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Cation Exchange Modification of Clinoptilolite Zeolite for Applications in Nitrogen Rejection

DOCTOR *of* PHILOSOPHY *in* CHEMICAL ENGINEERING
THESIS

By

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ABSTRACT

Natural gas and biogas are increasingly important resources to the global energy mix. With the growth in the development of unconventional resources, contaminate gases within natural gas mixtures are growing challenges for industry. Inert gases such as N_2 cannot be more than 4%vol. in order to meet pipeline specifications. This is done in an effort to increase the heating value and reduce the compression volume of the natural gas. While approximately 15% of natural gas reserves in the United States do not meet this threshold, additional sources including fugitive methane emissions from gas wells and coal bed gas also contain large amounts of N_2 relative to CH_4 . For these kinds of gases to be used commercially they need to be treated. Conventional treatment methods such as cryogenic distillation are energy intensive; requiring large economies of scale and intense process integration to improve efficiency. Therefore, the development of some unconventional natural gas resources proves to be very difficult particularly for small and more remote operations. As the easier and better quality fuel stocks become more difficult to extract, the need to improve overall processing techniques by exploring energy efficient and cost effective separation systems becomes more important. The integration of adsorption technology within existing natural gas upgrading processes has the potential to achieve a more economical separation of N_2 from hydrocarbon mixtures. However, such technologies have shown limited commercial success as almost all adsorbents are only moderately selective for CH_4 over N_2 , with only a few adsorbents being N_2 selective. The screening and characterization of new adsorbent materials is thus necessary prior to implementing such separation technologies on a greater scale.

Following an extensive adsorbent screening study, clinoptilolite was found to be a material of interest due to both favourable kinetic and equilibrium separation properties. The objective of this research was thus to modify clinoptilolites through cation exchange to improve the separation of N_2 and/or CO_2 from natural gas or biogas resources. Clinoptilolite is a naturally occurring aluminosilicate zeolite with a very narrow effective pore size distribution. This adsorbent is unique as it may be either CH_4 selective or N_2 selective. Since the framework charge of clinoptilolite is negative, charges balancing extra framework cations occupy the channels of the zeolite. This zeolite may be modified through cation exchange to induce favourable separation properties by altering the morphology of the material. Following screening, the adsorption characteristics of CO_2 , CH_4 , and N_2 on the adsorbents were evaluated and their performances were related to the underlining morphology and elemental composition of these materials. Temperature effects and experimental CH_4 and N_2 mixture adsorption measurements were compared to multicomponent extensions of single gas adsorption isotherms. These adsorbent materials are promising candidates for the

application of natural gas refining. Their implementation into various adsorption technologies are considered.

Findings from this research showed the possibility of improved CH_4/N_2 equilibrium selectivity over natural clinoptilolite using Cs^+ and Fe^{3+} exchanged varieties. Additionally, the possibility of N_2/CH_4 selective kinetic separations were demonstrated for Ni^{2+} and Li^+ exchanged clinoptilolites. Ag^+ exchanged clinoptilolite was shown to be N_2 selective over CH_4 for potential equilibrium adsorption separations. Finally, the idea of membranes formed of clinoptilolite and a glass binder supported by a porous ceramic alumina support were presented for the first time.

SOMMAIRE

Le gaz naturel et le biogaz sont des ressources qui deviennent de plus en plus importantes au niveau énergétique mondial. Grace à la croissance dans le développement de ressources non-conventionnelle, les gaz contaminants dans les mélanges de type gaz naturel poses présentement des défis industriels. Les gaz inertes tel que N_2 devraient être présents à des quantités plus basses que 4 %vol. afin de répondre aux spécifications du pipeline. Ces spécifications sont imposées afin d'augmenter la pouvoir calorifique et de réduire le volume de compression du gaz naturel. Environ 15% des réserves de gaz naturel aux États-Unis excède ce seuil de gaz contaminants. De plus, d'autres sources de gaz tel que les émissions fugitives de méthane provenant des puits de gaz ainsi que les gaz de couche contiennent aussi des quantités élevées de N_2 par rapport au CH_4 . Des étapes de traitement sont alors nécessaires pour que ces types de gaz puissent être utilisés commercialement. Les méthodes de traitement conventionnelles tel que la distillation cryogénique requièrent beaucoup d'énergie, ce qui nécessite des grandes économies et des efforts d'intégration de procédés afin d'améliorer l'efficacité technologique. Le développement de ressources de gaz naturel non-conventionnel est alors très difficile, surtout pour les opérations isolées et à petite échelle. Au fur et à mesure que les réserves de carburant deviennent plus difficiles à extraire, le besoin de technologies de séparation rentable et à faible consommation devient de plus en plus important. L'intégration de la technologie d'adsorption avec des procédés existants d'extraction de gaz naturel possède le potentiel d'améliorer la rentabilité de la séparation de N_2 des mélanges gazeux d'hydrocarbure. Cependant, jusqu'à date ces technologies ont démontrées des limitations dans leurs succès commerciale puisque presque toutes les adsorbants sont seulement modérément sélectifs envers le CH_4 par rapport au N_2 . De plus, seulement quelques adsorbants sont sélectifs envers le N_2 . Le dépistage et la caractérisation de nouveaux adsorbants et alors nécessaires avant que ces technologies de séparations puissent être utilisées à l'échelle commerciale.

À la suite d'une étude approfondie, la clinoptilolite s'est révélée être un d'intérêt. L'objectif de cette recherche est d'effectuer le dépistage de différents types de cations qui sont appliqués dans la modification de clinoptilolite afin d'améliorer la séparation de N_2 et CO_2 des mélanges de gaz naturel ou biogaz. Le clinoptilolite est une zéolithe d'origine naturelle ayant une distribution de grandeur de pore très étroite. Cet adsorbant est unique dû au fait qu'il peut être sélectif envers soit le CH_4 ou le N_2 . Puisque la charge naturelle du clinoptilolite est négative, des cations qui balancent la charge occupent les canaux de la zéolithe. Ce zéolithe peut être modifié par échange de cations afin d'améliorer ses propriétés de séparation en altérant la morphologie du matériel. Par la suite, les caractéristiques d'adsorption de CO_2 , CH_4 et N_2 sur les clinoptilolite modifiés ont été évaluées et ces résultats ont été reliés à la morphologie et

la composition des matériaux en questions. L'effet de température ainsi que les mesures expérimentales d'adsorption de mélanges de CH_4/N_2 ont été comparés à des extensions d'isothermes d'adsorption permettant l'analyse de plusieurs composées. Ce matériel est un candidat promettant comme adsorbant pour des applications dans le raffinement du gaz naturel, et sont implémentation en plusieurs technologies d'adsorption est d'abord considérés.

Ces recherches ont montré une amélioration de la sélectivité à l'équilibre CH_4/N_2 par rapport à la clinoptilolite naturelle à l'aide de variétés échangées avec Cs^+ et Fe^{3+} . De plus, la possibilité de séparations cinétiques sélectives N_2/CH_4 a été montrée pour les clinoptilolites échangées avec Ni^{2+} et Li^+ . La clinoptilolite échangée avec Ag^+ s'est révélée être sélective pour N_2 par rapport à CH_4 pour les séparations par adsorption à l'équilibre. Enfin, des membranes formées de clinoptilolite et d'un liant à base de verre ont été présentées pour la première fois.

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III. THESIS STRUCTURE and ORGANIZATION

This thesis consists of nine chapters and two appendix chapters which is based upon a culmination of articles submitted or published in peer reviewed academic journals. **A complete list of the published manuscripts and conference presentations corresponding this thesis is provided in Appendix B.**

Chapter 1 consists of a brief introduction relating the relevance of this work to practical applications of adsorption and membrane based processes for the separation of gas species present in natural gas and biogas mixtures. Also presented within this section is a brief outline of the overall objectives and goals of this work.

Chapter 2 relates to an article published in the *Journal of Chemical and Engineering Data* titled “Pure and Binary Adsorption Equilibria of Methane and Nitrogen on Activated Carbons, Desiccants, and Zeolites at Different Pressures”. This article contains a brief review of the literature and presents new information in the form of a pure component adsorption screening of common adsorbents for potential CH₄ and N₂ gas separations. Included within this article is a discussion related to the effects of competitive adsorption of binary CH₄ – N₂ gas mixtures for the most promising commercially available adsorbents.

Chapter 3 is based upon an article published in *Microporous and Mesoporous Materials* titled “Cation Exchange Modification of Clinoptilolite – Screening Analysis for Potential Equilibrium and Kinetic Adsorption Separations Involving Methane, Nitrogen, and Carbon Dioxide”. In this chapter, clinoptilolite, a natural zeolite, was modified with different cations. The effects of which were analysed in terms of the physicochemical properties of the materials and the related single gas adsorption behaviour of CO₂, CH₄ and N₂ gases.

Chapter 4 explores the temperature effects of CO₂, CH₄, and N₂ adsorption on various promising clinoptilolite types which were modified with Fe³⁺, Cs⁺, and Ca²⁺ cations (which were selected based upon the findings shown in Chapter 3). Included in this discussion is a detail comparison on the effect of temperature on the adsorption characteristics of raw and cation exchanged clinoptilolite using temperature dependent isotherm models. The article is titled “Cation Exchange Modification of Clinoptilolite – Thermodynamic Effects on Adsorption Separations of Carbon Dioxide, Methane, and Nitrogen” and it was published in *Microporous and Mesoporous Materials*.

Chapter 5 builds on the findings related to the previous two chapters and presents the binary adsorption behaviour of CH₄ and N₂ gas mixtures on Fe³⁺ and Cs⁺ clinoptilolite compared to natural

unmodified clinoptilolite. These materials were of interest as they showed higher CH₄/N₂ adsorption selectivity compared to others. A detailed analysis pertaining to the effects of the cation type on the observed adsorption behaviour as it relates to the material properties of the clinoptilolites is discussed. Also included in this section is a discussion related to the applicability of different predictive binary isotherm models for this gas mixture system. The article has been published in *Adsorption* and is titled “Pure and Mixture Adsorption Equilibria of Methane and Nitrogen onto Clinoptilolite: Effects of Cs⁺ and Fe³⁺ Exchanged Cations on Separation Performance”.

Chapter 6 presents the physicochemical and adsorption characteristics of CH₄ and N₂ gasses on different types of clinoptilolite cation-exchanged with AgNO₃. This material modification was of interest as it demonstrated unconventional N₂/CH₄ adsorption selectivity as most other adsorbents are CH₄ selective for this type of separation. The article is titled, “The Effect of Ag⁺ Cations on the Micropore Properties of Clinoptilolite and Related Adsorption Separation of CH₄ and N₂ Gases” and it has been published in *Microporous and Mesoporous Materials*.

Chapter 7 shows the application of natural clinoptilolite in a novel inorganic composite membrane. The corresponding article was titled, “Vitreous Composite Clinoptilolite Membranes: Synthesis and Preliminary Gas Permeation Properties” it has been submitted to *Chemical Engineering Communications*.

Chapter 8 contains an article published in the *Canadian Journal of Chemical Engineering* titled, “Pore Plugging Synthesis and Characterization of Silicalite-1 Membranes using Tubular TiO₂ Supports: Effect of Support Pore Size on Membrane Performance”. While not directly related to the overall content of this thesis, many of the principles and concepts discussed in this section are relevant to the fundamental understanding of adsorption effects in gas membrane separations processes.

Chapter 9 provides an overall discussion and gives conclusions and recommendations that have resulted from this work. A summary of the original research contribution that this thesis provides to the advancement to the field of adsorption is discussed.

An appendix section is also provided at the end of this thesis.

Appendix A contains an elaboration on background material regarding the description of the experimental apparatus as well as relevant experimental methods used in this thesis.

Appendix B contains a current curriculum vitae corresponding to my scientific contributions during my academic studies which includes work that has resulted from this thesis.

IV. CONTRIBUTION of COLLABORATORS

The experiments were performed using the equipment provided by my supervisor Dr. F. Handan Tezel, and the facilities at the University of Ottawa. The lab-scale binary adsorption apparatus including the gas chromatograph was modified and maintained by myself with the guidance of Louis Tremblay and Franco Ziroldo. The membrane permeation apparatus used for the experiments outlined in Chapter 2 was designed and built by Lauren Rose with help from the technical staff (Louis Tremblay, Gerard Nina, Franco Ziroldo, and James Macdermid). The volumetric adsorption system was repaired and calibrated by myself with assistance from Christa Abou-Zeid. The gravimetric adsorption system was maintained with the assistance of Sean Wilson and Dr. Ye Hua.

The single and binary gas chromatography experiments presented in Chapter 2 were completed in part by Emily Trudeau and Maja Mujčin. Experiments related to the papers presented in Chapter 4 and Chapter 5 were performed with the assistance of Maja Mujčin and Christa Abou-Zeid as part of their undergraduate thesis projects. Some of the cation exchange experiments required from Chapter 6 were completed with the assistance of Mohamad Khanafer. The experimental results given in Chapter 7 are based in part from preliminary work completed by Talal Omar as part of his undergraduate thesis. Finally, Chapter 8 pertains to research that was conducted alongside David Carter who trained me on various membrane characterization techniques along with Muhammad Tawalbeh.

In addition, some of the material analysis was performed with assistance by others. The powdered x-ray diffraction measurements shown in Chapters 3 to 7 were performed by Dr. Bulat Gabadullin (Department of Physics, University of Ottawa). The nitrogen sorption tests and material textural analysis presented in Chapters 4 to 6 was completed by Dr. Yong Yang from the Centre for Catalysis Research and Innovation (University of Ottawa). Scanning electron microscopy and electron diffraction spectroscopy measurements shown in Chapters 3 to 6 were completed with the help of Glenn Poirier from the Microanalysis Lab (Department of Earth and Environmental Sciences, University of Ottawa).

In accordance with the rules established by the University of Ottawa., this thesis manuscript is original and is entirely the product of the author's own work. Contributions made by co-authors are listed below and are used with their full knowledge and consent. Some of the work was done in collaboration with various undergraduate and graduate students at the University of Ottawa after having been trained by me with respect to methodology and technique. A brief outline of the contribution of the authors for each thesis chapter is outlined below for transparency:

Chapter 1

Author	Author's Role & Contribution
Dean Kennedy	• Manuscript writing and corrections (100%)
Dr. F. Handan Tezel	• Editorial comments and corrections

Chapter 2

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Sample preparation • Single component adsorption isotherm experiments and experimental screening • Binary mixture chromatography experiments • Single gas chromatography experiments • Experimental Data analysis • Manuscript writing and corrections (100%)
Maja Mujcin	• Sample preparation • Binary mixture gas chromatography experiments
Emily Trudeau	• Single gas chromatography experiments
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 3

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Sample preparation • Single component adsorption isotherm experiments and experimental screening • Data analysis • Manuscript writing and corrections (100%)
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 4

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Sample preparation • Single component adsorption isotherm experiments and experimental screening • Data analysis • Manuscript writing and corrections (100%)
Maja Mujcin	• Sample preparation • Single gas chromatography experiments
Christa Abou-Zied	• Single gas chromatography experiments
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 5

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Sample preparation • Single component adsorption isotherm experiments. • Data analysis (50%) • Manuscript writing and corrections (80%)
Maja Mujcin	• Sample preparation • Binary mixture gas chromatography experiments (100%) • Data analysis (50%) • Manuscript writing (20%)
Tatum Alenko	• MATLAB programming code development for binary isotherm modelling.
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 6

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Sample preparation • Single component adsorption isotherm experiments. • Experimental data analysis • Manuscript writing and corrections (100%)
Mohamad Khanafer	• Sample preparation
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 7

Author	Author's Role & Contribution
Dean Kennedy	• Experimental design • Membrane preparation and permeation experiments. • Verification of clinoptilolite properties following heat treatment. • Single component adsorption isotherm experiments. • Experimental data analysis • Manuscript writing and corrections (90%)
Maja Mujcin	• Clinoptilolite powder preparation. • Membrane preparation and permeation experiments
Talal Omar	• Membrane preparation and permeation experiments. • Manuscript writing (10%)
Dr. F. Handan Tezel	• Guidance and feedback on all aspects of project • Editorial comments and corrections

Chapter 8

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David Carter	• Experimental design & training • Membrane preparation and permeation experiments (25%) • Editorial comments and corrections
Sean Wilson	• Gravimetric adsorption experiments
Dr. B. Kruczek	• Editorial comments and corrections
Dr. F. Handan Tezel	• Editorial comments and corrections

Chapter 9

Author	Author's Role & Contribution
Dean Kennedy	• Manuscript writing and corrections (100%)
Dr. F. Handan Tezel	• Editorial comments and corrections

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VI. AUTHOR'S STATEMENT

I declare that I am the sole author and primary contributor to the experimental work described herein within this thesis. Contributions made by various co-authors are detailed in Section IV and are acknowledged at the beginning of each chapter section for all co-authored works. I designed all of the experimental studies and performed the subsequent data analysis in addition to having written all of the chapters contained in this thesis. This work was completed under supervision of Dr. F. Handan Tezel (Department of Chemical and Biological Engineering, University of Ottawa) who provided experimental guidance and helpful editorial corrections that have improved the quality and breadth of this work.

References to the original publications that form the basis of each chapter are provided for the content of this thesis that has already been published to date in peer reviewed journals.

Signature: _____

Date: _____

CHAPTER 1

Introduction

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1.1. MOTIVATION

The intention of this thesis is to research new adsorbent materials which increase the adsorption separation efficiency of CH_4 gas from N_2 and/or CO_2 gas mixtures for applications of natural gas and/or biogas treatment. Pursuant to this objective, the development of practical adsorbent materials was considered. A practical adsorbent material in this respect is considered to be a material for which it is highly selective, is easy to obtain with robust characteristics such as durability, chemical stability, and is cost effective for implantation into large scale applications.

1.2. NATURAL GAS

Natural gas is a light hydrocarbon rich fuel composed of primarily methane which is an increasingly relevant and important resource. The development of natural gas fields has been spurred in part by the adoption of new technologies that have improved the recoverability and increased the economic viability of unconventional natural gas reserves where development was previously thought to be uncompetitive. While better technology and recoverability of natural gas reserves have improved the economic practicality of this resource in recent years, the introduction of increased environmentally stringent emission regulations have favoured the development of natural gas resources over other fossil fuels. As the worldwide demand for energy increases, natural gas, as the cleanest and most efficient hydrocarbon resource will play an increasingly important role in the global energy mix [1]. Several studies have indicated that conventional natural gas is a less carbon intensive energy source than other fossil fuels such as coal [2,3]. Importantly, reported 100 year life cycle analysis of properly regulated shale gas extraction showed the potential to achieve an 18 to 41% lower greenhouse gas footprint than that of coal without the use of carbon capture and storage technology [4–6]. However, other studies have disputed this claim mainly due to the impact of the contribution of methane leakage from upstream and downstream processing of unconventional shale gas [7–9]. This is of particular interest when assessing the role of natural gas as reliable and alternative to coal or oil while renewable technology matures, particularly with respect to electrical production [10,11]. In order to meet the long-term demand for natural gas, exploitation of unconventional and nitrogen contaminated low BTU natural gas reserves must be considered. The growth in unconventional resource recovery and the addition of environmental regulations requiring capture and sequestration of carbon dioxide and stricter regulation of methane emissions from production facilities are resulting in interesting natural gas processing challenges [12]. Continued use of this resource facilitates the need to explore energy efficient and cost effective separation systems to improve natural gas processing techniques throughout the lifecycle of the resource.

Currently, it is estimated that natural gas comprises a market share of between 21.4% and 23.7% of the global primary energy demand. This represents an increase of about 34% in market share over a 30 year period from 1973 – 2013 [13]. During a similar period, global natural gas production has increased from about 1.20×10^{12} m³/yr to over 3.50×10^{12} m³/yr [13]. It is expected that the world demand for natural gas will increase at an annualized rate of between 1.2% and 1.9 %, and by 2020 natural gas will account for the largest share of growth in global energy consumption [14]. The contribution of unconventional natural gas to the total share of natural gas production will continue to increase over this period. In the United States for example, in 2013, of the 0.69×10^{12} m³/yr of dry natural gas production, the combined contribution of tight and shale gas to this number was 64% [15]. It is further expected that most of the future growth in onshore natural gas production in North America will be through expansion of the extraction of shale or tight natural gas reserves [15]. Coalbed methane, which has long been a hazard for safety in coal mining operations [16,17], is another increasingly important hydrocarbon source and has seen an appreciable growth in extraction.

1.2.1. NATURAL GAS SOURCES and COMPOSITION

Conventional natural gas reserves may be found alongside oil reservoirs in porous sedimentary rock formations such as sandstone [18,19]. With respect to unconventional natural gas, the gas produced from these reservoirs is not always associated with oil. Furthermore, the gas contained within the reservoir is not as easy to recover compared to conventional natural gas. This is due to the complex and often less porous structure of the geological formations, as such the gas is less likely to permeate through reservoir bed. Common examples of unconventional natural gas sources include shale gas and tight gas which is a broad term for natural gas found in low-permeable rock formations including: shale, sandstone, siltstone, limestone, among others [20]. In recent years, the development of enhanced natural gas recovery techniques, such as horizontal wells, multi-stage hydraulic fracturing, and multi-lateral drilling has unlocked this resource [18,21].

Raw natural gas from either conventional or unconventional reserves are similar in nature and contain variable amounts of contaminants that must be removed in order to meet the required specifications for transport and utilization. Methane composes the bulk constituent of natural gas, however other components include C₂+ paraffinic hydrocarbons, aromatics, water, carbon dioxide, nitrogen, sulfur containing compounds, small amounts of helium (<1 vol.%), and mercury (5 – 1000 µg/m³). When found together with oil reserves, typically the natural gas is usually richer with heavier paraffinic hydrocarbons and is classified as *wet* natural gas when the C₂+ content is higher than 10 vol.%.

Natural gas may also be *sweet* or *sour* if the content of acid gas contamination in the natural gas exceeds 1 vol.% for hydrogen sulphide and 2 vol.% for carbon dioxide.

Coalbed methane, can be of biogenic, thermogenic, or mixed origin and is the result of degradation of the coal within reserves [22–24]. In general, coalbed gas contains mostly methane, with variable quantities of inert gases with carbon dioxide being the predominant contaminant, and small amounts of nitrogen, water, and hydrogen sulfide also present. The quality of the methane found within coal beds is dependent on the original coal deposit and the predominant degradation process. Coalbed gas quality has been shown to be related to the depth of the deposit, with deeper locations containing gas of thermogenic origin, and shallower deposits containing a mixture of gas of biogenic and thermogenic origin however this is not universal across all basins [22,25,26]. Low quality deposits such as lignite are associated with higher carbon dioxide content due to the influence of anaerobic biogenic degradation of the coal a result of higher organic content. Areas with higher quality deposits of coal are more associated with thermogenic processes where carbon dioxide is a less predominant contaminant.

Landfill gas is a methane rich biogas produced from the anaerobic decomposition of landfill waste which has approximately half of the heating value of natural gas [27]. On average, methane is usually the most dominant component in landfill gas with concentrations consisting of between 40% and 60%. Carbon dioxide is the main contaminant along with smaller amounts of nitrogen, and trace amounts of hydrogen sulphide, ammonia, as well as other volatile organic compounds [28,29]. Variations in landfill gas composition is attributed to both the waste composition and the biodegradation stage of the landfill [30,31]. The components found in landfill gas are similar to other biogas sources which include anaerobic digesters used in sewage sludge treatment and used in treatment of agricultural biowastes (silage, manure, food wastes) [29].

The methane yield and composition of the natural gas source is highly variable and depends on the reservoir basin and/or source. Table 1.1 presents the reported general range of components found in natural gas, coalbed gas, and biogas sources on a dry basis. It follows that in addition to the raw composition, the transportation requirements and the specifications for end user applications dictate the separation and conditioning needs for gas enrichment. The degree of nitrogen contamination within the natural gas sources is quite variable. However it is usually quite significant with only water vapour and acid gases such as carbon dioxide being more prominent contaminants.

Table 1.1. Principle gaseous constituents found in natural gas sources on a dry basis (% vol.)

Component	Conventional and Unconventional Natural Gas [14,32–34]	Coalbed Gas (biogenic and/or thermogenic origin) [35–37]	Biogas inc. Landfill Gas [29–31,38,39]
Methane	<i>Typical Range</i> 80 – 95 <i>Extreme Range</i> 30 - 99	<i>Typical Range</i> 85 – 95 <i>Extreme Range</i> 1 - 99	40-70
Carbon Dioxide	<i>Typical Range</i> ≤ 5 <i>Extreme Range</i> ≤ 40	<i>Typical Range</i> ≤ 5 <i>Extreme Range</i> ≤ 30	30-50
Nitrogen	<i>Typical Range</i> ≤ 10 <i>Extreme Range</i> ≤ 25	<i>Typical Range</i> ≤ 5 <i>Extreme Range</i> ≤ 50	<i>Typical Range</i> ≤ 2 <i>Extreme Range</i> ≤ 20
Ethane	<i>Typical Range</i> 1 – 6 <i>Extreme Range</i> ≤ 15	<i>Typical Range</i> ≤ 2 <i>Extreme Range</i> ≤ 11	Trace – 0.2
Propane	0.2– 6	<i>Typical Range</i> ≤ 2 <i>Extreme Range</i> ≤ 6	Trace
Butane	0.25 – 3	<i>Typical Range</i> Trace – 0.1 <i>Extreme Range</i> ≤ 1	Trace
Pentanes+	0.5 – 3	Trace	Trace
Helium	Trace – 1	-	Trace
Hydrogen Sulfide	Trace – 5	Trace	15 – 430 ppm
Oxygen	Trace	Trace – 8	≤ 1
Other contaminants (oxosilanes, mercury, etc..)	Trace	Trace	Trace

1.2.2. NITROGEN CONTENT in NATURAL GAS

While the specifications for pipeline quality natural gas may vary according to local standards, typical specifications indicate a minimum threshold heating value of 950 BTU/cft ($\approx 35000 \text{ kJ/m}^3$). Low BTU natural gas is often contaminated with high amounts of inert gases such as nitrogen which do not contribute to the heating value of the gas and thus may be considered sub quality in nature due to nitrogen contamination [40]. Subquality natural gas is defined as containing equal to or more than 2% carbon dioxide, 4% nitrogen, and 4 ppm of hydrogen sulfide [12]. Natural gas that falls within the criteria of sub

quality natural gas constitutes roughly 1.7 trillion m³ of known US natural gas reserves [40]. Figure 1.1 shows the distribution of nitrogen content within known natural gas reserves in the United States.

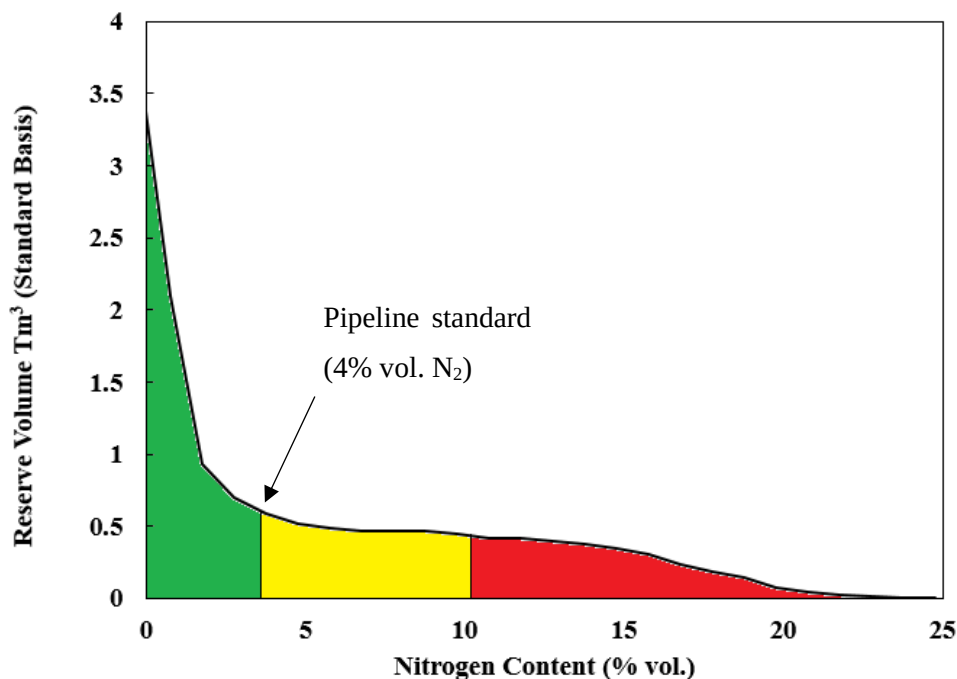


Figure 1.1. United States natural gas reserve volume compared to nitrogen concentration [41].
Colour code - green: $N_2 < 4\%$ vol. (meets threshold for pipeline standard), yellow: $4\% \text{ vol.} < N_2 < 10\% \text{ vol.}$ (blending or treatment required to meet pipeline standard), red: $10\% \text{ vol.} < N_2$ (extensive treatment required to meet pipeline standard).

Specifically, for nitrogen contamination it is estimated that between 11% and 17% of US natural gas reserves contain excess amounts of nitrogen with the bulk of this being in between 5% and 18% nitrogen content [41–45]. In mature and depleted natural gas fields, commercial enhanced recovery techniques such as direct carbon dioxide or nitrogen injection are employed to improve the life of existing natural gas wells, resulting in lower quality natural gas and increased downstream processing requirements. These aforementioned resources require blending with higher BTU gas or removal to meet pipeline and/or liquefied natural gas (LNG) specifications. If these are to be exploited, the need for development of nitrogen removal technologies will increase [41].

Historically, the development of unconventional natural gas reserves contaminated with an excess of nitrogen have been avoided as conventional resources have been more economical as they are both easier to extract and refine. In this respect, development of natural gas fields with particularly high nitrogen content in the 10 – 25% range has been largely overlooked. This accounts for about 300 billion m³ of US reserves with an estimated value of \$30 billion [41,43,46]. While large scale gas producers have been able to economically extract and process high volumes of contaminated natural gas using conventional separation techniques such as cryogenic distillation, smaller operators cannot benefit from

such economies of scale [40]. As a result, a large portion of subquality natural gas reserves controlled by small operations cannot be produced in an economical fashion [40]. Some of this gas may also be released to the atmosphere in the form of methane leakage or as fugitive emissions. Methane is a strong greenhouse gas, with a global warming potential of between 28 and 36 times greater than that of carbon dioxide [47]. Thus, in many instances it is actually preferred to burn such waste hydrocarbon gases in lieu of directly releasing them into the atmosphere. To exploit more of these reserves, cost effective and simple technologies applicable to the treatment of small and dilute natural gas streams is required [41]. Recent developments in commercial nitrogen rejection technologies using pressure swing adsorption and to a lesser extent membrane separation have become a tool in unlocking these resources particularly for mid-scale operations [12,14].

Another aspect relating to nitrogen contamination in natural gas are dilute methane rich nitrogen containing gas mixtures resulting from fugitive methane emissions from natural gas recovery in shale and tight gas, and coal bed methane, as well as flare gas. These emissions are both growing environmental and economic concerns. Estimates of total fugitive methane emissions or leakage from shale gas has accounted for losses of on average between 1.6% and 5.8% of the total methane produced in these natural gas systems [4–6,8,11,48,49]. In these cases, the majority of the loss of methane has been attributed to venting of the gas during well completion, flow back following high-volume hydraulic fracturing, and methane slip from process exhaust, with the remaining methane emissions coming from leaks in downstream process equipment [5,50]. Additionally, fugitive methane emitted from coal mine ventilation and in seam gas draining alone account for about 8% of the world's anthropogenic methane emissions [51]. While the quantity and context of methane leakage is highly variable, the preventative release and/or processing of this gas has several economic and environmental implications. Particularly, the economic loss associated with residual methane gas emissions is not limited in terms of direct loss of profit. The diminished perception of the lifecycle environmental benefits of natural gas resources compared to other fossil fuels undermines the credibility of this resource as a transition fuel going forward in a 21st century energy economy and will need to be addressed by the industry.

1.3. NATURAL GAS CONDITIONING

Natural gas as produced from the well head contains a mixture of both productive hydrocarbon gases which contribute to the overall heating value of the gas (mainly methane, but also ethane, C₃, and other hydrocarbons) and non-productive gases (water vapour, inert gases, acid gases, etc....). Following resource extraction, gas conditioning is applied to the raw natural gas to meet specifications for transportation and downstream processes and both industrial and commercial end user applications (Table 1.2) [14,32]. With respect to liquefied natural gas, LNG is considered as the preferred means of gas transportation compared to a pipeline when the distance between the origin of the gas and the end user is greater than 4800 km [14]. Several published works have previously discussed in detail the broad conventional and alternative conditioning operations implemented in commercial upgrading, as such herein lays a brief overall summary of the major operations [12,14,18,19,32,52]

Table 1.2. Overview of composition specifications for natural gas pipeline delivery and liquefied natural gas feed specifications [14,32,46].

Component	Pipeline Specification	Liquefied Natural Gas Feed Specifications
CO ₂	< 2%	<50ppm
H ₂ O	< 120-150ppm	<0.1ppm
Inert Gases (N ₂ and He)	<3-4vol%	<1 vol%
Total Sulfur	< 4ppm	<20ppm
C ₃	950-1050 Btu/scf dewpoint: <-20°C	-
C ₄	-	<2 vol.%
C ₅	-	<0.1 vol.%
aromatics	-	<2ppm

1.3.1. OVERVIEW of NATURAL GAS PROCESSING

Today natural gas production stems in most part from large fields where the gas is processed in high volumes using central upgrading facilities following field extraction [40]. The typical unit operations that may be employed for natural gas processing include: inlet gas compression, acid gas removal, dehydration, natural gas liquid recovery, nitrogen rejection, and outlet compression/liquefaction (Figure 1.2) [12]. The requirement for nitrogen rejection is dependent on the quality and composition of the inlet feed gas. Various natural gas conditioning processes have been developed in order to facilitate the removal of different impurities to meet end user specifications,

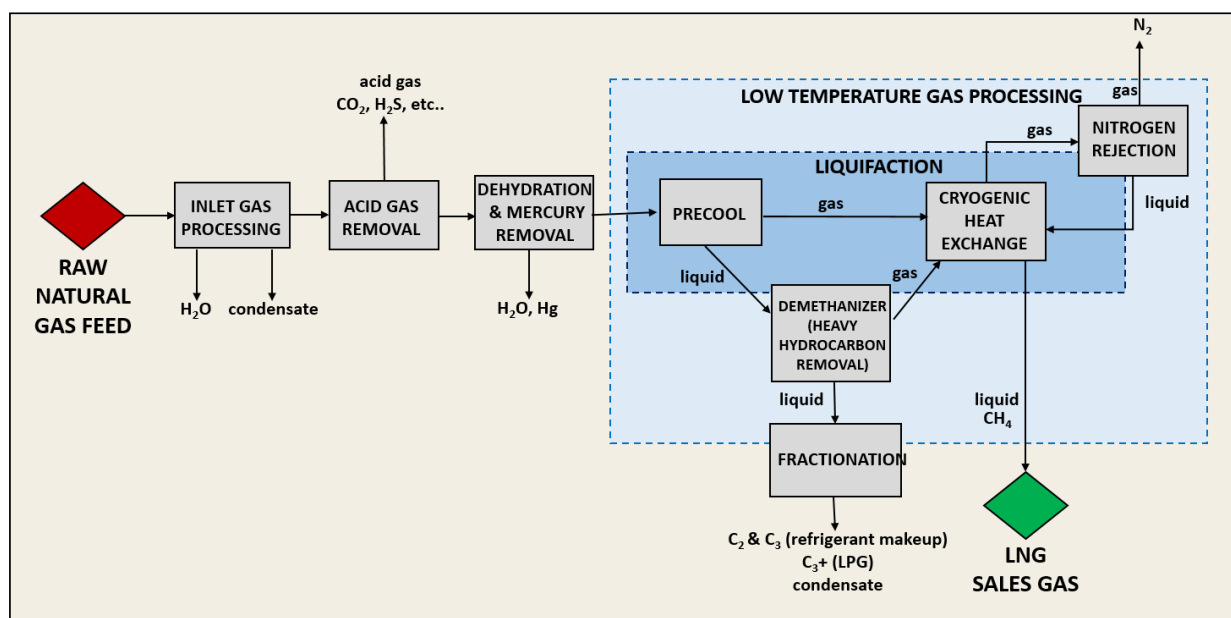


Figure 1.2. Representative BFD depicting general natural gas processing unit operations for LNG [12].

Water may be found in raw natural gas following field gas extraction. The removal of excess water is essential to prevent pipe corrosion in the presence of acid gases and reduce the risk of condensation or hydrate formation and subsequent blockages or fouling of equipment within cryogenic processes and natural gas pipelines. This can be initially done with a combination of compression with rapid expansion and cooling to condense out excess liquid water prior to further processing. This process also removes some of the *wet* natural gas liquids (C_3+ hydrocarbons) from the raw gas at the same time which is recovered as natural gas condensate. However, while the removal of excess liquid water is quite simple, the removal of water vapour requires additional unit operations. Absorption gas dehydration processing using organic solvents such as triethylene glycol or diethylene glycol is the most commonly implemented strategy. Adsorption based gas dehydration using solid desiccants such as activated alumina, silica gel, or molecular sieves such as 3A zeolite may also be used for further treatment for water vapour removal, particularly following compression cycles.

Acid gases such as carbon dioxide and hydrogen sulfide pose significant risk of corrosion to natural gas infrastructure. They may also lead to solids formation within cryogenic units and therefore these components are to be removed as soon as possible following gas extraction. Above the risk of equipment damage, environmental regulations require a low hydrogen sulfide content within the fuel to reduce harmful sulfur dioxide emissions upon combustion. While some natural gas sources contain little to no sulfur compounds, the need for gas sweetening for carbon dioxide removal is more universal since most deposits contain carbon dioxide contamination in some amount of significance. Regardless, the use of aqueous amine absorption/stripping for natural gas sweetening processes is the standard practice for this separation [53]. In this process, two towers are used, first the acid gases are absorbed from the bulk

natural gas usually at high pressure, and reacts with the amine at low temperatures (-40°C). Following acid gas stripping, often a combination of low pressure and high temperatures are used to release the absorbed components from the saturated amine which is then recycled. Conventional absorption processes require a large capital investment and are both labour and energy intensive due to the required high temperatures to regenerate the large volume of solvent[46,53]. Alternative processing methods that have been either commercialized or show economic potential for this separation include adsorption, and membrane technology.

Typically, natural gas containing greater than 3-4 vol. % of inert gases such as nitrogen is required to be removed to meet pipeline specifications for nitrogen content in sales gas in particular to increase the heating value of the gas [12]. Further specifications of 1 vol. % of nitrogen content in natural gas for LNG processes is required to ensure efficient natural gas compression and liquefaction as well as the reduce amount of boil off during storage and transportation [45]. In some instances, nitrogen rich natural gas may be blended with low nitrogen sources to meet pipeline specifications, this is usually done only when the nitrogen content is below 10 vol. % [45]. For inlet feed conditions whereby high amounts of nitrogen are observed, the generally accepted industrial standard for nitrogen removal from natural gas are cryogenic processes. Cryogenic distillation fractioning units may be used to reject nitrogen and other inert non-productive gases from natural gas due to the large differences in relative volatility of inert gases such as nitrogen ($T_{\text{nbp}} = 77\text{K}$) and helium ($T_{\text{nbp}} = 4\text{K}$) compared to methane ($T_{\text{nbp}} = 112\text{K}$). Cryogenic distillation technologies for nitrogen rejection are the most commonly used technologies on the commercial scale [54]. These systems are capable of treating large quantities of natural gas for variable quantities of nitrogen contained within the feed, giving a high hydrocarbon recovery of over 99%[54]. Cryogenic nitrogen rejection may exist in several different schemes integrated within the cold box associated with natural gas liquid recovery with process designs accounting for various configurations based on local refining requirements [45]. Variations on single column and multiple column designs may be used to treat natural gas with a nitrogen content varying from 3 mol% up to as high as 60 mol%[45]. However, while these designs are capable of being highly productive with respect to product recovery, in general this is at the expense of process efficiency as it relates to energy requirements for cooling, and controllability of variable gas feed types [45]. These units benefit from economies of scale and are more suited for large gas recovery operations and usually only economically viable for natural gas process plants processing greater than $4.25 \times 10^5 \text{ m}^3/\text{d}$ of natural gas although higher flow rates of $1.42 \times 10^6 \text{ m}^3/\text{d}$ are recommended [14,53,55]. The requirement for high natural gas throughput with respect to optimizing the economic favourability of cryogenic systems for nitrogen rejection inhibits the use of these systems for smaller and more remote gas suppliers [40].

1.4. ALTERNATIVE GAS PROCESSING TECHNOLOGIES

To date, economically efficient exploitation of low quality natural gas contaminated with high amounts of nitrogen using noncryogenic nitrogen separation processes has remained a relatively small market. This is due to the processing limitations available with current mainstream commercial technologies. Some commercially available alternative technologies that have been developed include pressure swing adsorption (PSA) using either N_2 or CH_4 selective adsorbents, or membrane technology [46]. The idea of these units are attractive as unlike cryogenic distillation units, they can be easily sized and engineered in modular units suitable for the exploitation of smaller and more remote gas reservoirs [14]. However, neither of these technologies have been widely adopted as of yet as they both suffer higher hydrocarbon losses and lower methane recoveries when compared to cryogenic distillation [45].

1.4.1. PRESSURE SWING ADSORPTION SYSTEMS

Physical adsorption is a reversible surface phenomenon described as an increase in the concentration of a substance formed on the interface between a fluid and solid surface. This behaviour is attributed to wall effects formed on the surface due to van der Waals forces caused by interactions between the surface polarity of the adsorbent and the combined polarizability, dipole, and quadrupole moment of the adsorbing species. An adsorptive separation may be achieved through exploiting differences in the adsorptive behaviour of one or more components within a mixture through one of two properties which are the adsorption kinetics and the adsorption equilibrium capacity. Adsorption equilibrium based separations are made possible based on the differences in adsorption equilibrium capacity of the different species to be separated. Kinetic adsorption separations are made possible through differences in the rates of the intracrystalline diffusion within the micropores of an adsorbent. These differences can be attributed to many factors which include molecular steric effects, wall effects, adsorbent pore size, and uniformity. An extension of the kinetic separation mechanism is the steric effect, in which access to the adsorbent pore is restricted based on molecular size, thus acting as a molecular sieve. Therefore, some components may have access to pore network and adsorb on the surface, whereas other components are excluded. This behaviour is unique to adsorbents with a narrow and uniform pore size distribution such as zeolites or carbon molecular sieves for example.

The implementation of adsorption processes as an alternative to cryogenic distillation units has been proposed for the separation of nitrogen from natural gas for small to mid-scale natural gas producers. This is because the typical processing volumes for PSA technology is limited to a capacity of between $6.0 \times 10^4 \text{ m}^3/\text{d}$ and $4.3 \times 10^5 \text{ m}^3/\text{d}$ [45], however some processes can have higher capacities. These systems are of particular interest because adsorption-based processes are less energy intensive and require lower capital investment than cryogenic technologies [53]. Adsorption based separation processes for

natural gas separation involve cyclic unsteady state configurations which are an expansion of the original patent on the 2 stage, 4 step Skarstrom PSA cycle developed in 1960 [56]. While research and development efforts have led to variations on the original PSA separation process, all cyclic PSA processes involve an adsorption step followed by a desorption/regeneration step. During the adsorption step, the packed bed is exposed to a higher pressure gaseous feed where the components of the feed are contacted with the adsorbent and selectively adsorbed within the bed. At the end of the adsorption step, the adsorbent bed will reach saturation capacity. The adsorbed components are released by lowering the pressure within the column during the desorption/regeneration step. Separation is achieved because the less strongly adsorbed components will pass through the bed more readily thus enriching the raffinate stream, whereas the strongly adsorbed components enrich the extract stream following desorption/regeneration [14].

PSA processes for nitrogen rejection from natural gas using methane selective adsorbents have also been developed. Particularly common are the use of activated carbons which have been employed by CH₄ selective N₂ rejection systems developed and currently marketed by companies such as IACX Energy and their Nitrogen Sponge® technology. This system has been marketed for applications with low pressure (up to 5 atm) and low volume streams with current available configuration providing $1.41 \times 10^5 \text{ m}^3(\text{STP})/\text{d}$ of natural gas per separation train [12,54]. These units may treat natural gas with a nitrogen content of up to 40% in the feed with up to 92% hydrocarbon recovery [54]. The main issue with this configuration is that the processed natural gas is produced at low pressure, thus incurring additional recompression costs to achieve pipeline pressure [45].

For the application of these gas separations using adsorption, typical areas of research focussed primarily on the development alternative adsorbents such as carbon molecular sieves [57–59], and other small pored zeolite structures including clinoptilolite[60–63], zeolite 4A [53,64], and chabazite [53,65]. Many studies have been published on particularly for CO₂ selective adsorbents for the separation of CO₂ from CH₄ and N₂ containing mixtures on LTA type zeolites [66,67], MFI type zeolites[68–72], various activated carbons [73,74], and chabazites [75], among many others. Rufford et al. has already presented a recent and detailed literature review on these potential adsorbents for N₂ and CO₂ removal from natural gas [12]. While high CO₂ selectivity are commonly reported, the underlying issue for many adsorbent materials is the modest CH₄/N₂ selectivity ranging anywhere from 1.7 up to 5.5 [64,69,76–81]. Factors such as surface area and potential of the adsorbents obviously affect the adsorption capacity of these gases on the adsorbents. However, the low CH₄/N₂ selectivity observed with these materials is likely due to the physical properties of both nitrogen and methane. Specifically, differences in quadrupole, and molecular polarization energy, presented in Table 1.3, influence the adsorption potential of the gases. N₂ gas is the least adsorbed of the three components as it has only a weak field quadrupole moment and lower

polarizability compared to the other two gases. On the other hand, CH₄ benefits from higher polarizability. While CO₂ exhibits the most adsorbing potential because of the combination of having a high quadrupole moment and higher polarizability compared to the other two gases.

Table 1.3. Physio-chemical properties of CO₂, CH₄ and N₂ gases. [82–84]

Property	CO ₂	CH ₄	N ₂
Kinetic diameter (Å)	3.33	3.82	3.64
Polarizability ($\times 10^{-25}$ cm ³)	29.1	26.0	17.4
Quadrupole moment ($\times 10^{-26}$ esu·cm ²)	4.30	0	1.52
Normal boiling point, T_b (K)	194.7*	111.7	77.4
Critical Temperature, T_c (K)	304.2	190.6	126.2
Molecular weight (g·mol ⁻¹)	44	14	28
* T_b for CO ₂ is the normal temperature for sublimation at 1 atm total pressure.			

The choice of PSA systems is dependent on the adsorbent material and the subsequent adsorption cycle process refinements. An alternate PSA process using a N₂/CH₄ selective adsorbent material is regarded to be the most preferred technical solution. In principle these PSA processes may produce enriched methane at high pressure as the raffinate instead of in the low pressure extract stream, thus reducing gas recompression requirements [14]. Based on the gas properties presented in Table 1.3, this may be achieved by using adsorbents whereby the larger methane molecule (kinetic diameter = 3.82 Å) is restricted; inducing a favourable separation towards the smaller nitrogen gas molecule, (kinetic diameter = 3.64 Å). Such molecular sieves are thereby N₂ selective based on a combination of adsorption equilibria and kinetic effects induced by steric limitations.

Guild Associates uses a propriety system called Molecular Gate®. It builds on the principle on using exclusively N₂/CH₄ selective adsorbents, and thus has generated significant interest in nitrogen selective adsorption in the natural gas industry [54,85]. This system has a design pressure of up to 56 atm with a capability of treating natural gas with a nitrogen content of up to 30% in the feed with up to 90% methane recovery [54]. The current available configuration allows for the treatment of between 1.4×10^5 m³(STP)/d and 2.3×10^6 m³(STP)/d of natural gas per separation train [12,54]. Their proprietary titanosilicate ETS-4 has been proven to be tailored as a N₂ selective molecular sieve through activation at temperatures between 543 and 588K resulting in a contracted pore structure [86]. One limitation of this adsorbent is the relatively low capacity for N₂ gas with a reported equilibrium saturation N₂ adsorption capacity of between 0.5 and 0.6 mmol/g at ambient temperatures [86–88]. Nonetheless, titanosilicate ETS-4 remains the benchmark for N₂/CH₄ selective gas separations. Microporous carbon molecular sieves have been investigated as possible alternatives to ETS-4, for possible equilibrium or kinetic separations of

CO₂ and N₂ from CH₄ mixtures for natural gas or landfill gas upgrading [57,59,89,90]. Although CMS has a higher equilibrium capacity for CH₄ compared to N₂, it is kinetically selective for N₂ due to the narrow micropore size distribution which leads to a delay in the adsorption uptake of the larger CH₄ molecule over the smaller N₂ molecule since it is more difficult for CH₄ to access the micropores of the adsorbent. Cavenati et al. proposed a layered PSA system containing CMS 3K and 13X zeolite layered in a packed bed which was capable of producing 92% pure methane with 43.5% recovery from a mixed CO₂-CH₄-N₂ gas feed [91]. Similarly, small pored LTA structured zeolites such as zeolite 4A has been proposed for a possible kinetic separation of N₂ from CH₄. However, the proposed PSA process is limited to low temperatures (below 277K) and CH₄ feeds of greater than 90%. While increasing interest in the application of newer metal organic framework (MOF) materials such as MIL-100(Cr) for this separation; some issues remain with respect to the stability of MOFs for long term PSA type applications [92]. Amongst zeolites various cation exchanged clinoptilolites (Ca⁺², Mg⁺², and mixed Mg⁺²/Na⁺¹ for example) have shown great potential for N₂/CH₄ selective adsorption[63,93,94]. However, Frankiewicz and Donnelly observed that the use of N₂/CH₄ selective Ca²⁺ rich clinoptilolite in a demonstration PSA system resulted in a product that was below pipeline quality [60]. Subsequent research using different cation exchanged variants of this material have pointed to favourable properties such as high N₂/CH₄ kinetic selectivity, or N₂/CH₄ adsorption separation performance similar to that of ETS-4 [63,93–96].

1.4.2. MEMBRANE SYSTEMS

Although several companies have offered CO₂ removal using different polymeric membrane types, the application of membrane technology for nitrogen rejection has been inhibited due to limitations with respect to material performance and integration with further processing requirements. Similarly to PSA systems, a nitrogen selective membrane material is regarded to be the most preferred technical solution thus reducing compression requirements [14]. The typical flow capacities for membrane systems range between 1.0×10⁴ m³(STP)/d and 7.1×10⁵ m³(STP)/d of natural gas which is suitable for smaller operations[45]. Table 1.4 outlines the the current commercial availability of membrane separation system by Membrane Technology and Research Inc. (MTR) marketed for natural gas nitrogen rejection.

MTR has developed proprietary membranes and a two stage separation process for nitrogen rejection produces pipeline quality gas and nitrogen-rich fuel from raw natural gas [44,54]. These hydrophobic rubbery polymeric membranes are selectively permeable to hydrocarbons (CH₄, C₂H₆, and higher hydrocarbons), whereas nitrogen is less permeable. The reported methane selectivity of these membranes range from 3 to 4 with a theoretical maximum of 6 to 7 at low temperatures (below 253K) [44]. In this configuration, the membrane separates the feed mixture into a hydrocarbon rich permeate which is recompressed and fed to the pipeline, and a nitrogen rich retentate which is used as a fuel [45]. The membrane system is designed for a maximum feed inlet pressure of 85 atm, with a pressure drop

of between 12 and 50 atm per separation cartridge resulting in recompression of the product gas [54]. While MTR membrane system presents a viable commercial solution, there are some limitations in the application of this system for a lower quality natural gas feedstock such as those with high N₂ values and other contaminants such as CO₂ present.

Table 1.4. Commercially available membrane technologies for natural gas nitrogen rejection.

Commercial Name	Vendor - Licensor	Membrane Material and configuration	Natural Gas Separation Type	Capacity (m ³ /d)	Ref.
NitroSep™	MTR inc.	Rubbery Polymer	CH ₄ selective, N ₂ reduced from 50% to 4% in product gas	1.13×10 ⁴	[12,54] www.mtrinc.com
		Silicon rubber		–	
		Spiral wound		2.83×10 ⁶	

When assessing the applicability of various materials for potential applications in membrane nitrogen rejection from natural gas, it is important to first consider the physio-chemical properties of the primary constituents that are to be separated which are nitrogen and methane (given in Table 1.3). Until recently, little attention with respect to membrane research has been focussed specifically on nitrogen rejection from natural gas due to difficulties in membrane separation based on size or condensability [97]. For this reason, limited mixture separation data is found in the literature when compared to other membrane separations. This is partly attributed to the fact that separation of these two components using membranes is inherently difficult when compared to temperature-based separations such as cryogenic distillation where higher selectivity and recoveries are possible. The primary factor that has inhibited the adoption of membrane based nitrogen rejection from natural gas is that current membranes are not selective and productive enough to avoid excessive loss of methane [98].

Membranes, such as glassy polymeric membranes, rubbery polymeric membranes, inorganic membranes, and mixed matrix membranes have been considered for the separation of N₂ from CH₄. In Figure 1.3, the experimental membrane productivity based on a literature survey is plotted as the N₂/CH₄ selectivity vs. the N₂ permeability [99,100,109–118,101,119–128,102,129–135,103–108]. The experimental values are compared to Robeson's 2008 upper bound for N₂/CH₄ membrane separations [136].

With respect to polymeric membranes for gas separation, two categories of polymeric materials exist: rubbery polymers and glassy polymers. This classification is dependent on the glass transition temperature of the polymer relative to the operating temperature of the membrane for the separation conditions. Glassy polymers occur when the operating temperature is below the glass transition temperature, the opposite is true for rubbery polymers. Glassy polymeric membranes are composed of rigid polymer chains, whereas rubbery polymers are more flexible because these polymers have sufficient energy to allow for movement and elasticity along the polymeric chain [137]. The elasticity of the

polymeric chains within rubbery polymeric membranes results in a larger free volume when compared to glassy polymers. This results in less diffusion resistance therefore the effect of the molecular size is reduced[46,138]. As such rubbery polymers preferentially let methane permeate over nitrogen as these membranes separate gases principally by solubility which is dependent on the component condensability[46]. For glassy polymers, the difference in the kinetic diameter of the permeating gases is largely responsible for the observed selectivity, therefore they tend to preferentially let nitrogen permeate more than methane[46]. In this respect, since the kinetic diameters of N_2 and CH_4 are very similar separation by size is very difficult, as such N_2/CH_4 selectivity is typically about 2.5-3 for the best glassy polymers [12,46,139]. With respect to rubbery polymers, similar gas component condensabilities result in CH_4/N_2 selectivity only as high as 3-5 for the best rubbery polymers [12,46]. Recently, more promising materials using thermally rearranged (TR) polyimide polymers were shown to maintain N_2/CH_4 ideal selectivity of about 3 but with permeance of about 2 orders of magnitude higher than first generation glassy polymers [131–133]. A key issue with rubbery polymeric membranes is the effect of plasticisation of the membrane materials resulting from adsorption of highly soluble hydrocarbons present in the natural gas stream. This results in degradation on the membrane performance over time [46].

Although inorganic membranes are more expensive and structurally more brittle than polymeric membranes, these membranes are temperature and wear resistance, and are chemically inert [134]. Inorganic composite membranes derived from small pored zeolites or carbon molecular sieve materials represent the greatest progress in improving N_2/CH_4 membrane selectivity for this separation. This is because these membranes possess the ability to achieve a stable and uniform pore size distribution which is advantageous for applications as a molecular sieve within a membrane. It is for this reason that large pore adsorbent membranes are not considered practical for this separation, as both CH_4 and N_2 are weakly adsorbed components with CH_4 being only slightly more adsorbed[139]. Membranes developed from ion exchanged ETS-4 were shown to be N_2 selective with a selectivity of 5.4 at 308K, however these membranes have low permeability between 2.3 - 4.1 Barrer[130]. Ma et al. developed CMS membranes derived from polymeric materials that have a high N_2 selectivity of 7.7 with higher permeability of 6.7 Barrer at 308K [135]. The low permeance of these membranes is a key issue with these performance of inorganic membranes. While the low permeance of polymeric membranes may be overcome through the ability to produce high surface area designs such as hollow fibre or spiral wound configurations, this is not possible with inorganic membranes. Therefore, high gas permeability is a necessary requirement to reduce the required membrane surface area. Recently, SAPO-34 and SSZ-13 zeolite membranes with the small pored chabazite structure have shown to be the most promising new development. Wu et al. found that SAPO-34 membranes prepared using the secondary growth method exhibit higher N_2/CH_4 selectivity of between 5.4 and 7 with N_2 permeability as high as 4000 Barrer[139]. However, when these researchers added 5% propane to a CH_4-N_2 mixture, membrane fouling was

observed resulting in a reduction in the permeance of the membrane, however the selectivity was maintained[97].

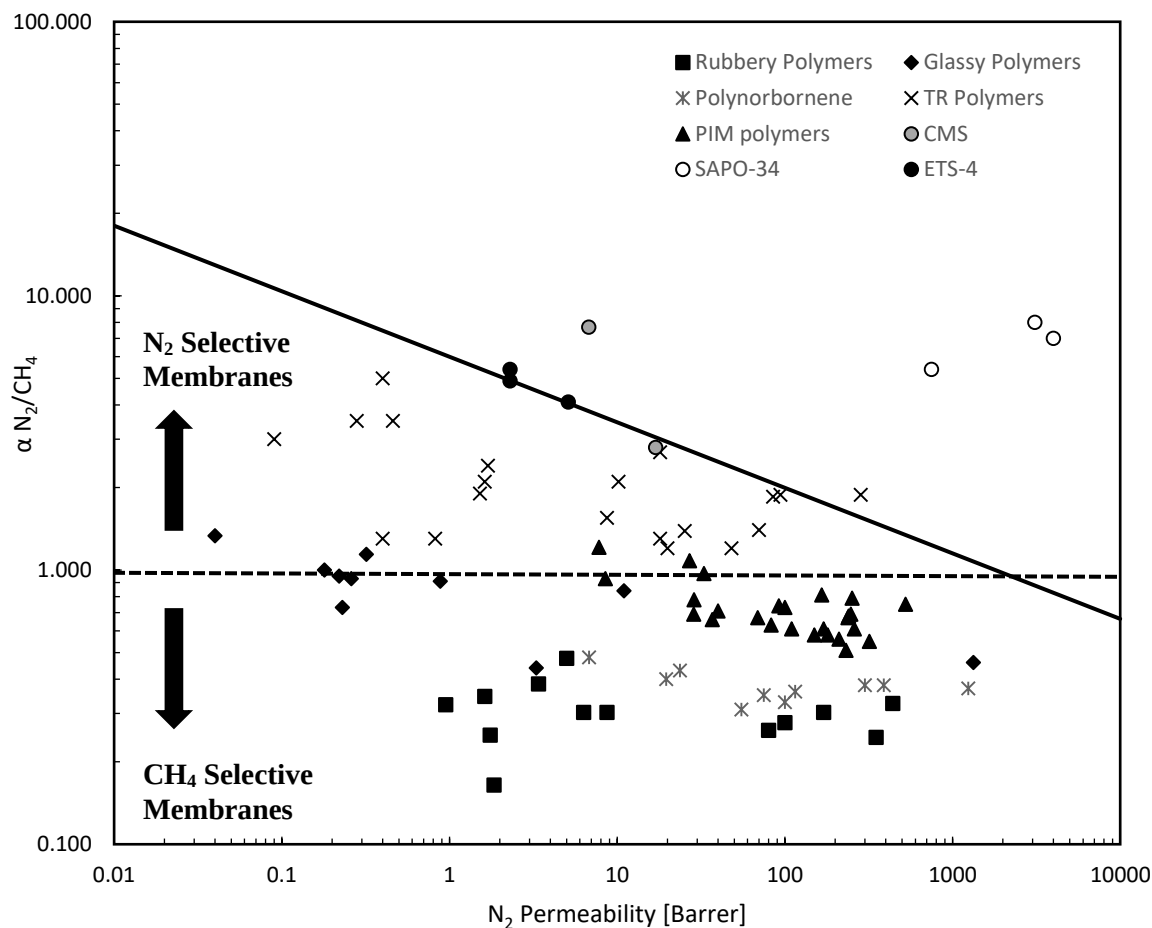


Figure 1.3. Literature data showing the N_2/CH_4 ideal separation factor versus N_2 permeability at temperatures between 293K and 308K for polymeric and inorganic membranes compared to the Robeson 2008 upper bound (black solid line) [99,100,109–118,101,119–128,102,129–134,136,103–108].

1.5. HYPOTHESIS and THESIS OBJECTIVES

Given the established limitations of current adsorption and membrane technologies for the treatment of natural gas and biogas as described in Section 1.4. There is a requisite need for material development in order to foster growth of alternative natural gas treatment technologies. Therefore, the overall objective of this thesis pertains to the development and characterization of a practical adsorbing materials that have the capability of improving the separation of N_2 , and/or CO_2 from CH_4 containing mixtures which are common gas separations in natural gas related industries.

Many smaller sub-objectives were necessary for this project in order achieve the overall project objectives. First, commercially available adsorbents were screened for CH_4 and N_2 adsorption equilibrium capacity. This was done to establish the current limitations for commonly used adsorbents and to compare the experimental results of this study with previous works as determined from a review of the literature. Following this step, clinoptilolite (a type of natural zeolite) emerged as a possible candidate material that was selected to be modified to augment the separation of N_2 , and/or CO_2 from CH_4 . It should be noted that cation exchange was chosen specifically for this adsorbent based upon the dual effect on the channel pore geometry and related surface potential as a result of cation exchange modification. Details pertaining to the physicochemical properties and characterization of the original clinoptilolite sample are elaborated on in Chapters 3 to 6 and are thus omitted from this introduction for sake of brevity.

In consideration of the overall project objective and following a review of the literature, the hypothesis of this thesis was developed and was as follows:

Cation exchange modification of clinoptilolite zeolite will modify both the effective pore size of select zeolites and the surface chemistry due to changes in the extra framework cation charge and coordination within the pores of the zeolite. This change will affect the gas adsorption properties of the zeolite, and may facilitate improved selectivity and separation efficacy of CH_4 from N_2 , and/or CO_2 compared to non-modified zeolites.

Clinoptilolite zeolite was modified using cation exchange and a variety of different cations. The modified materials were characterized using XRD and EDS and the adsorption proprieties of CO_2 , CH_4 , and N_2 gases were measured through a systemic screening process for each new material. The most promising materials were selected for further study, and subsequent characterization.

Specifically, the objectives of this project for each chapter of this thesis were as follows:

CHAPTER 2 – Pure and Binary Adsorption Equilibria of Methane and Nitrogen on Activated Carbons, Desiccants

Evaluation of commercially available adsorbent performance through screening analysis of CH₄ and N₂ adsorption equilibria and the effect of binary CH₄-N₂ gas mixtures on adsorption performance.

- Literature review and experimental screening CH₄ and N₂ adsorption equilibria on commercially available adsorbents.
- Characterization of the best available commercial adsorbent materials in terms of CH₄ and N₂ adsorption equilibria, CH₄/N₂ ideal selectivity, Henry's region experimental K constants, and heats of adsorption for both gases.
- Examination of the effect of gas mixtures on adsorption behaviour through binary CH₄-N₂ gas adsorption experiments using the concentration pulse chromatographic technique. Comparison of the effect of binary mixtures on CH₄/N₂ selectivity and X-Y phase diagrams.

CHAPTER 3 – Cation Exchange Modification of Clinoptilolite – Screening Analysis for Potential Equilibrium and Kinetic Adsorption Separations Involving Methane, Nitrogen, and Carbon Dioxide

Evaluation of different cation exchanged clinoptilolites through a screening analysis of CO₂, CH₄, and N₂ gas adsorption equilibria and kinetics. Establishment of the influence of the cation type on the adsorption properties of CO₂, CH₄, and N₂ gases on clinoptilolite including:

- The effect of pore blocking by various extra framework cations in relation to the adsorption uptake rate and equilibrium adsorption capacity of CH₄.
- The effect of cation charge density and extra framework coordination on the clinoptilolite surface using N₂ and CO₂ as probe gases.
- Systemic examination of the effect of highly exchanged cations on clinoptilolite using XRD for structural and EDS for compositional verification.

CHAPTER 4 – Cation Exchange Modification of Clinoptilolite – Thermodynamic Effects on Adsorption Separations of Carbon Dioxide, Methane, and Nitrogen

Examination of the temperature effects of CO₂, CH₄ and N₂ adsorption on selected cation exchanged clinoptilolites. Promising cation exchanged clinoptilolites were chosen including N₂/CH₄

selective Ca^{2+} clinoptilolite and Fe^{3+} and Cs^{+} exchanged clinoptilolite which were both CH_4/N_2 selective. These results were compared to natural clinoptilolite.

- Measurement of the pure component CO_2 , CH_4 , and N_2 adsorption equilibria over a wide experimental temperature range. Show the relationship between the observed gas adsorption uptake rate and the pore textural properties of these materials using N_2 adsorption at 77K.
- Determination of the adsorption temperature dependence through a comparison of different adsorption models.
- Characterization was made for the selected clinoptilolites in terms of CO_2/CH_4 and CH_4/N_2 ideal selectivity predictions and the practical operating conditions for these separations were considered.

CHAPTER 5 – Methane-Nitrogen Binary Behaviour over Cs^{+} and Fe^{3+} Cation - Exchanged Clinoptilolite

Characterization of promising CH_4/N_2 selective clinoptilolites (Cs^{+} and Fe^{3+} cation exchanged clinoptilolite) and determination of mixed binary CH_4 and N_2 adsorption at different temperatures and comparison with pure clinoptilolite.

- Characterization of Cs^{+} and Fe^{3+} exchanged clinoptilolite with XRD, SEM. EDS, FTIR-ATR, comparison with natural clinoptilolite.
- Demonstration of the effect of mixtures on the adsorption behaviour through binary CH_4 - N_2 gas adsorption experiments using the concentration pulse chromatographic technique. Comparison of the effect of binary mixtures on CH_4/N_2 selectivity and X-Y phase diagrams to illustrate adsorption separation potential.

CHAPTER 6 – Cation Exchange Modification of Clinoptilolite – Effect of Silver Cation Composition on Micropore Properties and Related Adsorption of CH_4 and N_2

The use of Ag^{+} cation exchange for N_2/CH_4 selective adsorption separation was explored, as this material was demonstrated to be a molecular sieve with respect to the adsorption of N_2 over CH_4 .

- The effect of concentration of the initial AgNO_3 cation exchange solution was studied to elucidate the effect of Ag^{+} cation composition on the CH_4 and N_2 adsorption properties.

- The chemical and physical structural properties of the modified materials were measured using XRD, SEM. EDS, FTIR-ATR, and N₂ adsorption at 77K. The results were compared with natural clinoptilolite.

CHAPTER 7 – Vitreous Composite Clinoptilolite Membranes: Synthesis and Preliminary Gas Permeation Properties

In considering the potential of inorganic membranes for the application of N₂/CH₄ gas separation, the idea of inorganic composite membranes formed of clinoptilolite powder and glass sealant as a binder supported by a porous ceramic alumina is explored.

- The effect of exposure to high temperatures required for glass vitrification on the physical and adsorption properties of clinoptilolite was examined.
- The effect of the ratio of clinoptilolite to glass on the membrane morphology and the related membrane permeation properties using single gases (CO₂, CH₄, N₂, He) were studied.

1.6. NOMENCLATURE

Barrer	$1 \text{ Barrer} = \frac{10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}}{\text{s} \cdot \text{cm}^2 \cdot \text{cmHg}}$
BTU	British thermal unit (conversion: 1 BTU/cft = 37.259 kJ/m ³)
CMS	carbon molecular sieve
ETS-4	Engelhard titanosilicalite-4
HEU	heulandite zeolite
LNG	liquefied natural gas
LTA	Linde type A zeolite
MOF	metal organic framework
MTR	Membrane Technology and Research Inc.
NBP	normal boiling point
NGL	natural gas liquids
PIM	polymer of intrinsic microporosity
PSA	pressure swing adsorption
STP	standard temperature and pressure (T = 273K, P = 1atm)
TCF	trillion cubic feet (conversion: 1TCF = 28.32 billion m ³)
TR	thermally reduced
TSA	temperature swing adsorption
VSA	vacuum swing adsorption
VPASA	vacuum pressure swing adsorption
ZIF	zeolitic imidazole framework

1.7. REFERENCES

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CHAPTER 2

Pure and Binary Adsorption Equilibria of Methane and Nitrogen on Activated Carbons, Desiccants, and Zeolites at Different Pressures

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ABSTRACT

In this study, several commercially available adsorbents that show promise for the separation of CH_4 from N_2 including different activated carbons, desiccants, and zeolites were evaluated using single component adsorption isotherms of pure methane and nitrogen that were measured at 303K for pressures of up to 10 atm using the gravimetric method. Following the screening, adsorption of binary gas mixtures composed of methane and nitrogen were studied at 303K and 2 different pressures on the adsorbents with the highest capacity for CH_4 of each of the activated carbons, desiccants, and zeolites. These selected adsorbents included commercial zeolite 13X (Siliporite Nitroxy Pro from CECA Arkema Group), activated carbon (Xtrusorb A754 from Calgon Carbon Corp.), and silica gel (SG-B127 from Grace & Co). Concentration pulse chromatographic method was used to determine the pure component CH_4 and N_2 Henry's Law constants, heats of adsorption, and the experimental binary adsorption isotherms for the three selected adsorbents. The effect of pressure on the binary CH_4 - N_2 system was examined at 1 and 4 atm total pressures. The experimental equilibrium binary adsorption isotherm behaviour was compared to the predictions based on the Extended Langmuir Model and the Ideal Adsorbed Solution Theory using the parameters from the pure component adsorption isotherms. The experimental equilibrium data for each adsorbent were compared through X-Y phase diagrams and selectivity curves. Both binary models show only a modest ability to describe adsorption equilibria of the binary system on activated carbon, silica gel, and 13X. The experimental binary CH_4/N_2 selectivity was shown to be different than the pure component data suggests for all of the adsorbents, indicating some competitive adsorption of CH_4 and N_2 in the binary system. Results of this study showed that for this system, 13X zeolite had a combination of the lowest binary selectivity and the highest heats of adsorption. Silica gel had low heats of adsorption for both N_2 and CH_4 , but higher methane selectivity at high methane concentrations. Activated carbon provided high binary equilibrium selectivity and high capacity among the studied adsorbents, which has good implications for this gas separation application of natural gas treatment.

Key Words:

Binary adsorption, methane, nitrogen, activated carbon, 13X, silica gel, methane nitrogen separation

2.1 INTRODUCTION

Natural gas, composed of mainly CH_4 , is an important energy resource. The increasing role of this resource within the global energy mix is driven by several key factors. Chief among them is the introduction of new technologies that have improved the recoverability and increased the economic viability of natural gas reserves such as shale gas, where development was previously thought to be uncompetitive. The introduction of carbon pricing by various governments as an effort to mitigate greenhouse gas emissions is further reasoning for the development of these natural gas resources. Several studies have routinely indicated that conventional natural gas is a less carbon intensive energy source when compared to coal [1,2]. Importantly, recently reported 100 year life cycle analysis of properly regulated shale gas showed the potential to achieve an 18 to 41% lower greenhouse gas footprint than that of coal without the use of carbon capture and storage technology [3–5]. For this reason, natural gas has been suggested to serve as a possible bridge fuel while renewable technology matures, particularly with respect to electrical production.

Sub-quality natural gas has been defined as having a composition containing more than 2% CO_2 , 4% N_2 , and 4 ppm of H_2S by volume [6]. The further refinement of this gas is necessary to prevent pipeline corrosion and meet regulatory fuel standards. Field analysis of unconventional natural gas sources have been shown to have considerable variability in gas content, particularly containing higher quantities of CO_2 and N_2 [7,8]. The significant reserve volume of unconventional natural gas facilitates the need to explore more efficient gas separation processes.

Traditionally, N_2 is removed from the natural gas using a cryogenic distillation unit integrated within the liquefaction process [6]. Although this method provides high equilibrium selectivity between N_2 and the hydrocarbon; it is at the expense of efficiency which requires extensive process integration to reduce operational costs[9]. Pressure swing adsorption separation processes have lower initial capital investment costs and has the potential to achieve greater process efficiencies than cryogenic distillation. Dynamically, adsorption separation processes can be carried out at more moderate temperatures and are more adaptive than cryogenic distillation to changing process conditions which can be advantageous for variable feed compositions [10]. However, a major challenge with the development of adsorption separation systems for natural gas enrichment is the inherent low selectivity for CH_4/N_2 gas separation. The selection of adsorbents that have a combination of both high capacity and selectivity, which can be easily regenerated, is necessary for the development of more efficient and economical pressure swing adsorption systems [11].

Previous studies that have evaluated $\text{CH}_4\text{-N}_2$ binary adsorption behaviour are primarily focussed on zeolites; including 4A, 5A, 13X, and MFI type zeolites with different $\text{Si}^{+4}:\text{Al}^{+3}$ ratios including H-

ZSM-5 and silicalite [12–17]; or activated carbon [11,18–22]. In these studies, the performance of zeolite materials have been reported to have only modest CH_4/N_2 selectivity ranging from 1.7 to 5 at 50% CH_4 loading [12–16]. Activated carbons have been shown to have a combination of higher selectivity and capacity than zeolites, with reported CH_4/N_2 selectivity ratios ranging from 2.1 to 5.5 under similar conditions [11,18,19]. All of these materials have an internal pore aperture greater than the kinematic diameter of both N_2 and CH_4 gases at 3.6 Å and 3.8 Å, respectively. Therefore, separations of this kind rely on equilibrium based on differences in adsorption affinity of the components towards the adsorbent [23]. Specifically, differences in dipole, quadrupole, and molecular polarization energy, presented in Table 2.1, influence the adsorption potential of the gases, with CH_4 usually being more adsorbed than N_2 . ZSM-5 type zeolites with high $\text{Si}^{+4}/\text{Al}^{+3}$ ratios such as silicalite and high surface area activated carbons show the best binary CH_4/N_2 selectivity [11,13]. These zeolites along with activated carbons have homogeneous surfaces, as they contain less or no counter balancing cations within pore network which can interact with the quadrupole moment of N_2 leading to increased charge induced adsorption. The generally less expensive nature of activated carbon is also favourable for the commercial application of natural gas upgrading as compared to other synthetic zeolites. Newer adsorbent materials such as metal organic framework (MOFs) and zeolitic imidazolate frameworks (ZIFs) have also been evaluated and show comparable selectivity to most zeolites with generally higher adsorption capacity [24,25]. However the cost and lack of stability of these materials is still a challenge [11].

Alternatively, separation of nitrogen from methane containing mixtures using adsorbent molecular sieves with inverse selectivity for N_2 over CH_4 have also been of interest as a possible alternative to methane selective adsorbents. The adsorption characteristics of N_2 and CH_4 of natural and various cation exchanged clinoptilolites (Ca^{+2} , Mg^{+2} , and mixed $\text{Mg}^{+2}/\text{Na}^{+1}$) show some potential for this application [26–28]. The work of Kuznicki et al. showed that titanosilicates such as Ba-ETS-4 can have tunable pore sizes which can limit access of larger gases such as methane to the micropores through size exclusion, thus producing a N_2 selective adsorbent [29,30]. This promising work has resulted in the commercial solution known as Molecular Gate Adsorption Technology® which has the ability to achieve high methane recovery from methane streams contaminated with CO_2 and/or N_2 . However, a key issue for the application of ETS-4 for large scale methane recovery is the relatively low productivity of these materials.

Some PSA systems are packed with a layer of desiccant such as silica gel or activated alumina near the inlet feed zone which acts as a pre-treatment for conditioning of the raw natural gas for the removal of excess water prior to entering the adsorbent packed column[31]. The addition of this layer is needed to protect the adsorbent bed from degradation over time. Mulgundmath et al. considered the performance of activated alumina for this application which showed a binary CH_4/N_2 separation factor of

about 2 at 313K [32]. The knowledge of the adsorptive behaviour of CH₄-N₂ gas systems on silica gel is more applicable for this separation for appropriate modelling and development of PSA based separation systems for natural gas purification since these systems occur at moderate temperatures. Although some research has been performed on the use of silica gel for the enrichment of methane, particularly with respect to CO₂-CH₄ separation[33,34], little work has been done to evaluate the binary behaviour of CH₄-N₂ on silica gel for the purpose of natural gas upgrading.

Table 2.1. Relevant adsorption properties of CH₄ and N₂ gases used[35]

Gas	Kinematic diameter (Å)	Polarizability (x10 ⁻²⁵ cm ³)	Dipole moment (x 10 ¹⁸ esu·cm)	Quadrupole moment (x 10 ⁻²⁶ esu·cm ²)
CH ₄	3.8	26.0	0	0
N ₂	3.6	17.6	0	1.52

2.2 OBJECTIVE

The purpose of this study was to evaluate different types of commercially available adsorbents that show potential for the separation of N₂ from natural gas mixtures under ambient temperatures and moderate pressures. An initial screening study was performed which compared the pure component adsorption performance of CH₄ and N₂ on various commercial activated carbons, desiccants, and zeolites for this application. Single gas N₂ and CH₄ pure component adsorption isotherms were determined using the gravimetric method for different samples of these commercial adsorbents at 303K. Concentration pulse chromatographic method was used in this study to determine the initial loading effects and the isosteric heat of adsorption of pure N₂ and CH₄ as well as the mixture behaviour of CH₄ and N₂ with the promising adsorbents as determined from the initial screening study. Although raw natural gas contains a mixture of various gases such as light hydrocarbons, water vapour, carbon dioxide, nitrogen, and sulfur dioxide, for the purpose of this study, only the binary behaviour of CH₄ and N₂ was considered as representative of preconditioned gas prior to entering a potential pressure swing adsorption (PSA) system. Binary isotherms for CH₄-N₂ gas mixtures are presented at 303K and compared at system total pressures of 1 atm and 4 atm. Separation factor plots and x-y phase diagrams were determined at 303K comparing the influence of pressure on all of the systems studied.

2.3 MATERIALS and EXPERIMENTAL METHODS

2.3.1 MATERIALS

Single and binary gas adsorption experiments were conducted using high purity N_2 , and CH_4 gases. High purity He gas was used as a purge gas for the binary isotherm experiments and for buoyancy correction for the single gas isotherm experiments carried out in the gravimetric system. All gases were supplied by Linde Canada Ltd (Ottawa, Canada) and were of 99.995, 99.99, and 99.99 % purity for He, N_2 , and CH_4 gases, respectively. The adsorbents studied were commercially available forms of silica gel, activated carbon, and 13X zeolite. Details on the studied adsorbents are presented in Table 2.2.

Table 2.2. Manufacturers and commercial names of the studied adsorbents (Activated carbons, desiccants and zeolites, classified, respectively)

Adsorbent Type	Commercial Name	Manufacturer	City
Activated Carbon	Xtrusorb A754	Calgon Carbon Corp.	Pittsburgh PA, USA
Activated Carbon	BPL	Calgon Carbon Corp.	Pittsburgh PA, USA
Activated Carbon	F-400	Calgon Carbon Corp.	Pittsburgh PA, USA
Silica Gel	SG B-127	Grace & Co.	Cambridge, MA, USA
Activated Alumina	AA-300	Alcan	Brockville, ON, Canada
13X zeolite	Nitroxy Pro	CECA Arkema Group	Honfleur, France
4A	4A	Davison Chemicals	Baltimore, MD, USA
5A	5A	Union Carbide	Danbury, CT, USA
CaX	20049-56-12A	Zeochem	Louisville, KY, USA
Silicalite	HISIV 3000	UOP	Des Plaines, IL, USA

2.3.2 SINGLE GAS HENRY'S LAW and ADSORPTION ISOTHERMS

For the determination of the Henry's Law constants for single gases, concentration pulse chromatographic method was used. The pure component Henry's Law experiments were carried out using helium as the carrier gas with flow rates ranging from 15 – 40 sccm and 1 atm total pressure at different temperatures of 303K, 318K, 333K, and 348K. The experiments were conducted using a modified gas chromatograph equipped with a thermal conductivity detector (GOW-MAC Series 400) purchased from

GOW-MAC Instrument Co. (Bethlehem, Pennsylvania, USA). A 0.25cc pulse of the sample gas (CH_4 or N_2) was injected into the packed adsorbent column with He as the carrier gas passing through the column. Although helium has been shown to have some non-negligible adsorptive interaction with solids under specific conditions[36], for the purposes of these experiments helium was assumed to be a non-adsorbing gas.

Single gas CH_4 and N_2 adsorption experiments were performed on the adsorbent samples using a microgravimetric analyser purchased from VTI Corp. (Hialeah, Florida, USA). All samples were regenerated under vacuum conditions of approximately 10^{-8} atm at a temperature of 573K. Following regeneration, the adsorbents were exposed to a sample gas and were evaluated at increasing pressures from 0 to 10 atm at 303K. At each pressure step, equilibrium was indicated by a weight change of less than 0.015 wt% over a period of 15 minutes, at which time the equilibrium adsorption measurement was recorded. The samples were also exposed to helium at similar pressures and temperatures in order to correct for buoyancy.

2.3.3 BINARY GAS ADSORPTION EXPERIMENTS

Concentration pulse chromatographic method was used to determine the binary adsorption isotherms. A detailed description concerning the experimental apparatus and procedure for the binary gas adsorption experiments is described in our previous papers[12,37,38].

The system dead time was determined by an injection of N_2 gas into a 50 sccm helium carrier using a column packed with 40x50 standard U.S. mesh (0.297 – 0.420 mm) glass beads. The glass beads were supplied by Sigma Aldrich (Mississauga, Ontario, Canada) and were sieved to the desired mesh size range. For each experiment, the selected adsorbents were crushed to a particle size with a standard U.S. mesh size of 40x50 (0.297 – 0.420 mm) and packed within a sample column 10.4 cm in length with an inner diameter of 0.46 cm. The column diameter to particle size ratio was maintained above 10 in order to minimize the wall effects on the adsorbent sample analysis. Prior to commencing an experiment, the adsorbent samples were regenerated at 1.0 atm total pressure under helium purge of 20sccm for 12 hours at 523K. The binary gas adsorption experiments were conducted at 303K at 1.0 and 4.0 atm total pressures using different CH_4 - N_2 gas mixture compositions using a total carrier gas flow rate of 50 sccm. Details concerning the experimental and column specification used in this study are outlined in Table 2.3.

For the binary gas adsorption experiments, the packed adsorption column was exposed to CH_4 - N_2 mixed gas carriers with increasing mole fraction of CH_4 in the gas feed from 0 to 1. For this method, it is important to start with the carrier gas that is void of the suspected preferentially adsorbed gas (in this case CH_4) so as to avoid unwanted occupation of the preferentially adsorbed gas on the adsorbent. The gas composition of the carrier feeds into the column were controlled using two mass flow controllers. The

flow of each gas stream was calibrated prior to each experiment to ensure accuracy. Following a change in carrier gas composition, the system was left to approach an equilibrium state which is indicated by a stable baseline response from the TCD detector measurements at the outlet of the column. In this case, CH₄, being the preferentially adsorbed gas, is considered the primary gas component, whereas N₂ is considered the secondary gas component. Therefore, a 0.25 cc pulse of each sample gas was injected into the column at increasing primary carrier gas concentrations ranging from 0 to 1 for mole fraction of CH₄. For a binary system, the sample pulse injection creates an equilibrium disturbance within the carrier gas mixture composition which effects the column response time. In relation to the primary component, when a primary component sample is injected, the mixture composition in the carrier gas increases slightly towards the primary component. This is opposite for a secondary component injection, where the mixture composition decreases slightly for the primary component. When possible, the average column response to 3 of each sample gas injections was used for computational analysis.

Table 2.3. Details of the binary and single gas experimental and column specifications for the concentration pulse chromatography experiments.

Column	Length Inner diameter Packing mesh size Packing particle size range Packing type Void fraction determined with glass beads Sample gas injection volume	10.4 0.46 40 x 50 0.297 - 0.420 glass beads, all the adsorbents listed in Table 2.2 0.39 0.25	cm cm US std. mesh mm dimensionless cc
Henry's Law Constant Experimental	Carrier gas Sample gases Total carrier gas flowrate Total pressure Temperature	He CH ₄ , N ₂ 15 – 50 1.0 303, 318, 333, 348	 sccm atm K
Binary Adsorption Experimental	Carrier gases Sample gases Total carrier gas flowrate Total pressure Temperature	CH ₄ , N ₂ CH ₄ , N ₂ 50 1.0, 4.0 303	 sccm atm K
Regeneration	Purge Gas Used Regeneration Temperature Regeneration Pressure Regeneration Time	He 523 1 12	 K atm h

2.3.4 PURE COMPONENT and MIXTURE ADSORPTION MODELS

Several pure component adsorption isotherm models have been proposed and employed in the literature to describe pure component adsorption equilibria [23,39–42]. Two parameter Freundlich and Langmuir isotherms are among the simplest models.

The Freundlich isotherm model assumes that the amount adsorbed is limited by the porous media morphology and the ability of the adsorbing species to interact with the surface [42,43].

$$q = k P^{1/n} \quad (1)$$

where q is the amount adsorbed; P is the pressure; while k and n are constant parameters [40]. However, the Freundlich isotherm does not adequately describe gas adsorption behaviour at higher pressures or low temperatures[40].

The Langmuir model relies on the assumption that adsorption is limited by a fixed number of adsorptive sites and there is no interaction between adsorbed molecules [23,42].

$$\theta = \frac{q}{q_m} = \frac{BP}{1+BP} \quad (2)$$

where θ is the fractional coverage; q is the amount adsorbed; q_m is the saturation adsorption capacity; B is the affinity constant; and P is the pressure [13]. The use of two parameters for Freundlich and Langmuir models leads to less flexibility over systems with a large range of pressures and temperatures.

The Sips model is essentially a combination of the parameters in both the Langmuir and Freundlich isotherm models as follows:

$$\theta = \frac{q}{q_m} = \frac{BP^n}{1+(BP)^n} \quad (3)$$

This three parameter model equation has been shown to describe single gas CH_4 and N_2 systems accurately on activated carbon and LiX zeolite and thus satisfies both the low and high pressure range of the isotherm [44]. The Sips isotherm along with the Toth isotherm models are thermodynamically consistent, thus the adsorption equilibria data can be interpolated over a range of different temperatures [13,38]. For this work, the Sips model has been employed on the isotherm data at 303K in order to model the single gas adsorption behavior.

When two components exist within an adsorbing system, there is added complexity as there exists the possibility of both components competing for the adsorption sites. Several models have been developed to predict multiple gas adsorption behaviour from the single gas pure component isotherms. The Extended Langmuir Model (ELM) prediction of binary gas adsorption behaviour is the simplest and is shown below [13,45]

$$\theta_1 = \frac{q_1}{q_{m1}} = \frac{B_1 P_1}{1 + B_1 P_1 + B_2 P_2} \quad (4)$$

where the subscripts 1 and 2 represent binary gas components in the system, and q_m is the maximum amount adsorbed of the most adsorbed component (component 1 in this case), determined from the pure component adsorption data. The Ideal Adsorbed Solution Theory (IAST) may also be used to predict multicomponent mixture adsorption behaviour and is thermodynamically consistent [46].

Previous studies have examined the validity of the theoretical model predictions of the ELM, IAST, and the Vacancy Solution Theory (VST) models among others for binary adsorption gas systems and compared these models to experimentally obtained data [11,13,17,38]. Most have shown very similar predictions with only a modest ability of the model to represent the binary adsorption data for highly selective systems, and fairly good applicability for low to moderate selective systems. However these binary models can only show, at best, an indication of adsorption behaviour and are not good representation of what is physically occurring within a binary system. For this reason, only the ELM and IAST models were chosen to predict the binary isotherms in order to give an indication of the deviation of the experimental binary data from the model predictions.

2.3.5. CONCENTRATION PULSE METHOD

The concentration pulse method (CPM) has been used previously to characterize the adsorption properties of single and binary gas systems [12,13,17,37,38,47–58]. The CPM has been shown to be consistent with static binary adsorption methods [17,49,59]. With this method, the initial loading of an adsorbent sample can be measured that describes the Henry's Law constant (K_p) which is the initial slope of the adsorption isotherm. For the pure component K_p experiments, following a very small sample gas injection into a He carrier gas, the response of a packed adsorbent column to the disturbance is monitored. The mean retention time (μ) of the sample is calculated from the response peak concentration (c) as a function of time (t) measured at the outlet of the column. The dimensionless Henry's Law constant (K) is derived from the packed bed parameters including the bed porosity (ϵ), bed length (L), fluid velocity (v) as shown in Equation 5:

$$\mu = \frac{\int_0^\infty c(t - \mu_D) dt}{\int_0^\infty c dt} = \frac{L}{v} \left[1 + \frac{(1 - \epsilon)K}{\epsilon} \right] \quad (5)$$

The porosity of the column, ϵ , was measured by using the same size glass beads as the adsorbent particles in the column and filling the voids in the column with deionized distilled water and measuring the exact volume or the weight of the water with its density.

The dimensional Henry's Law constant is determined from a conversion factor dependant on temperature (T) and adsorbent pellet density (ρ_p), where R is the universal gas constant as defined in Equation 6:

$$K_p = \frac{K}{RT\rho_p} \quad (6)$$

When pure component K_p values are determined at different temperatures, the limiting heat of adsorption (ΔH) can be calculated from the slope of the Van't Hoff plot ($\ln K_p$ vs. $1/T$) as defined from Equation 7:

$$K_p = K_o e^{\left[\frac{-\Delta H}{RT}\right]} \quad (7)$$

The ΔH value for a gas with an adsorbent is important to consider when designing an adsorption separation process. A low heat of adsorption is preferred in order to minimize localized heating across the bed during the adsorption step. Since adsorption is an exothermic process, increases in the column temperature during the adsorption step will decrease the adsorption capacity of the adsorbed species, resulting in a less efficient process.

For a binary mixture, the column response to a small sample injection is measured over a range of compositions for a binary mixture carrier gas. For this method, the K_p dimensional equilibrium constant is related to the slopes of both of the isotherms of the components within the binary gas mixture as follows:

$$K_p = (1 - y_1) \frac{dq_1}{dP_1} + y_1 \frac{dq_2}{dP_2} \quad (8)$$

where dq_1/dP_1 and dq_2/dP_2 are the slopes of the individual component binary isotherms, and y_1 refers to the mole fraction of the preferentially adsorbed component in the gas phase. For the $\text{CH}_4\text{-N}_2$ binary system, CH_4 is the preferentially adsorbed species, and therefore it is component 1.

This method relies on the fact that for binary systems, the experimental K_p data is a representation of the contribution of the equilibrium adsorption capacity of both gases at different partial pressures on the adsorbent. The development and applicability of several mathematical functional forms to different binary systems has been explored in the literature using this method [12,37,52,54,60]. The modified polynomial approach originally developed by Van der Vlist and Van der Meijden [54] (MVV-CPM) is among the simplest methods, and proves to represent the less selective systems very well [13]. However, for binary systems with a large difference in the adsorption capacities of the two components the MVV-CPM does not adequately describe the binary behaviour. For this study, the MVV-CPM was used for the $\text{CH}_4\text{-N}_2$ binary adsorption system data, since it showed a good representation of the experimental data obtained.

2.3.6. COMPUTATIONAL METHODS

In this study, the 4 parameter MVV-CPM, which uses a polynomial function, was used to determine the binary isotherms from the experimental K_p data [54]:

$$K_p = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3 \quad (9)$$

The binary isotherm slope functions are derived from the derivative of the 4 parameter primary function as follows:

$$dq_1/dP_1 = B_0 + B_1 y_1 + B_2 y_1^2 \quad (10a)$$

$$dq_2/dP_2 = C_0 + C_1 y_1 + C_2 y_1^2 \quad (10b)$$

Substituting Equations 10a and 10b into Equation 8 yields the K_p function used to model the experimental K_p data.

$$K_p(model) = (1 - y_1)[B_0 + B_1 y_1 + B_2 y_1^2] + y_1[C_0 + C_1 y_1 + C_2 y_1^2] \quad (11)$$

To ensure a proper model fit to the experimental data, a minimization of the sum of the squared residuals (SSR) was used as the objective function to be minimized as follows:

$$SSR = \sum_{y=y_{min}}^{y=y_{max}} \{K_p(experimental) - K_p(model)\}^2 \quad (12)$$

The B_i and C_i coefficients from Equation 11 were optimized to the global minimum function, SSR. A broad range of initial values were considered in order to ensure that the global minimum was achieved for each binary isotherm. After the determination of the B_i and C_i coefficients, the individual binary adsorption isotherms were determined through the integration of the binary isotherm slope functions presented in Equations 10a and 10b as follows:

$$q_1 = \left[B_0 y_1 + \left(\frac{B_1}{2} \right) y_1^2 + \left(\frac{B_2}{3} \right) y_1^3 \right] P_T \quad (13a)$$

$$q_2 = \left[C_0 (1 - y_1) + \left(\frac{C_1}{2} \right) (1 - y_1)^2 + \left(\frac{C_2}{3} \right) (1 - y_1)^3 \right] P_T \quad (13b)$$

The CPM function must properly represent the K_p experimental data in order to accurately reflect the actual binary isotherms, as such, several constraints have been proposed to the K_p model function and systems of equations to properly reflect the binary system [37,52,61]. Since at low system pressures, the fractional loading of the adsorbed phase is low, the individual binary isotherm slopes should remain positive over the entire range of the concentration profile, therefore there should be no maximum observed in the isotherms [61]. The K_p model function must pass through the endpoints of the

experimental K_p values which occurs at $y_1=0$ and $y_1=1$ [52]. Harlick and Tezel proposed that the endpoints of the binary isotherms determined from Equations 13a and 13b should be equal to the values of the corresponding pure component isotherms at the same total pressure [52]. Little work has been done on binary systems using CPM at higher system pressures. Therefore, the applicability of the proposed constraints is in question for highly selective systems, and systems at higher pressures as these systems may deviate more from ideality.

2.3.7. SEPARATION FACTORS

The binary adsorption separation relies on differences in the component equilibrium adsorption capacities. The pure component data serves as an indicator of separation potential of a particular adsorbent system. The ideal equilibrium selectivity is defined as the ratio of the pure component adsorption equilibrium capacities.

$$\alpha_{ideal,1/2} = \frac{n^a_1}{n^a_2} \quad (14)$$

Where n^a_1 and n^a_2 are the pure component equilibrium adsorption capacities of component 1 and 2, respectively.

After determining the binary adsorption isotherms, the equilibrium separation factor is defined as a more realistic parameter to be used for the separation of components 1 and 2, in the presence of each other:

$$\alpha_{1/2} = \frac{x_1/y_1}{x_2/y_2} \quad (15)$$

where x_1 , x_2 , y_1 , and y_2 are the mole fractions of components A and B in the adsorbed and the gas phases at equilibrium, respectively.

2.4 RESULTS and DISCUSSION

2.4.1 PURE GAS ISOTHERMS

Pure adsorption isotherms for CH_4 and N_2 gases with different types of activated carbon, desiccants, and zeolites at 303K were determined using gravimetric method and are shown in Figure 2.1. The Sips isotherm model is shown to appropriately represent the data over the pressure range studied. The regression parameters for the Sips isotherm models are presented in Table 2.4.

For all of the studied adsorbents, CH₄ was adsorbed more than N₂ because of the stronger polarizability of CH₄ compared to N₂. N₂ only has a weak quadrupole moment and lower polarizability; therefore it was not adsorbed as much as CH₄[62]. As expected, activated carbons are shown to have the highest adsorption capacity for CH₄, followed by the zeolites, and the desiccants. However a slightly different trend is observed with respect to N₂ adsorption, where for the studied pressure range, a similar amount of N₂ is adsorbed on 13X, CaX, 5A, and 4A as the three activated carbons, resulting in lower ideal CH₄/N₂ selectivity for zeolites compared to activated carbons. The difference in adsorbed capacities clearly show that both electrostatic forces and dispersion forces affect the adsorption dynamics of the studied adsorbents. The interaction of N₂ and CH₄ with silica gel, activated alumina, activated carbons, and silicalite is limited to the dispersion forces, where the adsorption capacity is limited to the available adsorption sites, since these adsorbents have homogeneous surfaces with no cation present [11]. Since the adsorbents have relatively homogeneous surfaces, the nonpolar CH₄ molecules are attracted more to adsorbent compared to N₂. As can be seen in Figure 2.1, the capacity of both CH₄ and N₂ on activated carbon is much higher compared to silica gel, activated alumina, and silicalite, with the adsorption capacity of CH₄ being much higher for activated carbon compared to that of N₂. Since the difference in adsorption capacities for CH₄ and N₂ gases are similar for these aforementioned adsorbents, it can be concluded that the available surface area is the principle driver for the observed differences in capacity, as activated carbons generally have higher surface areas, followed by zeolites, and desiccants.

Zeolites 13X, CaX, 5A, and 4A have low SiO₂/Al₂O₃ ratios with Al³⁺ and Si⁴⁺ atoms imbedded within the pore structure along with counter balancing cations. The presence of cations imbedded within the adsorption sites of these zeolites results in electrostatic interaction between the polarizability of CH₄ and N₂, and the weak quadrupole moment of N₂ [14]. In particular, the interaction of Na⁺ cations with the N₂ quadrupole moment results in higher capacity of N₂ for 13X when compared directly to silicalite which have no counterbalancing cation charge on the adsorbent surface. This is evident by the higher difference in adsorption capacities of CH₄ and N₂ for silicalite compared to 13X and the other zeolites. This trend has been shown on other zeolites such as in the work of Harlick and Tezel with ZSM-5 zeolite with different SiO₂/Al₂O₃ ratios and counterbalancing Na⁺ cation [12,17,52] .

The data from the experimental pure adsorption isotherms shows that for the studied pressure range the adsorbents with the highest capacity for CH₄ in each of the different groups of adsorbents were Xtrusorb A754 among the activated carbons, Grace B-127 silica gel among the desiccants, and Nitroxy Pro 13 X zeolite among the zeolites. These three adsorbents were chosen to be studied further and used to determine the ideal CH₄/N₂ equilibrium selectivity using Equation 14 at 303K and at different total pressures. The results are presented in Figure 2.2. Comparing the three adsorbents, the highest equilibrium selectivity, in general, occurs with activated carbon, followed by silica gel, and 13X zeolite.

The ideal equilibrium selectivity approaches 4 and 4.1 for activated carbon and silica gel, respectively, at low pressures. Below a pressure of 3 atm, the selectivity decreases with increasing pressure for both silica gel and activated carbon, whereas it increases for 13X. At higher pressures, the ideal selectivity plateaus at approximately 2.1 for both silica gel and activated carbon, and 1.2 for 13X which is consistent with the fact that the adsorbents approach saturation capacity at higher pressures.

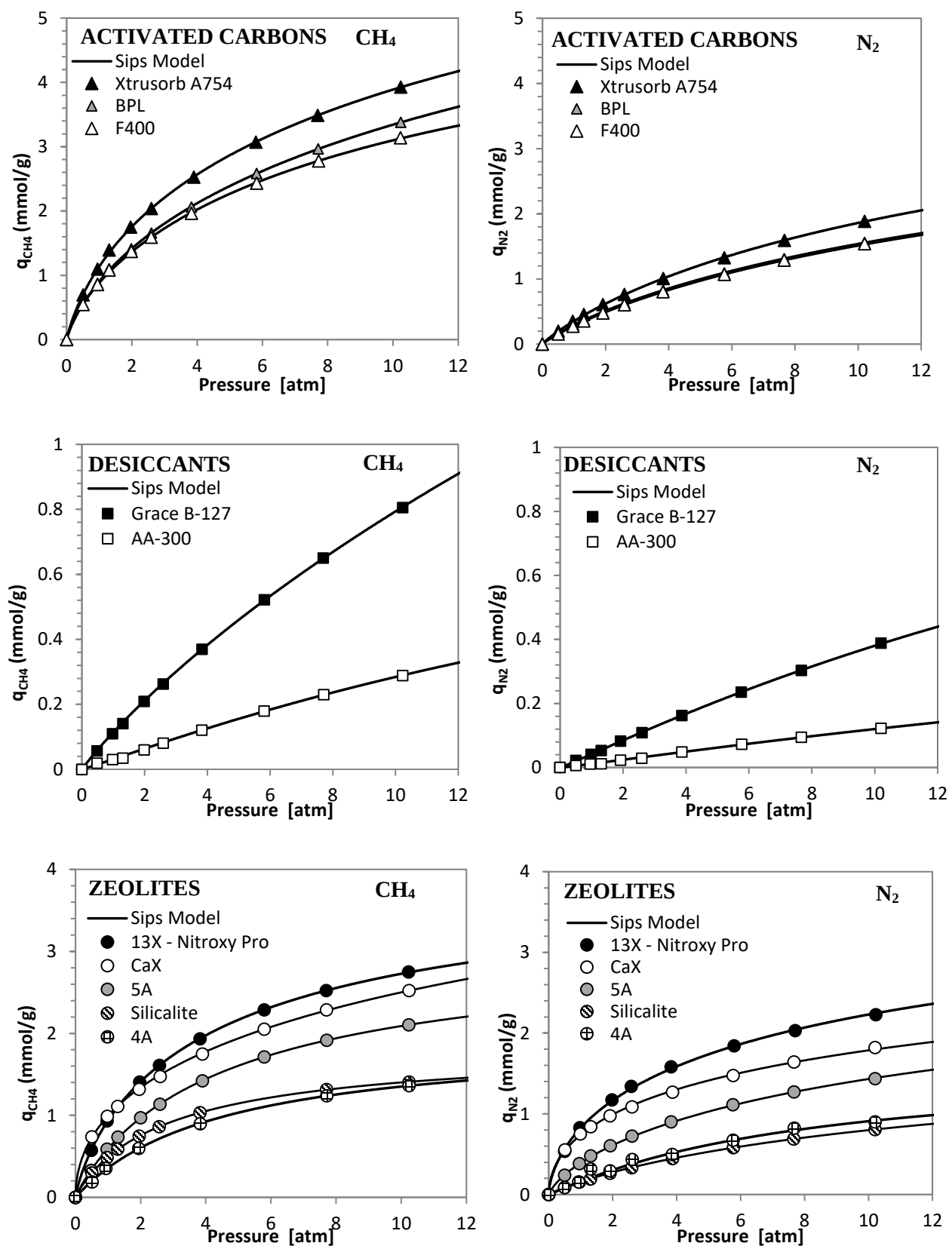


Figure 2.1. Pure component Sips adsorption isotherms for CH_4 (left) and N_2 (right) on different activated carbons, desiccants, and zeolites at 303K.

Table 2.4. Pure component Sips isotherm model parameters for CH₄ and N₂ on different activated carbons, desiccants, and zeolites at 303K.

Adsorbent Types	CH ₄			N ₂		
	q _m (mmol·g ⁻¹)	B (atm ⁻¹)	n	q _m (mmol·g ⁻¹)	B (atm ⁻¹)	n
<u>Activated Carbons</u>						
Xtrusorb A754	7.837	0.097	0.765	4.967	0.056	0.890
BPL	7.329	0.079	0.776	4.474	0.047	0.871
F400	6.601	0.085	0.759	4.312	0.050	0.891
<u>Desiccants</u>						
Silica Gel (SG-B127)	2.839	0.038	0.980	1.183	0.051	1.129
Activated Alumina – AA300	1.141	0.036	1.073	0.679	0.025	1.094
<u>Zeolites</u>						
13X (Nitroxy Pro)	4.110	0.228	0.824	3.675	0.176	0.714
CaX	5.723	0.059	0.551	4.506	0.045	0.524
5A	3.130	0.211	0.931	2.937	0.092	0.784
Silicalite	1.867	0.329	0.924	1.850	0.074	0.911
4A	1.959	0.223	0.996	1.609	0.127	1.065

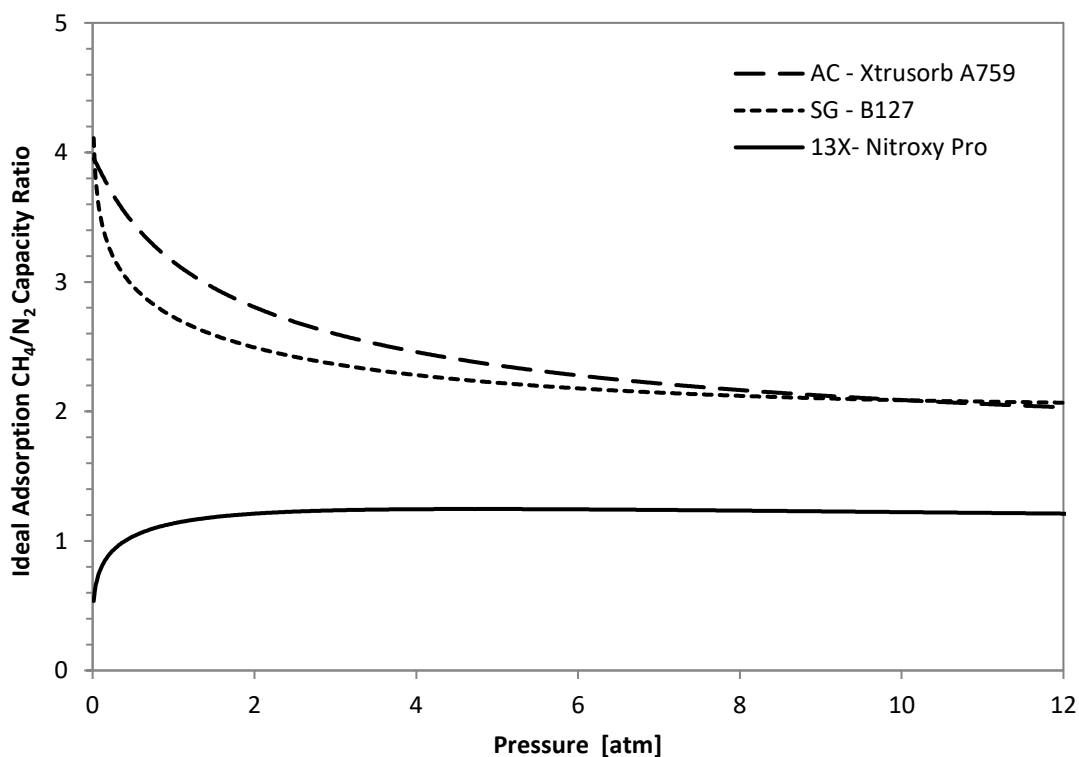


Figure 2.2. Ideal pure component adsorption CH₄/N₂ capacity ratios for activated carbon (Xtrusorb A754), silica gel (SG – B127), and 13X zeolite (Nitroxy Pro) at 303K.

2.4.2 INITIAL LOADING and HEAT of ADSORPTION

To better understand the adsorbing system at temperatures consistent within the operating parameters of a fixed bed adsorption process for CH₄ recovery, the knowledge of the heat of adsorption values are necessary. Ideally, a smaller ΔH is preferred to minimize localized temperature variations during the adsorption and desorption steps, which could lower the working capacity of the adsorbent. Although the literature does provide substantial information for the heat of adsorption for CH₄ and N₂ on the studied adsorbent types, the parameters in these studies are quite variable and often times the authors omit the specific adsorbent brand, which is a crucial information for adsorbent selection to maximize industrial process efficiency.

The experimentally determined Henry's Law constants at different temperatures for CH₄ and N₂ gases are plotted on the Van't Hoff plot shown in Figure 2.3 and the corresponding data are presented in Table 2.5. The corresponding heat of adsorption values determined from the slopes of the Van't Hoff plots are presented in Table 2.6 and may be compared with the literature data given for similar adsorbents in Table 2.7. The experimental heats of adsorption values obtained in this study tend to agree with the overall trends shown in the literature where the magnitude of the heats of adsorption is in the following order for both N₂ and CH₄: 13X > activated carbon >> silica gel. Compared to the literature data, the heat of adsorption for N₂ and CH₄ on silica gel and activated carbon is lower, whereas 13X is about the same. This indicates that activated carbon, Xtrusorb A745, and the silica gel, SG-B127, would be better adsorbents for this process with low heat of adsorption values.

Furthermore, the magnitude of the difference between the experimental K_p data is as expected for these adsorbents as they are following similar trends in the initial slopes that can be derived from the pure component isotherms given in Figure 2.1.

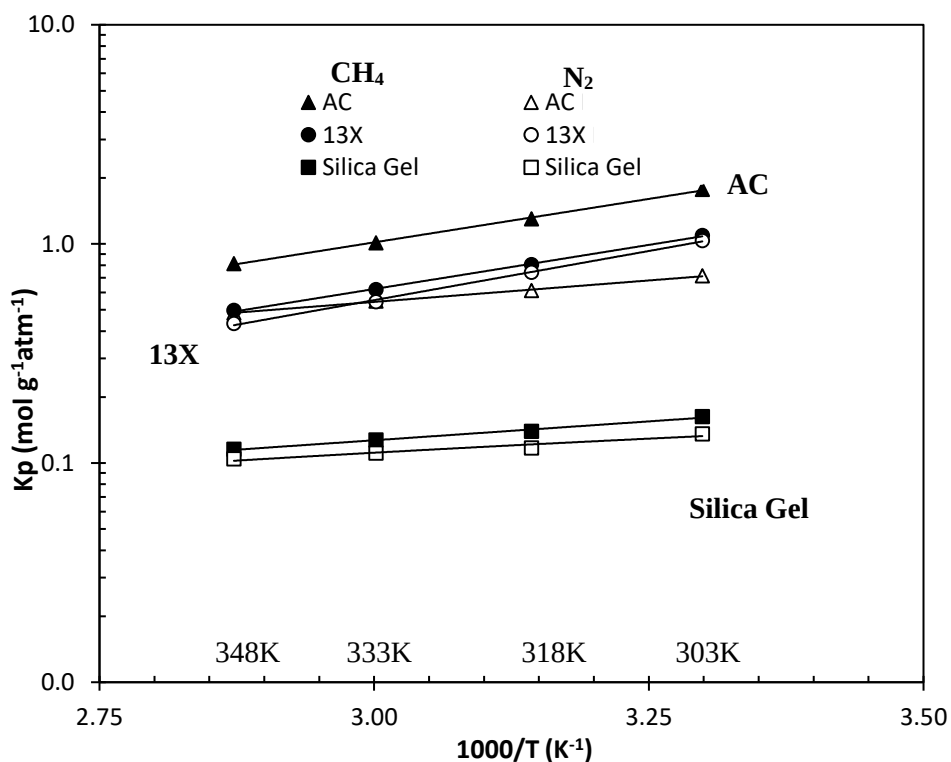


Figure 2.3. Van't Hoff plots of the Henry's Law constants of activated carbon (Xtrusorb A754), 13X zeolite (Nitroxy Pro), and silica gel (SG-B127) for pure component CH₄ (closed points) and N₂ (open points) injections into helium carrier gas, as a function of inverse temperature.

Table 2.5. Henry's Law constants at different temperatures as determined with CPM for CH₄ and N₂ gases for activated carbon, 13X zeolite, and silica gel. ^a

T(K)	Activated Carbon <i>Xtrusorb A754</i>		Silica Gel <i>SG-B127</i>		13X Zeolite <i>Nitroxy Pro</i>	
	K _p (mmol·g ⁻¹ ·atm ⁻¹)		K _p (mmol·g ⁻¹ ·atm ⁻¹)		K _p (mmol·g ⁻¹ ·atm ⁻¹)	
	CH ₄	N ₂	CH ₄	N ₂	CH ₄	N ₂
303	1.774	0.715	0.163	0.136	1.094	1.036
318	1.301	0.612	0.140	0.117	0.804	0.741
333	1.011	0.548	0.127	0.111	0.618	0.544
348	0.814	0.485	0.116	0.105	0.497	0.433

^a Standard uncertainties *u* are *u*(T) = 1K, and the combined relative standard uncertainty *u_r* is *u_r*(K_p) = 0.059.

Table 2.6. Experimental heat of adsorption values for CH₄ and N₂ with activated carbon, silica gel, and 13X zeolite determined in this study. ^a

Adsorbent	Temperature range (K)	CH ₄ Experimental -ΔH (kJ·mol ⁻¹)	N ₂ Experimental -ΔH (kJ·mol ⁻¹)
activated carbon <i>Xtrusorb A754</i>	303 -348	15.22 +/- 0.67	7.52 +/- 0.16
silica gel <i>SG-B127</i>	303 -348	6.62 +/- 0.55	4.96 +/- 1.06
13X zeolite <i>Nitroxy Pro</i>	303 -348	15.55 +/- 0.60	17.20 +/- 0.75

^a Standard uncertainties u are u(T) = 1K

Table 2.7. Heat of adsorption values for CH₄ and N₂ for various commercial activated carbons, silica gels, and 13X zeolites found in the literature.

Adsorbent Description	CH ₄ -ΔH (kJ·mol ⁻¹)	Ref.	N ₂ -ΔH (kJ·mol ⁻¹)	Ref.
<u>activated carbon types</u>				
<i>Maxsorb</i>	15.3, 16.3	[63,64]	-	-
<i>BPL</i>	16.1	[64]	-	-
<i>A10</i>	16.2	[64]	-	-
<i>Mast Carbon</i>	19.5	[65]	12.2	[65]
<i>Norit -R1 Extra</i>	20.6	[64]	-	-
<i>Sutcliffe Speakman</i>	21.3	[66]	17.2	[66]
<i>Columbia</i>	22.3	[66]	17.4	[66]
<u>silica gel types</u>				
<i>Davison Chemical</i>	11.7	[67]	-	-
<i>Davison Chemical</i>	12.5	[68]	-	-
<i>Davison Chemical– Grade 15</i>	13.7	[69]	-	-
<u>13X zeolite types</u>				
<i>CECA</i>	15.3	[70]	12.8	[70]
<i>Linde Union Carbide</i>	17.6	[71]	18.4	[71]
<i>Not specified</i>	19.2	[72]	19.7	[72]

2.4.3 BINARY ADSORPTION ISOTHERMS for the CH₄-N₂ SYSTEM

The pure component adsorption isotherms given in Figure 2.1 were also fitted to the Langmuir isotherm model for the selected activated carbon, silica gel, and 13X zeolite, so that Extended Langmuir (EL) Model and IAST (Ideal Adsorbed Solution Theory) Model predictions can be carried out for the

binary CH₄-N₂ system for these adsorbents and can be compared to the experimental ones. Table 2.8 shows the model parameters for these Langmuir adsorption isotherm fits for pure CH₄ and N₂ gases.

For the determination of the experimental binary adsorption isotherms, following adsorbent regeneration at 523K under He purge, the experimental K_p values were determined by increasing the CH₄ concentration within the binary CH₄-N₂ carrier gas from $y_{CH_4} = 0$ to 1 at 1 and 4 atm total system pressures. A series of 0.25 cc injections of each gas were performed after the column reached equilibrium with different CH₄-N₂ mixtures in the carrier gas, as indicated by a steady baseline on the GC measuring output from the column. The resultant experimental K_p values were calculated using Equations 5 and 6. The experimental binary K_p data for CH₄ and N₂ obtained for different carrier gas compositions on the selected activated carbon (Xtrusorb A754), silica gel (SG-B127), and 13X zeolite (Nitroxy Pro) at 303K and at 1 and 4 atm total pressure are presented in Figure 2.4 with error bars indicating the range of K_p values measured. The MVV-CPM non-linear regression was performed on the experimental K_p data using Equations 11 and 12. The results of these regressions are presented in Figure 2.4 and the corresponding B_i and C_i parameters are presented in Table 2.9. Due to the fact that the binary CH₄-N₂ adsorption system is not very selective and non-ideal, the MVV-CPM provided a good representation of the experimental K_p as can be seen from Figure 2.4, while maintaining simplicity within the functional form. The K_p values at lower total pressure (1 atm) are higher than the K_p values for higher total pressure (4 atm). This is expected, since the slope of the adsorption isotherms decreases as pressure increases, as can be seen in Figure 2.1 for the pure component isotherms.

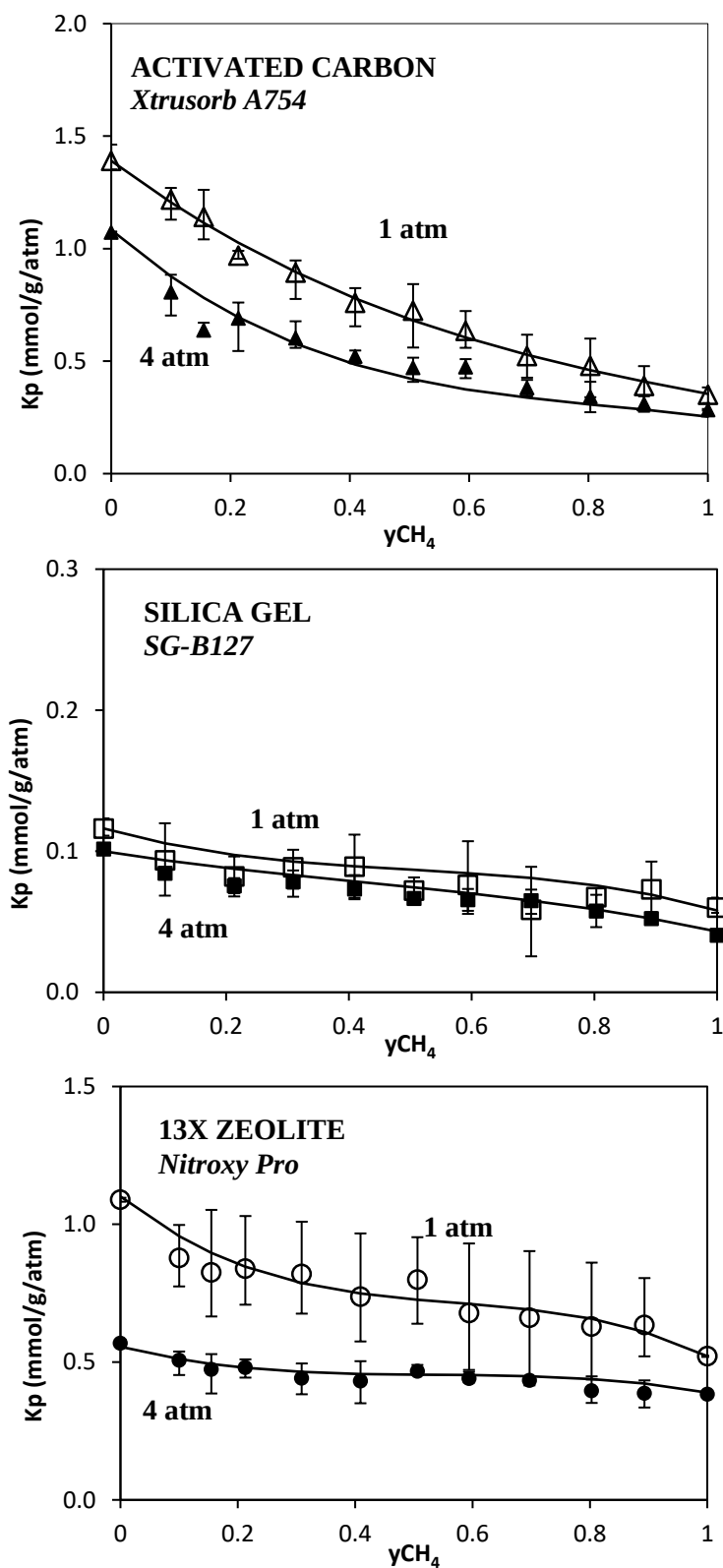


Figure 2.4. Regressions for the CH_4/N_2 binary K_p experimental data by MVV-CPM for activated carbon (top), silica gel (middle), and 13X zeolite (bottom) at different carrier gas compositions and 1 and 4 atm total pressure at 303K. The hollow points represent the 1 atm total pressure data, and the filled data points represent the 4 atm total pressure data.

Table 2.8. Pure component Langmuir Model parameters for adsorption of CH₄ and N₂ on chosen activated carbon, silica gel, and 13X zeolite at 303K.

Model	Parameter	Activated Carbon <i>Xtrusorb A754</i>		Silica Gel <i>SG-B127</i>		13X Zeolite <i>Nitroxy Pro</i>	
		CH ₄	N ₂	CH ₄	N ₂	CH ₄	N ₂
Langmuir	q _m (mmol·g ⁻¹)	5.352	3.715	2.654	2.077	3.435	2.652
Model	B (atm ⁻¹)	0.246	0.099	0.051	0.022	0.358	0.427

Table 2.9. MVV-CPM parameters for the binary CH₄/N₂ adsorption system on activated carbon, silica gel, and 13X zeolite at 303K and 1 and 4 atm total pressure.

MVV-CPM parameter	units	activated carbon <i>Xtrusorb A754</i>		silica gel <i>SG-B127</i>		13X zeolite <i>Nitroxy Pro</i>	
		1 atm	4 atm	1 atm	4 atm	1 atm	4 atm
B ₁	mmol·g ⁻¹ ·atm ⁻¹	1.390	1.082	0.116	0.100	1.100	0.556
B ₂	mmol·g ⁻¹ ·atm ⁻¹	-0.816	-1.499	-0.049	-0.015	-2.004	-0.336
B ₃	mmol·g ⁻¹ ·atm ⁻¹	0.203	0.995	0.141	0.060	2.350	0.359
C ₁	mmol·g ⁻¹ ·atm ⁻¹	0.234	0.281	0.040	0.045	1.402	0.358
C ₂	mmol·g ⁻¹ ·atm ⁻¹	0.304	-0.047	0.009	-0.011	-1.803	0.261
C ₃	mmol·g ⁻¹ ·atm ⁻¹	-0.184	0.020	-0.008	0.009	0.920	0.230

The experimental binary isotherms for components CH₄ and N₂ were calculated from the B_i and C_i parameters as determined using the MVV-CPM and Equations 13a and 13b. They are presented for the selected activated carbon, silica gel, and 13X zeolite at 303K and at 1 and 4 atm total pressures in Figure 2.5 and are compared to the ELM and IAST model predictions in the same figure. Comparison of the binary CH₄-N₂ isotherms relative to the ELM and IAST predicted binary isotherms for these adsorbents shows the effect of the binary competitive adsorption of CH₄ relative to N₂ on different adsorbent surfaces.

As expected, as the composition of CH₄ in the binary mixture increases, the adsorption capacity of CH₄, q_{CH_4} , increases, whereas q_{N_2} decreases. Adsorption capacity increases with increasing system pressures, which is in agreement with the fact that total surface occupancy increases with pressure. The

total amount adsorbed, q_{total} , increases with increasing y_{CH_4} for both activated carbon and silica gel at both of the studied system total pressures. However this is not the case for 13X zeolite at 1 atm total pressure where q_{total} decreases with increasing composition of CH_4 in the gas until $y_{CH_4} = 0.6$, and increases afterwards. This is due to the fact that both CH_4 and N_2 are affected negatively in the binary system compared to the ideal ELM and IAST binary behaviour, as can be seen from Figure 2.5. At 4 atm total system pressure for 13X zeolite, q_{total} does not change much with increasing CH_4 composition in the gas phase. This can be attributed to the relatively non selective nature of this binary system at higher pressure, and therefore less competitive adsorption.

The non-polar surface of the activated carbon is attracted to the non-polar N_2 and CH_4 molecules at both pressures and this effect is larger at higher pressures. The models represent the N_2 component adsorption isotherm quite well at low pressures for activated carbon, whereas CH_4 is slightly more favourably adsorbed. This result is consistent with previous studies which showed that CH_4 is adsorbed more in the binary systems, compared to the pure component model predictions suggest whereas N_2 behaviour was similar to the binary isotherm model predictions for binary CH_4 - N_2 systems at 1atm total pressure [11]. At higher system pressure, both N_2 and CH_4 are more adsorbed by activated carbon than predicted by ELM and IAST. This can be attributed to the fact that activated carbon has a broad availability of adsorption sites and therefore the two gases are not heavily competing for the sites and forming a non-ideal adsorption system at higher pressures.

For silica gel, the N_2 binary isotherms are in somewhat agreement with the model predictions for low and high pressures. CH_4 is less adsorbed than the model prediction for both of the studied pressures for silica gel.

The requirements of a good adsorbent for CH_4 - N_2 bulk separations are a combination of high capacity, high selectivity, and good durability. Figure 2.6 presents the binary CH_4 - N_2 adsorption phase diagrams for the studied adsorbents at 303K and at 1 and 4 atm total pressures determined from the experimental binary adsorption isotherms. Lower pressure data were shown to give better separation since the phase diagram curves at lower pressures are further away from the 45° line. This is expected looking at the shape of the CH_4 and N_2 isotherms as well as the ideal pure component adsorption CH_4/N_2 capacity ratios. As can be seen in Figure 2.6, at lower y_{CH_4} ($y_{CH_4} < 0.7$), activated carbon is shown to give the best separation for this binary gas pair, whereas at high y_{CH_4} ($y_{CH_4} > 0.7$) both activated carbon and silica gel show similar separation behaviour for both of the studied pressures. 13X zeolite shows the lowest performance of the studied adsorbents.

Using Equation 15, the experimental equilibrium CH_4/N_2 selectivity values were determined from the experimental binary isotherms and are presented in Figure 2.7. The CH_4/N_2 selectivity is shown to be

the highest at low y_{CH_4} for activated carbon, followed by silica gel, and 13X zeolite, whereas silica gel shows better separation performance than activated carbon at higher y_{CH_4} . For all three adsorbents, the binary CH_4/N_2 selectivity is observed to decrease with increasing system pressure, which is consistent with previous reports showing that the limited capacity of the adsorbent at increased loading leads to a decrease in selectivity. At 1 atm total pressure, the binary CH_4/N_2 selectivity at $y_{CH_4} = 0.5$ is 3.4 for activated carbon which is consistent with the 2.1 – 5.5 range reported for CH_4/N_2 selectivity outlined in Wu et al. for comparable activated carbon samples[11]. The selectivity of silica gel was between 2.4 and 3.4, and increases with increasing y_{CH_4} . This range of selectivity is higher than the binary selectivity of about 2 reported in the literature for activated alumina at 313K [32]. This suggests that silica gel can be an alternative to activated alumina for pre-treatment of natural gas, coal bed gas, or landfill gas since it has a higher capacity for CH_4 compared to activated alumina, and better selectivity. For 13X zeolite, the CH_4/N_2 selectivity ranges from 1.3 to 1.7 slightly increasing with increasing y_{CH_4} , as can be seen from Figure 2.7. For 13X the observed trend of increasing selectivity for CH_4 with increasing y_{CH_4} is quite minimal and can be considered insignificant, however this differs somewhat from the work reported by Mofarahi and Bakhtyari where selectivity ranged from 1.9 – 2.1 and in most cases the selectivity was reported to be slightly higher or constant for lower concentrations of y_{CH_4} [14]. This is different than the trend and the range of values (2.2- 3.0) that what is reported by Mulgundmath et al. for 13X at 313K where selectivity was observed to be the highest at $y_{CH_4} = 0.5$ [32]. The observed binary CH_4/N_2 selectivity trends for both silica gel and 13X may be attributed to the fact that CH_4 is slightly more polarizable compared to N_2 . Thus CH_4 may be interacting with the polar surface of the silica gel and the 13X zeolite more than N_2 . This effect may be more pronounced at higher concentrations of CH_4 in the binary mixture since it is suspected that the two gases are competing for the same adsorbing sites thus forming a non-ideal system. Figure 2.7 shows that the binary selectivity values differ from the pure component selectivity values given in Figure 2.2. The pure component selectivity can therefore only serve as a guide when determining suitable adsorbents for practical purposes.

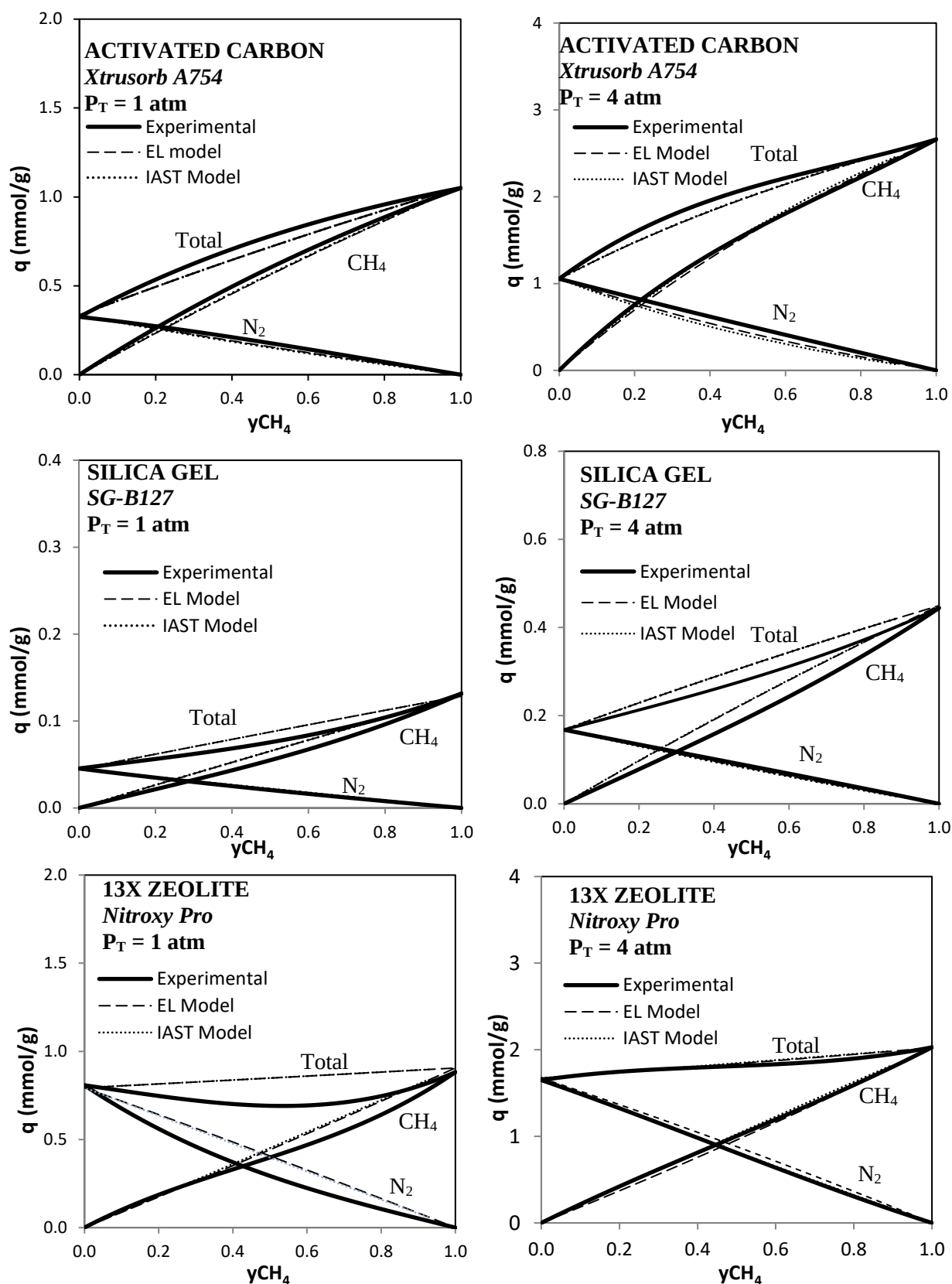


Figure 2.5. Experimental binary isotherms determined from the MVV - CPM, compared with the EL and IAST model predictions for CH_4/N_2 with activated carbon (top), silica gel (middle), and 13X zeolite (bottom) at 1 atm (left) and 4 atm (right) total pressure and 303K.

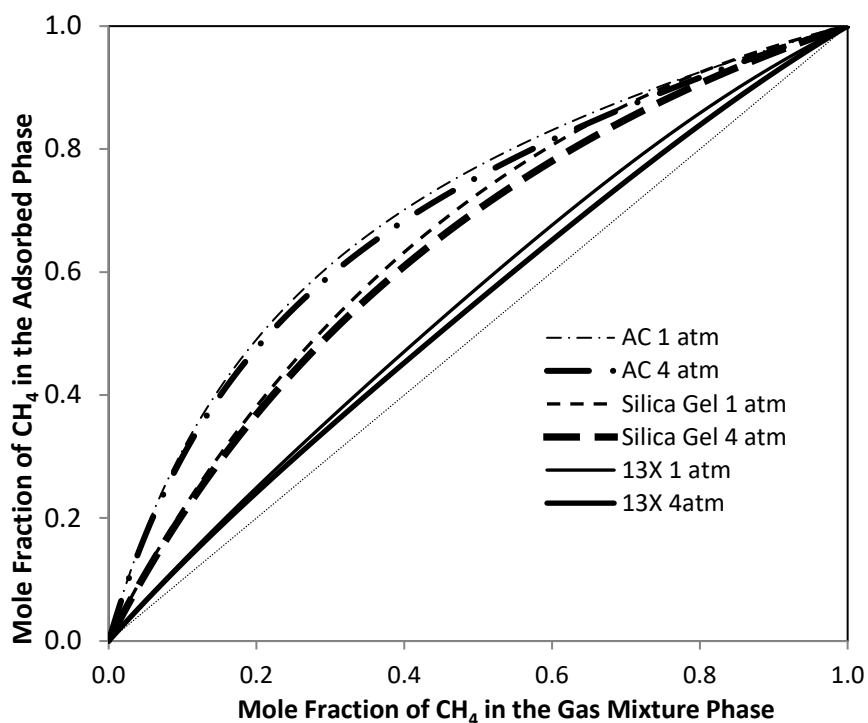


Figure 2.6. X-Y phase diagrams for CH_4/N_2 binary adsorption system with activated carbon (Xtrusorb A754), silica gel (SG-B127), and 13X zeolite (Nitroxy Pro) at 1 and 4 atm total pressures at 303K obtained from MVV-CPM.

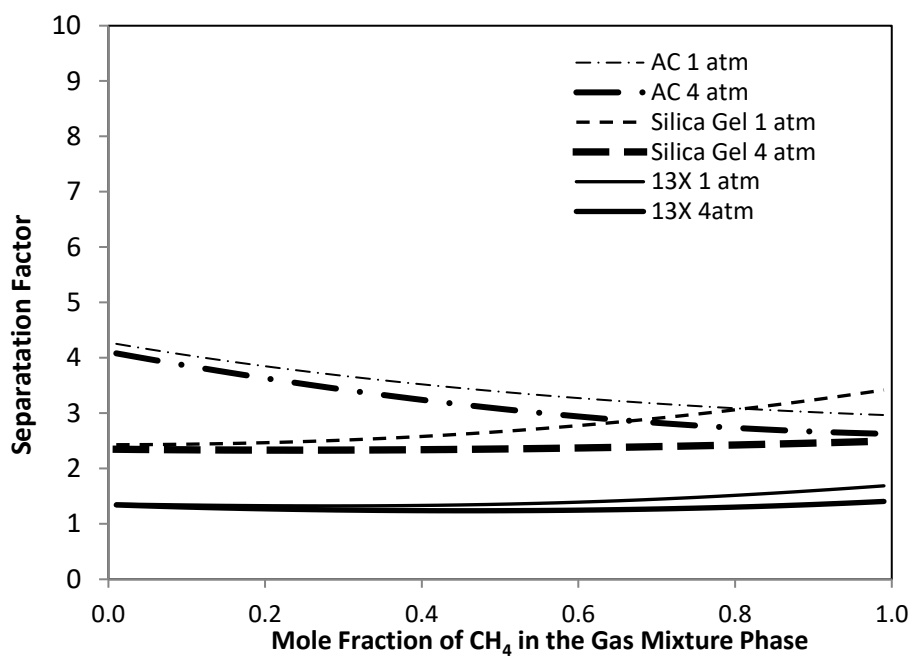


Figure 2.7. Separation factor as a function of mole fraction of CH_4 in the gas phase for CH_4/N_2 binary system with activated carbon (Xtrusorb A754), silica gel (SG-B127), and 13X zeolite (Nitroxy Pro) at 303K and 1 and 4 atm total pressure obtained from MVV-CPM.

2.5 CONCLUSIONS

In this present study, pure component adsorption isotherms for N_2 and CH_4 were obtained at 303K for several different commercially available adsorbents (activated carbons, desiccants, and zeolites) that have shown promise for the application of CH_4 capture for CH_4 - N_2 systems. In general, activated carbons show the highest equilibrium adsorption capacity for CH_4 , followed by the zeolites, and the desiccants. Of the activated carbons, Xtrusorb A754 shows the highest capacity for CH_4 , followed by BPL and F400. Of the desiccants, silica gel SG B-127 had better performance compared to activated alumina (AA-300). Of the zeolites, the order of increasing capacity for CH_4 was: 4A, silicalite, 5A, CaX, and 13X. Ideal CH_4/N_2 selectivity is shown to be the highest for the activated carbons, followed by the desiccants and the zeolites. Of these studied adsorbents, activated carbon Xtrusorb A754 from Calgon Carbon Corp., 13X from CECA, and silica gel from Grace, were studied in greater detail for the separation of CH_4 from N_2 gases, since they had the largest CH_4 adsorption capacity in their categories. The pure component heat of adsorption values were determined from the slope of the adsorption Henry's Law constants as a function of inverse temperature as Van't Hoff plots. The experimental heat of adsorption values were the lowest for silica gel, followed by activated carbon, and then 13X. From the binary CH_4 - N_2 experiments, the MVV-CPM was shown to provide a good representation of the K_p data for all of the experimental binary CH_4 - N_2 adsorption systems for these three studied adsorbents both at 1 atm and 4 atm total pressures. Binary isotherm predictions using the ELM and IAST show a deviation from experimental binary CH_4 and N_2 data for the studied adsorbents.

For the application of CH_4 capture in natural gas processes where y_{CH_4} ranges between 0.7 – 0.9, the CH_4/N_2 separation factor determined from the binary isotherms at $y_{CH_4} = 0.80$ at 1atm total pressure shows to be the highest for activated carbon and silica gel at 3.1, followed by 13X zeolite at 1.6, and decreases with increasing pressure. However in terms of applicability of these adsorbents in pressure swing adsorption processes for methane capture from N_2 for natural gas production, activated carbon Xtrusorb A754 is the best among the studied adsorbents as it has the highest capacity for CH_4 and the comparatively high binary adsorption CH_4/N_2 selectivity.

2.6 NOMENCLATURE

A,B,C	parameters used for the MVV-CPM in Equations 9 to 13b, [$\text{mmol} \cdot \text{g}^{-1} \cdot \text{atm}^{-1}$]
ΔH	limiting heat of adsorption [$\text{kJ} \cdot \text{mol}^{-1}$]
K	dimensionless Henry's Law constant, [dimensionless]
K_p	dimensional Henry's Law constant, [$\text{mmol} \cdot \text{g}^{-1} \cdot \text{atm}^{-1}$]
L	length of the column, [m]
n^a	amount of gas adsorbed for pure systems, [$\text{mmol} \cdot \text{g}^{-1}$]
P	pressure, [atm]
q	amount adsorbed, [$\text{mmol} \cdot \text{g}^{-1}$]
q_m	amount adsorbed at 100% surface occupancy, [$\text{mmol} \cdot \text{g}^{-1}$]
R	universal gas constant, [$\text{L} \cdot \text{atm} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$]
t	time, [s]
T	temperature, [K]
x	mole fraction in the adsorbed phase, [dimensionless]
y	mole fraction in the gas phase, [dimensionless]

Subscripts

1	component 1
2	component 2
i	index
max	maximum
min	minimum
total	total

Greek Symbols

α	adsorption separation factor, [dimensionless]
ε	bed porosity, [dimensionless]
μ	mean retention time, [s]
μ_D	system dead time, [s]
v	Interstitial velocity, [$\text{cm} \cdot \text{s}^{-1}$]

Abbreviations

CPM	concentration pulse method

ELM	Extended Langmuir Model
GC	gas chromatograph
IAST	Ideal Adsorbed Solution Theory
MOF	metal organic framework
MVV-CPM	modified Van der Vlist and Van der Meijden – concentration pulse method
PSA	pressure swing adsorption
SSR	sum of square residuals
TCD	thermal conductivity detector
VST	Vacancy Solution Theory
ZIF	zeolitic imidazolate framework

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CHAPTER 3

Cation Exchange Modification of Clinoptilolite – Screening Analysis for Potential Equilibrium and Kinetic Adsorption Separations Involving Methane, Nitrogen, and Carbon Dioxide

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ABSTRACT

In this study, natural clinoptilolite was modified by cation exchange using alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), alkaline earth metal cations (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}), transition metal cations (Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Ce^{3+}), and acid treatment (H^+). The composition and structural properties of the modified samples were assessed using EDS and XRD analysis, and compared to the original clinoptilolite sample. Adsorption isotherms for CO_2 , N_2 , and CH_4 gases were measured using a microgravimetric adsorption analyser. For all of the clinoptilolite samples, the adsorption equilibria and the diffusion rates were measured at 303K over a pressure range from 0 to 8atm. The results of this screening analysis show that the cation exchanged clinoptilolites exhibit a wide range of adsorption characteristics, which make them suitable for a variety of gas separation applications by pressure swing adsorption. The high adsorption selectivity towards CO_2 and CH_4 found with the Cs^+ exchanged clinoptilolite makes it advantageous for possible CH_4/N_2 and CO_2/N_2 equilibrium separations. Reduced CH_4 equilibrium capacity resulting from pore blocking in the Ca^{2+} exchanged clinoptilolite leads to high selectivity for CO_2/CH_4 and N_2/CH_4 selective adsorbent. However, the potential of this material is limited due to increased microporous diffusion resistance. While both Li^+ and Ni^{2+} clinoptilolites exhibit low CH_4/N_2 ideal selectivity, they present high N_2/CH_4 kinetic selectivity, thereby making them suitable for possible N_2/CH_4 kinetic separations.

Key Words:

Clinoptilolite, pressure swing adsorption, cation exchange, adsorbent screening, CO_2 , N_2 , CH_4 , adsorption separation

3.1. INTRODUCTION

The development and application of new or modified small pored adsorbent materials for gas separations using adsorption technology is of interest for a broad range of industrial separations. The separation of carbon dioxide, methane, and nitrogen containing mixtures are of particular importance due to potential economic and environmental implications. Specifically, the capture of CO₂ from industrial flue gases containing N₂, as well as the separation of CO₂ and N₂ from CH₄ in applications of enhanced natural gas and coal bed gas recovery, biogas production, and control of fugitive methane emissions have been important areas of research. The potential application of pressure swing adsorption (PSA) technology for these separations may be accomplished through exploiting differences in adsorption equilibrium and kinetic properties of the gases with the adsorbents.

Adsorption separations are governed by equilibrium and kinetic effects [1]. Due to differences in their molecular properties as shown in Table 3.1, the equilibrium adsorption potential of the gases in the order of increasing capacity is: N₂ < CH₄ < CO₂, in general. The electrostatic surface potential is the highest for CO₂ as it has a combination of high polarizability and strong quadrupole moment which favours its adsorption over both CH₄ and N₂. Due to its low polarizability and a weak quadrupole moment compared to the other two gases, N₂ generally has the lowest adsorption potential compared to both CO₂ and CH₄.

Table 3.1. Relevant molecular properties of CO₂, CH₄, and N₂ gases[2,3]

gas	Molecular weight (g·mol ⁻¹)	kinetic diameter (Å)	polarizability (x10 ⁻²⁵ cm ³)	dipole moment (x 10 ¹⁸ esu·cm)	quadrupole moment (x 10 ⁻²⁶ esu·cm ²)
CO ₂	44	3.33	29.1	0	4.30
CH ₄	14	3.82	26.0	0	0
N ₂	28	3.64	17.4	0	1.52

For the implementation of an economical PSA process for biogas or natural gas recovery, it is ideal to employ a PSA cycle in such a way that the desired component (CH₄) remains in the high pressure raffinate stream. This is to limit the requirement for recompression of the product gas following the gas separation step. For this to be achieved, the adsorption of CH₄ should be limited in such a way that the affinity towards the adsorbent follows the trend of CH₄ < N₂ < CO₂. The desired properties may be achieved in such a way that adsorption of the larger CH₄ gas molecule is inhibited thus inducing a favourable separation towards the smaller gases. However, separation of these gases through kinetic and molecular sieving is difficult, since their kinetic diameters are very similar.

For the application of these gas separations using adsorption, the idea of porous solids with discrete and uniform micropores ranging in size between 3Å and 4Å coupled with high pore volume are of interest. Typical areas of research for separation of N₂ from CH₄ containing mixtures have focussed on the development small pored adsorbents, such as ordered microporous carbon molecular sieves (CMS)[4], titanosilicates (ETS-4)[5–7], small pored LTA structured zeolites (4A)[8], and cation exchanged clinoptilolite zeolites[9–12]. Additionally, many contributions exist regarding CO₂ removal from CH₄ and N₂ containing mixtures using various materials, including: LTA type zeolites [13,14], MFI type zeolites[15–19], activated carbons[20,21], chabazites [22] , among many others [23,24].

Microporous carbon molecular sieves have been investigated for possible kinetic separations of CO₂ and N₂ from CH₄ mixtures for natural gas or landfill gas upgrading [25–28]. Although CMS has higher equilibrium capacity for CH₄ compared to N₂, it is kinetically selective for N₂ due to its narrow pore size distribution and small micropore size. This leads to a delay in the adsorption uptake of CH₄ over N₂ since it is more difficult for the larger CH₄ to access the pores of the adsorbent. Cavenati et al. proposed a layered PSA system containing CMS and 13X zeolite layered in a packed bed which was capable of producing 92% pure methane with 43.5% recovery from a mixed CO₂-CH₄-N₂ gas feed[29]. Similarly, small pored LTA structured zeolites such as zeolite 4A has been proposed for a possible kinetic separation of N₂ from CH₄. However, the proposed PSA process is limited to low temperatures (below 277K) and CH₄ feeds of greater than 90%. With respect to N₂/CH₄ selective adsorbents using adsorption equilibria as a means of separation, titanosilicate ETS-4 has been proven to be tailored as a N₂ selective molecular sieve through activation at temperatures between 270°C and 315°C resulting in a contracted pore size[5]. ETS-4 has some industrial success for methane recovery under the commercial name Molecular Gate Adsorption Technology®. While substantial N₂/CH₄ equilibrium selectivity has been reported, an ongoing limitation of this adsorbent is the relatively low capacity for N₂ gas with a reported equilibrium saturation N₂ adsorption capacity of between 0.5 and 0.6 mmol/g at ambient temperatures[5–7]. MIL-100(Cr) which is a metal organic framework (MOF) material has shown promise for N₂/CH₄ equilibrium selective separations, however issues remain with respect to the stability of MOF type materials for long term PSA type applications[30]. Additionally changes in the cation composition of modified zeolite rho has shown to effect the pore size of this zeolite, thus inducing favourable adsorption and molecular sieving properties for CO₂, CH₄, and N₂ separations[31].

Clinoptilolite is an abundant naturally occurring microporous zeolite with a two dimensional channel structure that is isostructural to the heulandite (HEU) group of zeolites[32]. As described by Ackley and Yang [9,11], clinoptilolite is composed of a framework of alternating 10 and 8-membered rings which form two parallel channels (channels A and B respectively) that intersect with a third channel composed of an 8-membered ring (channel C). The approximate dimensions of the channels are as

follows: channel A = $7.2\text{\AA} \times 4.4\text{\AA}$, channel B = $4.7\text{\AA} \times 4.1\text{\AA}$, and channel C = $5.5\text{\AA} \times 4.0\text{\AA}$. The framework of clinoptilolite is composed of SiO_4 and AlO_4^{-1} tetrahedra with typical Si/Al ratios for natural clinoptilolite ranging from 4 to 5.2 [33]. This results in an unbalanced negative framework with charge balancing cations occupying sites within the channel pore network of clinoptilolite, where Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are the most common naturally occurring charge balancing cations.

The crystal structure and cation organization of clinoptilolite is very interesting due to the existence of multiple extra framework cation sites and high cation exchange capability. Previous work completed by Koyama and Takeuchi established the existence of 4 extra framework cation sites denoted M(1) through M(4) [34]. These locations correspond to the locations of the naturally occurring cations present in HEU type zeolites: Na^+ , Ca^{2+} , K^+ , and Mg^{2+} , respectively. Since this early work, extensive crystallographic studies on the location of other cations in HEU type zeolites have proved the cation exchange ability and identified several different extra framework locations for samples exchanged with cations including: Ag^+ , Pb^{2+} , Cd^{2+} , Mn^{2+} , Hg^{2+} , Ba^{2+} , Rb^+ , Cs^+ , Zn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} and NH_4^+ [35–44]. Figure 3.1 presents the framework structure of clinoptilolite and the approximated extra framework cation locations M(1) through M(4) for the naturally occurring cations.

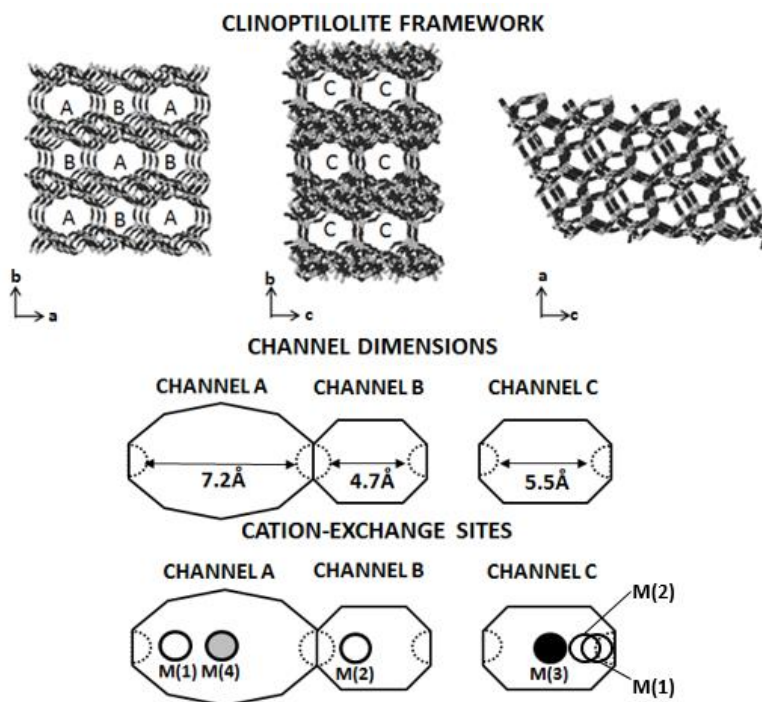


Figure 3.1. The framework structure of clinoptilolite zeolite as described by the International Zeolite Association with the channel dimensions and approximated M(1) through M(4) exchangeable cation positions for the naturally occurring cations[9,45].

The M(1) through M(4) extra framework cation sites are the most well understood positions. The distribution of the cation exchange locations are variable and depend on the cation size and charge, and may also be coordinated with the zeolite framework and/or water molecules [34,44,46,47]. For example, variable cation coordination and migration has been demonstrated with Zn^{2+} , K^+ , and Na^+ exchanged clinoptilolite and heulandite type zeolites at higher temperatures as a result of framework dehydration [42,46,48]. Godelitsas and Armbruster have demonstrated that the positions of several cations are also influenced by the positioning of water molecules present within the channels of the zeolite[43].

The distribution and location of the major exchangeable cation sites residing within the channels of clinoptilolite influences the overall adsorption equilibrium and the diffusion characteristics of gases within the zeolite[9,11,49]. Within the channel network, the M(1) and M(2) sites have been reported to be preferred to be occupied by Na^+ and Ca^{2+} cations, respectively, whereas the M(3) site has been shown to be preferred by K^+ , and the M(4) site is preferred by Mg^{2+} and Li^{2+} respectively. It has been speculated by Jayaraman et al. based on pure CH_4 and N_2 adsorption data that Ce^{3+} cations may prefer to occupy the M(4) and M(3) sites[50]. Table 3.2 shows a summary of the location of the naturally occurring exchangeable cations given in the literature limited to M(1) through M(4) sites for simplicity[45]. Due to the proximity of some of the cation exchange sites, only some of the sites may be occupied simultaneously in pair combinations, with the adjacent M(1)-M(3) and M(1)-M(4) site combinations not always possible because of steric hindrance due to restrictions of the atomic size and positions within the sites.

Table 3.2. Preferred positions for the naturally occurring extra-framework cations present in clinoptilolite[9]

Cation Exchange Position	Channel	Channel Dimension (Å × Å)	Known Exchangeable Cations
M(1)	A	7.2×4.4	$\text{Na}^+ > \text{Ca}^{2+}$
M(2)	B	4.7×4.1	$\text{Ca}^{2+} < \text{Na}^+$
M(3)	C	5.5×4.0	K^+
M(4)	A	7.2×4.4	Mg^{2+}

Clinoptilolite has been shown to exhibit interesting adsorption equilibria and diffusion behaviour due to its unique channel geometry and cation exchange capability. This variable kinetic and equilibrium gas separation capability is derived from the two dimensional pore structure and the pore blocking effects of the highly exchangeable extra framework cations within the channels[9]. Frankiewicz and Donnelly

observed that the presence of partially exchanged divalent Ca^{2+} cations in naturally occurring clinoptilolite results in a N_2/CH_4 kinetic and equilibrium selective adsorbent, however further study into the use of this adsorbent in a PSA process resulted in a product that was below pipeline quality [51]. Ackley and Yang characterised the pure component equilibrium adsorption, diffusion uptake, and isosteric heat of adsorption data of N_2 and CH_4 on clinoptilolites exchanged with Na^+ , K^+ , H^+ , Mg^{2+} , and Ca^{2+} [9,11,12]. They found that N_2/CH_4 selective equilibrium adsorption was achieved with clinoptilolites modified with Na^+ and partially modified (89%) with Ca^{2+} cations. These cations occupy the M(1)-M(2) extra-framework sites, effectively blocking CH_4 from accessing channels B and C respectively. The Mg^{2+} cations occupying the M(4) position were not exchanged, and were suspected to block channel A in the partially exchanged samples[11,12]. Chromatographic studies by Triebe and Tezel confirmed that microporous diffusion of N_2 and CO is dominant in natural clinoptilolite[52]. Binary $\text{N}_2 - \text{CH}_4$ modelling conducted by Predescu et al. showed predicted azeotropic CH_4/N_2 selectivity behaviour at moderate temperatures for naturally rich Ca^{2+} Turkish clinoptilolite[53]. The temperature effects on N_2 and CH_4 adsorption on natural clinoptilolite showed increased N_2/CH_4 selectivity on natural clinoptilolite at low temperatures due to diffusion limitations of CH_4 , with natural clinoptilolite being N_2 selective at 273K[54]. Aguilar-Armenta et al. studied the adsorptive equilibria and kinetics of several light gases including CO_2 , N_2 , and CH_4 on partially cation exchanged clinoptilolite; with K^+ and Ca^{2+} exchanged clinoptilolite shown to be effective for kinetic separations of CO_2/CH_4 and N_2/CH_4 mixtures[55]. However, it should be mentioned that the presence of Mg^{2+} cations in these partially exchanged samples may have contributed to the observed kinetic selectivity as observed in previous studies[11,12]. Jayaraman et al. studied the effects of single and mixed cations including Mg^{2+} , Na^+ , Ca^{2+} , Li^+ , Sr^{2+} and Ce^{3+} exchanged clinoptilolites on N_2 and CH_4 adsorption equilibria and kinetic uptake [50,56]. These results showed that several different ion exchange combinations including partially exchanged mixed $\text{Na}^+/\text{Mg}^{2+}$, $\text{Ca}^{2+}/\text{Mg}^{2+}$, and Na^+/Li^+ cations induce favourable kinetic and equilibrium N_2/CH_4 gas separations comparable to that of titanosilicate ETS-4[50,56]. Karousos et al. showed that natural clinoptilolite shows some promise for CO_2/N_2 gas separations, with significant selectivity at a higher temperature of 403K[57]. The effect of acid treatment on natural clinoptilolite tuff showed that H^+ ions tend to open the channels of the zeolite leading to greater CH_4 adsorption[12,58].

3.2. OBJECTIVE

Several research contributions have demonstrated the adsorptive and diffusive properties of CO_2 , CH_4 , and N_2 gases on various natural and cation exchanged clinoptilolites. These studies have been limited to modification using naturally occurring cations (Na^+ , K^+ , Mg^{2+} , and Ca^{2+}) with some other

cations including Li^+ , Ce^{3+} , and Sr^{2+} . The type of charge balancing cation influences the effective pore size of this zeolite, and the acid-base properties of the zeolitic framework.

This study attempts to build on work of previous systemic screening studies of this type[9–11,50,59]. In this work, natural and several different cation exchanged clinoptilolites were analyzed in order to screen for potential equilibrium and diffusion selective characteristics for CO_2 , CH_4 and N_2 gases. Clinoptilolite was modified with three different groups of cations; alkali metals, alkaline earth metals, and transition metals. Single gas CO_2 , CH_4 , and N_2 adsorption isotherms and kinetic adsorptive uptake curves were measured using the gravimetric method at 303K to identify the most promising cations to be used for these separations.

3.3. MATERIALS and EXPERIMENTAL METHODS

3.3.1. MATERIALS

Natural clinoptilolite zeolite tuff originating from deposits in Nevada, USA was purchased from Ash Meadows Zeolite LLC. (Amargos Valley, NV.). The clinoptilolite was received as +140 US. Std. mesh powder. The skeletal density of the raw clinoptilolite was assessed to be 2.12 g cm^{-3} using a Micromeritics volumetric adsorption analyser and helium gas as the probe gas. The cation exchange salt solutions were prepared using deionized water and cation containing reagent salts as presented in Table 3.3. Where possible, salts containing chloride ions as the counterbalancing negative ion for each reagent were used to reduce the risk of additional variation within the screening process.

Single gas adsorption experiments were conducted using high purity CO_2 , N_2 , and CH_4 gases; high purity He gas was used for buoyancy correction for the single gas adsorption isotherm experiments. All gases purchased from Linde Canada Ltd. (Ottawa, Canada) and had the following specifications for purity: 99.995% He, 99.99% N_2 , 99.99% CH_4 , and 99.99% CO_2 .

Table 3.3. Cation sources and reagent supplier information used in this study.

Exchangeable Cation	Chemical Reagent	Purity	Supplier
Ba ²⁺	barium chloride dihydrate (BaCl ₂ ·2H ₂ O)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Be ²⁺	beryllium sulphate tetrahydrate (BeO ₄ S·4H ₂ O)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Ca ²⁺	calcium chloride (CaCl ₂)	96.0%	EMD Chemicals Inc., Gibbstown, NJ
Ce ³⁺	cerium(III) chloride heptahydrate (CeCl ₃ ·7H ₂ O)	98.0%	Sigma-Aldrich Canada Co., Oakville, ON
Cs ⁺	cesium chloride (CsCl)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Cu ²⁺	copper(II) sulfate pentahydrate (CuO ₄ S·5H ₂ O)	98.0%	Sigma-Aldrich Canada Co., Oakville, ON
H ⁺	hydrochloric acid (HCl)	37% solution	Acros Organics, Geel, Belgium
Fe ³⁺	iron(III) chloride hexahydrate (FeCl ₃ ·6H ₂ O)	99.0%	BDH Inc., Toronto, ON.
Li ⁺	lithium chloride (LiCl)	99.0%	Fisher Scientific Company, Ottawa, ON.
Mg ²⁺	magnesium chloride hexahydrate (MgCl ₂ ·6H ₂ O)	99.0%	Fisher Scientific Company, Ottawa, ON.
Na ⁺	sodium chloride (NaCl)	99.0%	Anachemia Canada Inc., Montreal, QC
Ni ²⁺	nickel(II) chloride hexahydrate (NiCl ₂ ·6H ₂ O)	99.9%	Sigma-Aldrich Canada Co., Oakville, ON
K ⁺	potassium chloride (KCl)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Rb ⁺	rubidium chloride (RbCl)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Sr ²⁺	strontium chloride hexahydrate (SrCl ₂ ·6H ₂ O)	99.0%	Sigma-Aldrich Canada Co., Oakville, ON
Zn ²⁺	zinc(II) sulfate heptahydrate (ZnO ₄ S·7H ₂ O)	99.0%	Fisher Scientific Company, Ottawa, ON.

3.3.2. PREPARATION of the CATION EXCHANGED CLINOPTILOLITES

The preparation of the adsorbent prior to cation exchange was carried out in a similar fashion as described in the literature[11,50,56]. The raw clinoptilolite powder was mixed with deionized water with a ratio of 1g of clinoptilolite to 80 mL of deionized water. The mixture was heated to between 80°C and 90°C under minimal agitation for a minimum of 1 hour. Following this step, the solution is decanted and the remaining clinoptilolite is rinsed with 50 mL of deionized water, this step is repeated twice to ensure

that the raw clinoptilolite is purified of any undesirable soluble salts. The washed clinoptilolite was then placed in an oven and dried at 105°C overnight.

In a 50 mL Teflon lined autoclave; a ratio of 1g of the washed dry clinoptilolite was mixed with 50 ml of 0.2 M cation salt solution. The amount of exchangeable cations with the clinoptilolite is in excess with this ratio of solution to clinoptilolite at this concentration[56]. The autoclave is put into the oven while it is at room temperature and heated in the oven to 135°C for 10 hours. Then it is removed from the oven and is cooled to room temperature over 2 hours under ambient conditions. The 0.2M salt solution is then decanted, leaving behind partially cation exchanged clinoptilolite.

The procedure indicated in the above paragraph is repeated once more to increase the exchange of the cations into the clinoptilolite. Following the decanting of the exchange solution, the clinoptilolite is rinsed twice with 50 mL of deionized water, and dried at 105°C for 24 hours and cooled down to room temperature. Afterwards, the clinoptilolite is activated at 300°C.

3.3.3. SAMPLE CHARACTERIZATION

The purity of the original natural clinoptilolite sample was verified through x-ray diffraction (XRD) analysis. The powdered samples were examined at room temperature using a Rigaku Ultima IV powder diffractometer in Bragg-Brentano geometry, using Cu K α radiation ($\lambda = 1.5418$ Å). The 2θ range of 2° to 90° was covered with a 0.02° step width and 6°/min scan speed. The XRD diffraction patterns were analysed using the Rietveld refinement method and X'Pert Highscore Plus analysis software. The diffraction patterns of the samples were compared to the characteristic patterns for clinoptilolite established by the International Zeolite Society (IZA)[60].

Electron Dispersive Spectroscopy (EDS) analysis was used to verify the atomic composition of the cation exchanged clinoptilolite samples. A JEOL JSM-6610LV series scanning electron microscope equipped with an Oxford INCA large area SDD detector was used with the following configuration: 20kV acceleration voltage, 10 mm working distance, and 4000X magnification.

3.3.4. SINGLE GAS ADSORPTION EXPERIMENTS

The single gas CO₂, CH₄ and N₂ adsorption isotherms and uptake-rate measurements were performed using the gravimetric method with a microgravimetric analyser equipped with a Cahn balance from VTI Corp. (Hialeah, Florida, USA) following a similar method as our previous study[61]. This equipment allows for the concurrent monitoring of both the static equilibrium and dynamic adsorption uptake measurements. Experiments were carried out using a Cahn microbalance that has an accuracy of

$\pm 1 \mu\text{g}$ enclosed within a stainless steel chamber. The experimental temperature was controlled using a jacketed water bath installed around the adsorption chamber and was monitored using a thermocouple with an accuracy of $\pm 0.01\text{K}$. The samples were regenerated under high vacuum conditions of approximately 10^{-8} atm using a high vacuum turbo molecular pump at a temperature of 573K . The samples were considered to be fully regenerated once the sample weight remained unchanged over a period of 1 hour.

Following regeneration, the adsorbents were exposed to the sample gas and were evaluated at increasing pressure steps ranging from 0 to 10 atm at 303K . For each pressure step change, the dynamic adsorption uptake was monitored and recorded as the change in sample weight as a function of time. Sufficient time was allowed for the system to reach equilibrium, which was determined to be achieved once a weight change of less than $0.015 \text{ wt\%}$ over a period of 15 minutes was observed, at which time the equilibrium adsorption measurement was recorded. The reversibility of the adsorption process was tested for each sample by measuring desorption isotherms and observing the sample weight change at decreasing pressure steps. The experimental sample weight was corrected for buoyancy by exposing the sample to high purity helium at similar pressures and temperatures. Since helium is a much smaller molecule than the gases used in this study, it will have access to smaller micropores than what CO_2 , CH_4 , and N_2 gases will have access to. Therefore, after the buoyancy correction, we will actually be reporting the excess amount adsorbed for these systems[62], and those values were fit to different isotherm models used in this study.

3.4. ADSORPTION MODELS

3.4.1. MODELLING SINGLE COMPONENT ADSORPTION EQUILIBRIA

If the adsorption isotherm exhibits type I behaviour as classified by Brunauer, Deming, Deming, and Teller (BDDT), the equilibrium adsorption data for each sample can be described simply with the Langmuir adsorption isotherm regression[63]. The Langmuir approach relies on the assumptions that adsorption is in a state of dynamic equilibrium, limited by a fixed number of localized adsorptive sites, with monolayer adsorption where there is no interaction between adsorbed molecules within the adsorbed sites, and that the energy of adsorption is consistent over all sites [64,65].

$$\theta = \frac{q}{q_m} = \frac{BP}{1+BP} \quad (1)$$

Here, θ is the fractional coverage on the adsorbent surface; q is the amount adsorbed; q_m is the saturation monolayer adsorption capacity; B is the affinity constant; and P is the pressure [16,65].

The Toth model equation carries much of the same conventions as the Langmuir approach, however it allows for greater flexibility for the prediction of adsorption systems. At very low pressures the Toth isotherm equation reduces to the Henry's law isotherm equation and is thermodynamically consistent, thus the adsorption equilibria data can be interpolated over a range of different temperatures and pressures [16,17]

$$\theta = \frac{q}{q_m} = \frac{BP}{[1+(BP)^n]^{\frac{1}{n}}} \quad (2)$$

The additional n parameter is dimensionless. When the n parameter equals 1, the Toth model equation reduces to the Langmuir equation.

3.4.2. MODELLING ADSORPTION KINETICS

In order to interpret the adsorption transport diffusivity from the experimental kinetic uptake rate data, a diffusion model must be applied to determine the diffusion coefficients. It is important to envision the clinoptilolite as a semi-infinite plane whereby microporous gas diffusion may occur within the A, B, and C channels in a 2 dimensional pore arrangement. Differences in access to the pores is governed by the gas type and variations in the channel structure resulting from the occupation of various cations within the pores [11]. In reality the evaluation of this kinetic behaviour is fairly complicated. However, in order to rapidly quantify the kinetic uptake data for comparison purposes between different materials, a simplified approximation is undertaken using the Linear Driving Force (LDF) model as shown in Equation 3 [64,66–70].

$$\frac{\partial q}{\partial t} = k_{LDF}(q_e - q(t)) \quad (3)$$

This approach relies on the assumption of a homogenous adsorbent media whereby the mass transfer coefficient, k_{LDF} is independent of adsorbate concentration. To apply the LDF model, the experimental pressure step change response is monitored as the amount adsorbed $q(t)$ at different times (t). The change in q as a function of time gives the slope, dq/dt , that is plotted as a function of $q(t)$ for different times. Since the q_e value is known as the amount adsorbed at equilibrium, the slope of this plot gives k_{LDF} specific to the system.

The LDF diffusion model is valid in the fractional uptake region $\frac{q(t)-q_0}{q_e-q_0}$ of between 0.6 or 0.7 and less than 0.99 [64,71]. Intracrystalline diffusion resistance within the micropores of clinoptilolite is

an influential transport rate controlling mechanism. The diffusion time constant, D_e/R_p^2 , is used to better reflect the effective intracrystalline diffusion within the zeolite as shown in Equation 4 [67].

$$k_{LDF} \approx \frac{15D_e}{R_p^2} \quad (4)$$

Where D_e/R_p^2 is the diffusion time constant [s^{-1}] which is the effective transport diffusivity, D_e , divided by the squared radius of the pellet, R_p .

3.4.3. EVALUATING GAS ADSORPTION SEPARATION POTENTIAL

Comparison of the pure component adsorption equilibria for different gases is a first step required to assess the potential applicability of the adsorbent materials for a particular gas separation. The ideal selectivity, α , and separation factor, S , are good tools to initially screen for the most promising adsorbent materials for a particular separation process.

The adsorption equilibrium separation factor is the ratio of the adsorbed phase and gas phase for the separating components in a mixture. It can be expressed as the ratio of the Langmuir isotherm parameters outlined in Equation 1 as derived from the Extended Langmuir prediction for a gas mixture as shown in Equation 5 [8,72].

$$\alpha_{i,A/B} = \frac{X_A \cdot Y_B}{X_B \cdot Y_A} \approx \frac{q_{mA} B_A}{q_{mB} B_b} \quad (5)$$

The more strongly adsorbed component is labelled with the subscript A , whereas the weakly adsorbed component is labelled with subscript B . For a gas mixture, the adsorbed phase mole fraction is denoted as X , whereas the gaseous phase mole fraction of a mixture is denoted as Y .

The adsorption equilibrium selectivity, S , is calculated using Equation 6. It is evaluated based on the ratio of the working adsorption capacities for species A and B , Δq_A and Δq_B , which is the difference in the adsorption capacity at the adsorption pressure and desorption pressure, respectively[72]. For this analysis, the adsorption working capacity ratios was assessed for pressure ranges from 0.1 – 1 atm, and from 1 – 10 atm for prospective VSA and PSA performances, respectively.

$$S = \alpha_{i,A/B} \frac{\Delta q_A}{\Delta q_B} \quad (6)$$

The narrow channels of small pored structured clinoptilolite zeolites coupled with the variable cation exchange positions located within the channels offer the possibility of a kinetically driven separation. The kinetic selectivity, $K_{A/B}$, is employed to approximate separation performance based on the diffusivity ratio (which is the same as the ratio of kinetic mass transfer coefficients) determined from Equations 3 and 4, and the ideal adsorption equilibrium separation factor calculated for two different adsorbed components (Equation 7)[8,73].

$$K_{A/B} = \alpha_{i,A/B} \sqrt{\frac{k_{LDF_A}}{k_{LDF_B}}} \quad (7)$$

3.5. RESULTS and DISCUSSION

3.5.1. COMPOSITIONAL ANALYSIS

The composition of the modified clinoptilolite samples were analysed using EDS. The results are compared to the raw clinoptilolite and are presented in Table 3.4. In this table, the elemental composition is normalized to the approximated amount of aluminum atoms present in the unit cell for clinoptilolite. The total amount exchanged is quantified as the percent difference between the natural occurring cations (K^+ , Ca^{2+} , Mg^{2+}) present in the exchanged clinoptilolite sample compared to those present in the original raw clinoptilolite sample.

As can be seen in Table 3.4, following the cation exchange procedure, a significant portion of the naturally occurring exchangeable cation types present in the raw sample were substituted. These results suggest that a high proportion of non-native cations are capable of occupying the channels of the zeolite, which is consistent with previous studies that indicated an overall high potential exchangeability of the extra-framework cations[74]. The Si/Al ratio of the raw zeolite sample is 5.10 and follows the range reported in the literature for clinoptilolite [33,75]. Due to limited EDS detector probe sensitivity, the atomic compositions for the H^+ , Li^+ and Be^{2+} cations are unquantified. Comparisons may be drawn with previous studies which showed sufficient Li^+ cation exchangeability and tendency to occupy the M(4) position in the middle of channel B (see Figure 3.1), with no indication of incorporation within the lattice structure of the clinoptilolite[50,54]. Neglecting the results of the H^+ , Li^+ and Be^{2+} cation exchanged samples, the average silicon to aluminum ratio of all of the cation exchanged samples 5.05 ± 0.25 , and is similar to the raw sample. The Fe^{3+} cation exchanged sample presents a high silicon to aluminum ratio of 5.85, indicating a decrease in the absolute amount of aluminum present compared to the raw clinoptilolite.

Table 3.4. Unit cell elemental composition of prepared clinoptilolite samples obtained using EDS.

<u>SAMPLE</u>	Cation	atoms/unit cell							Exchanged Cation	% of Natural Cations Exchanged ‡	Si:Al
		O	Al	Si	K	Ca	Mg	Fe			
raw clinoptilolite	-	111.19	6.00	30.65	1.49	1.68	0.71	0.27	-	-	5.10
acid treated clinoptilolite †	H ⁺	128.30	6.00	39.53	0.46	0.83	0.46	-	†	57.8	6.59 [†]
Li – clinoptilolite †	Li ⁺	140.47	6.00	43.10	0.76	1.36	0.53	0.05	†	34.9	7.18 [†]
Na – clinoptilolite	Na ⁺	103.36	6.00	31.96	1.09	0.90	-	-	3.46	52.1	5.32
K – clinoptilolite	K ⁺	101.98	6.00	28.87	4.79	0.89	0.32	0.09	4.79	68.6	4.81
Rb – clinoptilolite	Rb ⁺	112.69	6.00	29.49	-	1.35	-	0.28	4.24	60.7	4.91
Cs – clinoptilolite	Cs ⁺	115.87	6.00	31.20	0.38	1.12	-	0.29	5.60	56.7	5.20
Be – clinoptilolite †	Be ²⁺	103.08	6.00	29.97	0.69	1.04	0.57	0.24	†	39.0	5.00 [†]
Mg – clinoptilolite	Mg ²⁺	109.03	6.00	31.28	0.58	1.15	2.18	-	2.18	58.4	5.21
Ca – clinoptilolite	Ca ²⁺	98.46	6.00	29.72	0.54	3.23	0.50	0.41	3.23	65.1	4.95
Sr – clinoptilolite	Sr ²⁺	117.51	6.00	29.86	0.38	1.26	-	0.15	2.16	56.7	4.98
Ba – clinoptilolite	Ba ²⁺	110.01	6.00	31.15	0.35	0.67	0.19	0.09	3.18	68.6	5.19
Fe – clinoptilolite	Fe ³⁺	123.55	6.00	35.10	0.51	0.21	-	1.94	1.94	82.5	5.85
Ni – clinoptilolite	Ni ²⁺	116.98	6.00	31.20	-	0.68	-	0.51	5.15	71.3	5.20
Cu – clinoptilolite	Cu ²⁺	110.76	6.00	31.76	0.74	0.86	-	-	2.39	61.6	5.29
Zn – clinoptilolite	Zn ²⁺	98.54	6.00	29.65	0.84	0.99	-	-	3.68	56.0	4.94
Ce – clinoptilolite	Ce ³⁺	122.89	6.00	30.98	0.60	0.83	0.55	0.14	1.11	48.9	5.16

† Limited EDS detector sensitivity was not capable of accurately measuring the exchanged cation.
‡ Quantified as the % difference between the natural cations (K⁺, Ca²⁺, Mg²⁺) present in the exchanged clinoptilolite sample compared to those present in the raw clinoptilolite sample.

3.5.2. STRUCTURAL SCREENING ANALYSIS

The XRD pattern of the raw and modified clinoptilolite samples are presented in Figure 3.2. The samples were compared visually to the characteristic patterns identified in the literature for clinoptilolite minerals [36,76,77]. The crystal structure was assessed using the Rietveld method provided in X'Pert Highscore Plus Software [78]. This interpretation showed that the original material is primarily composed of clinoptilolite (71 wt.%). The remaining portion of the mineral phase consisted mostly of stilbite (18 wt.%) with smaller quantities of mordenite, quartz type material, and other alumina silicate impurities such as feldspar identified. The material is monoclinic with the lattice unit cell parameters of the raw sample having the following measurements: $a = 14.6 \pm 4.0 \text{ \AA}$, $b = 10.9 \pm 4.0 \text{ \AA}$, $c = 9.1 \pm 0.5 \text{ \AA}$ and $\beta = 109.6 \pm 12.3^\circ$. The measured lattice parameters of the material differ from the accepted cell parameters for clinoptilolite which are: $a = 17.662 \text{ \AA}$, $b = 17.991 \text{ \AA}$, $c = 7.407 \text{ \AA}$ and $\beta = 116.4^\circ$ [34], and may be explained by the presence of the natural impurities of the different phases within the sample. The measured purity was considered sufficient for the screening study, particularly since mordenite is the only

impurity known to exhibit significant gas adsorption tendencies and the quantity of mordenite was low and consistent across all the experimental data set.

Distinctions between the XRD profiles of the raw clinoptilolite and the cation exchanged samples shows that cation exchange appears to alter the position and intensity of some of the characteristic peaks. Small changes in the arrangement of the structure of the clinoptilolite and/or the atomic positions within the unit cell may be inferred by the differences presented in the diffraction patterns. Detailed analysis of the crystal structure have been the subject of several research contributions [43,47,48,79–81], as such this was beyond the scope of this study.

Some changes with respect to the peak intensity of the diffractograms given in Figure 3.2 may be explained by the properties of the cations given in Table 3.5. Substitution of the cations with a higher charge to ionic radius ration, such as H^+ , Li^+ , Be^{2+} , Mg^{2+} , and Fe^{3+} results in less defined diffraction patterns. This likely indicates a change in the atomic density and increased disorder resulting in generally lower crystallinity of the zeolite framework [75]. These patterns may also be partially caused by the relative acidity attributed to ion exchange environment, as demonstrated by Alver and Sakizci where a loss of crystallinity was observed with increasing HCl concentrations in the exchange environment [58]. The lowest peak intensities are observed for the clinoptilolite exchanged with Fe^{3+} cations indicating increased framework disorder.

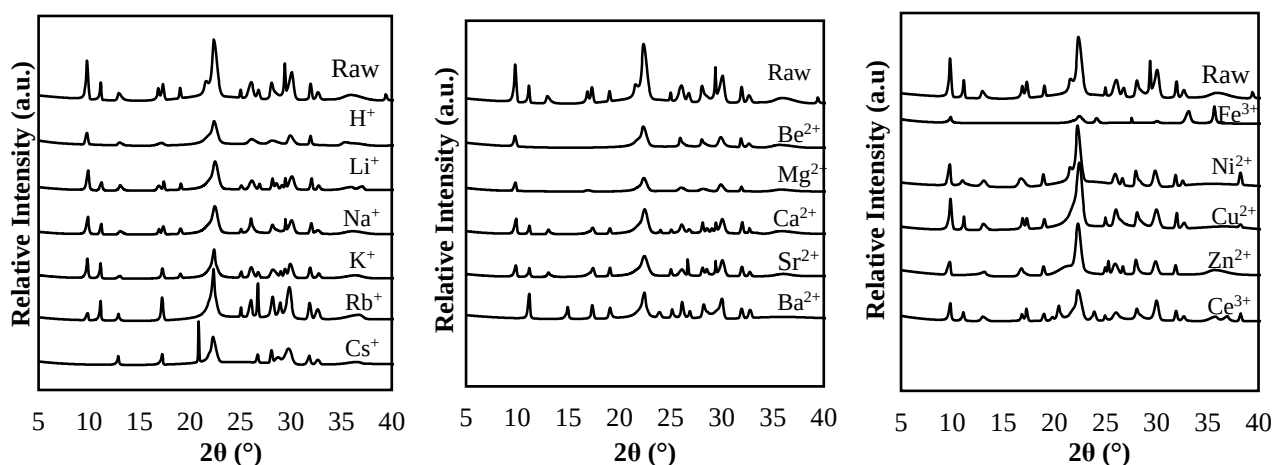


Figure 3.2. Experimental XRD patterns for the raw and prepared cation exchanged clinoptilolite samples obtained at room temperature. The peak intensity patterns were used to quantify the structural purity and unit cell lattice parameters of the samples.

Table 3.5. Physical properties of the exchanged cations[82,83].

Group	Cation	Effective Ionic Radius (Å)	Hydrated Radius (Å)	Charge to Ionic Radius Ratio
-	H ⁺	~0.10	0.25	~10.0
alkaline earth metal	Be ²⁺	0.45	1.05	4.44
transition metal	Al ³⁺	0.53	1.25	5.66
transition metal	Fe ³⁺	0.55	1.40	5.45
transition metal	Ni ²⁺	0.69	1.35	2.89
alkaline earth metal	Mg ²⁺	0.72	1.50	2.78
transition metal	Cu ²⁺	0.73	1.35	2.74
transition metal	Zn ²⁺	0.74	1.35	2.70
alkali metal	Li ⁺	0.76	1.45	1.32
alkaline earth metal	Ca ²⁺	1.00	1.80	2.00
transition metal	Ce ³⁺	1.01	1.85	2.97
alkali metal	Na ⁺	1.02	1.80	0.98
alkaline earth metal	Sr ²⁺	1.18	2.00	1.69
alkaline earth metal	Ba ²⁺	1.35	2.15	1.48
alkali metal	K ⁺	1.38	2.20	0.72
alkali metal	Rb ⁺	1.52	2.35	0.66
alkali metal	Cs ⁺	1.67	2.60	0.59

The XRD diffraction patterns presented in Figure 3.2 were analyzed using Rietvelt refinement analysis, and the dimensions of lattice parameters for the unit cell were evaluated for all of the different clinoptilolite samples as shown in Figure 3.3[a] and 3[b]. The majority of the cation exchanged structural dimensions are fairly consistent with respect to the original raw clinoptilolite sample given the precision of this screening method. The most significant change in the unit cell lattice parameters with respect to the different cation exchanged samples are observed for the *a* and *b* directions. These coordinates follows along the same plane as channels A and B as presented in Figure 3.1. This observation is the most evident for clinoptilolite exchanged with the smaller cations, including Be²⁺, Fe³⁺, Zn²⁺, and Ni²⁺ where the lattice measurements show a reduction in the *b* direction.

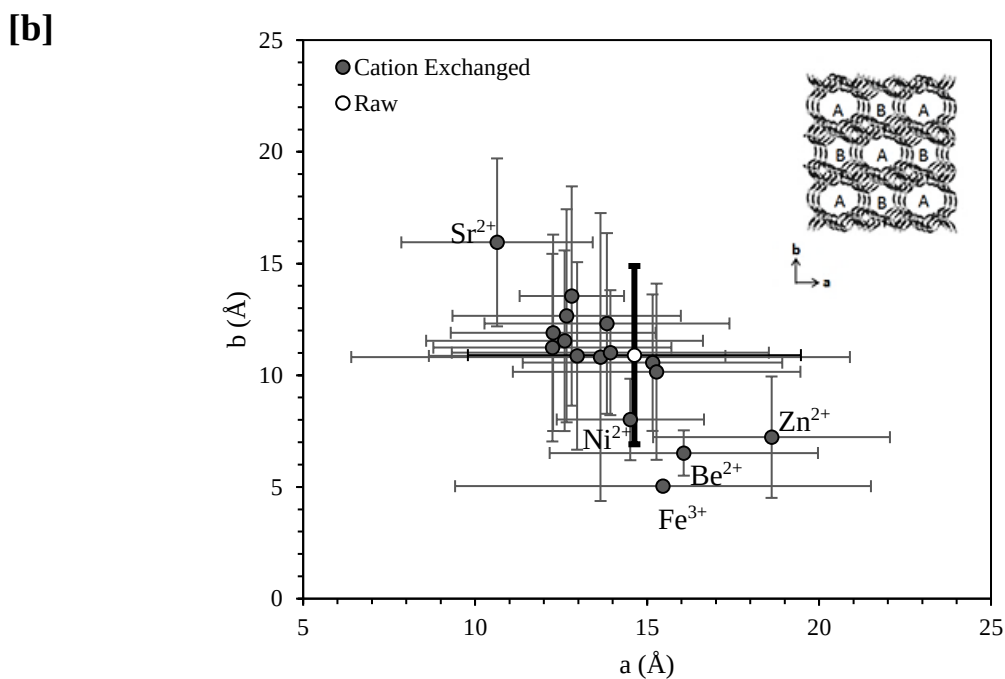
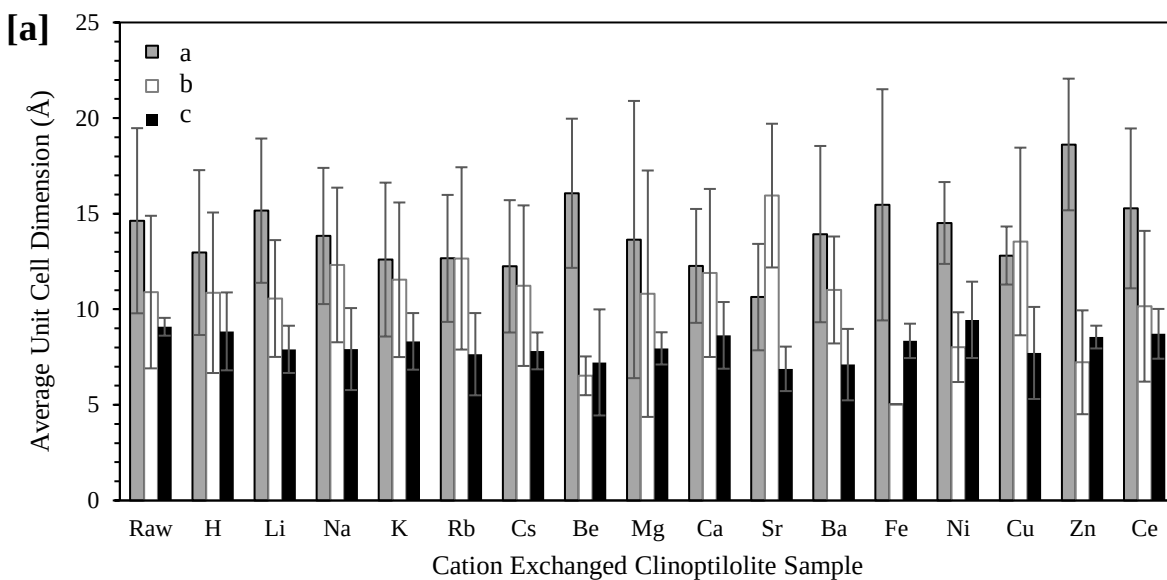


Figure 3.3. [a] Experimentally determined lattice dimensions of the prepared clinoptilolite samples compared to raw clinoptilolite determined using the Rietveld refinement method on XRD powder patterns at room temperature. **[b]** Comparison of experimentally determined lattice dimensions in the $a - b$ axis determined from the Rietveld refinement method on XRD powder patterns at room temperature.

3.5.3. PURE COMPONENT CO₂, CH₄, and N₂ ADSORPTION EQUILIBRIA

Physical adsorption is governed by the der Waals forces of dispersion and repulsion, and the electrostatic interactions which comprise of polarizability, dipole and quadrupole interactions the effect of which are largely influenced by the degree of energetic heterogeneity of the zeolite surface[64]. With respect to small pored zeolites such as clinoptilolite, physical adsorption is also influenced by steric effects with respect to access to the zeolite pore network. The capability of a broad variation in the adsorption equilibria for different gases on clinoptilolite is due to the positioning and type of extra-framework cations located within the zeolite channels[49]. In addition, the cation charge, size, and location in relation to the framework influences the available surface area and local acid sites on the surface of the zeolite.

Experimental equilibrium adsorption isotherms of pure CO₂, CH₄, and, N₂ gases on the different cation exchanged clinoptilolites were performed as described in Section 3.4. In general, the adsorption equilibria data for the studied gases on clinoptilolite can be considered as type I adsorption isotherms as classified by BDDT over the experimental pressure range [63]. Therefore, Langmuir and Toth isotherm models were employed on the experimental data, and the corresponding parameters are presented in Table 3.6.

3.5.3.1. RAW and ACID TREATED CLINOPTILOLITE

Raw clinoptilolite consists of different types of naturally occurring cations whose quantity and proportions depend on the local source of the mineral deposits. The raw clinoptilolite used in this study consisted of a distribution of Ca²⁺, K⁺, Mg²⁺, and Fe³⁺ extra framework cations. Figure 3.4 shows that the observed adsorption equilibria follows the expected trend with CO₂ as the most readily adsorbed component, followed by CH₄ and N₂. The greater adsorption equilibrium capacity for CH₄ compared to N₂ indicates that access to the pore network is not impeded by the distribution of the naturally occurring cations in the raw sample for the larger CH₄. While the Ca²⁺ cation has been shown to successfully block access of CH₄ gas to the pore network [51], there exists insufficient quantities of Ca²⁺ cation present in the natural sample for this to occur.

Acid treatment results in partial replacement of the naturally occurring cations occupying the channels of the zeolite, thereby opening up access to the channels for adsorption to occur[49,58]. Differences may be observed with respect to the adsorption equilibria capacity of the acid treated clinoptilolite compared to the raw clinoptilolite. At higher pressures CO₂ capacity is greater for the acid treated clinoptilolite, whereas CH₄ and N₂ adsorption capacities of the acid treated clinoptilolite are approximately equivalent to that of the raw clinoptilolite sample.

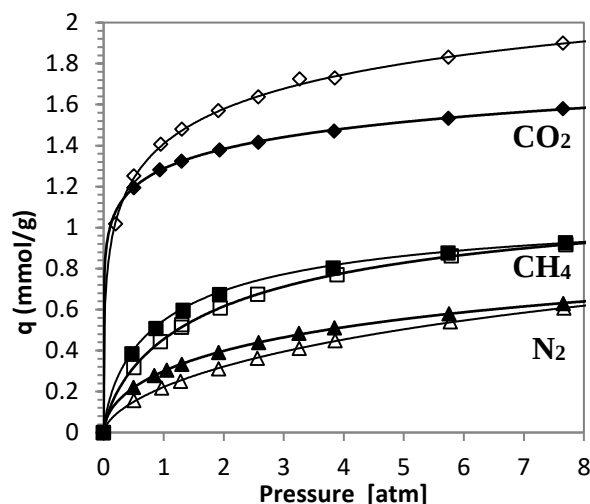


Figure 3.4. Experimentally determined adsorption isotherms with Toth model fit for CO₂, N₂, and CH₄ at 303K for raw clinoptilolite (filled points) and 0.2M HCl acid treated clinoptilolite samples (open points).

3.5.3.2. ALKALI METAL CATION EXCHANGED CLINOPTILOLITE

Figure 3.5 presents the single gas adsorption equilibrium isotherms for CO₂, CH₄, and N₂ gases performed at 303K on the alkali metal cation exchanged clinoptilolite samples. In all cases, the observed adsorption equilibria capacities follow the expected trend of CO₂ > CH₄ > N₂. Adsorption of CO₂ follows the trend in the ionic radii of the substituted cations, where CO₂ adsorption capacity is observed follow the order of: Li⁺ ≈ Na⁺ > K⁺ > Rb⁺ > Cs⁺, with Cs⁺ being the largest cation and Li⁺ being the smallest (see Table 3.5). Similar trends in CO₂ adsorption capacity were observed for other small pored zeolites exchanged with alkali cations including: chabazite [22], zeolite beta [84], zeolite X and zeolite Y [85]. It is thought that the greater electrostatic charge density of the smaller cations results in higher surface potential. In addition, smaller cations take up smaller space in the channels opening up more space for molecules to be adsorbed. The net result is greater adsorption potential for CO₂[22]. The presence and size of these cations within the channel cavity also follow the expected trends with the larger cations occupying a greater space thus limiting the absolute amount of CO₂ adsorbed.

The CH₄ adsorption equilibria were greater than that of N₂, with the order of CH₄ adsorption equilibria being: K⁺ > Na⁺ > Rb⁺ > Li⁺ > Cs⁺ for the alkali cation exchanged samples. This compares to N₂ adsorption equilibria capacity being in the order of: Na⁺ > K⁺ > Rb⁺ > Li⁺ > Cs⁺. Yang and Armbruster studied the crystal structure of alkali metal cation exchanged heulandite. They confirmed the existence of cation coordinated positions for Rb⁺ and Cs⁺ adjacent to the framework in the 10 member ring in channel A, and within the centre of the 8 member ring in channel B [37]. Importantly, this means that the Mg²⁺

cations originally occupying the M(4) position in the middle of channel A are completely removed following cation exchange (see Table 3.4). Therefore, channel A is open and facilitates access of the studied gas molecules to the inner channels of the zeolite for adsorption. In comparison Li^+ is the smallest of the alkali cations, however the Li^+ exchanged clinoptilolite shows a lower adsorption capacity for both N_2 and CH_4 than most of the other alkali cations. This effect may be explained by also considering the presence of the natural Ca^{2+} , Mg^{2+} , and K^+ cations present in the Li^+ exchanged sample (see Table 3.4). It is likely that coordination of the Li^+ cations with the natural cations results in occupying positions within the channels which limits access to the studied CH_4 and N_2 gases.

The composition and distribution of the naturally occurring cations within the original starting clinoptilolite sample affects the adsorption properties of the sample following cation exchange. In this study, the parent clinoptilolite sample contained a distribution of Ca^{2+} , K^+ , Mg^{2+} , and Fe^{3+} cations, with no Na^+ cations. Kouvelos et. al. showed that samples originally rich in Na^+ cations and treated with an acid bath prior to the Li^+ cation exchange procedure showed higher uptake of CH_4 and N_2 compared to Na^+ form of clinoptilolite [54]. Natural clinoptilolite originally rich in Ca^{2+} cations and exchanged with Na^+ cations resulted in a reduced equilibrium adsorption capacity for CH_4 and inverse N_2/CH_4 equilibrium selectivity [56].

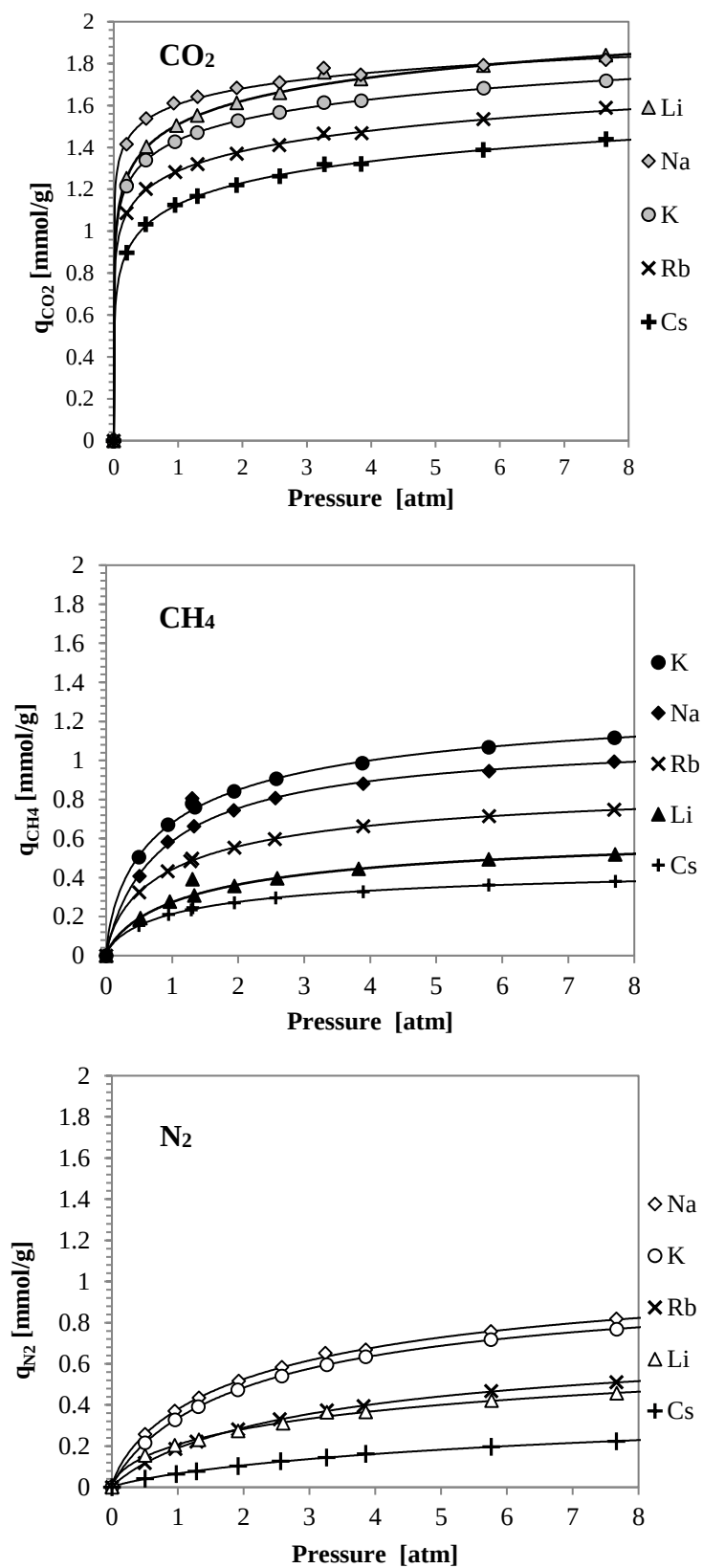


Figure 3.5. Experimentally determined adsorption isotherms with Toth model fit for CO₂ (top), CH₄ (middle) and N₂ (bottom) at 303K for acid treated and alkali +1 cation exchanged clinoptilolite samples.

3.5.3.3. ALKALINE EARTH METAL CATION EXCHANGED CLINOPTILOLITE

Figure 3.6 presents the single gas adsorption equilibrium isotherms performed at 303K for CO₂, CH₄, and N₂ gases on the alkaline earth metal cation exchanged samples. The alkaline earth metal cation exchanged clinoptilolite samples exhibit different gas adsorption behaviour compared to the alkali metal cation exchanged samples. The sequence of CO₂ adsorption for the different cation exchanged samples are as follows: Ba²⁺>Sr²⁺>>Be²⁺ ≈ Mg²⁺ >Ca²⁺. Similar trends are exhibited with the N₂ equilibrium adsorption capacity where the order of the adsorption capacity is as follows: Ba²⁺>Sr²⁺>>Mg²⁺>Be²⁺>Ca²⁺. Differences in CO₂ adsorption capacity were lower than those for CH₄ and N₂ gases.

The Ba²⁺ and Sr²⁺ cation exchanged clinoptilolite samples both have a noticeably higher adsorption capacity for all three studied gases compared to the exchanged samples with the three smaller alkaline earth cations. These two alkaline earth cations occupy different positions in the clinoptilolite than the smaller Mg²⁺, Be²⁺, and Ca²⁺ cations. Previous research contributions have shown that the Ba²⁺ cations occupy spaces adjacent to the framework in the vicinity of the M(1) and M(3) positions [42,86]. Similar observations have also been found for Sr²⁺ cations, with a greater preference for the M(1) position [87]. Since these cations occupy areas closer to the side of the channel, rather than the middle of it, the overall cavity volume accessible to the studied gases is likely higher. Additionally, the positioning of the Sr²⁺ and Ba²⁺ cations in the M(1) site and the large hydrated radii of these cations (Table 3.5) results in displacement and reduction of the Mg²⁺ cation (see Table 3.4) residing in the M(4) position, opening up channel A for gas adsorption. The result is an open channel A, which is associated with increased gas uptake during adsorption compared to the other cations.

The influence of the cation positions are demonstrated particularly with respect to the observed CH₄ adsorption equilibria where three distinct CH₄ adsorption isotherm patterns are observed in Figure 3.6. CH₄ adsorption capacity is in the order of: Ba²⁺ > Sr²⁺ >> Be²⁺ ≈ Mg²⁺ >> Ca²⁺. The Ca²⁺ clinoptilolite shows effective pore blocking of the channels, thereby limiting access of the larger CH₄ gas molecules to the pores through steric hindrance, an effect which is extensively described in detail in the literature[12,51]. This results in inverse equilibrium selectivity for N₂ over CH₄. The Mg²⁺ and Be²⁺ cation exchange varieties, along with the Sr²⁺ and Ba²⁺ clinoptilolites show similar behaviour as explained for the CO₂ and N₂ adsorption equilibria.

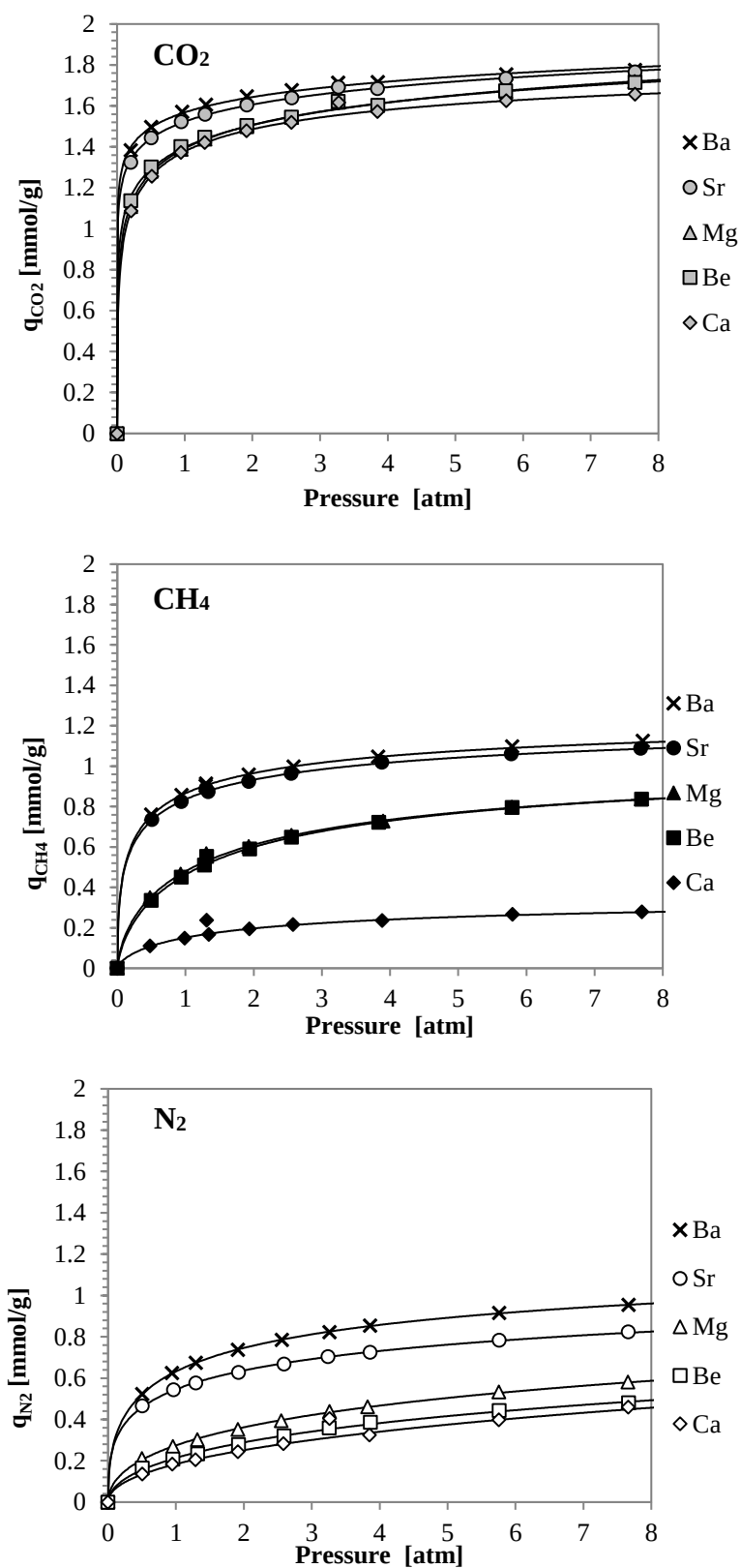


Figure 3.6. Experimentally determined adsorption isotherms with Toth model fit for CO_2 (top), CH_4 (middle) and N_2 (bottom) at 303K for alkaline earth +2 cation exchanged clinoptilolite samples.

3.5.3.4. TRANSITION METAL CATION EXCHANGED CLINOPTILOLITE

Figure 3.7 presents the single gas adsorption equilibrium isotherms determined at 303K for CO₂, CH₄, and N₂ gases on the transition metal cation exchanged clinoptilolite samples. The gas adsorption behaviour for these clinoptilolites is fairly complex, however some expected trends are followed such as the sequence of adsorption capacity which was CO₂ > CH₄ > N₂ in all cases. For each of the studied gases separately, the adsorption behaviour is confined to a narrow range on the samples exchanged with the +2 transition metal cations. It follows that these cations have very similar properties such as similar charge density and ionic radii (see Table 3.5).

The sequence of CO₂ adsorption for the different transition metal cation exchanged samples at higher loadings at 303K are as follows: Ni²⁺ ≈ Ce³⁺ > Zn²⁺ > Cu²⁺ > Fe³⁺. Overall the differences in adsorption capacity between the different cation clinoptilolite in this category were smaller compared to the other types of cation exchanged clinoptilolites, especially for CH₄ and N₂ gases.

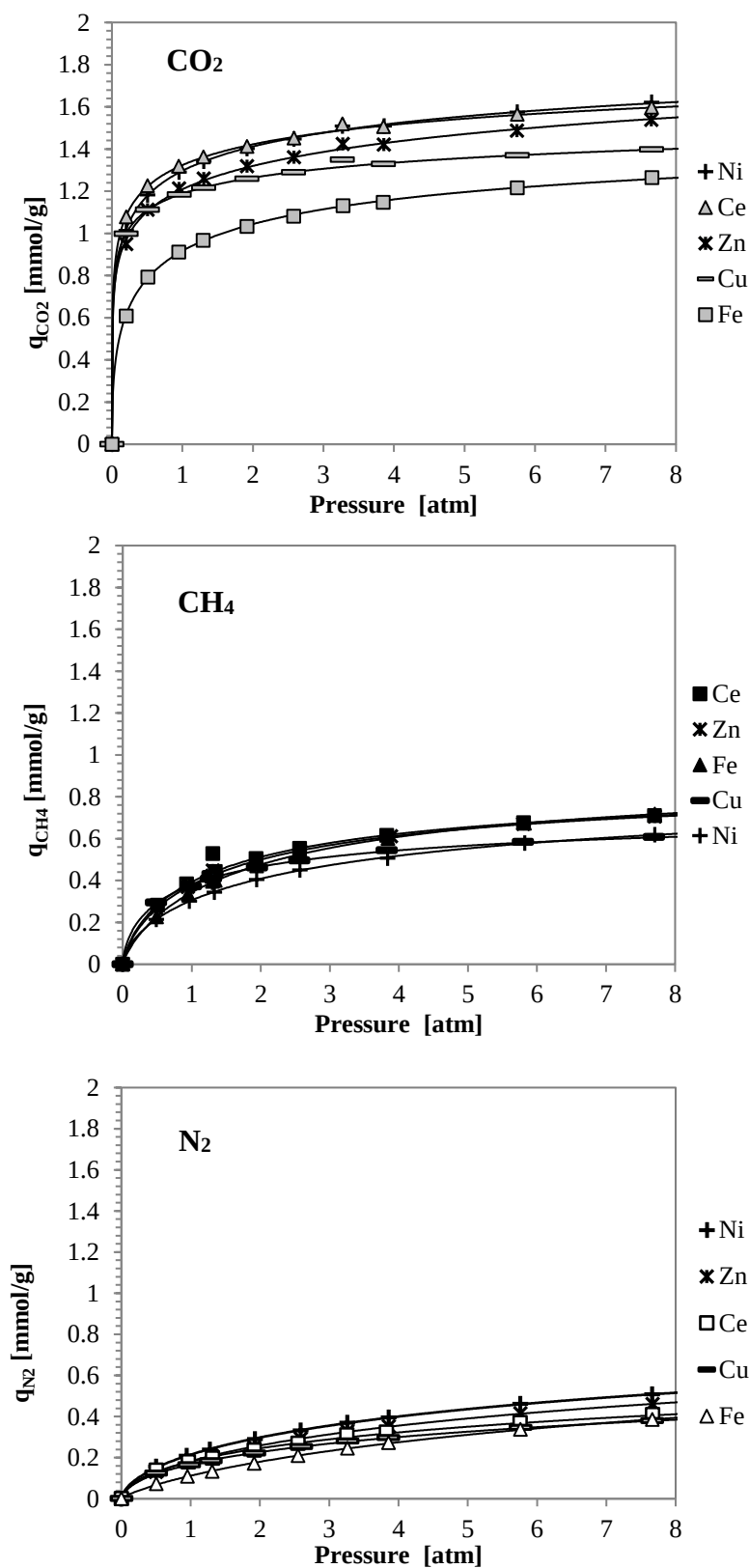


Figure 3.7. Experimentally determined adsorption isotherms with Toth model fit for CO_2 (top), CH_4 (middle) and N_2 (bottom) at 303K for transition metal cation exchanged clinoptilolite samples.

Table 3.6. Langmuir and Toth isotherm model parameters for pure component nitrogen, methane, and carbon dioxide adsorption isotherms on prepared cation-exchanged clinoptilolite samples at 303K.

ion-exchanged clinoptilolite sample		Langmuir Isotherm Parameters						Toth Isotherm Parameters								
		nitrogen		methane		carbon dioxide		nitrogen			methane			carbon dioxide		
		q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	n (-)	q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	n (-)	q _m (mmol ·g ⁻¹)	B (atm ⁻¹)	n (-)
raw clinoptilolite		0.721	0.686	1.019	1.154	1.579	4.958	1.178	1.184	0.474	1.087	1.425	0.482	2.168	513.0	0.288
Acid treatment H ⁺		0.925	0.263	1.077	0.706	2.049	1.893	4.325	0.391	0.281	1.454	1.245	0.549	2.904	318.7	0.269
exchanged alkali metal +1 cations	Li ⁺	0.607	0.470	0.594	0.835	1.916	3.760	1.880	1.822	0.279	0.692	1.211	0.680	2.632	1507	0.253
	Na ⁺	0.987	0.597	1.095	1.149	1.861	5.778	1.277	0.858	0.611	1.162	1.431	0.816	2.042	223.1	0.416
	K ⁺	0.959	0.522	1.216	1.276	1.813	2.997	1.094	0.765	0.605	1.436	2.517	0.606	1.950	219.8	0.396
	Rb ⁺	0.701	0.363	0.823	1.148	1.691	2.647	0.809	0.396	0.767	0.966	2.056	0.629	1.940	221.29	0.348
	Cs ⁺	0.387	0.177	0.423	0.995	1.501	2.369	0.575	0.201	0.604	0.519	1.841	0.594	1.894	261.1	0.316
exchanged alkaline earth metal +2 cations	Be ²⁺	0.615	0.470	0.939	0.953	1.663	8.825	1.605	2.565	0.287	1.159	1.742	0.593	2.118	305.9	0.342
	Mg ²⁺	0.702	0.585	0.946	1.061	1.819	3.773	2.110	4.394	0.259	1.189	2.341	0.540	2.148	284.5	0.332
	Ca ²⁺	0.680	0.370	0.329	0.557	1.601	8.443	1.682	2.301	0.275	0.393	1.679	0.582	2.108	266.1	0.330
	Sr ²⁺	0.915	1.143	1.119	3.254	1.861	6.868	1.368	6.099	0.398	1.250	6.246	0.621	2.010	154.7	0.421
	Ba ²⁺	1.001	1.712	1.140	3.329	1.825	6.462	1.761	13.46	0.329	1.286	6.308	0.640	2.007	267.9	0.401
exchanged transition metal cations	Fe ³⁺	0.654	0.190	0.855	0.653	1.341	1.967	1.076	0.165	0.607	0.992	0.826	0.718	1.789	53.92	0.342
	Ni ²⁺	0.656	0.443	0.727	0.676	1.729	2.505	2.423	1.155	0.278	1.089	1.424	0.482	1.982	157.3	0.359
	Cu ²⁺	0.492	0.433	0.654	1.381	1.453	7.031	1.930	1.344	0.262	0.799	3.519	0.548	1.494	81.02	0.462
	Zn ²⁺	0.621	0.373	0.803	0.876	1.599	3.653	1.875	0.623	0.332	0.953	1.355	0.651	1.850	38.19	0.432
	Ce ³⁺	0.511	0.501	0.799	0.952	1.533	9.526	1.742	1.750	0.274	0.938	1.520	0.653	1.862	76.19	0.431

3.5.4. IDEAL ADSORPTION SEPARATION FACTOR

Table 3.7 presents the calculated ideal adsorption equilibrium separation factors (α) determined using Equation 5 with the fitted Langmuir isotherm parameters shown in Table 3.6. The results show the strong influence of the different exchanged cations which are capable of altering the separation factors dramatically compared to the raw clinoptilolite sample. These observed differences show that the degree of energetic surface heterogeneity (influenced by the positioning and the type of the exchanged cation), and steric factors affect the adsorption behaviour.

The CO_2/N_2 ideal adsorption equilibrium separation factor is highest for the Ce^{3+} and Ca^{2+} exchanged clinoptilolite with a values of 57.0 and 53.6, respectively. This is over 3 times higher than the CO_2/N_2 separation factor for the raw clinoptilolite found in this work. These values are similar to those of other small pored zeolites summarized a review by Cheung and Hedin, including 4A and 5A zeolite, Li-chabazite, and zeolite T [88] and but lower than 13X zeolite[14,89]. With respect to potential CO_2/CH_4 separations, the highest CO_2/CH_4 ideal adsorption equilibrium separation factor is for the Ca^{+} clinoptilolite with a value of 73.6. This value is higher compared to other small pored zeolites which range from 3 to 17 for zeolite 4A, 2 to 10 for zeolite 5A, and 2 to 8 for chabazite and H-mordenite under comparable conditions [8,90]. However, this is lower than the reported values of about 43 and 177 for CaX and 13X determined at 313K [91]. As noted in the literature, regarding the Ca^{2+} clinoptilolite, the improved CO_2/CH_4 equilibrium separation factor comes at the expense of less desirable slower kinetics since access of the gases to the pores is restricted by the presence of the cation [54,92]. The CH_4/N_2 ideal adsorption equilibrium separation factor is the highest for the Cs^{+} and Fe^{3+} exchanged clinoptilolites, with values of 6.1 and 4.5, respectively. These values are over 2 times higher than the value for the raw clinoptilolite which was 2.4. This is of particular significance since many zeolites and activated carbons reported in the literature have calculated CH_4/N_2 equilibrium selectivity in the range of 1.7–5 for activated carbons, and 2.1 - 5 for zeolites under similar conditions[16,93–98].

The data from the presented experimental pure adsorption isotherms were then used to determine corresponding equilibrium selectivity values using Equation 6. The equilibrium selectivity values give a better idea of potential adsorbent separation performance by taking into consideration the shape of the individual isotherms as quantified by the adsorption capacity ratios at different pressures. The results are presented in Figure 3.8. For this analysis, the adsorption working capacity ratios were assessed for pressure ranges of 0.1 – 1 atm, and 1 – 10 atm for separations involving CH_4/N_2 , CO_2/CH_4 , and CO_2/N_2 . These calculated values are the highest for CO_2/N_2 separations, followed by CO_2/CH_4 and CH_4/N_2 separations.

The calculated CH_4/N_2 equilibrium selectivity values in Figure 3.8 for the Fe^{3+} and Cs^+ exchanged clinoptilolites are 13.9 and 20.6, respectively, in the vacuum region, and are 5.5 and 5.7, respectively, in the higher pressure region. These values for Cs^+ and Fe^{3+} clinoptilolite is comparable to that of silicalite calculated from our previous work, which ranges from 15.8 in the vacuum region to 7.3 in the pressurized region at 303K[61]. The Cs^+ cation has a lower charge density compared to the original Ca^{2+} , Mg^{2+} , or K^+ cations present in the raw clinoptilolite (see Table 3.5). As a result, increased CH_4/N_2 equilibrium selectivity for Cs^+ and Fe^{3+} cation exchanged clinoptilolite could be due to greater surface homogeneity and a lower surface charge distribution compared to the pure clinoptilolite. With respect the Fe^{3+} clinoptilolite, it is important to consider that the hydrated charge density of the Fe^{3+} cations is lower than Al^{3+} (see Table 3.5). Therefore possible dealumination and incorporation of Fe^{3+} cations within the zeolite lattice structure during the cation exchange procedure may result in a similar net change in the surface environment as Cs^+ clinoptilolite. A more homogeneous surface interacts with the non-polar CH_4 gas better than the N_2 gas with quadrupole moment, provided that CH_4 is not hindered by steric factors[92].

A similar explanation relates to the observed CO_2 and N_2 adsorption equilibrium selectivity shown in Figure 3.8. These values are by far the highest for the Cs^+ exchanged clinoptilolite with values ranging from 770 to 105, compared to 50 to 11 for raw clinoptilolite in the vacuum region and the higher pressure region, respectively. CO_2 gas has greater than 3 times the quadrupole moment strength and higher polarizability compared to N_2 [2]. In this case, CO_2 interacts strongly with framework surface for all of the modified clinoptilolites. The strong CO_2 surface interaction with clinoptilolite results in a much higher uptake in the vacuum region compared to N_2 . This is presented as a more rectangular isotherm shape for CO_2 , whereas the N_2 isotherm shape is more linear. This adsorption behaviour explains the great reduction in the experimental CO_2/N_2 equilibrium selectivity going from the vacuum region to the higher pressure region which is calculated from the CO_2 and N_2 gas working capacity values.

Additionally the CO_2/CH_4 equilibrium selectivity is also the highest for the Ca^{2+} cation exchanged clinoptilolite with values ranging from 269 to 53, in the vacuum region and in the higher pressure region, respectively. The location of the Ca^{2+} cation within the zeolite channels greatly limits the accessibility of the larger CH_4 gas molecule while not effecting the smaller CO_2 gas molecule, which explains the reduced CH_4 capacity. The same effect is also observed with respect to the Ca^{2+} clinoptilolite for potential CH_4/N_2 separations. Figure 3.8 shows that the CH_4/N_2 equilibrium selectivity is 0.55 for this material (inverse value is 1.8 for the N_2/CH_4 equilibrium selectivity). This confirms that Ca^{2+} clinoptilolite is more selective for N_2 over CH_4 as reported in the literature [12,56]. However, this N_2/CH_4 equilibrium selectivity for Ca^{2+} clinoptilolite is fairly low compared to other materials reported in the literature, such

as titanosilicate NaSr-ETS-4 and MIL-100(Cr) which range from 4 to 10 and 9 to 18, respectively, under similar conditions [5,30].

Table 3.7. Summary of the calculated ideal adsorption equilibrium separation factor (α) values determined from the pure component CO₂, N₂, and CH₄ isotherms at 303K.

Cation exchanged clinoptilolite sample	α_{CH_4/N_2}	α_{CO_2/CH_4}	α_{CO_2/N_2}
Raw	2.4	6.7	15.8
Acid treatment H ⁺	3.1	5.1	15.9
Li ⁺	1.7	14.5	25.3
Na ⁺	2.1	8.5	18.2
K ⁺	3.1	3.5	10.9
Rb ⁺	3.7	4.7	17.6
Cs ⁺	6.1	8.4	51.9
Be ²⁺	3.1	16.4	50.8
Mg ²⁺	2.4	6.8	16.7
Ca ²⁺	0.7	73.6	53.6
Sr ²⁺	3.5	3.5	12.2
Ba ²⁺	2.2	3.1	6.9
Fe ³⁺	4.5	4.7	21.2
Ni ²⁺	1.7	8.8	14.9
Cu ²⁺	4.2	11.8	49.9
Zn ²⁺	3.0	8.3	25.2
Ce ³⁺	3.0	19.2	57.0

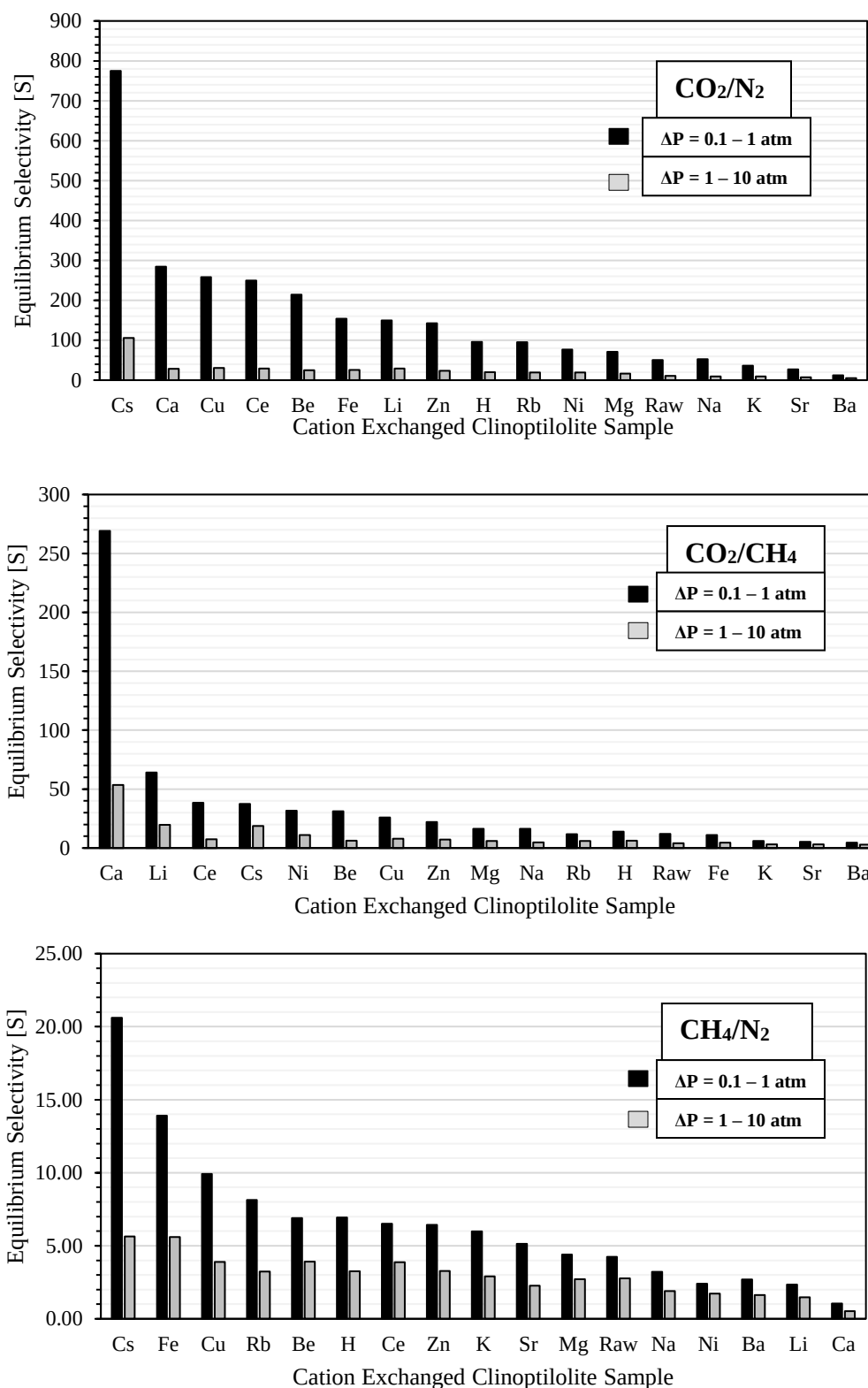


Figure 3.8. Experimentally determined adsorption equilibrium selectivity values for gas mixtures involving CO₂-N₂, CO₂-CH₄, and N₂-CH₄ with various prepared cation exchanged clinoptilolites at 303K.

3.5.6. KINETIC MODELLING and CH₄/N₂ KINETIC SELECTIVITY

Intra crystalline diffusion resistance is dominant in microporous zeolites such as clinoptilolite[99,100]. Therefore, it is important to understand the influence of adsorption mass transfer kinetics particularly with respect to the implications of potential diffusional limitations on possible PSA cycles[101]. Single gas adsorption uptake rates of CO₂, CH₄, and N₂ were studied on the cation exchanged clinoptilolites for a pressure step change of 0.5 to 1 atm at 303K. It is important to clarify the limitations of the accuracy of the reported kinetic rate constants due to the large pressure steps used for this analysis. It is likely that a significant influence of gas flows in the initial uptake phase results in less accurate measurements. Nonetheless, since the focus of this article is to provide a ranking of adsorbent materials, the resulting fractional uptake curves were used to assess the diffusional time constant from the LDF approximation given in Equations 3 and 4. The results are summarized in Table 3.8. The calculated diffusion time constants range from as low as $2.05 \times 10^{-5} \text{ s}^{-1}$ for CH₄ diffusion in Li⁺ clinoptilolite, to as high as $7.73 \times 10^{-3} \text{ s}^{-1}$ for N₂ diffusion in Rb⁺ clinoptilolite. The observed variability in diffusional uptake shows that the organization of the different cation distributions, the channel geometry, and the size of the diffusing gas effects the adsorption rate data, with N₂ (kinetic diameter = 3.6Å) or CO₂ (kinetic diameter = 3.3 Å) being the fastest and CH₄ (kinetic diameter = 3.8Å) having the slowest kinetics.

Figure 3.9 shows the experimental adsorption uptake rate curves and LDF model fit for CO₂, CH₄, and N₂ adsorption on the raw, acid treated, and selected cation exchanged (Li⁺, Fe³⁺, Ca²⁺) clinoptilolites. Using the raw clinoptilolite as a reference, the diffusion uptake rate follows the trend of N₂ > CO₂ >> CH₄. This trend is due to the random distribution of the naturally occurring cation mixture present within the raw sample. For the raw sample, Ca²⁺ occupies the M(1) and M(2) positions, K⁺ occupies the M(3) position and Mg²⁺ occupies the M(4) position. However, none of the cations are dominant, therefore all of the channels are only partially blocked. Since the pore structure of clinoptilolite is two dimensional, this cation arrangement gives greater resistance to diffusion of the larger CH₄ molecule within the pores [10]. For the Ca²⁺ cation exchanged clinoptilolite, the increased amount of Ca²⁺ cations within channels A and B, and the continued presence of K⁺ and Mg²⁺ cations (Table 3.4) results in limited access to the channels for both N₂ and CH₄, as indicated by the slower observed transport diffusivity. A similar channel blocking effect is observed in the case of the Li⁺ clinoptilolite, whereby the cation arrangement offers little diffusional resistance to N₂ compared to CH₄. Conversely, the acid treated clinoptilolite (H⁺ exchanged one) showed faster adsorption uptake for all three gases compared to the raw sample. This is reflective of the more open pore structure as a result of the acid treatment thereby decreasing the microporous diffusion resistance[9].

CH₄ is thermodynamically favoured over N₂ for adsorption equilibria onto the clinoptilolite surface. This explains the higher equilibrium adsorption capacity compared to N₂ in most cases as shown in Figures 3.5, 3.6, and 3.7. Nonetheless as shown in Table 3.7, the CH₄/N₂ equilibrium ideal adsorption equilibrium separation factor is quite modest for many of the clinoptilolite samples. Despite this limitation, some research contributions have proposed employing cation exchanged clinoptilolites for possible kinetic separations of CH₄-N₂ gas mixtures[9–11,50]. Since CH₄ is a larger molecule, it is more kinetically hindered than N₂ due to some of the cation positions within the channels of the two dimensional clinoptilolite structure[10,54]. This reduces the ability of the CH₄ to diffuse within the channels and access the adsorption sites. This is reflected in the order of magnitude difference in the observed adsorption rate between N₂ and CH₄ in the raw clinoptilolite, and some of its cation exchanged derivatives as shown in Table 3.8. The net result is that the kinetic selectivity is the reverse of the equilibrium selectivity and it favors nitrogen over methane [9,10,54,55,95,102].

In Figure 3.10, the overall diffusion coefficients for Li⁺, Ca²⁺, and raw clinoptilolite are presented as a function of the total amount adsorbed for N₂ and CH₄ gases. The observed transport diffusivity values increase as loading increases for both gases (the exception being N₂ gas on raw clinoptilolite where the observed transport diffusivity decreased slightly). This trend is largely consistent with the findings of Ackley and Yang for various clinoptilolites whereby it was postulated that a combination of slow and rapid microporous diffusion occurs within the parallel channels of the clinoptilolite [11]. N₂ is the smaller gas molecule, therefore gas transport occurs more rapidly than CH₄ since it has more access to the channels that facilitate rapid transport diffusivity. Microporous materials such as clinoptilolite initially induce a resistance on the movement of gas particles. At higher loadings the transport of the gases increases due to a greater frequency of both intermolecular and surface interactions with the zeolite.

Figure 3.11 presents the N₂/CH₄ ideal kinetic selectivity values calculated using Equation 7. As expected, the acid treated clinoptilolite has the lowest N₂/CH₄ kinetic selectivity (≈ 1) which can be explained by the more open pore structure of this material. The Li⁺ and Ni²⁺ clinoptilolites have higher kinetic selectivity compared to the raw clinoptilolite with values of 105 and 35, respectively. In previous studies, each of Mg²⁺, Na⁺, Sr²⁺, Ce³⁺, and mixed Na⁺-Li⁺ exchanged clinoptilolites have been shown to have improved kinetic selectivity in favour of N₂ over CH₄ compared to that of natural clinoptilolite [9,50,54–56]. Both Ackley et al. and Jayaramen et al. reported that Mg²⁺ exchanged clinoptilolite had the highest N₂/CH₄ kinetic selectivity[9,56]. Jayaramen et al. also showed lower kinetic selectivity for Li⁺ clinoptilolite compared to that of purified clinoptilolite which is opposite of the observed findings in this study. Importantly in those studies, the quantity of naturally occurring cations in the raw clinoptilolite starting material was in the order of Na⁺ > K⁺ > Ca²⁺ > Mg²⁺ [50,56]. In this study, the cation content in the original raw clinoptilolite was different. The order of the naturally occurring cations in this study was

$\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} \gg \text{Na}^+$. The results from this study suggest that the starting cation type, content, and distribution within the natural clinoptilolite plays an important role in determining the outcome of the adsorbent kinetic effects upon cation exchange.

Table 3.8. Diffusion time constants for pure nitrogen, methane, and carbon dioxide adsorption on cation-exchanged clinoptilolite samples determined at 303K with a pressure step change from 0.5 to 1 atm using the LDF approximation.

ion-exchanged clinoptilolite sample		$D_e/R_p^2 \text{ (s}^{-1}\text{)}$		
		nitrogen	methane	carbon dioxide
raw clinoptilolite		4.35×10^{-3}	1.12×10^{-4}	2.55×10^{-4}
Acid treatment	H^+	4.70×10^{-3}	3.83×10^{-3}	1.61×10^{-3}
exchanged alkali metal +1 cations	Li^+	3.92×10^{-3}	2.05×10^{-5}	3.50×10^{-4}
	Na^+	3.93×10^{-4}	3.44×10^{-4}	3.60×10^{-3}
	K^+	2.15×10^{-3}	7.53×10^{-4}	2.52×10^{-3}
	Rb^+	7.73×10^{-3}	6.42×10^{-4}	7.16×10^{-4}
	Cs^+	4.94×10^{-3}	4.16×10^{-4}	2.19×10^{-3}
exchanged alkaline earth metal +2 cations	Be^{2+}	2.83×10^{-3}	2.55×10^{-4}	5.32×10^{-4}
	Mg^{2+}	6.34×10^{-3}	1.37×10^{-4}	6.09×10^{-4}
	Ca^{2+}	8.39×10^{-5}	3.66×10^{-5}	1.01×10^{-4}
	Sr^{2+}	6.72×10^{-3}	5.67×10^{-4}	5.37×10^{-4}
	Ba^{2+}	2.83×10^{-3}	4.43×10^{-3}	7.41×10^{-4}
exchanged transition metal cations	Fe^{3+}	2.93×10^{-3}	2.48×10^{-3}	2.68×10^{-3}
	Ni^{2+}	4.89×10^{-3}	8.32×10^{-5}	4.29×10^{-3}
	Cu^{2+}	3.54×10^{-3}	6.46×10^{-4}	3.43×10^{-4}
	Zn^{2+}	5.47×10^{-3}	5.67×10^{-4}	5.99×10^{-4}
	Ce^{3+}	3.49×10^{-3}	5.49×10^{-5}	1.42×10^{-3}

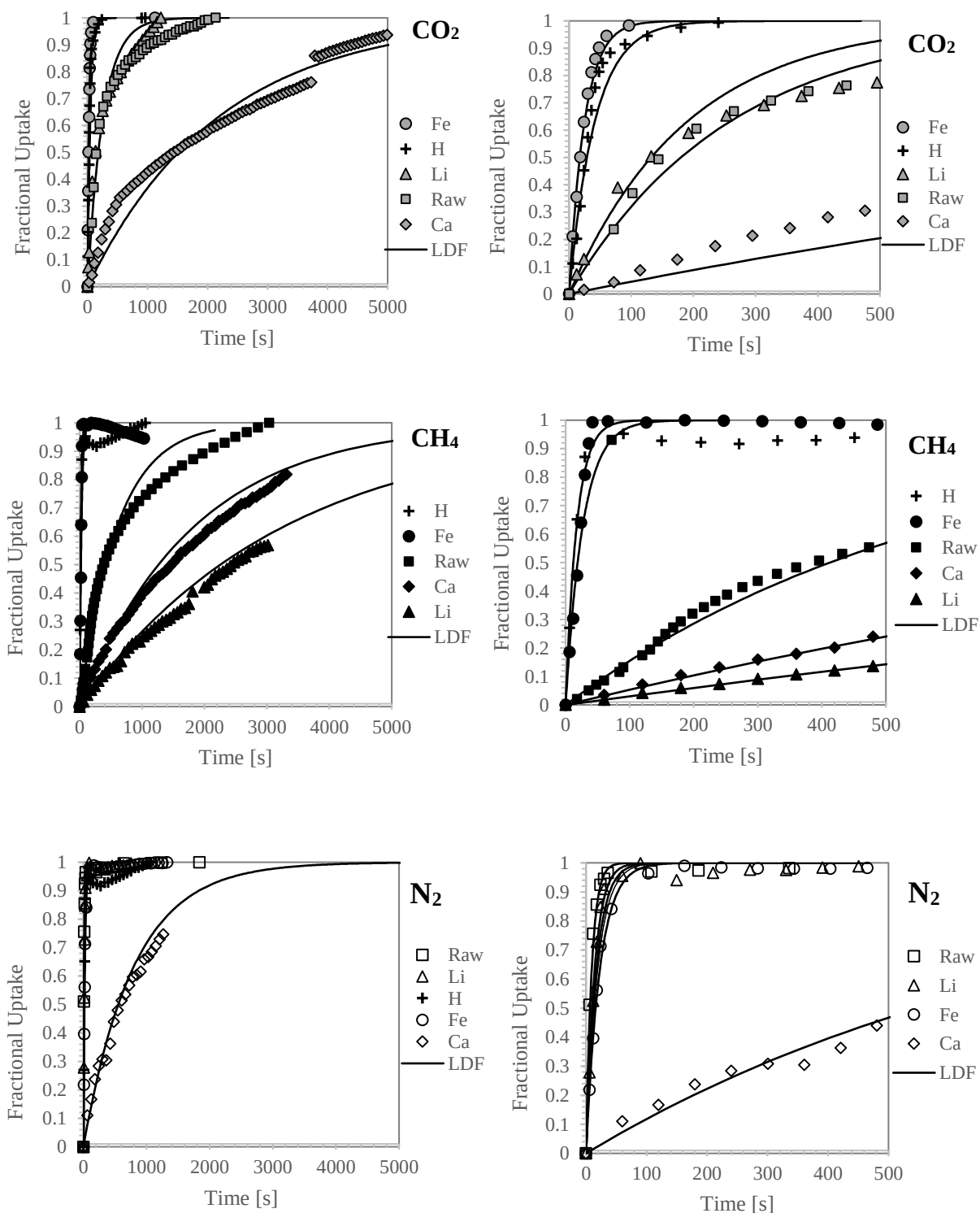


Figure 3.9. Experimental adsorption fractional uptake rate curves and fitted LDF model for selected pure carbon dioxide (top), methane (middle), and nitrogen (bottom) adsorption on prepared clinoptililite samples determined at 303K with a pressure step change from 0.5 to 1 atm. The plots on the left are for the long time, the plots on the right are for the short time.

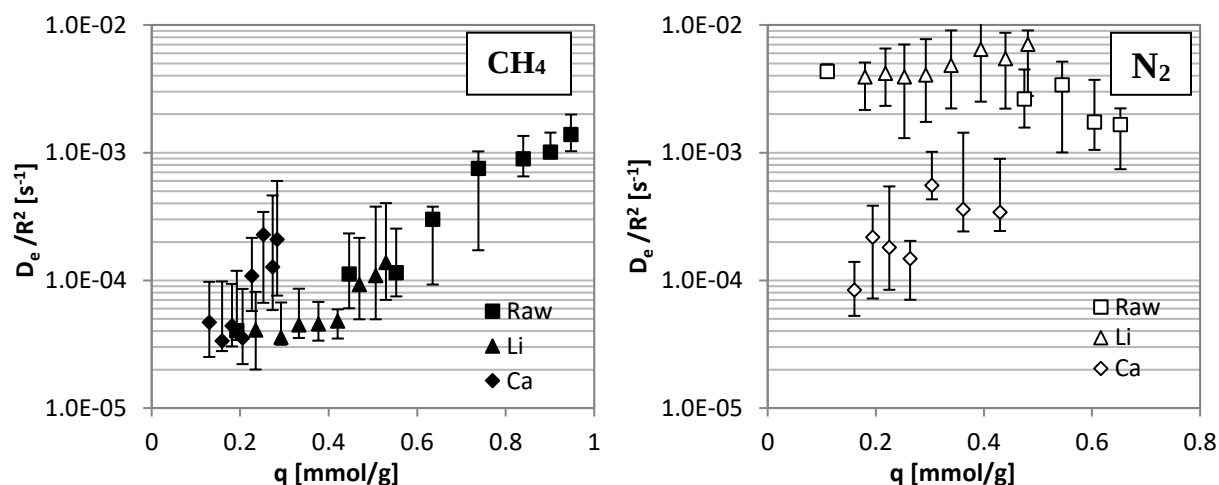


Figure 3.10. Experimentally determined diffusion time constants as a function of total adsorbate concentration for pure nitrogen and methane on raw, Li^+ , and Ca^{2+} clinoptilolite samples determined at 303K.

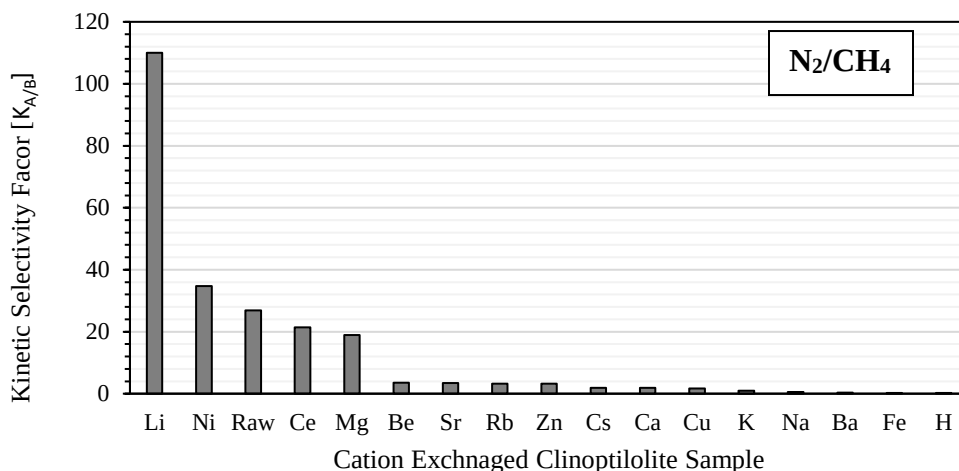


Figure 3.11. Experimentally determined kinetic selectivity factors for kinetic gas separations involving N_2 - CH_4 with various prepared cation exchanged clinoptilolites at 303K. The mass transfer coefficients obtained from the uptake data from a pressure step change of 0.5 to 1 atm was used.

3.6. CONCLUSIONS

The influence of acid treatment and cation exchange modifications of natural clinoptilolite using monovalent, bivalent, and trivalent cations was studied. The compositional and structural properties of the samples were assessed using EDS and XRD analysis. Cation exchange is shown to slightly alter the structure of the clinoptilolite and/or the extra framework atomic positions within the unit cell, as quantified by small changes observed in peak intensity of the XRD diffractograms. This is particularly evident following the substitution of the more acidic cations H^+ , Li^+ , Be^{2+} , Mg^{2+} , and Fe^{3+} . Dealumination of the zeolite lattice and incorporation of Fe^{3+} into the framework structure is hypothesized based upon the high amount of Fe^{3+} exchanged and the higher Si/Al ratio of 5.85 compared to a value of 5.1 for the naturally occurring raw clinoptilolite.

The adsorption characteristics of pure CO_2 , N_2 , and CH_4 gases were measured for all of the clinoptilolite samples. Langmuir and Toth isotherms were fitted to the experimental adsorption equilibrium data and the resultant parameters of these isotherms were determined. Diffusion time constants were assessed using the LDF approximation of the experimental gas uptake rate data. The positioning and type of charge balancing cations greatly influences the adsorption characteristics of the studied gases on the modified clinoptilolites compared to the original raw clinoptilolite. The results from this study establish that the starting cations found within the natural clinoptilolite influence the outcome of the adsorption equilibria and kinetic effects following cation exchange.

The adsorption equilibrium separation factor, and the kinetic selectivity factor were used for assessing the adsorbent performance for all of samples. This screening analysis shows that Cs^+ exchanged clinoptilolite has superior performance for possible CH_4/N_2 and CO_2/N_2 equilibrium separations. While the Ca^+ exchanged clinoptilolite exhibits promising equilibrium selectivity for CO_2/CH_4 , this comes at the expense increased microporous diffusion resistance for both CO_2 and CH_4 . Both Li^+ and Ni^{2+} clinoptilolites show favourable kinetic selectivity for possible N_2/CH_4 kinetic separations.

3.7. NOMENCLATURE

a, b, c	unit cell coordinate parameters	[Å]
B	adsorption affinity constant	[atm ⁻¹]
D_e	effective (transport) diffusivity	[m ² /s]
D_e/R_p^2	diffusion time constant	[s ⁻¹]
k_{LDF}	kinetic rate constant	[s ⁻¹]
$K_{A/B}$	kinetic selectivity	[dimensionless]
n	dimensionless Toth model parameter	[dimensionless]
P	pressure	[atm]
q	adsorption capacity	[mmol/g of adsorbent]
$q(t)$	amount absorbed at time t	[mmol/g of adsorbent]
q_e	adsorption capacity at equilibrium	[mmol/g of adsorbent]
q_m	adsorption capacity at saturation	[mmol/g of adsorbent]
R_p	radius of particle	[m]
t	time	[s]
T	temperature	[K]
S	adsorption equilibrium selectivity	[dimensionless]
X	mole fraction in the gas phase	[dimensionless]
Y	mole fraction in the gas phase	[dimensionless]

Subscripts

A	component A
B	component B

Greek Symbols

α	ideal adsorption equilibrium separation factor	[dimensionless]
β	unit cell angle between a-c coordinates	[°]
θ	adsorption surface coverage	[dimensionless]

Abbreviations

BDDT	Brunauer, Deming, Deming, and Teller
CMS	carbon molecular sieve
EDS	electron dispersive spectroscopy
HEU	heulandite
IZA	international zeolite association
MOF	metal organic framework
PSA	pressure swing adsorption
LDF	linear driving force
VSA	vacuum swing adsorption
XRD	x-ray diffraction

3.8. REFERENCES

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CHAPTER 4

Cation Exchange Modification of Clinoptilolite – Thermodynamic Effects on Adsorption Separations of Carbon Dioxide, Methane, and Nitrogen

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ABSTRACT

This study details an experimental analysis of the thermodynamics of adsorption equilibrium behaviour of pure CO₂, CH₄, and N₂ gases on raw, Fe³⁺, Ca²⁺, and Cs⁺ cation exchanged clinoptilolite. Equilibrium adsorption isotherms were experimentally determined for CO₂, CH₄, and N₂ at three different temperatures ranging from 303K up to 363K, at pressures up to 8.0atm using the microgravimetric technique. Kinetic adsorption uptake data was measured at different temperatures for CH₄ and N₂ gases, and the results were compared for raw and Ca²⁺ clinoptilolite. Heat of adsorption values were calculated for all three gases on the studied clinoptilolite samples using the chromatographic method. These results were compared to the isosteric adsorption enthalpies determined from the adsorption isotherms at different temperatures. The isosteric heat of adsorption was the highest for CO₂ followed by CH₄, and N₂. Temperature dependent Sips, Toth, and Dual-Site Langmuir isotherm models were fitted with experimental data and selectivity factor values were calculated for CO₂/CH₄ and CH₄/N₂ gas separations using the regressed isotherm models. Ca²⁺ clinoptilolite shows the best potential for CO₂/CH₄ separations due to its high selectivity. However, higher temperatures are needed in order to compensate for the slow kinetic behaviour. For potential CH₄/N₂ separations, Fe³⁺ clinoptilolite displays both high equilibrium selectivity values and less variability compared to Cs⁺ clinoptilolite over a broader range of temperatures and pressures.

Key Words:

Cation exchanged clinoptilolite, adsorption, CO₂, N₂, CH₄, gas separation

4.1. INTRODUCTION

Natural gas currently represents almost one quarter of global energy consumption[1]. While long term predictions suggest that renewable energy will one day replace fossil derived resources, growing demand for natural gas is expected to result in a 30 % increase in consumption through to 2030[2]. This trend has been driven by increased consumer demand and improved economic viability of previously entrapped unconventional natural gas sources through advanced extraction techniques. While raw natural gas contains predominately CH₄ (80 – 95%), a number of different components including CO₂ (typically <5%) and N₂ (typically <10%) are also present in natural gas mixtures among many others[3]. Some of these additional gases would need to be removed depending on the local conditions of the natural gas field relative to gas composition and heating value regulatory standards. Inert gases such as N₂ are to be rejected from the bulk gas to increase the heating value of the natural gas fuel and to improve the compression efficiency by reducing the total gas volume. Additionally, CO₂ is to be removed as a means to prevent freezing and corrosion within the gas processing and delivery equipment.

4.1.1. CO₂ and N₂ REMOVAL from NATURAL GAS TYPE MIXTURES

Conventionally, CO₂ removal from natural gas is achieved using aqueous amine absorption scrubbing, whereas excess N₂ is rejected using cryogenic distillation technologies[4]. These methods are capable of achieving high equilibrium selectivity, however they both have several process disadvantages[5]. Some concerns with respect to amine absorption include: environmental concerns resulting from fugitive amine emissions and operation issues regarding premature process equipment corrosion. Additionally, a large amount of energy is required to achieve solvent regeneration temperatures for CO₂ stripping and for cooling to liquefaction temperatures in the case of nitrogen rejection. Production of sub-quality natural gas from remote locations, unconventional sources, or degraded fields requiring enhanced production techniques such as N₂ gas injection puts additional strain on these separation methods[6]. This is because the per-volume gas processing efficiency decreases rapidly with lower capacity. Additional gas treatment costs are incurred based on the volume of CO₂ and N₂ gas to be removed from the natural gas mixture. These limitations facilitate the need to explore alternative processing technologies capable of reducing the CO₂ and N₂ volume in raw gas feed. Pressure swing adsorption (PSA) and Vacuum Swing Adsorption (VSA) are proposed as possible alternative solutions for separation of CO₂ and N₂ from natural gas type mixtures. These technologies are particularly attractive for smaller scale field processing volumes and for treating nitrogen-rich natural gas streams[7,8]. Additionally, sources of fugitive methane emissions from appreciably lower quality stocks including coal-bed gas, coal-mine ventilation gas, as well as biogas are also targets for CH₄ enrichment through PSA processes due to the high volume of contaminants CO₂ and/or N₂ gases. For a pressure swing adsorption

process directed towards natural gas upgrading, there exists a desirability of having the CH_4 as the least adsorbed component so that it remains in the high pressure raffinate stream following the adsorption step. While not absolutely essential, this configuration reduces the mechanical work needed to re-pressurize the refined CH_4 gas.

4.1.1.1. ADSORBENTS for CO_2 REMOVAL from CH_4

Several adsorbent materials have been proposed and screened for the separation CO_2 from CH_4 including various zeolite types[9–18], activated carbons[19–26], metal organic frameworks (MOFs) [27–34], and many others[5]. Enhanced CO_2 selectivity has been achieved using novel amine surface functionalized adsorbents[23,35–39]. However, thermally induced structural degradation and reactive deactivation of the supported amine in the presence of common natural gas contaminants has shown to effect the long term stability of these materials[40–42]. With respect to MOFs, while exceptional CO_2 adsorption capacities have been reported, the vulnerability of metal – ligand framework to moisture, and thermal degradation is well documented and has been the subject of several contributions[43–48]. Therefore, zeolites and activated carbons are still considered advantageous in this regard due to their better temperature and chemical stability. Kacem, et al. directly screened and compared the function of various zeolites and activated carbons for the separation of CO_2 - CH_4 mixtures[49]. Generally, activated carbons exhibit higher CO_2 loadings at high pressures compared to zeolites (5A and 13X), whereas the zeolites showed higher CO_2/CH_4 equilibrium selectivity at low to moderate pressures, especially in the vacuum pressure region. Experimental cyclic PSA studies ($T = 298\text{K}$, $P = 1 - 30 \text{ atm}$) showed repeatable reversability for both material types after 2 – 3 cycles, with CH_4 purity and recoveries being higher for zeolite 13X compared to activated carbon for an equimolar CO_2 - CH_4 gas feed mixture[49]. Similarly, Cavenati, et al. proposed a VPSA system ($T = 299\text{K}$, $P = 0.05 - 5 \text{ atm}$) which showed that CH_4 recoveries of greater than 80% were possible for a (60% CH_4 + 20% CO_2 + 20% N_2) mixture, giving a CH_4 product purity of about 80% using 13X zeolite[9]. To date, several successful commercial adsorption based applications for CO_2 / CH_4 separation have been implemented most involving the use of activated carbons or some other proprietary adsorbent material. A review conducted by Rufford, et al. presents an excellent summary of these commercialized technologies[5].

4.1.1.2. ADSORBENTS for N_2 REMOVAL from CH_4

In most cases, CH_4/N_2 adsorption equilibrium selectivity is only moderate and typically ranges between 2.1-5.5 for activated carbons[50,51] and 1.3-1.7 for many zeolites[52,53] under standard conditions. However, CH_4 is larger than N_2 (kinetic diameter is $3.84\text{\AA}$ for CH_4 vs. $3.60\text{\AA}$ for N_2), therefore microporous adsorbents with a similarly small pore size have also been explored for this separation. Small pored adsorbents compound the effect of steric limitations and have a favourable

influence on inducing a desired N_2/CH_4 gas separation[54]. Microporous materials such as zeolite 4A [55], chabazite[55,56], mordenite[55,57], clinoptilolite[58–60], carbon molecular sieve [26,61–63] (CMS), and MOF[64] have all been studied in this regard. However, most are moderately CH_4 equilibrium selective, but have high N_2/CH_4 kinetic selectivity. In some cases, equilibrium selectivity for CH_4 over N_2 can be reversed such that N_2 is the more adsorbed component. This is the case with titanosilicate ETS-4, whereby the pore size of this material may be tailored to achieve preferential adsorption of smaller gases such as N_2 over larger gases such as CH_4 or C_2H_6 [65]. Guild Associates' Molecular Gate Adsorption Technology® remains the benchmark for commercial N_2/CH_4 selective adsorption based separations using proprietary synthetic titanosilicate ETS-4 adsorbents[65].

4.1.1.3. CLINOPTILOLITES for CO_2 and N_2 REMOVAL from CH_4

Clinoptilolite is a zeolite which has high cation exchange capability [60,66,67]. To that end, several gas adsorption equilibria and diffusion studies have been conducted to explore the effect of different cation exchanged clinoptilolite types on the potential gas separations including CH_4 upgrading[58,68–74]. While 13X zeolite has been given much of the attention for CO_2/CH_4 separations, Arefi Pour et al. directly compared natural clinoptilolite and 13X zeolite for this separation[74]. 13X zeolite showed slightly better equilibrium selectivity than natural clinoptilolite; however systemic cation exchange may improve its CO_2/CH_4 separation performance. The work of Yang and coauthors is amongst the most detailed and thoroughly investigated in this regard for natural clinoptilolite and its cation exchanged derivatives[58,60,75–77]. Results from these studies showed that different cation exchange combinations may result in favourable N_2/CH_4 selective properties with comparable separation performance to that of titanosilicate ETS-4[76,77]. In the case of CH_4 selective adsorption, clinoptilolite cation-exchanged with H^+ , Fe^{3+} , Cs^+ , K^+ have shown improved CH_4/N_2 equilibrium selectivity [71,75,78]. However, a notable key issue with some of these materials have been the reported slow diffusion kinetics [58,70,75,79–81]. Frankawitz and Donnelly pointed out that this tends to reduce the performance efficiency of the material in a dynamic PSA environment, especially for CH_4/N_2 separations. However, acid treated clinoptilolite successfully opens the pores leading to greater CH_4 adsorption, and faster uptake kinetics[75,78]. Similar effects have also been observed for both Cs^+ and Fe^{3+} exchanged clinoptilolite that showed improved adsorption kinetics for CH_4 over natural and Ca^{2+} exchanged clinoptilolite[71].

4.1.2. OBJECTIVES

Several modified forms of clinoptilolite show potential for improved separations involving CO_2 , CH_4 , and N_2 gas mixtures. However, only a limited number of studies have investigated the effects of temperature on the adsorption properties and all of these studies have been limited to natural

clinoptilolite[72,81,82]. Results from our previous work showed improved separation potential using Ca^{2+} , Cs^+ , and Fe^{3+} clinoptilolite for these gases[71]. Given the large temperature and pressure distributions present in current natural gas processing facilities, it is prudent to establish the effectiveness of these materials over a broad range of operating conditions. Therefore, in this study, these cation exchanged clinoptilolite types were screened and compared to the natural clinoptilolite for the adsorption separation of CO_2 , CH_4 , and N_2 gases at different temperatures and relatively high pressures.

4.2. MATERIALS and CHARACTERIZATION

Natural clinoptilolite was purchased from Ash Meadows Zeolite LLC (Amargosa, NV, USA). The clinoptilolite was received in the powdered form (+140 US. Std. mesh) or as small granules and was sourced from natural deposits located in Amargosa Valley, Nevada in USA. All gases that were used for the experimental analysis were purchased from Linde Canada Ltd. (Ottawa, Ontario, Canada) and had the following specifications for purity: 99.999% for He, 99.999% for N_2 , 99.99% for CH_4 , and 99.99% for CO_2 . The following reagents were used to carry out the cation exchange process: calcium chloride (CaCl_2 , 96.0%, EMD Chemicals Inc., Gibbstown, NJ, USA), cesium chloride (CsCl , 99.0%, Sigma-Aldrich Canada Co., Oakville, Ontario, Canada), and iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%, BDH Inc., Toronto, Ontario, Canada). The granular clinoptilolite was crushed to a 60 x 80 US. Std. mesh size prior to commencing the experiments. The adsorbent was washed with deionized water and underwent a cation exchange procedure in the same manner as described in our previous study[71].

In our previous contribution, we verified the phase structure and elemental composition of the clinoptilolite samples using powdered x-ray diffraction (XRD) analysis and electron dispersive spectroscopy (EDS) respectively[71]. The predominant cations present in the original clinoptilolite sample are Ca^{2+} , Mg^{2+} , and K^+ . Cation exchange was confirmed for all three clinoptilolite variants (Ca^{2+} , Cs^+ , and Fe^{3+}). Standard N_2 sorption experiments were performed at 77K using a Micromeritics ASAP – 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA). The samples were degassed under high vacuum for 8 hours at 200°C prior to the experimental analysis. The specific surface area was then calculated from the N_2 sorption data at 77K, using the Brunauer – Emmett – Teller (BET) method [83]. The micropore volumes were calculated using the Horvath – Kawazoe (HK) approach [84,85].

4.3. METHODS and ANALYSIS

4.3.1. EXPERIMENTAL SET-UP and PROCEDURE

The equilibrium and kinetic adsorption properties for the clinoptilolite samples were measured using a microgravimetric analyser (VTI Corp., Hialeah, Florida, USA). Samples were independently

exposed to CO₂, CH₄, and N₂ gases at three different temperatures (303K, 323K, and 343K for Cs⁺, Fe³⁺ and raw clinoptilolite; 323K, 343K and 363K for Ca²⁺ clinoptilolite). The adsorbents were exposed to the sample gases at increasing pressures ranging from 0 to 10 atm. For each pressure step, the dynamic adsorption uptake was monitored as the change in sample weight as a function of time using a Cahn microbalance. Each equilibrium adsorption measurement was recorded once the sample weight stabilized following a pressure step change. The equilibrium criteria was set to less than 0.015 wt% weight change over a period of 15 minutes. The reversibility of the adsorption process was tested for each sample through measuring desorption isotherms. High purity helium gas was used for each equilibrium adsorption measurement to correct for buoyancy effects. A detailed account of this experimental technique is provided in our previous contributions [51,71].

The concentration pulse chromatography technique was used to determine the CO₂, CH₄, and N₂ Henry's Law adsorption constants (K_p) [86–89]. These experiments were performed using a modified GOW-MAC Series 400 gas chromatograph (GC) equipped with a thermal conductivity detector purchased from GOW-MAC Instrument Co. (Bethlehem, Pennsylvania, USA). Granular clinoptilolite samples (particle size = 180- 250 μ m) were packed into custom made column (L = 3.4 cm, I.D. = 0.18 cm) and were installed in the GC. The samples were first regenerated over a period of 12h overnight at 523K using helium as the purge gas with a flowrate of 8sccm. In this case, since helium exhibits only highly limited adsorption behavior, it is assumed to be non-interacting[90]. Therefore, helium was used as the carrier gas with a flow rate of 4sccm for all experiments and 1 atm pressure (negligible pressure drop was measured across the packed column). Following the regeneration step, the system temperatures were adjusted using either the GC oven for higher temperatures or an insulated water-cooled coil installed around the column for lower temperatures. For the CO₂ experiments, the experimental temperature range was 428 – 563 K, and for the CH₄ and N₂ experiments, the temperature range was 288 – 363K. The packed sample columns were independently exposed to CO₂, CH₄, and N₂ gases by injecting a single 0.1 cc volume pulse of these pure gases into the column. Table 4.1 shows the details of the experimental setup for the concentration pulse chromatography experiments. The complete experimental setup and procedure has been described in our previously published papers [51,91].

Table 4.1. Details of the single gas experimental specifications for the concentration pulse chromatography experiments.

Column	Length Inner diameter Packing type Packing mesh size Void fraction determined with 60 x 80 US Std. mesh glass beads Sample gas injection volume	3.4 0.18 Raw, Ca ²⁺ , Cs ⁺ , Fe ³⁺ clinoptilolite 60 x 80 180-250 0.39 0.1	cm cm US Std. mesh μ m d'less cc
Henry's Law Constant Experimental	Carrier gas Sample gases Total carrier gas flowrate Total pressure Temperatures (CH ₄ and N ₂ experiments) Temperatures (CO ₂ experiments)	He CO ₂ , CH ₄ , N ₂ 4 1.0 288, 303, 318, 333, 348, 363 428, 443, 458, 473, 488, 503, 518, 533, 548, 563	sccm atm K K
Regeneration	Purge Gas Used Regeneration Temperature Regeneration Pressure Regeneration Time	He 563 1 12	K atm h

4.3.2. DATA ANALYSIS

For the chromatographic experiments, the gas concentration (c) is expressed in the form of a voltage signal and is measured at the column outlet. The sample gas injections create a disturbance in the adsorption equilibrium inside the adsorbent packed columns. Following the gas injection, the concentration at the column outlet is measured as a function of time. The mean retention time of the injected gas (μ) may thus be determined by using Equation 1: [88,92,93]

$$\mu = \frac{\int_0^{\infty} c(t - \mu_D) dt}{\int_0^{\infty} c dt} = \frac{L}{v} \left[1 + \frac{(1 - \epsilon)K}{\epsilon} \right] \quad (1)$$

The calculated mean retention time is directly related to the dimensionless Henry's Law constant (K) by using the packed bed parameters such as porosity (ϵ), bed length (L), and fluid velocity (v), according to Equation 1. The dimensional adsorption Henry's Law constant (Kp) is determined from a conversion factor dependant on the system temperature (T) and the adsorbent pellet density (ρ_p) as shown in Equation 2.

$$K_p = \frac{K}{RT\rho_p} \quad (2)$$

The dimensional K_p values are measured at different temperatures. The limiting heat of adsorption (ΔH) is thus calculated from the slope of the van't Hoff plot ($\ln K_p$ vs. $1/T$) as shown in Equation 3, where K_0 is the pre-exponential constant for Henry's law constant, K , and R is the gas constant.

$$K = K_0 e^{\left[\frac{-\Delta H}{RT}\right]} \quad (3)$$

To properly model the experimental adsorption isotherms across different temperatures, an accurate representation of the adsorption characteristics is required. In this study, the equilibrium adsorption data was regressed using the Sips, Toth, and Dual-Site Langmuir isotherm models which are shown in Equations 4 through 6, respectively. These isotherms are more flexible than the Langmuir approach, as they account for greater heterogeneity and non-uniformity with respect to adsorbent surfaces[94–97].

$$\theta = \frac{q}{q_m} = \frac{BP^{1/n}}{1+(BP)^{1/n}} \quad (4)$$

$$\theta = \frac{q}{q_m} = \frac{BP}{[1+(BP)^n]^{\frac{1}{n}}} \quad (5)$$

$$q_i = \frac{q_{mA}B_{iA}P}{1+B_{iA}P} + \frac{q_{mB}B_{iB}P}{1+B_{iB}P} \quad (6)$$

Here, θ is the fractional coverage; q_m is the saturation adsorption capacity; B is the Langmuir affinity constant [98]. For the Sips and Toth isotherms, the n parameter is dimensionless and represents limited site availability at increasing surface concentration. The subscripts A and B represent adsorption sites A and B which are independent of each another.

Adsorption is an exothermic process, therefore the effect of temperature must be considered since adsorption processes are non-isothermal and any change in the column temperature will affect the adsorption capacity. The q_m , B , and n parameters as functions of temperature for the temperature dependent Sips and Toth isotherm models (given in Equations 4 and 5) are shown in Equations 7 through 9 [98].

$$B = B_0 e^{\left[\frac{Q}{RT_0}\right]\left[\frac{T_0}{T}-1\right]} \quad (7)$$

$$q_m = q_{m0} e^{\chi\left[1-\frac{T}{T_0}\right]} \quad (8)$$

$$n = n_0 + \alpha_n \left[1 - \frac{T}{T_0}\right] \quad (9)$$

Here, B_0 is the adsorption affinity constant at reference temperature T_0 , q_{m0} is the saturation adsorption capacity at T_0 , and n_0 is the parameter n at T_0 , whereas χ and α_n are constant parameters. Substitution of Equations 7 through 9 into Equations 4 and 5 will give six parameter functions where the parameters (B_0 , Q , q_{m0} , χ , n_0 , α_n) are obtained by regressing the model to fit the experimental data obtained at different temperatures.

Similarly, the temperature dependent parameters for the Dual-Site Langmuir model are described in Equations 10 and 11.[99]

$$q_m = k_1 - k_2 T \quad (10)$$

$$B = k_3 e^{\left[\frac{k_4}{T}\right]} \quad (11)$$

The k_1 , k_2 , k_3 , and k_4 constants are thus determined by fitting experimental data obtained at different temperatures. The model that best described the experimental data was determined by the lowest sum of the squared residuals (SSR).

The adsorbate-adsorbent interactions at different temperatures manifest itself in the isosteric heat of adsorption which is a good indicator of the adsorption strength[100]. The isosteric heat of adsorption, ΔH , is calculated at zero fractional loading as shown in Equation 3. Under the Langmuir assumption ΔH is constant, as it is considered to be independent of surface coverage. In reality, the isosteric heat of adsorption may be slightly variable, as it is effected by the local surface heterogeneity and additional molecular interactions which occur at higher loadings. This effect may be observed by calculating the ΔH directly from experimental isotherms at different temperatures using the Clausius-Clapeyron equation.

$$\left(\frac{\Delta H_{iso}}{R}\right) = \left(\frac{\partial \ln P}{\partial \left(\frac{1}{T}\right)}\right)_q \quad (12)$$

According to this equation, the change in natural logarithm of pressure (P) with respect to the change in inverse temperature (T) at constant q is related to heat of adsorption. ΔH is determined from the slope of the plot of $\ln(P)$ against $1/T$ at constant q .

Adsorption kinetics is an important factor to consider when evaluating adsorbent performance, as well. In our previous paper, we showed that the Linear Driving Force (LDF) model can be an acceptable tool to rapidly quantify the kinetic uptake data for comparison purposes between different materials[71]. The LDF model is shown in Equation 13a [82,94,100–105].

$$\frac{\partial q}{\partial t} = k_{LDF}(q_e - q(t)) \quad (13a)$$

$$k_{LDF} \approx \frac{15D_e}{R_p^2} \quad (13b)$$

The dynamic system response to a pressure step change is measured as the change in q as a function of time, t . The uptake rate, dq/dt , is plotted as a function of $(q_e - q(t))$ at different times, and the slope of this plot gives the mass transfer coefficient, k_{LDF} , that is specific to the system. As shown in Equation 13b, k_{LDF} , can be interpreted as diffusion time constant, D_e/R_p^2 , to better reflect intracrystalline diffusion within the zeolite [100]. However, as reported by others, this method is only valid strictly for comparison purposes and has no practical application in overall PSA design due to existing limitations inherent with respect to the measuring approach[55,102].

Regarding screening for a particular gas separation, as first step is to determine the ideal single gas equilibrium selectivity, $\alpha_{1/2}$. This may be crudely calculated as the ratio of the pure component adsorption capacities (q_1 and q_2) at the same temperature and pressure for gases 1 and 2 [28,55]. While convenient, caution should be used with this approach is highly simplistic and limited in scope to the actual conditions as it assumes that there is no interaction between the different gases that are adsorbed.

$$\alpha_{1/2} = \frac{q_1}{q_2} \quad (14)$$

4.4. RESULTS and DISCUSSION

Figure 4.1a presents the experimental adsorption-desorption isotherms as a function of relative pressure for N₂ at 77 K on the raw and cation exchanged clinoptilolite samples. N₂ was used to assess the pore distribution of the material. It should be noted for future studies other potential probe gases may be more desirable since in this case N₂ is one of the adsorbing species being studied in this investigation. The N₂ adsorption – desorption behaviour is similar for all of the clinoptilolite types and shares the similar characteristics as others have reported in the literature [66,81]. It may be summarized as follows: At low relative pressures (P/P_0 below 0.1) an initial increase in N₂ adsorption is observed. Between the values of $0.1 < P/P_0 < 0.8$ the N₂ adsorption isotherms stay relatively consistent and only begin to increase quickly again at relative pressures greater than 0.8. Desorption behaviour shows the presence of a hysteresis loop at relative pressures in the range of $0.5 < P/P_0 < 1$ for all of the clinoptilolite types. The increase in N₂ adsorption at low relative pressure is expected for these materials and shows presence of microporosity. Whereas, the shape of the adsorption curve above relative pressures of 0.8 indicates the presence of mesopores and macropores. The hysteresis loop, is characteristic of clinoptilolites samples, and can be attributed to factors such as multilayer adsorption and capillary condensation within the mesopore space [55].

The micropore size of clinoptilolite is only slightly larger than the size of N₂. Therefore, at the experimental temperatures of 77K, N₂ diffusion within the pores of clinoptilolite is difficult, which may result in a reduction in the measured adsorption N₂. This means that the estimated surface area calculated using the BET model may not account for all of the micropore space. While the HK and BET methods may not accurately depict the adsorbent surface characteristics, they can still present valuable information, and have thus been used by many contributions in the literature. A summary of the calculated pore properties and surface area of the adsorbents is provided in Table 4.2. As can be seen from this Table, the calculated BET surface area is the highest for Fe³⁺ variant compared to the other forms of clinoptilolite. This trend is indicative of the limited access of N₂ to the micropores as previously discussed. Figure 4.1b shows the distribution of the micropore volume for raw, Ca²⁺, Cs⁺, and Fe³⁺ cation exchanged clinoptilolite determined from the N₂ sorption experiments using the Horvath-Kawazoe (HK) method. The calculated effective micropore volume for the different types of clinoptilolite is in the order of: Fe³⁺ > raw $\approx$ Cs⁺ > Ca²⁺. From Figure 4.1b, it is clear that the Fe³⁺ cation exchanged clinoptilolite likely has a more open micropore structure compared to the other three types of clinoptilolite studied, thus allowing access to N₂.

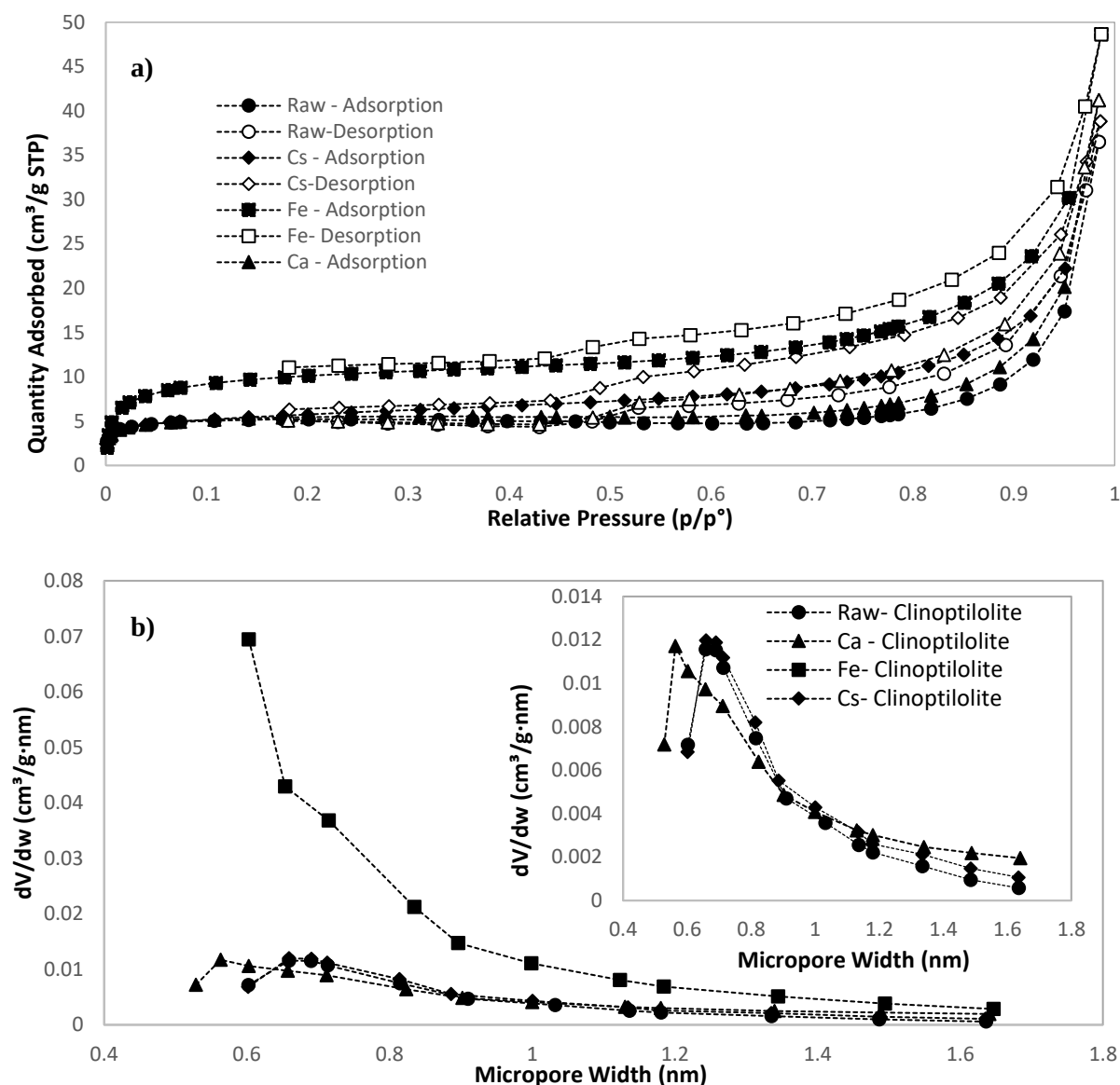


Figure 4.1. a) N_2 adsorption (solid symbols) –desorption (open symbols) isotherms for raw, Ca^{2+} , Cs^+ , and Fe^{3+} cation exchanged clinoptilolite at 77K. b) Distribution of the micropores for raw, Ca^{2+} , Cs^+ , and Fe^{3+} cation exchanged clinoptilolite determined from the sorption experiments with N_2 at 77K using the HK distribution method.

Table 4.2. BET surface area, HK micropore volume, and total pore volume for raw, Ca^{2+} , Cs^+ , and Fe^{3+} cation exchanged clinoptilolite determined from the sorption experiments with N_2 at 77K.

Sample	BET Surface area (m^2/g)	HK Micropore volume (cm^3/g)	Micropore area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter ($\text{\AA}$)
raw clinoptilolite	19.0861	0.007068	15.7022	0.054171	292.213
Cs – clinoptilolite	18.8545	0.006262	13.9378	0.060032	288.338
Fe – clinoptilolite	121.1814	0.046986	18.1502	0.068392	168.991
Ca - clinoptilolite	20.4073	0.003460	12.6242	0.061328	188.150

4.4.1. PURE COMPONENT CO_2 , CH_4 and N_2 ADSORPTION EQUILIBRIA

The pure CO_2 , CH_4 , and N_2 adsorption isotherms were determined for raw, Ca^{2+} , Cs^+ , and Fe^{3+} cation exchanged clinoptilolite at different temperatures for pressures up to 8 atm. Figures 4.2 through 4.4 show these experimental adsorption isotherms and the temperature dependant (TD) Toth, Sips, and Dual-Site (DS) Langmuir model fits for each adsorbent. Table 4.3 presents the calculated parameters for these adsorption isotherm models. The accuracy of these models is assessed using the SSR values between the calculated and experimental results. All of the experimental adsorption isotherms conform to the expected behaviour: adsorption capacity is shown to increase with increasing pressure and decreasing temperature.

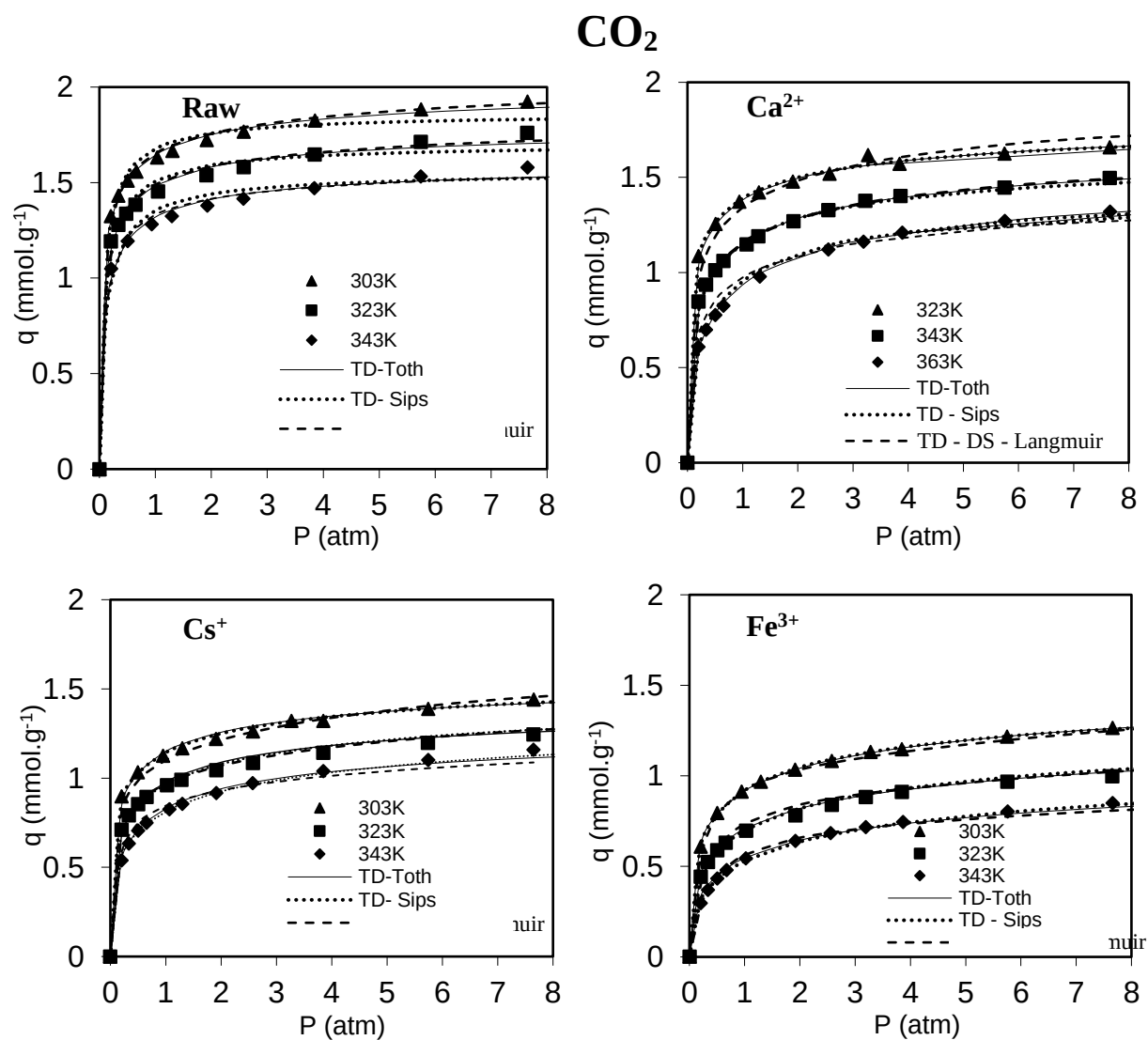


Figure 4.2. Experimentally determined adsorption isotherms for CO₂ at different temperatures for raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged samples. The experimental data points were fitted with temperature dependant Toth, Sips, and Dual Site Langmuir models.

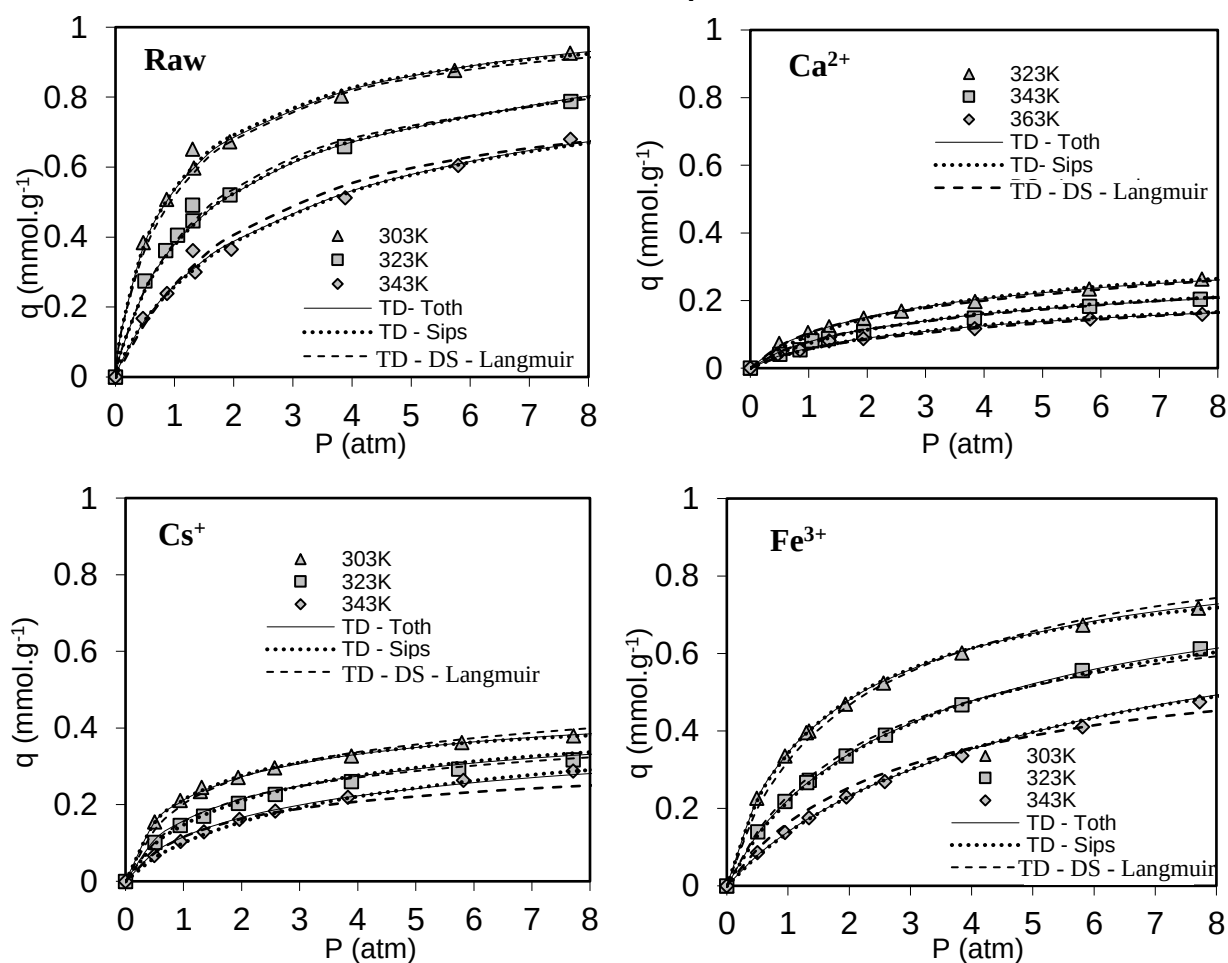


Figure 4.3. Experimentally determined adsorption isotherms for CH₄ at different temperatures for raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged samples. The experimental data points were fitted with temperature dependant Toth, Sips, and Dual Site Langmuir models. *

*Caution - It should be noted that in the case of Ca²⁺ and raw clinoptilolite due to the slow kinetics of CH₄ adsorption within these materials, the experimentally determined adsorption isotherm values may not have achieved total equilibrium.

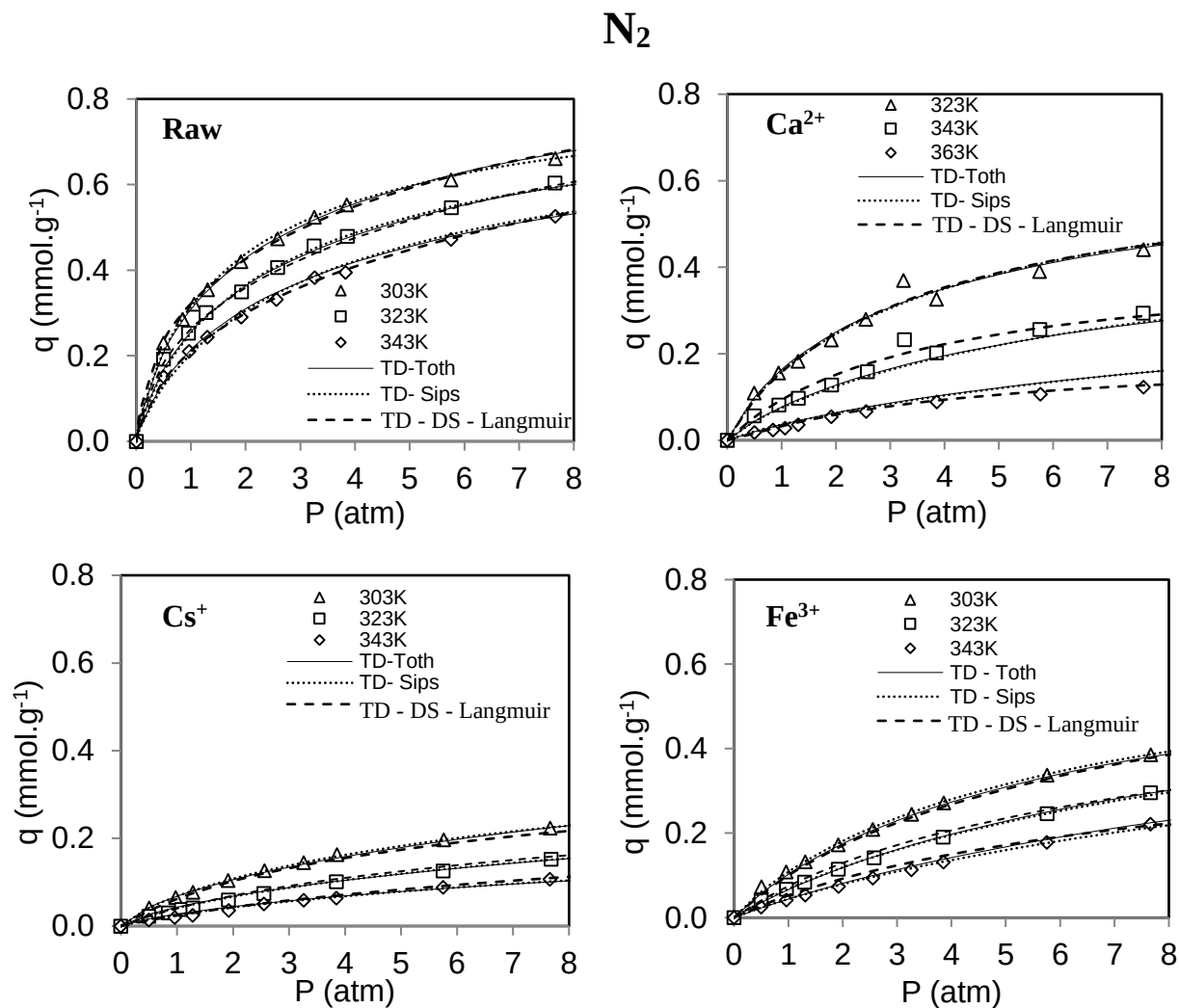


Figure 4.4. Experimentally determined adsorption isotherms for N_2 at different temperatures for raw clinoptilolite compared to Fe^{3+} , Ca^{2+} , and Cs^+ exchanged samples. The experimental data points were fitted with temperature dependant Toth, Sips, and Dual Site Langmuir models.

Table 4.3. Temperature dependent Sips, Toth, and Dual Site Langmuir model parameters for CO₂, CH₄ and N₂ adsorption on raw clinoptilolite and Ca²⁺, Cs⁺, and Fe³⁺ cation-exchanged clinoptilolites.

Model	Parameter	Clinoptilolite Type											
		Raw			Ca ²⁺			Cs ⁺			Fe ³⁺		
		CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂
TD – Toth	n _o (mmol/g)	0.493	0.692	0.574	0.434	0.617	0.740	0.405	0.538	0.316	0.315	0.757	0.870
	α _n	0.851	0.025	0.001	0.000	0.003	0.002	0.045	0.194	0.175	0.002	0.200	0.002
	χ	1.759	0.493	0.948	0.811	2.986	3.659	1.279	0.598	4.605	2.179	0.019	0.066
	T ₀ (K)	303.15	303.15	303.15	323.15	323.15	323.15	303.15	303.15	303.15	303.15	303.15	303.15
	Q(kJ/mol)	20.995	26.951	9.440	39.150	7.293	33.321	21.374	25.362	13.160	21.820	29.769	20.785
	q _{mo} (mmol/g)	2.061	1.168	1.122	1.911	0.462	0.743	1.697	0.564	2.133	1.883	0.978	0.736
	b ₀ (atm ⁻¹)	77.376	1.616	0.848	77.376	0.505	0.374	77.391	1.969	0.116	77.389	0.778	0.175
SSR		0.031	0.003	0.003	0.008	0.001	0.013	0.012	0.001	0.002	0.004	0.001	0.001
TD – Sips	n _o (mmol/g)	1.155	1.175	1.207	2.088	1.100	1.136	2.494	1.301	1.248	2.059	1.090	1.075
	α _n	0.007	0.003	0.000	1.188	0.000	0.000	0.001	0.755	0.001	0.001	0.389	0.006
	χ	1.347	0.669	0.451	1.674	3.343	3.429	0.636	0.057	2.620	1.668	0.658	0.464
	T ₀ (K)	303.15	303.15	303.15	323.15	323.15	323.15	303.15	303.15	303.15	303.15	303.15	303.15
	Q(kJ/mol)	6.916	22.190	11.451	12.921	3.653	29.695	13.067	23.689	15.041	14.127	24.329	20.228
	q _{mo} (mmol/g)	1.867	1.084	0.882	1.879	0.388	0.717	1.766	0.477	0.515	1.612	0.890	0.710
	b ₀ (atm ⁻¹)	8.782	0.984	0.555	2.833	0.325	0.283	1.832	0.803	0.152	1.325	0.623	0.180
SSR		0.084	0.004	0.005	0.014	0.002	0.014	0.013	0.002	0.002	0.003	0.002	0.001
TD - DS Langmuir	K ₁₁ (mmol/g)	1.465	1.199	0.815	1.838	0.871	3.778	2.470	1.343	1.070	3.639	2.030	1.643
	K ₂₁ (mmol/g K)	0.004	0.001	0.000	0.004	0.002	0.010	0.005	0.003	0.001	0.009	0.005	0.004
	K ₃₁ (atm ⁻¹)	0.103	0.009	0.008	0.153	0.056	0.147	0.415	0.102	0.006	0.005	0.009	0.036
	K ₄₁ (K)	274.6	1337.2	906.8	274.6	854.4	200.4	1053.2	704.2	100.6	610.0	1330.0	85.17
	K ₁₂ (mmol/g)	3.847	1.227	0.862	3.917	395.51	0.515	2.755	2.640	1.217	3.578	1.594	1.593
	K ₂₂ (mmol/g K)	0.0071	0.0036	0.0018	0.0082	0.0047	0.0015	0.0069	0.0067	0.0032	0.0083	0.0040	0.0040
	K ₃₂ (atm ⁻¹)	1.5085	0.6486	0.0232	1.5380	0.0000	0.6339	0.0574	0.0099	0.0113	0.0482	0.0384	0.0516
	K ₄₂ (K)	660.4	843.3	1503.6	660.4	894.0	354.0	373.8	109.0	1003.0	1406.1	433.3	493.42
SSR		0.044	0.009	0.001	0.073	0.001	0.007	0.035	0.005	0.001	0.020	0.009	0.003

Looking down each column in Table 4.3, the SSR values for each model fit are directly compared for each individual isotherm. Among the three isotherm models used in this study, in most cases the experimental adsorption data is better represented by the TD -Toth model as shown in Table 4.3 where the lowest SSR values are highlighted for each isotherm. In principle, the extra parameters used with Dual-Site Langmuir model should give this isotherm model greater flexibility compared to the other isotherm types. However, the temperature dependent parameters for the Dual-Site Langmuir model that have been proposed in the literature and thus used in this study are inherently more restrictive compared to those of the TD Toth and Sips equations. This temperature variance is represented as a linear function for the DS Langmuir model and is limited only to changes in the adsorption affinity parameter and saturation adsorption capacity with temperature. This is compared to the temperature variation being modelled as an Arrhenius type relationship for the Sips and Toth isotherms. Additionally, this behaviour is extended to not only the B and q parameters, but also the dimensionless surface parameter, n , for the Sips and Toth isotherms. It is supposed that the DS Langmuir model may be modified in a similar context, particularly as it relates to the q parameter. However, this will result in an isotherm equation which is far more complicated than that depicted in Equations 6, 10, and 11 and is beyond the scope of this current study. In its current form, the temperature dependence in the q_m parameter is modelled as a linear function. This function inherently implies that at some temperature the saturation adsorption capacity will be negative, which is not possible. Since the temperature dependence can only be modelled accurately over a limited temperature range, careful attention must be given to ensure that the results are thermodynamically consistent.

As can be seen in Figures 4.2 through 4.4, the adsorption behaviour of the different gases on the clinoptilolite samples is different, which is typical for this material [58,59,75,77,81,106]. In general, CO_2 is the most adsorbed gas on the clinoptilolite, followed by CH_4 and then N_2 , (the exception being Ca^{2+} clinoptilolite where more N_2 is adsorbed compared to CH_4). This behaviour is influenced by both the characteristics of the modified zeolite and the properties of the adsorbate; both of which ultimately govern the effect of the adsorption interaction parameters[11,94]. Tables 4.4 and 4.5 show the relevant properties of the adsorbed gases and the zeolite extra framework cations which are important to better understand their implication on the experimental observations.

Table 4.4. CO₂, CH₄, and N₂ gas properties[107].

Gas	Kinetic diameter (Å)	Polarizability ($\times 10^{-25} \text{ cm}^3$)	Quadrupole moment ($\times 10^{-26} \text{ esu} \cdot \text{cm}^2$)
CO ₂	3.33	26.5	4.30
CH ₄	3.80	26.0	0
N ₂	3.64	17.6	1.52

Table 4.5. Physical properties of the zeolite extra framework cations [108,109].

Cation	Effective Ionic Radius (Å)	Hydrated Radius (Å)	Charge to Ionic Radius Ratio
Fe ³⁺	0.55	1.40	5.45
Mg ²⁺	0.72	1.50	2.78
Ca ²⁺	1.00	1.80	2.00
Na ⁺	1.02	1.80	0.98
K ⁺	1.38	2.20	0.72
Cs ⁺	1.67	2.60	0.59

As shown in Table 4.4, CO₂ has a larger polarizability and quadrupole moment compared to CH₄ and N₂ which result in greater electrostatic potential for CO₂. Therefore, the higher capacity for CO₂ gas can be explained by the quadrupole interaction with the cations present on the zeolite surface. However, the trend in CO₂ adsorption is nuanced, whereby the sequence of adsorption on the clinoptilolite is in the following order: Fe³⁺ < Cs⁺ < Ca²⁺ < Raw. Some factors that influence CO₂ adsorption behaviour include the cation type and the distribution in relation to the zeolite framework. These cations impact the surface electrostatic potential and local acid/base environment[110–112]. The raw clinoptilolite exhibits the greatest amount of CO₂ adsorption. The composition and distribution of cations within the raw clinoptilolite consist of a mix of alkali and alkali earth cations (predominately Mg²⁺, Ca²⁺, and K⁺) whereby none of the cations are dominant. The cationic variability induces increased surface charge heterogeneity which is conducive to stronger electrostatic interactions. This is supported by the fact that the raw clinoptilolite also shows the highest adsorption capacity for both CH₄ and N₂ in comparison to all of the other cation exchanged variants studied as well. In contrast, Fe³⁺ clinoptilolite has the lowest CO₂ capacity, despite being the smallest cation with the greatest charge density among the studied cations. This behavior runs counter to previous reports which show that in general, smaller extra framework cations (H⁺) result in greater CO₂ adsorption on zeolites[111]. CO₂ is a moderate Lewis acid, therefore its

adsorption behaviour is dictated by the local acid–base surface properties of the zeolite. Extra framework cations provide acid sites and the framework oxygen atoms nearest to the cation act as basic sites. The charge of a particular site is influenced by the position and type of extra framework cation in relation to the framework oxygen atoms [110–112]. In principle, three negative framework charges are required to be balanced with each individual Fe^{3+} cation. However, transition metal cations such as Fe^{3+} may react to form additional oxygen containing compounds onto the zeolite surface [113–115]. To the best of our knowledge, this behaviour has not been documented in the case of Cs^+ or Ca^{2+} cation exchanged zeolite variants. This means that for the Fe^{3+} clinoptilolite, there is likely increased opportunity for basicity of the framework. It has also been hypothesized that the zeolite framework may be partially dealuminated following Fe^{3+} cation exchange as evidenced by changes in the Si/Al ratio and decreased crystallinity observed through XRD [71]. It is likely that the combination of these effects results in the total amount adsorbed being the lowest for CO_2 on the Fe^{3+} clinoptilolite.

It is evident that the overall adsorption capacity of CO_2 on the Cs^+ clinoptilolite is lower than the raw clinoptilolite. The Cs^+ cation is the largest and has the lowest charge density of the studied cations exchanged into the clinoptilolite. These combined effects, in addition to the large molecular weight of Cs^+ may be detrimental to the overall CO_2 uptake [74,111]. Based on this behavior, it is likely that the Cs^+ cation is occupying the space within the pore cavity but is not actually blocking the channels. While this limits the overall gas uptake, it has little effect on the microporous diffusion resistance to the same extent as Ca^{2+} clinoptilolite as documented in our previous study. [71]

The adsorption of CH_4 on the clinoptilolite is in the following order: $\text{Ca}^{2+} < \text{Cs}^+ < \text{Fe}^{3+} < \text{Raw}$, whereas the adsorption of N_2 is in the order of $\text{Cs}^+ < \text{Fe}^{3+} < \text{Ca}^{2+} < \text{Raw}$. Both CO_2 (3.33 Å) and N_2 (3.64 Å) are smaller than CH_4 (3.80 Å). With respect to Ca^{2+} clinoptilolite, CH_4 adsorption is restricted since it cannot access the pores at all. [70,81] Therefore, for the Ca^{2+} clinoptilolite it is likely that the pore aperture is limited due to the positioning of the Ca^{2+} cation within the channels. With the exception of the Ca^{2+} clinoptilolite, preferential adsorption of CH_4 compared to N_2 is observed for all clinoptilolite types, and follows similar patterns as the CO_2 adsorption mechanism. Since clinoptilolite has a variable surface charge distribution, the higher polarizability of CH_4 means that it has a greater tendency to form instantaneous dipoles with the surface. This effect allows for greater surface occupancy compared to N_2 .

4.4.2. ADSORPTION KINETICS

Microporous diffusion resistance is dominant for natural clinoptilolite and many of its derivatives [79,106]. For gas separations involving CH_4 the influence of the dynamic behaviour on the adsorption separation performance for this material is profound. Some studies even report N_2/CH_4 kinetic

selectivity to be in the 100's for Mg^{2+} , Ni^{2+} , or Li^{+} cation exchanged clinoptilolite among many [59,71,106]. In this study, with respect to the Cs^{+} and Fe^{3+} clinoptilolite, the studied adsorbates are known to diffuse with less resistance within the micropores and have little if any kinetic selectivity[71]. Therefore, the channels are likely not as obstructed by the presence of the extra framework Cs^{+} or Fe^{3+} cations to the same extent as the raw or Ca^{2+} clinoptilolite. Since, CH_4 is the slowest adsorbing of the studied gases[60,71]; this essentially presents the lower limit for diffusional uptake. Slower kinetic behavior elongates the effective adsorption/desorption propagation fronts and contributes to reduced separation performance in dynamic adsorption environments. Figure 4.5 depicts the kinetic adsorption uptake rates in response to a pressure step change for CH_4 and N_2 on raw and Ca^{2+} modified clinoptilolite. The corresponding diffusion constants for CH_4 are presented and these values are compared to N_2 at different temperatures for raw and Ca^{2+} clinoptilolite. Due to the modest CH_4/N_2 adsorption equilibrium selectivity for raw and Ca^{2+} clinoptilolite, the influence of the molecular dynamics becomes more meaningful for this separation. There is a positive correlation between the microporous diffusion rate and temperature which is to be expected based upon the increased kinetic energy of the molecules. For CH_4 , Some notable diffusional resistance exists for the raw clinoptilolite which is likely due to the mix of cations present in the natural deposits. The diffusion constants for both gases are the lowest for the pore blocking Ca^{2+} exchanged clinoptilolite, as can be seen from Figure 4.5c. These findings suggest that higher temperature is required in order to achieve more efficient separation. However, this will ultimately need to be balanced with subsequent reduced adsorption capacity and changes to the gas adsorption equilibrium selectivity at different temperatures.

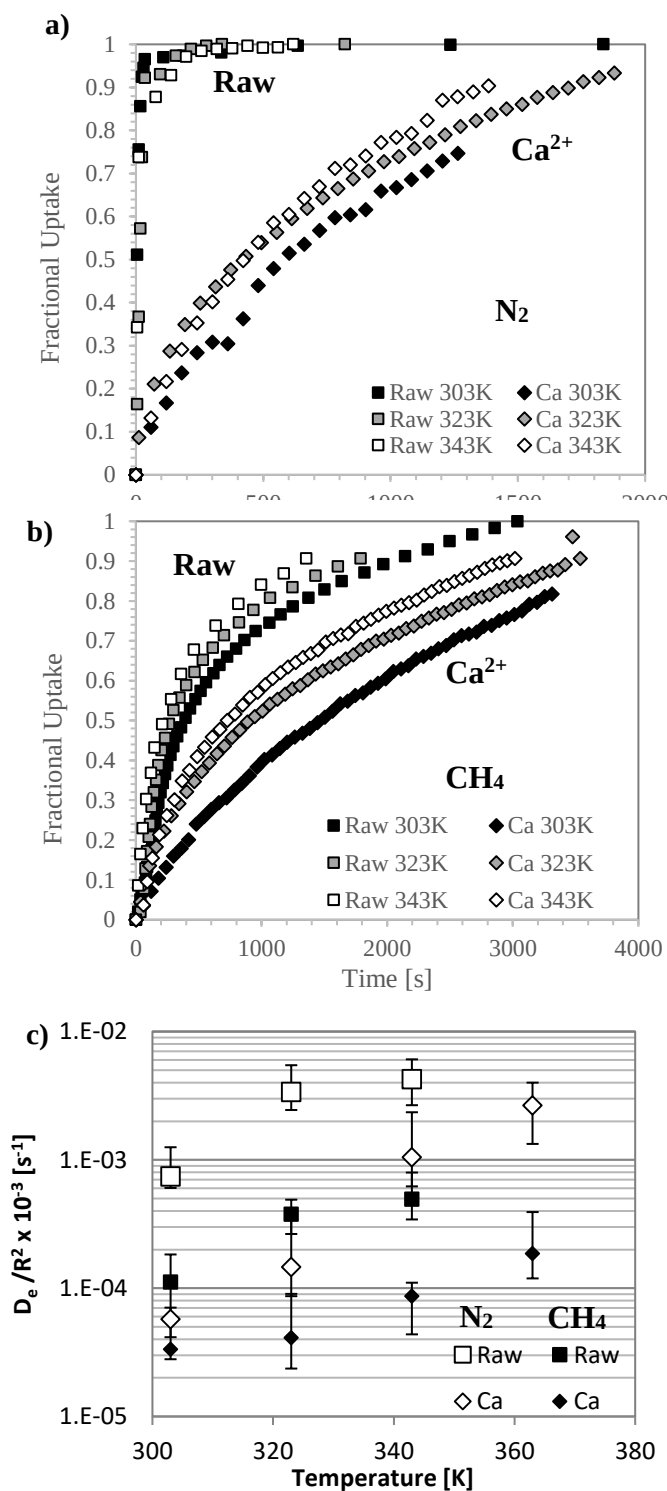


Figure 4.5. a) Experimental adsorption fractional uptake rate curves for a) N₂ and b) CH₄ gas adsorption on raw and Ca²⁺ clinoptilolite samples determined at 303K, 323K, and 343K with a pressure step change from 0.5 to 1 atm. c) Experimentally determined diffusion time constants calculated from the LDF model as a function of temperature for N₂ and CH₄ gas adsorption on raw and Ca²⁺ clinoptilolite samples. For graph c) the solid points are CH₄ and the hollow points are N₂.

4.4.3. HENRY'S LAW CONSTANTS and HEAT of ADSORPTION

In Henry's Law region, adsorbate-adsorbent forces are the most dominant adsorption mechanism since at near zero coverage additional forces which are dependent on adsorbate-adsorbate effects are minimized. The experimental Henry's Law constants were determined for pure CO₂, CH₄ and N₂ gases by using concentration pulse chromatography method (CPM) using Equations 1 and 2. These values are displayed in Table 4.6 for different temperatures. Henry's Law constants are related directly to the shape of adsorption isotherm curves at low pressures. Adsorption isotherms of CO₂ on all clinoptilolite types and at all temperatures have the highest slope in the low pressure region. The K_p values are the highest for CO₂. They show the following trend for CO₂: $Fe^{3+} < Cs^+ < Ca^{2+} < Raw$. These higher values indicate a high level of interaction between the CO₂ adsorbate molecules and the surface as discussed in Section 4.1.

As can be seen in Table 4.6, both CH₄ and N₂ show significantly weaker interaction with all of the adsorbents compared to CO₂. The K_p values determined using the CPM are low for CH₄ and N₂. The range of K_p values are fairly similar for both gases, with CH₄ being slightly higher than N₂ for Fe³⁺, and Cs⁺ clinoptilolite, are similar for raw clinoptilolite and are lower for Ca²⁺ clinoptilolite. It is evident that there is likely reduced interaction for both of the N₂ and CH₄ since the Henry's Law constant values are lower compared to CH₄. This can be a consequence of the steric effects resulting from restricted micropore access for these gases. Figure 4.6 presents the van't Hoff plots for the Henry's Law constants measured for CO₂, CH₄, and N₂ for the studied adsorbents. As can be seen in Figure 4.6, the slope of the van't Hoff plots are fairly flat for the CH₄ and N₂ gases compared to CO₂. This trend may be explained by the influence of microporous diffusion resistance in the micropores of this zeolite. The chromatographic method is a dynamic method because the flow rate of the He carrier gas influences the exposure of the gas molecules to the micropores of the adsorbent. Microporous diffusion limitations would manifest itself with lower observed K_p values, which is indicative of less interaction between the gas and the adsorbent. For example, Ca²⁺ clinoptilolite (which is known to have smaller effective micropore size and slower diffusion rates[60]) shows the smallest K_p values for CH₄ thus indicating less interaction between the large CH₄ molecule and the small micropores of the adsorbent. On the other hand, the Fe³⁺ clinoptilolite (which has much lower microporous diffusion resistance[71]) exhibits higher K_p values and a greater slope than Ca²⁺ clinoptilolite. While great care is given to ensure that the CPM experimental conditions were optimal (carrier gas flow rate, temperature, sample gas injection volume etc..) the microporous diffusional limitation inherent with this material makes it difficult to achieve reliable results with this method. CPM also has its limitations as a method to measure adsorption characteristics. If the Henry's Law constants and the diffusivities are very low, it is impossible to measure the Henry's Law constants accurately due to the assumptions made for the equations used for the calculations.

Table 4.7 shows the calculated limiting heat of adsorption values determined from the CPM technique according to the van't Hoff equation (Equation 3) using the K_p values determined. While the heat of adsorption values for CO_2 are similar, they are far lower than the accepted literature values for CH_4 and N_2 on raw clinoptilolite[74,82]. Given this discrepancy, and the questionable use of CPM for very low K_p values as explained in the above paragraph, the heat of adsorption values were also estimated from the experimental isotherm data obtained at different temperatures (Figures 4.2, 4.3, and 4.4) using the Clausius-Clapeyron equation (Equation 12). Adsorption is an exothermic process. Therefore increasing the temperature will decrease the adsorbate–adsorbent interaction and lower the adsorption capacity. The effect of adsorbate surface loading on the thermodynamic tendencies presents itself as the isosteric heat of adsorption which is presented in Figure 4.7. The isosteric heat of adsorption values at near zero coverage are determined using the y-axis intercept of this Figure and are presented in Table 4.8. The isosteric heats of adsorption calculated for all of the clinoptilolite types at low loadings are in the order of $\text{N}_2 < \text{CH}_4 < \text{CO}_2$. Comparing these values with literature, the isosteric heat of adsorption values differ only slightly than the values found for raw clinoptilolite[74,82]. The differences are likely due to the variations in clinoptilolite composition which depends on the local mineral source.

Considering only the heat of adsorption values for CO_2 ; both Fe^{3+} and Ca^{2+} clinoptilolite have the highest isosteric heat of adsorption at higher loadings (see Figure 4.7). CO_2 interactions with these adsorbents are concentrated towards the highly charged cationic sites meaning that adsorbate - adsorbent interactions have the strongest temperature dependence due to the close proximity of the adsorbed gases. The isosteric heat for CO_2 increases as loading increase, these interactions dominate as loading increases for all of the clinoptilolite types. This trend is the most pronounced on the Ca^{2+} clinoptilolite, and is actually observable for all three gases. This makes sense given that intermolecular interactions are expected to increase when the effective pore size is more restricted.

Table 4.6. Average Henry's Law constants at different temperatures as determined with CPM for CO₂, CH₄ and N₂ gases on raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged samples.

	Raw Clino. K _p * (mmol·g ⁻¹ ·atm ⁻¹)	Ca ²⁺ Clino. K _p * (mmol·g ⁻¹ ·atm ⁻¹)	Cs ⁺ Clino. K _p * (mmol·g ⁻¹ ·atm ⁻¹)	Fe ³⁺ Clino. K _p * (mmol·g ⁻¹ ·atm ⁻¹)
T(K)	CO₂			
428			0.738 +/- 0.026	0.656 +/- 0.015
443			0.500 +/- 0.018	0.539 +/- 0.007
458			0.348 +/- 0.042	0.414 +/- 0.012
473			0.258 +/- 0.025	0.313 +/- 0.021
488			0.201 +/- 0.011	0.261 +/- 0.010
503	3.144 +/- 0.073	1.868 +/- 0.087	0.135 +/- 0.038	0.222 +/- 0.004
518	2.586 +/- 0.063	1.513 +/- 0.084		
533	2.068 +/- 0.036	1.180 +/- 0.041		
548	1.789 +/- 0.046	0.802 +/- 0.019		
563	1.480 +/- 0.039	0.648 +/- 0.029		
T(K)	CH₄†			
303	0.334 +/- 0.042	0.083 +/- 0.028	0.216 +/- 0.009	0.851 +/- 0.017
318	0.324 +/- 0.013	0.060 +/- 0.060	0.206 +/- 0.016	0.700 +/- 0.018
333	0.301 +/- 0.026	0.067 +/- 0.067	0.204 +/- 0.008	0.631 +/- 0.006
348	0.273 +/- 0.054	0.057 +/- 0.057	0.188 +/- 0.017	0.507 +/- 0.019
363	0.227 +/- 0.086	0.052 +/- 0.052	0.181 +/- 0.019	0.399 +/- 0.006
T(K)	N₂†			
303	0.401 +/- 0.028	0.129 +/- 0.012	0.194 +/- 0.008	0.460 +/- 0.007
318	0.351 +/- 0.107	0.114 +/- 0.022	0.195 +/- 0.007	0.387 +/- 0.005
333	0.323 +/- 0.069	0.089 +/- 0.014	0.189 +/- 0.002	0.324 +/- 0.042
348	0.201 +/- 0.063	0.071 +/- 0.022	0.186 +/- 0.004	0.290 +/- 0.006
363	0.168 +/- 0.075	0.056 +/- 0.004	0.180 +/- 0.006	0.227 +/- 0.018
*K _p = average of n = 3 individual experiments with the range as the standard deviation. The experimental uncertainty u(K _p) ≈ 13.5%.				
† The calculated CH ₄ and N ₂ experimental K _p values determined from the CPM method are too low to be considered reliable				

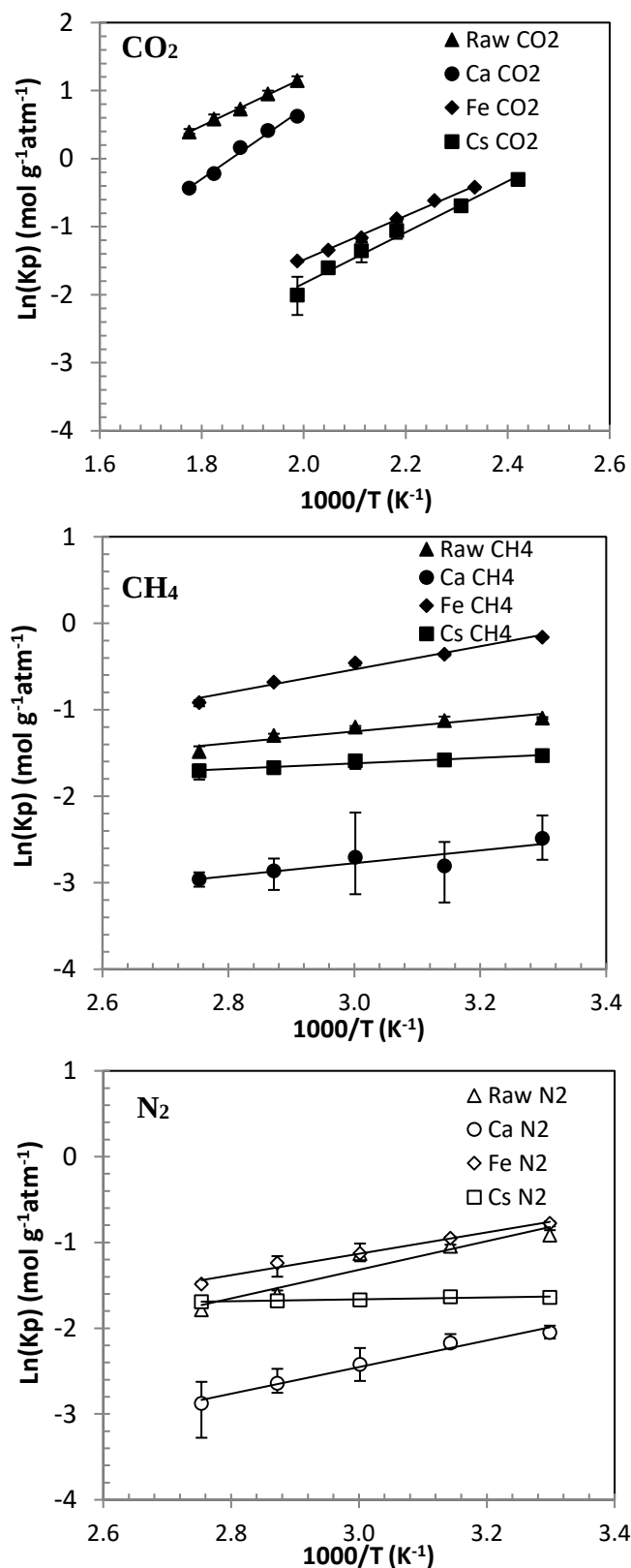


Figure 4.6. van't Hoff plots of the average Henry's Law constants for pure component CO₂, CH₄, and N₂ injections into helium carrier gas, as a function of inverse temperature using the CPM method. The error bars represent the maximum and minimum experimental K_p values for the repeats.

Table 4.7. Experimental limiting heat of adsorption values for CO₂, CH₄ and N₂ with raw and different cation exchanged clinoptilolite determined using the CPM method.

Adsorbent	Experimental $-\Delta H$ (kJ·mol ⁻¹)		
	CO ₂	CH ₄ [†]	N ₂ [†]
Raw Clinoptilolite	29.3	5.7	13.9
Ca ²⁺ Clinoptilolite	43.1	6.4	12.9
Cs ⁺ Clinoptilolite	31.2	1.0	2.8
Fe ³⁺ Clinoptilolite	27.8	9.7	9.6
† The calculated CH ₄ and N ₂ experimental $-\Delta H$ values determined from the CPM method are considered not accurate due to the very low K _p values obtained			

Table 4.8. Experimental isosteric heat of adsorption at near zero coverage calculated from the adsorption equilibria data and comparison with literature.

Adsorbent	$-\Delta H$ (kJ·mol ⁻¹)			Ref.
	CO ₂	CH ₄	N ₂	
Raw Clinoptilolite	24.5	28.4	17.6	Current Study
Ca ²⁺ Clinoptilolite	19.9	16.3	20.7	
Cs ⁺ Clinoptilolite	25.2	26.6	18.9	
Fe ³⁺ Clinoptilolite	28.6	29.7	20.9	
natural Clinoptilolite	42.3	-	24.9	[82]
natural Clinoptilolite	21.0	11.62	-	[74]

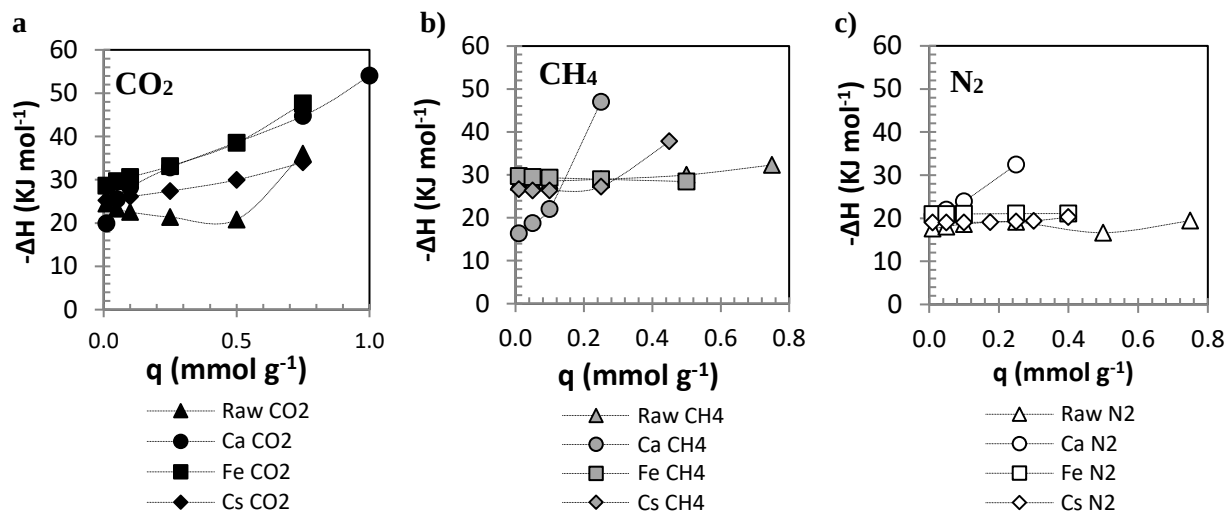


Figure 4.7. Isosteric heat of adsorption values for a) CO₂, b) CH₄, and c) N₂ for raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged clinoptilolite. The best temperature dependent adsorption model fit was used, which was determined from the lowest sum of the squared residuals between the experimental and predicted adsorption capacities.

4.4.4. EQUILIBRIUM SEPARATION PREDICTIONS of CO₂ and N₂ from CH₄

Figures 4.8 and 4.9 present the ideal equilibrium adsorption selectivity for CO₂/CH₄ and CH₄/N₂, respectively, on the different clinoptilolite types which were calculated using Equation 14 from the pure component adsorption data. The best isotherm model was chosen for the regression of the experimental values as described in Section 4.1 using the selected parameters given in Table 4.3. The temperature and pressure bounds, which were between 273 to 373K and 0.001 to 10 atm, respectively, were chosen to display the ideal equilibrium selectivity with reasonable confidence. However, caution should be taken when using the single gas isotherm regressions to extrapolate to full scale adsorption systems. This is due to the inherent limitations of this approach as it discounts the effects of kinetic behaviour and competitive adsorption which is present in adsorbing gas mixtures such as in this system[51,98,116–118]. Nonetheless, the ideal selectivity values provide a basic initial assessment for identifying the best criteria for augmenting the separation performance of these materials[55].

The ideal selectivity changes dramatically depending on the type of cation exchanged which confirms the findings as discussed in our previous study for Ca²⁺, Cs⁺, and Fe³⁺ cation exchanged clinoptilolite[71]. As shown in Figure 4.8, the CO₂/CH₄ ideal selectivity increases with decreasing pressure for all of the clinoptilolite types and is the greatest at pressures below 1 atm. This is the result of the more rectangular shape of the CO₂ isotherms as can be seen in Figure 4.2, compared to the ones for CH₄ in Figure 4.3. Ca²⁺ clinoptilolite has the highest CO₂/CH₄ ideal selectivity among all of the clinoptilolite types and is over 300 at 273K and 0.001 atm. Above 1 atm, the temperature and pressure effects on the ideal CO₂/CH₄ selectivity are less dramatic and the ideal selectivity value change from about 4.5 at 273K and 10 atm to 25 at 373K and 1 atm for Ca²⁺ clinoptilolite.

It is generally accepted in the literature that Ca²⁺ clinoptilolite shows high microporous diffusion resistance [60,71,81]. However, at higher temperatures this effect is minimized as shown in Figure 4.5. Therefore, while adsorbent capacity decreases with increasing temperature; greater ideal selectivity and faster adsorption kinetics may compensate for this behaviour at higher temperatures. This is also apparent for the CH₄/N₂ ideal selectivity on the Ca²⁺ clinoptilolite which shows the greatest sensitivity to temperature and pressure for this separation. As shown in Figure 4.9, the CH₄/N₂ ideal selectivity ranges from 0.3 (N₂/CH₄ selective) at 273K and 0.001atm up to 5.5 at 373K and 0.001atm for this adsorbent. Both Cs⁺ and Fe³⁺ clinoptilolite show higher CH₄/N₂ ideal selectivity values compared to the raw clinoptilolite that has values close to unity for this separation. The CH₄/N₂ ideal selectivity approaches unity for Cs⁺ clinoptilolite at 273K and 10atm and increases to 10 at 373K and 0.001atm, and generally increases with increasing temperature and decreasing pressure. In comparison, Fe³⁺ clinoptilolite has

CH₄/N₂ separation values which are less sensitive and range from 3 to 6 across the range of temperatures and pressures studied.

CO₂/CH₄

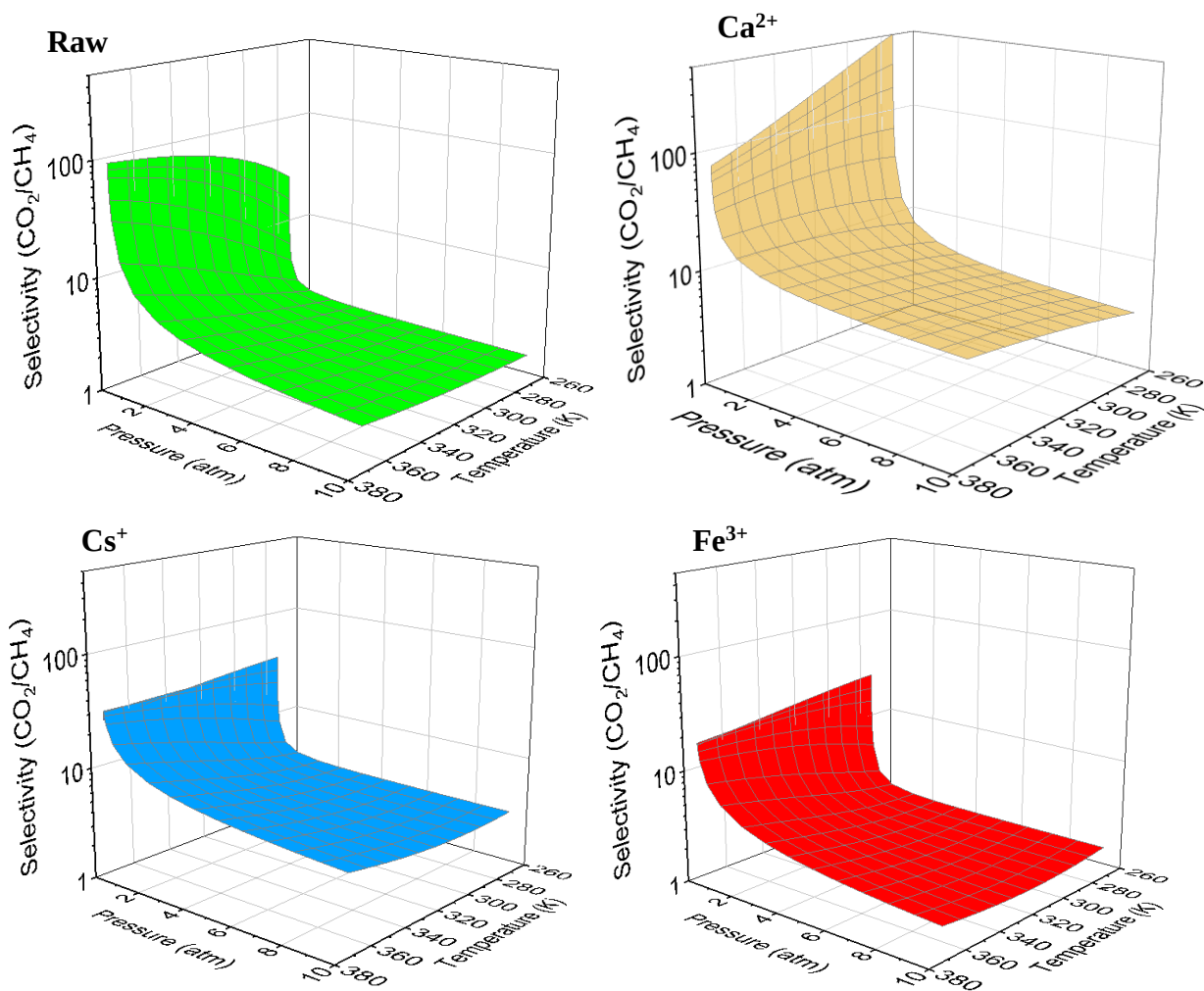


Figure 4.8. Predicted CO₂/CH₄ ideal selectivity for raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged clinoptilolite over a temperature range of 273K to 373K and pressure range of 0.001 atm to 10 atm.

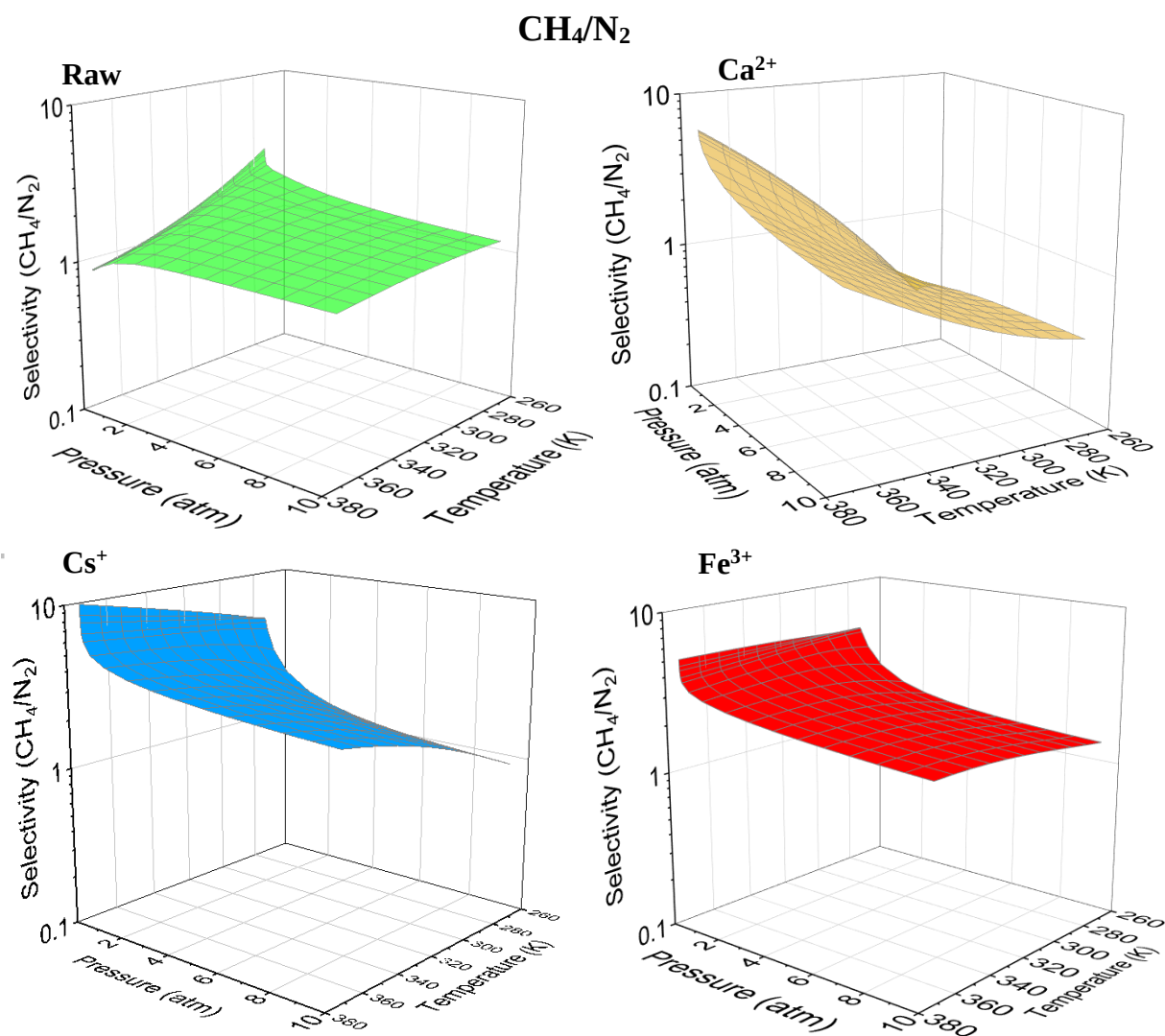


Figure 4.9. Predicted CH₄/N₂ ideal equilibrium selectivity for raw clinoptilolite compared to Fe³⁺, Ca²⁺, and Cs⁺ exchanged clinoptilolite over a temperature range of 273K to 373K and pressure range of 0.001 atm to 10 atm.

4.5. CONCLUSIONS

The effect of temperature on the adsorption characteristics of CO₂, CH₄, and N₂ gases was studied on raw and cation exchanged clinoptilolite with Ca²⁺, Fe³⁺, and Cs⁺ cations. Temperature dependent isotherm models were curve fitted with experimental data to determine the best model to represent the data. Ideal equilibrium selectivity factor values were calculated for CO₂/CH₄ and CH₄/N₂ gas separation applications using the regressed isotherm models that had the best representation of the experimental data. The CH₄ and N₂ adsorption kinetics were determined and compared for raw and Ca²⁺ clinoptilolite. These results showed higher microporous diffusion resistance for Ca²⁺ clinoptilolite for both gases which dissipates with increasing temperatures. The isosteric heat of adsorption value was the highest for CO₂ followed by CH₄, and N₂, and was shown to increase with the amount of surface coverage for clinoptilolite types for CO₂, and all three gases for Ca²⁺ clinoptilolite. Among the different types of clinoptilolites, Ca²⁺ clinoptilolite shows the best potential for CO₂/CH₄ separations due to its higher ideal equilibrium selectivity. However, it is recommended that higher adsorption temperatures be used for this adsorbent in order to compensate for the slow kinetic behaviour at low temperatures. For CH₄/N₂ separations, Both Cs⁺ and Fe³⁺ display higher ideal equilibrium selectivity values compared to the raw clinoptilolite which had values close to unity. However, the Fe³⁺ clinoptilolite ideal equilibrium selectivity displays less variability which means that it would be most effective over a broader range of temperatures and pressures for this separation compared to the Cs⁺ form. The ideal equilibrium selectivity plots serve only as a guide to define suitable operating ranges for these new materials. However, further study is necessary to determine the true performance of these materials using mixture adsorption analysis.

4.6. NOMENCLATURE

B	adsorption affinity constant	[atm ⁻¹]
B_0	adsorption affinity constant at reference temperature	[atm ⁻¹]
D_e	effective (transport) diffusivity	[m ² /s]
D_e/R_p^2	diffusion time constant	[s ⁻¹]
ΔH	limiting heat of adsorption	[kJ/mol]
k_1	TD - DS Langmuir parameter	[mmol/g]
k_2	TD - DS Langmuir parameter	[mmol/g K]
k_3	TD - DS Langmuir parameter	[atm ⁻¹]
k_4	TD - DS Langmuir parameter	[K]
K	dimensionless Henry's Law constant	[dimensionless]
K_p	dimensional Henry's Law constant	[mmol/g atm]
k_{LDF}	LDF model kinetic rate constant	[s ⁻¹]
L	length of the column	[m]
n	dimensionless model parameter	[dless]
n_0	dimensionless model parameter at reference temperature	[dless]
P	pressure	[atm]
P_0	saturation pressure	[atm]
q	amount adsorbed	[mmol/g of adsorbent]
$q(t)$	amount absorbed at time t	[mmol/g of adsorbent]
q_e	adsorption capacity at equilibrium	[mmol/g of adsorbent]
q_m	adsorption capacity at saturation	[mmol/g of adsorbent]
q_{m0}	adsorption capacity at reference temperature	[mmol/g of adsorbent]
Q	heat of adsorption model parameter	[kJ/mol]
R	universal gas constant	[m ³ Pa/ K mol]
R_p	radius of particle	[m]
t	time	[s]
T	temperature	[K]

Subscripts

1	component 1
2	component 2
A	adsorption site A

B adsorption site B

Greek Symbols

$\alpha_{1/2}$	apparent adsorption equilibrium selectivity factor,	[dimensionless]
α_n	dimensionless model parameter at reference temperature	[dimensionless]
β	kinetic selectivity factor	[dimensionless]
ε	bed porosity	[dimensionless]
θ	adsorption surface coverage	[dimensionless]
χ	dimensionless model parameter at reference temperature	[dimensionless]
μ	mean retention time	[s]
μ_D	system dead time	[s]
v	Interstitial velocity	[cm/s]
ρ_p	adsorbent pellet density	[g/cm ³]

Abbreviations

BET	Brunauer – Emmett – Teller
CMS	carbon molecular sieve
CPM	concentration pulse method
DS	dual site
EDS	electron dispersive spectroscopy
ETS-4	Engelhard Titanosilicate 4
FD	Fickian Diffusion model
GC	gas chromatograph
HEU	Heulandite
HK	Horvath-Kawazoe
LDF	linear driving force
MOF	metal organic framework
PSA	pressure swing adsorption
SSR	sum of the squared residuals
TCD	Thermal conductivity detector
TD	Temperature dependent
VPSA	vacuum pressure swing adsorption
VSA	vacuum swing adsorption

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CHAPTER 5

Pure and Mixture Adsorption Equilibria of Methane and Nitrogen with Clinoptilolite: Effects of Cs^+ and Fe^{3+} Exchanged Cations on Separation Performance

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ABSTRACT

Cation-exchanged clinoptilolite has emerged as an adsorbent that may be used for the treatment of natural gas type mixtures containing excess amounts of nitrogen. In this study, natural clinoptilolite was modified through Fe^{3+} and Cs^+ cation exchange. The resultant mineral phase and elemental composition were verified and the extra framework cation type, charge, and distribution is shown to have a profound effect on the observed adsorptive properties. Single gas adsorption isotherms were conducted at 288K and/or 303K for CH_4 and N_2 using a microgravimetric adsorption analyser, and the ideal equimolar CH_4/N_2 selectivity values were determined for the natural and modified clinoptilolites. Natural clinoptilolite presents selectivity values close to 1. However, we demonstrate that clinoptilolite cation-exchanged with Cs^+ and Fe^{3+} cations is rendered preferentially adsorptive for CH_4 over N_2 with a higher CH_4/N_2 selectivity than many adsorbents reported in the literature.

The experimental $\text{CH}_4\text{--N}_2$ binary adsorption behavior was evaluated for the first time on raw clinoptilolite and was compared to the modified clinoptilolites with Cs^+ and Fe^{3+} exchanged cations using the concentration pulse chromatographic technique. The experimental binary isotherms showed non-ideal behavior with competitive adsorption between CH_4 and N_2 . In most cases, the theoretical models could not adequately describe the experimental adsorption behavior. Within the temperature range studied of at 288K and 303K, the binary CH_4/N_2 separation factors range from 2.7 to 5.3, and 3.9 to 7.3 for Cs^+ and Fe^{3+} exchanged clinoptilolite, respectively. These results are comparable or better than those found in literature for activated carbon which typically ranges from 2.1 to 5.5 and may serve as an alternative adsorbent for this type of separation which warrants further investigation.

5.1. INTRODUCTION

Natural gas is considered a more favourable energy alternative with the promise of achieving lower greenhouse gas footprints comparatively to other fossil fuels such as coal [1]. According to the 2017 Edition of BP Energy Outlook, over the next few years the production of natural gas could grow quicker than that of other fossil fuels. It is hypothesized that the growth of unconventional natural gas sources, such as US shale gas, would be leading these tendencies [2]. One hallmark of unconventional natural gas resources is the presence of higher amounts of unwanted contaminants, such as N_2 , which can lead to lower gas heating values and increased compression volumes. In fact, 15% of US natural gas reserves contain more than 10% N_2 and are thus considered to be sub-quality in nature [3]. Fugitive emissions are additional sources of dilute methane that is contaminated with a higher nitrogen content. Such sources account for estimated losses of between 1.6% and 5.8% of the total methane produced from shale gas [4–10]. Additionally, ventilation in coal mines and in seam gas draining are also significant sources which account for about 8% of the world's anthropogenic methane emissions [11]. The emergence of gas processing technologies in the context for preventative methane release and recovery has several attractive economic and environmental implications to which Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) may be applicable.

Traditionally, N_2 removal is carried out through an energy-intensive cryogenic distillation process, using natural gas which emerged from the well head at higher pressure. Such a process requires high gas throughputs and process integration to improve operating efficiency. A proposed alternative is the incorporation of a PSA unit for this gas processing step, which offers the advantage of lower capital and operating costs compared to its cryogenic equivalent. However, since natural gas extracted from the field is at high pressures, if PSA is to replace a cryogenic unit, then an N_2 selective adsorbent is the preferred choice as this is able to give CH_4 as the higher pressure raffinate product. In this case the main operating costs associated with the use of a PSA unit may be mitigated, since it is associated with gas recompression and not liquefaction, as is the case in cryogenic distillation [12]. What has slowed the implementation of PSA as the main N_2 removal technique is the absence of suitable adsorbent materials with satisfactory performance characteristics. One such example of a successful commercial application of an N_2/CH_4 selective adsorbent are titanosilicates such as Ba-ETS-4²⁹. This patented material remains the benchmark for N_2 rejection within PSA systems, which has been commercialized by Guild Associates with their Molecular Gate Adsorption Technology® [13–16].

Over the last several years, with the exception of the aforementioned titanosilicate ETS-4, some carbon molecular sieves [17,18], and a limited number of zeolites (various cation exchange clinoptilolites)[19,20], the current body of research has shown that most adsorbent materials are selective for CH₄ over N₂. This is due to the differences in the electrostatic potentials of the two gases. N₂ has a slight quadrupole moment of 1.52×10^{-26} esu·cm², CH₄ has the advantage of being more polarisable than N₂ (26.0×10^{-25} compared to 17.6×10^{-26} cm⁻³) [21]. The higher polarizability of CH₄ promotes preferential interactions between adsorbent surfaces and gas molecules which are stronger than those achieved due to the quadrupole moment of N₂. Thus, most adsorbents including activated carbons, zeolites, silica gels, and activated alumina, have proven to be CH₄ selective over N₂, albeit only moderately [22–32]. The main issue with , CH₄/N₂ selective materials is that this configuration requires the processed natural gas to be produced at low pressure, thus incurring additional recompression costs to achieve pipeline pressure. However, CH₄/N₂ selective materials may be attractive in the case of recovery of fugitive methane sources provided that an adsorbent material has high selectivity thus reducing subsequent adsorption cycle process refinements.

Modification of clinoptilolite where variations in cation composition are known to alter the effective micropore size of this material [33–35] These alterations have been shown to have a profound influence on the adsorption separation characteristics of this material, and therefore it has been studied in variety of applications including natural gas purification, flue gas removal, and air purification [20,36–44]. Ackley and Yang proposed that the observed changes in the adsorption properties of adsorption of N₂ and CH₄ gas was dependent on the location of the cations in clinotpilolite channels. For instance, various adsorption diffusion and equilibria studies show that the presence of Ca²⁺ and Na⁺ cations within the clinoptilolite pore network lead to a preferential selectivity for N₂ over CH₄ [20,45–48]. Thus, Ca²⁺ and Na⁺ occupy sites that permit the blocking of CH₄ and exploit the slight kinetic diameter difference between CH₄ and N₂ molecules (3.8 compared to 3.6 Å) [21] by permitting the N₂ molecules to diffuse into the micropores of clinoptilolite. Studies into these cation exchange effects have shown high N₂/CH₄ kinetic selectivity values reaching into the 100's for Li⁺, Mg²⁺, or Ni²⁺ exchanged clinoptilolites among many others [45,47,49]. While clinoptilolite may be modified through cation exchange to be N₂ selective of CH₄ the reported slow diffusion kinetics reduces the performance of the material in a dynamic environment such as in PSA [20,45,50,51].

The presence of multiple extra-framework cation sites makes it an ideal candidate to assess the effectiveness of cation exchange on improving the adsorbent CH₄/N₂ selectivity for this gas system. Natural clinoptilolite may present some minimal preferential selectivity for CH₄ over N₂ with unfavourable diffusion rates. However, clinoptilolite cation-exchanged with H⁺, K⁺ and Mg²⁺ has shown improved CH₄/N₂ equilibrium selectivity [20,42,45,52]. In our previous works, the effect of multiple types of cations

individually exchanged with clinoptilolite and single gas CO_2 , CH_4 , and N_2 adsorption were studied. Both Cs^+ and Fe^{3+} exchanged clinoptilolite were the most promising candidates for the alternate CH_4/N_2 selective separation as they exhibited the greatest CH_4/N_2 ideal selectivity factors [47]. Beyond the higher CH_4/N_2 equilibrium selectivity, they exhibited a faster adsorption uptake rate with values = to that of for natural clinoptilolite or other modified forms. With N_2/CH_4 kinetic selectivity values of 1 and 10 for Fe^{3+} and Cs^+ clinoptilolite, respectively.

The purpose of the present study has been to assess the effect of cation-exchange with Cs^+ and Fe^{3+} clinoptilolite on the adsorption characteristics of CH_4 and N_2 for both single gas and binary gas mixtures. Raw clinoptilolite was modified through cation-exchange with solutions containing Cs^+ and Fe^{3+} cations. Single gas isotherms for CH_4 and N_2 on raw clinoptilolite at 303K and on the cation-exchanged samples at 288K and 303K were measured. From these, ideal equimolar CH_4/N_2 selectivity values were obtained. Experimental CH_4 – N_2 binary isotherms were determined using the Van der Vlist-Van der Meijden concentration pulse method. The binary isotherms were plotted and compared to the theoretical results predicted from the Extended Langmuir (ELM), Extended Dual Site Langmuir (DSL), Ideal Adsorbed Solution Theory (IAST), and Flory-Huggins Vacancy Solution Model (FH-VSM) theoretical models. From the binary isotherms, x-y phase diagrams as well as the CH_4/N_2 separation factors were determined.

5.2. MATERIALS and EXPERIMENTAL METHODS

5.2.1. MATERIALS

Raw clinoptilolite pellets were obtained from Ash Meadows Zeolite LLC. (Amargosa Valley, NV, USA). The pellets were crushed to a 60×80 standard US mesh size (180-250 μm). Iron chloride (FeCl_3 , 99.0%, BDH Inc., Toronto, ON, Canada) and cesium chloride (CsCl , 99.9%, Sigma-Aldrich, Oakville, ON, Canada) powders were dissolved in deionized water. These solutions were then used as source of cations during the cation exchange process. For the pure gas adsorption experiments, the studied clinoptilolite samples were exposed to CH_4 (99.99%) and N_2 (99.999%). High purity He gas (99.9995%) was used for buoyancy correction during the pure gas adsorption experiments. All of the gases were purchased from Linde Canada Ltd. (Ottawa, ON, Canada). In the case of binary gas adsorption experiments, CH_4 and N_2 were used as both the carrier and injection gases. Prior to the initiation of the binary adsorption experiments, clinoptilolite samples were regenerated at 573K using high purity He gas as the purge gas.

5.2.2. PREPARATION of ADSORBENTS

5.2.2.1. RAW CLINOPTILOLITE WASHING

Crushed raw clinoptilolite was washed with deionized water to remove any soluble salts. A ratio of 80 mL of water for 1 g of raw clinoptilolite was used. The mixture was heated for 1 hour, at 353K and was continuously stirred using a magnetic stirrer. Following this step, the clinoptilolite samples were rinsed with deionized water using a ratio of 100 mL of water to 1 g of crushed raw clinoptilolite. Finally, the samples were decanted and placed in an oven at 373K for 12 hours to remove any presence of water. A small sample of the washed raw clinoptilolite was characterized by powdered x-ray diffraction, while the rest was used for cation exchange.

5.2.2.2. CATION EXCHANGE

The cation exchange procedure was carried out in a similar manner as reported in the literature [20,45,49,53–55]. Solutions of 0.2 M Fe^{3+} and Cs^+ cations in deionized water were used as cation sources at a ratio of 25 mL of solution for 0.5 g of washed raw clinoptilolite. The cation exchange solutions were transferred into a Teflon-lined beaker containing the crushed raw clinoptilolite. The whole beaker was inserted into an autoclave then placed into an oven, preheated to 408K and maintained at that temperature for 10 hours. The autoclave was cooled in the oven with the door open over a period of 2 hours until it

reached room temperature, and the cation exchange solution was decanted and replaced with a fresh solution. The process was repeated one more time for each sample, leading to the samples being cation-exchanged twice. The samples were then rinsed with 100 mL of deionized water before being placed in an oven at 373K for 12 hours to remove any presence of water.

5.2.3. ADSORBENT MATERIAL CHARACTERIZATION

Powdered x-ray diffraction (XRD) was used to verify the phase characteristics of the original and modified clinoptilolite samples. The powdered clinoptilolite was analyzed at room temperature using a Rigaku Ultima IV powder diffractometer in Bragg-Brentano geometry, using Cu K α radiation ($\lambda = 1.5418$ Å). The 2θ range of 2° to 90° was covered with a 0.02° step width and $6^\circ/\text{min}$ scan speed. FT-IR analysis of the clinoptilolite samples was carried out using a Cary 630 FTIR with ATR (Agilent Technologies, Mississauga, ON, Canada). The infrared spectra range of 650 to 4000 cm^{-1} was used and a total of 100 sample scans were conducted per individual sample at a 4 cm^{-1} resolution. A JEOL JSM – 7500F Field Emission Scanning Electron Microscope (SEM) equipped with a Tracor-Northern Series Z – II electron dispersive spectrometer (EDS) (JEOL, Tokyo, Japan) was used to verify the elemental composition of the raw, and cation-exchanged clinoptilolite samples. SEM imagery of the samples were performed with a Phenom Pro SEM (Nanoscience Instruments, Alexandria, VA, USA) using accelerating voltage of 5kV.

5.2.4. PURE GAS ADSORBENT EXPERIMENTS

A microgravimetric analyzer (VTI Corp., Hialeah, Florida, USA), equipped with a Cahn microbalance, was used to determine the pure gas adsorption isotherms. Initially, the cation-exchanged clinoptilolite samples were regenerated at a 10^{-8} atm absolute pressure and 573K temperature. Subsequently, the samples were exposed to CH₄ or N₂ at different pressures. The absolute pressure of the adsorbing gas was increased from 0 to 10 atm, while temperatures were maintained constant at either 288K or 303K using a thermal bath. At each pressure increment, an equilibrium adsorption measurement was taken. A change of adsorbent mass of less than 0.015% over a period of 30 min was considered as an indication of equilibrium having been achieved [25]. Helium gas was used on the samples to correct for buoyancy. A full description of the single gas isotherm apparatus and experimental technique is detailed in our previous studies [25,47]

5.3. ADSORPTION MODELS for SINGLE COMPONENT DATA

At low pressures, the Henry's law adsorption isotherm given in Equation 1 represents the physical adsorption behaviour under dilute conditions [56].

$$q = K_p P \quad (1)$$

Where q is the amount adsorbed, P is the pressure of a component being adsorbed, and K_p is the Henry's constant. However, at higher pressures, the limitations of available adsorbing sites becomes apparent as the adsorbent reaches its saturation capacity denoted as q_∞ .

Langmuir proposed that at equilibrium the adsorbed gases occupy a portion of a finite number of adsorption sites [57]. This model, shown in Equation 2, assumes ideal behaviour and monolayer adsorption. Whereby, each adsorbing site can only accept one molecule, the adsorption energy of each site is homogeneous, meaning that it is uniform with no interactions between adsorbed molecules on the different sites [57,58].

$$\theta_i = \frac{q_i}{q_i^\infty} = \frac{b_i P}{1 + b_i P} \quad (2)$$

Thus, at high pressure the maximum amount adsorbed for component, i , at equilibrium is determined as the limiting adsorption capacity, q_i^∞ . The equilibrium constant for a component, b , can be determined from the initial slope of the isotherm, and is essentially the Henry's constant, since at very low pressures as $P \rightarrow 0$ atm, the Langmuir isotherm simply reduces to the Henry's form given in Equation 1.

For adsorbents such as zeolites, in most cases the adsorbent surface is energetically heterogeneous. This is attributed to the presence of extra framework cations dispersed amongst the micropores of the zeolite, therefore creating different adsorption regions on the surface of the zeolite [59]. The Dual Site Langmuir (DSL) Isotherm accounts for this fact by applying the exact same assumptions of the Langmuir model, but to two separate patches which are independent of one another as shown in the following equation:

$$q_i = \left(\frac{q_{i,A}^\infty b_{i,A} P_i}{1 + b_{i,A} P_i} \right)_{\text{Site A}} + \left(\frac{q_{i,B}^\infty b_{i,B} P_i}{1 + b_{i,B} P_i} \right)_{\text{Site B}} \quad (3)$$

For this model, flexibility is introduced to reflect the energetic heterogeneity of the adsorbent surface by way of the independent adsorption sites A and B. Similar to the Langmuir isotherm, for the DSL isotherm the overall limiting adsorption capacity, q^∞ is simply the sum of those of the independent adsorption sites A and B. Additionally, as $P \rightarrow 0$ atm, the DSL isotherm simply reduces to the Henry's form.

For the reasons discussed above, both the Langmuir and DSL models are thermodynamically consistent. The adsorption energy of component i on an adsorption site or heat of adsorption, $-\Delta H_{j,i}$, is the effect of temperature on adsorption equilibrium constant b as shown in Equation 4.

$$b_{j,i} = b_{j,i_o} \exp\left(\frac{-\Delta H_{j,i}}{RT}\right) \quad (4)$$

Thus, since adsorption is an exothermic process, it is inversely correlated with temperature.

5.4. THEORETICAL MODELS for PREDICTION of GAS MIXTURE ADSORPTION

Several models have been described for predicting the gas mixture adsorption equilibria using only the pure component experimental data. Many of which have been evaluated systematically for accuracy with respect to experimental binary systems in the literature [23,60]. In this work, the single gas adsorption isotherms were determined experimentally for both CH₄ and N₂ and were used to predict the multicomponent behaviour of these gases. The Extended Langmuir Model (ELM), Dual Site Langmuir Model (DSL), the Ideal Adsorbed Solution Theory (IAST) and the Flory-Huggins Vacancy Solution Model (FH-VSM) were all used to compare to the experimental binary adsorption data.

5.4.1. EXTENDED LANGMUIRE MODEL (ELM)

The ELM is the multicomponent extension of the Langmuir model with the same assumptions. It is shown in Equations 5a and 5b for each component in a binary mixture [61]. The partial pressures of the two gases, were determined by simply multiplying the mole fraction of each gas in the assumed mixture by the total pressure of the system.

$$q_1 = \frac{q_1^\infty b_1 y_1 P_t}{1 + b_1 y_1 P_t + b_2 y_2 P_t} \quad (5a)$$

$$q_2 = \frac{q_2^\infty b_2 y_2 P_t}{1 + b_1 y_1 P_t + b_2 y_2 P_t} \quad (5b)$$

5.4.2. DUAL SITE LANGMUIR MODEL (DSL)

The multicomponent extension of the DSL has already been discussed in detail by Ritter et. al. [62]. Similarly to the reasons outlined in Section 5.3, for mixed-gas adsorption the saturation capacity for each component, is allowed to be different and the adsorbent free energies are assigned to either site A or site B

to reflect the independent adsorption sites. It is shown in Equations 6a and 6b for each component in a binary mixture.

$$q_{1,m} = \left(\frac{q_{1,A}^{\infty} b_{1,A} y_1 P_t}{1 + b_{1,A} y_1 P_t + b_{2,A} y_2 P_t} \right)_{\text{Site A}} + \left(\frac{q_{1,B}^{\infty} b_{1,B} y_1 P_t}{1 + b_{1,B} y_1 P_t + b_{2,B} y_2 P_t} \right)_{\text{Site B}} \quad (6a)$$

$$q_{2,m} = \left(\frac{q_{2,A}^{\infty} b_{2,A} y_2 P_t}{1 + b_{1,A} y_1 P_t + b_{2,A} y_2 P_t} \right)_{\text{Site A}} + \left(\frac{q_{2,B}^{\infty} b_{2,B} y_2 P_t}{1 + b_{1,B} y_1 P_t + b_{2,B} y_2 P_t} \right)_{\text{Site B}} \quad (6b)$$

5.4.3. IDEAL ADSORBED SOLUTION THEORY (IAST)

The IAST [63,64], just like the ELM, assumes the ideal solution behavior of the mixture. However, with this technique the adsorption equilibria between the gas phase, y , and the adsorbed phase, x , is expressed similar to Raoult's law as shown below:

$$P_1 = y_1 P_t = x_1 P_1^0 \quad (7)$$

$$P_2 = (1 - y_1) P_t = (1 - x_1) P_2^0 \quad (8)$$

P_1^0 and P_2^0 represent the equilibrium pressure of a pure component at the same constant temperature and spreading pressure, π , as the adsorbed mixture.

The spreading pressure can be calculated using the data from the pure gas isotherm experiments as shown in Equation 9.

$$\frac{\pi_1^0 A}{RT} = \int_0^{P_1^0} \frac{q_1^0}{P} dP = \int_0^{P_2^0} \frac{q_2^0}{P} dP = \frac{\pi_2^0 A}{RT} \quad (9)$$

Here, A is the surface area covered by adsorbed gas molecules. For an ideal adsorbed solution in a binary mixture, it is assumed that there is no enthalpy change and the surface area covered by the adsorbed gases remain constant upon mixing. Using Equation 9, the integral may be defined using the pure component adsorption isotherms for each adsorbate. The Langmuir parameters obtained from the single component isotherm may be used if the experimental pure component isotherms have good fits to the Langmuir model. Using this method, the three unknowns (the two equilibrium pressures (P_1^0 and P_2^0) and the composition in the adsorbed phase, x_1), can be solved at constant temperature and fixed total pressure for different compositions in the gas phase, y_1 , (from Equations 7-9, 3 equations with 3 unknowns).

Afterwards, the total adsorbed capacity of both components in a binary mixture, q_t , is determined from q_1^0 , q_2^0 and x_1 and x_2 as follows:

$$\frac{1}{q_t} = \frac{x_1}{q_1^0} + \frac{x_2}{q_2^0} \quad (10)$$

Finally, the adsorbed capacity of each component in the binary mixture can be obtained from Equations 11 and 12, for each y_1 value for us to be able to plot the binary isotherms (the plot of q_1 and q_2 as a function of y_1) at the fixed temperature and the total pressure:

$$q_1 = x_1 q_t \quad (11)$$

$$q_2 = (1 - x_1) q_t \quad (12)$$

5.4.5. FLORY-HUGGINS VACANCY SOLUTION MODEL (FH-VSM)

The FH-VSM has the capacity to predict certain types of non-ideal behavior with limited accuracy such as azeotropes [65–70]. Using this model, first the pure gas capacities obtained at different pressures were fitted to the pure component FH-VSM equation below:

$$P_{calc,i} = \frac{q_1^\infty}{b_1} \left(\frac{q_{1,i}/q_1^\infty}{1 - q_{1,i}/q_1^\infty} \right) \exp \left(\frac{\alpha_{1v}^2 q_{1,i}/q_1^\infty}{1 + \alpha_{1v} q_{1,i}/q_1^\infty} \right) \quad (13)$$

The values of q_1^∞ , b_1 and α_{1v} were determined by minimizing the SSR between the experimental and calculated values as shown in Equation 14.

$$SSR = \sum_{i=1}^n (P_{exp,i} - P_{calc,i})^2 \quad (14)$$

Since FH-VSM does not assume the solution to be ideal, the activity coefficients can be calculated from the constants previously obtained. The activity coefficients, γ_i^s , describe the non-idealities caused by interactions between the two gas species, 1 and 2, and the vacancy, v , in the adsorbed phase, s . After the determination of the pure component isotherms for each component, to get the binary isotherms, the total pressure, P , and the temperature, T are fixed and the following calculations are used for each adsorbed phase composition, x_1 . The set of equations below is used to determine the activity coefficients:

$$\ln(\gamma_1^s) = -\ln \left(\frac{X_1^s}{\alpha_{11} + 1} + \frac{X_2^s}{\alpha_{12} + 1} + \frac{X_v^s}{\alpha_{1v} + 1} \right) + \left[1 - \left(\frac{X_1^s}{\alpha_{11} + 1} + \frac{X_2^s}{\alpha_{12} + 1} + \frac{X_v^s}{\alpha_{1v} + 1} \right)^{-1} \right] \quad (15)$$

$$\ln(\gamma_2^s) = -\ln \left(\frac{X_1^s}{\alpha_{21} + 1} + \frac{X_2^s}{\alpha_{22} + 1} + \frac{X_v^s}{\alpha_{2v} + 1} \right) + \left[1 - \left(\frac{X_1^s}{\alpha_{21} + 1} + \frac{X_2^s}{\alpha_{22} + 1} + \frac{X_v^s}{\alpha_{2v} + 1} \right)^{-1} \right] \quad (16)$$

$$\ln(\gamma_v^s) = -\ln \left(\frac{X_1^s}{\alpha_{v1} + 1} + \frac{X_2^s}{\alpha_{v2} + 1} + \frac{X_v^s}{\alpha_{vv} + 1} \right) + \left[1 - \left(\frac{X_1^s}{\alpha_{v1} + 1} + \frac{X_2^s}{\alpha_{v2} + 1} + \frac{X_v^s}{\alpha_{vv} + 1} \right)^{-1} \right] \quad (17)$$

The parameters of the equations above are determined from Equations 18 to 22, using the parameters obtained from pure component data for FH-VSM.

$$q_t^\infty = x_1 q_1^\infty + x_2 q_2^\infty \quad (18)$$

$$X_i^s = x_i \frac{q_t}{q_t^\infty} \quad (19)$$

$$X_v^s = 1 - \frac{q_t}{q_t^\infty} \quad (20)$$

$$\alpha_{ij} = \frac{\alpha_{iv} + 1}{\alpha_{jv} + 1} - 1 \quad (21)$$

$$\alpha_{vi} = \frac{1}{\alpha_{iv} + 1} - 1 \quad (22)$$

Equations 15 through 22 were combined into the gas-phase composition relations below for the prediction of the binary mixture isotherms for each x_1 value.

$$Y_1 = \frac{\gamma_1^s x_1}{P_t} \frac{q_t}{q_t^\infty} \frac{q_1^\infty}{b_1} \left[\frac{\exp(\alpha_{1v})}{1 + \alpha_{1v}} \right] \exp \left\{ \left[\left(\frac{q_1^\infty - q_t^\infty}{q_t} \right) - 1 \right] \ln(\gamma_v^s X_v^s) \right\} \quad (23)$$

$$Y_2 = \frac{\gamma_2^s x_2}{P_t} \frac{q_t}{q_t^\infty} \frac{q_2^\infty}{b_2} \left[\frac{\exp(\alpha_{2v})}{1 + \alpha_{2v}} \right] \exp \left\{ \left[\left(\frac{q_2^\infty - q_t^\infty}{q_t} \right) - 1 \right] \ln(\gamma_v^s X_v^s) \right\} \quad (24)$$

Acknowledging that $Y_1 + Y_2 = 1$, q_t was determined for different compositions in the adsorbed phase, x_1 , and the predicted adsorption capacities for each gas in the binary mixture were deduced by Equation 25.

$$q_1 = x_1 q_t \quad , \quad q_2 = (1 - x_1) q_t \quad (25)$$

5.4.6. ASSESSING GAS SEPARATION PERFORMANCE

To predict the CH_4/N_2 gas separation performance in both the single gas and gas mixture systems for the ion-exchanged clinoptilolites studied, the selectivity may be determined as shown Equation 26.

$$\alpha_{1/2} = \frac{x_1/y_1}{x_2/y_2} \quad (26)$$

Alternatively, simply the ratio of pure gas adsorption capacities is a quick method of assessing adsorbent performance, and is roughly equivalent to the ideal selectivity for an equimolar mixture of both components as shown in Equation 27.

$$\alpha_{1/2}^0 = \frac{q_1^0}{q_2^0} \quad (27)$$

5.5. BINARY GAS ADSORPTION MEASUREMENTS

Knowledge of the adsorption properties of gas mixtures is crucial for the assessment of the true performance of prospective adsorbents for use in gas separations. However, multicomponent adsorption isotherm measurements are challenging due to the added complication of analysis of the mixture composition in the adsorbed phase. Several reliable experimental multicomponent adsorption measurement techniques have been developed and are described in the literature including dynamic systems such as: breakthrough measurements,[29,71], differential column analysis [72], zero length column chromatography [73], chromatography [74–76], isotope exchange technique[77]; and static systems such as: gravimetric or volumetric methods [26,78–81].

5.5.1. CONCENTRATION PULSE CHROMATOGRAPHY

Concentration pulse chromatography was used in this study to measure the CH₄-N₂ binary isotherms on the different clinoptilolite samples. The setup has been described in previously published papers [82–85]. Packed adsorbent columns, were installed in a modified GOW-MAC Series 400 gas chromatograph containing a thermal conductivity detector (GOW-MAC Instruments Co., Bethlehem, Pennsylvania, USA). At the initiation of the adsorption experiments, the cation-exchanged clinoptilolite samples were packed into a column and were regenerated using He as the purge gas. He is assumed to be non-adsorptive, albeit it may present negligible adsorptive behaviors under specific conditions [86]. In the case of binary gas adsorption experiments, CH₄ and N₂ were used as carrier and injection gases. Once a constant baseline voltage was measured by the TCD (indicating adsorption equilibrium), volumes of 0.1 cc of CH₄ and N₂ were injected into the column. The gas injections created disturbances in the adsorption equilibrium. The concentration of the gas samples exiting the column, c , were measured as a function of time in the form of voltage response peaks at the column outlet following the sample gas injection. The mean retention time, μ , was determined by integrating under the response peaks and it was related to the dimensionless Henry's Law constant, K , with the relationship as follows: [76,87–89]

$$\mu = \frac{\int_0^\infty c(t - \mu_D)dt}{\int_0^\infty cdt} = \frac{L}{v} \left[1 + \frac{(1 - \varepsilon)K}{\varepsilon} \right] \quad (28)$$

The dimensionless constant, K , is related to the dimensional Henry's law constant, K_p , which is the same constant that is used in Equation 1 to describe the physical adsorption behaviour under dilute conditions. It is dependant on temperature (T) and adsorbent pellet density (ρ_p) which is defined in the following equation:

$$K_p = \frac{K}{RT\rho_p} \quad (29)$$

For the pure component systems, the Henry's law constant represents the initial slope of an adsorption isotherm at low pressures approaches zero as shown in Equation 1. When the K_p values are obtained from mixture of two components, these measurements are a function of the slopes of both of the individual isotherms of component 1 (CH_4) and component 2 (N_2) in the binary gas mixture, according to Equation 30 below:

$$K_p = (1 - y_1) \frac{dq_1}{dP_1} + y_1 \frac{dq_2}{dP_2} \quad (30)$$

This equation demonstrates the contribution of both components of the carrier gas mixture to the K_p and by extension to the binary adsorption isotherms. Details of the experimental conditions used in this study for the concentration pulse chromatography experiments are shown in Table 5.1.

Table 5.1. Details of the binary gas experimental and column specifications for the concentration pulse chromatography experiments.

Column Specificalitons	Length (cm) Inner diameter (cm) Packing Type Mesh size (US std.Mesh) Particle size range (μm) Void fraction determined with glass beads (dless) Sample gas injection volume (cc)	3.4 0.18 Raw, Cs^+ , Fe^{3+} clinoptilolite 60 x 80 180-250 0.4 0.1
Binary Adsorption Experimental Conditions	Carrier gases (0 to 100% composition) Sample gases Total carrier gas flowrate (sccm) Total pressure (atm) Temperature (K)	CH_4 - N_2 mixture CH_4 , N_2 4 1.0 288, 303
Regeneration Conditions	Purge Gas Used Regeneration Temperature (K) Regeneration Pressure (atm) Regeneration Time (h)	He 573 1 12

For the binary gas adsorption experiments, the experimental column temperature was maintained at either 288 or 303K after regeneration and the system total pressure was held at 1.0 atm. A mixture of CH_4 and N_2 at different concentrations was used as the carrier gas. The carrier gas was sent through a 3.4 cm-long packed column with internal diameter of 0.18 cm. A void fraction of 0.4 in the column was determined with glass beads of the same particle size range as the clinoptilolite pellets (180-250 μm). Dead volume retention times were determined by injecting N_2 in a column packed with 60 $\times$ 80 standard US mesh size (180-250 μm) glass beads using He as the carrier gas at a 4 sccm flowrate. Additionally, the pressure drop across the packed column was measured and determined to be insignificant. The columns packed with the cation-exchanged clinoptilolite samples were regenerated for 12 hours at a column temperature of 573K and a total pressure of 1.0 atm and at 8 sccm He flowrate. At the end of the regeneration, the column temperature was brought down to either 288K or 303K, using a water-cooled coil around the column, and N_2 was sent through the column at a flowrate of 4 sccm.

Varying the composition of the carrier gas, the experimental K_p values were determined at CH_4 concentrations ranging from 0 to 100% in the carrier gas. Between 0 and 10% CH_4 , the carrier gas CH_4 concentrations were increased by increments of 2.5%. Then, until 20% CH_4 , they were increased by 5%

increments. From 20%, the concentrations of CH₄ were incremented by 10% until 100% CH₄ was present in the carrier gas feed. Three sample injections of CH₄ and N₂ respectively were done for each carrier gas mixture concentration. The K_p values determined for each binary composition were the averages of the K_p values obtained for both CH₄ and N₂ injections. These K_p values were used to determine the effects of CH₄ concentration in the carrier gas on the adsorption capacity of each ion-exchanged clinoptilolite sample.

5.5.2. VAN der VLIST and VAN der MEIJDEN – CONCENTRATION PULSE METHOD

Several mathematical models were developed to interpret binary gas K_p values and quantify the contributions of the gases studied [82,84,87,90–92].

The VV-CPM [87] is a third-degree polynomial model suitable for less competitive adsorption systems. The primary four-parameter polynomial used is shown below:

$$K_p = A_0 + A_1y_1 + A_2y_1^2 + A_3y_1^3 \quad (31)$$

Taking the derivatives of Equation 31 leads to the slope functions of the binary adsorption isotherms and is shown below for component 1 and 2, respectively.

$$\frac{dq_1}{dP_1} = B_0 + B_1y_1 + B_2y_1^2 \quad (32)$$

$$\frac{dq_2}{dP_2} = C_0 + C_1y_1 + C_2y_1^2 \quad (33)$$

Integrating Equations 32 and 33 gives the binary adsorption isotherms for components 1 and 2 as shown below.

$$q_1 = \left[B_0y_1 + \frac{B_1}{2}y_1^2 + \frac{B_2}{3}y_1^3 \right] P_T \quad (34)$$

$$q_2 = \left[C_0(1 - y_1) + \frac{C_1}{2}(1 - y_1)^2 + \frac{C_2}{3}(1 - y_1)^3 \right] P_T \quad (35)$$

Equations 32 and 33 can be substituted into Equation 30 to yield the model used to analyze the experimental K_p data for binary gas systems which is shown below:

$$K_p = (1 - y_1)(B_0 + B_1y_1 + B_2y_1^2) + y_1(C_0 + C_1y_1 + C_2y_1^2) \quad (36)$$

For the model to fit the experimental data properly, the coefficients B and C were determined to ensure the minimization of the SSR between the model K_p given in Equation 36 and the experimental K_p data as follows.

$$SSR = \sum_{y_1=0}^{y_1=1} [K_p(model) - K_p(experimental)]^2 \quad (37)$$

Several different constraints have been proposed so that various functions determined using the CPM can properly reflect the binary adsorption isotherm data and are summarized as follows [84,90,93]. The modelled K_p values at the endpoints should be equal to the experimental values [90], as shown in Equations 38 and 39. The binary adsorption capacities at the end points should be equal to their pure isotherm counterparts at the same operating pressure and temperature [90], as illustrated in Equations **Error!** **Reference source not found.** and 41.

$$K_p(model)|_{y_1=0} = K_p(experimental)|_{y_1=0} \quad (38)$$

$$K_p(model)|_{y_1=1} = K_p(experimental)|_{y_1=1} \quad (39)$$

$$q_1(binary)|_{y_1=1} = q_1^o(pure) \text{ at } P_T \quad (40)$$

$$q_2(binary)|_{y_1=0} = q_2^o(pure) \text{ at } P_T \quad (41)$$

Since, the pure component isotherms likely represent the maximum amount adsorbed at a certain T and P at the endpoints. There should be no maximums observed in the binary adsorption isotherms [93]. Therefore, for the individual isotherm slopes of CH₄ and N₂ in a binary mixture, given in Equations 32 and 33, the values must remain positive throughout the total range of different concentrations in carrier gas studied [93].

5.5.3. THERMODYNAMIC CONSISTENCY

To establish the reliability of the measured binary adsorption data, the validity of the experimental pure component isotherms and experimental binary isotherm correlations should be checked. The thermodynamics of pure and binary gas adsorption systems has been investigated and discussed in detail using the Gibbsian Surface Excess (GSE) model as proposed by Sircar.[94–96]. In this model, the integral across different paths can be used to establish the consistency between the pure gas and binary gas mixture adsorption isotherms. This is shown in Equation 42.

$$\left(- \int_0^P \frac{q_2^o}{P} dP \right) - \left(- \int_0^P \frac{q_i^o}{P} dP \right) = \int_0^1 \frac{[q_1(1-y_1) - q_2 y_1]}{y_1 (1-y_1)} dy_1 \quad y_1 + y_2 = 1, T, P \text{ constant} \quad (42)$$

Here, q_1^o and q_2^o are the amounts adsorbed of pure gas components 1 and 2, respectively. Whereas q_1 and q_2 , are the amounts adsorbed of components 1 and 2 in a binary gas mixture. The integral of the right hand side (RHS) of Equation 42 is the potential for adsorption calculated from the binary gas system at constant T and P. The values for the terms on the left hand side (LHS) are calculated from the pure gas adsorption data from components 1 and 2 at given values of P and T. The level of accuracy of the binary adsorption equilibria measurements can therefore be checked by comparing both sides of Equation 42, and the % difference between the two values is expressed using Equation 43.

$$\%Difference = \frac{|RHS-LHS|}{LHS} \cdot 100 \quad (43)$$

5.6. RESULTS and DISCUSSION

5.6.1. MATERIAL PROPERTIES

The unit cell basis for clinoptilolite can be expressed by the simplified chemical formula: $(X)_6 (Al_6Si_{30}O_{72}) \cdot 20H_2O$, where X denotes the exchangeable extra framework cations (+1 charge basis) [42,97]. Table 5.2 summarizes the composition of the raw and modified clinoptilolite samples, analysed using EDS as a function of the average unit cell for clinoptilolite as a basis. The average Si/Al ratio of the raw zeolite sample ranges from 5.52 – 6.21 which is in the typical range for clinoptilolite [97,98]. The extra-framework cations present in the raw clinoptilolite sample were K^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , and to a lesser extent Na^+ . Elemental analysis of the clinoptilolite samples confirms that a large portion of the naturally occurring extra-framework cations were substituted with Fe^{3+} or Cs^+ in the cation-exchanged samples. The analysis shows that the Si/Al ratio for the exchanged samples also fall within a similar range with respect to the parent clinoptilolite material. It is worth noting that the Si/Al ratio is the highest for the Fe^{3+} exchanged clinoptilolite. This may indicate the removal of the framework Al^{3+} during cation exchange. Ultimately this value is not significant based upon the degree of precision of this analysis method. However, it is clear that the Fe^{3+} exchanged clinoptilolite appears to have a higher amount of Fe^{3+} cations than otherwise would be expected. The unit cell of clinoptilolite is expected to have negative charge of about - 6 as a result of the AlO_4^{-1} tetrahedra incorporated within the framework. This negative charge is balanced by extra framework cations. The elemental analysis in Table 5.2 shows the presence of almost 9 Fe atoms per unit cell. This value is greater than the number of Fe^{3+} cations expected to be exchanged within clinoptilolite unit cell. For each Fe^{3+} cation, it is expected that a corresponding three negative zeolite framework charges are required to remain in balance[99]. Thus it has been proposed by others that the additional Fe^{3+} cations (or any other metallic cations) present in over exchanged zeolites may form oxodic or hydroxodic metallic species. These species have a lower overall charge difference compared to the original Fe^{3+} cation, They may be formed freely or incorporated on the internal and external zeolite surface depending on the chemical environment [99–102].

Table 5.2. Unit cell elemental composition of raw, Cs⁺, and Fe³⁺ cation exchanged clinoptilolite samples obtained using EDS analysis. The elements were analyzed on a %wt basis, and the values were converted to unit cell atomic composition on the basis of 6 Al atoms.

Sample /Cation	Unit Cell Elemental Composition								Si:Al
	O	Al	Si	K	Ca	Mg	Na	Fe	
raw clinoptilolite	85.39 +/- 5.76	6.00	35.20 +/- 2.06	1.76 +/- 0.30	1.76 +/- 0.16	1.01 +/- 0.38	0.17 +/- 0.06	1.79 +/- 0.39	5.52 - 6.21
Cs⁺ clinoptilolite	79.79 +/- 3.68	6.00	32.90 +/- 1.41	0.48 +/- 0.01	-	0.33 +/- 0.15	-	0.52 +/- 0.22	5.24 - 5.71
Fe³⁺ clinoptilolite	90.91 +/- 0.84	6.00	36.11 +/-0.09	0.26 +/-0.02	0.09 +/-0.03	-	-	8.94 +/- 0.74	6.00 - 6.04
The uncertainty was quantified as the standard deviation between the sample averages of two separate samples, with n = 10 independent collection points for each sample.									

Figure 5.1 presents the X-ray diffractograms for the raw natural clinoptilolite. The sample exhibits the characteristic XRD pattern which is attributed to clinoptilolite as evidenced by the correlation of the peaks denoted by “*” on the XRD pattern [52,103–107]. This means that it is likely that clinoptilolite phase forms the majority mineral component present in the raw zeolite sample. Moreover, the raw clinoptilolite shows a high degree of crystallinity, as demonstrated by the sharp characteristic peaks. Modification of the clinoptilolite through cation exchange shows that the material maintains many of the characteristic peaks albeit with a lower intensity. For the Cs⁺ clinoptilolite, there is a noted absence of the peaks at 9.88° and 11.20°. These differences are to be expected and may be due to the reorganization of the extra framework cation distribution[108]. The low intensity peaks of the XRD pattern of Fe³⁺ cation-exchanged clinoptilolite indicates framework disorder and follows closely to those reported by others [47,99]. Fe³⁺ clinoptilolite displays additional peaks at 41.0°, 49.6°, and 54.3° that do not appear in any significance in the raw clinoptilolite sample. This may correspond to additional iron containing phases not present in the parent clinoptilolite sample. These phases have likely formed as a result of chemical reactions within the cation exchange environment.

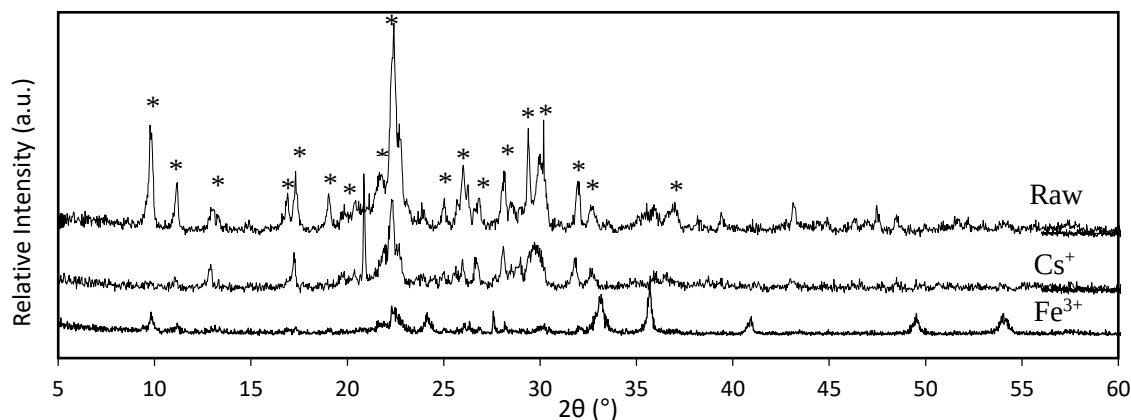


Figure 5.1. XRD pattern of the raw natural clinoptilolite compared to the Cs^+ and Fe^{3+} cation exchanged clinoptilolite. The star symbol (*) signifies the characteristic peaks typical of clinoptilolite [52,103–107,109].

The FT-IR spectra of the clinoptilolite samples are presented in Figure 5.2. This confirms that based upon the observed spectral range of 650 to 4000 cm^{-1} , the exchanged material retains much of the basic characteristics of the parent clinoptilolite sample. However a few differences may be observed within some of the spectral band regions. Doula (2002, 2007) and Mozgawa et al. (2009) have described in detail the IR spectra for clinoptilolite and the corresponding effect of cation exchange. All of the samples show bands at approximately 3605 cm^{-1} which correspond to the bridging —OH molecules present within the framework structure [109,110]. However, only the Fe^{3+} clinoptilolite shows an additional broad band present at 3353 cm^{-1} ; this behaviour resembles the findings reported by Doula (2007). In that study, it was suspected that this vibration band corresponds to intermolecular hydrogen bonding present within oxodic or hydroxodic species. Another possibility may be that excess Fe salts could form complexes in the solution and adsorb onto the clinoptilolite surface. This supports the idea that the cation exchange environment with FeCl_3 salt may result in the formation of additional iron containing phases on the surface of the clinoptilolite.

Slight differences may be observed for the Cs^+ and Fe^{3+} clinoptilolite compared to the parent sample in the spectra range of 650 to 1250 cm^{-1} . This region corresponds to the internal Si and Al oxide tetrahedra bond vibrations and pseudo-lattice vibrations [99,109,111]. Small but notable shifts may be identified with respect to the band at 1038 cm^{-1} for the raw clinoptilolite compared to the Cs^+ and Fe^{3+} clinoptilolite (1029 and 1043 cm^{-1} , respectively for the samples). This band is sensitive to the presence of the framework Si and Al content [99,112]. This small deviation suggests a limited change in the Si and Al content within the overall zeolite lattice. While some small distinctions are observed between the different IR spectra, caution

should be taken when interpreting these results due to the complicated physiochemical properties of these materials.

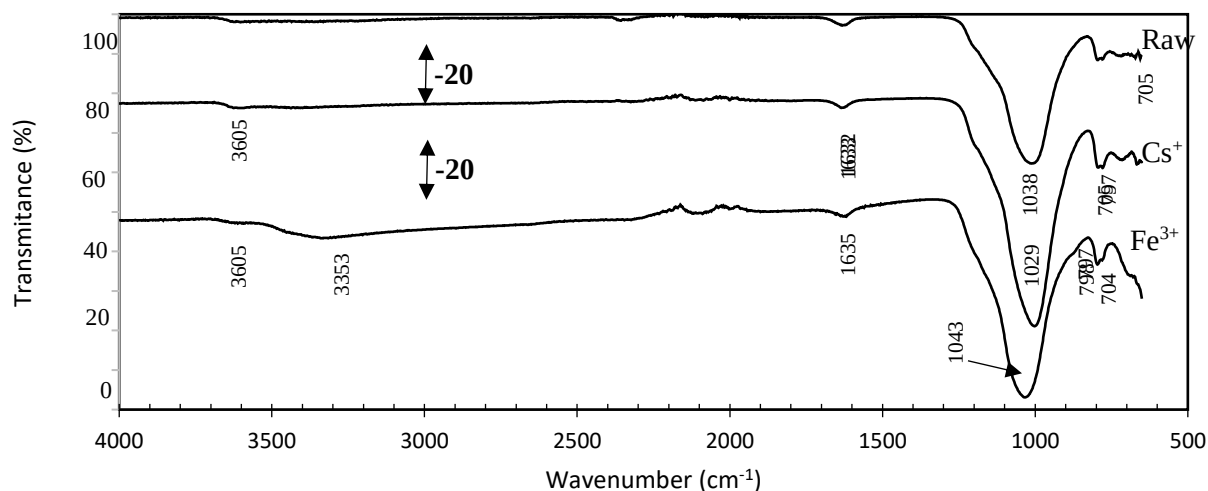


Figure 5.2. FT- IR spectra of the raw natural clinoptilolite compared to the Cs^+ and Fe^{3+} cation exchanged clinoptilolite. A separation of -20% transmittance is applied between each spectra.

SEM images of the clinoptilolite samples are shown in Figure 5.3. Qualitatively, no distinctions may be drawn between the Cs^+ clinoptilolite and the raw clinoptilolite. However it is clear that the Fe^{3+} clinoptilolite displays a greater quantity of fragmentation following cation exchange. In this sample, distinct amorphous microparticles are observed to be dispersed amongst the larger clinoptilolite particles. It is suspected that these particles are composed of various Fe species. They were likely formed following dissolution of the various impurities present in the parent clinoptilolite sample by cation exchange environment.

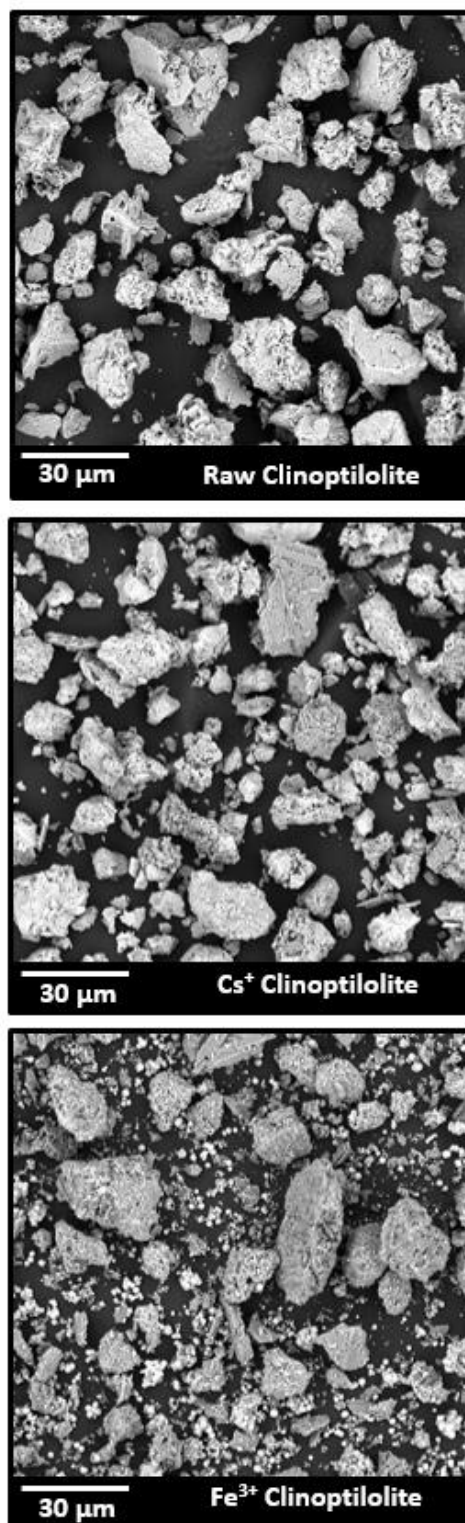


Figure 5.3. SEM images of the natural clinoptilolite (top) compared to the Cs⁺ (middle), and Fe³⁺ (bottom) cation exchanged clinoptilolite (magnification 2000X).

5.6.2. PURE GAS ADSORPTION

Pure gas adsorption equilibrium isotherms for CH₄ and N₂ obtained at 303K and the corresponding CH₄/N₂ ideal selectivity values are shown in Figure 5.4 for the unmodified raw clinoptilolite. It should be noted that the ideal selectivity values shown in this Figure that are below a pressure of 0.5 atm are not accurate since this region is not accounted for with the experimental data. The experimental data is shown to be fairly well represented by both the Langmuir and DSL model isotherms and the regression parameters are summarized in Table 5.4.

A notable characteristic of clinoptilolite in comparison to other adsorbents is that it can exhibit adsorptive preference for either N₂ or CH₄. Due pore network geometry, the charge-balancing extra-framework cations are located within channels and can block access to the adsorption sites [19,20,42,45,49]. The positioning of Ca²⁺ and/or Na⁺ cations indicates that the channel dimensions may be reduced. Therefore, the larger CH₄ gas molecules may have to overcome some initial steric inhibition while smaller N₂ gas molecules are not impeded. The raw clinoptilolite used in this study consists of a distribution of cations in such a way that the quantity of Ca²⁺ cations is insufficient to fully block access of the larger CH₄ gas to the channel network. While access of CH₄ to the pore network may be limited to some degree, it is not fully impeded by the random distribution of natural cations.

The presence of different types of charge-balancing cations means that the natural clinoptilolite exhibits a high degree of surface charge heterogeneity. The variable surface charge distribution leads to a higher degree of electrostatic surface interactions. At low surface loadings, these interactions are more favoured for the N₂ molecule since it is smaller and has quadrupole moment. The adsorption of CH₄ may also be hindered by the placement of the natural cations within the channels. However, as surface loadings increase, the effect of lateral dispersion and repulsion interactions within the adsorbed phase are more pronounced. The N₂ molecules in the adsorbed phase experience a degree of close-range repulsion induced by the quadrupole moment. These repulsion forces are greater compared to that of CH₄. The same trend for raw clinoptilolite has been reported for CH₄ and N₂ adsorption for Ca²⁺ and Mg²⁺ cation rich Turkish Bigadic clinoptilolite [113].

For natural clinoptilolite, even though it is rich in divalent cations (Ca²⁺, Mg²⁺), the positioning of these cations within the channels mitigates the adsorption capacity of CH₄ since some of the sites are blocked due to steric factors. The adsorption capacity of CH₄ on natural clinoptilolite variants may be subject to underreporting the equilibria values. This may be due to the combined effect of slower molecular motion at lower temperatures and limited access to the channel network due to steric effects [51]. In fact,

Kouvelos et al. (2007) observed that CH_4 adsorption capacity slightly decreased with temperature and thus reported the adsorption capacity as ‘pseudo-equilibria’ values. Similar properties were shown with pore constricted ETS-4 titanosilicate, where CH_4 adsorption remained constant regardless of the temperature [114]. Obviously, these observations run counter to the fundamental understanding of adsorption phenomena. Therefore, in order to observe the true CH_4 and N_2 adsorption equilibria for Cs^+ and Fe^{3+} clinoptilolite, great care was taken to obtain values following prolonged equilibrium gravimetric measurements (discussed in Section 5.2.4).

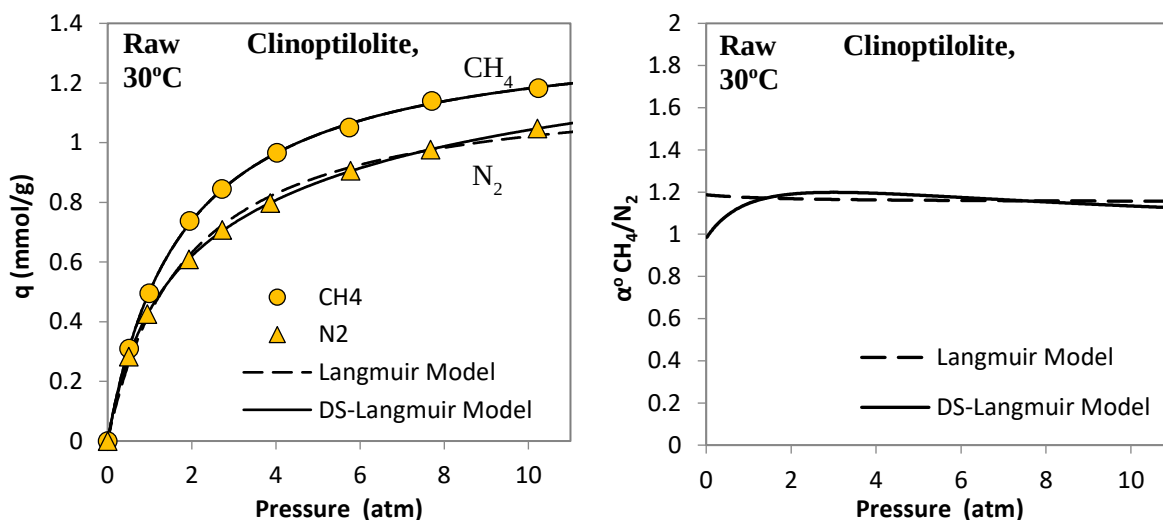


Figure 5.4. CH_4 and N_2 pure component adsorption isotherms fitted with Langmuir and DS Langmuir models (left) and the CH_4/N_2 adsorption capacity ratios (right) for raw clinoptilolite at 303K.

Table 5.3. Regression results for the Langmuir, DSL, and FH-VSM parameters for pure CH₄ and N₂ adsorption isotherms on raw clinoptilolite at 303K.

Model	Parameter	Raw Clinoptilolite	
		CH ₄	N ₂
Langmuir	q^{∞} (mmol g ⁻¹)	1.391	1.208
	b (atm ⁻¹)	0.565	0.548
	SSR	0.00032	0.00232
DS-Langmuir	q_A^{∞} (mmol g ⁻¹)	0.081	0.769
	q_B^{∞} (mmol g ⁻¹)	1.311	0.689
	b_A (atm ⁻¹)	0.437	0.954
	b_B (atm ⁻¹)	0.574	0.101
	SSR	0.00031	0.00028
FH-VSM	q_1^{∞} (mmol g ⁻¹)	1.680	1.325
	b_1 (atm ⁻¹)	0.915	1.132
	α_{lv}	1.083	1.608

Figure 5.5 presents the CH₄ and N₂ adsorption isotherms for the Fe³⁺ and Cs⁺ cation-exchanged variants obtained at 288 and 303K from the microgravimetric measurements. The corresponding regression parameters of the pure component isotherm model used are summarized In Table 5.4. As the temperature is increased, the adsorption capacity of both CH₄ and N₂ decreases. This trend is consistent with the fact that physical adsorption is an exothermic process and is supported by the findings of our previous study for these materials[115]. Cs⁺ and Fe³⁺ clinoptilolite are both CH₄ selective in a pure gas setting. It is supposed that the two cations studied do not occupy the exact same cation sites as those of the naturally occurring cations [116]. The type and charge of cation can explain the preferential adsorption of CH₄ over N₂. The Fe³⁺ clinoptilolite adsorption capacities for both CH₄ and N₂ at either temperature are superior to those of the raw clinoptilolite and the Cs⁺ variant. The Fe³⁺ cation is smaller than Cs⁺ (ionic radius= 0.55 Å vs. 1.67Å) or the natural cations present in the raw clinoptilolite: Mg²⁺, Ca²⁺, K⁺, (ionic radii = 0.72Å, 1.00Å, and 1.38Å respectively) [117,118]. Therefore this allows for a greater volume of space within the pore cavity for the adsorbed gases to gain access. In contrast, the Cs⁺ cation is the largest of the studied cations and it is evident that the overall adsorption capacity of the Cs⁺ clinoptilolite is much lower than both Fe³⁺ and natural clinoptilolite. The higher charge density and greater polarizing strength of the trivalent Fe³⁺ cation can induce higher adsorption potential for both gases on the surface compared to the Cs⁺ cation which has a lower charge density. The potential for greater surface heterogeneity is also possible since there is a larger number Fe³⁺ cations compared to Cs⁺ cations (as shown in Table 5.2). It is suspected that the Fe³⁺

cations may have been oxidized into a lower charged state (based on the high number of Fe atoms exchanged), the induced surface heterogeneity the surface may actually alter the adsorption behavior.

Figure 5.6 presents the ideal equimolar CH_4/N_2 selectivity as the ratio of amounts adsorbed in Figure 5.5 for both Cs^+ and Fe^{3+} clinoptilolite at the two studied temperatures. These materials are CH_4 selective, with the clinoptilolites modified with Cs^+ and Fe^{3+} showing improved CH_4/N_2 equilibrium selectivity compared to that of natural clinoptilolite given in Figure 5.4. The CH_4/N_2 separation factors decrease with increasing pressure, which is correlated to the shape of the individual adsorption isotherms of CH_4 and N_2 . At lower pressures ($P < 1\text{atm}$), the CH_4/N_2 ideal selectivity ranges from 3.0 to 6.7 for Cs^+ clinoptilolite and from 2.9 to 6.7 for Fe^{3+} clinoptilolite. These values are greater than the selectivity reached by many activated carbons, which exhibit the best CH_4/N_2 separation performances [25]. At higher pressures ($P > 1\text{ atm}$) the ideal CH_4/N_2 selectivity is comparable to other adsorbent materials including activated carbons, silicalite, and zeolite 5A as reported in the literature [25,27–29,90,119]. The selectivity is observed to increase with increasing temperature. The observed trends in the selectivity with respect to temperature are consistent with our previous study on the temperature effects on these materials [115].

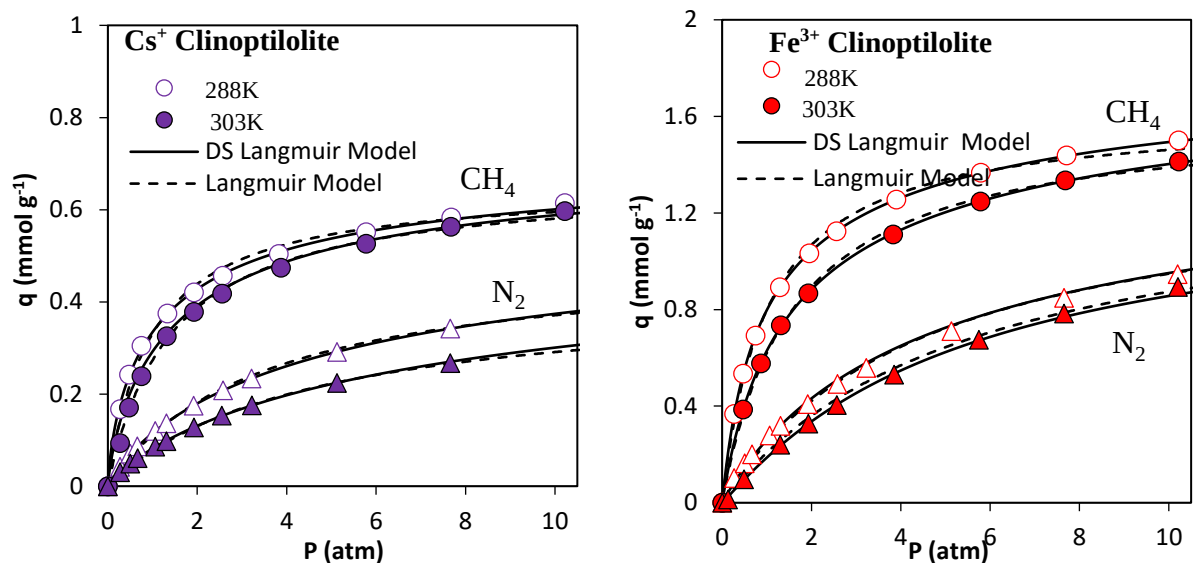


Figure 5.5. CH₄ and N₂ pure component adsorption isotherms fitted with the Langmuir and DSL models for clinoptilolite cation exchanged with Cs⁺ (right) and Fe³⁺ (left) at 288K and 303K.

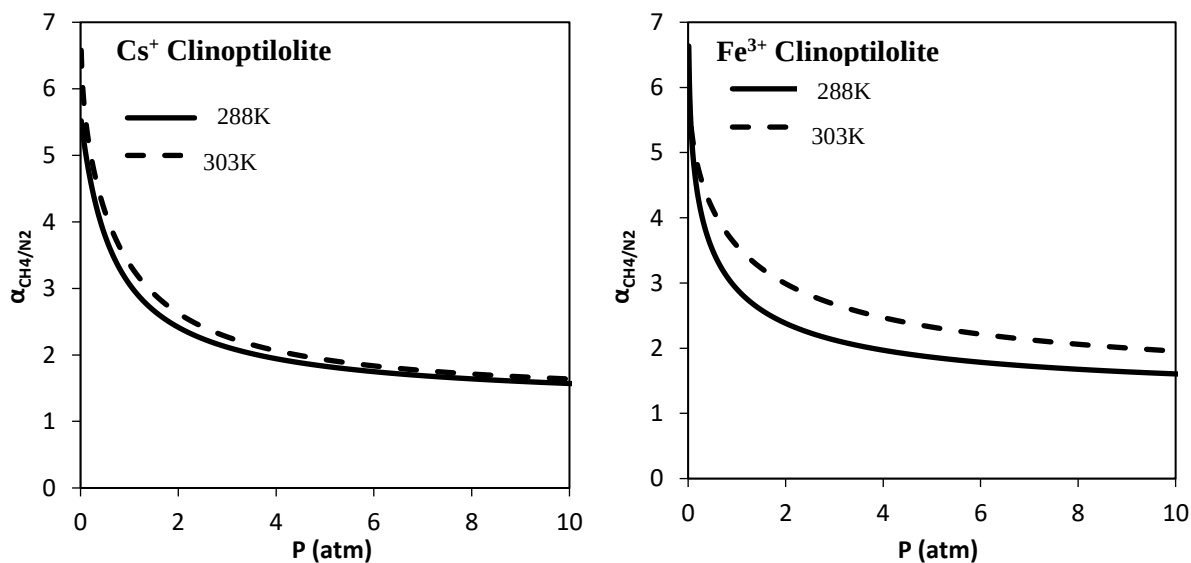


Figure 5.6. Ratio of amounts adsorbed for CH₄ over N₂ for clinoptilolite cation-exchanged with Cs⁺ (left) and Fe³⁺ (right) at 288K and 303K determined using the DSL adsorption isotherm.

Table 5.4. Regression results for the Langmuir, DSL, and FH-VHM parameters for pure CH₄ and N₂ adsorption isotherms on cation exchanged clinoptilolite with Cs⁺ and Fe³⁺ at 288K and 303K.

Model	Parameter	Cs ⁺ Clinoptilolite				Fe ³⁺ Clinoptilolite			
		CH ₄		N ₂		CH ₄		N ₂	
Langmuir	q^{∞} (mmol g ⁻¹)	0.651		0.458		1.610		1.379	
	b_0 (atm ⁻¹)	1.075		0.337		0.985		0.220	
	$-\Delta H$ (kJ/mol)	18.006		26.023		21.895		14.197	
	SSR	0.00377		0.00061		0.00718		0.00445	
DS-Langmuir	q_A^{∞} (mmol g ⁻¹)	0.458		0.133		1.194		0.634	
	q_B^{∞} (mmol g ⁻¹)	0.305		0.423		0.594		0.823	
	b_{A0} (atm ⁻¹)	1.953		0.832		1.489		0.104	
	b_{B0} (atm ⁻¹)	0.137		0.149		0.172		0.323	
	$-\Delta H_A$ (kJ mol ⁻¹)	27.930		13.570		24.005		3.664	
	$-\Delta H_B$ (kJ mol ⁻¹)	0.979		31.133		15.959		21.262	
	SSR	0.00073		0.00003		0.00012		0.00328	
FH-VSM	T (K)	303	288	303	288	303	288	303	288
	q_1^{∞} (mmol g ⁻¹)	0.547	0.927	0.352	0.631	1.574	1.618	1.316	1.632
	b_1 (atm ⁻¹)	0.906	0.134	0.186	0.518	2.011	1.394	0.460	0.228
	α_{1v}	0.121	2.287	0.479	0.234	0.735	1.023	1.379	0.625

5.6.3. GAS MIXTURE ADSORPTION

5.6.3.1. CH₄–N₂ K_p MEASUREMENTS and VV-CPM MODEL FIT

The average experimental binary CH₄-N₂ K_p data obtained at 288K and 303K and 1 atm total pressure were plotted graphically as a function of the CH₄-N₂ composition of the carrier gas (y_{CH_4}) and are presented in Figure 5.7. These K_p values were determined by changing the CH₄-N₂ composition of the carrier gas from $y_{CH_4} = 0$ to 1 and alternating CH₄ and N₂ pulse injections into the carrier gas fed to the adsorbent packed column. The error bars represent the range of the measured K_p values. The non-linear VV-CPM model regression shown provided a good fit for the experimental data. The optimized parameters used for

the fit are summarized in Table 5.5 as well as the corresponding SSR values as determined by using Equation 37, and the constraints highlighted in Equations 38 – 41.

For raw clinoptilolite, the binary $\text{CH}_4\text{-N}_2$ K_p values initially decrease rapidly with increasing y_{CH_4} in the carrier gas feed up to $y_{\text{CH}_4} = 0.2$. Between the range of $0.2 < y_{\text{CH}_4} < 0.7$ the K_p values remain relatively constant (increasing very slightly), and decrease after $y_{\text{CH}_4} = 0.7$. A similar (although less pronounced) trend in binary $\text{CH}_4\text{-N}_2$ K_p values were observed with 13X zeolite for this gas system[25]. In the case of Fe^{3+} and Cs^+ clinoptilolite, the experimental binary $\text{CH}_4\text{-N}_2$ K_p values are observed to decrease continuously with increasing y_{CH_4} in the carrier gas feed. This trend is consistent with the findings from the pure component isotherms (shown in Figure 5.5), where the initial slope of the CH_4 adsorption isotherm is greater than that of N_2 . This indicates a stronger attraction for CH_4 on the surface of clinoptilolite compared to N_2 . Therefore, at low y_{CH_4} , the injected gas disturbance has a greater opportunity to interact with the surface, resulting in higher K_p values. In the case of Fe^{3+} clinoptilolite, since the pure gas isotherms predict higher adsorption capacities for both CH_4 and N_2 compared to the Cs^+ clinoptilolite, the overall experimental K_p values are higher. The K_p values are only at best marginally lower at higher system temperatures (within experimental error). This may be due to the inadequacy of the CPM to describe the temperature effects on this particular system given the selected temperature difference of on 288K and the degree of variability of the K_p measurements. It is expected that since adsorption is an exothermic adsorption process, there should be less interaction at higher temperatures.

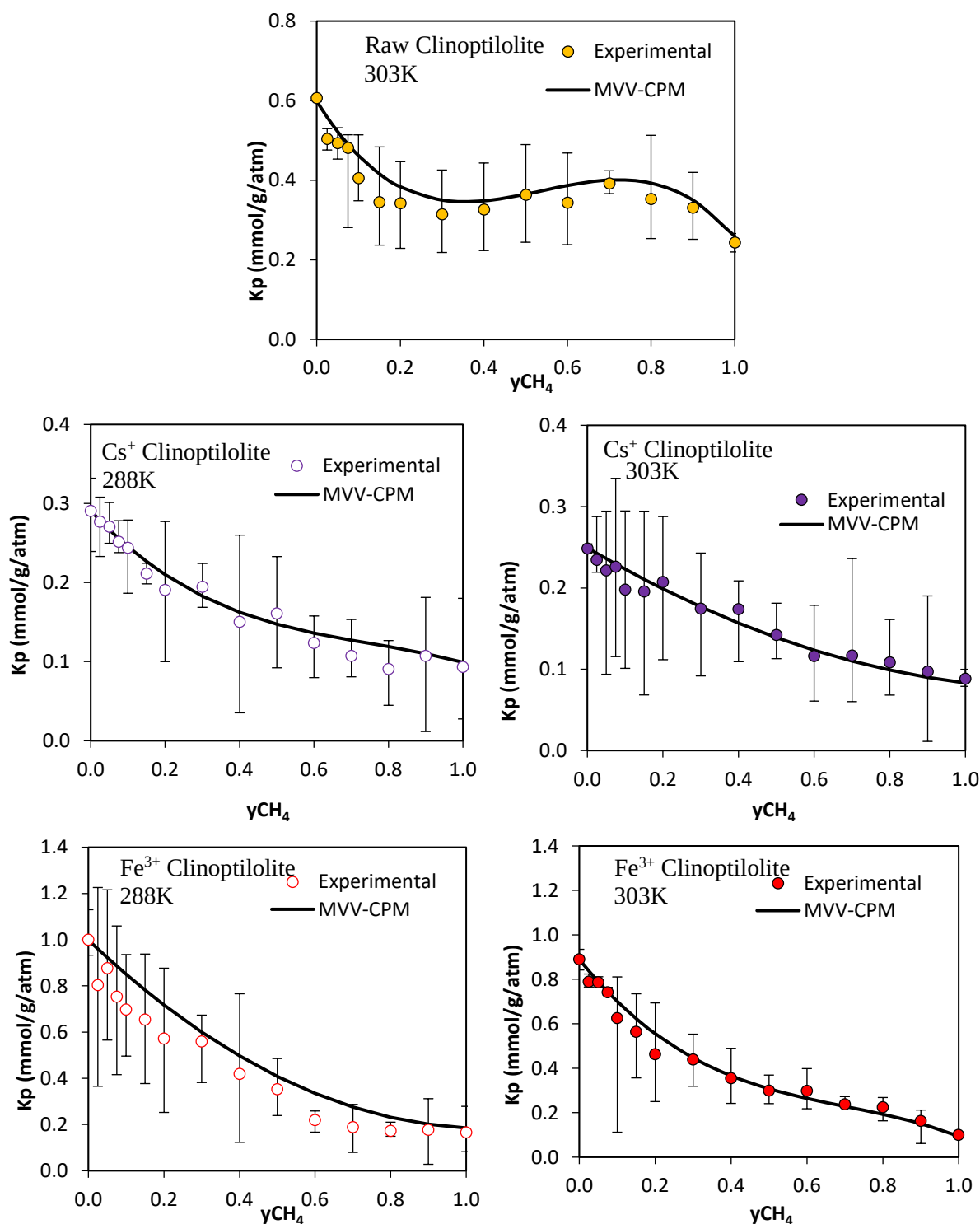


Figure 5.7. VV-CPM regressions for the binary $\text{CH}_4\text{-N}_2$ experimental K_p values as a function of carrier gas composition for raw clinoptilolite (top) cation-exchanged with Cs^+ (middle) and Fe^{3+} (bottom) at 288K and 303K and 1 atm.

5.6.3.2. COMPARISON of the BINARY ADSORPTION ISOTHERMS with THEORETICAL MODELS

Using the VV-CPM parameters from Table 5.5, binary adsorption isotherms for CH₄ and N₂ were developed using the procedure explained in Section 5.2.4 and are illustrated in Figure 5.8. In this Figure, the binary isotherms are presented alongside the predictions by the ELM, IAST and FH-VSM models determined from the single component CH₄ and N₂ isotherm data.

Some binary CH₄-N₂ adsorption systems, like those on activated carbons, have been shown to behave fairly consistently with the binary predictions [25,29]. Other binary CH₄-N₂ adsorption systems, for example those occurring on zeolites including silicalite, 13X, 4A, and 5A, have shown substantial deviation from the mixture model predictions [22,25,26,28,120,121]. Binary gas mixture model predictions derived from pure gas adsorption data are not always accurate for assessing the actual separation performances in a binary setting. Non-idealities induced by the energetic heterogeneity of the zeolite surface and competitive adsorption account for much of this lack of accuracy. While these observations are particularly true for highly selective binary systems (e.g.: CO₂ - N₂ mixture adsorption) [84,122].

Table 5.5. VV-CPM parameters for binary CH₄/N₂ adsorption experiments on clinoptilolite cation-exchanged with Cs⁺ and Fe³⁺ at 288K and 303K and 1 atm.

Parameter	Cation				
	Raw	Cs ⁺		Fe ³⁺	
	303K	288K	303K	288K	303K
B ₀	0.605	0.29398	0.250	0.980	0.890
B ₁	-2.250	-0.622	-0.274	-1.376	-1.808
B ₂	3.020	1.073	0.509	1.408	1.903
C ₀	0.720	0.387028	0.248	0.804	0.571
C ₁	-0.790	-1.079	-0.674	-2.008	-1.190
C ₂	0.311	0.791	0.509	1.389	0.713
SSR	0.005	0.001	0.0018	0.080	0.021

As shown in Figure 5.8, all the CH₄-N₂ binary theoretical models present some degree of divergence from the experimental data. In all cases, the ELM, DSL, IAST and FH-VSM binary isotherm models overestimate the adsorption capacities for both CH₄ and N₂ on the raw, Cs⁺, and Fe³⁺ clinoptilolite. A degree of caution should be used when interpreting the accuracy of the single gas isotherm models with the multicomponent predictions for this system. Judging from the experimental binary adsorption isotherms

given in Figure 5.8, it is clear that all of the predictive binary models overestimate the amount adsorbed for CH_4 and N_2 , and that some level of competitive adsorption is observed with CH_4 - N_2 binary adsorption on clinoptilolite.

The discrepancies between the experimental adsorption capacities and the isotherm model predictions though ELM, DSL, and IAST are a clear indicator of non-ideal behavior. Since both of these models are based upon an extension of the Langmuirian assumption for single gas isotherms, there is an implied assumption that the binary adsorbed phase would behave like an ideal solution. Based on the results shown in Figure 5.8, it is clear that different non-ideal phenomena could be occurring in the binary CH_4 - N_2 system, explaining the deviation presented by the predicted data. The binary adsorption isotherms for both gases exhibit a degree of concavity. This indicates that it is likely that CH_4 and N_2 molecules are competing for the same adsorption sites [22,23,123,124]. In particular, the energetic surface heterogeneity of clinoptilolite induces greater non-ideality which leads to a non-uniform selectivity from one adsorption site to another. As previously mentioned, clinoptilolite is composed of three microporous channels with multiple cations, differing in charge and size, occupying space within the cavity, therefore their presence effects the local adsorption properties. The binary results suggest that CH_4 and N_2 are attempting to occupy the same sites. The effect is compounded by the small pore diameter of clinoptilolite, whereby lateral interactions between the molecules in the adsorbed phase are more pronounced. These factors are a result of differences in adsorbate properties such as the molecular size and electrostatic potential. If the binary isotherms are compared at different temperatures, it can be observed that the difference between the predictions by ELM, DSL, IAST and FH-VSM and the experimental data is larger at the lower temperature of 288K, both for Cs^+ and Fe^{3+} , compared to the difference at 303K.

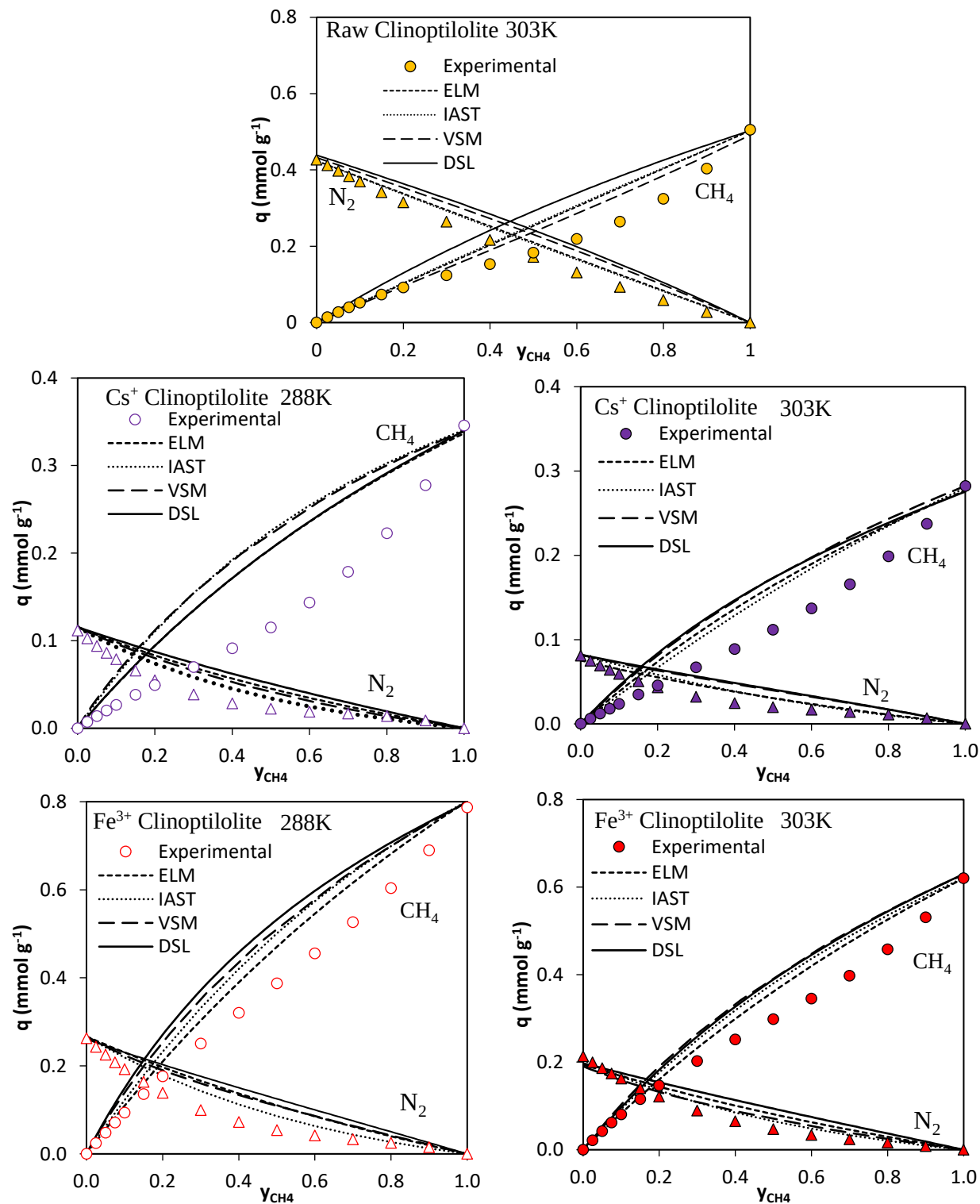


Figure 5.8. Experimental binary adsorption isotherms for CH_4 , N_2 for raw clinoptilolite (top), cation-exchanged with Cs^+ (middle) and Fe^{3+} (bottom) at 288K and 303K and 1 atm, compared to the corresponding ELM, IAST and FH-VSM binary isotherm predictions.

5.6.3.3. EQUILIBRIUM BINARY PHASE DIAGRAMS and CH₄/N₂ SELECTIVITY

The phase equilibrium diagrams at different temperatures were determined from the experimental binary isotherms and are presented in Figure 5.9. In the same Figure, these values are compared to the binary predictions determined using the ELM, IAST and FH-VSM models. The separation potential may be assessed qualitatively by measuring the distance between the phase diagrams and the 45° line. It is obvious that raw clinoptilolite shows a very low separation potential for either CH₄ or N₂, and is essentially non selective. In contrast, both of the Cs⁺ and Fe³⁺ modified clinoptilolites exhibit a much higher separation potential in favour of CH₄. All of the theoretical models show a slight deviation in the binary phase behavior compared to the experimental values for Cs⁺ and Fe³⁺ clinoptilolite. At both temperatures, the experimental binary phase diagrams for both Cs⁺ and Fe³⁺ clinoptilolite are furthest from the 45° line at about $0.40 < y_{\text{CH}_4} < 0.60$ indicating the greatest separation potential in this region.

The separation factor coefficients for the binary CH₄/N₂ separation are presented in Figure 5.10. For raw clinoptilolite at 303K these binary CH₄/N₂ separation values are close to unity; ranging from 1.05 to 1.65. For Cs⁺ clinoptilolite the CH₄/N₂ separation coefficients range from 2.7 to 5.2 and from 3.5 to 5.3 at 288K and 303K, respectively. The highest selectivity value is achieved at CH₄ concentration of $y_{\text{CH}_4} = 0.55$ for Cs⁺ clinoptilolite at both temperatures. Fe³⁺ clinoptilolite has consistently superior CH₄/N₂ separation performance compared to those of either raw or Cs⁺ clinoptilolite. At 288K, the selectivity coefficients range from 3.9 to 7.3, and reach a maximum value at $y_{\text{CH}_4} = 0.60$. At 303K the CH₄/N₂ selectivity is similar, and reaches a maximum value of 7.2 at $y_{\text{CH}_4} = 0.80$ for Fe³⁺ clinoptilolite. Similar experimental binary behavior showing an increase in separation factors at low concentrations of a particular gas until a maximum is reached followed by a decrease in separation factor has also been reported by others [83,122].

The binary CH₄/N₂ separation performance of the modified clinoptilolites is summarized in Table 5.6. These results are compared to the ideal equimolar selectivity under the similar conditions ($P = 1\text{atm}$, $288\text{K} \leq T \leq 323\text{K}$ ($15^\circ\text{C} \leq T \leq 50^\circ\text{C}$)) alongside the performances of other small pored zeolites or activated carbons reported in literature for this separation. The CH₄/N₂ separation performance of both Cs⁺ and Fe³⁺ clinoptilolite compares favorably with many of these adsorbents. In the case of Fe³⁺ clinoptilolite, under similar conditions the selectivity for CH₄ over N₂ is comparable or superior to that of various activated carbons and silicalite which rank amongst the best materials for this separation.

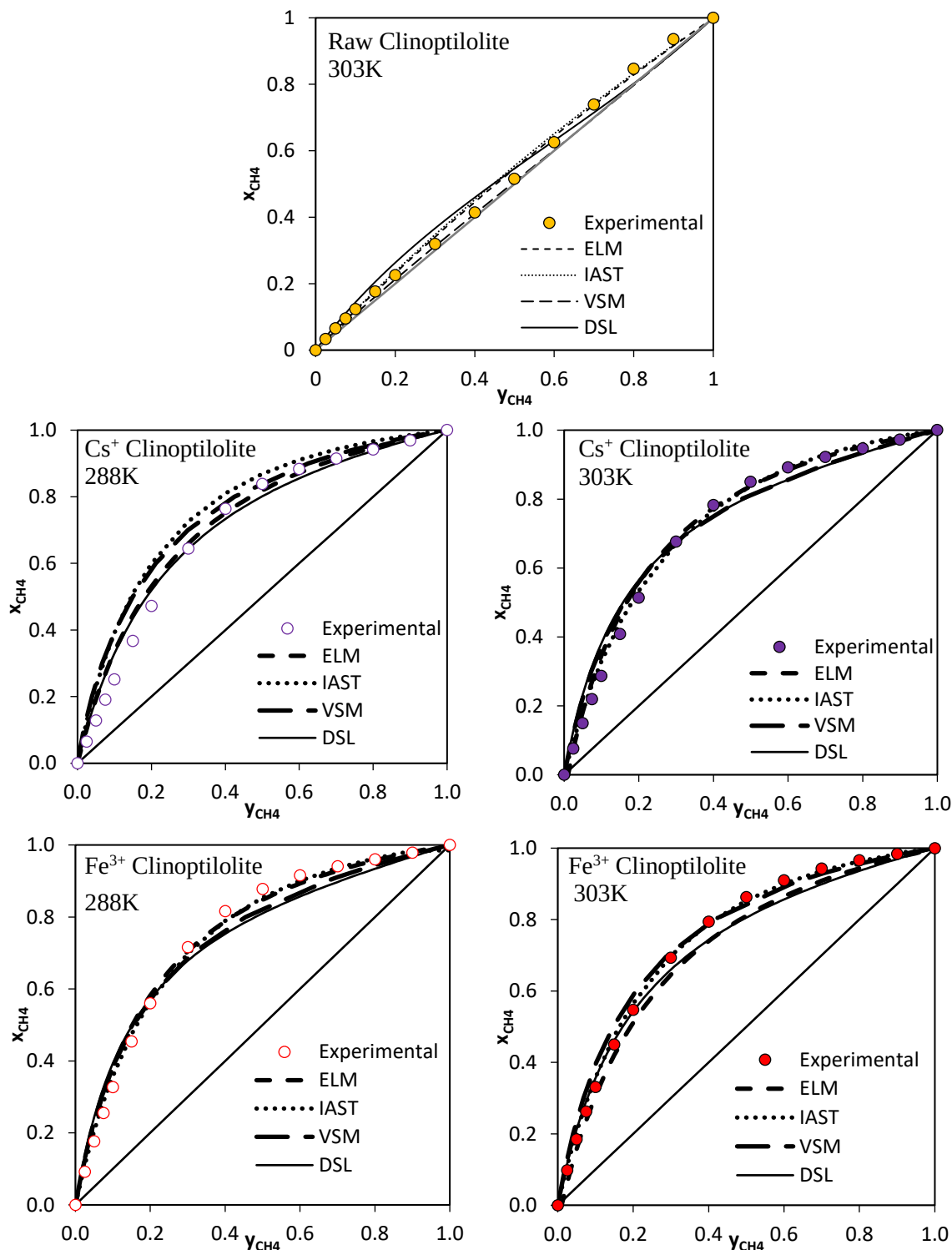


Figure 5.9. x-y phase diagrams for the experimental binary adsorption of CH₄ for raw clinoptilolite, as well as the cation-exchanged ones with Cs⁺ and Fe³⁺ at 288K and 303K and 1 atm total pressure, compared to the corresponding ELM, IAST and FH-VSM x-y phase diagram predictions.

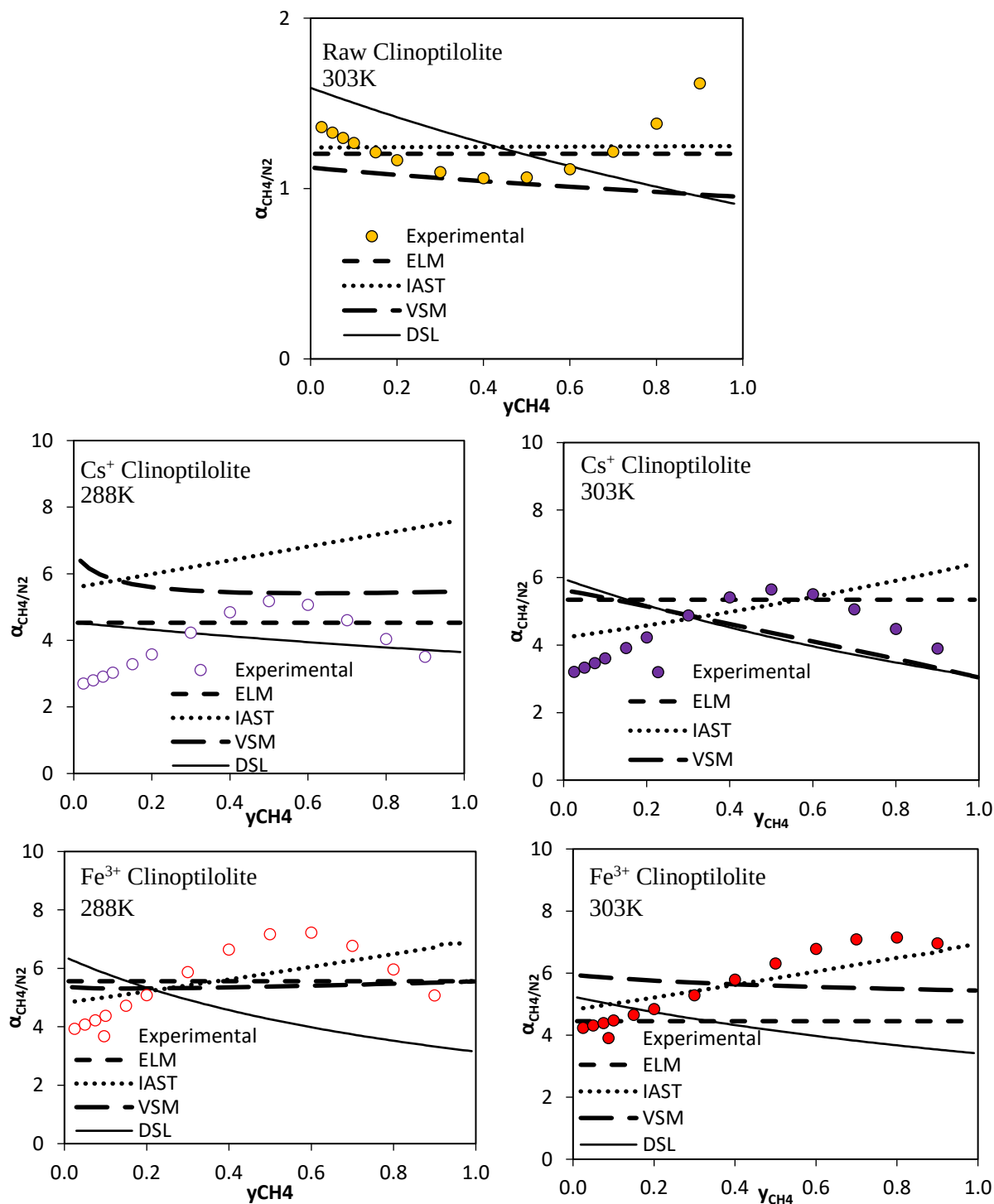


Figure 5.10. Selectivity coefficients for CH₄ over N₂ for raw clinoptilolite, as well as the one cation-exchanged with Cs⁺ and Fe³⁺ at 288K and 303K and 1 atm total pressure, compared to corresponding ELM, IAST and FH-VSM selectivity coefficients.

Table 5.6. Experimental CH₄/N₂ separation performances for raw, Cs⁺, and Fe³⁺ cation exchanged clinoptilolite at 288K and 303K at 1 atm total pressure in comparison to values reported for different adsorbents in the literature under similar experimental conditions.

Adsorbent	T (K)	Ideal Equimolar CH ₄ /N ₂ Selectivity	Binary CH ₄ /N ₂ Selectivity Range	Reference
Cs ⁺ Clinoptilolite	288	3.0	2.7 – 5.2	Present study
	303	3.4	3.5 – 5.3	
Fe ³⁺ Clinoptilolite	288	2.9	3.9– 7.3	Present study
	303	3.6	4.1– 7.2	
Raw clinoptilolite	303	1.2	1.05 -1.65	Present study
Silicalite	313	2.7	3.3 – 4.9	[22]
ZSM – 5 (SiO ₂ /Al ₂ O ₃ = 30)	313	2.5	3.0 – 3.6	[23]
Silica gel	303	2.7	2.4 – 3.4	[25]
Activated Alumina	313	1.8	1.8 – 2.1	[27]
Zeolite 5A	303	1.3	1.4 – 1.9	[26]
	323	1.6	1.6 – 1.7	
Zeolite 13X	303	1.2	1.3 – 1.7	[25]
	313	1.8	2.2 – 3.0	[27]
	303	1.7	1.8 – 2.2	[28]
	323	1.9	1.9 – 2.1	
Activated Carbon	303	3.2	3.2 – 4.2	[25]
	303	3.3	5.2 – 5.9	[29]

5.6.3.4. THERMODYNAMIC CONSISTENCY

Table 5.7 present the results for the integral thermodynamic consistency test from the GSE model between the experimental pure component and the binary isotherms determined using Equation 42. As can be observed in this Table, the values for raw clinoptilolite and even Fe³⁺ clinoptilolite are fairly reasonable, and comparable with previous works for similar CH₄-N₂ gas systems presented in the literature that usually range between 2% and 30% difference [22,26,28]. However, the difference in values for Cs⁺ clinoptilolite are substantial, indicating a disagreement between the LHS and RHS of Equation 42. Therefore, caution should be taken when interpreting these CH₄-N₂ binary isotherm values since there is considerable deviation in the thermodynamic consistency requirement for this system. Thus, the combination of the experimental pure component isotherms, the binary predictions, and the experimental binary results should be used to paint the overall picture of the performance of these materials, particularly for Cs⁺ clinoptilolite.

Table 5.7. Integral thermodynamic consistency test for the experimental pure and binary CH₄ and N₂ adsorption data for raw, Cs⁺, and Fe³⁺ cation exchanged clinoptilolite at 288K and 303K at 1 atm total pressure determined using Equation 42.

Adsorbent	Temperature (K)	LHS of Eq. 42 (mmol · g ⁻¹)	RHS of Eq.42 (mmol · g ⁻¹)	% Difference LHS/RHS
Cs⁺ Clinoptilolite	288	0.395	0.202	96.0
	303	0.280	0.155	81.2
Fe³⁺ Clinoptilolite	288	0.831	0.667	24.6
	303	0.636	0.539	18.2
Raw clinoptilolite	303	0.096	0.094	1.6

5.7. CONCLUSIONS

Natural clinoptilolites cation-exchanged with Cs⁺ and Fe³⁺ emerge as promising adsorbents for the separation of CH₄ from N₂ in natural gas. In the present study, raw and cation exchanged clinoptilolites were characterized through XRD, EDS, FT-IR ATR spectroscopy, and SEM. These results confirmed alterations with respect to the elemental composition following cation exchange. Small but noteworthy physicochemical differences were observed between the raw and modified samples. Clinoptilolite comprised the majority of each sample. Single gas isotherms of CH₄ and N₂ were conducted on the raw and modified clinoptilolite samples. For the non-modified clinoptilolite, the ideal selectivity of CH₄ over N₂ is close to unity. The pure adsorption equilibria selectivity values were higher for both of the modified samples. CH₄-N₂ binary gas experiments were carried out at 288K and 303K on the raw and cation-exchanged samples. This led to the development of experimental binary gas isotherms. To assess performance of experimental the binary CH₄-N₂ adsorption behavior, these isotherms were plotted against the theoretical binary isotherm predictions (ELM, DSL, IAST, FH-VSM) determined from the single component isotherm data. The binary model predictions showed significant deviations from the experimental data, implying competitive adsorption behavior. At the range of CH₄ concentrations corresponding to natural gas content, $0.8 < y_{CH_4} < 0.9$, the binary separation factors at 288K are 4.1 and 5.8 for Cs⁺ and Fe³⁺ cation-exchanged clinoptilolite, respectively. At 303K, these values are 4.5 and 7.1, respectively. Clinoptilolite cation-exchanged with Fe³⁺ presents superior separation characteristics, ranking well compared to many adsorbents reported in the literature and would be an interesting alternative to explore for applications in CH₄/N₂ gas separations.

5.8. ACKNOWLEDGEMENT

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5.9. NOMENCLATURE

$A_0, A_1, A_2, A_3,$	parameters used for the primary 4 parameter MVV-CPM fit
B_0, B_1, B_2	parameters used for MVV-CPM fit describing the slope functions of the binary adsorption isotherms
b	equilibrium constant parameter (atm^{-1})
C_0, C_1, C_2	parameters used for MVV-CPM fit describing the slope functions of the binary adsorption isotherms
c	adsorbate concentration at the outlet of the column (expressed as mV)
K	dimensionless Henry's Law constant
K_p	dimensional Henry's Law constant ($\text{mmol g}^{-1} \text{atm}^{-1}$)
L	length of column (m)
n	dimensionless Sips isotherm model parameter
P	pressure (atm)
P^0	equilibrium vapor pressure of a pure component at the same temperature and spreading pressure as the adsorbed hypothetical mixture (atm)
q^∞	limiting (maximum) amount adsorbed (mmol g^{-1})
q	amount adsorbed (mmol g^{-1})
q^0	pure gas adsorption capacity (mmol g^{-1})
R	universal gas constant ($\text{atm m}^3\text{mol}^{-1}\text{K}^{-1}$)
t	time (s)
T	absolute temperature (K)
v	interstitial fluid velocity ($\text{cm}\cdot\text{s}^{-1}$)
x_i	mole fraction of component i in the adsorbed phase
X_i^s	mole fraction of component i in the solution representing the adsorbed phase predicted using the FH-VSM
y_i	mole fraction of component i in the gas phase
Y_i	mole fraction of component i in the gas phase predicted using the FH-VSM

Superscripts

0	pure component for IAST
∞	limiting (maximum) value
S	component in solution for FH-VSM

Subscripts

1	component 1
2	component 2
$1/2$	subscript used for expressing selectivity of component 1 over component 2
$calc.$	calculated
exp	experimental
i	component i
j	component j
m	maximum
t	total
v	vacancy

Greek Symbols

$\alpha_{1/2}$	binary adsorption separation factor for component 1 over component 2
$\alpha^0_{1/2}$	ideal adsorption selectivity for component 1 over component 2
α_{ij}	empirical constant of FH-VSM describing non-idealities cause by interactions of species i and j
ε	bed porosity
μ	mean retention time (s)
μ_D	system dead time (s)
π	spreading pressure (atm)
γ_1^S	activity coefficient of component 1 in the surface phase for FH-VSM
γ_2^S	activity coefficient of component 2 in the surface phase
γ_v^S	activity coefficient of the vacancy in the surface phase
ρ_p	adsorbent density without the void space (kg/m^3)

Abbreviations

ATR	attenuated total reflection
CPM	concentration pulse method
DS	Dual Site (Langmuir model)
DSL	Dual Site Langmuir
EDS	electron dispersive spectroscopy
ELM	Extended Langmuir Model
ETS-4	Engelhard Titanosilicate 4
FH-VSM	Flory-Huggins Vacancy Solution Model
FT-IR	Fourier Transform Infra-Red
GSE	Gibbs Surface Excess
IAST	Ideal Adsorbed Solution Theory
LHS	Left Hand Side (applies to Equation 42)
PSA	pressure swing adsorption
RHS	Right Hand Side (applies to Equation 42)
SCCM	Standard cubic centimeters per minute at 1atm total pressure and 0°C
SEM	scanning electron microscopy
SSR	sum of square residuals
TCD	thermal conductivity detector
VSM	Vacancy Solution Model
VV-CPM	Van der Vlist and Van der Meijden – concentration pulse method
XRD	X-ray diffraction

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CHAPTER 6

The Effect of Ag^+ Cations on the Micropore Properties of Clinoptilolite and Related Adsorption Separation of CH_4 and N_2 Gases

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ABSTRACT

In this study, we report on the effects of Ag^+ cations exchange within clinoptilolite zeolite in relation to both the physicochemical and the gas adsorption characteristics. Clinoptilolites cation-exchanged with AgNO_3 to varying degrees were investigated and the influence of naturally occurring cations (Mg^{2+} , Ca^{2+} , K^+) distributed within the material is discussed. The morphology and elemental composition of the untreated clinoptilolite and the Ag^+ cation exchanged variants were characterized by XRD, EDS, FTIR, and N_2 sorption experiments performed at 77K. From the pore property analysis, we show that a slight reduction in the micropore distribution occurs for the highly exchanged Ag^+ clinoptilolite compared to the untreated clinoptilolite, indicating a likely decrease in the average effective micropore size. Equilibrium adsorption isotherms of CH_4 and N_2 were measured at 303 K. The adsorption uptake rate of both gases was also studied and it slowed by the addition of Ag^+ cations. The modified samples showed decreasing adsorption capacity for the larger CH_4 gas molecule, whereas adsorption of the smaller N_2 gas was less affected. This effect was most pronounced for the highly exchanged Ag^+ clinoptilolite samples (AgNO_3 exchange solution above 0.2M) whereby more N_2 was adsorbed than CH_4 . At 1 atm and 303K, the N_2/CH_4 equilibrium selectivity values of highly exchanged Ag^+ clinoptilolite ranged from 2.8 to 7.6, which are higher than many clinoptilolite types.

6.1. INTRODUCTION

Microporous zeolites as defined according to IUPAC are aluminosilicate materials having a characteristic pore diameter of less than $20\text{\AA}$ [1]. Within this pore size range, various types of adsorbent materials have been developed that may induce molecular sieve separations based upon steric factors in which some components are excluded based on size. One such application of this principle is in adsorption separation tailored for natural gas or landfill gas treatment. For this kind of separation, the removal of CO_2 and N_2 contaminants from CH_4 mixtures is required in order to meet natural gas specifications for transportation and/or end user applications [2–4]. For this application it is advantageous to have the larger CH_4 (and other larger hydrocarbons) to be the lesser adsorbed component compared to the smaller CO_2 and N_2 gases (kinetic diameter = $3.80\text{\AA}$ for CH_4 vs. $3.3\text{\AA}$ and $3.64\text{\AA}$ for CO_2 and N_2) [5]. This means that CH_4 and other hydrocarbons are retained within the higher pressure raffinate stream following the separation step, thus limiting requirements for re-pressurisation [3,6]. An adsorbent material with narrow pore opening between $3.64\text{\AA}$ and $3.80\text{\AA}$ is required to achieve this separation goal so as to selectively block the larger CH_4 gas molecule from accessing the adsorbent pores, while permitting the smaller gases to be adsorbed. Only a few materials satisfy the small pore size requirements for this separation including carbon molecular sieves (CMS) [7–11], titanosilicates[12–14], metal organic frameworks (MOFs) [15], and zeolites (SAPO-34, AIPO-18, clinoptilolites etc.)[16,17,26–29,18–25]. Guild Associates applies this principle for commercial applications in the natural gas industry with their Molecular Gate Adsorption Technology® system[30,31]. Titanosilicate ETS-4 is the adsorbent that is used within this system. This proprietary and synthetic material exhibits tunable pore sizes through systemic contraction of the crystal lattice upon dehydration at temperatures between 270°C and 315°C [12–14]. While ETS-4 remains the benchmark for N_2/CH_4 gas separations, its structural stability is sensitive to the effects of thermal treatment resulting in a limitation to potential applications[32,33].

Zeolites have a crystalline framework structure composed of silicon and aluminum oxides which are covalently interconnected to form a repeating framework of cages or channels making them porous. The framework is negatively charged due to differences in the oxidation states of the SiO_4 and AlO_4^{-1} tetrahedra. The residual negative charge as a result of the AlO_4^{-1} tetrahedra is balanced by extra framework cations that occupy sites within the zeolite cage to maintain neutrality[34]. The type of extra framework cation influences the pore properties of a zeolite. The most ubiquitous example of pore size modification through cation exchange with zeolites belongs to the Linde Type A (LTA) family of zeolites [35–38]. These materials retain specific pore sizes of 3.0 , 3.8 , and $4.3\text{\AA}$, resulting from the different extra framework charge balancing cations of Na^+ , K^+ , and Ca^{2+} , respectively [36]. More recently, cation gating effects have been demonstrated using so called ‘trap door’ zeolites. This group of zeolites includes modified forms of

zeolite A[39,40], chabazite[41], and zeolite rho[23]. These materials are capable of achieving high CO₂ adsorption separation selectivity from CH₄ or N₂ gas containing mixtures. With the ‘trap door’ mechanism; highly interactive molecules (CO₂ or H₂O) are capable of accessing the adsorbed sites while the extra-framework cations may exclude larger and less interactive species (CH₄ or N₂) [23,41]. Essentially, with the ‘trap door’ mechanism, the interactive adsorbing species can alter the positioning of the charge balancing cation within the zeolite pores enough so as to gain access to the adsorbing sites. Zeolites have been developed specifically for inducing molecular sieve type separations targeted towards N₂ removal from CH₄ gas mixtures [16–24]. Amongst these zeolites, the use of small pore molecular sieves such as SAPO-34 and AlPO-18 are notable particularly for applications in N₂/CH₄ selective molecular sieve membrane separations [27,29,42]. Cation exchanged clinoptilolite has also been of interest for this same separation due to its variable adsorption properties including high N₂/CH₄ kinetic selectivity, and the possibility of N₂/CH₄ equilibrium selectivity [19,43–51].

6.1.1. CLINOPTILOLITE ZEOLITE

Clinoptilolite is a natural zeolite and is a member of the heulandite (HEU) structural family. The framework possesses a two dimensional channel structure and consists of alternating 8-membered and 10-membered rings which form two parallel channels. Perpendicular to these two channels intersects a third channel composed of an 8-membered ring. The approximate dimensions of these channels are as follows: the two parallel channels; channel A = 7.2 Å x 4.4 Å, channel B = 4.7 Å x 4.1 Å, and the perpendicular channel; channel C = 5.5 Å x 4.0 Å [19,52]. The unit cell of clinoptilolite is monoclinic and is contained within the following dimensions: $a = 17.62 \text{ Å}$, $b = 17.91 \text{ Å}$, $c = 7.30 \text{ Å}$, with $\alpha = 90.0^\circ$, $\beta = 116.267^\circ$, $\gamma = 90.0^\circ$ [53–56]. The unit cell basis for clinoptilolite may be represented by 72 oxygen atoms, with typical Si/Al ratios for clinoptilolite ranging from 4 to 5.2[57]. Thus, the representative chemical formula for the unit cell of clinoptilolite is: $(X)_6 (Al_6Si_{30}O_{72}) \cdot 20H_2O$, where X denotes the exchangeable extra framework cations[56]. The most common naturally occurring charge balancing extra framework cations are Na⁺, K⁺, Ca²⁺, and Mg²⁺ [58]. Extensive crystallographic studies on HEU type zeolites exchanged with a variety of cation types have identified several different extra framework locations within the zeolite channels[58,59,68,60–67]. The distribution of these locations is dependent on the cation properties (eg: size, charge, etc...) and coordination with the framework lattice and/or extra framework water molecules [58,66,68–71]. For reference, the framework structure and the common extra framework cation sites for clinoptilolite is given in the supplementary information of this article.

The extra framework cations are known to significantly affect the gas adsorption behaviour of clinoptilolite, as such, this has been the subject of several different systemic adsorption studies [19,43–

49,56,72]. Frankiewicz and Donnelly were amongst the first to successfully identify the relationship between the presence of extra framework Ca^{2+} cations in clinoptilolite and resultant N_2/CH_4 adsorption selectivity[16]. Pursuant to this work, Ackley and Yang systematically examined the effect of naturally occurring cations on pure N_2 and CH_4 adsorption on clinoptilolite [19,56,72]. Clinoptilolites modified with Na^+ or Ca^{2+} cations were found to exhibit molecular sieve type behaviour for this gas separation. Subsequent studies have confirmed similar properties utilizing single, mixed, and partially exchanged clinoptilolites including Mg^{2+} and Li^+ in the presence of Ca^{2+} and/or Na^+ cations [73,74]. The balance of evidence suggests that the observed CH_4 molecular sieving effects is dependent on the cation sites occupied by Ca^{2+} and Na^+ , and to a certain extent Li^+ and Mg^{2+} within the channels of clinoptilolite. The cation arrangement is such that the larger CH_4 molecule is blocked, while the smaller N_2 molecules are capable of diffusing into the micropores.

To gain a better appreciation between the location of the extra framework cations and the adsorption behaviour, it is best to envision the clinoptilolite as a semi-infinite plane with a 2 dimensional channel arrangement. When the channels are ‘open’ such as through HCl acid treatment, both CH_4 and N_2 gases are free to diffuse along the pore network[45,75]. Only when the channels are blocked by cations do we observe molecular sieve type behaviour for CH_4 gas adsorption. Conventionally, for the HEU structured zeolite the main cation site designations are denoted as M(1) through to M(4) [76]. The Ca^{2+} and Na^+ cations occupy both the M(1) and M(2) positions. The M(1) position lays off centre within the 10 membered ring which forms channel A, and the M(2) position lays within the eight member ring of channel B. Both the M(1) and M(2) positions are slightly distended and occupy some space within the perpendicular cross channel (channel C); reducing the effective pore aperture of this channel as well. The M(3) site which is located towards the centre of channel C is preferred by K^+ . However, the presence of cations in the M(1) or M(2) positions block access to this site due to steric effects. Likewise, the Mg^{2+} cations occupy the M(4) position which is directly in the centre of channel A, which is the largest channel. The presence of some cations in the M(1) location may block access to the M(4) cation position, causing the channel to be more open after the cation exchange.

Extra framework Ag^+ cations have been demonstrated to significantly enhance the adsorption characteristics of N_2 in some faujisite zeolites [77–79]. Additionally, silver exchanged LTA type zeolites have shown molecular sieve separation behaviour; albeit this has been limited to larger gases such as ethylene/ethane separations[80]. These properties make Ag^+ exchanged clinoptilolite a good candidate for examination into potential molecular sieve type gas separations involving N_2 and CH_4 . The cation exchange properties of Ag^+ clinoptilolite are well known; this material has been exploited for its antimicrobial properties and water treatment applications [81–90]. Recent screening studies into cation exchanged

clinoptilolites for N_2/CH_4 selective adsorption separations have demonstrated the effectiveness of Ag^+ as a pore blocking cation for this separation [51]. In this work, the relationship between the concentration of Ag^+ cations exchanged on different clinoptilolites and the nature of the adsorption of pure N_2 and CH_4 gases is presented. The physicochemical and structural properties of the modified materials were verified and are compared to the non-modified clinoptilolite.

6.2. EXPERIMENTAL

6.2.1. MATERIALS

Clinoptilolite in the powdered form (+140 U.S. Std. mesh ($<105\ \mu\text{m}$)), and pellet form (20 x 60 U.S. Std. mesh, (250 - 841 μm)) was sourced from deposits located in Amargosa Valley, Nevada, USA and were purchased from Ash Meadows Zeolite LLC (Amargosa, NV, USA). Cation exchange was carried out using silver nitrate (AgNO_3 , $\geq 99.0\%$) (Sigma Aldrich, Oakville, ON, Canada). All gases that were used for the experimental analysis were purchased from Linde Canada Ltd. (Ottawa, ON, Canada) and had the following specifications for purity: 99.999% He, 99.999% N_2 , 99.99% CH_4 .

6.2.2. METHODS

6.2.2.1. CATION EXCHANGE

Prior to Ag^+ exchange, the raw clinoptilolite powder was washed with deionized water (a ratio of 1g of adsorbent per 80mL of deionized water was used) and dried at 378K overnight. The adsorbents underwent a cation exchange procedure in the exact same manner as described in our previous paper [75]. A total of 0.5g of Ag^+ clinoptilolite was produced per sample batch using 25mL of AgNO_3 cation exchange solution with the following concentrations: 0.002M, 0.01M, 0.05M, 0.10M, 0.20M, and 0.40M. The samples were cation exchanged sequentially with each experimental batch being exposed to the above-mentioned exchange solution concentrations twice. Following the cation exchange procedure, the samples were washed with deionized water to remove all salts and dried at 378K overnight prior to analysis.

6.2.2.2. MATERIAL CHARACTERIZATION

The level of Ag^+ cations exchanged within the different clinoptilolite samples was measured using Electron Dispersive Spectroscopy (EDS). A JEOL JSM – 7500F Field Emission Scanning Electron Microscope (SEM) equipped with a Tracor-Northern Series Z – II electron dispersive spectrometer was used (JEOL, Tokyo, Japan). For these measurements the SEM had the following working parameters: 20kV acceleration voltage, 10 mm working distance, and 4000X magnification.

Powdered X-Ray Diffraction analysis (XRD) was used to verify the phase structure of the untreated and cation exchanged clinoptilolite samples. Powdered samples were analyzed at room temperature using a Rigaku Ultima IV powder diffractometer in Bragg-Brentano geometry, using Cu K α radiation ($\lambda = 1.5418$ Å). A 2θ range of 2° to 90° was used with a 0.02° step resolution and $6^\circ/\text{min}$ scan speed.

Fourier Transform Infrared (FT-IR) spectroscopic analysis was conducted using a Cary 630 FT-IR with ATR (Agilent Technologies, Mississauga, ON, Canada). A spectral range of 650 to 4000 cm^{-1} was used and a total of 100 scans were carried out for each sample with a resolution of 4cm^{-1} .

The surface properties of the samples were analyzed using N_2 sorption experiments performed at 77K using a Micromeritics ASAP – 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA). The specific surface area was calculated from the Brunauer – Emmett – Teller (BET) method [91]. The micropore volume was calculated using the Horvath – Kawazoe (HK) method and the mezopore volume space was calculated using the Barrett-Joyner-Halenda (BJH) method [92–94]. Prior to the experimental analysis, all of the samples were degassed under high vacuum for 8 hours at 473K.

6.2.2.3. ADSORPTION MEASUREMENTS

Single gas adsorption measurements were performed using a microgravimetric analyser (VTI Corp., Hialeah, Florida, USA) equipped with a Cahn microbalance. The gases used consisted of helium (as a purge gas and for buoyancy correction) and CH_4 or N_2 as sorption gases. Approximately 30 to 50 mg of the clinoptilolite sample was placed inside a stainless-steel sample bucket and degassed at 573K under high vacuum (vacuum pressure of 10^{-8} atm). The samples were considered to be fully regenerated once the sample weight remained unchanged over a period of 1 hour at these conditions. Gas adsorption isotherms were measured for each clinoptilolite sample at 303K with CH_4 and N_2 for pressures ranging from 0 to 10 atm. Adsorption equilibrium was achieved once the sample weight stabilized following a pressure step change (criteria: less than 0.015 wt% weight change over a period of 15 minutes). The transient adsorption conditions were monitored concurrently and were recorded using a data acquisition system. To correct for buoyancy effects, helium gas was used since this gas is assumed to be non-interacting under these conditions[95]. A complete description of the experimental setup and procedure has been already described in our previous contributions [75,96].

The adsorption measurements were used to obtain the excess adsorption isotherms for the CH_4 and N_2 uptake on the different clinoptilolite samples. The data was regressed using the Sips isotherm model [97].

$$\theta = \frac{q}{q_m} = \frac{BP^{1/n}}{1+(BP)^{1/n}} \quad (1)$$

Where, θ is the fractional coverage; q_m is the saturation adsorption capacity; B is the Langmuir affinity constant, and n is dimensionless.

At the same temperature and pressure, the ratio of the pure component adsorption capacities (q_1 and q_2) for the different gases gives a good ideal of the adsorption separation performance, $\alpha_{1/2}$ [21].

$$\alpha_{1/2} = \frac{q_1}{q_2} \quad (2)$$

The rate of adsorption was studied by way of the fractional uptake response to a pressure step change. This was determined by plotting the fractional uptake $\left(\frac{q(t)-q_0}{q_e-q_0}\right)$ as a function of time (t) following a pressure step change. Where $q(t)$ is the amount adsorbed at time t , and the q_0 and q_e values are the amount adsorbed at equilibrium prior to and following the pressure step change respectively [98,99]. Measurement inaccuracies resulting from gas flows in the initial uptake phase limit the reliability of this method, as such it was only used to qualitatively assess the differences between the clinoptilolite samples.

6.3. RESULTS and DISCUSSION

6.3.1. PHYSICOCHEMICAL PROPERTIES

Table 6.1 presents the elemental composition of the clinoptilolite samples obtained from the EDS analysis. The elemental analysis was carried out on a %wt. basis and the values were converted to numbers per average unit cell for clinoptilolite on the basis of 6 Al atoms. The Si/Al ratio of the untreated zeolite sample is between 5.14 and 5.98 which is expected for clinoptilolite [57,100]. For the untreated clinoptilolite, Mg^{2+} , Ca^{2+} and K^+ are identified as major extra framework cations. Following treatment with $AgNO_3$, no significant change in the Si/Al ratio is observed for all of the samples. The data shows that a significant portion of these cations were substituted by the Ag^+ which agrees with the results found in the literature [82,101]. A small amount of Fe is observed for all of the samples, and remains relatively consistent regardless of Ag^+ cation exchange solution concentration. This suggests that in lieu of extra framework cation sites, some of the Fe may be incorporated into the framework or may correspond to impurities such as additional Fe phases. This is to be expected given that the clinoptilolite is derived from a natural source.

Table 6.1. Unit cell elemental composition of untreated and AgNO₃ cation-exchanged powdered clinoptilolite samples obtained using EDS analysis. The individual elements analyzed on a %wt. basis and the values were converted to unit cell atomic composition on the basis of 6 Al atoms.

Clinoptilolite AgNO ₃ Treatment Concentration [M]	Unit Cell Elemental Composition								Si:Al
	O	Al	Si	K	Ca	Mg	Fe	Ag	
0 (untreated)	79.79 +/- 3.35	6.00	33.36 +/- 1.39	1.66 +/- 0.56	1.12 +/- 0.76	0.38 +/- 0.35	0.80 +/- 0.68	0.00 +/- 0.00	5.14 – 5.98
0.002	75.90 +/- 4.34	6.00	31.43 +/- 2.51	1.01 +/- 0.23	1.75 +/- 0.49	0.59 +/- 0.04	0.75 +/- 0.83	0.37 +/- 0.23	4.62 – 5.86
0.01	77.63 +/- 7.32	6.00	32.56 +/- 3.72	0.64 +/- 0.24	1.32 +/- 0.28	0.63 +/- 0.23	0.41 +/- 0.40	1.34 +/- 0.20	5.30 – 5.55
0.05	75.80 +/- 2.54	6.00	31.40 +/- 0.76	0.73 +/- 0.39	0.68 +/- 0.18	0.41 +/- 0.01	0.49 +/- 0.28	3.76 +/- 1.20	5.16 – 5.31
0.10	78.24 +/- 0.92	6.00	32.07 +/- 0.46	0.74 +/- 0.12	0.28 +/- 0.14	0.49 +/- 0.04	1.01 +/- 0.03	5.05 +/- 0.10	5.23 – 5.45
0.20	73.04 +/- 1.68	6.00	30.30 +/- 0.66	0.26 +/- 0.36	0.26 +/- 0.07	0.10 +/- 0.15	0.32 +/- 0.01	5.13 +/- 0.69	4.87 – 5.24
0.40	72.74 +/- 3.85	6.00	30.00 +/- 2.22	0.34 +/- 0.20	0.01 +/- 0.01	0.30 +/- 0.19	0.45 +/- 0.23	5.26 +/- 0.17	4.82 – 5.28
The uncertainty is quantified as the standard deviation between the sample averages of two separate samples, with n = 10 independent EDS analysis collection points for each sample.									

Figure 6.1 shows the effect of AgNO₃ treatment on the quantity of extra framework cations present in the clinoptilolite samples. Prior to Ag⁺ cation exchange, natural extra framework cations are present in the order of: K⁺ > Ca²⁺ > Mg²⁺. As expected, the amount of Ag⁺ cations is observed to increase with increasing AgNO₃ exchange solution. This increase in the exchanged cations comes at the expense of the original cations (with Ca²⁺ and K⁺ cations showing the greatest decrease) which is similar to the findings of others in the literature [73,75,82,101]. The Si/Al ratio is about 5.14 – 5.98 for untreated clinoptilolite compared to values of 4.82 – 5.28 for the clinoptilolite treated with the 0.4M AgNO₃ solution. This means that the framework retains a negative charge that is balanced by the extra framework cations in the more Ag⁺ exchanged clinoptilolite. It is evident that the amount of Ag⁺ cations exchanged approaches saturation at concentrations greater than 0.1M AgNO₃ as beyond this concentration the amount of Ag⁺ cations stays relatively constant [82]. At this concentration, about 5 Ag⁺ cations per unit cell are balanced with the negative framework and any residual charge difference is balanced by the remaining natural cations which are still present albeit in far lower quantities, in the order of: K⁺ ≈ Mg²⁺ > Ca²⁺.

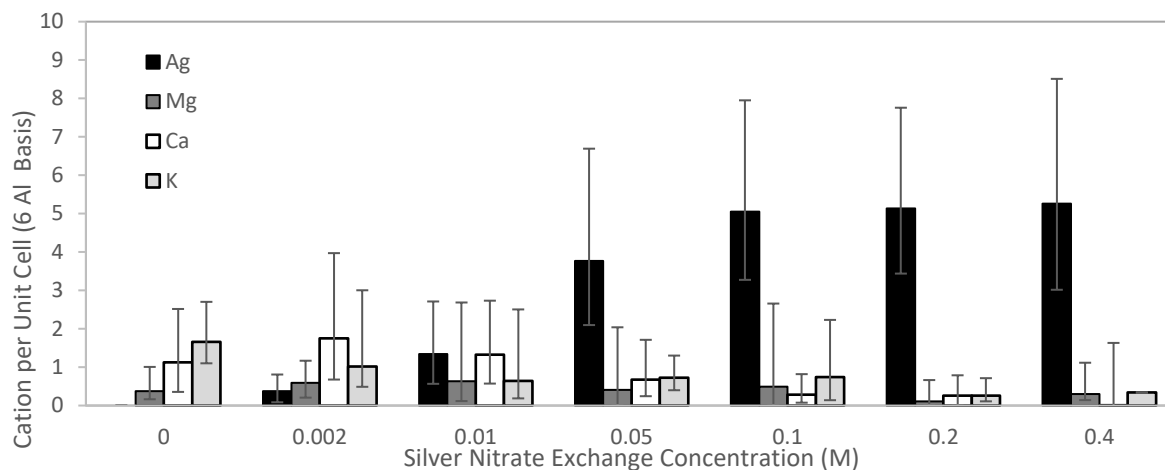


Figure 6.1. Unit cell elemental composition of the extra framework cations present in untreated and AgNO_3 cation-exchanged clinoptilolite samples obtained using EDS analysis. The error bars represent the range of the maximum and minimum measured values for each cation.

Figure 6.2 presents the IR spectra covering a spectral range of 650 to 4000 cm^{-1} for the clinoptilolite samples obtained from the FT-IR ATR analysis. All of the IR spectra share comparable properties which are consistent with that of clinoptilolite.[81,102]. All samples show characteristic bands at about 3610 cm^{-1} , 1630 cm^{-1} , 1040 cm^{-1} , 795 cm^{-1} , and 705 cm^{-1} . The spectra range of 650 to 1250 cm^{-1} corresponds to the internal Si and Al oxide tetrahedra bond vibrations and pseudo-lattice vibrations. The signal in this spectra region is sensitive to the framework ring structure and the Si/Al content [81,103–105]. These results confirm that the overall zeolite lattice is mostly unaffected by the presence of additional Ag^+ cations, particularly for lower concentrations of AgNO_3 exchanged [83]. While we are confident that the modified material retains much of the same properties as the reference sample, a degree of caution should be taken due to the complicated physicochemical makeup of these materials. Additionally, the spectral range corresponding to Ag – O bond stretching (spectral range of 253–206 cm^{-1}) is not included in this analysis [106]. Therefore, we cannot say for certain as to whether silver complexes have also been formed following the AgNO_3 cation exchange.

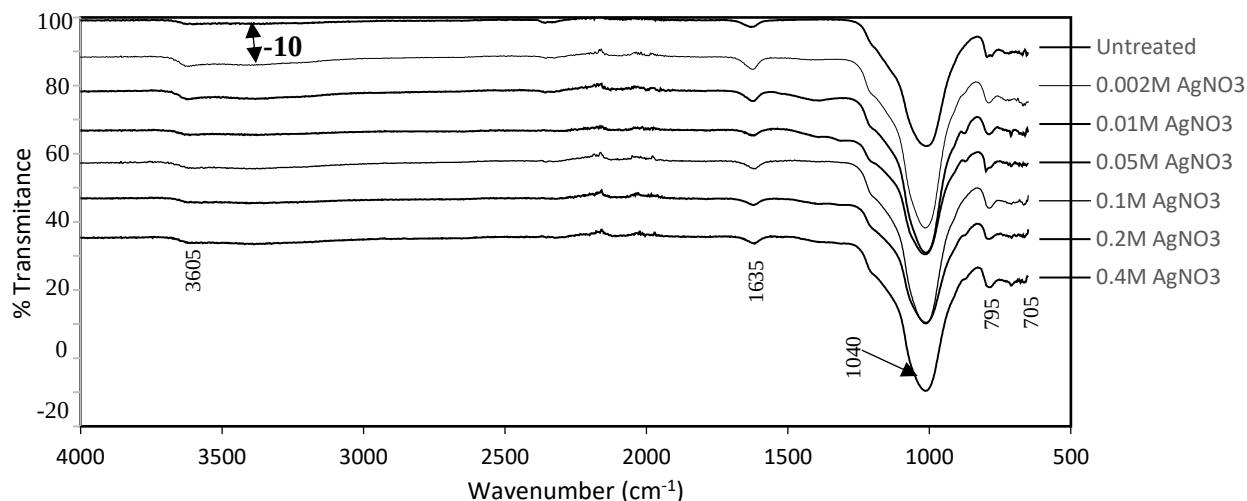


Figure 6.2. FTIR spectra for the untreated powdered natural clinoptilolite compared to the Ag^+ cation exchanged clinoptilolite samples. A separation distance of -10% transmittance is applied between each spectra.

Figure 6.3 presents the x-ray diffractograms for the untreated clinoptilolite powder and the Ag^+ cation exchanged clinoptilolite samples. The characteristic XRD pattern for clinoptilolite is evident along with some additional peaks representing impurities which is to be expected given that the sample is naturally sourced [45,55,107–110]. Following cation exchange with AgNO_3 , the overall diffractogram pattern is essentially maintained. However, the peak intensity is observed to decrease with increasing concentration of AgNO_3 . This suggests increased disorder is induced by the conditions of the cation exchange environment at higher concentrations of AgNO_3 resulting in decreased crystallinity.

A notable difference is observed with the peak intensity at about 9.88° . This peak is shown to decrease substantially between the untreated sample and the highest AgNO_3 solution concentration. Changes in the XRD peak intensity such as this are thought to be the result of significant alterations in the crystal form. Alternatively, Unadi et al. and Dimova et al. both observed similar tendencies in the XRD diffractograms for clinoptilolite exchanged with heavy cations. In these studies it was speculated that the incorporation of the large cations within the channel cavity of the clinoptilolite may account for this observation [83,101,111].

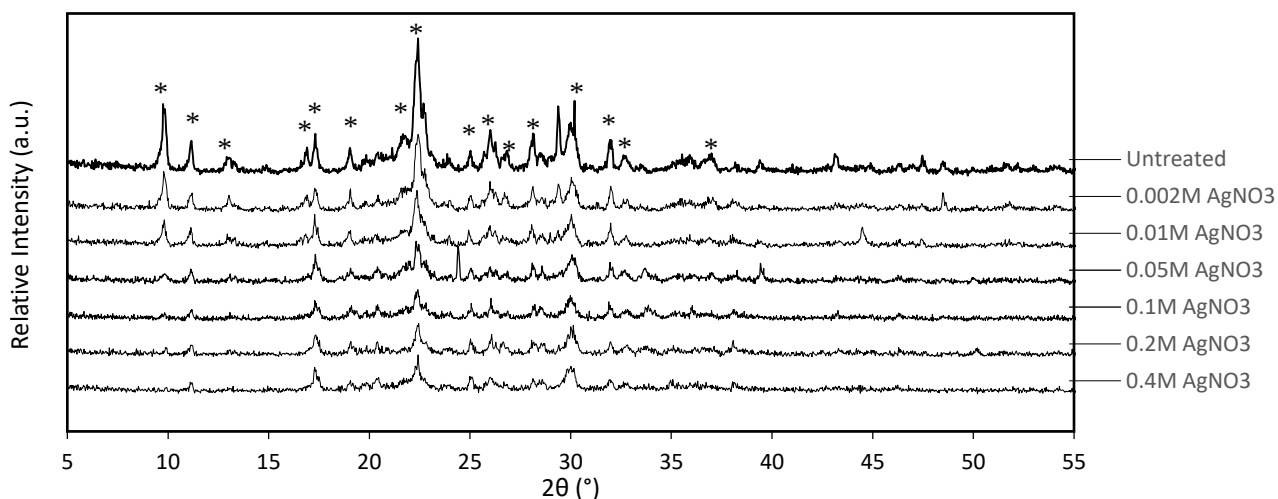


Figure 6.3. XRD pattern of the untreated natural clinoptilolite compared to the Ag^+ cation exchanged clinoptilolite samples. The characteristic of clinoptilolite pattern is evident, the characteristic peaks are denoted with a (*) symbol [45,55,107–110].

Figure 6.4 shows adsorption-desorption isotherms as a function of relative pressure for the N_2 sorption experiments at 77 K. It should be noted for future studies other potential probe gases may be more desirable since in this case N_2 is one of the adsorbing species being studied in this investigation. The corresponding HK and BJH pore volume distribution for the untreated and Ag^+ exchanged clinoptilolite samples treated with 0.2M AgNO_3 solution are also shown as Sample 1 and Sample 2, respectively. The N_2 sorption behaviour resembles those presented for clinoptilolite and other small pored zeolite types [21,47,52]. The BJH pore distribution is similar between the untreated and AgNO_3 samples which indicates little effect of the AgNO_3 treatment on the mesopore distribution. Distinctions may be drawn by observing changes in the HK distribution (which describes the slit micropore dimensions). A small but noticeable reduction in the micropore width is observed for both Ag^+ clinoptilolite samples compared to the untreated clinoptilolite. The maximum point of the HK micropore distribution is observed to shift from about 0.7nm to about 0.55nm indicating a possible reduction in the average micropore size. The micropore size of clinoptilolite is only slightly larger than the size of N_2 . Therefore, N_2 diffusion is very slow at the experimental temperatures of 77K. Consequently, the measured N_2 adsorption may not be accurate and the pore properties as described by the HK and BET methods may not account for all of the micropore space. Nonetheless, the experimental data presented in Figure 6.4b qualitatively suggests a reduction in the effective micropore size for the clinoptilolite treated with 0.2M AgNO_3 compared to the untreated samples.

With this information in mind, a summary of the calculated pore properties and surface area of the adsorbents is provided in Table 6.2. The calculated BET surface area and average pore diameter decreases with the presence of extra framework Ag^+ cations within the clinoptilolite pores. The calculated micropore area is also reduced for the Ag^+ clinoptilolite compared to the parent sample. This is the sign of a reduction in the channel aperture due to the position of the Ag^+ cations; resulting in decreased access of N_2 into the micropore space.

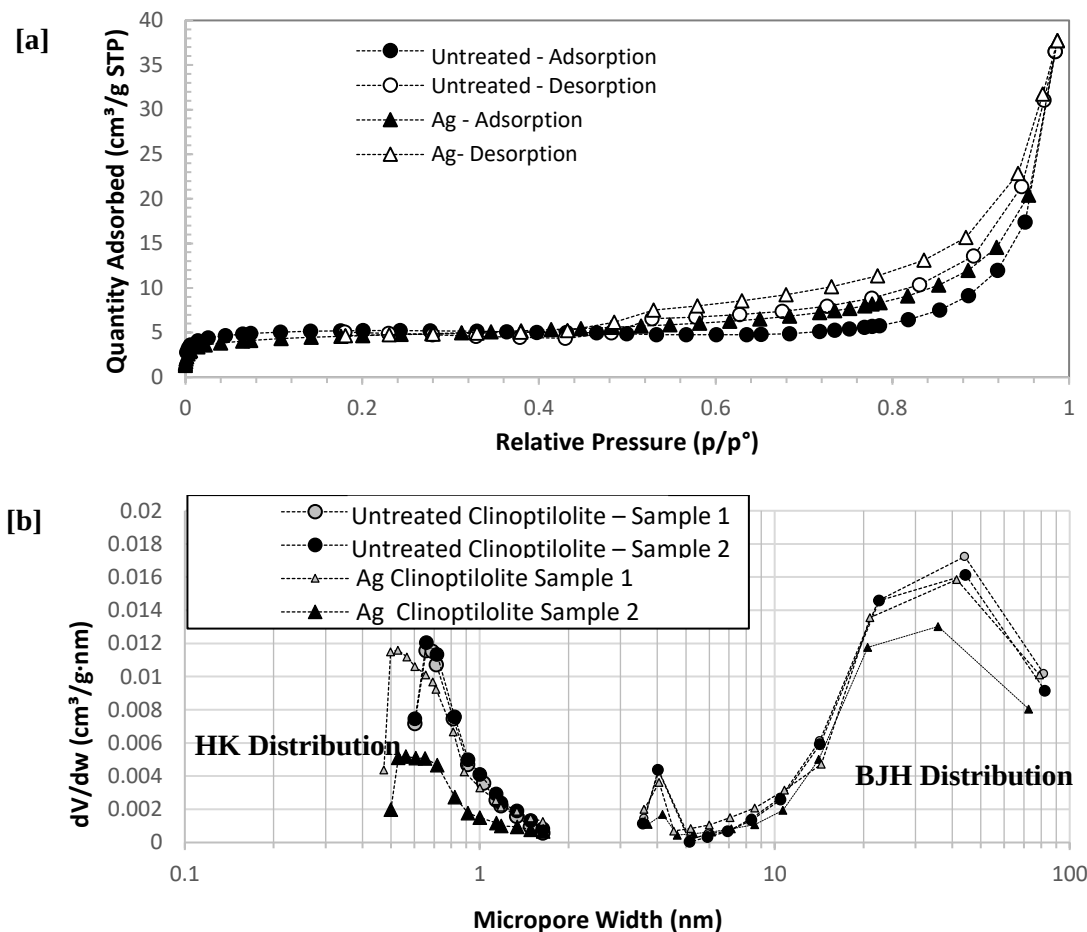


Figure 6.4. [a] N_2 adsorption (solid symbols) – desorption (open symbols) isotherms for powdered untreated and Ag^+ cation exchanged (a 0.2M AgNO_3 cation exchange solution was used for both samples 1 and 2) clinoptilolite at 77K. [b] Distribution of the micropores and mesopores for untreated and Ag^+ cation exchanged clinoptilolite determined from the sorption experiments with N_2 at 77K.

Table 6.2. BET surface area, HK micropore volume, and total pore volume for powdered untreated and 0.2M AgNO₃ cation exchanged clinoptilolite determined from the sorption experiments with N₂ at 77K. †

Sample	BET Surface area (m ² /g)	HK Micropore volume (cm ³ /g)	Micropore area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
Untreated clinoptilolite Sample 1	18.3307	0.007290	16.2409	0.052208	304.254
Untreated clinoptilolite Sample 2	19.0861	0.007068	15.7022	0.054171	292.213
Ag ⁺ clinoptilolite Sample 1	14.8929	0.003845	8.7482	0.056070	260.327
Ag ⁺ clinoptilolite Sample 2	7.5347	0.001470	3.3735	0.016830	161.707
† The calculated values may be underrepresented due to the difficulty of N ₂ diffusion in the clinoptilolite micropores at 77K.					

6.3.2. ADSORPTION PROPERTIES

Figure 6.5 presents the excess CH₄, and N₂ adsorption isotherms for untreated and Ag⁺ cation exchanged clinoptilolite powders at 303K for pressures up to 10 atm. As expected the adsorption uptake for both gases increases with increasing pressure. The corresponding calculated parameters for the Sips adsorption isotherm models using Equation 1 are given in the supplemental material for reference.

6.3.2.1. N₂ ADSORPTION ISOTHERMS

The adsorption equilibria for N₂ on the clinoptilolite samples show that the adsorption uptake increases for the clinoptilolite exchanged with smaller amounts of Ag⁺ cations, followed by a slight decrease with greater quantities of Ag⁺ cations. Using a pressure of 10 atm as a reference, the presence of the lesser amounts of Ag⁺ cations increases the N₂ adsorption capacity from about 0.65 mmol/g (untreated clinoptilolite) to 0.91 mmol/g for the sample exchanged with the 0.002M AgNO₃ solution. Following this effect, the N₂ uptake is shown to decrease slightly with increasing presence of Ag⁺ cations within the clinoptilolite. The enhanced N₂ uptake observed with small amounts of Ag⁺ cations may be due to the increased heterogeneity of the adsorbent surface. Following the cation exchange with the 0.02M AgNO₃ solution the clinoptilolite is only partially exchanged (as shown in Figure 6.1). Therefore, there is a complex distribution of Ag⁺ cations that is mixed amongst the naturally occurring Ca²⁺, K⁺ and Mg²⁺ cations. This variable cation charge distribution may actually interact with the N₂ quadrupole moment thus increasing the adsorption capacity of this gas. Similar tendencies have been reported for N₂ adsorption equilibria on some faujisite zeolites partially exchanged with Ag⁺ cations [77–79].

6.3.2.2. CH₄ ADSORPTION ISOTHERMS

It is clear that the adsorption uptake is the highest for the untreated clinoptilolite for CH₄ and that amount adsorbed for this gas decreases with the presence of Ag⁺ cations. For this discussion, the untreated clinoptilolite will be compared to the clinoptilolite treated with 0.1 – 0.4 M AgNO₃ since at that concentration range the amount of Ag⁺ cations exchanged was shown to stay relatively constant in Figure 6.1. Using a pressure of 10 atm as a reference, the presence of the Ag⁺ cations is shown to profoundly affect the equilibrium adsorption values for CH₄. The equilibrium adsorption capacity of CH₄ gas is shown to decrease from 0.97 mmol/g (untreated clinoptilolite) to between 0.09 and 0.49 mmol/g. Since N₂ (kinetic diameter = 3.64 Å) is smaller than CH₄ (kinetic diameter = 3.80 Å), the distribution of the Ag⁺ cations with the remaining residual natural cations (Ca²⁺, K⁺, Mg²⁺) are contributing to blocking of the larger CH₄ gas while having little blocking effect on N₂ gas. A similar affect has been well documented in the case of Ca²⁺ clinoptilolite [16,47]. It has been reported by others that the observed pore blocking for CH₄ is in a delicate balance and may be effected by the distribution of other extra framework cations present in the zeolite[73]. An increased CH₄ adsorption capacity for the clinoptilolite after treatment with 0.4M AgNO₃ was observed compared to the 0.2M AgNO₃. A combination of variations in the distribution of cations in the naturally sourced material and slightly higher K⁺, Mg²⁺, and Fe³⁺ content following treatment with 0.4M AgNO₃ vs. 0.2M AgNO₃ (Table 6.1) is suspected to explain the observed increase in CH₄ adsorption capacity.

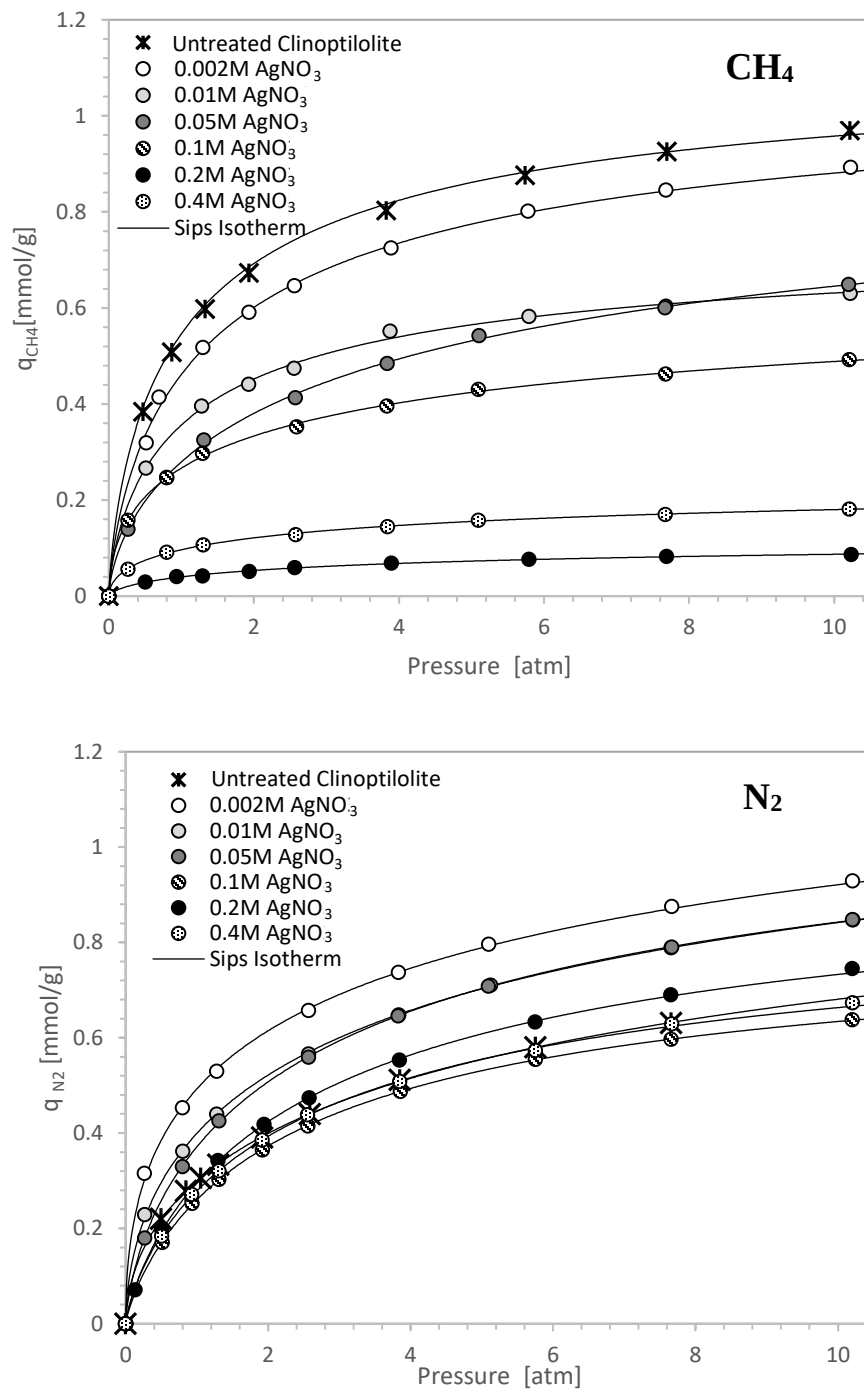


Figure 6.5. Experimental CH₄ (top) and N₂ (bottom) adsorption isotherms at 303K with Sips model fits for untreated and the Ag⁺ cation exchanged clinoptilolite powder exchanged with different concentrations of AgNO₃ solution.*

*Caution - It should be noted that due to the slow kinetics of CH₄ adsorption within these materials, the experimentally determined adsorption isotherm values may not have achieved total equilibrium.

6.3.2.3. N₂/CH₄ ADSORPTION EQUILIBRIUM SELECTIVITY

The ideal N₂/CH₄ equilibrium selectivity values were calculated using Equation 2. The results are plotted with respect to pressure and are presented in Figure 6.6 for the clinoptilolite samples exchanged with different concentrations of AgNO₃ solutions. More CH₄ is adsorbed compared to N₂ for the untreated clinoptilolite sample. This observation is to be expected given that in most cases the adsorption of CH₄ is thermodynamically favoured over N₂. The greater adsorption equilibrium capacity for CH₄ compared to N₂ indicates that access to the pore network is not impeded by the mix of Ca²⁺, K⁺ and Mg²⁺ extra framework cations present within the untreated sample. It follows that increasing the amount of Ag⁺ extra framework cations results in higher N₂/CH₄ selectivity. Treatment with 0.02M to 0.10M AgNO₃ solution results in a slightly N₂ selective material. The presence of smaller amounts of Ag⁺ cations means that there is likely insufficient quantities of extra framework Ag⁺ cations present in these samples to limit the uptake of CH₄ within the channel network. However, treatment of the clinoptilolite with the 0.2M and 0.4M AgNO₃ solution resulted in higher N₂/CH₄ selectivity which ranged from 2.9 to 8.4 for these samples. The reduced CH₄ capacity can be explained by the blocking effect of the positions of the extra framework Ag⁺ cations.

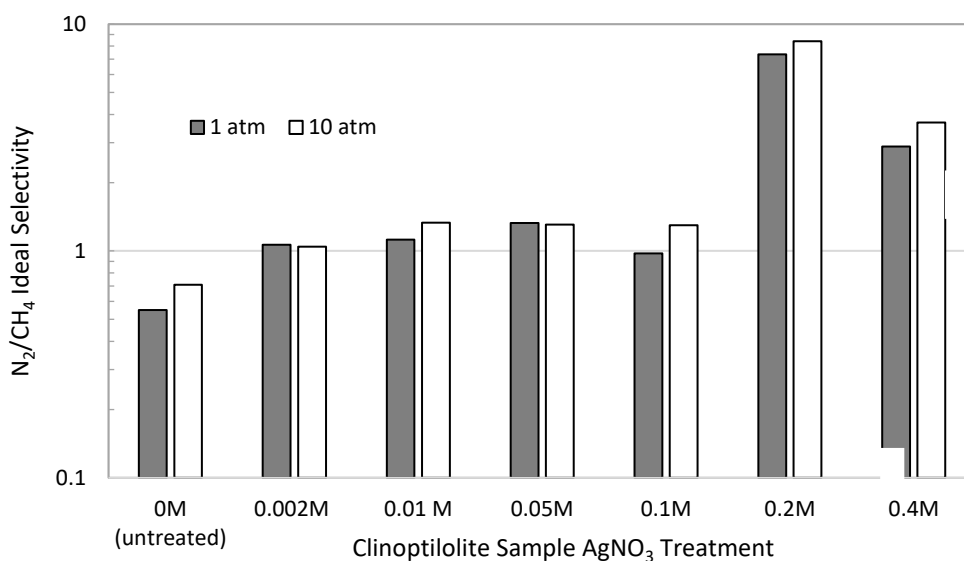


Figure 6.6. N₂/CH₄ ideal equilibrium selectivity values as a function of pressure for untreated clinoptilolite compared to the different Ag⁺ exchanged clinoptilolite samples at 303K.*

*Caution - It should be noted that due to the slow kinetics of CH₄ adsorption within these materials, the experimentally determined adsorption isotherm values may not have achieved total equilibrium.

6.3.2.4. CH₄ and N₂ ADSORPTION on CLINOPTILOLITE PELLETS vs. POWDER

Untreated clinoptilolite pellets with a 20X60 U.S. Std. mesh size were cation exchanged in the exact same manner as previously described with a 0.2M AgNO₃ solution. Following the cation exchange procedure, the presence of elemental Ag was confirmed using EDS and the results are compared to the untreated clinoptilolite pellets which are presented in the supplemental material for reference. The majority of the original cations are removed with Ca²⁺ and K⁺ being the most affected in the same manner for the pellets as was observed with the Ag⁺ exchanged clinoptilolite powder (See Table 6.5 in the supplemental material).

Figure 6.7 shows the results of the adsorption studies on these materials. The excess CH₄, and N₂ adsorption isotherms for the untreated and Ag⁺ cation exchanged clinoptilolite pellets were conducted at 303K for pressures up to 10 atm. As can be observed, compared to the values for the powdered samples, the clinoptilolite pellets showed an overall higher adsorption capacity for both CH₄ and N₂ for the untreated samples. However, these materials behaved in a similar manner as described in the previous section for the adsorption of CH₄ and N₂ following the AgNO₃ cation exchanged procedure. The CH₄ is being blocked from accessing the channel pores due to the presence of the extra framework Ag⁺ cations and perhaps the residual natural cations still occupying some sites. The differences observed between the pellets and the powdered clinoptilolite may be the result of natural variation of impurities between the samples. Additionally, the effect of crushing may reduce the available surface area for adsorption to occur, thus lowering the adsorption capacity for the powdered samples compared to the pellets which were not crushed to the same extent.

The fractional adsorption uptake rate response for N₂ and CH₄ gases on selected clinoptilolite samples is shown in Figure 6.8. For clinoptilolite, diffusional resistance within the micropores is dominant [112,113]. This leads to the notable issue of slow diffusion kinetics which must be evaluated when considering the use of cation exchanged clinoptilolites for prospective CH₄/N₂ gas separations [43,72,114]. From Figure 6.8, it can be observed that the larger CH₄ gas has a slower diffusion rate compared to the smaller N₂ gas regardless of the material type. As shown with the clinoptilolite samples treated with 0.002M AgNO₃, even the presence of a small amount of Ag⁺ cations induces slower kinetic uptake for both gases, with CH₄ being the most affected gas. The highly exchanged variants of the Ag⁺ clinoptilolite result in a slower CH₄ uptake rate which is indicative of molecular sieve type behaviour. In comparison to the

clinoptilolite powder, the pellets show slower uptake rates for both N_2 and CH_4 . The observed slower mass transfer of the gases in pellets as compared to powders is expected and has been demonstrated previously with respect to small pored zeolites for heterogeneous catalysis[115].

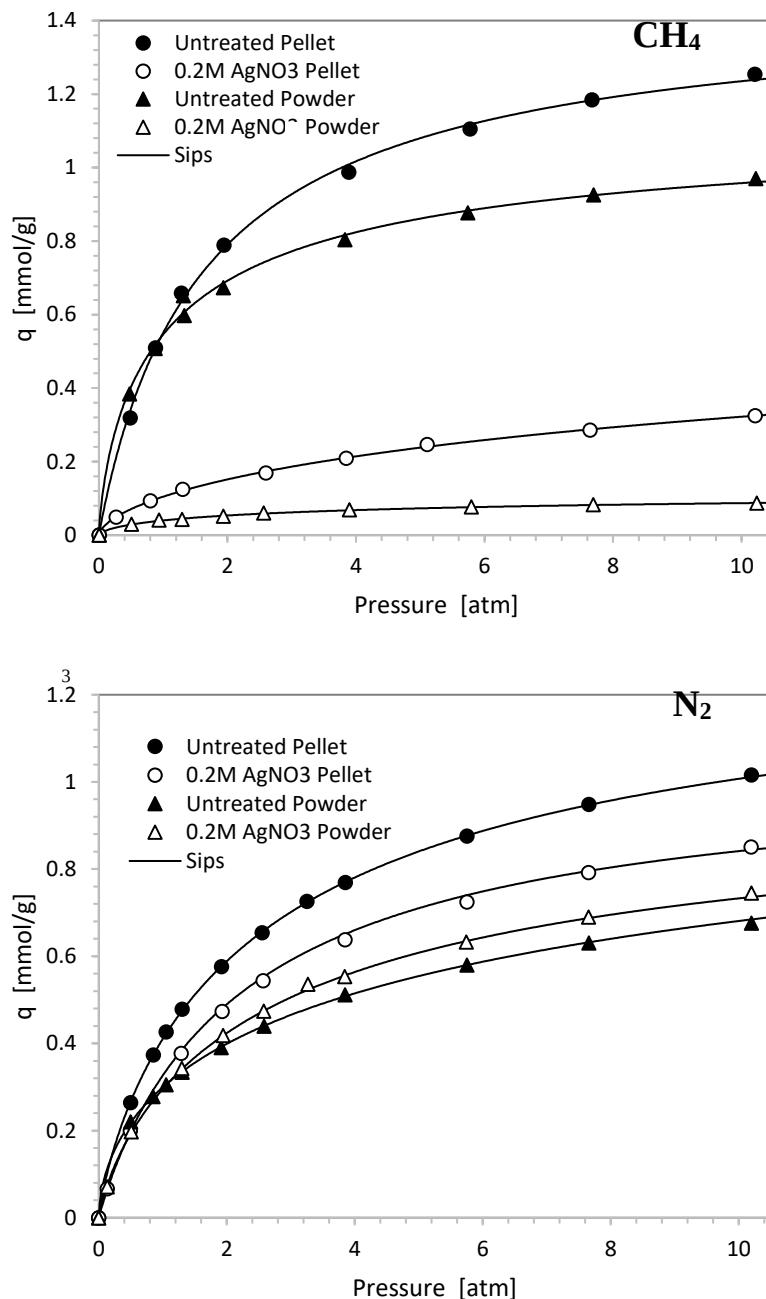


Figure 6.7. Experimental CH_4 (top) and N_2 (bottom) adsorption isotherms at 303K with Sips model fits for untreated and Ag^+ cation exchanged clinoptilolite powder compared to pellets exchanged with 0.2M $AgNO_3$ solution.*

*Caution - It should be noted that due to the slow kinetics of CH₄ adsorption within these materials, the experimentally determined adsorption isotherm values may not have achieved total equilibrium.

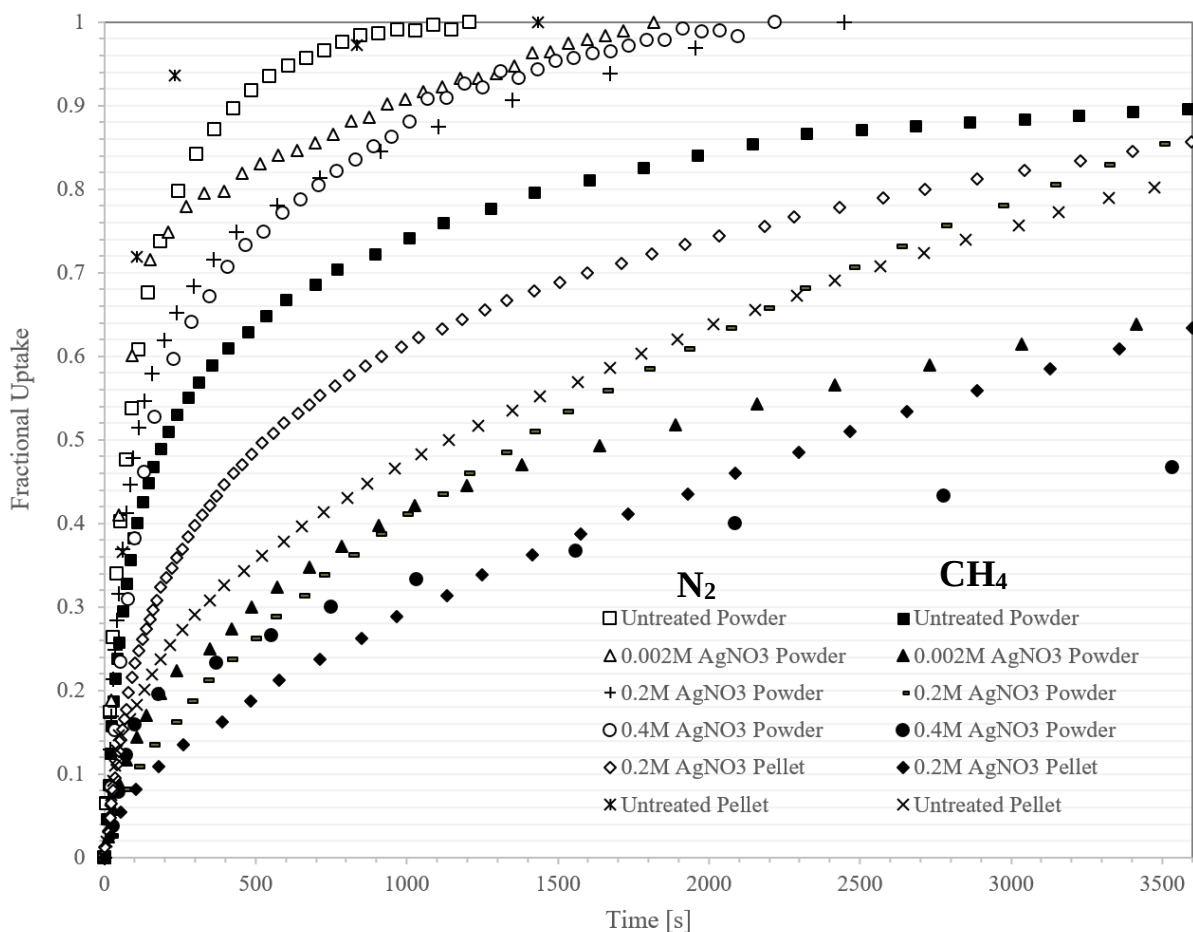


Figure 6.8. Experimental adsorption fractional uptake rate curves for pure CH₄ (closed points) and N₂ (open points) gas adsorption on powdered untreated and Ag⁺ exchanged clinoptilolite samples determined at 303K with a pressure step change from 3 to 4 atm. 0.2 M AgNO₃ treated pellets are also shown for comparison.

6.3.3. INFLUENCE of the Ag⁺ CATION SITES on PORE BLOCKING

The distribution of the natural extra framework cations present within the parent clinoptilolite sample effects the adsorption properties of the modified material [47,74]. Lihareva et al. showed the propensity of the Ag⁺ cations to replace the naturally occurring extra framework cations in the order of: Na⁺ > Ca²⁺ > K⁺ > Mg²⁺ [82]. In this work, we show that the tendency for the Ag⁺ cations to exchange the original cations in the following manner: Ca²⁺ > K⁺ >> Mg²⁺, with Mg²⁺ being the least exchanged. The

presence of the native cations are a consideration when examining the change in CH_4 adsorption capacity and pore blocking of clinoptilolite after AgNO_3 treatment.

The apparent N_2/CH_4 equilibrium selectivity of the highly exchanged Ag^+ clinoptilolite samples likely stems from the location of the Ag^+ cations within the channels of the clinoptilolite. It is speculated that the location of the extra framework Ag^+ cations serve to reduce the effective pore size of the clinoptilolite in a similar manner as demonstrated by Ca^{2+} and Na^+ cation exchanged variants [16,19,56,72]. Detailed crystallography studies by Dimova and colleagues using the Rietvelt refinement technique presented the possible locations of the extra framework Ag^+ cations of highly exchanged Ag^+ clinoptilolite [101]. Figure 6.9 depicts the Ag^+ cations in the approximated locations as determined by Dimova et al [101]. As can be seen in this Figure, the Ag(1) and Ag(2) positions are similar to the extra framework cation locations M(1) and M(2) determined by Koyama and Takéuchi [76]. Since Ca^{2+} occupies the M(1) and M(2) positions, this explains the large reduction observed for Ca^{2+} cations following Ag^+ cation exchange [76]. Additionally, the position of Ag(3) site may also facilitate a decrease in the effective pore size of the clinoptilolite. The position and size of the exchanged Ag^+ cations explains the apparent decrease in the average micropore width for the Ag^+ exchanged clinoptilolite sample observed in Figure 6.4 and the decrease in CH_4 adsorption equilibria.

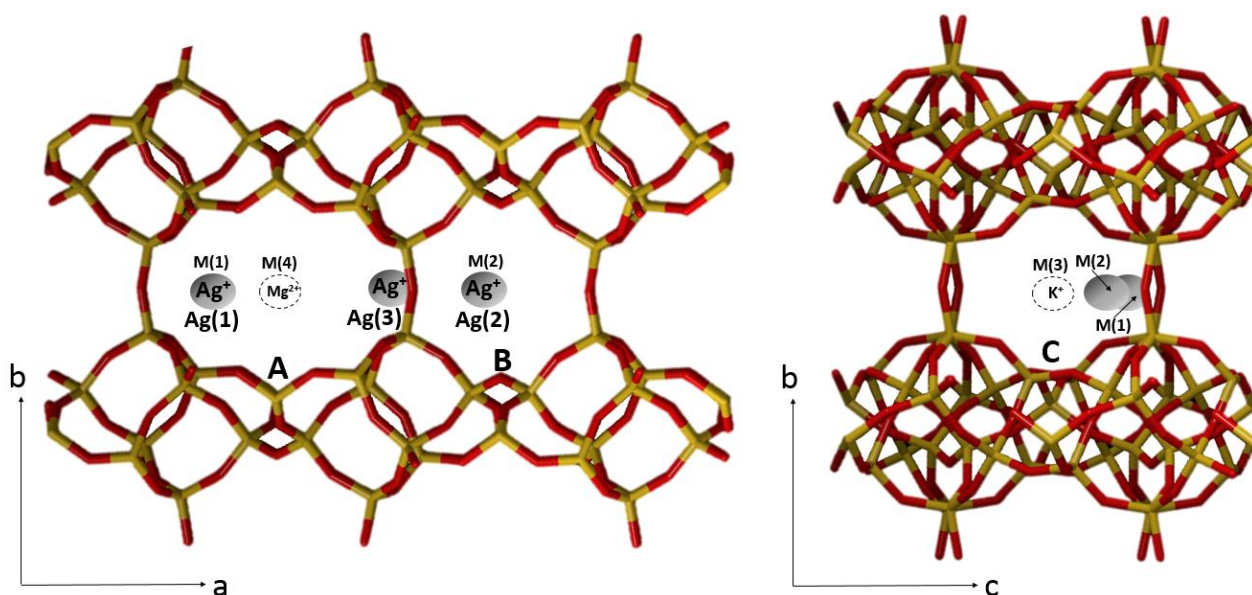


Figure 6.9. The framework structure of clinoptilolite zeolite as described by the IZA with the approximated cation site occupancies of Ag^+ in relation to the framework and the M(1) through M(4) cation positions as adapted from Dimova et. al. [19,76,101]. (The cation size and precise positions are not to scale).

Table 6.3 presents the physical properties of some of the cations that have been the subject of adsorption studies involving the cation modification of clinoptilolite [51,72,73,75,113,116]. In the absence of any direct evidence, the cation size and charge can be used to evaluate whether the pores may be blocked. Conventional wisdom would argue that the inclusion of even larger cations than Ag^+ would effectively block much of the accessible pore space within the channels of clinoptilolite. In reality, steric factors are also a consideration when evaluating whether the pores may be blocked. Larger Ba^{2+} and Sr^{2+} cations behave differently compared to the smaller Mg^{2+} and Ca^{2+} cations even though they are all alkaline earth cations. Clinoptilolite exchanged with Ba^{2+} and Sr^{2+} actually exhibits higher adsorption capacity for both N_2 and CH_4 [75]. Both Ba^{2+} and Sr^{2+} cations occupy spaces adjacent to the framework in the vicinity of the M(1) and/or M(3) positions [66,117,118]. However, the large hydrated radii of these cations causes displacement of cations residing in the M(4) position, opening up channel A. Similar steric effects are also observed for Rb^+ and Cs^+ cations which reside adjacent to the M(1) and M(2) cation positions [61]. From Table 6.3, it is clear that the radius of the Ag^+ cations lays in between the cation sizes which decrease the channel aperture (Na^+ , Ca^{2+}) and those which open the channel due to steric displacement (Ba^{2+} , Sr^{2+} , Rb^+ , and Cs^+). Judging from the N_2/CH_4 selective behaviour that is presented with Ag^+ clinoptilolite, it is clear that the presence of Ag^+ cations can effectively block the pores to CH_4 .

Table 6.3. Physical properties of the clinoptilolite extra framework cations [119,120].

Cation	Effective Ionic Radius (Å)	Hydrated Radius (Å)	Charge to Ionic Radius Ratio
Mg^{2+}	0.72	1.50	2.78
Ca^{2+}	1.00	1.80	2.00
Na^+	1.02	1.80	0.98
Ag^+	1.15	1.60	0.87
Sr^{2+}	1.18	2.00	1.69
Ba^{2+}	1.35	2.15	1.48
K^+	1.38	2.20	0.72
Rb^+	1.52	2.35	0.66
Cs^+	1.67	2.60	0.59

Table 6.4 shows the CH_4 and N_2 capacity and N_2/CH_4 equilibrium selectivity of various forms of nitrogen selective clinoptilolites which are compared to the benchmark titanosilicate ETS-4, as well as other promising materials. Since this is a simple screening of various materials, for simplicity the process conditions were limited to a pressure region of 0.2, 1, and 8 atm to signify the ideal separation performance for prospective separation systems, including membrane, VSA or PSA systems. For this analysis, the temperature range was limited to between 273 and 323 K based upon the available data in the literature. Over this pressure range, the Ag^+ clinoptilolite N_2/CH_4 equilibrium selectivity ranges from 2.8 to 7.6. While

the N_2/CH_4 ideal selectivity is observed to not change substantially over this pressure range, it is evident that the ideal selectivity is sensitive to the extent of the cation exchange within the clinoptilolite as was shown in Figure 6.6. The N_2/CH_4 ideal selectivity values show variation between powdered and pellet samples with the powdered samples having higher values. This difference may be caused by the greater quantity of larger mesopores which are present in the pellets as the pellets were subject to a less crushing force compared to the powder. None the less, both the powdered and pellet form of the Ag^+ exchange clinoptilolite show good separation potential and are consistent with the result of previous studies for Ag^+ exchanged clinoptilolite [51]. However, the N_2/CH_4 selectivity of titanosilicate Sr-ETS-4 is higher and ranges from 5.8 to 12 under comparable conditions. In comparison, SAPO-34 and AlPO-18 display adsorption equilibria that is CH_4 selective over N_2 . However, the molecular sieve properties of these zeolites induce N_2/CH_4 selectivity when applied to membrane based separations[28,29].

Table 6.4. Comparison of CH₄ and N₂ capacity and N₂/CH₄ equilibrium selectivity for nitrogen selective clinoptilolites.

Adsorbent Description Material Type	T (K)	P (atm)	CH ₄ capacity (mmol/g)	N ₂ Capacity (mmol/g)	N ₂ /CH ₄ equilibrium selectivity	Ref.
Ag ⁺ clinoptilolite powder (treated with 0.2M AgNO ₃)	303	0.2	0.03	0.19	6.3	Current study
		1	0.04	0.27	6.8	
		8	0.09	0.68	7.6	
Ag ⁺ clinoptilolite 20X60 pellets (treated with 0.2M AgNO ₃)	303	0.2	0.04	0.12	3	Current study
		1	0.10	0.33	3.3	
		8	0.29	0.81	2.8	
Ag ⁺ clinoptilolite	298	1	0.03	0.20	6.53	[51]
Ca ²⁺ clinoptilolite	303	0.2	0.07	0.12	1.7	[75]
		1	0.15	0.22	1.5	
		8	0.24	0.42	1.8	
Ca ²⁺ clinoptilolite	300	0.2	0.05	0.12	2.4	[43]
		1	0.07	0.22	3.2	
Ca ²⁺ clinoptilolite	295	0.2	0.05	0.19	3.8	[74]
		1	0.15	0.41	2.7	
Na ⁺ clinoptilolite	300	0.2	0.12	0.16	1.3	[43]
		1	0.23	0.47	2.1	
Na ⁺ clinoptilolite	295	0.2	0.06	0.14	2.3	[74]
		1	0.27	0.60	2.2	
Na ⁺ clinoptilolite	298	1	0.05	0.37	7.25	[51]
Mixed Mg ²⁺ /Na ⁺ clinoptilolite (50%/50%)	295	1	0.36	0.62	1.7	[73]
		8	1.9	1.3	1.5	
Mixed Li ⁺ /Na ⁺ clinoptilolite (80%/20%)	295	0.2	0.11	0.20	1.8	[73]
		1	0.40	0.60	1.5	
Sr-ETS-4, (activated at 588K) titanosilicate	295	0.2	0.01	0.11	11.0	[74]
		1	0.02	0.24	12.0	
Sr-ETS-4, (activated at 543K) titanosilicate	298	0.2	0.03	0.26	8.3	[13]
		1	0.08	0.46	5.8	
AlPO-18	298	1	0.42	0.14	0.33	[29]
SAPO-34	295	1	0.40	0.15	0.37	[28]
		8	2.05	0.90	0.44	

6.4. CONCLUSIONS

Natural clinoptilolite, originally rich in Ca²⁺, K⁺, and Mg²⁺ cations was cation-exchanged with Ag⁺ cations and was found have suitable adsorption properties for the selective separation of N₂ from CH₄. The physicochemical properties of the untreated parent clinoptilolite and the Ag⁺ variants were characterized through XRD, EDS, FTIR, and N₂ sorption experiments performed at 77K. The amount of extra framework Ag⁺ cations increases at the expense of native Ca²⁺, K⁺ and Mg²⁺ cations following controlled AgNO₃ cation exchange experiments. Single gas isotherms of CH₄ and N₂ performed at 303K showed that the extent of the Ag⁺ cation exchanged influences the adsorption behaviour of the powdered clinoptilolite

samples. Prior to cation exchange, for untreated clinoptilolite CH_4 is adsorbed at a higher capacity than N_2 . Following cation exchange with Ag^+ , the modified samples showed decreasing capacity for CH_4 while N_2 was only moderately affected. This resulted in an N_2 selective molecular sieve for the exchanged Ag^+ clinoptilolite samples (above 0.2M AgNO_3 cation exchange solution concentration). Similar behaviour was also observed for Ag^+ cation exchanged clinoptilolite pellets.

It is uncertain as to whether the observed adsorption behaviour is due to the Ag^+ cations alone or with coordination the residual naturally occurring cations (Ca^{2+} , K^+ and Mg^{2+}) that are still present to some degree following cation exchange. However, it was noted that the diffusion uptake of all of the modified materials was slow, with CH_4 being slower than N_2 . The slow kinetics may make this material difficult to implement in a dynamic PSA environment. Between pressures of 0.2 to 8 atm and at temperatures of 303K, the N_2/CH_4 equilibrium selectivity of highly exchanged Ag^+ clinoptilolite ranged from 2.8 to 7.6 which compared well to other N_2 selective clinoptilolite types but was lower than the values reported in the literature for titanosilicate ETS-4. Nonetheless, the properties make this material an interesting alternative for further research into potential separations of N_2 from CH_4 in adsorption processes.

6.5. NOMENCLATURE

a, b, c	unit cell coordinate parameters	[Å]
B	adsorption affinity constant	[atm ⁻¹]
n	dimensionless Sips model parameter	[dimensionless]
P	pressure	[atm]
q	adsorption capacity	[mmol/g of adsorbent]
$q(t)$	amount adsorbed at time t	[mmol/g of adsorbent]
q_e	adsorption capacity at equilibrium	[mmol/g of adsorbent]
q_m	adsorption capacity at saturation	[mmol/g of adsorbent]
t	time	[s]
T	temperature	[K]

SUBSCRIPTS

1	component 1
2	component 2
i	component i
m	Maximum/saturation

GREEK SYMBOLS

α	ideal adsorption equilibrium separation factor	[dimensionless]
β	unit cell angle between a-c coordinates	[°]

θ adsorption surface coverage [dimensionless]

ABBREVIATIONS

BET	Brunauer – Emmett – Teller
BJH	Barrett-Joyner-Halenda
CMS	carbon molecular seive
EDS	electron dispersive spectrometer
ETS	Englehard titanosilicate
HEU	heulandite
HK	Horvath – Kawazoe
FT-IR	Fourier Transform Infrared
IR	infrared
IZA	International Zeolite Association
LTA	Linde type A
MOF	metal organic framework
PSA	pressure swing adsorption
SEM	scanning electron microscopy
VSA	vacuum swing adsorption
XRD	X-ray diffraction

6.6. REFERENCES

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6.7. SUPPLEMENTAL MATERIAL

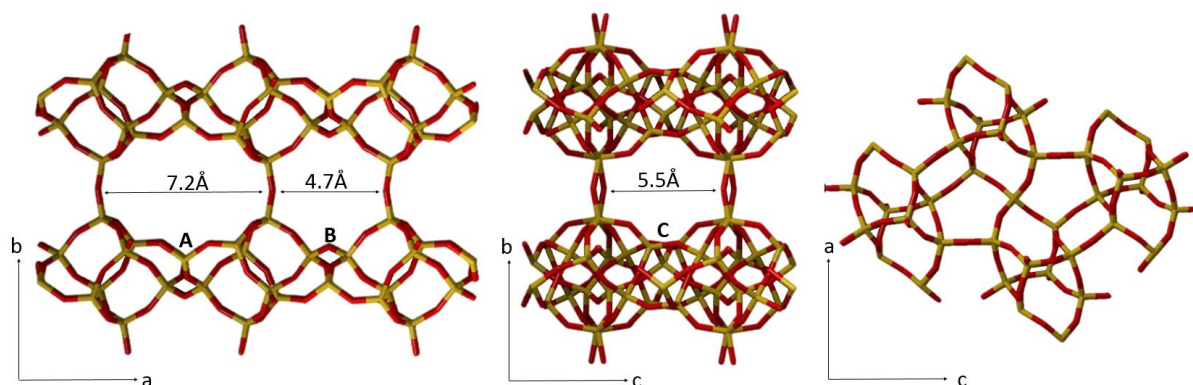


Figure 6.10. HEU framework structure and channel dimensions of clinoptilolite zeolite generated using structural database from the structure commission of the International Zeolite Association (IZA). The yellow sticks represent silicon or aluminum atoms and the red sticks represent the covalently shared oxygen atoms[76,121].

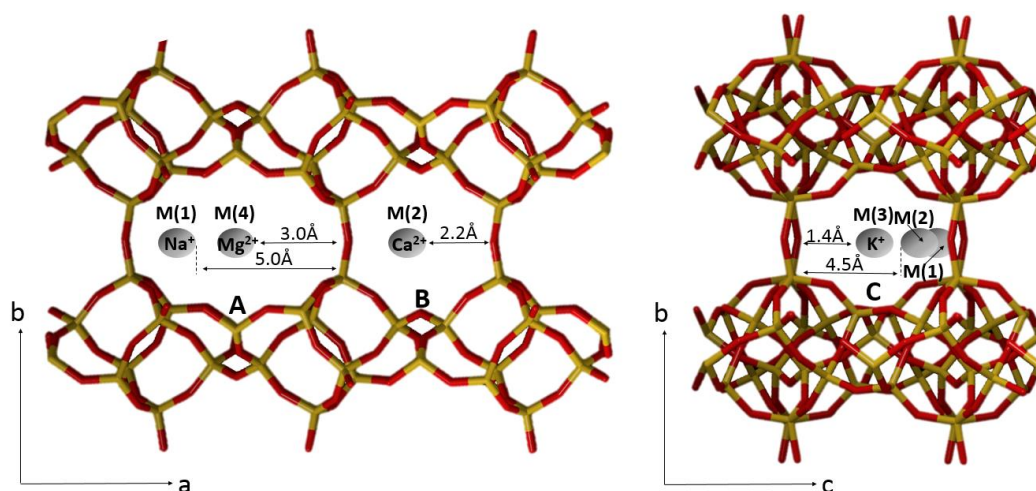


Figure 6.11. The framework structure of clinoptilolite zeolite as described by the IZA. The approximated M(1) through M(4) cation positions and corresponding dimensions of the channel openings are shown [19,76]. The yellow sticks represent silicon or aluminum atoms and the red sticks represent the covalently shared oxygen atoms. (The cations are not to scale)

Table 6.5. Unit cell elemental composition AgNO₃ cation-exchanged clinoptilolite 20x60 U.S. Std. Mesh pellets obtained using EDS analysis.

Clinoptilolite AgNO ₃ Treatment Concentration [M]	Unit Cell Elemental Composition							Si:Al
	O	Al	Si	K	Ca	Mg	Fe	
Untreated	81.39 +/- 7.59	6	35.19 +/- 2.48	2.44 +/- 0.21	0.74 +/- 0.07	0.75 +/- 0.09	0.61 +/- 0.30	0.00 +/- 0.00
0.2	75.5 +/- 4.46	6	30.47 +/- 0.27	0.06 +/- 0.05	0.04 +/- 0.05	0.26 +/- 0.03	0.53 +/- 0.20	5.56 +/- 0.06
Quantified as the standard deviation between the sample averages of two separate samples, with n = 10 independent EDS analysis collection points for each sample.								

Table 6.6. Sips isotherm model parameters for CH₄ and N₂ adsorption on different clinoptilolite samples used in this study at 303K.

Clinoptilolite AgNO ₃ Treatment Concentration [M]	N ₂			CH ₄		
	q _m (mmol·g ⁻¹)	B (atm ⁻¹)	n (-)	q _m (mmol·g ⁻¹)	B (atm ⁻¹)	n (-)
0 (untreated)	1.294	0.120	1.765	1.213	0.708	1.449
0.002	1.564	0.207	2.026	1.114	0.622	1.374
0.01	1.426	0.190	1.758	0.770	0.814	1.384
0.05	1.236	0.298	1.432	0.989	0.219	1.533
0.10	0.846	0.375	1.207	0.728	0.367	1.825
0.20	1.001	0.336	1.238	0.134	0.267	1.558
0.40	0.907	0.356	1.269	0.277	0.316	1.848
Untreated (20x60 pellet)	1.358	0.361	1.219	1.453	0.599	1.034
0.20 (20x60 pellet)	1.047	0.436	1.047	0.932	0.035	1.614

CHAPTER 7

Synthesis and Preliminary Gas Permeation Properties of Vitreous Composite Clinoptilolite Membranes

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ABSTRACT

In this study, we communicate our initial findings regarding the development of novel inorganic composite clinoptilolite membranes. The membranes were formed from natural clinoptilolite microparticles sintered together using specialty glass atop a porous Al_2O_3 porous disc that was used as a support. The ratio of glass sealant to clinoptilolite powder was varied from 50 wt. % to 100 wt. % with the balance being the clinoptilolite particles that were used as filler. FTIR and XRD analysis was used to confirm that the natural clinoptilolite used in this study maintains its overall structural conformation following heat treatment as high as 1073K. Surface and cross-sectional SEM imagery of the prepared membranes showed the formation of a porous clinoptilolite – glass composite layer and a mostly glass layer with lesser porosity. Single gas He, CO_2 , CH_4 , and N_2 permeation experiments were carried out to evaluate the initial performance parameters of the membranes. Single gas membrane permeation decreased with increasing amount of glass sealant, and ranged from $2 \times 10^{-7} \text{ mol/m}^2\text{sPa}$ for the membrane prepared with 30 wt. % clinoptilolite as filler to as high as $4 \times 10^{-6} \text{ mol/m}^2\text{sPa}$ for the 50 wt. % clinoptilolite membrane. The ideal selectivity was calculated from the single gas permeances for potential natural gas or biogas CH_4/N_2 and CO_2/CH_4 separations. These values were the highest at 1.7 ± 0.2 and 1.9 ± 0.1 for the membranes prepared with 40 wt. % and 30 wt. % clinoptilolite, respectively. While low, they are higher when compared to the theoretical Knudsen flow selectivity, suggesting possible gas surface flow across the zeolite. This proof of concept study demonstrates the potential of fabricating inorganic membranes prepared from raw zeolite powder and sintered in a glass binder. This idea lays the groundwork for future investigation in this area of inorganic membrane fabrication, in particular where the generation of a continuous phase of zeolite crystals is not possible.

Key Words:

clinoptilolite, inorganic membrane, CO_2 , N_2 , CH_4 , gas separation, natural gas upgrading

7.1 INTRODUCTION

In the natural gas industry, the content of acid or inert gases such as CO₂ or N₂ is required to be present in less than 2 or 4 vol.% , respectively, in order to reduce the corrosion risk (CO₂) and meet the heating value specifications and to decrease the compression volume for pipeline transport [1–3]. Typically, N₂ rejection from natural gas is carried out through a cryogenic distillation process. In the case of N₂ gas rejection, the significant difference in normal boiling points of N₂ and CH₄ ($T_{nb} = 77.4$ K for N₂, $T_{nb} = 111.7$ K for CH₄) allows for highly selective temperature based separations [4]. The potential for integration within an already required liquefaction process makes the cryogenic separation units desirable components for liquefied natural gas systems. However, in order to implement such systems very large capital costs and economies of scale are required to achieve acceptable process efficiencies [5]. Not surprisingly, this separation technique is best suited for high throughput natural gas processing with typical treatment volumes ranging from 2.8 -14.1 m³/d which do not fully translate to economic viability for smaller scale producers [6].

7.1.1. MEMBRANES for N₂ REJECTION

Various alternative approaches to cryogenic distillation for N₂ rejection have been explored including many membrane based and adsorption based separation processes [7]. In principle, these technologies are advantageous due to their predicted flexibility and ease of operation at moderate conditions thereby lowering the overall energy requirements and increasing operational savings. However, careful consideration of the material interactions with constituent gases are important when considering implementing these technologies on industrial scales[8]. Aside from temperature-based separations the properties of CH₄ and N₂ are such that the separation of these two components is inherently difficult by alternative methods (i.e.: adsorption or membrane-based separations). For example, CH₄ is only slightly larger than N₂ (kinetic diameter = 3.82 Å for CH₄ vs. 3.64 Å for N₂) [9] making it difficult to achieve molecular sieve type separations. For most adsorption based separations, adsorption of CH₄ is only slightly more favoured over N₂ due to electrostatic properties such as its slightly higher polarizability (26.0×10^{-25} cm³ for CH₄ vs. 17.6×10^{-25} cm³ for N₂) [9], whereas, N₂ has a weak quadrupole moment of 1.52×10^{-26} esu·cm² and CH₄ does not have one [9].

Commercial implementation of membranes for industrial N₂ rejection has been achieved by few companies. The advantages and barriers to industrial scale implementation of membrane technology for N₂ rejection are well documented [8]. Many proposed membrane materials are not selective nor productive enough to maintain acceptable rates of methane recovery to be used as commercial stand-alone systems

[10] Economic analysis have shown that based on current performance limits, the integration of a membrane separation system alongside a cryogenic distillation process may be the most effective solution [11].

Membrane Technology and Research Inc. has developed a two stage separation process for nitrogen rejection using proprietary hydrophobic rubbery polymeric membranes under the commercial name NitroSep™ [12,13]. For rubbery polymeric membranes, gaseous compounds are soluble within the matrix. The relative solubility between different gases can be determined by their critical temperature (T_c), with T_c being higher for CH_4 compared to N_2 ($T_c = 190.6\text{K}$ for CH_4 , vs. 126.2K for N_2) [4]. These kinds of polymeric membranes are selectively permeable to hydrocarbons (CH_4 , C_2H_6 +) over nitrogen. In this configuration, the membrane separates the feed mixture into a hydrocarbon rich permeate which is recompressed and fed to the pipeline, and a nitrogen rich retentate [14]. The reported methane selectivity of these membranes range from 3 to 4 with a possible maximum of 6 to 7 at low temperatures (below 253K) [13]. The membrane system is designed for a maximum feed inlet pressure of 85 atm, with a pressure drop of between 12 and 50 atm per separation cartridge resulting in recompression of the product gas [12]. Rubbery polymeric membranes such as these are subject to plasticisation as a result of interactions with the heavier hydrocarbons present within the natural gas feed [8].

PoroGen Inc. has recently developed and marketed a nitrogen selective glassy polymeric membrane composed of polyether ether ketone (PEEK) under the commercial name PEEK-SEP™. These membranes retain the ability to treat $1.41 \times 10^5 \text{ m}^3(\text{STP})/\text{d}$ of feed gas with 6% nitrogen content producing a product gas containing 2.25% nitrogen with a methane recovery of 87% [7]. The inlet feed pressure was 30 atm whereas the product gas had a pressure of 2 atm prior to recompression. For these kinds of glassy polymeric membranes, the rigidity of the polymer matrix results in lesser amounts of gas solubility, meaning that the relative differences in the sizes of the component to be separated is the main factor that dictates the potential membrane selectivity. Thus, since N_2 is slightly smaller than CH_4 , for the separation of these gases, glassy polymeric membranes are usually N_2 selective over CH_4 . Aside from the continued issue of low selectivity, degradation of membrane performance over time following prolonged exposure to natural gas is another ongoing limitation of these materials.

Inorganic membranes present an alternative approach to the use of polymeric materials. While issues pertaining to the costs and robustness of inorganic membranes exist, these materials are advantageous compared to their organic counterparts due to their greater temperature and chemical stability [15,16]. Examples of such types of membranes presented in the literature specifically for N_2 gas rejection from CH_4 have been limited to those formed from various microporous zeolites (chabazite, SAPO), titanosilicate ETS-4, or carbon molecular sieves [17–21]. The active layer material type and membrane morphology dictate the separation performance. In general, membranes of this type have displayed high selectivity and

permeability values for prospective N_2/CH_4 separations. They have also demonstrated superior performance to that of the 2008 Robeson upper bound for these types of separations [22].

7.1.2. CLINOPTILOLITE

Due to its extensive study with respect to adsorption based gas separation systems the application of membranes formed of clinoptilolite is of interest in this work. Clinoptilolite is a common and abundant natural zeolite with a simplified chemical formula that is as follows: $(X)_6 (Al_6Si_{30}O_{72}) \cdot 20H_2O$. The framework structure consists of alternating eight and ten member rings formed of silica and alumina oxides [23]. Therefore, charge balancing extra framework cations are necessary to balance the residual negative framework charge (this is represented by the X within the chemical formula which is equivalent to a +1 charge cation) [23,24]. For natural clinoptilolite, this can be a variable mix of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ cations that is dependent on the source of the local mineral deposit [23,25,26]. The channel pore arrangement is such that dimensions of the pore aperture may be altered by the arrangement of extra framework cations. This means that for the two parallel channels consisting of eight and ten membered rings; the effective channel window can vary in size from 3.1 to 7.5 Å and from 3.6 to 4.7 Å, respectively. Whereas the effective pore size of the intersecting third channel ranges from 2.8 to 5.5 Å [23]. The effect of different cations and alterations in the channel pore geometry induce favourable gas separation properties including molecular sieve effects [27–37].

7.1.2. CLINOPTILOLITE MEMBRANES

Zeolite membranes are usually prepared as composites on a porous support using some sort of crystallization technique (e.g.: in-situ crystallization or secondary growth via hydrothermal synthesis) [38,39]. The complex nature of clinoptilolite crystal formation even under tightly controlled synthesis conditions presents an obstacle to this approach [40–42]. This presents a significant barrier to scale up for clinoptilolite membranes of this kind. For this reason, very few studies have attempted to pursue the development of inorganic membranes formed from clinoptilolite [43–45].

In 2011, Kuznicki and colleagues fabricated clinoptilolite membranes directly from sheets of solid natural clinoptilolite mineral deposits that were machined into thin wafers [46–48]. Observations from these studies showed that these membranes exhibit favourable properties for H_2 selective gas separations in mixtures containing CO_2 gas. These characteristics were attributed to the dense makeup and high degree of crystallinity of the mineral phase which is composed of the membrane wafers. However, scale up of these membranes for applications in larger scale processes is likely quite difficult due to the high variability of defects in naturally derived materials. One successful example of such membranes are those formed from

mixing natural clinoptilolite powder and aluminum silicate into a slurry and coating a porous steel support [43]. Another method of manufacturing membranes of this kind is from a pressed matrix consisting of a mixture of clinoptilolite and copper powders with heat treatment at 923 K[45]. Functional molecular sieve membranes were made in this fashion, with results showing H_2/CO_2 selectivity similar to the natural wafer membranes machined from clinoptilolite mineral deposits[43,45,48]. However, the authors noted that these membrane types were subject to defects; reducing the selectivity. Defects are likely formed due to an uneven distribution of particles (agglomerations, air bubbles etc..) and differences in the thermal expansion coefficients between the substrate, the zeolite, and the support [49–52]. It was found that for these membranes, the areas for non-selective gas transport may be reduced by applying multiple coats [43].

The use of clinoptilolite particles as inorganic fillers dispersed amongst a continuous polymeric matrix have been developed for applications such as water and wastewater treatment, pervaporation, and gas separations[53,54]. These membranes propose to combine the superior mechanical toughness of polymeric materials with the high gas permeability and selectivity of inorganic membrane filler materials. Mixed matrix membranes (MMM) formed with 10 wt% clinoptilolite particles dispersed within polyether-block-amide matrix showed improved CH_4/CO_2 and CH_4/N_2 selectivity values as high as 37.36 and 1.87, respectively [55]. Similarly, a polysulfone polymer MMM with clinoptilolite has been developed and displayed higher selectivity than those of the neat polysulfone form for CH_4/CO_2 gas separations with selectivity values ranging from 32.2 to 145.6 [56].

7.2. OBJECTIVES

In this study, the development of composite inorganic membranes formed of natural clinoptilolite particles fused within a vitreous glass matrix formed atop a porous alumina ceramic support is investigated. Firing at high temperatures results in the creation of an amorphous ‘glass’ matrix that is thought to be impermeable. In principle, it is proposed that the glass acts as a kind of binder between the ceramic supports and the clinoptilolite particles. A defining limitation to this approach is the high glass transition temperatures usually required for traditional glaze which is well beyond the thermal stability of many zeolites. Whilst most other zeolites are considerably less stable under such high temperatures, the upper temperature range for clinoptilolite stability is 1170K to 1340K before the pore structure fully collapses (depending on the occupying cation, with K^+ cations being the most stable) [57,58]. Recent developments have led to so called ‘low temperature melting glass’ composed of primarily B_2O_3 and/or Bi_2O_3 as opposed to SiO_2 with other minerals as fluxes where the glass transition temperature (T_g) may be as low as 675 K. [59,60] The idea is that the glass sealant can successfully bind and create a seal atop ceramic support which will minimize the presence of pathways for non-selective gas transport. The effect of thermal treatment on clinoptilolite was assessed using Fourier Transform Infrared spectroscopy (FTIR) and

powdered x-ray diffraction (XRD) and single gas adsorption studies. The physical properties of the membranes were analysed using scanning electron microscopy (SEM). Single gas permeation behaviour of He, N₂, CO₂, and CH₄ gases was studied in an effort to determine the initial performance properties of these new materials.

7.3. MATERIALS and METHODS

7.3.1 MATERIALS

Raw clinoptilolite of the Ca²⁺ form was obtained from St. Cloud Mining (Tucson, AZ, USA) from mineral deposits located in Amargos Valley, NV, USA. The elemental composition, phase characteristics, and surface properties of this same clinoptilolite powder (sourced from the Amargos Valley, NV, USA) have been verified and discussed in detail in our previous work [61].

The clinoptilolite was received in the form of a powder +325 U.S. Std. mesh size ($d_p < 44\mu\text{m}$) and was sieved with a +400 U.S. Std. mesh sieve tray ($d_p < 37\mu\text{m}$) for 30 minutes using a Ro-Tap sieve shaker. The particles that were collected from the bottom of the sieve tray were used for cation exchange, particle analysis, and fabrication of the membranes. Specialty glass (SCHOTT Glass number – G018-266) was purchased from SCHOTT North America, Inc. (Southbridge, MA, USA). The glass was supplied as a fine powder with an average particle size (d_p) of 10 μm . This glass has a T_g of 870K and a sealing temperature of 1040K, it is designed to be compatible with alumina ceramics with a thermal expansion coefficient of $5.8 - 6.9 \times 10^{-6} \text{ K}^{-1}$. A proprietary acrylic based binder which was purchased from SCHOTT North America, Inc. was used to disperse the glass and clinoptilolite particle mixture. Chemical information regarding the binder makeup was not provided by the supplier. The membranes were fabricated on commercially available porous ceramic alumina discs purchased from TAMI Industries (Nyons, France). The discs had a diameter of 4.7 cm and a thickness of 2 mm. The surface of the disc contained an Al₂O₃ active layer with a pore size of 0.45 μm . The gases used for the membrane permeation experiments and the adsorption experiments were: CO₂ (99.995%), CH₄ (99.99%), N₂ (99.999%), and He gas (99.999%). All of the gases were purchased from Linde Canada Ltd. (Ottawa, ON, Canada).

7.3.2. PREPARATION of CLINOPTILOLITE POWDER and MEMBRANES

Prior to fabrication of the membranes, the sieved clinoptilolite powder was prepared according to the same washing procedure with deionized water to remove any excess soluble salts as outlined in our previous contribution [61]. Following this procedure, the clinoptilolite samples were rinsed with deionized water before being placed in a drying oven at 378 K for a minimum of 12 hours. The porous ceramic

alumina supports were all washed by submerging them into a beaker filled with deionised water for a period of 1 hour. Following this step, the disc supports were placed into a drying oven at 378K overnight. The supports were removed from the oven and stored in a dry desiccant bed prior to use. Coating slurry consisting of clinoptilolite and glass powder suspended in the liquid acrylic based binder was prepared. Ratios of 50, 40, and 30 wt. % clinoptilolite to glass powder were used. The two powders (glass powder and clinoptilolite) were first mixed together on a dry basis and then they were suspended in the liquid acrylic based binder at a ratio of 0.75g liquid binder per 1.0 g of powder mixture. To ensure an even distribution, a single coat of the slurry was applied to the top surface of the ceramic alumina disc supports using a brush applicator. Much of the suspension dried quickly following application, however the discs were left air-dried at standard ambient temperatures and pressures for 30 minutes. Next, a second coat of the slurry was applied however in perpendicular direction and the discs were allowed to dry in the same fashion as in the previous step. The prepared discs were placed into a programmable Neytech Vulcan 3-550 furnace purchased from Cole-Parmer Canada (Montreal, QC, Canada). The discs were heated at a rate of 1 K/min from room temperature up to 1040 K where the temperature was held for a period of 15 minutes. The membranes were cooled to 610 K at a cooling rate of 3 K/min, following this step, they were cooled to 323 K at a cooling rate of 0.5 K/min. After reaching 323K, the oven was turned off and the membrane discs were allowed to cool to standard ambient temperatures in the same oven with the door closed.

7.3.3. CHARACTERIZATION

Powdered x-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy was used to draw comparisons with respect to changes in the clinoptilolite phase structure and physicochemical properties following heat treatment. For this analysis, a 1g sample of clinoptilolite powder inside a ceramic crucible was placed into a programmable Neytech Vulcan 3-550 furnace. Separate samples of raw clinoptilolite powder were heated from room temperature at a rate of 1 K/min up to the experimental oven temperatures which were: 973K, 1043K, 1073K, 1173K, and 1273K. Each sample was held at the respective temperatures for 1 hour and then cooled to 323K at a cooling rate of 1K/min. Both the heat treated and non-heat treated powdered samples were analyzed at room temperature using a Rigaku Ultima IV powder diffractometer in Bragg-Brentano geometry for the XRD analysis, using Cu K α radiation ($\lambda = 1.5418$ Å). A 2θ range of 2° to 90° was used with a 0.02° step resolution and $6^\circ/\text{min}$ scan speed. A Cary 630 FT-IR with ATR (Agilent Technologies, Mississauga, ON, Canada) was used for the FT-IR analysis. A spectral range of 650 to 4000 cm^{-1} was used and a total of 100 scans were carried out for each sample with a resolution of 4 cm^{-1} .

Scanning Electron Microscope (SEM) imagery of the clinoptilolite particles and the synthesized membranes was carried out with a Phenom Pro SEM (Nanoscience Instruments, Alexandria, VA, USA) using accelerating voltage of 5kV. The powdered samples were mounted on aluminum sample holders (Ted Pella, Redding, CA, USA). The clinoptilolite powder particle size was measured using the SEM images at 2000X magnification using ImageJ software. An SEM image was divided into quadrants and the diameter of 400 particles (100 per each quadrant) were measured to assess the particle size distribution using Microsoft Excel. The synthesized membranes were fractured and small sections of the membrane were mounted on the sample holders prior to the analysis. The membrane cross section was used to approximate the thickness of the membrane atop the porous ceramic support.

7.3.4. SINGLE GAS ADSORPTION MEASUREMENTS

Pure component CO₂, CH₄, and N₂ adsorption isotherms were conducted on clinoptilolite powder samples at a temperature of 295K over a pressure range of 0 to 8 atm. These isotherms were compared to those obtained for the clinoptilolite that was subject to heat treatment at the membrane formation temperatures (1040K). A microgravimetric analyser VTI Corp. (Hialeah, FL, USA) was used. A complete description of the experimental setup and procedure has been previously described elsewhere [61,62]. The Sips isotherm given in Equation 1 was used to fit all of the experimental adsorption isotherms [63].

$$q = \frac{q_m \beta p^n}{1 + \beta p^n} \quad (1)$$

7.3.5. SINGLE GAS MEMBRANE PERMEATION MEASUREMENTS

For the gas permeation experiments, the prepared membranes were installed within a custom made stainless steel membrane cell. Figure 7.1 details the sequence of steps that was used to install the membranes within the permeation cell. Given the rigidity of the ceramic discs, steps were taken to prevent damage to the membrane and to improve the seal within the permeation cell. First, the outside edge of the membrane disc was wrapped with polytetrafluoroethylene (PTFE) tape. Next, a thin layer of silicone rubber was used to help seal the space between the edge of the PTFE wrapped membrane disc and the rubber O-rings of the permeation cell. The wrapped membrane was placed within the module such that the active layer containing the membrane surface was facing towards the inlet feed gas. In doing so, the bottom of the disc support was flush with the porous stainless steel support of the permeation cell. The membrane was enclosed within the pressure housing and the silicone rubber was allowed to set overnight. As the silicon rubber is required to cure, a continuous low flow rate of He gas (below 20ml (STP)/min was employed on the membrane as a purge. Figure 7.2 shows a cross section of the membrane installed within the permeation cell.

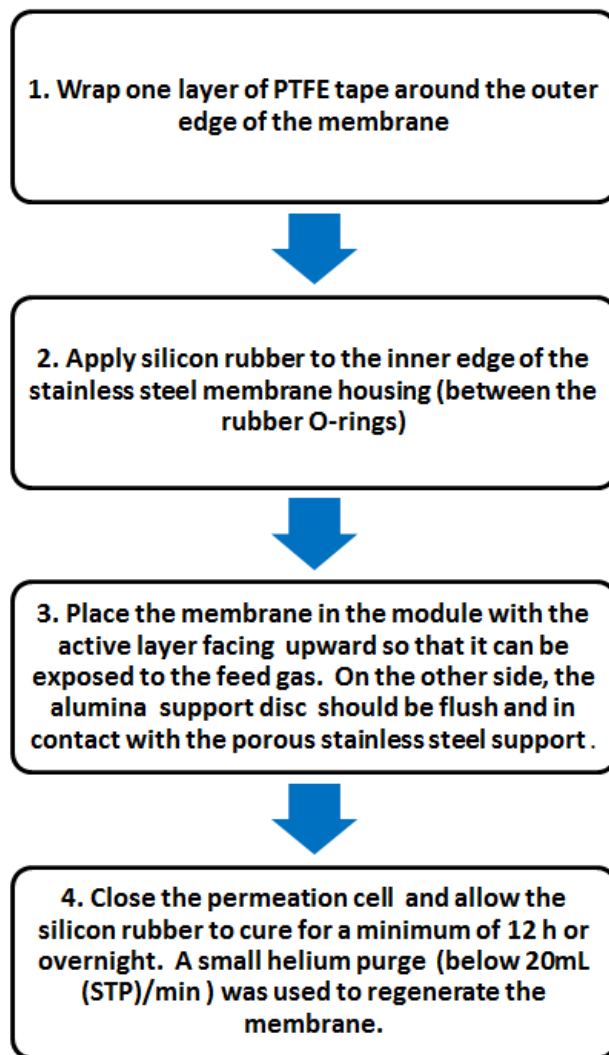


Figure 7.1. Diagram showing the sequence that was used for preparing and installing the ceramic disc membranes within the permeation cell.

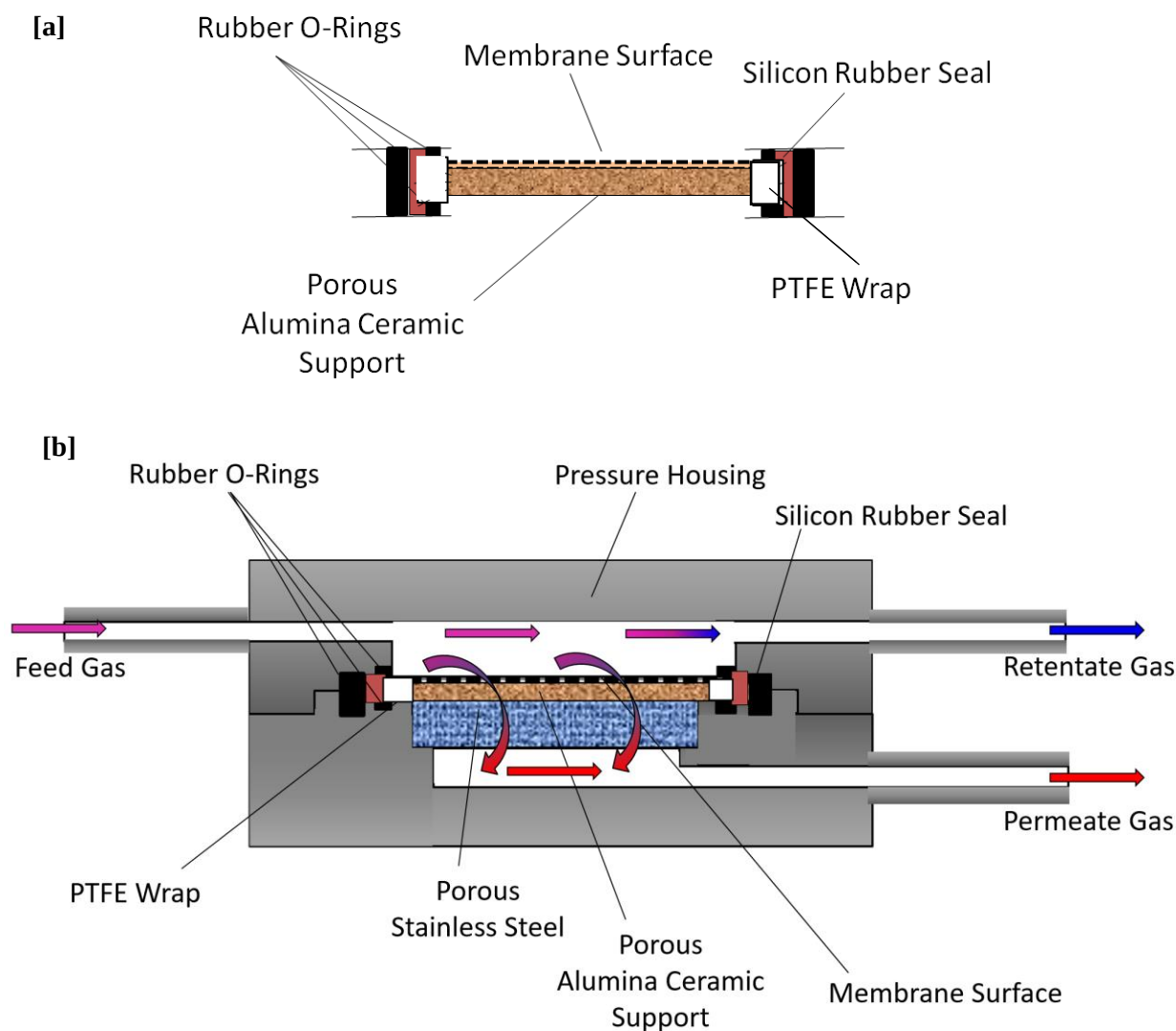


Figure 7.2 [a] Cross section of the membrane highlighting the seal around the outside edge of the disc that was installed inside the membrane permeation cell.; [b] Cross section of flat disc membrane permeation cell with the membrane shown in [a] installed.

The membrane cell depicted in Figure 7.2 was installed within the experimental setup shown in Figure 7.3 which was used for all of the membrane permeation experiments. For this study, the experiments were limited to single gas permeation with the different gases being fed individually towards the membrane permeation cell. A needle valve was used to control the feed gas flow rate which was monitored using a rotameter. A pressure gage was used to measure the pressure of the feed gas prior to entering the feed side of the membrane module. The feed pressure was controlled manually using a needle valve installed at the outlet (retentate side) of the membrane cell in order to regulate back pressure. The permeate flow rate was

measured using a 100mL soap film bubble flow meter, and the permeate pressure was monitored using a pressure gage installed directly following the permeation cell.

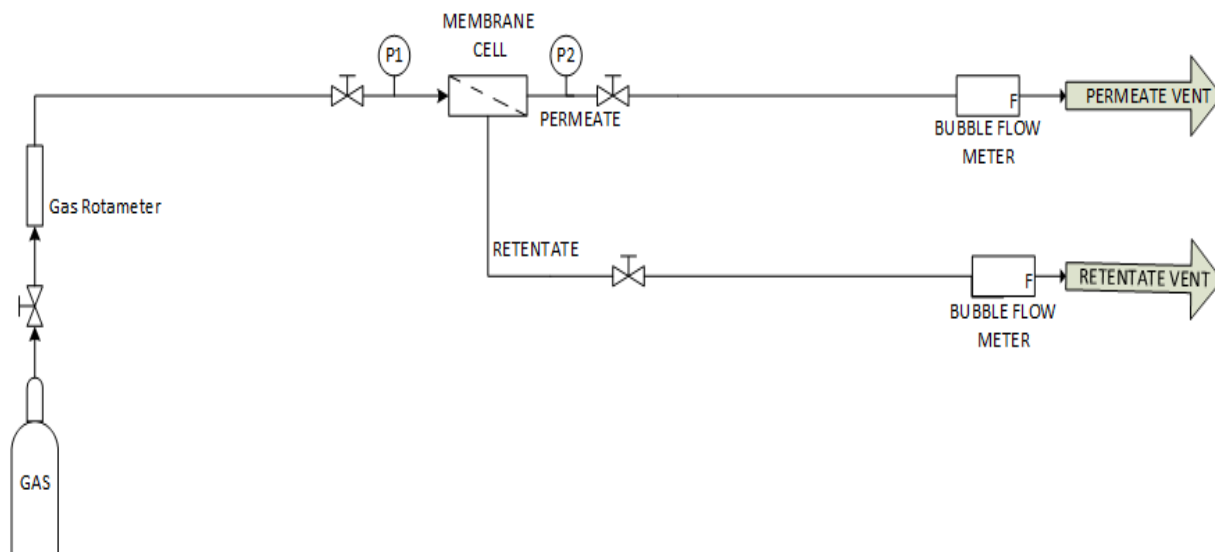


Figure 7.3. Schematic diagram of the membrane permeation set-up. For this experiment, the configuration was set up so that only the single gas permeation measurements were performed.

The initial performance parameters of the membranes were assessed by means of single gas permeation experiments using He, N₂, CH₄, and CO₂ gases at ambient temperatures (approximately 295 K). Prior to commencing each experiment, the membranes were sealed within the permeation cell and regenerated overnight under helium purge with a flow rate below 20 mL(STP)/min with the permeate side open to atmosphere. For all of the experiments the upstream feed side pressure was held at different pressures ranging from 1.25 atm and 2.5 atm while the permeate side was kept open to atmosphere (pressure ≈ 1 atm). Following each feed side pressure change, both the feed side pressure and the flow rate of the permeate were measure. The system reached steady state over a period of half an hour as indicated by no change in the measured values. Once steady state is achieved, the feed and permeate side pressures were recorded and the flow rate of the permeate gas was measured with the bubble flow meter. Equation 2 shows that the single gas permeance, P_i , is determined by normalizing the flux of the permeate, J_i , to the pressure difference across the membrane with $p_{i,F}$, and $p_{i,P}$, being the pressures of i at the feed and permeate side of the membrane, respectively.

$$P_i = \frac{J_i}{(p_{i,F} - p_{i,P})}, \text{ where } J_i = \frac{\dot{Q}}{(Area)} \quad (2)$$

An initial estimation of membrane separation performance is done by comparing the ideal selectivity, α_{ij}^* , which is defined as the ratio of single gas permeances of gases i and j as shown in Equation 3.

$$\alpha_{i/j}^* = \frac{P_i}{P_j} \quad (3)$$

With this information an initial assessment of the membrane productivity may be obtained.

7.4. RESULTS and DISCUSSION

Figure 7.4 presents the particle size distribution of the crushed and sieved clinoptilolite powder as determined from the SEM imagery using ImageJ software. The clinoptilolite powder has an average particle size of 10.8 μm with a standard deviation of 6.4 μm . In comparison to the filler used in conventional mixed matrix membranes which typically utilize particles in the nanometer size range, the clinoptilolite particle size is considerably large. For polymeric mixed matrix membranes, both the particle size and loadings effect the performance of these membranes[64]. However, a continuous phase composed of glass is thought to adhere more easily to the inorganic filler than as is the case for polymeric mixed matrix membranes where voids at the inorganic – polymeric interface are a common source of defects [65]. For these membranes, both the inorganic filler (clinoptilolite particles) and the continuous phase (glass) are more chemically similar to each other compared to mixed matrix membranes of the polymeric variety. In this case they are both inorganic, the continuous phase is amorphous and clinoptilolite filler retains an ordered structure. The particle size distribution is broad and is skewed towards the smaller particles. Given the high particle loading for these membranes (clinoptilolite loadings of 30 wt. % - 50 wt. %) discrepancies in the uniformity of the particle size may be sources of potential defects to consider when evaluating membranes of this type.

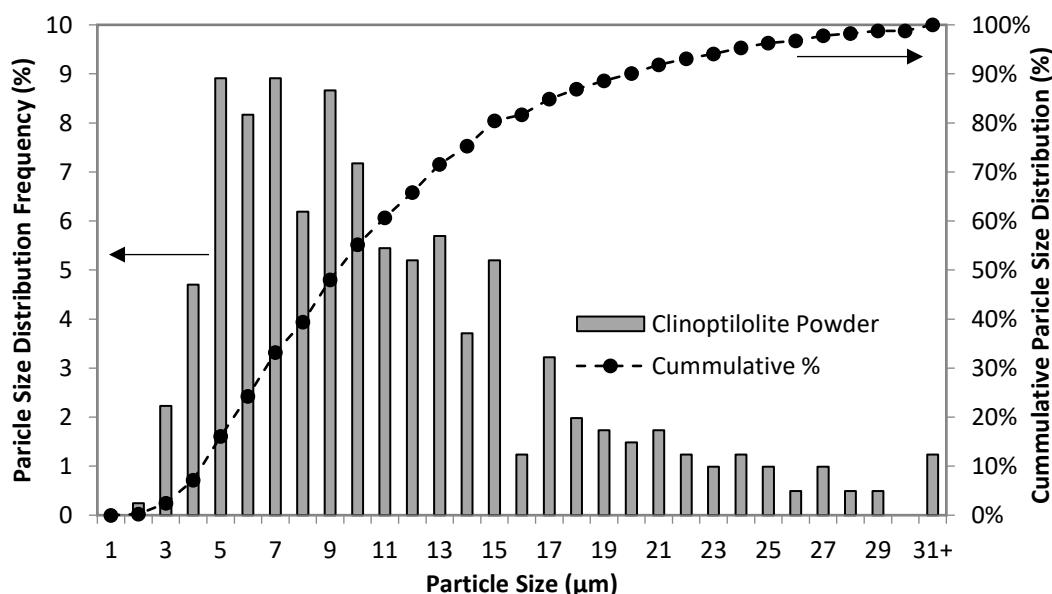


Figure 7.4. Histogram corresponding to the particle size diameter distribution of the untreated clinoptilolite powder. Particle size frequency % is the percent of each diameter counted of the total 400 particles.

The thermal stability of the clinoptilolite is important for establishing the processing temperature limits of the material for use in this application. Therefore, prior to fabricating the membranes, samples of clinoptilolite powder were subject to heat treatment at different temperatures. The physical and structural characteristics of the clinoptilolite were assessed and compared to the untreated clinoptilolite using XRD and FTIR. Figure 7.5 presents the XRD patterns for the untreated and the heat treated clinoptilolite samples at different temperatures. The original sample displays a typical XRD pattern that is synonymous with clinoptilolite [26,32,40,41,66,67]. This Ca^{2+} rich variety of clinoptilolite displays high thermal stability. However, as expected, heat treatment results in a deterioration of the sample crystallinity at higher temperatures which presents itself as a decrease in the prominence of the XRD peaks with an increase in treatment temperature. It is notable that many of the characteristic peaks are present up to a treatment temperature of 1073 K. At higher temperatures the clinoptilolite structure likely collapses, given that clinoptilolite typically exhibits high thermal stability at temperatures as high as 1170K to 1340K [57,58,68]. However, caution should be taken when selecting the source of the clinoptilolite. Thermal stability of clinoptilolite is dependent on the purity of the mineral source, the cation type and distribution, and ratio of Si to Al in the zeolite framework [58].

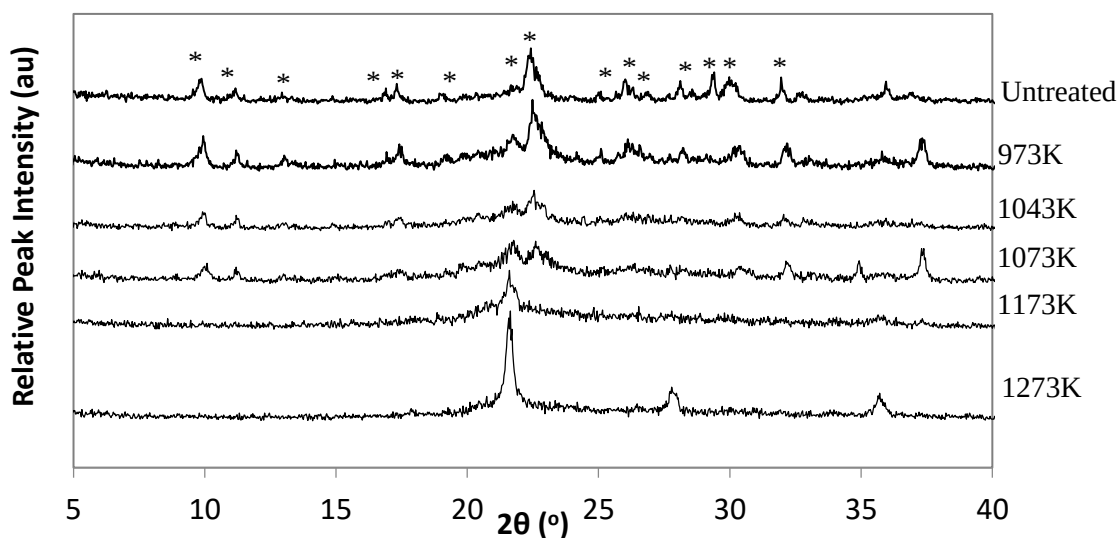


Figure 7.5. XRD diffractograms corresponding to the untreated clinoptilolite powder compared to the clinoptilolite subject to heat treatment at different temperatures. The intensity response of the untreated sample is equivalent to the characteristic XRD patterns (*) for clinoptilolite. [26,41,67,69]

The FT-IR spectra for the untreated clinoptilolite and the clinoptilolite subject to the membrane fabrication conditions outlined in Section 7.3.2 with temperatures as high as 973 K is presented in Figure 7.6. From the FT-IR spectra, it is clear that the heat treated clinoptilolite retains much of the characteristics of the untreated clinoptilolite sample. Small deviations within the spectra band region of 650 to 1250 cm^{-1}

suggest only a limited change in the overall zeolite lattice. This region is sensitive to the internal Si and Al oxide tetrahedra and the sub-lattice bond vibrations that form the framework and 8 and 10 membered rings consistent with this particular zeolite structure [69–72]. However, it is obvious that some differences may be observed between the spectra range of 3150 and 3650 cm^{-1} . These band vibrations correspond to bridging –OH molecules present in the framework or water residing in the zeolite micropores [32,69,73]. This change is to be expected since the majority of the physically adsorbed water and water coordinated with the extra framework cations is removed at temperatures between 343 and 423 K, whereas –OH groups are removed in the region of 573 and 873 K [68].

Overall, the information presented in Figures 7.5 and 7.6 suggests that while small structural changes are likely, the clinoptilolite used in this study is largely capable of withstanding the heat treatment conditions necessary for achieving the glass vitrifying temperatures that are necessary for membrane formation.

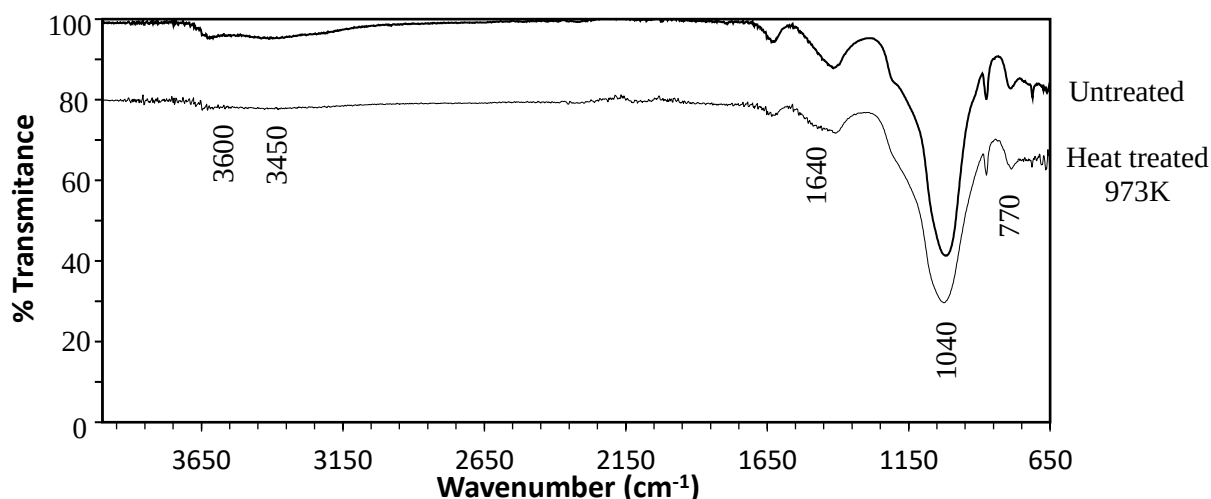


Figure 7.6. FT- IR spectra in the range of 650 to 4000 cm^{-1} for the untreated clinoptilolite compared to clinoptilolite subject to the same heat treatment procedure used for membrane formation outlined in Section 7.3.2. A separation of -20% transmittance is applied between each spectrum.

A combination of different transport mechanisms (ie: Poiseuille/viscous flow, Knudsen flow, surface flow etc...) may contribute to gas transport across these porous membranes. However, surface flow induced by the zeolite adsorption mechanism is a preferred mechanism due to the ability to achieve a higher gas separation selectivity [74]. The driving force for surface flow corresponds to the concentration profile across the membrane and is related to the difference in the adsorbate surface coverage between the higher

pressure feed side and the lower pressure permeate side [75]. Adsorption equilibria on the zeolite were measured experimentally and is related to the potential driving force behaviour for surface flow across the membrane. Figure 7.7 presents the single gas adsorption isotherms of CO₂, CH₄, and N₂ gases at 295K on both the untreated and heat treated clinoptilolite subject to the membrane formation temperatures outlined in Section 7.3.2. Corresponding Sips adsorption isotherm parameters are given in Table 7.1. As can be seen from this Figure, the model seems to represent the experimental isotherm data very well. The adsorption capacity for all of the gases increases with increasing pressure, with CO₂ being the most adsorbed, followed by CH₄ and N₂, which is to be expected for natural clinoptilolite of this variety [61]. However, the adsorption capacity of all of the gases for the heat treated clinoptilolite is lower than for the untreated samples. While the majority of the material is composed of clinoptilolite, natural impurities form some portion of the mineral phase which is to be expected since it is a naturally sourced material. It is suspected that the heat treatment may actually remove or alter some of the impurities that are less stable under higher temperatures. These impurities could actually influence the adsorption behaviour of the samples since they could have adsorption capacities themselves or block the pores if they become amorphous following treatment at high temperatures.

Since the channel pore size distribution of clinoptilolite is very narrow, molecular sieving and mass transfer resistance may also play an important role in the performance of this adsorbent. Most notably, investigations into these effects for clinoptilolite exchanged with different cations (Ca²⁺, mixed Na⁺ and Mg²⁺, Li⁺, and Ni⁺, among others) has demonstrated significantly altered gas adsorption behaviour with increased N₂/CH₄ kinetic selectivity due to blockage of larger gases such as CH₄ to a certain degree [27–29,37,61]. These tendencies have been proven to be translated into the gas transport and separation behaviour with clinoptilolite based membranes showing improved H₂/CO₂ and CO₂/CH₄ separations [46,56]. In this present study, the natural form of clinoptilolite was used as a proof of concept. Anecdotally, the transport diffusivity is the slowest for CH₄ is slower than the other studied gases. Gas transport appears to be slower for the heat treated clinoptilolite compared to the untreated clinoptilolite. It is suspected based on previous studies that the framework structure of clinoptilolite undergoes a slight contraction following activation between temperatures of 523K to 773K. This contraction reduces the effective size of the micropore channels and thus can alter the gas adsorption behaviour [76,77]. It is suspected that the slower gas transport diffusivity of the gases within the clinoptilolite may be an indication of a slight decrease in the micropore size following heat treatment resulting in a blockage of the pores.

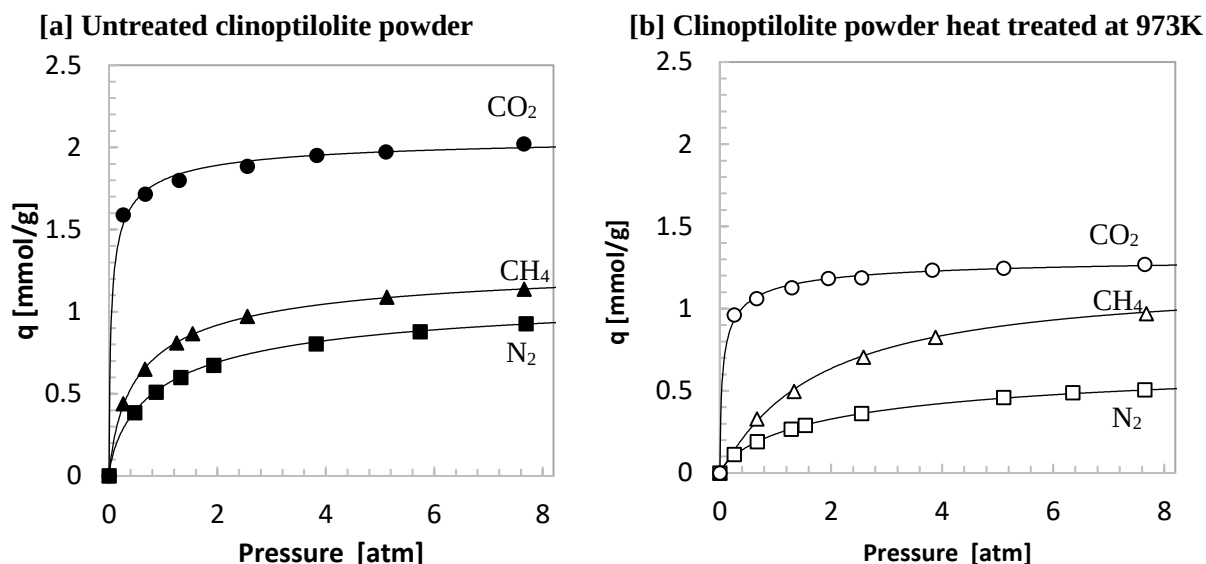


Figure 7.7. CO₂, CH₄ and N₂ pure component adsorption isotherms at 295K fitted with Sips model for [a] untreated clinoptilolite powder [b] clinoptilolite powder treated at 973K subject to the same heat treatment procedure used for membrane formation outlined in Section 7.3.2.

Table 7.1. Sips isotherm model parameters for CO₂, CH₄ and N₂ adsorption at 295 K on raw clinoptilolite powder and clinoptilolite powder heat treated at 973 K subject to the same heat treatment procedure used for membrane formation.

Sips Parameter	Untreated			Heat Treated		
	CO ₂	CH ₄	N ₂	CO ₂	CH ₄	N ₂
n	0.734	0.773	0.558	0.722	1.057	0.773
q _m (mmol/g)	2.045	1.309	1.331	1.300	1.181	0.718
β(atm ⁻¹)	16.443	1.513	0.109	13.374	0.577	0.399

Figure 7.8 presents the SEM imagery of the surface of a prepared membrane from the same batch as those used in the permeation experiments prepared using a mixture of 30 wt. % clinoptilolite filler and 70 wt. % glass, it is compared to the surface of an alumina support modified with a layer of glass with no clinoptilolite used as filler. As expected, the surface of the 100 wt. % glass layer formed on top of the alumina support appears to be fairly uniform and non-porous with only minor abrasions present on the top layer. In contrast, the surface of the prepared membrane shows distinct areas of fused glass mixed in between clinoptilolite particle agglomerations. The membrane appears to be fairly porous with some void areas evident on the surface.

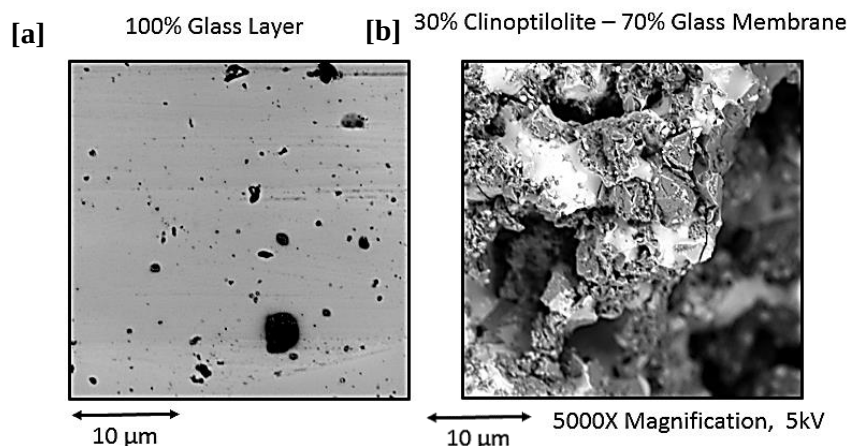


Figure 7.8. SEM images with 5000x magnification of the membrane surface that is in contact with the gas feed.

[a]The support surface is coated with 100 wt. % glass.

[b]The support surface is coated with a membrane comprising of a mixture of 30 wt. % clinoptilolite and 70 wt. % glass.

Figure 7.9 shows the SEM imagery of the cross section of the same prepared membrane as described in Figure 7.8 [b]. For comparison, the cross section of this membrane is presented alongside that of an unmodified porous alumina support and an alumina support modified with a layer of glass with no clinoptilolite used as filler. As can be seen in Figures 7.9 [a] the alumina support is porous and contains distinct regions incorporating the active layer and the porous support, with the active layer extending about 20 μm from the support surface into the porous support. The prepared 100 wt.% glass layer shown in Figure 7 [d] appears to completely cover the active layer surface. However, small cracks are observed in the glass layer at the interface with the support. This is likely due to differences in the rates of thermal expansion between the two different materials. In this case, the mean coefficient of thermal expansion for the glass is about $6.9 \times 10^{-6} \text{ K}^{-1}$ as provided from the manufacturer for a temperature range of 293 K to 673 K. This compares to a range of $5.80 \times 10^{-6} \text{ K}^{-1}$ to $8.79 \times 10^{-6} \text{ K}^{-1}$ for $\alpha - \text{Al}_2\text{O}_3$ for the ceramic supports over a similar temperature range [78]. Figure 7.9 [b] shows the cross section of the prepared membrane. It is clear that two distinct layers have formed on top of the porous alumina support. The top layer that is in contact with the gas feed is more porous and appears to contain the majority of the fused clinoptilolite particles. Whereas, the second layer that is directly after the first layer is less porous and is formed of majority of the glass phase that is fused to the active layer of the ceramic alumina support. It is suspected that the glass and clinoptilolite may have actually formed two distinct layers during the glass vitrification process whereby the glass was able to flow towards the bottom layers over the course of several minutes. This may

also explain why there appears to be a lesser amount of glass and more clinoptilolite towards the top of membranes as shown in Figure 7.8.

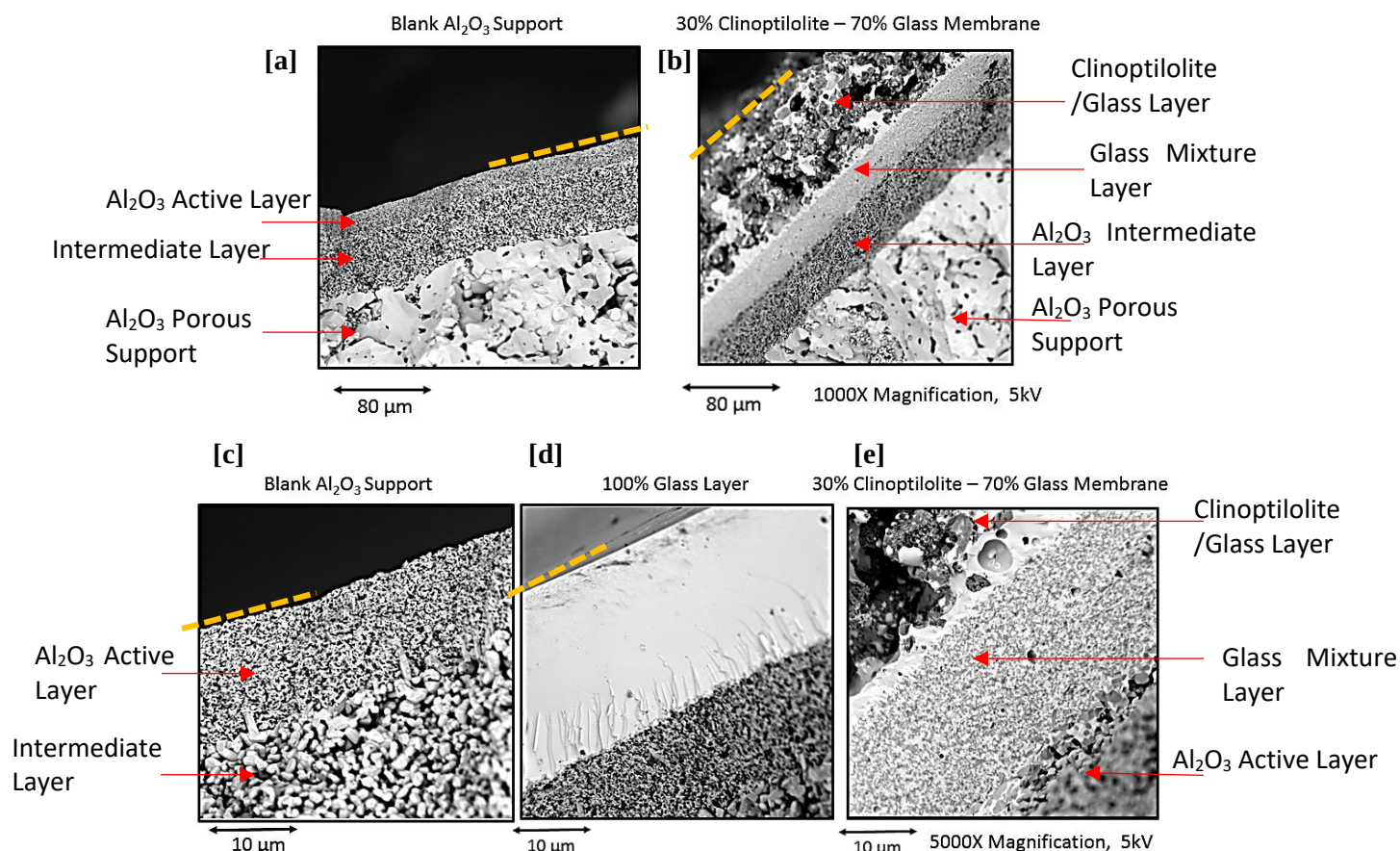


Figure 7.9. Cross sectional SEM images of the prepared membranes and the empty Al_2O_3 supports (the dashed line is the membrane surface in contact with the feed gas).

[a] 1000X magnification of the blank Al_2O_3 support (no coating)

[b] 1000X magnification of the Al_2O_3 support coated with 70 wt. % glass and 30 wt. % clinoptilolite

[c] 5000X magnification of the blank Al_2O_3 support (no coating)

[d] 5000X magnification of the Al_2O_3 support coated with 100 wt. % glass layer.

[e] 5000X magnification of the Al_2O_3 support coated 70 wt. % glass and 30 wt. % clinoptilolite

Figure 7.10 displays the single gas permeation results for He , N_2 and CH_4 gases as a function of the pressure differential across the different prepared and unprepared surfaces. From this Figure, comparisons may be drawn with the permeation values of the prepared membranes to that of a support covered in a 100 wt. % glass layer. As expected, the blank support with no membrane had the highest gas permeation values for all gases at about 3×10^{-5} to 5×10^{-5} $\text{mol/m}^2\text{sPa}$, increasing with increasing pressure differential. The support is not selective as no significant difference with regards to the permeation rates is

observed between the different gases. This is expected given the high porosity of the support observed with the SEM imagery as outlined in Figure 7.9 [c]. This translates into an overall lower resistance to gas transport, with viscous flow likely being the dominant gas transport regime for the porous unprepared discs. In comparison, the support covered with a 100 wt. % layer of glass displays by far the lowest permeation rates, with values ranging from 3×10^{-9} to 6×10^{-9} mol/m²sPa and increasing with increasing pressure differential across the membrane. This is to be expected since the glass is non porous and acts as an impermeable seal overtop the porous ceramic support. Therefore the observed low permeation values are likely a result of gaseous transport through the small micro-fractures shown in Figure 7.9 [d]. Compared to the 100 wt. % glass membrane, the membranes prepared with clinoptilolite filler show greater permeance values, indicating the possibility of additional surface interactions and gas transport as a result of adding clinoptilolite filler to the prepared membrane surface. It may be observed that the permeance rate is actually fairly proportional to the amount of clinoptilolite used as filler in the membrane. The rate of gas permeance increases from 2×10^{-7} mol/m²sPa for the membrane prepared with 30 wt. % clinoptilolite as filler to as high as 4×10^{-6} mol/m²sPa for the 50 wt. % clinoptilolite membrane,. All of the prepared membranes show increasing gas permeance values with increasing pressure differential across the membrane in a similar fashion as the blank support and 100 wt. % glass covered support, which is expected.

The permeation rates of the different gases are very high and essentially the same for the blank support, indicating non-selective viscous flow dominant gas transport across the unprepared support. However, the presence of clinoptilolite in the matrix of the membrane appears to alter the permeation rates of the different gases, resulting in an apparent induced selectivity. Whereas for the 30 wt. % and 40wt. % clinoptilolite membranes, the overall permeation rate is much lower, with the order being $\text{CH}_4 > \text{N}_2 \geq \text{He}$. In comparison, the permeation rates for the 100 wt. % glass covered support (with no clinoptilolite) are very low and are in the order is: $\text{He} \geq \text{CH}_4 > \text{N}_2$. For the membrane prepared with 50 wt. % clinoptilolite the permeation rate displays the following order: $\text{He} > \text{CH}_4 > \text{N}_2$, with the most permeable gas being the non-interacting He. Therefore, it is probable that transport through porous defects is dominant since the order of permeation follows the similar pattern as the 100 wt. % glass covered membrane where no zeolite is present. Given that the more interactive species (CH_4 and N_2) show preference for permeation for the 30 wt. % and 40 wt. % clinoptilolite membranes, this show an optimum amount of % clinoptilolite increases the separation performance of the membranes. This likely means that there is an increased proportion of molecular transport by surface diffusion through the zeolite for membranes prepared with 30 to 40% clinoptilolite compared to the other compositions. Since the continuous glass phase is non-porous, the overall rate of permeation decreases as the support surface is covered in a greater proportion of glass, thus blocking areas for non-selective gas transport. In general, it was noted that as the wt. % of clinoptilolite increases, it is more likely that there are increases in defects due to cracks or incomplete surface coverage

of the glass filler and although the permeance increases, selectivity decreases. When the support is covered with 100 wt.% glass and no zeolite, gas permeation follows closely with the expected Knudson and viscous flow behaviours with the lightest gas (He) being the most permeable gas and permeance positively correlated with the pressure differential. Given the morphology of the prepared membranes (as discussed in the previous section) subsequent refinements of the preparation method would focus on determining the best range for wt. % clinoptilolite in order to optimise for membrane selectivity.

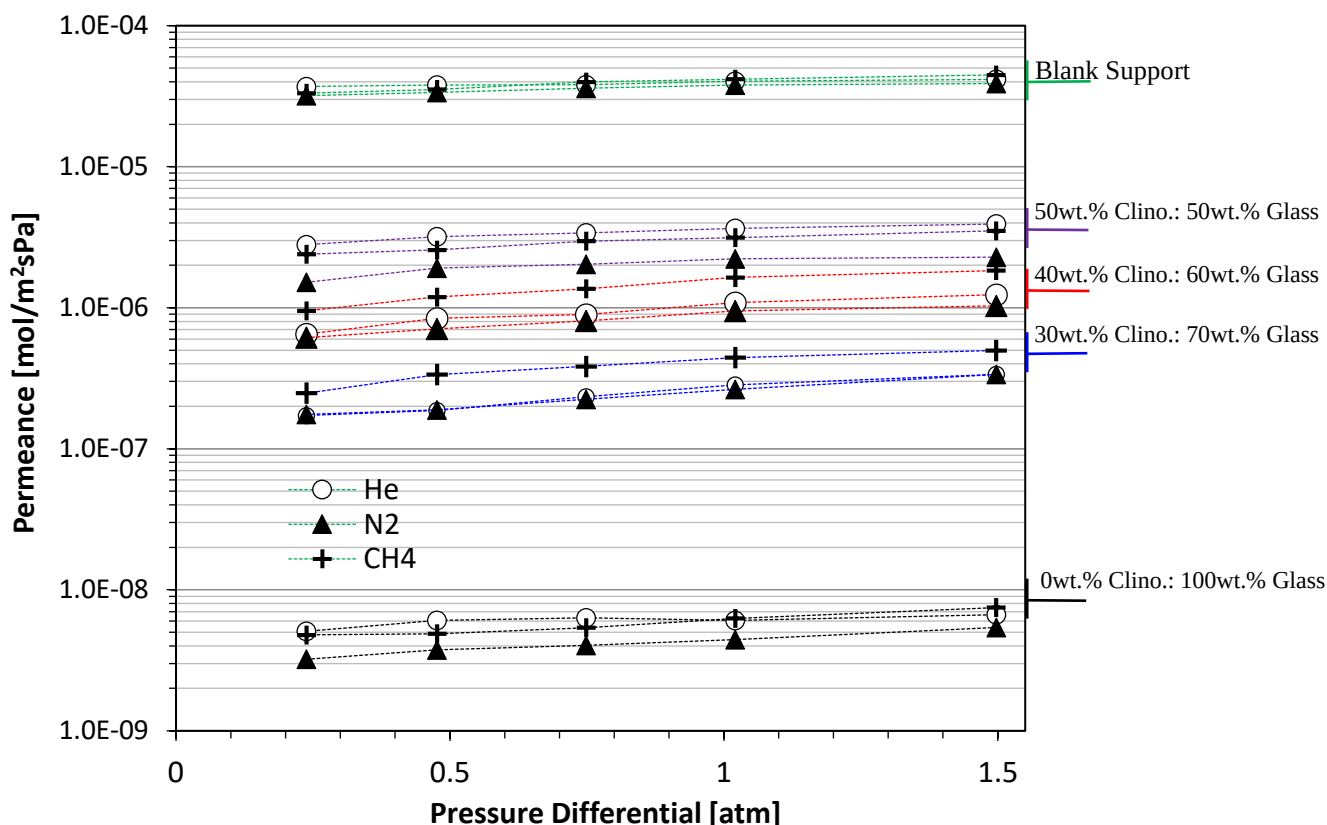


Figure 7.10. Single gas permeances of He, N₂, and CH₄ gases as a function of pressure differential for the empty Al₂O₃ support; Al₂O₃ support that is coated with 100 wt.% glass; Al₂O₃ support that is coated with different mixtures of glass and clinoptilolite. Experiments were performed at 293K with the permeate side open to atmospheric pressure. The dashed lines serve as guides for the eye.

Figure 7.11 depicts the ideal selectivity for potential CH₄/N₂ and CH₄/CO₂ gas separations based on the permeation values for the prepared membranes averaged over the entire studied pressure gradient given in Figure 7.10. The membranes synthesized with 30 or 40 wt. % clinoptilolite filler have the highest CH₄/N₂ and CH₄/CO₂ selectivity, with values of 1.7 ± 0.2 and 1.9 ± 0.1 , respectively. While these ideal

selectivity values are fairly low, they are greater than those of the unprepared support and the support coated with 100 wt. % glass where no clinoptilolite is present, while non selective viscous flow is the dominant transport mechanism for the unprepared supports. In the case of the 100 wt. % glass disc, sources of membrane defects include: incomplete surface coverage, void formations, or micro-fracturing. These defects may result in much of the observed gas permeance since no clinoptilolite is present. The net result is a combination of non-selective viscous flow or Knudsen flow (gas selectivity is directly related to the square root of the inverse ratio of the molecular weights) [79,80]. Figure 7.11[b] shows the ideal selectivity of the prepared membranes compared to the theoretical Knudsen flow selectivity (dashed line) and the viscous flow selectivity (solid line). The ideal Knudsen selectivity is 1.41 and 1.77 for CH_4/N_2 and CH_4/CO_2 , respectively. The results show that the ideal selectivity for both gas mixtures is slightly higher for the 30 wt. % and 40 wt. % clinoptilolite membranes. This suggests that there is an optimum for the ratio of clinoptilolite to glass filler whereas gas transport across the membrane would occur predominately by adsorption surface diffusion, and to a lesser extent Knudsen flow or viscous flow. For surface flow, the transport diffusivity for CH_4 gas across the membrane is higher compared to N_2 and CO_2 since the driving force is the gradient of surface occupancy caused by a pressure differential. Accordingly, while the absolute value of CO_2 adsorption capacity on clinoptilolite is the highest, there is less of a surface occupancy gradient (i.e. less difference in adsorption capacity) between the permeate side pressure ($p \approx 1\text{atm}$) and the feed side pressure ($p \approx 2.5\text{ atm}$) for CO_2 compared to CH_4 , as shown in Figure 7.7. Other MMM clinoptilolite membranes have demonstrated molecular sieve behaviour with CO_2/CH_4 and N_2/CH_4 selectivity values ranging from 37.36 to 145.6, and 1.87, respectively [55,56]. These observations indicate the potential of these membranes to be used for future natural gas separation, however the preparation technique would be subject to further refinements to reduce the quantity of membrane defects which is inhibiting the performance of these materials.

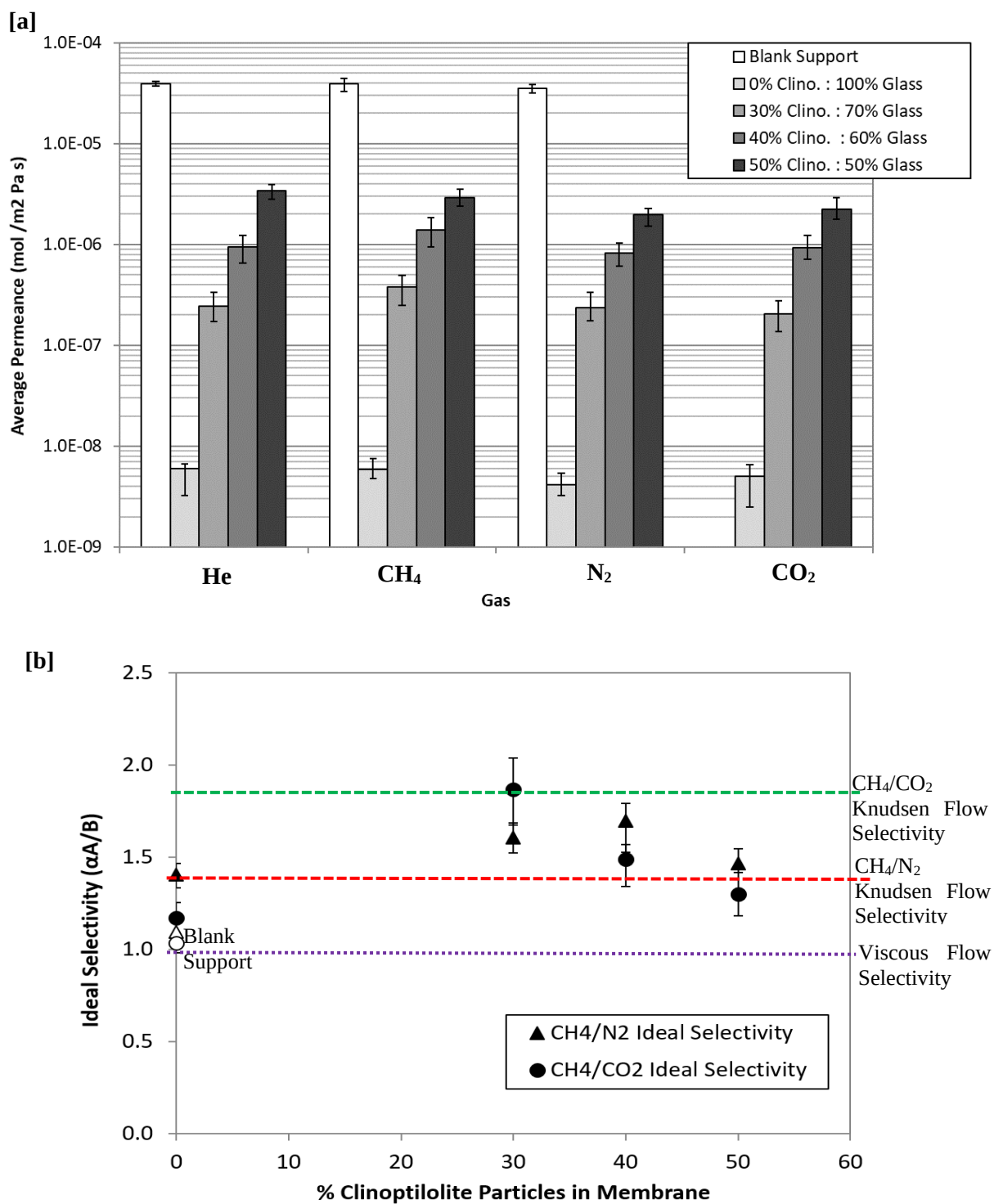


Figure 7.11. [a] Average single gas permeances for different prepared membrane surfaces membranes. [b] Average single gas CH₄/N₂ and CH₄/CO₂ ideal selectivity of the membranes compared to unmodified supports. The open points are the blank support, the closed points at 0% clinoptilolite are for the membranes prepared with 100% glass. Experiments were performed at 293 K with the permeate side open to atmospheric pressure.

7.5. CONCLUSIONS and RECOMMENDATIONS

The concept of inorganic membranes composed of a glass continuous phase as a binder and using clinoptilolite particles as a zeolite filler has been presented. Inorganic membranes were formed using a 50 wt. % to 100 wt. % ratio of specialty glass sealant to natural clinoptilolite particles on alumina disc supports. The raw clinoptilolite used in this study maintains much of its essential structure following heat treatment conditions necessary for achieving the membrane forming glass vitrifying temperatures as high as 1073 K. Two distinct layers were observed from the cross-sectional SEM imagery of the prepared membranes: one consisting of a porous clinoptilolite – glass mixture and one composed mostly of glass layer with lesser porosity. Single gas permeation experiments using He, N₂, CO₂, and CH₄ showed decreasing permeation rates with increasing amount of glass. The gas permeation rates ranged from 2×10^{-7} mol/m²sPa for the membrane prepared with 30 wt% clinoptilolite as filler to 4×10^{-6} mol/m²sPa for the 50 wt% clinoptilolite membrane. The ideal selectivity values were calculated for potential CH₄/N₂ and CO₂/CH₄ separations and were 1.7 ± 0.2 and 1.9 ± 0.1 for the membranes prepared with 40 wt. % and 30 wt. % clinoptilolite, respectively. While low, they are higher than the theoretical Knudsen flow selectivity, suggesting possible gas surface flow across the zeolite. Further refinements to this technique are necessary in order to minimize defects before it may be used as an alternative inorganic membrane fabrication approach when zeolite crystallization is difficult to achieve.

7.6 NOMENCLATURE

A_m	membrane area	(m ²)
d_p	particle diameter	(μ m)
J	membrane flux	(mol/m ² s)
l	thickness of the active layer of the membrane	(m)
n	dimensionless Sips model parameter	(dless)
p	pressure	(atm) or (Pa)
P	permeance	(mol/m ² sPa)
Q	flow rate	(mol/s)
q	adsorption capacity	(mmol/g of adsorbent)
q^{sat}	adsorption capacity at saturation	(mmol/g of adsorbent)
R	universal gas constant	(m ³ Pa/ K mol)

T	temperature	(K)
T _g	glass transition temperature	(K)

Greek Symbols

$\alpha^*_{A/B}$	ideal selectivity	
β	adsorption affinity constant	(atm ⁻¹)
θ_i	adsorption surface coverage of component <i>I</i>	

Abbreviations

EDS	electron dispersive spectroscopy
ETS-4	Engelhard Titanosilicate
FT-IR	Fourier Transform Infrared
GC	gas chromatograph
MFC	mass flow controller
PTFE	polytrafluoroethylene
SEM	scanning electron microscopy
TCD	thermal conductivity detector
XRD	x-ray diffraction spectroscopy

7.7. ACKNOWLEDGEMENTS

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CHAPTER 8

Pore Plugging Synthesis and Characterization of Silicalite-1 Membranes using Tubular TiO₂ Supports: Effect of Support Pore Size on Membrane Performance

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ABSTRACT

In this study, we present a detailed synthesis procedure and characterization of porous inorganic silicalite-1 membranes synthesized on tubular TiO_2 supports prepared using a pore plugging method with the inclusion of a 12 hour thermal break. Tubular, ceramic alumina supports with a TiO_2 active layer were used. The effect of the support pore size on membrane performance was examined with pore sizes ranging from 0.3 μm to 1.4 μm . Characterization using SEM and EDS analysis confirm the penetration and formation of silicalite-1 crystals within porous supports up to a depth of 10 – 12 μm for all membranes. With the exception of the membranes synthesized on the support with 1.4 μm pore size, all membranes were more permeable to probe gas N_2 compared to He. The highest ideal N_2/He selectivity of 2.3 ± 0.5 was observed for the membranes synthesized on supports with 0.8 μm pore size. Single gas permeance for the membranes were high; ranging between 0.2×10^{-6} and $5.2 \times 10^{-6} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$, and was independent of gas kinematic diameter with the order of permeation being $\text{CH}_4 > \text{CO}_2 > \text{N}_2 > \text{He}$. Binary equimolar CO_2/N_2 separation experiments show better membrane CO_2/N_2 permselectivity compared to the ideal selectivity calculated from the single gas experiments. Comparing the observed membrane gas diffusivity and the adsorbate gas uptake rate within the zeolite material alone shows that these favourable selective properties are the result of adsorption surface diffusion and that Knudsen diffusion is minimised.

Keywords

CO_2/N_2 separation, gas permeation, inorganic zeolite membranes, silicalite-1, porous membranes, effect of support pore size

8.1. INTRODUCTION

The development of separation processes using membrane technologies is promising due to the potential operational efficiency and predicted flexibility and ease of implementation into a broad array of systems and fields.[1] A current application that has seen great interest in recent years is post-combustion capture and separation of CO₂ from the industrial flue gases. In order to be viable, the addition of separation and sequestration technologies to fossil fuel based processes should not contribute to more than a 35% increase in generation costs.[2] Monoethanolamine (MEA) absorption is the current accepted practice for CO₂ capture, however this method is very energy intensive due to multiple process units required for solvent regeneration.[3] Additionally, the potential health and environmental impact of the release of fugitive MEA emissions to the atmosphere is also a major subject of concern for this application.[4,5] Membrane separation technologies may serve as an alternative to this current standard separation practice, and have thus gained considerable research attention.

Inorganic zeolite membranes have a high potential to be suitable for separation of gaseous process streams such as for post combustion CO₂ capture. These types of membranes can operate under a wide range of temperatures and pressures and have good solvent stability compared to polymeric membranes.[6] While recent progress with mixed matrix membranes to combine the advantages of polymer and inorganic membranes is promising, the fabrication of robust and defect free mixed matrix membranes is very difficult due to weak polymer – particle adhesion and potential particle agglomeration.[7] Zeolite membranes are generally characterized as a thin layer of crystalline silicates or aluminasilicates formed on top of a porous support with a uniform three dimensional microporous structure. Zeolite membranes may also be synthesized within the pores of a support via a pore plugging synthesis technique, forming a thin composite structure creating a thin selective zeolite layer. [8–11]

Three different adsorption separation mechanisms can be defined for adsorbent systems as they relate to steric, kinetic, and equilibrium effects.[12] The use of MFI type zeolites such as ZSM-5 and silicalite-1 have been of great interest due to a three dimensional lattice structure with an internal pore size of 5.1 Å to 5.6 Å (1Å = 0.1nm). [13,14] The pentasil structure of silicalite-1 leads to a large internal microporous network with high surface area. The internal aperture of silicalite-1 is larger than the kinetic diameter of the studied gases: 2.6 Å, 3.3 Å, 3.6 Å, and 3.8 Å for He, CO₂, N₂, and CH₄ respectively.[15] As such, since all of these sorbates are smaller than the pore size of silicalite-1, a steric separation through size exclusion is not possible. Instead, a separation may be achieved by exploiting differences in the equilibrium adsorption potential of the adsorbate gases and their differences in the diffusivity within the

zeolite pores. This is influenced by the electrostatic dispersion within the pore network and energies of adsorption as governed by differences in the dipole moment, quadrupole moment, and the molecular polarization energy of the different gases as shown in Table 8.1. [16] Adsorption potential for the studied adsorbate gases occurs in the following increasing order for silicalite-1: $\text{He} \ll \text{N}_2 < \text{CH}_4 < \text{CO}_2$. The maximum for CO_2 is attributed to high polarizability and a strong quadrupole interaction with the adsorption sites.[17–20] CH_4 has stronger polarizability compared to N_2 contributing to increased adsorption potential.

Table 8.1. Molecular properties of the studied adsorbate gases [21–23]

Gas	Molecular Weight [g · mol ⁻¹]	Kinetic Diameter [Å]	Polarizability [x10 ⁻²⁵ cm ³]	Quadrupole moment [x 10 ⁴⁰ cm ²]
CO ₂	44.01	3.3	29.1	-13.41
CH ₄	16.04	3.8	25.9	0
N ₂	28.01	3.6	17.4	-4.91
He	4.00	2.6	2.05	0

A combination of adsorption surface diffusion and pore diffusion (Knudsen diffusion or viscous flow) is responsible for gas transport across a zeolite membrane.[24,25] For a defect free zeolite membrane, the non-zeolitic pores which are responsible for pore diffusion are minimized. This results in surface diffusion as the dominant transport mechanism across the membrane, whereby enhanced membrane gas selectivity may be observed.

MFI type zeolite membranes have a larger uniform pore aperture which allow for comparatively greater flux compared to smaller pore sized zeolite membranes such as SAPO-34, DDR, and zeolite T.[14] The ability to achieve both a higher flux and a significant separation is an advantageous property of MFI type zeolite membranes which make them desirable for investigations into bulk industrial separations that require high gas throughputs. Unlike other MFI type zeolites, such as ZSM-5, the silicalite-1 zeolite does not possess any alumina ions (Al^{3+}) imbedded in the lattice structure of the crystal. This means that silicalite-1 zeolites contain no counterbalancing cations and exhibit more hydrophobic properties compared to their equivalent ZSM-5 type zeolites.[10] Along with zeolite type, the separation performance of the zeolite membrane depends largely on the continuity and thickness of the active zeolite layer. Most of the reported zeolite membranes have been synthesized using alumina in the active layer of the supports, which could lead to the possible incorporation of Al^{3+} ions into the final structure of zeolite membrane. Therefore the final product would not exhibit the properties of a true silicalite-1. Titanium

oxides are more chemically stable than alumina and have been the focus of previous studies.[10,26] However, little has been investigated regarding the effect of pure TiO_2 active layer pore size on silicalite-1 membrane performance.

The purpose of this study has been to determine the effect of support pore size on the development of high performing silicalite-1 membranes for gas separations. This was achieved by using a pore plugging synthesis method with a thermal break. Silicalite-1 crystals were synthesized within different tubular TiO_2 active layer supports forming thin composite structures. The effect of support pore size on the resultant membrane physical characteristics and gas permeation properties was examined. The physical properties of the membranes were analysed using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). Single gas permeation experiments were performed on all of the membranes using He and N_2 as probe gases to establish the contribution of non - zeolitic pores to gas transport. Single gas permeation behaviour of He, N_2 , CO_2 , and CH_4 gases was studied for the membrane with the best N_2/He ideal selectivity and the performance was compared to the literature for other silicalite membranes. This membrane was also tested with an equimolar binary CO_2 - N_2 gas mixture.

8.2. EXPERIMENTAL

8.2.1. MEMBRANE FABRICATION

A silicalite-1 membrane synthesis protocol using the pore plugging method with an 11 hour synthesis interruption was applied in this work.[10,11,26–28] The membranes were fabricated on commercially available ceramic porous tubes with an active layer containing only TiO_2 purchased from TAMI Industries (Nyons, France). The tubes were 6 cm in length with an outside diameter of 1 cm and thickness of 2 mm. The inside surface of the tube contained the TiO_2 active layer. A range of active layer pore sizes; 0.3 μm , 0.45 μm , 0.8 μm , and 1.4 μm , were investigated. A total of 9 membranes were synthesized in three different batches (batch A, B, and C, respectively).

8.2.1.2. PRECURSOR SOLUTION PREPARATION

In a Teflon (polytetrafluoroethylene (PTFE)) lined beaker under magnetic stirrer, 9.61g of fumed silica (SiO_2) (Sigma-Aldrich, Oakville, ON, Canada), used as a silicone (Si) source, was dissolved in 72 mL of 1 M tetrapropylammonium hydroxide (TPAOH) solution (Sigma-Aldrich, Oakville, ON, Canada), and 8 mL of deionized water was added. The resultant solution consisted of 2.0 M SiO_2 and 0.90 M TPAOH giving an overall molar ratio of 1 SiO_2 : 0.45 TPAOH : 27.8 H_2O . The solution was left under magnetic stirring for 3 days at room temperature in the Teflon beaker that was covered to prevent any evaporation of the solution. The solution was then centrifuged for 30 minutes at 4000 rpm to remove any undissolved particulates that may inhibit zeolite synthesis.

8.2.1.3. HYDROTHERMAL SYNTHESIS

Hydrothermal synthesis was performed in a 125 ml Teflon beaker, inserted inside a Parr model 4748 stainless steel autoclave (Parr Instrument Co., Moline, IL, USA). A programmable Neytech Vulcan 3-550 furnace purchased from Cole-Parmer Canada (Montreal, QC, Canada) was used for this step. For each batch, 4 ceramic tubular supports were covered with a thin layer of Teflon tape on the external surface to prevent the formation of zeolite crystals on the outside surface. The ceramic supports were inserted into the beaker vertically and were held in place by a home-made cradle to hold them in a vertical position to prevent shifting during the synthesis process. The zeolite precursor solution was poured into the beaker containing the supports until the supports were completely immersed in the solution. The

supports were submerged in the solution for 6 hours before hydrothermal synthesis, insuring sufficient penetration time of the solution into the pores of the support.

The autoclave was closed, insuring that there was less than 1 cm of free height between the solution and the lid of the autoclave. The autoclave was then inserted into the programmable oven and heated to 170°C at a rate of 1.0 °C/min and remained at that temperature for 12 h. To promote secondary crystal growth, a hydrothermal synthesis break of 11 hours was used by cooling the mixture in the same oven with the oven door closed until the oven temperature reached 50°C, then the oven was opened fully until the mixture temperature reached 30°C. Afterwards, the hydrothermal synthesis resumed with a heating rate of 1.0 °C/min until the system reached 170°C, then the temperature was held constant for 72 h, except for batch C which was for 75 h. At the end of the hydrothermal synthesis step, the autoclave was cooled gradually to room temperature within the oven over a period of 12 h. The membranes were removed from the autoclave, rinsed and submerged in distilled water for 24 hours. The washed membranes were then dried at 100°C for 24 h. The remaining zeolite solution was collected from the beaker, was washed with distilled water, and was poured into an evaporating dish. The remaining H₂O and TPAOH was evaporated in air inside a fume hood; resulting in a powder.

8.2.1.4. CALCINATION

The dried membranes were then subjected to a calcination step performed at 500°C for 4 h using a programmable oven (Vulcan 3-550) with a heating and cooling rate of 1.0 °C/min. After the membranes were removed from the oven, they were placed in a desiccator until use. The collected zeolite powder was also calcined in the same fashion and kept for subsequent characterization. The properties of synthesized zeolite powder were considered to be same as that of the zeolite synthesized within the supports regardless of the pore size of the active layer.

8.2.2. MEMBRANE and MATERIAL CHARACTERIZATION

8.2.2.1. MEMBRANE and PARTICLE MORPHOLOGY EXPERIMENTS

A Micromeritics ASAP-2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA) was used to analyse the zeolite powder in terms of the BET specific surface area and the BJH pore volume and pore size distribution using N₂ adsorption-desorption at 77K.[29,30] All samples were degassed under vacuum conditions and heated at 383 K prior to the analysis. The purity of the synthesized

silicalite-1 crystals was verified using powdered x-ray diffraction analysis (XRD). The powdered samples were examined at room temperature using a Rigaku Ultima IV powder diffractometer in Bregg-Brentano geometry, using Cu K α radiation ($\lambda = 1.5418$ Å). The 2θ range of 2° to 90° was covered with a 0.02° step width and $6^\circ/\text{min}$ scan speed.

Scanning electron microscope (SEM) and Electron dispersive spectrometer (EDS) analyses were performed using a JEOL JSM-7500F Field Emission Scanning Microscope (JEOL, Tokyo, Japan) with a Tracor-Northern Series Z-II spectrometer (Zeiss, Oberkochen, Germany) installed. SEM and EDS analyses were used as compositional and morphological verification of the active layer cross section of the synthesized membranes. The synthesized tubular membranes were fractured, and small sections of the membrane cross section were mounted on a specimen holder prior to the analysis.

8.2.2.2. SINGLE GAS ADSORPTION EXPERIMENTS

Single gas adsorption isotherms and adsorption kinetic behaviour were determined for the synthesized powder using a microgravimetric analyser purchased from VTI Corp. (Hialeah, FL, USA) equipped with a high sensitivity Cahn microbalance with a weighing resolution of ± 1 μg . Single gas adsorption isotherms were conducted at a temperature of 295K for CO₂, CH₄, and N₂ gases. All gases were purchased from Linde Canada Ltd. (Ottawa, ON, Canada) and were of 99.995, 99.99, and 99.999 % purity respectively. The analysed adsorbent sample weight was between 30 and 40 mg to minimize adsorption heat and kinetic mass transfer effects. Samples were regenerated at 573K under vacuum conditions at approximately 10^{-8} atm for about 1.5 hours. The equilibrium adsorption isotherms for each gas were evaluated at increasing pressures from 0 to 5 atm. For each isotherm point, equilibrium was determined when there was less than a 0.015% sample weight change over a 15 minute period. A buoyancy correction was performed using helium gas at similar pressures and temperatures as silicalite-1 has negligible adsorption capacity for helium.

To elucidate the effect of the intracrystalline diffusion on the rate of gas permeance across the silicalite-1 membrane, the single gas adsorption uptakes were also measured. The transient kinetic behavior was analysed under isothermal conditions for constant pressure step changes using the synthesized silicalite-1 powder. For each gas, the adsorption uptake curve response to a pressure step

change was determined as the fractional uptake at different times before adsorption equilibrium was achieved for the silicalite-1 powder.

8.2.2.3. SINGLE GAS PERMEATION and BINARY GAS SEPARATION EXPERIMENTS

Single gas permeation and binary gas separation experiments were used to characterize the membrane performance for a feed side pressure of between 1.5 atm and 5 atm with the permeate side open to atmosphere at ambient temperature (295 K). For the single gas permeation experiments, the gases that were studied were He, N₂, CH₄, and CO₂. Pure gases He and N₂ were used as probe gases to examine the permeation properties of non-adsorbing small gas(He) and adsorbing larger gas (N₂) on the membrane performance. For the binary gas separation experiments, an equimolar mixture of CO₂ and N₂ gases was used as the feed. Prior to commencing each single gas and binary gas permeation experiment, the membranes were regenerated under helium purge at ambient temperatures (295K) with a feed side pressure of 2 atm overnight. Single gas permeation experiments were performed in order of increasing gas affinity for the silicalite-1 as described in the literature, which is He < N₂ < CH₄ < CO₂. [18–20]

The tubular membranes were attached to tubular stainless steel supports on both ends using epoxy resin. A quick setting epoxy was used initially to fix the tubular supports in place. After 1 hour the membrane was firmly bound to the tubular supports. With the membrane spinning, a second layer of epoxy was used to form an airtight joint between the membrane and the stainless steel support. The epoxy was left to set for a minimum of 2 hours. The spinning motion allowed the epoxy to thin coat the membrane evenly which produced smooth rounded joints. The membrane was installed within a custom made membrane module. The dead volume of the permeate side of the membrane module was approximated to be 200 cm³. One of the main benefits of silicalite-1 membranes is the ability to achieve a high gas flux across the membrane, so that no sweeping gas was required for this setup. The experimental apparatus outlined in Figure 8.1 was used to carry out the single gas permeation and binary gas separation experiments.

The feed gas flow rate and composition were controlled by two mass flow controllers: MFC 1 and MFC 2. Feed pressure was controlled manually using a needle valve. The feed and permeate pressures were measured using electronic pressure transducers P1 and P2, respectively. Permeate flow was measured manually using a 100mL soap film flow meter. For the binary gas separation experiments, the

permeate gas composition was measured using a gas chromatograph equipped with a thermal conductivity detector. During the experiments both the feed and permeate side pressures, flow rate, and composition were monitored. After approximately 3 hours, the system reached steady state and the feed and permeate side pressures, and the composition and the molar flux of permeate were recorded. A total of 6 consecutive permeate flow measurements were recorded and the average value was used to calculate the molar flux of the permeate.

The membrane performance was evaluated by means of the single gas N₂ and He probe permeances, which are measures of the membrane productivity as described in Equation 1.

$$P_i = \frac{J_i}{(p_{i,F} - p_{i,P})} \quad (1)$$

where P_i is the permeance of gas i [mol/m²sPa], J_i is the total measured steady state flux of i in the permeate [mol/m²s], and $p_{i,F}$, [Pa] and $p_{i,P}$, [Pa] are the partial pressures of i at the feed and permeate side of the membrane, respectively. For the single gas permeation experiments, $p_{i,F}$ and $p_{i,P}$ were simply equal to the absolute total feed and permeate pressures.

The ideal selectivity (α_{ij}^*) is an estimation of membrane separation performance for a particular gas pair, as it is defined as the ratio of single gas permeance of gases i and j . This ratio is referred to as the permselectivity (α_{ij}) when the feed gas is a gas mixture (Equation 2).

$$\alpha_{i/j}^* = \frac{P_i}{P_j} \quad (2)$$

Membrane performance was evaluated by comparing the N₂/He ideal selectivity and the measured single gas permeance through each membrane. The best performing membrane having the highest N₂/He ideal selectivity was then selected for further analysis using single gases CO₂ and CH₄, and an equimolar binary mixture of N₂ and CO₂ gases. The corresponding permeance and permselectivity values were then determined.

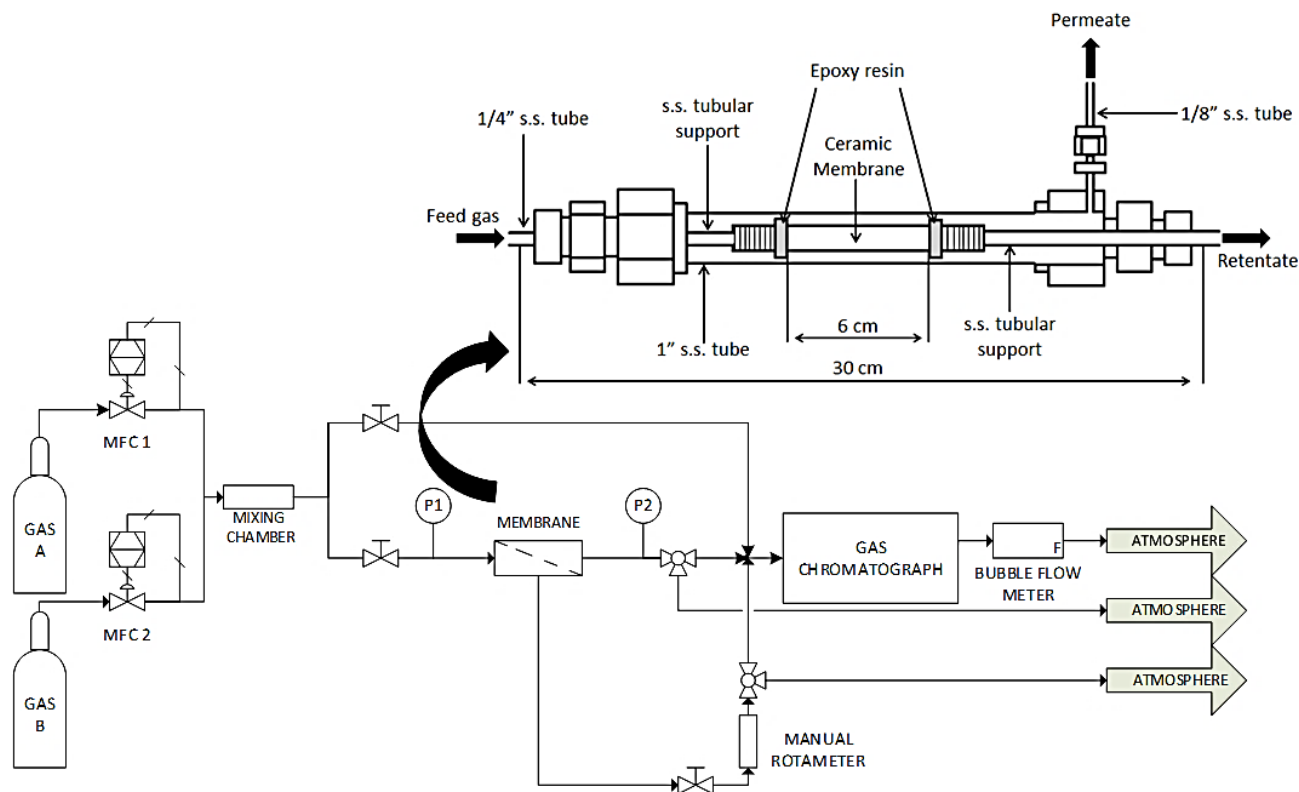


Figure 8.1. Single gas permeation and binary gas separation experimental set-up (MFC: mass flow controller, P1: feed side pressure transducer, P2: permeate side pressure transducer). The tubular permeation cell is shown in the top right.

8.3. MEMBRANE TRANSPORT CHARACTERISTICS

To better understand the measured permeation behaviour of the silicalite-1 membranes as described in Equation 1 it is important relate this information to the various transport mechanisms of gases through the membranes. Gaseous transport through porous membranes involves the contribution of pore flow (viscous flow (Poiseuille flow) and Knudsen flow) and surface flow based on adsorptive surface interactions with the gas adsorbate (Equation 3). [31–33]

$$J_i = J_i^P + J_i^S \quad (3)$$

Where J_i^P is the flux from pore flow and J_i^S is the flux from surface flow.

Pore flow consists of both Knudsen flow and viscous flow. The contribution of both of these factors to the total flux from pore flow is expressed in Equation 4 for a homogenous pore structure [31,33],

$$J_i^P = -\frac{\varepsilon}{\tau RT} [(D^{Vis}) + (D_i^{Kn})] \frac{\partial p_i}{\partial x} \quad (4)$$

Where, ε is the membrane porosity, τ is the tortuosity factor, R is the universal gas constant, T is the temperature, p_i is the pressure of component i , and x is the coordinate along the membrane corresponding to the thickness.

The influence of viscous flow to the overall membrane permeance may be assessed experimentally by considering that viscous transport is pressure dependant, whereas Knudsen flow is pressure independent. While both the viscous flow parameter (D_i^{Vis}) and the Knudsen diffusive parameter (D_i^{Kn}) are influenced by the pore size of membrane, D_i^{Kn} is influenced by the molecular weight of the diffusing gas, whereas D_i^{Vis} is independent of this value. [33] Viscous flow is inherently non selective, whereas selectivity from Knudsen flow is limited to the difference in the molecular weights of the diffusive species.

$$D_i^{Kn} = \frac{2r_p}{3} \sqrt{\frac{8 RT}{\pi M_i}} \quad (5)$$

$$D^{Vis} = \frac{r_p^2 p}{8\eta} \quad (6)$$

Where r_p is the pore radius of the membrane, M_i is the molecular weight of component i and η is the viscosity of the diffusive gas (or gas mixture), and p is the total pressure.

The influence of pore flow to the overall membrane flux may be minimized such that surface flow is the dominating transport mechanism. An advantage of the pore plugging membrane synthesis approach over other methods is that the pore size of the support serves as the maximal size of a potential membrane defect or crack since the silicalite-1 layer is formed within the pores of the support and not on the surface. Therefore, the contribution of pore flow to the total membrane flux may be localized.

For an ideal zeolite membrane formed through pore plugging synthesis, the dominating transport mechanism is attributed to surface flow and not pore flow.[25,34] For surface flow, the difference in equilibrium adsorption capacity between the high pressure feed side and the low pressure permeate side across this membrane is the driving force behind the gas transport. Gas molecules are adsorbed on the active sites within the pores of the adsorbent crystals and move in the direction of decreasing surface occupancy which corresponds to the concentration profile across the membrane. [35] Mass transfer resistance is ascribed to the intracrystalline diffusion resistance between the active sites along the length of the membrane. [36] For non-interacting gases such as He, gas transport is governed by primarily activated gaseous diffusion or Knudsen diffusion. [24]

The affinity of the gases within the pore network of the zeolite membrane plays an important role in the evaluation of membrane performance. With this in mind, it is necessary to quantify both the equilibrium adsorption and the diffusion characteristics of the adsorbent material composing the membrane to effectively describe the gas transport behaviour of the combined sorption and diffusion processes across the membrane. The flux from surface diffusion is derived from Fick's first law in relation to the surface coverage difference across membrane which represents the driving force for transport (Equation 7).[31,37,38] In the case of an ideal defect free membrane, the effective membrane diffusivity, D_e^m , is calculated from the rearrangement of Equation 7, using the experimentally determined membrane flux, J_i^s , and the physical characteristics of the membrane.

$$J_i^s = -\rho(1 - \varepsilon)q_i^{sat} \frac{D_e^m}{1 - \theta_i} \frac{\Delta\theta_i}{l} \quad , \quad D_e^m = \frac{J_i^s(1 - \theta_i)}{-\rho(1 - \varepsilon)q_i^{sat} \Delta\theta_i} \quad (7)$$

Where, ρ is the skeletal density of the adsorbent, ε is the porosity of the adsorbent, q_i^{sat} is the saturation adsorption capacity of component i , $\Delta\theta_i$ is the difference in absolute adsorption surface coverage of component i , between the high pressure feed side and low pressure permeate side across the length of the membrane, l is the thickness of the membrane, and the θ_i was calculated at the average pressure across the membrane.

The Sips isotherm model is used to represent the experimental isotherm data to calculate the surface coverage related to the single gas adsorption behavior. [12,16]

$$\theta_i = \frac{q_i}{q_i^{sat}} = \frac{\beta_i p_i^n}{1 + (\beta_i p_i)^n} \quad (8)$$

Where, q_i is the amount adsorbed of component i , β_i is the affinity constant, and n is the constant parameter. The Sips model parameters may be optimized from the minimization of the sum of the squared residuals between the model fit and the experimental data for the pure component adsorption isotherms.

The membrane effective diffusivity may be determined from single gas permeation experiments. However, due to the variability between different membrane sets composed of composite materials, it is difficult to determine this value appropriately. [31,36] Therefore the transport performance properties of the zeolite membrane may be evaluated by comparing the effective diffusivity of the membrane, (D_e^m), with the effective adsorption transport diffusivity evaluated from the zeolite material alone (D_e). This link between the gas adsorption behaviour of the zeolite material and the membrane permeation experiments establishes the performance parameters for an ideal zeolite membrane.

The adsorption mass transfer rate can be approximated using the Linear Driving Force (LDF) model proposed by Glueckauf and Coates and discussed in the literature [16,39–42] (Equation 9).

$$\frac{\partial q}{\partial t} = k_{LDF}(q_e - q(t)) \quad (9)$$

In this model, while single gas adsorption uptakes are determined experimentally, as mentioned in section 2.2.2, the amount adsorbed is monitored at different times as $q(t)$. The change in q as a function of time gives the slope, dq/dt , that is plotted as a function of $q(t)$ for different times. Since the q_e value is known as the amount adsorbed at equilibrium, the slope of this plot would give the value of k_{LDF} according to Equation 9.

The LDF diffusion model is valid in the uptake region of $\frac{q(t)-q_o}{q_e-q_o} > 0.6$ [43] or 0.7 [16]. The kinetic rate constant mechanism as shown with the LDF model only considers the surface resistance as a

barrier to mass transfer. In reality the silicalite-1 crystals are known to be microporous with a characteristic cuboid shape. To reflect the contribution of diffusion limitation within the micropores of the adsorbent, the LDF model may still be employed when considered as the reduced form of the Fickian Diffusion model for the isothermal diffusion gradient through a homogeneous spherical crystal, thus relating the effective intracrystalline transport diffusion term, D_e , to k_{LDF} . [16,42]

$$k_{LDF} \approx \frac{15D_e}{R_c^2} \quad (10)$$

Here D_e/R_c^2 is the diffusion time constant [s^{-1}] which is the effective transport diffusivity, D_e , divided by the squared radius of the crystal, R_c .

The values of the diffusion time constant of the adsorbing silicalite material alone, and the effective membrane transport diffusivity calculated from the permeation experiments may not be explicitly compared. However, an implicit comparison may be drawn from the selectivity ratios of D_e/R_c^2 and D_e^m respectively between the individual component species i and j (Equation 11).

$$\propto \frac{D_e}{R_{c,ij}^2} = \frac{D_e}{R_{c,i}^2} / \frac{D_e}{R_{c,j}^2} \quad , \quad \propto D_{e,ij}^m = D_{e,i}^m / D_{e,j}^m \quad (11)$$

An ideal zeolite formation within the porous membrane support is thought to have the same diffusivity characteristics and gas selectivity ratios as the zeolite material alone since surface diffusion would be dominant. Whereas, the contribution of pore diffusion from non zeolitic pores would result in a reduced effective membrane transport diffusivity selectivity.

8.4. RESULTS and DISCUSSION

8.4.1. MORPHOLOGICAL and COMPOSITIONAL ANALYSIS

The XRD patterns obtained (Figure 8.2) on the zeolite powder collected from the bulk solution in the autoclave following the hydrothermal synthesis and calcination, correspond well to the XRD patterns of MFI type zeolite previously reported in the literature [10,44–46], therefore confirming successful formation of silicalite-1 zeolite. Analysis of the N_2 volumetric adsorption measurements at 77K showed

an average BET surface area of $471.5 \text{ m}^2 \text{ g}^{-1}$. The BJH micropore area and the micropore volume were $21.89 \text{ m}^2 \text{ g}^{-1}$ and $0.302 \text{ cm}^3 \text{ g}^{-1}$, respectively. These values correspond well with literature values for silicalite-1 crystals. [47–50]

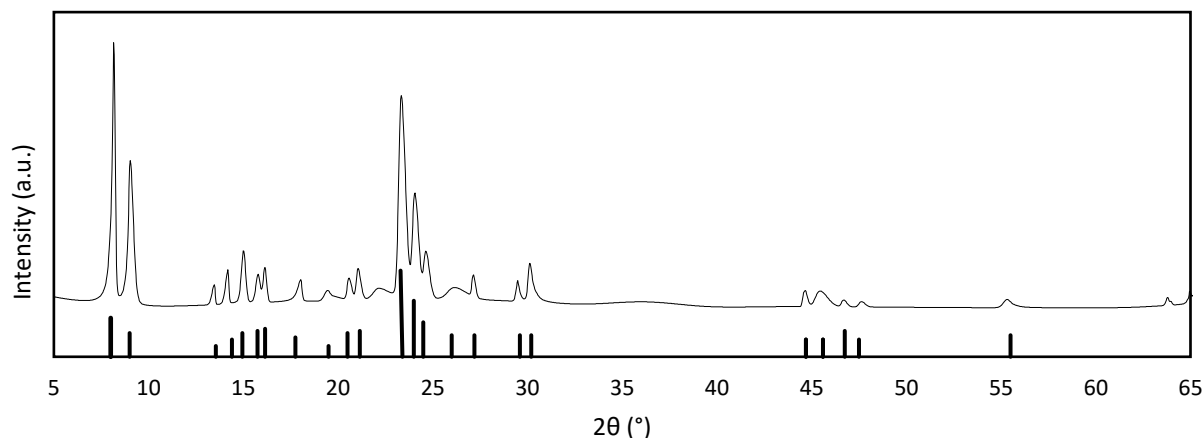


Figure 8.2. XRD patterns corresponding to the silicalite-1 powder recovered from the synthesis solution. The intensity response is equivalent to the characteristic XRD patterns for randomly orientated MFI type silicalite-1 crystals reported in the literature [10,44–46] represented by the lines at the base of the chart.

The extent of membrane formation through silicalite-1 pore plugging synthesis was examined using SEM (Figure 8.3) and EDS (Figure 8.4) analysis of the cross section for four different support pore sizes. Understanding the membrane cross sectional properties and not the surface gives a better idea with respect to the formation of the zeolite selective layer; since only a non-selective layer of randomly oriented crystal outgrowth is present on the surface it is not of interest. In Figure 8.3, the bottom part of each figure represents the surface of the tubular membrane which is exposed to the feed gas. For all pore sizes, the membrane MFI composite structure contains a thin packed layer of outgrowth containing randomly oriented silicalite-1 crystals with a variable thickness which is less than $2 \mu\text{m}$ on the membrane surface, followed by a layer of zeolite crystal growth within the pores of the TiO_2 support. This first layer is followed by an intermediate layer consisting of the internal pore network of the support with silicalite-1 crystals grown within the pores of the TiO_2 active layer. As shown with the SEM imagery (Figure 8.3), it is evident that following the synthesis of the silicalite-1, the pore network is occupied by zeolite crystals inter-grown within this active layer. Pore plugging is observed for the three membranes synthesized within the 3 smallest support pore sizes as indicated by a fairly continuous active layer agglomeration composed of composite silicalite-1 crystals formed within the pores of the support. The membrane synthesized on the support with a pore size of $1.4 \mu\text{m}$ shows incomplete pore blocking by the silicalite-1

crystals grown within the pores as evident by distinct voids forming visible channels within the pores of the support.

Compositional analysis of the composite membranes' cross section determined using EDS shows the SiO_2 and TiO_2 composition as a function of distance from the membrane surface (Figure 8.4). Since silicalite-1 zeolite is composed of SiO_4 tetrahedra, the presence of SiO_2 serves to quantitatively support the visual observations from the SEM imagery with respect to zeolite crystal growth. Crystal outgrowth is observed in the first top layers less than 2 μm from the membrane surface as the Si content is about 60% and 80% in this region for the membranes with support pore sizes of 0.3 and 1.4 μm , respectively. The variable thickness is consistent with other studies in the literature which report crystal outgrowth in the range of fractions of a micrometer to tens of micrometers.[10,51–53] The EDS analysis in Figure 8.4 supplements the SEM observations. Silicalite-1 penetration of approximately 30% up to the first 10 μm is observed within the composite TiO_2 layer for membranes with support pore sizes of 0.3, 0.45, and 0.8 μm . A consistent layer of SiO_2 within the first 10-12 μm from the membrane surface is observed, and is indicative of the presence of silicalite-1 crystals occupying the pores of the membrane active layer. A more uneven distribution of SiO_2 is observed in the active layer for the membrane with a support pore size of 1.4 μm , which is indicative of incomplete pore plugging and the presence of defects within the membrane as supported by the SEM imagery.[28]

Not depicted on the SEM images is porous alumina support which begins approximately 30 μm from the membrane surface. Additionally, the EDS analysis showed only the presence of SiO_2 and TiO_2 at a distance of up to 20 μm from the membrane surface with no aluminum present. This observation is in agreement with previous studies supporting the development of pure silicalite-1 membranes with no incorporation of aluminum from the porous alumina support into the membrane active layer. [10]

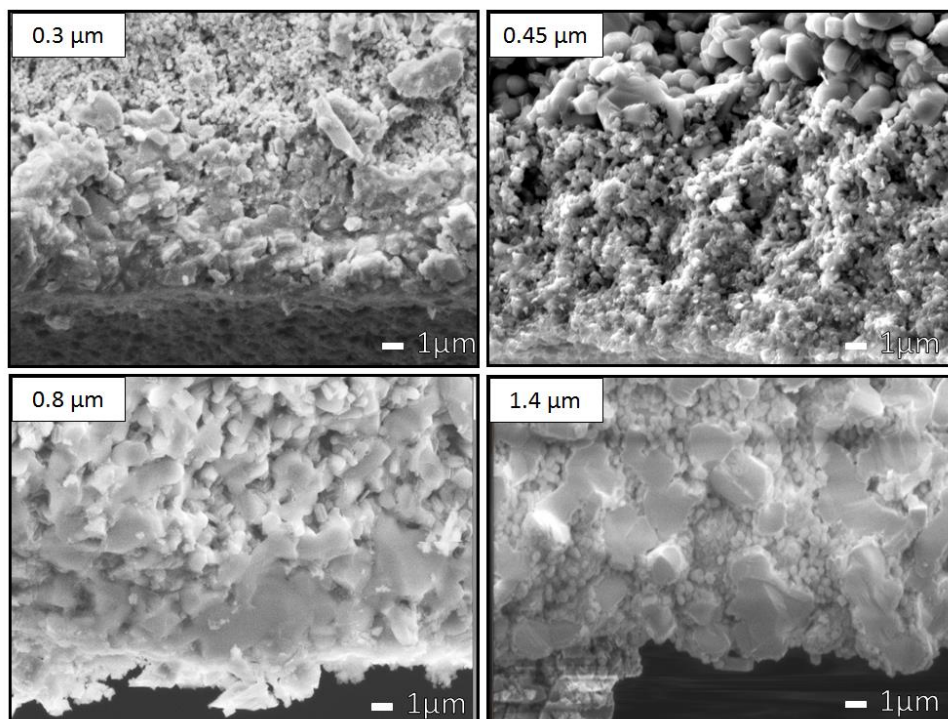


Figure 8.3. Cross sectional SEM images of synthesized silicalite-1 membranes for supports with pure TiO_2 in the active layer and pore sizes of 0.3, 0.45, 0.8, and 1.4 μm , (magnification 4000X). The bottom of each image is the membrane surface in contact with the feed gas. For the three smallest support pore sizes, a limited and variable amount of crystal outgrowth is observed, followed by a composite layer consisting of silicalite-1 zeolite intergrown within the active layer pores. Distinct void spaces between the support and the crystals are observed for the 1.4 μm membrane only, indicating defects.

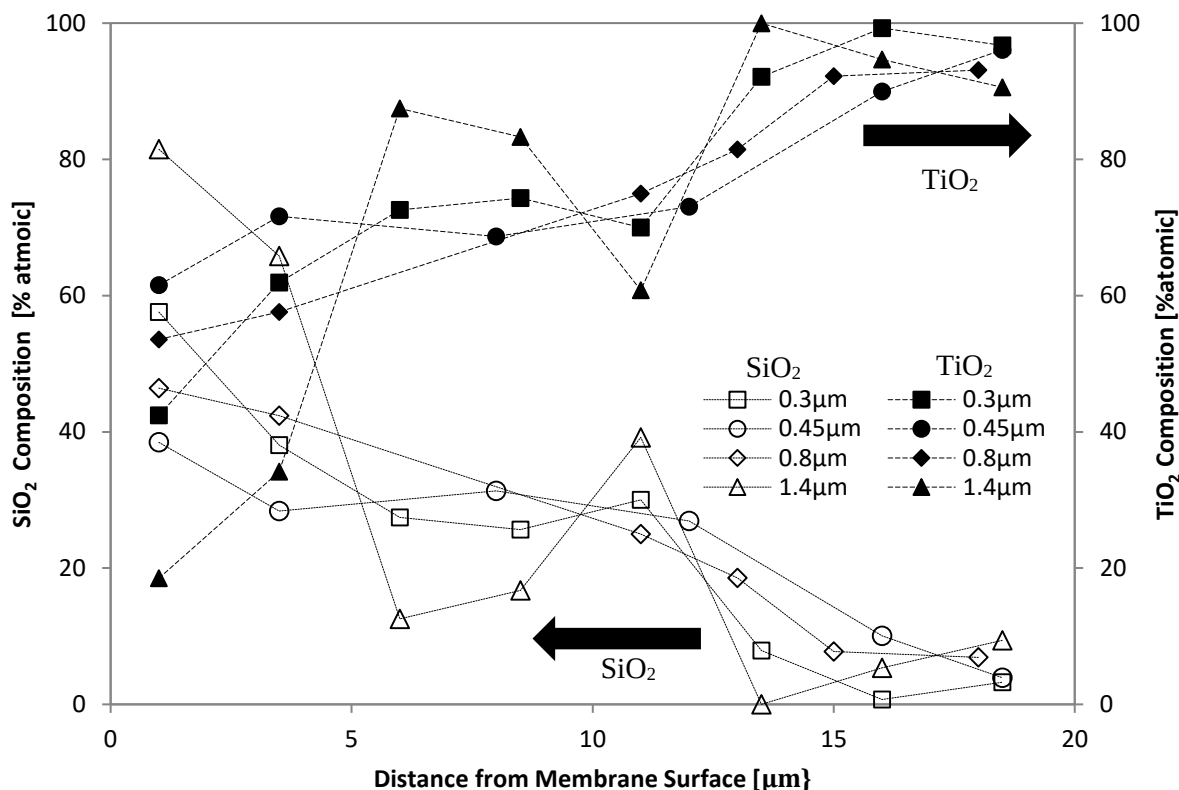


Figure 8.4. SiO₂ and TiO₂ composition as a function of distance from the top membrane surface for synthesized silicalite-1 membranes on supports with TiO₂ in the active layer for support pore sizes of 0.3, 0.45, 0.8, and 1.4 μm. The results were determined using EDS analysis with no Al₂O₃ or elemental aluminum detected. The dashed lines are to guide the eye.

8.4.2. SILICALITE-1 ADSORPTION ISOTHERMS and DIFFUSION KINETICS

Single gas adsorption equilibrium isotherms for CO₂, CH₄, and N₂ gases on the synthesized silicalite-1 powder were determined and are shown in Figure 8.5a. The adsorption capacity for CO₂ is the highest, followed by CH₄ and N₂. This is expected due to the strong quadrupole moment and greater polarizability of CO₂ contributing to increased adsorption potential.[17,23] The adsorption isotherms are in agreement with previous studies in the literature for the adsorption of these gases on silicalite-1.[10,18,19] Using the adsorption equilibrium isotherms, the corresponding ideal adsorption selectivity for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ gases were determined from the ratio of the equilibrium adsorption capacities, and the results are presented in Figure 8.5b. The ideal adsorption selectivity is the highest for CO₂/N₂ which approaches values greater than 20 and the lowest for CH₄/N₂ at 3.5 as pressure approaches 0 atm. However, from the perspective of membrane gas permeation and separation, 1 atm total pressure is the limiting value for the permeate side for a practical membrane. At that pressure, ideal CO₂/N₂ and

CH_4/N_2 selectivity values are 9 and 3, respectively. Although the adsorption capacities for all the gases increase with pressure, the rate of increase gradually decreases for both CO_2 and CH_4 . This compares to a relatively steady increase in N_2 adsorption capacity. As a result, this leads to a decrease in the ideal selectivity for CO_2/N_2 and CH_4/N_2 at increasing pressures. The ideal selectivity presents the equilibrium separation potential of silicalite-1 zeolite. However since molecular transport of these gases may occur by means of adsorptive surface diffusion within the pores of zeolite, the diffusivity of the gases must also be a considering factor for evaluating the separation potential.[35]

The experimental single gas uptake curves were modelled with the LDF model and effective diffusivity for different pressure steps have been determined from Equation 9. These effective diffusivity values are shown for different gas loadings in Figure 8.6. CH_4 has the fastest uptake on the silicalite-1 zeolite it has the highest transport diffusion time constant, followed by N_2 , and CO_2 . Interestingly, this means that although CO_2 has the highest adsorption capacity on silicalite-1 as shown in Figure 8.5a, it also has the highest resistance to intracrystalline transport diffusion within the micro-pores. As expected, the observed transport diffusivity values increase as loading increases for all three gases. The effective diffusivity in the order from the highest to the lowest is: $\text{CH}_4 > \text{N}_2 > \text{CO}_2$ which is in agreement with the trends previously reported for silicalite-1.[54,55] This behaviour is consistent with the fact that microporous materials initially induce a resistance on the movement of gas particles to the adsorbent sites due to the small porous structure. At higher loadings the transport of the gases tends to increase due to increases in the frequency for both intermolecular and surface interactions with the zeolite due to higher molecular concentrations.

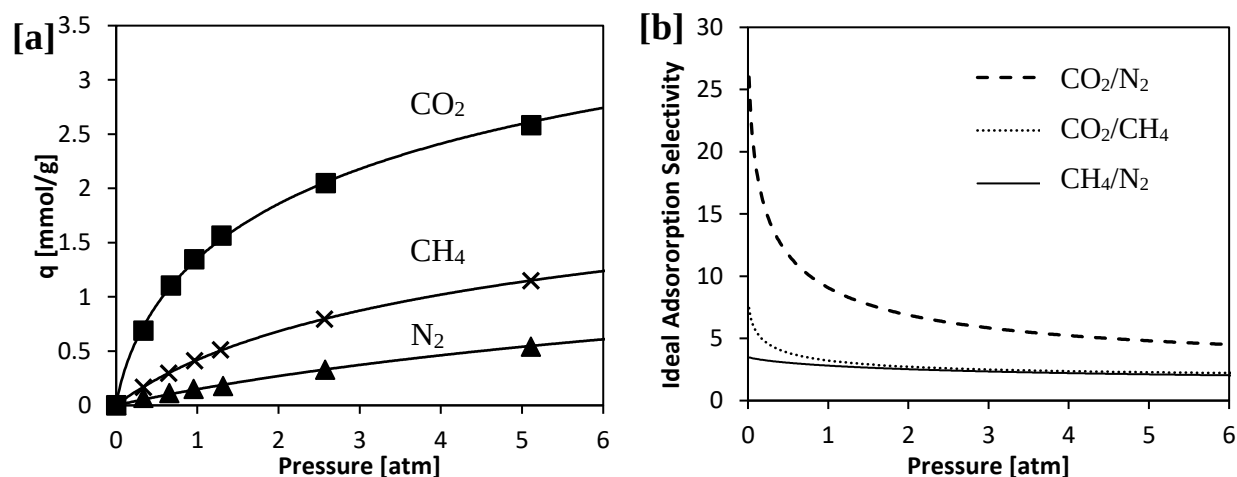


Figure 8.5. [a] Single component adsorption equilibrium isotherms and Sips model fit for CO_2 , N_2 , and CH_4 at 295K for the synthesized silicalite-1 powder. [b] Ideal adsorption selectivity for CO_2 , CH_4 , and N_2 gases as determined from the single component adsorption equilibrium isotherms in Figure 8.5[a].

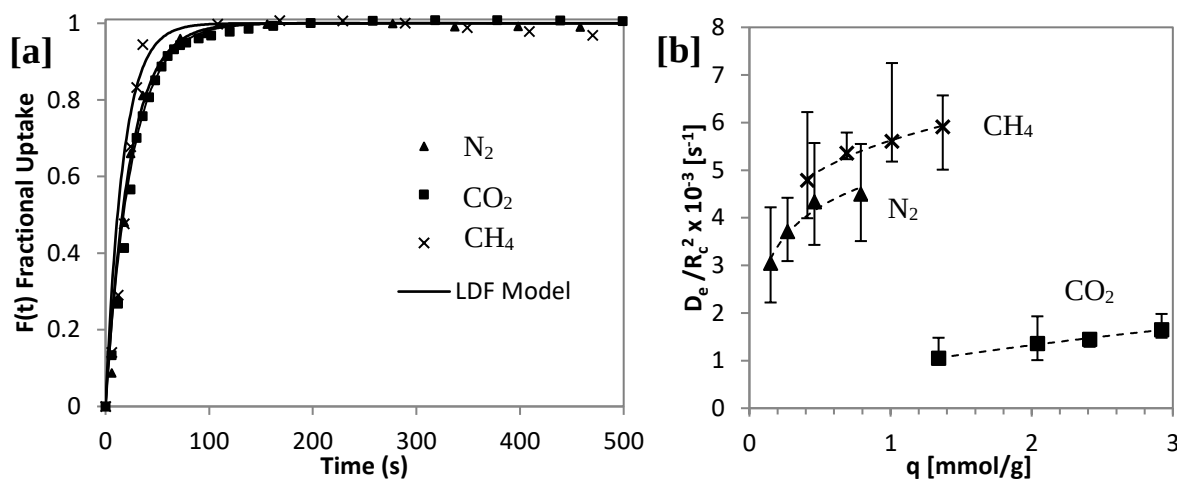


Figure 8.6. [a] Single component N_2 , CH_4 , and CO_2 gas uptake curves on synthesized silicalite-1 powder for a pressure step change of 0.5 atm to 1 atm at 295K. [b] Experimental transport diffusion time constants as a function of adsorption surface loading on synthesized silicalite-1 at 295K for pressure step changes of 0.5 - 1 atm, 1 - 2 atm, 2 - 4 atm, and 6 - 8 atm. The dashed lines are a guide to the eye.

8.4.3. SINGLE GAS MEMBRANE PERMEATION

Single gas permeation experiments were performed using N_2 and He gases to characterize the membrane performance with respect to effective pore plugging of the synthesized silicalite-1 inside the pores of the TiO_2 active layer. Four TiO_2 active layer pore sizes were studied: 0.3 μm , 0.45 μm , 0.8 μm , and 1.4 μm . A total of 9 membranes were fabricated from 3 different batches (batch A, B, and C, respectively). He and N_2 gases are of interest for characterization purposes as He is assumed to have little or no interaction within the zeolitic pores, whereas N_2 has some affinity to the silicalite-1 zeolite as observed from the adsorption equilibrium capacities shown in Figure 8.5. If the pores of the membrane support are sufficiently plugged with zeolite, N_2 gas transport across the membrane would occur by surface diffusion and to a lesser extent by Knudsen flow. However, the transport of the non-adsorbing He gas is limited to only Knudsen diffusion. For the surface diffusion, the driving force is the gradient of surface occupancy within the zeolite membrane caused by a pressure differential. This is why it was expected that N_2 gas, which has a higher adsorption capacity compared to He, would have a greater flux than He gas despite having a significantly larger kinetic diameter (3.6 Å for N_2 vs. 2.6 Å for He).

The permeance of N_2 and He gases for the non-synthesized supports were also examined as a reference and are shown in Figure 8.7. The average permeance of the porous supports with no membrane is on the order of $1.0 \times 10^{-4} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ with He being more permeable than N_2 . With respect to Knudsen flow, the square root of the inverse ratio of the molecular weights gives the ideal separation factor, whereas mass transfer through viscous flow is not selective at all.[56] For the case of N_2 and He gas permeance, as shown in Figure 8.10, He is more permeable than N_2 , the ideal He/ N_2 separation factor based on Knudsen flow alone should be 2.65 according to Equation 5. As expected, Knudsen flow is dominating the mass transfer across the supports with a contribution from viscous flow because these permeance measurements correspond to an ideal He/ N_2 selectivity ranging from to 1.25 - 1.53 (shown as the inverse value in Figure 8.10 for the supports), which is lower than the selectivity expected for gas transport by Knudsen diffusion alone.

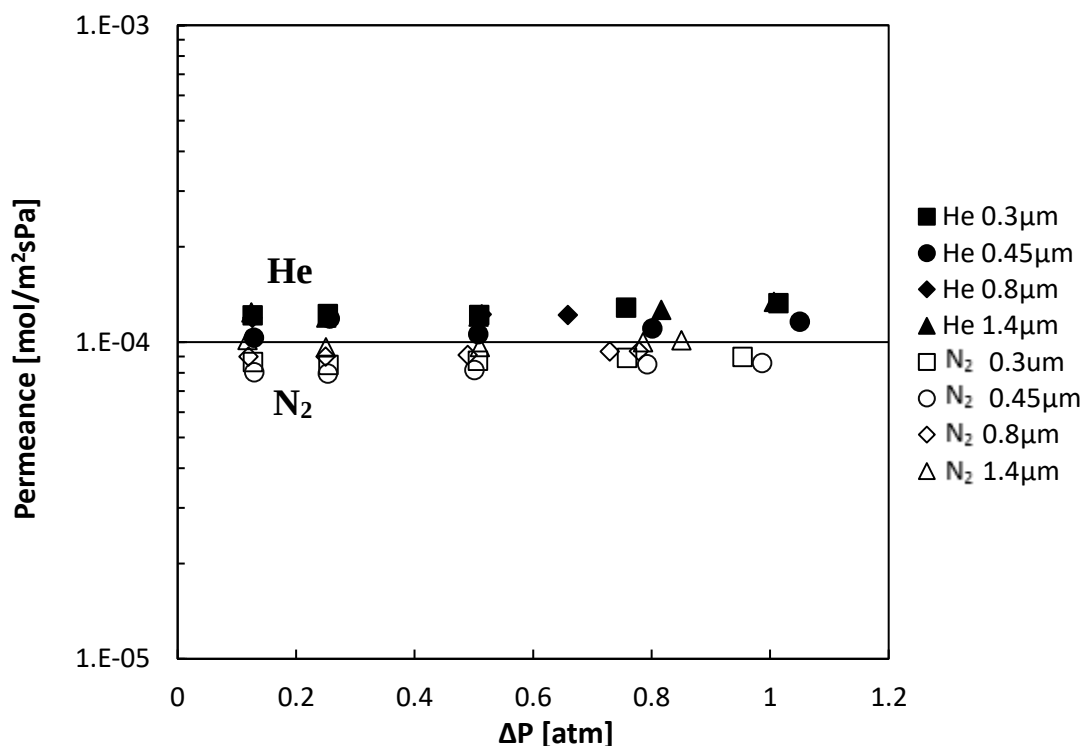


Figure 8.7. Single gas He (filled points) and N_2 (unfilled points) permeances as a function of differential pressure for membrane supports only, with pure TiO_2 in the active layer with pore sizes of 0.3, 0.45, 0.8, and 1.4 μm . Experiments were performed at 293K with the permeate side open to atmospheric pressure.

The single gas permeance values of He and N_2 gases as a function of the pressure differential for the synthesized membranes are shown for different support pore sizes in Figure 8.8. He permeances were

observed to be between 2×10^{-7} and 2×10^{-5} mol/m² s Pa, whereas N₂ permeances were observed to be between 4×10^{-7} and 2×10^{-5} mol/m² s Pa. In all cases, the permeance values for N₂ are higher than those for He, with the exception of the membranes synthesized using the 1.4 μ m pore size support. For the three smallest support pore sizes, N₂ is more permeable than He with the permeation measurements for both gases remaining consistent across the studied pressure gradients. Since this is the case, it can be concluded that the membranes with support pore sizes of 0.3 μ m, 0.45 μ m, 0.8 μ m are indeed sufficiently plugged with silicalite-1 zeolite, suggesting that the presence of defects has been minimized which is in agreement with the SEM and EDS analysis. The higher and consistent N₂ permeance over He is attributed to the interaction of N₂ with the silicalite-1 adsorption sites within the membrane. The relative linearity of the pure component adsorption equilibrium isotherms for N₂ (Figure 8.5), reinforces the fact that the gradient in pressure contributes to the adsorption driving force across the membrane through surface flow. He is an inert gas and is assumed to not interact with the zeolite, therefore the contribution of surface diffusion as a means of gas transport is quite small and Knudsen flow is the dominate transport mechanism for this gas. This results in N₂ selective membranes for the three smallest support pore sizes. Regarding the membranes synthesized on the 1.4 μ m support pore size; contribution of membrane defects to mass transport is highly likely since the membranes have a similar N₂/He ideal selectivity as the non-synthesized supports (Figure 8.10).

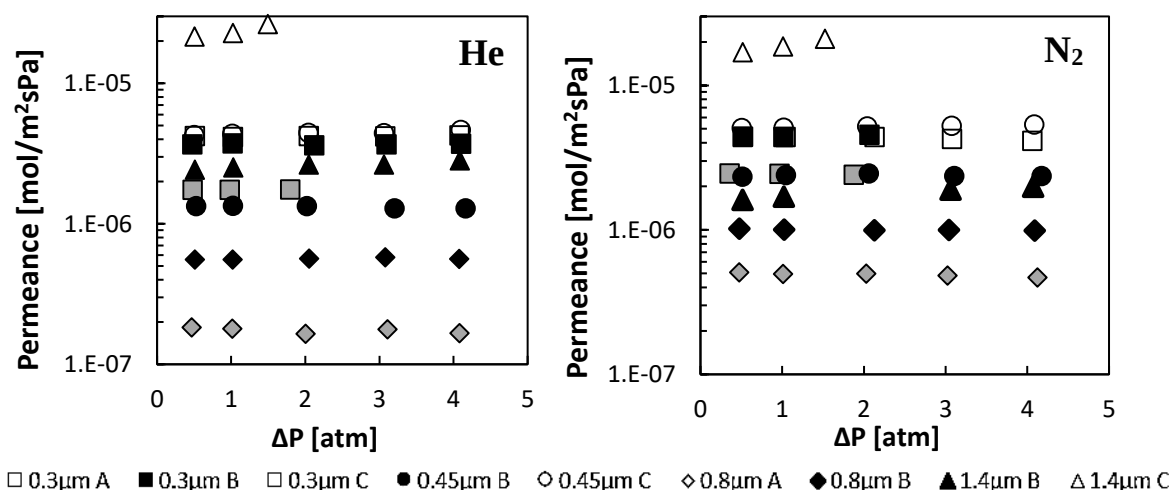


Figure 8.8. Single gas He (left) and N₂ (right) permeances as a function of differential pressure for synthesized silicalite-1 membranes with pure TiO₂ in the active layer with support pore sizes of 0.3, 0.45, 0.8, and 1.4 μ m. Experiments were performed at 293K with the permeate side open to atmospheric pressure.

Figure 8.9 shows the average single gas He and N₂ permeance values over the studied pressure range for the membranes with different support pore sizes from batches A, B, and C, respectively. With

the exception of the membranes synthesized on the 1.4 μm pore size support, single gas permeance ranged between about 0.2×10^{-6} and $5.2 \times 10^{-6} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ with N_2 gas being more permeable than He gas. The observed gas permeance decreases with increasing support pore size (excluding the 1.4 μm pore size support). The TiO_2 active layer pore size influences the amount of precursor zeolite solution diffusing into the support active layer during the pore plugging synthesis. Intuitively, the smaller support pore sizes are thought to be more conducive to easier plugging following the initial zeolite nucleation step. The zeolite active layer thickness and crystal formation may be inhibited due to the smaller pore size, thus decreasing the penetration of the precursor solution within the pores following nucleation. Conversely, larger pore sizes may result in a thicker composite membrane structure and an increase the prevalence of random crystal orientation up to a certain pore size. Thicker films result in lower gas permeances due to an increased resistance to mass transfer.[10,53] Zeolite growth may not be sufficient to completely fill the pores for supports with larger pore sizes (as shown with the membranes synthesized on the 1.4 μm support) thus leading to an increased presence of defects.[10,57] Therefore, an optimum support pore size should be considered which satisfies optimal gas permeation and high selectivity.

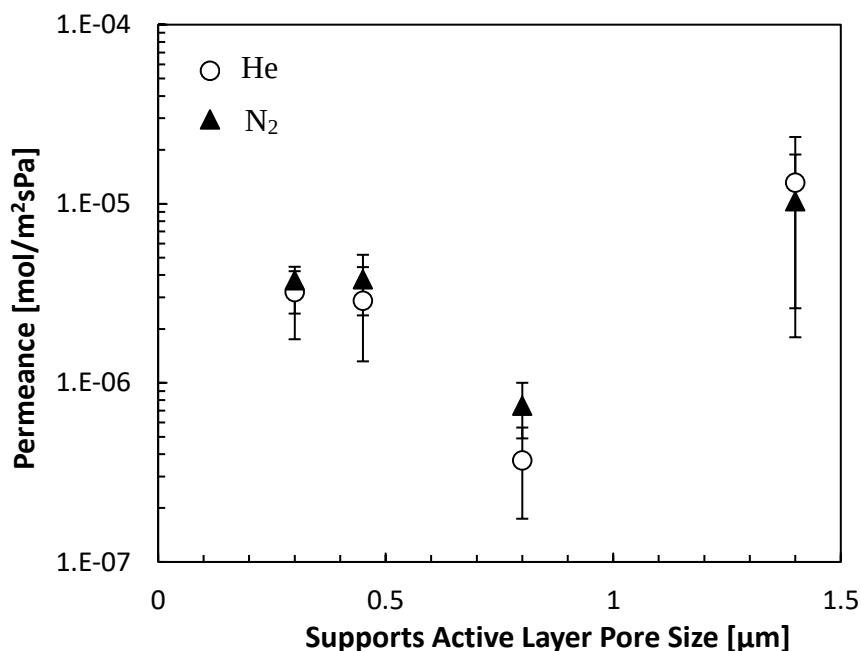


Figure 8.9. Average single gas He and N_2 permeances as a function of support active layer pore size for synthesized silicalite-1 membranes with pure TiO_2 in the active layer with support pore sizes of 0.3, 0.45, 0.8, and 1.4 μm . Experiments were performed at 293 K with the permeate side open to atmospheric pressure.

As can be seen in Figure 8.9, for the 1.4 μm membranes, He permeance is higher than N_2 whereas the other three membranes show the opposite behaviour. This indicates that for the 1.4 μm membranes,

gas transport through the non zeolitic pores is the primary means of permeation across the membrane. For the membranes synthesized on this support pore size, the permeances of both He and N₂ increase slightly with increasing pressure, indicating the presence of viscous flow (see Figure 8.8). These results support the initial findings from the SEM and EDS analysis of the which indicated the likely presence of defects due to incomplete pore plugging. This observation is consistent with previous studies that reported the likelihood of the MFI crystals' plugging the pores being inversely proportional to the support pore size.[10,28]

The ideal N₂/He selectivity values were calculated and presented in Figure 8.10. The average ideal selectivity approaches a maximum value of 2.3 ± 0.5 for the membranes synthesized on the support with the pore size of 0.8 μm in the active layer and is lower for the membranes synthesized on other support pore sizes. The ideal selectivity increases with increasing pore size of the support for the 3 membranes with the smaller pore sizes. This indicates that among these membranes, supports with larger pore sizes would have more volume of silicalite in their structure, increasing the contribution of mass transfer resistance. As a result, the contribution of adsorption surface diffusion to gas transport across the membrane increases, resulting in higher N₂/He selectivity.

The observed N₂/He permeance ratios are comparable to the values range of values reported in the literature which range from 1.6 to 3 for MFI type membranes, and are higher than most previously reported MFI type silicalite-1 membranes in the literature.[55,58–62] The observed N₂ and He permeances in this study are substantially higher than most other membranes of this type, with the exception of Hedlund et al., where N₂/He ideal selectivity was reported to be about 1.59 [59].

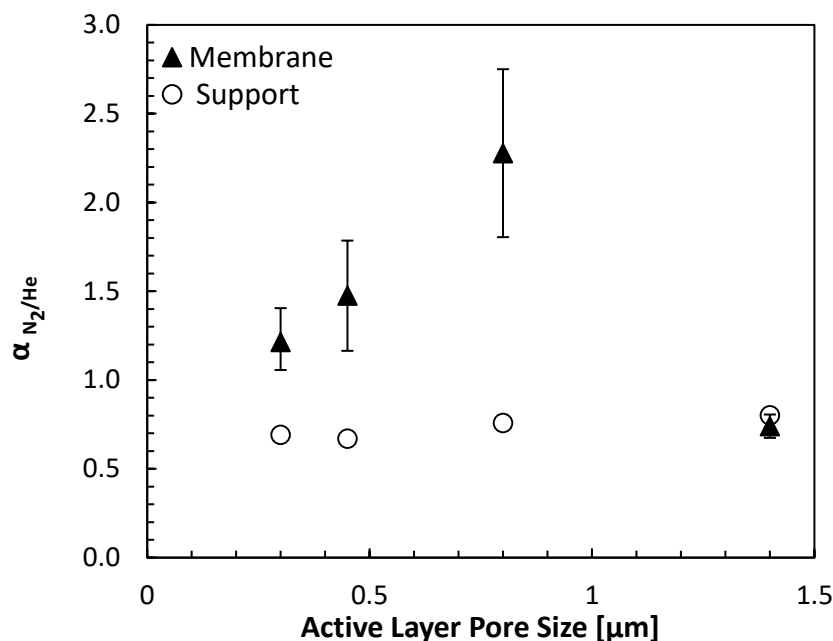


Figure 8.10. Average single gas N₂/He permeance ideal selectivities as a function of active layer pore size for synthesized silicalite-1 membranes with pure TiO₂ in the active layer with support pore sizes of 0.3, 0.45, 0.8, and 1.4 μm. The results are compared to the unsynthesized supports. Experiments were performed at 293 K with the permeate side open to atmospheric pressure.

The silicalite-1 membrane synthesized on the support with 0.8 μm pore size in batch A showed the highest N₂/He ideal selectivity indicating the most effective pore plugging silicalite-1 synthesis and minimal defects amongst the membranes studied. Therefore, additional single gas permeation experiments for He, N₂, CH₄, and CO₂ were performed with this membrane and results are given in Figure 8.11. As expected, the He and N₂ permeances remained relatively consistent with previous experimental results in this study and those reported in the literature.[55,63,64] Unlike He and N₂, The permeances of CO₂ and CH₄ decreased with increasing pressure difference. Adsorption diffusion across the membrane is the main mechanism for gas transport as these observations can be explained in terms of the shape of their respective isotherms shown in Figure 8.5a. The silicalite-1 adsorption capacity gradient (i.e. the slope of the adsorption isotherms) for CO₂ and CH₄ decreases with increasing pressure; this gradient represents the driving force that facilitates adsorptive surface flow across the membrane. In the absence of defects in the membrane structure, the permeance of CO₂ and CH₄ are expected to decrease with increasing feed pressure. On the other hand, since the N₂ isotherm has a more linear tendency, the permeance is expected to remain constant with increasing pressure differential. As can be observed from Figure 8.11, the decrease in permeance for CO₂, as the pressure difference increases is more than that of

CH₄. This is due to the fact that the CO₂ isotherm is more rectangular which results in a greater decrease in isotherm slope as pressure difference increases compared to CH₄.

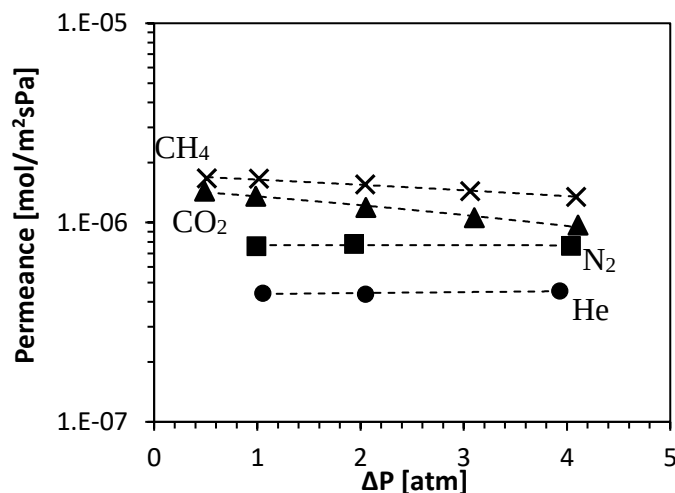


Figure 8.11. Single gas permeance of He, N₂, CO₂, and CH₄ gases as a function of pressure differential for the synthesized silicalite-1 membrane with pure TiO₂ in the active layer and support pore size of 0.8 μm. Experiments were performed at 293K with the permeate side open to atmospheric pressure [27]. The dashed lines are to guide the eye.

Figure 8.12a compares the diffusive ratios D_e and D_e^m for the different gases CH₄/CO₂, N₂/CO₂, and CH₄/N₂; where D_e was determined from the silicalite powder adsorption uptake experiments (Figure 12b). The D_e^m values were calculated from the single gas permeance data presented in Figure 11, and the membrane parameters shown in Table 8.2 (Figure 8.12c). While the absolute value of the different diffusion coefficients (D_e and D_e^m) for each gas may not be directly compared, comparing diffusion selectivity ratios shows the effectiveness of silicalite formation within the membrane pores compared to an ideal case where a membrane is assumed to be a single crystal. As expected, the increased surface occupancy at higher average pressures results in increased diffusivity in all cases due to an increase in the number of interactions between adjacent gas molecules.[27] It follows that the order of the diffusivity ratios are in the order of increasing selectivity: CH₄/N₂ < N₂/CO₂ < CH₄/CO₂, and are the same for both methods. However, in all cases, the D_e^m gas diffusivity ratios are lower than that of the D_e ratios. This indicates that while adsorption surface flow through the zeolite material is present in the membrane, there is still a sizeable contribution to flow through the non-zeolite pores.

Table 8.2. Sips adsorption isotherm parameters determined in this study at 295K for silicalite-1 for single gas CH₄, N₂, and CO₂; and estimated membrane parameters used for calculating the single gas diffusive property of the membrane, D_e^m .

Sips Model Parameters		CH ₄	N ₂	CO ₂
q ^{sat}	(mmol·g ⁻¹)	2.426	2.325	3.605
β	(atm ⁻¹)	0.180	0.076	0.870
n	(dless)	0.955	0.997	0.592
membrane thickness (x)		(μm)	~10-12 [†]	
silicalite-1 skeletal density (ρ) [65]		(g·cm ⁻³)	1.785	
Silicalite-1 porosity (ε) [48]		(dless)	0.428	
† the membrane thickness was estimated from EDS analysis of the membrane cross section given in Figure 8.4.				

Figure 8.13 presents the single gas permeance as a function of gas kinetic diameter for the studied gases observed at 293K for a pressure differential of 1 atm in this work compared to those reported in the literature under similar conditions. It is evident that the pore plugging method used in this study results in high gas permeance, while maintaining favourable gas permeation ratios consistent with the results from the literature (Table 8.3). Comparison with our previous work [10], shows that the gas permeation rate is significantly higher. It is suspected that the addition of an 11 hour thermal break during the hydrothermal synthesis procedure as described by Miachon et al. [11,44] may result in preferential orientation and formation of the zeolite crystals following the initial nucleation, thus explaining the higher gas permeation rates observed in this study. The experimental single gas permeance is not related to the gas kinetic diameter. Since the pores of the silicalite-1 membrane are greater than the kinetic diameter of all of the studied gases, if adsorption diffusion was not a mechanism of gas transport, smaller gases would be expected to have a higher rate of permeance. However, this is not the case as CH₄ is the most permeable (even though it is the largest) followed by CO₂, N₂, and He, which is indicative of adsorption surface flow across the membrane. It should be stressed that both the diffusivity and the equilibrium capacity for adsorption play key roles in determining the permeance of the components through the zeolite membrane. As such, this explains that although silicalite-1 has a lower equilibrium adsorption capacity for CH₄ compared to CO₂ (Figure 8.5a), the transport diffusivity for CH₄ gas across the membrane is higher compared CO₂ as indicated by the effective diffusivity values shown in Figure 8.6b. The experimental observations show combined high gas permeance and good ideal selectivity compared to the previous results in the literature. This is indicative of the ability to achieve synthesis of highly ordered silicalite crystals within the pores of the support, thus resulting in highly productive membranes in terms of both

flux and separation potential which is imperative to applications in industrial gas separations. The CO_2/N_2 and CO_2/CH_4 ideal selectivity are 1.77 and 1.23, respectively, these values are comparable to other silicalite-1 membranes reported in the literature (Table 8.3).

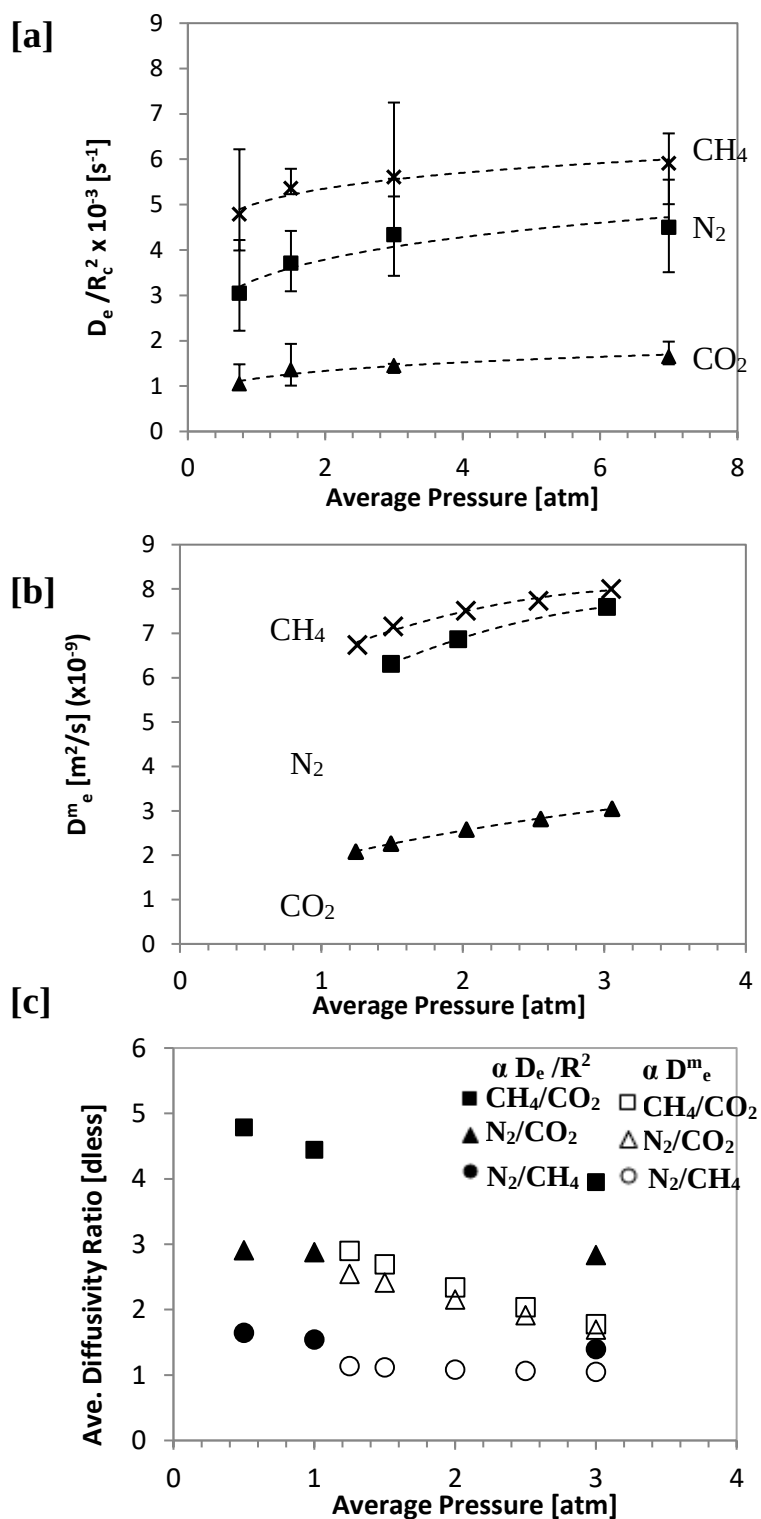


Figure 8.12. Single gas diffusivity coefficients determined from [a] the single gas adsorption uptake experiments for pure N₂, CO₂, and CH₄ gases on synthesized silicalite-1 shown in Figure 8.6 and [b] the single gas permeance of N₂, CO₂, and CH₄ gases shown in Figure 8.11. [c] Comparison of the experimental diffusivity ratios. The dashed lines are to guide the eye.

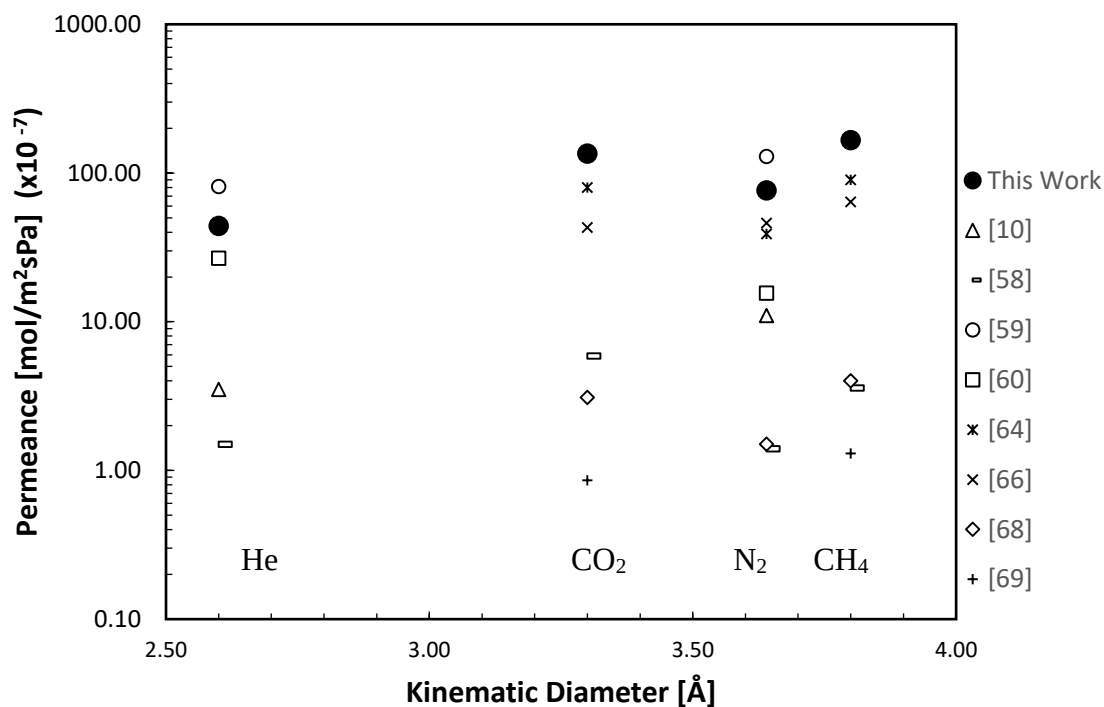


Figure 8.13. Single gas permeance of He, N₂, CO₂, and CH₄ gases at 1 atm pressure differential as a function of gas kinematic diameter for a synthesized silicalite-1 membrane with pure TiO₂ in the active layer and support pore size of 0.8 μ m. Experiments were performed with at 293K with a 1 atm pressure differential and the permeate side open to atmospheric pressure. The experimental results (filled points) are compared those reported in the literature [58–60,64,66–69] under comparable conditions.

Table 8.3. Comparison of single gas permeance and ideal selectivity with literature for a silicalite-1 membrane synthesized with pure TiO₂ in the active layer and pore size of 0.8 μm , experimental conditions for this work were evaluated at 293K with a 1 atm pressure differential and the permeate side open to atmospheric pressure

Reported Synthesis Description	Support type	T (K)	x [μm]	Permeance [$\text{mol}/\text{m}^2\text{sPa}$] ($\times 10^{-7}$)					Ideal Selectivity			Ref.
				P_{H_2}	P_{He}	P_{CO_2}	P_{N_2}	P_{CH_4}	$\alpha_{\frac{*N_2}{He}}$	$\alpha_{\frac{*CO_2}{N_2}}$	$\alpha_{\frac{*CO_2}{CH_4}}$	
Pore plugging and secondary growth	TiO₂ layer, α-Al₂O₃ tube	293	12	-	44.2	135.0	76.3	166.0	1.72	1.77	0.81	This work
pore plugging	TiO ₂ /ZrO ₂ layer, α -Al ₂ O ₃ tube	296	5	-	3.5	-	11	-	3.14	-	-	[10]
seeded growth	α -Al ₂ O ₃ disc	298	10	2.9	1.5	5.9	1.4	3.6	0.93	4.20	1.80	[58]
seeded growth	α -Al ₂ O ₃ disc	298	0.5	210	81	-	129	-	1.59	-	-	[59]
steam-assisted crystallization	α -Al ₂ O ₃ tube	298	5.5	-	1-18	-	0.43-20	-	~ 1	-	-	[61]
unseeded growth	α -Al ₂ O ₃ tube	300	10	44	26.7	-	15.6	-	0.58	-	-	[60]
unseeded growth	SS disc	300	50-60	2.5	0.8	3.0	1.3	3.8	1.62	2.31	0.79	[55]
seeded growth	α -Al ₂ O ₃ disc	298	17	86	-	80	39	90	-	2.05	0.89	[64]
in situ nucleation and secondary growth	α -Al ₂ O ₃ tube	298	2	79	-	43	46	64	-	1.07	0.67	[66]
unseeded growth	SS disc	298	50	2.5	-	3.1	1.5	4.0	-	2.06	0.78	[68]
pore plugging	TiO ₂ / ZrO ₂ layer, α -Al ₂ O ₃ tube	293	6.5	-	-	0.5	0.4	-	-	1.20	-	[26]
secondary growth	α -Al ₂ O ₃ disc	298	3	0.96	-	0.86	-	1.3	-	-	0.66	[69]
secondary growth	SS disc	303	20	-	-	2.3	-	0.7	-	-	3.28	[36]
seeded growth	α -Al ₂ O ₃ disc	300	10	-	1.4	-	-	-	-	-	-	[24]

8.4.4. MIXTURE MEMBRANE GAS PERMEATION

The single gas permeance of zeolite adsorbent membranes cannot be used to accurately predict mixed gas permeation performance. This is due to the fact that zeolites have a finite number of adsorptive sites which results in changes in zeolite mixture selectivity when compared to the single gas behaviour. Permeation experiments for the membrane with a support pore size of a 0.8 μm synthesized in batch A were carried out using an equimolar binary CO_2 - N_2 feed. The results are presented in Figure 8.14. The CO_2 permeance observed from the binary mixture is similar to the single gas permeance values shown in Figure 8.11. The N_2 permeance is lower for the binary CO_2 - N_2 system at about 1.8×10^{-7} to 2.0×10^{-7} $\text{mol}/\text{m}^2\text{sPa}$ compared to the single gas system at about 8.0×10^{-7} $\text{mol}/\text{m}^2\text{sPa}$. CO_2 has a much greater affinity towards the zeolite compared to N_2 , therefore it will be preferentially adsorbed to a site which may block access to N_2 which is favourable for increasing CO_2/N_2 permselectivity compared to the single gas CO_2/N_2 ideal selectivity. The CO_2/N_2 permselectivity ranges from 3 to 9 (Figure 8.14b) and decreases with increasing pressure differential which is consistent with the trends observed with respect to the ideal adsorption selectivity given in Figure 8.5b. These results are consistent with results that have been reported in the literature for binary mixtures involving CO_2 and N_2 on silicalite-1 pellets [20], and MFI type membranes [26,70]. Effectively, the permeance of N_2 in the mixture is affected much more than the permeance of CO_2 compared to their pure component permeance. Therefore, the presented permselectivity values for the mixtures are much higher than the ideal selectivity.

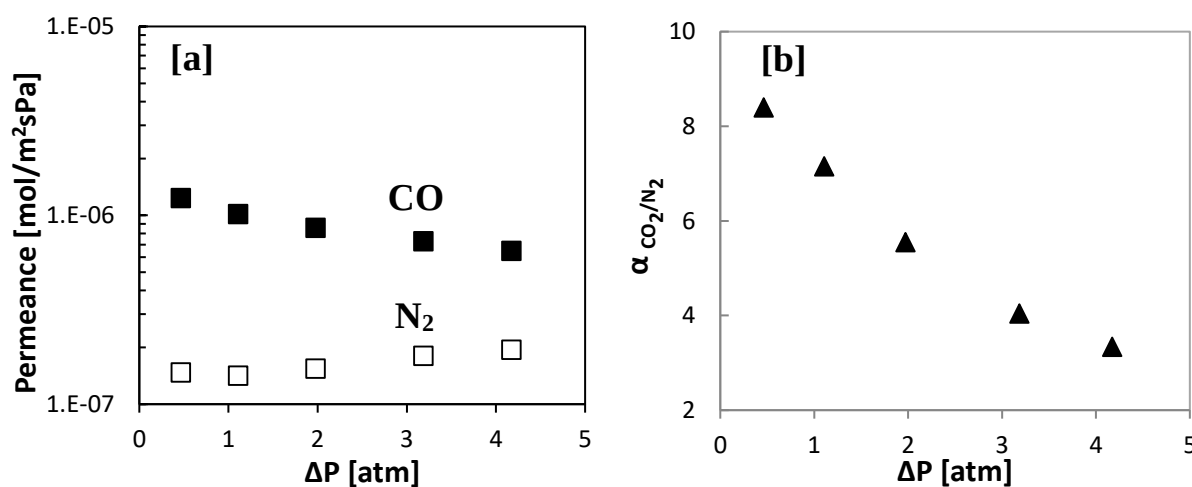


Figure 8.14. [a] Permeance and [b] CO_2/N_2 permselectivity of CO_2 and N_2 as a function of total pressure differential for a synthesized silicalite-1 membrane with pure TiO_2 in the active layer and support pore size of 0.8 μm . Experiments were performed at 293K with the permeate side open to atmospheric pressure using an equimolar binary CO_2 - N_2 feed.

8.5. CONCLUSIONS

Silicalite-1 membranes have been successfully synthesized on tubular supports with TiO₂ in the active layer using a modified pore plugging synthesis method with a thermal break of 11 hours. SEM and EDS analyses confirm the synthesis of silicalite-1 membranes with a thickness of approximately 10-12 μm with no Al⁺³ heteroatoms detected within the membrane composite structure in the active layer.

Single gas He and N₂ permeation experiments confirm the minimization of defects for membranes synthesized on supports with pore sizes of 0.3 μm , 0.45 μm , and 0.8 μm , with calculated membrane permeances ranging from 0.2×10^{-6} and $5.2 \times 10^{-6} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$. Ideal N₂/He permeance ratio was observed to be the highest at 2.3 ± 0.5 for the membranes with the support pore size of 0.8 μm which is equivalent to other MFI type membranes.

The effect of competitive adsorption within gas mixtures and surface diffusion was shown to induce favourable separation of CO₂ over N₂ with actual mixture permselectivity higher than the ideal gas selectivity calculated from the pure component data. A CO₂/N₂ permselectivity value as high as 9 was attained for an equimolar CO₂ – N₂ feed mixture. High gas permeability (calculated to be equivalent to about 33000 Barrer for CO₂ using the membrane thickness of about 10 – 12 μm determined from the EDS and SEM analysis) were observed which results in a similar material performance as described by the Robeson upper bound for CO₂/N₂ separations for polymeric materials.[71] The observed high permeances of these membranes coupled with the thermal and chemical stability of silicalite zeolite may show potential as an initial bulk separation step following industrial flue gas treatment, where polymeric materials are thought to be less stable and are subject to rapid physical aging.

8.6. NOMENCLATURE

A_m	membrane area	$[m^2]$
D_e	effective transport diffusivity	$[m^2/s]$
D_e^m	effective membrane diffusivity	$[m^2/s]$
D_e/R_c^2	diffusion time constant	$[s^{-1}]$
D_i^{Kn}	Knudsen diffusivity parameter	$[m^2/s]$
D_i^{vis}	Viscous flow parameter	$[m^2/s]$
J	membrane flux	$[mol/m^2 s]$
k_{LDF}	kinetic rate constant	$[s^{-1}]$
l	thickness of the active layer of the membrane	$[m]$
n	dimensionless Sips model parameter	[dless]
M	molar mass	$[g/mol]$
p	pressure	[atm] where 1 atm= 101325 Pa
P	permeance	$[ml(STP)/m^2sPa]$
q	adsorption capacity	$[mmol/g \text{ of adsorbent}]$
$q(t)$	amount absorbed at time t	$[mmol/g \text{ of adsorbent}]$
q_e	adsorption capacity at equilibrium	$[mmol/g \text{ of adsorbent}]$
q^{sat}	adsorption capacity at saturation	$[mmol/g \text{ of adsorbent}]$
R	universal gas constant	$[m^3 Pa/ K mol]$
R_c	radius of crystal	$[m]$
t	time	$[s]$
T	temperature	$[K]$
X	membrane thickness	$[\mu m]$

Greek Symbols

$\alpha_{A/B}$	permselectivity	[dless]
$\alpha^*_{A/B}$	ideal selectivity	[dless]
$\propto D_{e,ij}^m$	effective membrane transport diffusivity selectivity	[dless]
$\propto \frac{D_e}{R_c^2}$	effective silicalite-1 transport diffusivity selectivity	[dless]
β	adsorption affinity constant	$[atm^{-1}]$

ε	porosity of the silicalite in the membrane	[dless]
θ_i	adsorption surface coverage of component I	[dless]
ρ	skeletal density of the adsorbent	[g/cm ³]
τ	tortuosity factor	[dless]

Abbreviations

EDS	electron dispersive spectroscopy
LDF	linear driving force model
MEA	monoethanolamine
MFC	mass flow controller
PTFE	polytrafluoroethylene
SEM	scanning electron microscopy
TPAOH	tetrapropylammonium hydroxide
XRD	x-ray diffraction spectroscopy

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CHAPTER 9

Conclusions and Recommendations for Future Work

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9.1. OVERALL DISCUSSION

The purpose of this study was to characterize practical adsorbent materials to facilitate the separation of CH₄ from N₂, and/or CO₂ containing mixtures directed towards nitrogen rejection in natural gas or renewable biogas upgrading using adsorption technology.

Initially, an evaluation of adsorbents was performed consisting of a literature review and experimental adsorption screening of CH₄ and N₂ adsorption equilibria on commercially available adsorbents. Adsorption isotherms of CH₄ and N₂ were measured on commercially available activated carbons, zeolites, and desiccants at 303K using the gravimetric method. It was verified that in most cases for adsorption equilibria based separations, CH₄ is only moderately favoured over N₂. Activated carbons showed the best performance with a combination of the highest equilibrium adsorption capacity for CH₄ and CH₄/N₂ equilibrium selectivity. Zeolites also exhibited adsorption behaviour in favour of CH₄, with typically lower CH₄/N₂ equilibrium selectivity compared to activated carbons.

Given the difference in the size of the studied gases (CH₄ kinetic diameter = 3.8 Å vs. N₂ kinetic diameter = 3.6 Å) an alternative separation approach using a molecular sieve was considered. Whilst the titanosilicate ETS-4 presents the benchmark for such gas separations, several other molecular sieve type materials were reviewed including carbon molecular sieves and small pored zeolites (LTA type zeolites, chabazite, mordenite, SAPO-34 etc.). Of these materials, clinoptilolite, an aluminosilicate zeolite, was selected as an attractive candidate to explore this separation technique due to the narrow channel size. The possibility of manipulating the effective channel pore diameter using charge balancing extra framework cations was explored.

Natural clinoptilolite was modified through cation exchange and the influence of different extra framework cations was studied on the adsorption performance using a comprehensive screening process. Raw and cation exchanged clinoptilolites were characterized through XRD, EDS, FT-IR ATR spectroscopy, and SEM. The measured elemental composition demonstrated successful cation exchange for almost all of the studied cations. Through cation exchange, the amount of exchanged extra framework cations increases at the expense of native Ca²⁺, K⁺ and Mg²⁺ cations. Small variations were observed between the raw and some of the modified samples. Among the studied cations, H⁺, Li⁺, Cs⁺, Ag⁺, Be²⁺, Mg²⁺, Sr²⁺, and Fe³⁺ cations resulted in some alterations in the peak intensity of the XRD diffractograms compared to the original clinoptilolite samples. It is suspected that these alterations may be a result of an altered framework structure and/or different extra framework atomic positions within the unit cell compared to the parent clinoptilolite samples. In some cases, dealumination of the zeolite lattice was observed. Incorporation of Fe³⁺ cations and/or Fe containing complexes into the framework structure is hypothesized.

The adsorption characteristics (kinetic uptake, and equilibria) of pure CO₂, N₂, and CH₄ gases were measured for all of the clinoptilolite samples at 303K at pressures of up to 10 atm. Additionally, the adsorption temperature effects for these gases were studied for raw, Cs⁺, Fe³⁺, and Ca²⁺ cation exchanged clinoptilolite. The positioning and type of charge balancing cations influences the adsorption characteristics of the modified clinoptilolites compared to the original raw clinoptilolite which had an equilibrium selectivity of CH₄ over N₂ that is close to unity.

Extra framework cations such as Li⁺, Ni²⁺, Ca²⁺, and Ag⁺ were demonstrated to negatively influence the adsorption of CH₄ while N₂ was less affected. Specifically, Li⁺ and Ni²⁺ clinoptilolites showed favourable kinetic selectivity for possible N₂/CH₄ kinetic separations with kinetic selectivity values of 110 and 37, respectively. Both Ca²⁺ and Ag⁺ exchanged clinoptilolites showed equilibrium selectivity in favour of N₂ over CH₄. The pore size distribution (determined from N₂ sorption experiments performed at 77K) showed a decrease in average pore size for these forms for cation exchanged clinoptilolite. Pore blocking is suspected to limit access of the larger CH₄ gas to the pore network. The phenomena also extended to improved CO₂/CH₄ selectivity for Ca²⁺ clinoptilolite compared to raw clinoptilolite. However, as a consequence of the smaller channel pore size the diffusion uptake rate of these modified materials was much slower, which may limit the use of these materials in dynamic environments (such as a PSA). It is recommended that higher adsorption temperatures be used for this adsorbent in order to compensate for the slow kinetic behaviour at lower temperatures.

In contrast, natural clinoptilolites which were cation-exchanged with Cs⁺ and Fe³⁺ containing salt solutions showed moderately improved separation potential for CH₄/N₂ selective separations compared to those of the commercially available adsorbents. Experimental binary CH₄-N₂ adsorption behavior was assessed using the gas chromatographic technique. From the binary chromatography experiments, the MVV-CPM provided an adequate representation of the experimental data for all of the binary CH₄-N₂ adsorption systems. The resulting experimental binary isotherms were compared against the theoretical binary isotherm predictions (ELM, DSL, IAST, FH-VSM) determined from the single component isotherm data. The binary model predictions showed some deviations from the experimental data, particularly for zeolitic materials implying possible competitive or non-ideal adsorption behavior. Binary mixture CH₄/N₂ separation factor and X-Y phase behaviour were used to illustrate the improvement in the performance of Cs⁺ and Fe³⁺ exchanged clinoptilolite over natural clinoptilolite and commercially available adsorbents.

For the application of CH₄ capture in natural gas ($0.8 < y_{CH_4} < 0.9$), the binary separation factors at 303K and 1atm are 4.5 and 7.1 for Cs⁺ and Fe³⁺ cation-exchanged clinoptilolite, respectively. In comparison, the activated carbon (Calgon Xtrusorb A754) showed a binary CH₄/N₂ separation value of 3.1,

and 13X zeolite displayed a value of only 1.6. Therefore, clinoptilolite cation-exchanged with Fe^{3+} ranks well compared to many adsorbents reported in the literature and would be an interesting alternative to explore for applications in CH_4/N_2 gas mixture separations.

Finally, a preliminary exploration into the idea of inorganic membranes formed of clinoptilolite powder and glass sealant as a binder supported by a porous ceramic alumina was explored. A ratio of 50 to 100 wt. % specialty glass sealant to natural clinoptilolite particles was used. Raw clinoptilolite was found to maintain most of its essential properties following exposure to glass vitrifying temperatures of 1073 K. Single gas permeation experiments showed decreasing permeation rates with increasing amount of glass, with the membrane formed of 100 wt% glass being essentially impermeable (as expected). However, the ideal selectivity for these membranes was low. While adsorption based surface flow across the membrane is possible, the low selectivity is a result of defects in the membrane morphology which were observed from the cross sectional SEM imagery.

9.2. CONCLUSIONS & CONTRIBUTION to ORIGINAL KNOWLEDGE

The following conclusions and contributions to original scientific knowledge have been made as a result of this thesis project:

- A comprehensive review of the literature and systematic cation exchange screening process for modified natural clinoptilolite was performed using monovalent, divalent, and trivalent cations. The corresponding adsorption characteristics (kinetic uptake, and equilibria) of pure CO_2 , N_2 , and CH_4 gases were measured for all of the clinoptilolite samples and compared to others in the literature.
- Favourable N_2/CH_4 kinetic separation properties were demonstrated for the first time for Ni^{2+} exchanged clinoptilolites and were also verified for Li^+ exchanged clinoptilolites.
- The pore blocking effect of Ag^+ exchanged clinoptilolite exchanged with varying amounts of Ag^+ cations was demonstrated. It was shown for the first time that increasing N_2 / CH_4 equilibrium selectivity corresponds to increasing presence of Ag^+ cations in the structure.
- Improved CH_4/N_2 equilibrium selectivity was demonstrated for the first time with Cs^+ and Fe^{3+} exchanged clinoptilolite over natural clinoptilolite and most commercially available adsorbents. Binary mixture $\text{CH}_4\text{-N}_2$ adsorption behavior on these new materials was assessed experimentally

using the concentration pulse chromatographic technique, and compared to theoretical model predictions for mixture adsorption.

- The idea of membranes formed of clinoptilolite and a glass sealant binder supported by a porous ceramic alumina support was presented for the first time and show promise for further study for gas separations.

9.3. RECOMMENDATIONS for FUTURE WORK

This potential of adsorbents for CH₄ and N₂ adsorption separations was assessed experimentally and clinoptilolite was selected as a promising candidate material. It was then modified through cation exchange and the adsorption properties of CO₂, CH₄, and N₂ gases were measured, for both single gas and binary mixtures for the promising adsorbents. The experimental adsorption results were analyzed considering the factors that affect the material morphology, composition, and the related sorbent-sorbate interactions.

To build on this work, further evaluation of the merits of these new materials for adsorption based separation designs using the best cation exchange clinoptilolites for prospected CO₂/CH₄, CH₄/N₂ and N₂/CH₄ based separations is recommended. The following items are suggested:

- The clinoptilolite used in this study was sourced from a single location and supplier. It is recommended to source natural clinoptilolite from multiple different areas so as to ascertain if the starting material composition (cation composition, presence of impurities) may effect the outcome following cation exchange.
- Examination of the gas mixture adsorption behaviour by performing mixture gas adsorption experiments over a greater range of temperatures and pressures to obtain the working range of the materials is recommended.
- Detailed adsorption diffusion studies are necessary, particularly for the kinetically (Ag⁺, Li⁺, Ni²⁺) and equilibrium (Ag⁺, Ca²⁺) N₂/CH₄ selective clinoptilolites in relation to raw clinoptilolite and benchmark materials (ETS – 4) to better establish the kinetic properties of these materials.
- The above recommendations pertain to experimentally establishing parameters that effect of the optimal conditions to maximize the CH₄ purity and recovery. Modelling looking at predicting the positions of charge balancing extra framework cations within clinoptilolite may give greater insights into optimizing possible cation compositions to improve the separation properties of this material.

- The Extended Langmuir Model predictions for the binary isotherms deviated from the experimental binary isotherms due to non-idealities in the binary systems. It is recommended to calculate the activity coefficients for this system to determine the degree of nonideality of the binary systems.
- Experimental verification of the modelled performance using packed adsorbent columns and adsorption breakthrough curve experiments to establish the true adsorption separation potential and determine operating parameters such as temperature and pressure ranges for prospective adsorptive based systems, should be carried out.
- The concept of inorganic membranes composed of a glass continuous phase as a binder and using clinoptilolite particles as zeolitic fillers has been presented. Further refinements to this technique are necessary to determine an optimum ratio of wt. % clinoptilolite to glass to improve selectivity and to minimize defects. It is recommended to experiment with a reduced amount of clinoptilolite filler that was not studied in this thesis (between 0% and 20% clinoptilolite). Alternatively, mixed matrix polymeric membranes incorporating the clinoptilolite material may also be explored.

9.4 NOMENCLATURE

Abbreviations

CPM	concentration pulse method
DSL	dual site Langmuir Model
ELM	Extended Langmuir Model
IAST	Ideal Adsorbed Solution Theory
MVV-CPM	modified Van der Vlist and Van der Meijden – concentration pulse method
PSA	pressure swing adsorption
FH-VSM	Flory-Hudgins Vacancy Solution Method

APPENDIX A

APPARATUS and SUPPLEMENTAL MATERIAL

D. A. Kennedy

A. OVERVIEW of EXPERIMENTAL APPARTUS*

In order to fulfill the objectives discussed in this thesis project, three different were used to measure the gas adsorption behaviour; they are:

1. Gravimetric adsorption system
2. Constant volume adsorption system
3. Chromatographic system

***An expansion of the description of the experimental apparatus mentioned in Chapters 2 through 6 of this thesis.**

A.1. GRAVIMETRIC SYSTEM

The gravimetric adsorption system is the same system that was used in the work of Wilson (2015) which also described in his thesis works [1] . For this method, the single gas adsorption isotherms and uptake-rate measurements were performed on the adsorbent samples using a microgravimetric analyser purchased from VTI Corp. (Hialeah, Florida, USA). This equipment allows for the monitoring of both the static equilibrium and dynamic adsorption uptake measurements. The experiments were carried out using a sensitive Cahn microbalance that has an precision of $\pm 1 \mu\text{g}$ enclosed within a stainless steel chamber. The experimental temperature was controlled using a jacketed water bath installed around the adsorption chamber and was monitored using a thermocouple with an precision of $\pm 0.01\text{K}$. Figure A.1 presents the schematic of the microgravimetric adsorption analyser.

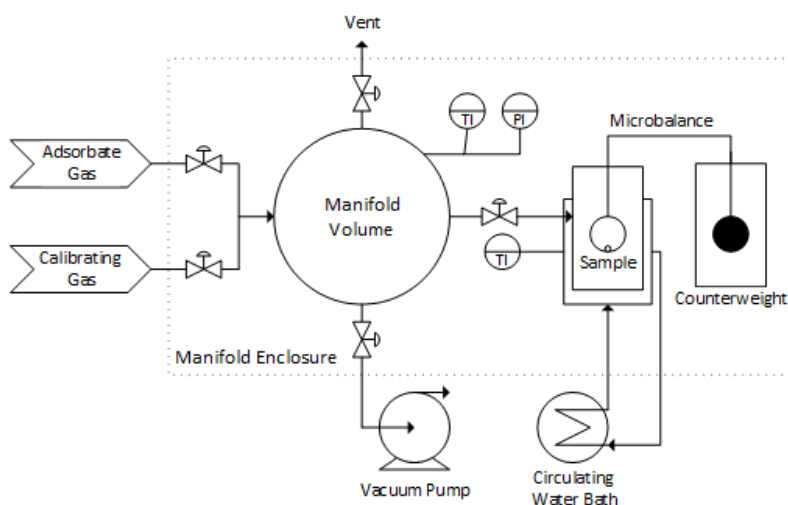


Figure A.1. Schematic diagram of the VTI Corp. microgravimetric adsorption analyser.[1]

Adsorbent samples are first regenerated under high vacuum conditions of approximately 10^{-8} atm using a high vacuum turbo molecular pump (Model# MTMH 071P, Pfeiffer Vacuum Inc., Nashua NH, USA) at a temperature of 573K. The samples were determined to be fully regenerated once the sample weight remained unchanged over a period of 1 hour. Following regeneration, the adsorbents were exposed to a sample gas and were evaluated at increasing pressure steps ranging from 0 to 10 atm at 303K. The samples were initially also exposed to helium at similar pressures and temperatures in order to correct for buoyancy. For each pressure step change, the dynamic adsorption uptake was monitored and recorded as the change in sample weight with time. Sufficient time was allowed for the system to reach equilibrium, which was determined to be achieved once a weight change of less than 0.015 wt% over a period of 15 minutes was observed, at which time the equilibrium adsorption measurement was recorded.

A.2 CONSTANT VOLUME ADSORPTION SYSTEM

For these adsorption measurements, a similar experimental procedure is used as described in the thesis of Predescu (1997) and Abdollahi (2013) [2,3]. The constant volume adsorption apparatus is used to determine the pure component adsorption equilibria isotherms limited to the low pressure region from 0 to 1.3 atm total pressure. A Micromeritics Instrument Co. Physical Adsorption Analyzer (Atlanta, GA) was used for this. The schematic diagram of the instrument is presented in Figure A.2. The system consists of three pressure transducers: one for the low pressure range (0.000 – 0.053 atm), one for the intermediate pressure range (0.000 – 1.312 atm), and an additional pressure transducer for higher pressures (0.00 - 10.88 atm), with an accuracy of $\pm 1\%$ of the pressure range respectively for each transducer. All pressure transducers were calibrated manually prior to the commencement of the experiment. A high accuracy pressure gage was used, the pressure transducer readings were corrected under high vacuum (corrected to 0 atm) and at atmospheric pressure conditions (corrected to 1 atm) respectively by comparing the value of the pressure gage to measurements given by the transducers and adjusting accordingly. The total volume of the apparatus was provided by the manufacturer and consists of the manifold, the interconnected tubing, and optional extra stabilization volume. These values were verified prior to commencing each experimental set. The experimental manifold is contained within an enclosed box, the temperature of the manifold is regulated to $303\text{K} \pm 1\text{K}$ during the experiments and is monitored with a thermocouple. The adsorbent sample is held within a glass sample flask equipped with a heating jacket to ensure consistent isothermal temperature conditions. A thermocouple is used to monitor the sample temperature during the experiments.

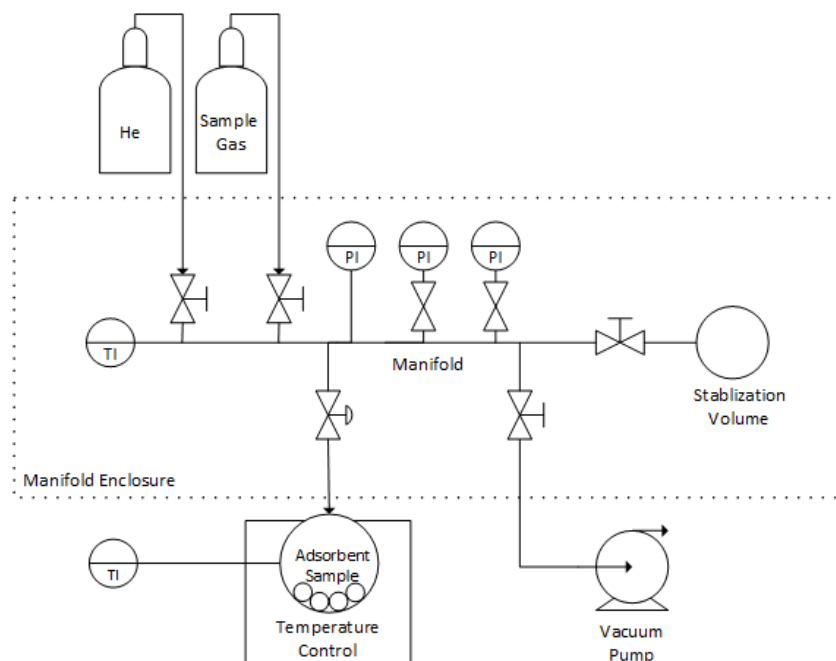


Figure A.2. Schematic diagram of the Micromeritics Accusorb Physical Adsorption Analyzer constant volume system that is used for pure component adsorption isotherm measurements [2–4].

Approximately 1 to 3 grams of a selected adsorbent sample is placed into the glass sample flask which is then installed into the experimental apparatus and regenerated under high vacuum conditions at a temperature of 573K over a minimum of 8 hours. Following sample regeneration, the experimental temperature is set and allowed time to reach equilibrium. Next, the total sample dead volume corresponding to the extra volume of the glass sample flask and the microporous void volume of the adsorbent is determined using helium gas. In a similar vein as the gravimetric adsorbent buoyancy correction, helium gas is used because it is assumed to be non-interacting and additionally, the small molecular size of helium gas (kinetic diameter of 2.6Å) permits access to the micropores of the sorbent thus permitting the calculation of the system volume. Following this step, the entire system and manifold is evacuated and the dosing valve to the adsorbent sample was closed. Next, the sample gas was released into the manifold and the initial manifold pressure was recorded. Finally, the adsorbent sample is exposed to the sample gas by opening the dosing valve, and the total system pressure is monitored and allowed to reach phase equilibrium conditions between the gas and the adsorbed phase. Equilibrium was determined to be achieved once the system pressure remained unchanged, this time is variable and may take several hours to several days depending on the nature of the gas adsorbing system. The calculations

A.3. COMPARISON of VOLUMETRIC and GRAVIMETRIC SYSTEMS

The measurements for the CH₄ and N₂ adsorptions isotherms on raw clinoptilolite were conducted using the gravimetric system and the volumetric system, the results are shown in Figure A.3. As can be seen in this Figure, the isotherms determined from either method are fairly consistent with one another. . It is supposed that some minor differences may between the two methods could be due to differences with the regeneration conditions. With the gravimetric method, a turbo-molecular vacuum pump was use used for the regeneration. This was not the case with the volumetric system, whereby a conventional vacuum pump was used. The different approach to the regeneration procedure could remove more contaminants from the surface using the gravimetric system. This is supported by the fact that the both of the N₂ and CH₄ adsorption isotherm measurements show slightly less amount adsorbed compared to the measurements using the gravimetric system. Additionally, the gravimetric system is equipped with measurement devices with higher precision compared to the volumetric system.

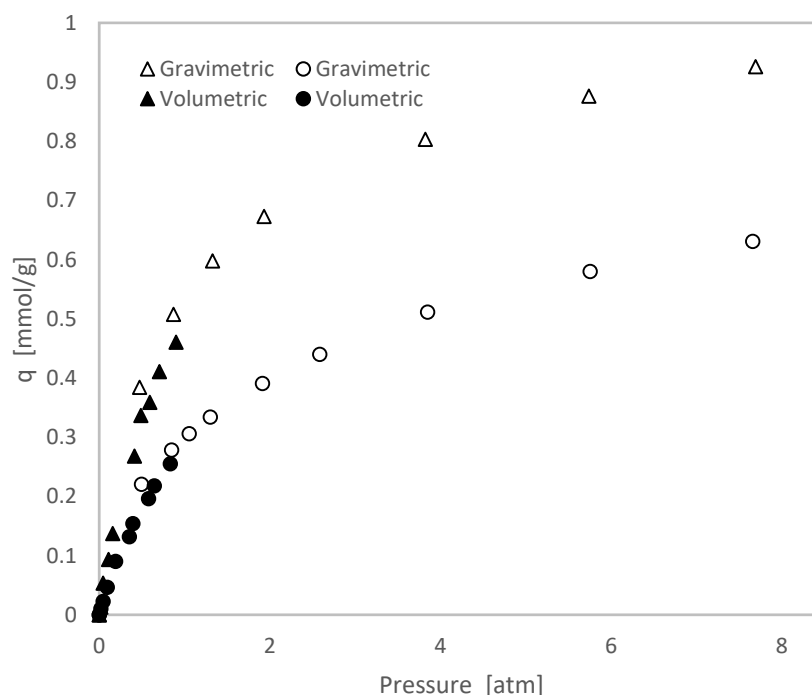


Figure A.3. Comparison of pure component adsorption isotherms for CH₄ and N₂ on raw clinoptilolite powder at 303K. The adsorption measurements were conducted with the volumetric system (filled points) and gravimetric system (open points) respectively.

A.4. REPRODUCIBILITY of GRAVIMETRIC MEASUREMENTS

The measurements for the CH₄ and N₂ adsorptions isotherms on raw clinoptilolite were conducted using the gravimetric system, the results are shown in Figure A.4. As can be seen in this Figure, the gravimetric isotherms are fairly consistent with one another. Considering that the findings from the initial adsorbent screening study were used as the basis for subsequent verification of the new materials, the differences in the measured results are likely not significant enough to fundamentally alter the broad conclusions or experimental findings.

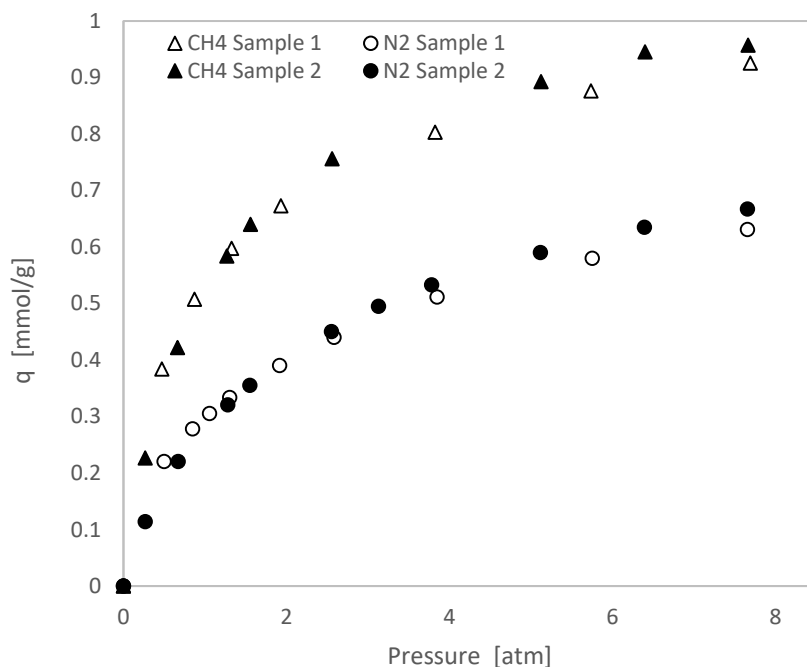


Figure A.4. Comparison of pure component adsorption isotherms for CH₄ and N₂ on raw clinoptilolite powder at 303K. The adsorption measurements were conducted with the gravimetric system and were repeated.

A.5. CHROMATOGRAPHIC SYSTEM

For the chromatography measurements, a similar experimental procedure is used as described in the thesis of Li (2007), and was discussed as the subject of my first publication Kennedy &Tezel (2014)[5,6].Figure A.5 depicts the experimental apparatus used to characterize the adsorption properties

of single and binary gas systems, which is known as the concentration pulse method (CPM) [5–22]. ***An expansion of the description of the experimental apparatus mentioned in Chapters 2 through 6 of this thesis.**

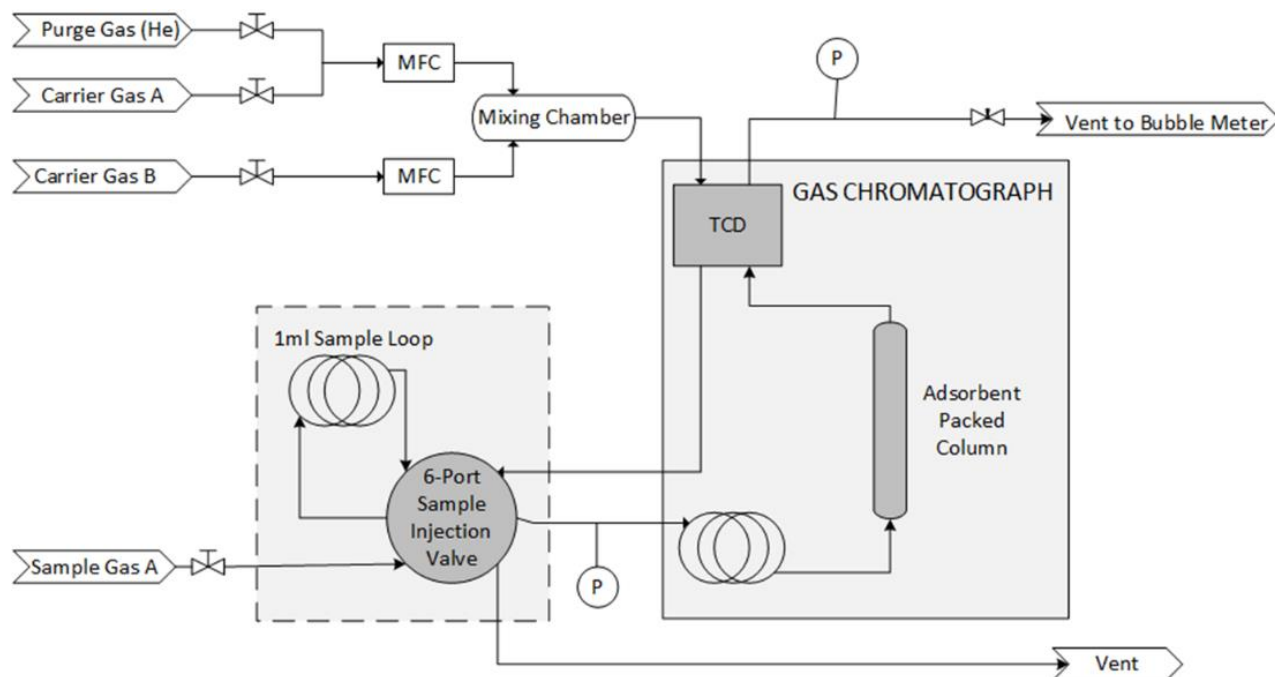


Figure A.5. Schematic diagram of the modified gas chromatograph setup used for the single component K_p , heat of adsorption experiments, and the binary gas mixture experiments [5,6].

With the chromatographic method the slope of an adsorption isotherm at very low gas concentrations (Henry's law constant (K_p)) can be determined by the system response to a dilute sample injection into an adsorbent filled column. A packed adsorbent column is installed in series within a modified GOW-MAC Series 400 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Initially, a packed adsorbent bed is regenerated at high temperature ($T > 250^\circ\text{C}$) under a constant inert gas purge (typically He). In the setup described in Figure A.5, the carrier gas flow rate is controlled by MKS mass flow controllers, and may be configured for either a single gas or a binary gas mixture. For a typical measurement, an injection of adsorbate sample gas is fed to the packed column. The response of the column to the sample injection was monitored at the outlet of the column with the TCD detector as the change in voltage as a function of time. Details on the column dimensions used in this project are listed in

Table A.1. Specific information pertaining to the column experimental conditions used for each study are elaborated on in the experimental section of Chapters 2, 4, and 6, respectively.

Table A.1. Details of the binary and single gas experimental and column specifications for the concentration pulse chromatography experiments.

Column 1*	Length	10.4	cm
	Inner diameter	0.46	cm
	Packing mesh size	40 x 50	US std. mesh
		300 – 425	μm
	Packing type	glass beads, crushed adsorbents	
	Void fraction determined with glass beads	0.39	dimensionless
	Sample gas injection volume	0.25	cc
Column 2*	Length	3.4	cm
	Inner diameter	0.18	cm
	Packing Type	glass beads, crushed adsorbents	
	Mesh size	60 x 80	US std. mesh
	Particle size range	180-250	μm
	Void fraction determined with glass beads	0.4	dimensionless
	Sample gas injection volume	0.1	cc
System Dead Time Experimental Conditions	Carrier gas	He	
	Injection sample gas	N ₂	
	Carrier gas flow rate range	column 1: 10 - 50 column 2: 0.75 – 8.0	cc/min cc/min
	Experimental temperature	318	K
<i>*Details pertaining to the specific column specifications and experimental conditions are listed in Chapters 2, 4, and 6.</i>			

Glass beads with the same particle size as the adsorbents were packed into the same sized columns as those used for the adsorption measurements (40 X 50 U.S. Std. Mesh for the large column and 60 x 80 U.S. std. Mesh for the smaller one). Figure A.6 shows the measured system dead time vs. the inverse of the carrier gas superficial velocity (v_s) for different sizes of columns used in this study

(columns 1 and 2, respectively). The system dead time (μ_D) is used to correct for the delay in system response due to volume associated with tubing and voids within the packed column. [5].

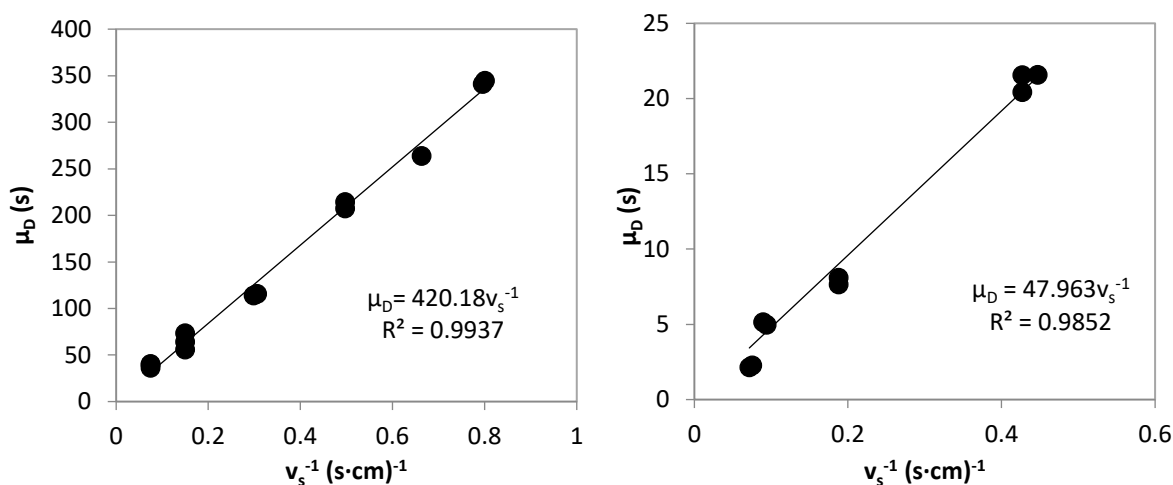


Figure A.6. Relationship between the system dead time (μ_D) and the v_s for column 1 (left) and column 2 (right) .

A.5.2. OUTLINE of the CONCENTRATION PULSE CHROMATOGRAPHIC METHOD FOR DETERMINATION of BINARY ISOTHERMS

To determine the K_p values, the mean retention time (μ) of the sample gas injection is calculated from the response peak as concentration (c) as a function of time (t) measured at the outlet of the column as detector voltage vs. time. Figure A.7 shows an example of a hypothetical response of an adsorbent packed column to an adsorbate gas injection with a constant He carrier gas flow rate.

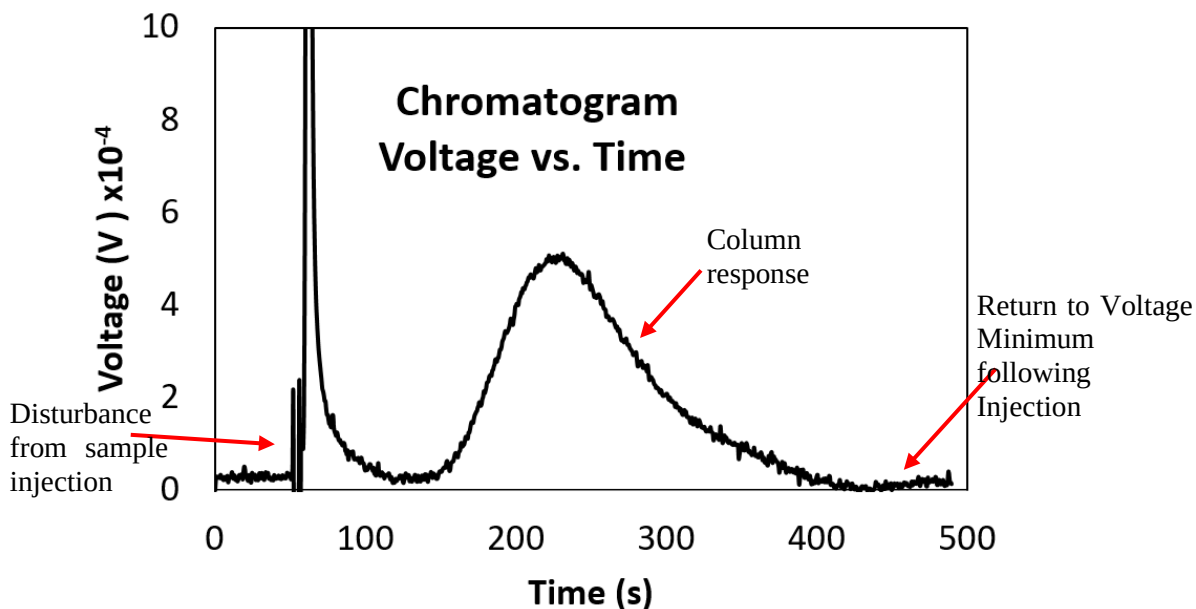


Figure A.7 Voltage vs. time plot of a hypothetical response of an adsorbent packed column to an adsorbate gas injection with a constant He carrier gas flow rate.

The dimensionless Henry's Law constant (K) is derived from the packed bed parameters including the bed porosity (ϵ), bed length (L), fluid velocity (v) as shown in Equation 1:

$$\mu = \frac{\int_0^{\infty} c(t - \mu_D) dt}{\int_0^{\infty} c dt} = \frac{L}{v} \left[1 + \frac{(1-\epsilon)K}{\epsilon} \right] \quad (1)$$

Figure A.8 shows a example of the Excel raw data file that was used to calculate the mean retention time (first moment) of the column calculated from the response peak to a sample injection given in Figure A.7 using Equation 1.

CH4 peak He Carrier @ 45C flow rate 15.0 cc/min activated carbon									
Voltage Minimum =		0.3784							
Room Temp =		23		C				Injection size 0.25	
Column Temp =		45		C				current 110	
Carrier Flowrate =		15.00		ml/min				det. Temp 55	
First Moment, μ =		90.8404 sec				$\int_0^{\infty} c dt$		inj Temp 45	
Calculated mean retention time (μ)						Sum: $\int_0^{\infty} c(t - \mu_D) dt$		Sum:	
$\mu = \frac{\int_0^{\infty} c(t - \mu_D) dt}{\int_0^{\infty} c dt}$						0.043759		3.975047	

$$K_p = \frac{K}{RT\rho_p} \quad (2)$$

When pure component K_p values are determined at different temperatures, the limiting heat of adsorption (ΔH) can be calculated from the slope of the Van't Hoff plot ($\ln K_p$ vs. $1/T$) as defined from Equation 3:

$$K_p = K_o e^{\left[\frac{-\Delta H}{RT}\right]}, \quad \ln K_p = \ln K_o - \frac{\Delta H}{RT} \quad (3)$$

For a binary mixture, the column response to a small sample injection is measured over a range of compositions for a binary carrier gas mixture. For binary systems, the experimental K_p data is related to the slopes of both of the isotherms of the components within the binary gas mixture as follows:

$$K_p = (1 - y_1) \frac{dq_1}{dP_1} + y_1 \frac{dq_2}{dP_2} \quad (4)$$

where dq_1/dP_1 and dq_2/dP_2 are the slopes of the individual component binary isotherms, and y_1 refers to the mole fraction of the preferentially adsorbed component in the gas phase.

The 4 parameter modified polynomial approach originally developed by Van der Vlist and Van der Meijden, was used to determine the binary isotherms from the experimental K_p data [15]:

$$K_p = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3 \quad (5)$$

The binary isotherm functions are derived from Equation 5 as follows:

$$\begin{aligned} dq_1/dP_1 &= B_0 + B_1 y_1 + B_2 y_1^2 & (6a) \\ dq_1 &= (B_0 + B_1 y_1 + B_2 y_1^2) dP_1 \\ P_1 &= P y_1 \\ dP_1 &= P dy_1 \\ \int_0^{q_1} dq_1 &= P_T \int_0^{y_1} (B_0 + B_1 y_1 + B_2 y_1^2) dy_1 \\ q_1 &= P_T \left[B_0 y_1 + \left(\frac{B_1}{2}\right) y_1^2 + \left(\frac{B_2}{3}\right) y_1^3 \right] & (6b) \end{aligned}$$

$$\begin{aligned} dq_2/dP_2 &= C_0 + C_1 y_1 + C_2 y_1^2 & (7a) \\ dq_2 &= (C_0 + C_1 y_1 + C_2 y_1^2) dP_2 \end{aligned}$$

$$\begin{aligned}
P_2 &= Py_2 \\
dP_2 &= Pdy_2 = -Pdy_1 \\
\int_0^{q_2} dq_1 &= -P_T \int_1^{y_1} (C_0 + C_1 y_1 + C_2 y_1^2) dy_1 \\
q_2 &= -P_T \left[C_0 (y_1 - 1) + \left(\frac{C_1}{2} \right) (y_1^2 - 1) + \left(\frac{C_2}{3} \right) (y_1^3 - 1) \right]
\end{aligned} \tag{7b}$$

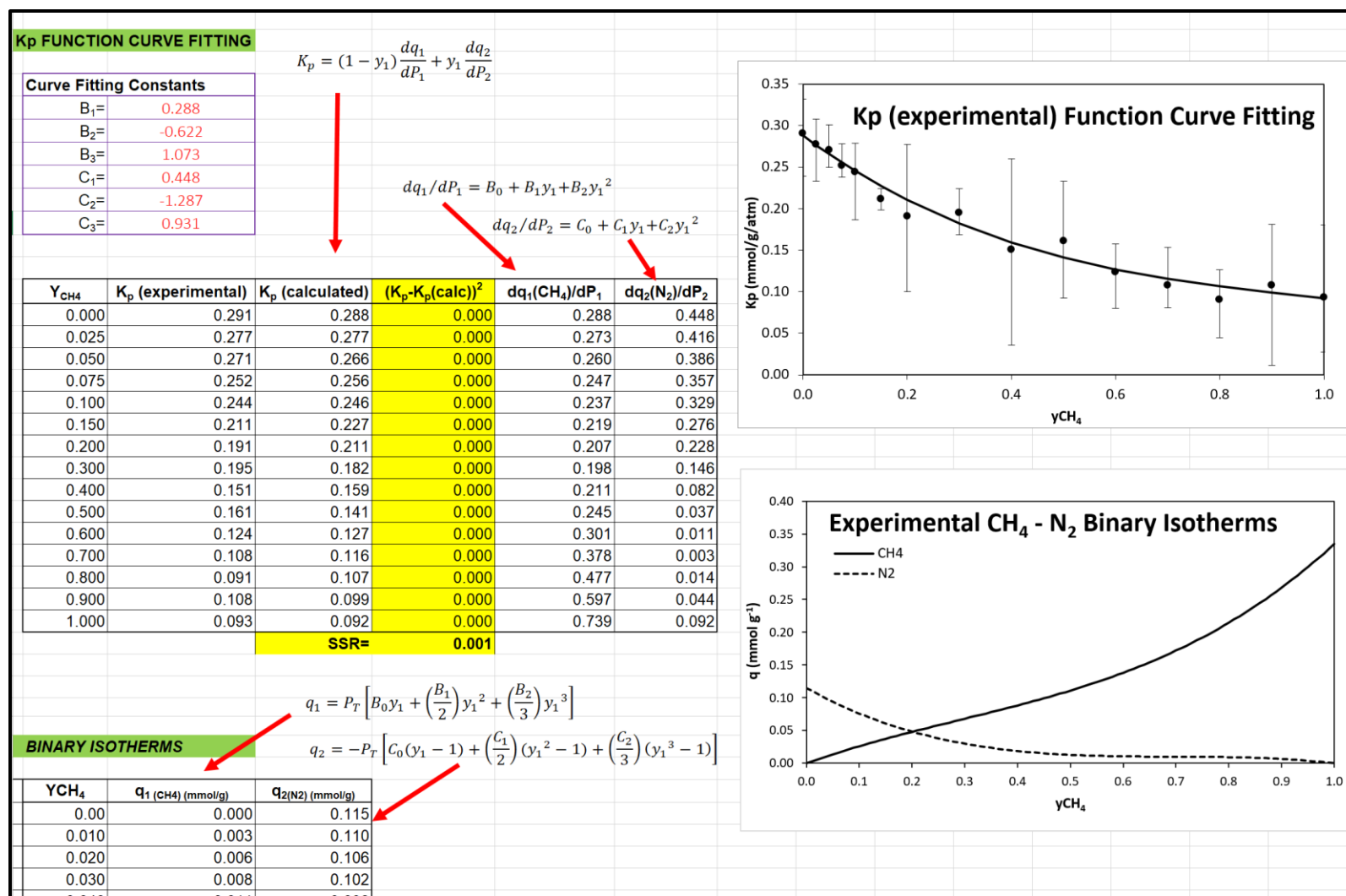
Substituting Equations 6a and 7a into Equation 4 yields the K_p slope function used to model the experimental K_p data.

$$K_p(model) = (1 - y_1)[B_0 + B_1 y_1 + B_2 y_1^2] + y_1[C_0 + C_1 y_1 + C_2 y_1^2] \tag{8}$$

The CPM function must properly represent the K_p experimental data. The B_i and C_i coefficients from Equation 8 are optimized based on minimizing the sum of the squared residuals between the experimental values and the model as follows:

$$SSR = \sum_{y=y_{min}}^{y=y_{max}} \{K_p(experimental) - K_p(model)\}^2 \tag{9}$$

Several constraints are imposed to the K_p model function and systems of equations to properly reflect the binary system are elaborated on in the experimental section of Chapters 2, 4, and 6, respectively [6,11,23]. Figure A.9 shows an example of the spreadsheet that was used to determine the binary isotherms from the experimental binary K_p data.

Figure A.9 Spreadsheet that was used to determine the binary isotherms from the experimental binary K_p data.

The applicability of different mathematical functions has been explored in the literature using this method [6,10–12,15,21,24]. Table A.2 shows a summary of some of the possible forms to different binary systems that may be considered for representing the experimental binary isotherm data using the chromatographic method.

Table A.2. Selected concentration pulse chromatographic methods used in the literature.

MVV-CPM (modified Van der Vlist and Van der Meijden – concentration pulse method)[15]	
4-parameter function	$K_p = A_0 + A_1 y_1 + A_2 y_1^2 + A_3 y_1^3$
Isotherm slope functions	$dq_1/dP_1 = B_0 + B_1 y_1 + B_2 y_1^2$
Binary isotherm functions	$dq_2/dP_2 = C_0 + C_1 y_1 + C_2 y_1^2$ $q_1 = \left[B_0 y_1 + \left(\frac{B_1}{2} \right) y_1^2 + \left(\frac{B_2}{3} \right) y_1^3 \right] P_T$ $q_2 = \left[C_0 (1 - y_1) + \left(\frac{C_1}{2} \right) (1 - y_1)^2 + \left(\frac{C_2}{3} \right) (1 - y_1)^3 \right] P_T$
MTT-CPM (modified Triebe and Tezel-concentration pulse method) [21]	
5-parameter function	$K_p = A_{-1}(y_1) + A_0 + \frac{A_1}{(\beta + y_1)} + \frac{A_2}{(\beta + y_1)^2}$
Isotherm slope functions	$dq_1/dP_1 = B_0 + \frac{B_1}{(\beta + y_1)} + \frac{B_2}{(\beta + y_1)^2}$ $dq_2/dP_2 = C_0 + \frac{C_1}{(\beta + y_1)} + \frac{C_2}{(\beta + y_1)^2}$
Binary isotherm functions	$q_1 = [B_0 y_1 + B_1 \ln[(\beta + y_1)/\beta] + B_2 y_1/\beta(\beta + y_1)^2] P_T$ $q_2 = [C_0 (1 - y_1) + C_1 \ln[(\beta + y_1)/(\beta + 1)] + C_2 (1 - y_1)/[(\beta + 1)(\beta + y_1)]] P_T$
HT-CPM (Harlick and Tezel-concentration pulse method)[24]	
5-parameter function	$K_p = A_1 + A_2 y_1 + A_3 y_1^2 + A_4 \ln y_1 + \lambda $
Isotherm slope functions	$dq_1/dP_1 = B_1 + 2B_2 y_1 + B_3 / (y_1 + \lambda)$ $dq_2/dP_2 = C_1 + 2C_2 y_1 + C_3 / (y_1 + \lambda)$
Binary isotherm functions	$q_1 = [B_1 y_1 + B_2 y_1^2 + B_3 \ln (y_1 + \lambda)/\lambda] P_T$ $q_2 = [C_1 (1 - y_1) + C_2 (1 - y_1^2) - C_3 \ln (y_1 + \lambda)/(1 + \lambda)] P_T$
KT – CPM (Kennedy and Tezel – concentration pulse method)[6]	
2-parameter function	$K_p = A_1 \ln (y_1 + \gamma) + A_2 e^{(\theta y_1)}$
Isotherm slope functions	$\frac{dq_1}{dP_1} = \frac{B_1}{(y_1 + \gamma)} + B_2 e^{(\theta y_1)}$ $\frac{dq_2}{dP_2} = \frac{C_1}{(y_1 + \gamma)} + C_2 e^{(\theta y_1)}$
Binary isotherm functions	$q_1 = P_T \left[B_1 \ln \left(\left \frac{y_1 + \gamma}{\gamma} \right \right) + \frac{B_2}{\theta} (e^{(\theta y_1)} - 1) \right]$ $q_2 = P_T \left[-C_1 \ln \left(\left \frac{y_1 + \gamma}{1 + \gamma} \right \right) + \frac{C_2}{\theta} (e^\theta - e^{(\theta y_1)}) \right]$

A.6. NOMENCLATURE

A,B,C	parameters used for the MVV-CPM in Equations 5 – 8	[mmol·g ⁻¹ ·atm ⁻¹]
A _m	membrane area	[m ²]
B	adsorption affinity constant	[atm ⁻¹]
B ₀	adsorption affinity constant at reference temperature	[atm ⁻¹]
ΔH	limiting heat of adsorption	[kJ·mol ⁻¹]
K	dimensionless Henry's Law constant	[dimensionless]
K _p	dimensional Henry's Law constant	[mmol·g ⁻¹ ·atm ⁻¹]
L	length of the column	[m]
P	pressure	[atm]
P	permeance	[ml(STP)/m ² sPa]
q	adsorption capacity	[mmol/g of adsorbent]
R	universal gas constant	[m ³ Pa/ K mol]
R _p	radius of particle	[m]
t	time	[s]
T	temperature	[K]
T ₀	reference temperature	[K]
$\dot{V}$	volumetric flow rate	[m ³ /s]
X	mole fraction in the gas phase	[dimensionless]
Y	mole fraction in the gas phase	[dimensionless]

Subscripts

1	component 1
2	component 2
i	index
max	maximum
min	Minimum

Greek Symbols

α	adsorption separation factor or membrane ideal selectivity	[dimensionless]
α _n	constant parameter	[dimensionless]
β	kinetic selectivity factor	[dimensionless]
ε	bed porosity	[dimensionless]
μ	mean retention time	[s]
μ _D	system dead time	[s]
v	interstitial velocity	[cm·s ⁻¹]
θ _i	adsorption surface coverage of component <i>i</i>	[dimensionless]
χ	constant parameter	[dimensionless]

Abbreviations

CPM	concentration pulse method

GC	gas chromatograph
IAST	Ideal Adsorbed Solution Theory
MFC	mass flow controller
MVV-CPM	modified Van der Vlist and Van der Meijden – concentration pulse method
SSR	sum of square residuals
TCD	thermal conductivity detector

A.7. REFERENCES

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APPENDIX B

Curriculum Vitae

D. A. Kennedy

(Current as of January, 2020)

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1. **D. A. Kennedy**, M. Khanafer, F. H. Tezel, (2019) “The Effect of Ag^+ Cations on the Micropore Properties of Clinoptilolite and Related Adsorption Separation of CH_4 and N_2 Gases”, *Microporous and Mesoporous Materials*, 281 (1), 123 – 133.
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3. **D. A. Kennedy**, M. Mujčin, C. Abou-Zied, F. H. Tezel, (2019) “Cation Exchange Modification of Clinoptilolite – Thermodynamic Effects on Adsorption Separations of Carbon Dioxide, Methane, and Nitrogen”, *Mesoporous Materials*, 262 (1), 235 – 250.
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5. **D. A. Kennedy**, D. Carter, S. Wilson, B. Kruczek, F. H. Tezel, (2017). “Pore Plugging Synthesis and Characterization of Silicalite-1 Membranes using Tubular TiO_2 Supports: Effect of Support Pore Size on Membrane Performance”, *Can. J. Chem. Eng.*, 96, 1597 – 1611.

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13. **D. A. Kennedy**, T. Omar, F. Handan Tezel, “Preparation and Characterization of Novel Clinoptilolite Membranes for the Treatment of Natural Gas Type Mixtures”, Euro-membrane 2018, Valencia, Spain, July 9 – 13, (2018).
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