dioxide adsorption isotherm of the parent sod-ZMOF activated at 55 °C with ethanol](image)
It was expected that adsorption tests on the cation-exchanged samples displayed in Table 4.1.1 would show greater improvements in the adsorption performance compared to the parent material. The cation-exchanged samples were washed with ethanol for three days, and then tested for their adsorption properties. The adsorption isotherms of the exchanged samples are shown in Figures 4.1.5 and 4.1.6. While the optimal pore volume of the parent sod-ZMOF is achieved by activation at 85 °C, the optimal pore volumes of the cation-exchanged samples were achieved at 55 °C, for this, comparison of plotted data represents only the isotherms that represent the optimal pore volume.

![Nitrogen adsorption isotherms of cation-exchanged sod-ZMOF in Preliminary Trial I.](image)

Figure 4.1.5: Nitrogen adsorption isotherms of cation-exchanged sod-ZMOF in Preliminary Trial I.

Interestingly, regardless of the cation and degree of cation-exchange, a large decrease in uptake is observed in both the N$_2$ and CO$_2$ isotherms. There is no clear correlation for the effect of the degree of exchange on the adsorption
behaviour on Na⁺ and Li⁺, while K⁺ shows the least decrease in N₂ uptake and most retention of Langmuir adsorption behaviour.

-of note however, is the difference in adsorption behaviour between the N₂ and CO₂ isotherms; in all cases, the decrease in CO₂ uptake from that of the parent is far less than the decrease in N₂ uptake as compared to the parent. This is particularly pronounced with the sample exchanged with the Mg²⁺ cation to a degree of 55%, its divalent nature would mean that the charge is essentially compensated for by 110%, indicating the complete exchange of the imidazole cation.

Initial experiments showed that the nitrogen and carbon dioxide adsorption performance of sod-ZMOF was only deteriorating with large degrees of cation-exchange. Therefore, a systematic study was devised in order to better understand the effect of cation exchange on the stability of sod-ZMOF.
Section 4.2.1: Preliminary Trial II – Part A: Cation-Exchange and Activation with Ethanol/Water

Following preliminary Trial I, adsorption tests were carried out on the parent sod-ZMOF which was washed with ethanol/water for three days, and then with ethanol for three days. The material showed a drastic drop in N₂ uptake compared to the parent material washed purely in ethanol as shown in Figure 4.2.1.1. This method of washing is likely a major cause of the large decline in the adsorption performance of the samples tested in Preliminary Trial I.

However other tests showed that, surprisingly, if sod-ZMOF is washed in ethanol/water for three days, and then immediately tested for adsorption without subsequent washing with ethanol, the material retains most of its N₂ adsorption capacity and reaches its optimal pore volume at elevated temperatures, as shown in Figure 4.2.1.2. It was deemed appropriate therefore, to conduct cation-exchange with ethanol/water and subsequently activate the samples without further washing with a more volatile solvent.

The use of water in the solvent mixture was deemed necessary in order to achieve a higher degree of cation-exchange within a shorter timeframe; this is because higher molar concentrations of metal nitrates can be dissolved in the presence of water. Previously, organic solvents such as a mixture of methanol/acetonitrile have also been used for cation-exchange experiments; this mixture can attain solubilities as high as 0.2 M for most of the metal nitrates tested in contrast to 1 M concentrations that are achievable with ethanol/water.
Figure 4.2.1.1: Nitrogen adsorption isotherms comparing sod-ZMOF exposed to water and thereafter washed with ethanol to sod-ZMOF without any prior exposure to H$_2$O.

Figure 4.2.1.2: Nitrogen adsorption isotherms comparing sod-ZMOF washed in ethanol/water and then activated without any subsequent washing with a volatile solvent.
A control experiment comparing the degree of cation-exchange attained with ethanol/water with that of methanol/acetonitrile showed that despite using the same molar concentration of metal nitrate solution; using ethanol/water for cation-exchange can yield a three-fold higher exchange rate. Ethanol/water was therefore deemed most appropriate as the cation-exchange solvent/mixture for preliminary Trial II, along with its use as the activation solvent.

For cation-exchanges conducted in Preliminary Trial II, cation-exchange was performed over shorter intervals of time and with a higher molar concentration of metal nitrate solution. The effect of cation-exchange was then studied with a 1 M concentration of sodium nitrate solution in ethanol/water.

<table>
<thead>
<tr>
<th>Exchange duration (h)</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of exchange</td>
<td>88%</td>
<td>77%</td>
<td>79%</td>
<td>65%</td>
</tr>
</tbody>
</table>

Table 4.2.1.1: Initial results from cation-exchange with Na⁺ performed over a 24 hour period

Tests carried out over a 24 hour period showed an overall decrease in the degree of exchange with increasing exchange duration (Table 4.2.1.1). At first, this result seemed to be inexplicable, considering that the amount of metal cations in solution were approximately a hundred times more than the number of imidazolium cations in the framework, thus, longer exchange times should have led to a greater displacement of the parent cations along and thus a greater degree of exchange.
It was supposed that this unexpected result may have been due to the post-exchange washing procedure performed for the experiment, which consisted of washing the exchanged material three times with 5 mL of ethanol/water, and then submerging the sample in 15 mL of ethanol/water for 18 hours. During submersion, these cations might have diffused out of the framework and into the solvent, thus decreasing the degree of exchange. In order to determine the effect post-exchange washing; several samples of sod-ZMOF were exchanged, washed in various ways and then analysed by elemental analysis.

<table>
<thead>
<tr>
<th>Washing</th>
<th>3X 0.1 mL</th>
<th>3X 5mL 18h</th>
<th>3X 15mL 18h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample1</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>Sample2</td>
<td>31%</td>
<td>33%</td>
<td>34%</td>
</tr>
<tr>
<td>Sample3</td>
<td>15%</td>
<td>18%</td>
<td>21%</td>
</tr>
<tr>
<td>Sample4</td>
<td>26%</td>
<td>26%</td>
<td>28%</td>
</tr>
<tr>
<td>Sample5</td>
<td>42%</td>
<td>42%</td>
<td>44%</td>
</tr>
</tbody>
</table>

Table 4.2.1.2: Results from a wash test showing the effect of washing on the degree of exchange of Na⁺-exchanged samples, samples washed immediately several times are compared to those washed over 18 hours.

The results from the wash test (Table 4.2.1.2); show that the extent of post-exchange washing has little effect on the degree of cation-exchange. Following this finding, washing was carried out post-cation-exchange by washing the cation-exchanged sample three times with 5 mL of solvent mixture.

The exchange experiment was then repeated again over a 24 hour period and it was found that, as desired; for longer exchange durations, a greater degree
of exchange was achieved and that full exchange of the parent cations with Na$^+$ can be achieved within 24 hours (Table 4.2.1.3). The PXRD patterns of the Na$^+$ exchanged samples showed that the material maintained its crystallinity after being exchanged (Figure 4.2.1.3).

<table>
<thead>
<tr>
<th>Exchange duration (h)</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of exchange</td>
<td>53%</td>
<td>73%</td>
<td>82%</td>
<td>102%</td>
</tr>
</tbody>
</table>

Table 4.2.1.3: Results from cation-exchange with Na$^+$ performed over a 24 hour period. The samples indicated in bold were tested by adsorption

Figure 4.2.1.3: X-ray diffraction patterns comparing cation-exchanged sod-ZMOF to the parent sod-ZMOF in preliminary trial II
The **sod-ZMOF** exchanged with \( \text{Na}^+ \) by 102% was then characterised by single-crystal x-ray diffraction to determine the position of the \( \text{Na}^+ \) cations in the framework. The \( \text{Na}^+ \) cation was found to be situated in the centre of six-member window; existing in a in a hydrated form where it is coordinated to 6 \( \text{H}_2\text{O} \) molecules (Figure 4.2.1.4 C). Observing the position of the \( \text{Na}^+ \) cation with a space-filling model elucidates the extent to which the cation restricts the size of the window; blocking access to the cavities of the framework (Figure 4.2.1.4 D). Full-exchange of the parent cation with sodium can thus lead to hydrated forms of the sodium cations being localised in the centre of the six-member window of **sod-ZMOF**, restricting access to intra-framework cavities.
Figure 4.2.1.4: A view of the six-member window of sod-ZMOF with the hydrated Na\(^+\) cation situated in the centre of the window in ball-and-stick and space-filling form. (A) and (B) are views of the window without cation-exchange, and (C) and (D) show a view of the window after cation-exchange with Na\(^+\). N.B. Hydrogen atoms are not shown on the water molecules.
The cation-exchanged samples were then tested for their N\textsubscript{2} and CO\textsubscript{2} adsorption performance (Figures 4.2.1.5 and 4.2.1.6). Clearly, a greater degree of cation-exchange results in a decrease in both the N\textsubscript{2} and CO\textsubscript{2} adsorption capacities. While all cation-exchanged samples show large reductions in their N\textsubscript{2} uptake, noticeably however, sod-ZMOF Na\textsuperscript{+} 53\% (blue circles) shows a marginal increase in the CO\textsubscript{2} uptake over the parent material also activated with EtOH/H\textsubscript{2}O (red circles).

Potentially, part of the reason why the N\textsubscript{2} and CO\textsubscript{2} adsorption performance decreases upon cation-exchange is the obstruction of the six-member windows by the hydrated cations. This can block access to the cavities of the framework, resulting in a significantly reduced uptake of N\textsubscript{2} and CO\textsubscript{2}. It is interesting to note that despite the single-crystal structure of the sod-ZMOF Na\textsuperscript{+} 102\% showing blocking of the six-member window by the hydrated cation; the adsorption isotherms of the material show that some N\textsubscript{2} and CO\textsubscript{2} is still adsorbed by the material. This could potentially be because while a number of the cations are situated in the centre of the six-member window, there may be some which are not located in the window and are instead in positions which still allow the passage of the gas to some of the cavities of the framework, thus allowing some uptake of N\textsubscript{2} and CO\textsubscript{2} gas.
Figure 4.2.1.5: Nitrogen isotherms of Na⁺ exchanged samples exchanged over a 24 hour period.

Figure 4.2.1.6: Carbon dioxide adsorption isotherms of Na⁺ exchanged samples exchanged over a 24 hour period.
Displayed also in Figure 4.2.1.6 is the CO₂ uptake achieved by the parent material using ethanol as an activation solvent without any prior exposure to H₂O. As mentioned earlier; while the N₂ uptake of sod-ZMOF does not decrease by much between using ethanol and ethanol/water as an activation solvent; the behaviour of the parent material for CO₂ adsorption shows that there is a decrease in the CO₂ uptake of approximately 50% upon using ethanol/water instead of ethanol as an activation solvent. Therefore, while the sod-ZMOF Na⁺ 53% outperforms sod-ZMOF activated in the same way with ethanol/water, it compares poorly to sod-ZMOF activated purely with ethanol. It is worthy to note here, that while sod-ZMOF is stable to water in regards to maintaining its crystallinity; adsorption studies show that the material is perhaps partially collapsing after exposure. As such, a different approach to cation-exchange was attempted in Preliminary Trial III where the sod-ZMOF framework is not exposed to water.
Section 4.2.2: Preliminary Trial II – Part B: Cation-Exchange and Activation with Ethanol/Water

Prior to the discovery that the use of water hinders sod-ZMOF's adsorption performance; further cation-exchange studies were conducted using ethanol/water as the solvent mixture. What follows is a more thorough discussion of the numerous experimental trials performed during preliminary Trial II.

Trials with a 1 M solution of sodium nitrate

Initial cation-exchange experiments with a 1 M solution of sodium nitrate yielded the results displayed in Table 4.2.2.1.

<table>
<thead>
<tr>
<th>Exchange duration (h)</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>18</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of exchange</td>
<td>53%</td>
<td>73%</td>
<td>82%</td>
<td>43%</td>
<td>28%</td>
<td>134%</td>
<td>130%</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>102%</td>
<td>205%</td>
</tr>
</tbody>
</table>

Table 4.2.2.1: Cation-exchange experiments conducted with 1M sodium nitrate solution. The numbers in bold were tested for their adsorption performance. Anomalous results are highlighted in red.

At first, it was thought that using a 1 M solution of sodium nitrate was appropriate due to past references of use in the literature. However, 24 hours after preparation of the 1 M solution, crystals of sodium nitrate begin to noticeably recrystallise in the original solution due to the high concentration and did not then re-dissolve. As such, using a 1 M solution of sodium nitrate was abandoned in favour of a less concentrated sodium nitrate solution to avoid recrystalisation of the salt.
Trials with a 0.6 M solution of sodium nitrate

Following verification that sodium nitrate would not recrystallise in solution, cation-exchange experiments were then conducted with a reduced concentration of sodium nitrate of 0.6 M, results of which are displayed below (Table 4.2.2.2).

<table>
<thead>
<tr>
<th>Exchange duration (h)</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>12</th>
<th>24</th>
<th>40</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of exchange</td>
<td>14%</td>
<td>19%</td>
<td>34%</td>
<td>28%</td>
<td>23%</td>
<td>59%</td>
<td>42%</td>
<td>48%</td>
</tr>
</tbody>
</table>

Table 4.2.2.2: Cation-exchange experiments conducted with 0.6M sodium nitrate solution.

While the use of 0.6 M sodium nitrate generally produced more consistent results than the use of 1 M sodium nitrate; due to the slow rate of exchange obtained at room temperature with 1 M lithium and magnesium nitrate, it was decided that further cation-exchange experiments would be performed at higher temperatures.

Trials with 1 M solutions of lithium and magnesium nitrate

Alongside the cation-exchange experiments performed with sodium nitrate, 1 M solutions of lithium and magnesium nitrate were also employed for cation-exchange experiments. It was found that recrystallisation did not occur in these solutions.

Even over a period of 120 hours, it was found that both lithium and magnesium nitrate yielded very low degrees of exchange (Tables 4.2.2.3 and 4.2.2.4).
In order to increase the exchange rate, further trials were carried out with regular refreshing of the metal nitrate solution (every two hours), results of which are displayed in Tables 4.2.2.5 and 4.2.2.6.

These results revealed that despite using a high molar concentration of solution and maintaining a high driving force for cation-exchange by refreshing in intervals of two hours; a sufficiently high degree of exchange could not be attained at room temperature. Therefore, it was more appropriate to conduct further cation-exchange trials at higher temperatures of 70 °C.

0.6M sodium nitrate refreshing in intervals of 2 hours at 70°C

Experiments with 0.6 M of sodium nitrate were conducted over a period of 10 hours at room temperature and at 70 °C, the results of which are displayed in Tables 4.2.2.7 and 4.2.2.8.
Figure 4.2.2.1 illustrates that increasing the temperature to 70 °C can result in a 4-fold increase in the exchange rate. However, prior to testing these samples for their adsorption performance, as described earlier in Section 4.2.1; adsorption tests were performed on the parent material exposed to ethanol/water (Figure 4.2.1.6), and it was found that the presence of water was detrimental to the CO₂ adsorption uptake of sod-ZMOF.
Preliminary Trial II – Conclusion

During the course of preliminary Trial II, it was found that while a 1 M sodium nitrate solution can be prepared in ethanol/water, the sodium nitrate in the solution begins to noticeably recrystallise after 24 hours; these crystals do not then re-dissolve, and lead to anomalies in the subsequent elemental analysis of cation-exchanged samples. Further studies were then carried out with a reduced concentration of sodium nitrate of 0.6 M, and 1 M solutions of lithium and magnesium nitrate which do not recrystallise.

However, it was not until after numerous experiments had been carried out in preliminary Trial II, that it was observed that washing with ethanol/water drastically reduces the carbon dioxide adsorption performance of the parent material. For this reason, ethanol/water was then abandoned as a feasible solvent mixture for cation-exchange.
Section 4.3: Preliminary Trial III: Cation-Exchange and Activation with Methanol/Acetonitrile

Following unsuccessful experiments using ethanol/water, methanol/acetonitrile was selected as a solvent mixture for cation-exchange. Due to the constraint of methanol/acetonitrile only being able to solubilise up to a 0.2 M sodium nitrate solution, in order accelerate the exchange process; cation-exchange was conducted at 22 °C and 60 °C and the resulting adsorption performance was compared.

After numerous trials, it was found that a degree of exchange of 17 % could be attained in 24 hours at 22 °C and in 4 hours at 60 °C (Table 4.3.1).

Two such samples were then tested for their adsorption performance, the results of which are shown in Figures 4.3.2 and 4.3.3. For both cation-exchange materials, the overall adsorption uptake decreases compared to the parent; with the decrease in N₂ uptake being distinctly different between the two materials while the CO₂ uptake remains approximately the same. Also of note, is that the sample exposed for a shorter time to the metal nitrate solution at 60 °C retains its optimal pore volume at a higher temperature than the sample exchanged for a longer time at 22 °C. As such, although it was found that the rate of cation-exchange could indeed be accelerated at higher

<table>
<thead>
<tr>
<th>Exchange temperature</th>
<th>22</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange duration (h)</td>
<td>24h</td>
<td>4h</td>
</tr>
<tr>
<td>Degree of exchange</td>
<td>17%</td>
<td>17%</td>
</tr>
</tbody>
</table>

Table 4.3.1: Comparing the effect of temperature on the degree of cation-exchange using methanol/acetonitrile
temperatures, it would also lead to a greater decrease in surface area than one exchanged at room temperature for longer periods of time.

Figure 4.3.1: PXRD patterns comparing the crystallinity of sod-ZMOF cation-exchanged at different temperatures in methanol/acetonitrile
Figure 4.3.2: Nitrogen adsorption results from sod-ZMOF exchanged 17% with sodium at different temperatures.

Figure 4.3.3 Carbon dioxide adsorption results from sod-ZMOF exchanged 17% with sodium at different temperatures.
The CO$_2$ adsorption isotherms were then compared to published cation-exchange results (Chen et al. 2011) as shown in Figure 4.3.4. Strikingly, the CO$_2$ uptake of the sod-ZMOF reported by Chen et al. is almost 50% lower than the CO$_2$ uptake achieved by sod-ZMOF in this study and in past studies by our research group. As such, despite the reported increases in the CO$_2$ uptake of sod-ZMOF upon cation-exchange found in the literature, the increase remains less than the parent and cation-exchanged materials produced in this study. While the reported N$_2$ uptake of the parent sod-ZMOF measured by Chen et al. is consistent with measurements in this study, there is no mention of the N$_2$ uptake achieved by the cation-exchanged; as such as full comparison between the two studies cannot be made.

Following the findings that cation-exchange would be better performed with a solvent mixture of methanol/acetonitrile at room temperature, more experiments were planned in order to investigate the development of the adsorption performance with greater degree of exchange.
Conclusion

From all the results reported in this study, the adsorption performance of cation-exchanged sod-ZMOF did not show any improvements over the parent material. In part, this was due to the exposure of the sod-ZMOF framework to a solvent mixture containing water, which reduced the overall uptake of nitrogen and carbon dioxide gas. While exposure of the framework to ethanol/water did not affect the structural integrity of the framework as observed by the powder x-ray diffraction, it was later found that the adsorption performance was indeed affected.

In retrospect, the parent sod-ZMOF material should have been screened by nitrogen and carbon dioxide adsorption after exposure to various solvent mixtures to determine the most suitable solvent mixture for the cation-exchange investigation. However, in the course of these experiments, this screening was performed much later during the investigation and as such did not allow sufficient time to repeat the full investigation with a more appropriate solvent mixture.

After identification of the negative effect of ethanol/water on the adsorption performance, a solvent mixture of methanol/acetonitrile was then selected for cation-exchange following verification that it did not affect the adsorption performance of sod-ZMOF. Cation-exchange performed over a period of 24 hours with sodium did not yield any improvements in the nitrogen and carbon dioxide performance.

Single-crystal analysis of sod-ZMOF fully exchanged with sodium cations showed that the hydrated cation can block the windows leading to the internal
cavities of the framework. This would explain why large degrees of cation-exchange with sodium can lead to decreases in the adsorption capacities in the material.

Indeed, all of the inorganic cations tested in the course of this investigation had hydrated diameters larger than the size of the framework window. While elemental analysis confirms that cation-exchange does indeed take place, it is thought that the high salt concentrations and long lengths of time required to achieve complete cation-exchange increases the likelihood of the pores being blocked by the hydrated forms of these cations, and as such, generally leads to a decrease in the adsorption uptake of N$_2$ and CO$_2$.

In order to avoid blocking of the windows of the sod-ZMOF framework, it was thought prudent to conduct further cation-exchange experiments with cations whose maximum dimensions did not exceed the size of the framework’s window. For this reason, experiments with various other organic cations were planned, however, time did not allow for full completion of this investigation.
Section 4.4: References


