Sorption, Transport and Gas Separation Properties of Zn-Based Metal Organic Frameworks (MOFs) and their Application in CO₂ Capture.

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ABSTRACT

Adsorption, separation and conversion of CO₂ from industrial processes are among the priorities of the scientific community aimed at mitigating the effects of greenhouse gases on the environment. One of the main focuses is the capture of CO₂ at stationary point sources from fossil fuel emissions using porous crystalline materials. Porous crystalline materials can reduce the energy costs associated with CO₂ capture by offering high adsorption rates, low material regeneration energy penalties and favorable kinetic pathways for CO₂ separation. MOFs consist of polymeric inorganic networks with adjustable chemical functionality and well-defined pores that make them ideal for these applications. The objective of this research was to test the potential for CO₂ capture on Zn-based MOFs by studying their sorption, transport and gas separation properties as adsorbents and continuous membranes.

Three Zn-based MOFs with open Zn-metal sites were initially studied. Zn₄(pdc)₄(DMF)₂•3DMF (1) exhibited the best properties for CO₂ capture and was investigated further under realistic CO₂ capture conditions. The MOF exhibited preferential CO₂ adsorption based on a high enthalpy of adsorption and selectivity of CO₂ over N₂ and CH₄. Sorption dynamics of CO₂ indicated fast adsorption and a low activation energy for sorption. Diffusion inside the pores is the rate-limiting step for diffusion, and changes in the process temperature can enhance CO₂ separation. Desorption kinetics indicated that CO₂ has longer residence times and lower
activation energies for desorption than N$_2$ and CH$_4$. This suggests that the selective adsorption of CO$_2$ is favored.

MOF/Polymer membranes were synthesized via a solvothermal method with structural defects sealed by a polymer coating. This method facilitates the permeation measurements of materials that cannot form uniform-defect-free layers. The membrane permeation of CO$_2$, CH$_4$, N$_2$ and H$_2$ exhibited a linear relation to the inverse square root of the molecular weight of the permeant gases, indicating that diffusion occurs in the Knudsen regime. Permselectivity was well-predicted by the Knudsen model with no temperature dependence, and transport occurs inside the pores of the membrane. MOF (1) exhibits ideal properties for future applications in CO$_2$ capture as an adsorbent.
ABSTRACT (PUBLIC)

Separation and conversion of carbon dioxide from industrial processes are among the priorities of the scientific community aimed at mitigating the effects of greenhouse gases on the environment. One of the main focuses is the retention and capture of harmful atmospheric gases at stationary point sources from fossil fuel emissions (such as power plants). Research using materials formed by porous crystalline structures where gases can travel at different rates is key for these applications. Porous crystalline materials can reduce the energy costs associated with carbon dioxide capture by offering high adsorption rates, low material regeneration energy penalties and favorable differences in gas velocities and transport properties for the separation of greenhouse gases. MOFs consist of polymeric networks linked by transition metal ions, and have adjustable chemical functionalities and well-defined pores that make them ideal for these applications. The objective of this research was to test the potential for carbon dioxide capture on MOF materials containing Zinc ions by studying their gas adsorption and desorption, the transport of gases through their crystalline pores and their gas separation properties as adsorbents and continuous membranes.

Three crystalline materials were initially tested, with Zn4(pdc)4(DMF)2•3DMF, (1) for simplicity, exhibiting the best properties for the capture and retention of CO2 among the materials. (1) was investigated further under realistic CO2 capture conditions – the conditions of pressure and temperature common in flue gases generated from the production of energy in power plants. MOF
(1) exhibited preferential CO$_2$ adsorption based on a higher bonding energy between the gas molecules and the surface of the material and the preferential adsorption of CO$_2$ molecules over other relevant species present in combustion gases. It was determined that CO$_2$ molecules are transported rapidly through the inside of the pores of the material to reach sites where they are adsorbed, and the energetic requirements to start this process are low. The traveling velocities of gases inside the pores of the material are limited by the physical characteristics of the pores of the crystals, and changes in the process temperature can enhance the separation of carbon dioxide. The regeneration of the material was studied to understand the energy required to take the material back to its original state and reuse it. It was determined that, on average, carbon dioxide spends more time on the surface before going back to the bulk gas and it needs less energy to leave the surface of the MOF when compared to nitrogen and methane. This suggests that the adsorption of CO$_2$ is selective over other typical products of combustion on (1).

Porous crystalline materials can also be applied as selective barriers to gas molecules in a membrane configuration. MOF/Polymer membranes were synthesized and their structural defects were sealed using a polymer coating. This method facilitates the measurements of the transport of gas molecules on materials that cannot form uniform-defect-free layers. The transport of gases through a membrane of (1) is dependent upon the weight of the gas molecules and the relative transport of gases inside the membrane is independent of the temperature in the system. It was concluded that MOF (1) exhibits ideal properties for future applications in CO$_2$ capture as an adsorbent.
To my parents and my sister.
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Chapter 1. Introduction.

1.1. Motivation and thesis overview.

Metal Organic Frameworks (MOFs) are crystalline porous materials composed by a network of transition metal ions and bridging organic ligands\(^1\), they consist of polymeric inorganic networks with high surface areas, defined pore sizes and adjustable chemical functionality. Their chemical functionality, surface area and pore size can be tuned by choosing metal centers and organic ligands that are more appropriate to each application\(^2,3\).

The increasing concern over the deleterious effects of greenhouse gas emissions on the environment has garnered the scientific community’s attention for the search of novel technologies that can minimize their environmental impact; carbon dioxide separation is a critical step when addressing ways for mitigating global warming effects\(^1\). From an energy point of view, a material that is efficient, inexpensive and selective for CO\(_2\) capture and conversion is desirable for these applications\(^3\). Adsorption separation processes by porous materials are among the most promising methods for CO\(_2\) removal from flue gas. MOFs materials have shown potential for gas mixtures separations, specifically in power plant emissions and to a lesser extent in natural gas processing. Industrial applications for CO\(_2\) capture materials can be designed to separate CO\(_2\) from stationary point sources as pre-combustion or post-combustion processes, the approach for separation and the required material properties will be different and unique for each type of separation\(^8\).

For pre-combustion CO\(_2\) capture, promising MOFs exhibit moderately high internal surface areas at pressures/temperatures relevant to CO\(_2\)/H\(_2\) separations, since the nature of their pore surface can be adjusted, interactions of the surfaces with CO\(_2\) can be tuned to increase the gas adsorption and separation. Selectivity of CO\(_2\) over H\(_2\) can be enhanced due to their high surface areas as H\(_2\) packs more efficiently due to its smaller molecular size\(^4\). Pre-combustion occurs at
high pressures, slightly elevated temperatures and high CO\textsubscript{2} concentrations\textsuperscript{3}. Interestingly, it has been previously suggested that high surface areas and extraordinary CO\textsubscript{2} uptake may not make materials ideal for pre-combustion separations, an enhancement in the strength of the sites of adsorption is more determinant for CO\textsubscript{2}/H\textsubscript{2} separations, and this can be achieved with the presence of metal cation sites. Due to the high pressures involved in pre-combustion separation processes, membrane separations become an attractive strategy for CO\textsubscript{2} capture, the pressure of the gas mixture can be used as the driving force to achieve separations, and diffusion will play a central role among the properties that a material requires to successfully serve as a CO\textsubscript{2} separation barrier.

In gas membrane separation applications is primarily important to develop continuous membrane films that are permeable and selective, it has been proven that MOFs materials have properties that make them appropriate for gas separation and adsorption in a membrane configuration\textsuperscript{5,6}. CO\textsubscript{2} capture in MOFs can also be applied as a post-combustion process, in this case the material will be working at low pressures and low CO\textsubscript{2} concentrations, and CO\textsubscript{2}/N\textsubscript{2} will be the mixture to be separated from flue gases; an adequate material should have a high selectivity, high adsorption, a rapid diffusion, since the process is already at low pressures the gas must be desorbed readily with minimum energy costs\textsuperscript{5}. In post-combustion separations a material that enhances the separation through interactions with functionalized pore surfaces will be preferred, due to the similarities in the kinetics diameters of CO\textsubscript{2} and N\textsubscript{2} and the low concentration and partial pressure of CO\textsubscript{2} in the mixture. It is ideal to report adsorption data in the correct range of pressures and temperatures (313 K – 333 K, 150 mbar for CO\textsubscript{2} and 750 mbar for N\textsubscript{2}) and these studies should be preferably done as multicomponent isotherms or in case of using single-component isotherms\textsuperscript{3}, a reliable method that considers interactions in the mixtures should be employed, the ideal adsorbed solution theory (IAST)\textsuperscript{2,4} has been largely used in MOFs and similar functionalized materials for
selectivity predictions. The presence of surface functionality by Nitrogen bases or Organic Functional groups and the accessibility of exposed metal cation sites has been suggested as a mean to improve selectivity, they serve as binding sites with high charge density favoring CO₂ adsorption as it is more polar and possess a greater quadrupole moment. In the case of membrane separations, materials that favor kinetic based separations are priority.

Generally speaking and as described above, there are some desirable characteristics of a material that can successfully capture or separate CO₂: a high adsorption rate, a low desorption energy and a kinetic pathway that favors CO₂ capture in the presence of other gases. Adsorption and membrane separation can be limited by the diffusion of the material to the adsorption sites and by the thermodynamics of adsorption once the gas molecules are at the vicinity of active adsorption sites. An understanding of the mechanisms that govern the sorption and diffusion of gases through adsorbent materials is key in the development of new sustainable methods for CO₂ separation.

There are two main approaches to take advantage of the MOF structures and chemical properties when separating gases: Kinetic-based separations and Thermodynamic separations, the preferred approach will depend upon the properties of the material and the characteristics of the system being separated. In kinetic based separations the diffusivities of gases to the surface and inside the pores of the material are the parameters to model, three main mechanisms describe the diffusion of gases inside pores of crystalline materials, viscous flow, Knudsen diffusion and surface flow, depending on the relative size to the gas molecules, the interactions among gases and between gases and pores, and the driving force that makes diffusion possible. In the case of thermodynamic separations, the affinity and interactions of the material with each of the components in the gas stream is the key parameter. Numerous studies have studied both kinetic-based and thermodynamic-based processes using MOF materials as CO₂ adsorbents and as gas
separation membranes, the fabrication of continuous MOF films has found application in different areas as supported catalysis, molecular sensors and gas separation membranes. 2, 8.

The synthesis of MOF as continuous films for gas separation membranes has been relatively successful and the methods used for membrane synthesis are dependent on the MOF used, the materials used for support and the potential application for the membrane8.

The objective of this research work is to study newly synthesized Zn(II)-based MOF materials with surface functionalities, metal sites and surface areas that favor CO2 separation from flue gas under conditions that mimic CO2 capture in pre-combustion and post-combustion processes, as well as other potential applications in natural gas processing. The main focus is on the investigation of the sorption thermodynamics and kinetics of sorption, as well as the development of continuous MOF membrane films and the study of the diffusion mechanism that reign the transport of gases. This knowledge will be used to determine the best potential applications for the materials and to compare the different kind of separations and transport mechanism for different MOF capture and separation applications, a theoretical base for the study of the sorption and separation properties of crystalline materials is also developed. Chapter 2 introduces the topic through a literature review and theoretical background to have a context of the current research goals in the area CO2 capture with porous crystalline materials. Chapter 3 studies the physical and thermodynamic properties of the sorption of CO2 and N2 on two newly synthesized Zn(II)-based MOFs with aims to determine the best CO2 adsorbent. Chapter 4 studies thermodynamic properties of gas sorption on a microporous MOF with open Zn(II) coordination sites under conditions relevant to pre-combustion and post-combustion CO2 capture; describing the adsorption dynamics and kinetics of desorption on this material to understand the diffusion mechanisms for sorption. Chapter 5 provides a method for MOF membrane formation and an study of its permeability, selectivity and
gas transport mechanism through a porous MOF membrane. **Chapter 6** contains a summary of the main findings and conclusions, including a report on the best applications for these materials and suggestions for future work in the CO₂ capture and separation use of porous crystalline MOFs.

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Chapter 2. Literature review and theoretical background.

2.1. Metal Organic Frameworks. (MOFs)

Metal organic frameworks (MOFs) are a class of porous solids composed by polymeric inorganic networks consisting of metal nodes bridged by organic linkers forming three-dimensional crystalline structures\(^1\). Due to their properties, high surface areas, tunable pore surface and adjustable chemical functionality, they find potential applications in gas storage, gas separations, heterogeneous catalysis and drug delivery\(^2,3\). Among these applications a material that is efficient, inexpensive and selective for CO\(_2\) capture and conversion is desirable due to the increasing levels of greenhouse gas in the atmosphere, porous materials like MOFs have shown potential for gas mixtures separations, specifically in power plant emissions and in natural gas processing\(^1,29\), as separation materials from power plant emissions, CO\(_2\) capture and separation in MOFs can be applied pre-combustion or post-combustion, different material properties are desired for each process\(^1,4\). The main focus of current research is on materials that can be used as preferential CO\(_2\) adsorbents or as gas separation membranes with high selectivity towards CO\(_2\), their use is dependent on the properties of the MOF and the relative diffusion properties and interactions of the gases in the pores of the MOF\(^31\).

2.1.1. MOFs in Pre-Combustion Capture.

For pre-combustion CO\(_2\) capture promising MOFs exhibit moderately high internal surface areas at pressures/temperatures relevant to CO\(_2/H_2\) separations, since the nature of their pore surface can be adjusted, interactions of the surfaces with CO\(_2\) can be tuned to increase the gas adsorption separation\(^1,30\). Selectivity of CO\(_2\) over H\(_2\) can be enhanced due to their high surface areas as H\(_2\) packs more efficiently due to its smaller molecular size\(^4\). Pre-combustion occurs at high pressure, slightly elevated temperatures (5-40 bar and 313) and high CO\(_2\) concentrations\(^1\). It
has been previously suggested that high surface areas and extraordinary CO\textsubscript{2} uptake may not make them ideal for these kind of separations, an enhancement in the strength of the sites of adsorption is more determinant for CO\textsubscript{2}/H\textsubscript{2} separations, and this can be achieved with the presence of metal cation sites. Selectivity is the determining factor for evaluating the efficacy of an adsorbent, in the case of CO\textsubscript{2}/H\textsubscript{2} separations the CO\textsubscript{2} working capacity is equally important, this capacity is measured as the difference in the amounts adsorbed at flue gas pressure and at the lower purge pressure, this parameter would reduce the amount of adsorbent needed to perform the separation efficiently, therefore studying the desorption rate of CO\textsubscript{2} is important to develop materials that are ideal for pre-combustion capture.

Due to the high pressures involved in pre-combustion separation processes, membrane separations become an attractive strategy for CO\textsubscript{2} capture, the pressure of the gas mixture can be used as the driving force to achieve separations, and diffusion will play a central role among the properties that an adsorbent requires to successfully serve as a CO\textsubscript{2} separation barrier. In gas membrane separation applications is primarily important to develop continuous membrane films that are permeable and selective, it has been proven that MOFs materials have properties that make them appropriate for gas separation and adsorption as membrane materials\textsuperscript{3,5}

2.1.2. MOFs in Post-Combustion Capture.

CO\textsubscript{2} capture in MOFs can also be applied in power plant emissions as a post-combustion process, in this case the material will be working at low pressures and low CO\textsubscript{2} concentrations, and CO\textsubscript{2}/N\textsubscript{2} will be the mixture to be separated; a promising material should have a high selectivity, high adsorption, a rapid diffusion and since the process is already at low pressures the gas must be desorbed readily with minimum energy costs\textsuperscript{1}. In post-combustion separations a material that enhances the separation through interactions with functionalized pore surfaces will
be preferred, due to the similarities in the kinetics diameters of CO$_2$ and N$_2$ and the low concentration and partial pressure of CO$_2$ in the mixture. It is ideal to report adsorption data in the adequate range of pressures and temperatures (313 K – 333 K, 150 mbar for CO$_2$ and 750 mbar for N$_2$) and these studies should be preferably done as multicomponent isotherms or in case of using single-component isotherms$^5$, a reliable method that considers interactions in the mixtures should be employed, the ideal adsorbed solution theory (IAST)$^{1,21}$ has been largely used in MOFs and similar functionalized materials for selectivity predictions. The presence of surface functionality by Nitrogen bases or Organic Functional groups and the accessibility of exposed metal cation sites has been suggested as a mean to improve selectivity, they serve as binding sites with high charge density favoring CO$_2$ adsorption as it is more polar and possess a greater quadrupole moment$^6$. In the case of membrane separations, materials that favor kinetic based separations are priority; the parameters to investigate are the relative size of the pores of the membrane to the gas molecules, the interactions among gases and between gases and pores, and the driving force that makes diffusion possible$^{31,32}$.

2.2. Adsorption theory.

Adsorption is a surface phenomenon characterized by an increase in the density of a fluid in the vicinity of a surface due to bonding deficiencies. In the case of adsorption of gases on solid surfaces, adjacent molecules will interact with the surface of a solid permanently leaving the gas phase, the length of the stay of these molecules will depend on various factors: the nature of the surface and its physical characteristics, the nature of the adsorbed gas, the number of layers formed and number of molecules being adsorbed as well as their kinetic energy, among others.

Experimentally, adsorption is measured by volumetric or gravimetric methods, they differ in the way changes in adsorbed amounts on the sample are measured. Volumetric methods measure
changes in pressure as a gas is expanded inside a known volume containing the sample; Gravimetric methods measure changes in weight as the gas is expanded inside a chamber containing a microbalance and the solid adsorbent. Both methods are used to estimate adsorbed amounts as pressure changes and isothermal conditions are fulfilled under certain assumptions that will be discussed in the following section.

A simplified system will be used to understand adsorption measurements, the system will consist of three phases, a pure solid (s, the adsorbent), a gas phase (g, gas in the bulk) and an adsorbed gas phase (a, gas adsorbed into the solid surface). The system will be kept at constant temperature and pressure, while the composition in the adsorbed phase/gas phase will change until equilibrium is reached. For the purposes of this system there will be three different values of fluid density, the density of the adsorbate inside the solid phase will be zero as we are assuming physisorption only; the density at the solid surface and beyond will vary until it reaches a point at a distance \( r \) from the surface of the solid where the density of the gas will be equal to that of the bulk gas (often assumed as equal to the hydrostatic pressure).

2.2.1. Types of adsorption.

Adsorption characteristics will vary depending on the strength of interactions between gas molecules and the solid surface, a gas molecule colliding can undergo three different types of interactions with the surface: chemical adsorption (chemisorption), physical adsorption (physisorption) and, if the energy is greater, absorption. Activation energy plays a determinant role to differentiate the type of adsorption present in a given system. Adsorption occurs when a single gas molecule collides inelastically with a surface having a change in its energy, the molecule must have enough energy to escape the surface or it will become adsorbed, in the case of weak interactions (Van der Walls forces) the molecule may diffuse from site to site before returning to
the gas phase. If stronger interactions exist, electron transfer may occur as the energy may be enough to create a chemical bond (chemical adsorption) and in this case the gas can also penetrate the bulk of the material being now governed by laws of diffusion (absorption). The following discussion will focus on physical adsorption where no chemical bonds are formed and the gas molecules do not penetrate the bulk of the material.

2.2.2. Physical Adsorption.

Physical adsorption occurs due to attractive dispersion forces, short range repulsive forces and electrostatic forces, known altogether as Van der Waals forces. These are forces formed in electrically neutral molecules, the particular case of physisorption of a nonpolar molecule on a nonpolar surface occurs due to dispersion forces. A deeper understanding of physical adsorption and adsorption equilibrium can be achieved by studying the thermodynamics and kinetics of sorption processes, the following discussion will focus on the description of thermodynamics and kinetics of single-gas monolayer adsorption as this will be the theoretical basis for mixed gas-multilayer adsorption, in case this multilayer description is needed to better characterize adsorption on MOF materials.

2.3. Thermodynamics of Physical Adsorption.

Thermodynamics of physical adsorption have been previously described elsewhere,\textsuperscript{7,8} three main assumptions about the adsorbed phase must be made in order to simplify the system and obtain a reasonable thermodynamic solution: (1) The adsorbent is assumed to be thermodynamically inert, any change in thermodynamic properties in the adsorbent surface is assumed to be negligible if compared to changes in the adsorbate phase. (2) The available area for adsorption is invariable in the conditions of temperature/pressure used for the experiments, this
assumption seems reasonable as this work is based on stable/nonflexible MOF crystals. (3) The Gibbs definition of adsorption applies, this point will be further discussed in this section.

2.3.1. Excess Adsorption.

Adsorption measurements are performed by changes in composition (gas expansions) while holding the temperature and pressure of the system constant. In the usual cases of liquid-vapor or solid-vapor equilibrium it would not be possible to vary composition while keeping temperature and pressure constant, there are only 2 degrees of freedom in the system; however, in the case of adsorption, the area of adsorption is an additional thermodynamic variable (related to the constant volume/ mass of the sample for volumetric/gravimetric methods), and the adsorbent is considered thermodynamically inert, therefore there will be three degrees of freedom in the system.

\[
DOF = (# \text{ of components}) - (# \text{ of phases}) + 3 = 3
\]

Equation 2-1

Adsorption of substances below their critical point is considered a process where a gas adsorbed on a surface undergoes a phase transformation, the gas phase becomes an adsorbed film and the amount of heat necessary for this process equals the enthalpy of sublimation for the substance. A film is assumed to be forming on the surface, therefore gas molecules are no longer present in the gas phase and it follows that the adsorbed amount is equal to the change in volume/weight measured by a volumetric or gravimetric method. In cases where adsorption is measured near or above the critical point of the adsorbate, this assumption is no longer valid as, by definition, the substance only exists as a gas, the adsorbed amount cannot be determined directly. Gas molecules will be present in the system as both adsorbed gas molecules and bulk gas molecules, near the surface they will both affect the volume displaced when measuring the adsorption, a sorption measurement will include both types of molecules when defining a vacuum
state with no molecules present in the system, this excess adsorption \( n_e \) was defined by Gibbs as a function of the absolute adsorption \( n_a \) and the adsorbed amount \( V_{ads} \rho \):

\[
n_e = n_a - V_{ads} \rho (P, T)
\]

Equation 2-2

This reference molecules (bulk gas near the surface) will affect the measured value and as the pressure increases, the difference defined by equation 2 will decrease until the increase in adsorption is equal to the increase in density of the bulk gas reaching the Gibbs excess maximum, after this point the measured adsorption will decrease continuously.

Thermodynamically, adsorption is a spontaneous process, where the total free energy of the system decreases, it follows that the Gibbs free energy of the system will decrease, therefore,

\[
\Delta G = \Delta H - T \Delta S < 0
\]

Equation 2-3

In the absence of vibrational entropy, translational entropy is lost as the gas goes from the bulk phase to the adsorbed film, thus \( \Delta S < 0 \), which implies that adsorption must be an exothermic process where \( \Delta H < 0 \). This equation will be the basis for thermodynamic calculations as enthalpy and entropy are available experimentally.

2.3.2. An approximation to thermodynamic calculations.

Gas sorption is measured as a change in concentration as temperature and pressure are kept constant. In a gas-solid adsorption system, under the thermodynamic assumptions previously presented, there will be two phases present in the system, the free gas \( g \) and the adsorbed gas \( a \), each phase is characterized by a chemical potential defined as a function of the Gibbs free energy,

\[
\mu_g = \left( \frac{\partial G_g}{\partial n_g} \right)_{T,P}
\]

Equation 2-4

\[
\mu_a = \left( \frac{\partial G_a}{\partial n_a} \right)_{T,P}
\]

Equation 2-5
A fluctuation in pressure in the system due to an increase in the number of free gas molecules $dn_g$ will move the system from equilibrium. This will result in mass transfer from the free gas to the adsorbed phase as the system must move in the direction of lower free energy, adsorption will occur. The free energy in the system will reach a minimum when the chemical potentials of both phases are equal resulting in a net change of Gibbs free energy equal to zero,

$$dG = (\mu_a - \mu_g)dn_a = 0$$

Equation 2-6

And,

$$\mu_a = \mu_g$$

Equation 2-7

It follows that adsorption results can be used to understand the equilibrium in the system and to find valuable thermodynamic information.

### 2.3.2.1. Enthalpy of adsorption.

Classical thermodynamics calculations at equilibrium under certain assumptions are needed in order to calculate the changes in enthalpy upon adsorption. Calculations can be divided depending on the characteristics of the system; its temperature, pressure and the gas being adsorbed. For most practical cases in this section the ideal gas assumption will be accurate enough to perform any thermodynamic calculations.

#### 2.3.2.1.1. Calculations below the critical temperature of the adsorbed gas.

If the adsorbed gas is below its critical point the Clausius-Clapeyron equation is valid to calculate thermodynamic variables, the following assumptions about the system will be made: (1) The gas phase volume is greater than the volumes of the solid phase or liquid phase, therefore $\Delta V_{sublimation} \ or \ \Delta V_{vaporization} \cong \nu_{gas}$. This also implies a phase change upon adsorption and it will not be valid near or above the critical point of the gas, above the critical point no phase change is possible as there is no equilibrium line in a phase diagram. (2) The enthalpy of adsorption is
equal to the enthalpy of vaporization, the energy for adsorption is equal to the energy necessary to make the gas phase change to liquid phase on the surface of the solid. (3) The gas phase is an ideal gas, $v_{\text{gas}} = \frac{RT}{P}$, this assumption is valid for most practical cases.

From equation 2-7 taking the total derivative, using the Gibbs definition of adsorption,

$$
\mu_a = \mu_g \quad \text{Equation 2-8}
$$

$$
-s_a dT + v_a dP = -s_g dT + v_g dP \quad \text{Equation 2-9}
$$

Rearranging the terms for the vaporization of a substance and substituting equation 3, the classical form of the Clausius-Clapeyron equation can be found,

$$
\left( \frac{dP}{dT} \right)_{\text{vaporization}} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V} \quad \text{Equation 2-10}
$$

Using the ideal gas assumption to find an expression to calculate the enthalpy of adsorption,

$$
\left( \frac{dP}{dT} \right)_{\text{vaporization}} = \frac{p\Delta H}{RT^2} \quad \text{Equation 2-11}
$$

Integrating equation 2-10 from an initial temperature/pressure $(T_1, P_1)$ to a final state at $T_2, P_2$,

$$
\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) = \frac{\Delta H}{RT_1} - \frac{\Delta H}{RT_2} \quad \text{Equation 2-12}
$$

Alternatively, if conditions at the second state are referred to as a constant reference state $C$, the following expression is obtained,

$$
\ln P = -\frac{\Delta H}{RT} + C \quad \text{Equation 2-13}
$$

Thus, if isothermal adsorption data can be fitted to a model which relates pressure and concentration, $P$ can be substituted in equation 2-11 and enthalpy of adsorption information can be calculated as the difference between two states of the system. Equation 2-10 presents the more general case where no assumptions about the gas phase have been made, a different equation of state can then be substituted in equation 2-10 to consider interactions between gas molecules and the surface of the solid. (Van der Waals, Peng-Robinson, Virial EOS among others).
The Clausius-Clapeyron equation approximation has been successfully used to calculate enthalpy of adsorption of numerous porous materials as in the case of zeolites and MOFs. A description of the methodology to calculate heats of adsorption from isothermal data on MOFs has been presented. Sumida et al. reported a review on the values of isosteric heats of adsorption and zero coverage heats of adsorption of CO$_2$ molecules on numerous MOFs, they were calculated from the virial equation and other mathematical fittings to adsorption data. An et al. studied the enthalpy of adsorption of CO$_2$ in a MOF exhibiting Pyridine and Amino-decorated pores. Isosteric heats of adsorption of zeolites 5A and 13X and of MOFs MOF-5 and MOF-177 for CO have been estimated from the Clausius-Clapeyron equation, Choi et al. reported values for the zero coverage heat of adsorption of MOF-5.

2.3.2.1.2. Calculations above the critical temperature of the adsorbed gas.

In cases where the substance is above its critical point, as shown in figure 2-1, an equilibrium line no longer exists in the phase diagram of the adsorbed gas, no assumptions about the energy of adsorption can be made as condensation is not possible.

![General phase diagram](image)

**Figure 2-1.** General phase diagram. No phase equilibrium above the critical point of the substance.
The most general approximation given by the Van’t Hoff equation is pertinent in this case to perform adsorption thermodynamic calculations, starting from the Gibbs-Helmholtz equation at constant pressure,

\[
\left[ \frac{d(\Delta G/\ell)}{d(1/T)} \right]_P = \Delta H \quad \text{Equation 2-14}
\]

Also, the Gibbs free energy of the system is related to its adsorption equilibrium constant by,

\[
\frac{\Delta G}{T} = -R \ln K_{ads} \quad \text{Equation 2-15}
\]

\(K_{ads}\) is the adsorption equilibrium constant which can be found by fitting isothermal data to an adsorption model (i.e. Langmuir), it is a constant that relates the changes in pressure and concentration inside an adsorption system. Substituting equation 2-15 in equation 2-14,

\[
\left[ \frac{d \ln K}{d(1/T)} \right]_P = -\frac{\Delta H}{R} \quad \text{Equation 2-16}
\]

Integrating equation 2-16 to get the final expression,

\[
\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) - \frac{\Delta H}{R T_1} - \frac{\Delta H}{R T_2} \quad \text{Equation 2-17}
\]

Thus, once again, if the isothermal data if fitted to a model to find values of \(K_{ads}\), equation 2-17 can be used to calculates changes in enthalpy upon adsorption. It is remarkable to note that Van’t Hoff equation does not make assumptions about the gas phase of the system.

The Van’t Hoff equation approximation and its plot has been applied to numerous systems to describe the energy of adsorption of gases on porous materials. Valenzano et al\(^3\) reported values of CO and CO\(_2\) molecules physisorbed on the coordinately unsaturated Zn(II) metal sites of MOF-74-Zn, while values of enthalpies of adsorption of CO\(_2\), CH\(_4\) and C\(_2\)H\(_2\) on microporous mixed MOFs were reported by Zhang et al\(^{11}\) following a similar approach.
2.3.2.2. Entropy of adsorption.

For calculations below the critical temperature, the Clausius-Clapeyron equation gives a general relationship to calculate changes in entropy upon adsorption under the assumptions previously mentioned,

\[
\left(\frac{dp}{dT}\right)_{\text{vaporization}} = \frac{\Delta S}{v_g} = \frac{\Delta H}{Tv_g} \quad \text{Equation 2-18}
\]

From equation 2-18 the change of enthalpy upon adsorption is a function of the amount of gas adsorbed on the solid phase, and can be calculated as,

\[
\Delta S_{ads} = \left(\frac{dp}{dT}\right)_{\text{vaporization}} v_g \quad \text{Equation 2-19}
\]

In cases where the enthalpy of adsorption has been previously calculated, equation 2-19 takes the following form,

\[
\Delta S_{ads} = \frac{\Delta H_{ads}}{T} \quad \text{Equation 2-20}
\]

Similarly the Van’t Hoff equation can be used above the critical temperature of the gas species to obtain an expression to calculate the entropy upon adsorption, using the definition \( \Delta G = \Delta H - T\Delta S \) (equation 2-3) and substituting in equation 2-17 the final form of the equation is presented,

\[
\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{Equation 2-21}
\]

Another useful set of thermodynamic relationships come from combining the Clausius-Clapeyron equation and the Van’t Hoff equation, in cases where the Clausius-Clapeyron equations are still valid, if we take equation 2-12 as equal to equation 2-17, we obtain the following expression,

\[
\ln \frac{p_2}{p_1} = \ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2-T_1}{T_1T_2}\right) \quad \text{Equation 2-22}
\]

Consequently, from equation 2-13 and equation 2-20,

\[
C = \frac{\Delta S}{R} = \frac{\Delta H}{RT} \quad \text{Equation 2-23}
\]
Then,

\[ \ln K = \ln P = -\frac{\Delta H}{R T} + C = -\frac{\Delta H}{R T} + \frac{\Delta S}{R} \]  \hspace{1cm} \text{Equation 2-24} \]

Equation 2-23 relates the adsorption equilibrium constant to the pressure of the system in order to calculate the enthalpy and entropy of adsorption.

Once the enthalpy and entropy of adsorption have been defined, the Gibbs free energy of the system and therefore its equilibrium can be calculated from equation 2-3 or equivalently equation 2-15, the system must necessarily reduce its energy upon adsorption.

2.3.3. **Fitting experimental data to adsorption isotherm models.**

Experimental adsorption data using gravimetric or volumetric methods to measure amounts of gas adsorbed under isothermal conditions can be used to calculate thermodynamic adsorption variables, the accuracy of these calculations will rely on the applicability of the assumptions made to develop the thermodynamic theory and on the exactitude of the chosen fit equations to describe experimental data. For the general purposes of the gases and pressure/temperature range used during experimentation, it is safe to consider the ideal gas assumption and to approximate the absolute adsorption as the excess adsorption, this was described in the previous section from the Gibbs adsorption theory. Under this conditions, adsorbed amounts can be obtained directly from a gravimetric or volumetric adsorption at constant temperature, therefore data representing concentration as a function of pressure will be available by fitting any experimental data to a sorption model.

Adsorption models differ among them in the type of interactions that are considered (adsorbate-adsorbent, adsorbent-adsorbent, among others), the number of layers of adsorption on the surface of the solid and the homogeneity of the surface among others. Under the experimental
conditions, 5 different models will be considered to fit isothermal experimental data; the linear interpolation model, the virial fitting equation, the Freundlich isotherm model, the Langmuir isotherm model and the Langmuir-Freundlich model.

The simplest way to fit isothermal data is through a linear interpolation, in this case no fitting equation is used and the interpolation is used to correlate values of pressure to concentration, this method does not provide any certainty or general method to calculate values of enthalpies of adsorption. Experimental data can also be fitted to a virial-type equation, where

\[ \ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \]  

Equation 2-25

where \( P \) is the pressure, \( N \) is the amount of gas adsorbed, \( T \) is the temperature, \( m \) and \( n \) are the number of virial coefficients required for fitting, and \( a \) and \( b \) are virial coefficients. The number of virial coefficients \( a \) and \( b \) can be adjusted in this model to best fit the data to this empirical model, nonetheless, it must be considered that as with any polynomial model a higher number of terms will increase the coefficients \( n \) and \( m \) introducing an undesirable curvature among data points, the higher number of terms will also reduce the physical significance of the virial coefficients obtained from the fit. Another problem always found in fitting data to virial-type equation is the presence of multiple minima in the data, a non-linear least squares regression may produce multiple fits that represent the data accurately under different values of \( a \) and \( b \) virial coefficients, this can be overcome by having an initial estimate of the values of the virial coefficients in order to have a better initial guess to approximate the data.

The virial coefficients \( a_0 \) and \( b_0 \) are related to the zero coverage heat of adsorption and the Henry's law adsorption constant \( K_H \). Then, the advantage of the virial-type equation is that it can be used to estimate the zero-coverage heat of adsorption as it has a limit as the pressure goes to
zero. From this equation, enthalpies of adsorption can be estimated as a function of surface coverage, using the Clausius Clapeyron equation,

\[ Q_{st} = -R \left( \frac{d\ln P}{dT} \right)_N = -R \sum_{i=0}^{m} a_i N^i \]  

Equation 2-26

Then, the Henry’s law value of enthalpy can be estimated as the zero-coverage isosteric heat of adsorption, to be written as Equation 2-27,

\[ Q_{st} = -R \lim_{N \to 0} \left( \sum_{i=0}^{m} a_i N^i \right) = -Ra_0 \]  

Equation 2-27

Values of \( b_0 \) are also related to the physically meaningful quantity \( K_0 \) which is related to the Henry’s law adsorption constant \( K_H \) by equation 2-28,

\[ K_H = K_0 \exp \left( \frac{q_0}{RT} \right) \]  

Equation 2-28

\[ K_0 = \exp(-b_0) \]  

Equation 2-29

In the limit where pressures are low and gases behave as ideal gases, adsorption will be a straight line and a simple way to represent this behavior is given by Henry’s Law, this approach is also useful to estimate single gas adsorption when coverage goes to zero as will be mentioned in the next section. As pressure increases this model will be too simple to describe the system,

\[ C_a = K_H P \]  

Equation 2-30

where \( C_a \) represent the adsorbed gas concentration. A different approach is to consider adsorption a kinetic process with an energy of adsorption that describe interactions between the surfaces and gas molecules, treating the mass transfer between them with the kinetic theory. The rates of adsorption and desorption must be equal if the system is in dynamic equilibrium for a monolayer of adsorbent on the surface. For the particular case of the Langmuir model\(^1\) the following assumptions are made: (1) gas molecules are treated as ideal gases, (2) the available adsorption sites are identical, (3) the energy of adsorption is independent of the adsorption sites
that each molecule is occupying. We must first define a fractional coverage of the adsorption sites, \( \theta \), which relates the number of molecules on the surface \( (n_a) \) to the total number of molecules that will cover a monolayer on the surface \( (n_s) \),

\[
\theta = \frac{n_a}{n_s}
\]

Equation 2-31

The rate of adsorption on the surface of the material can be expressed in terms of first order kinetics,

\[
 r_{\text{ads}} = k_{\text{ads}} c_{\text{gas}} c_{\text{ads sites}} = k_{\text{ads}} c_{\text{gas}} (1 - \theta)
\]

Equation 2-32

Where \( k_{\text{ads}} \) is the adsorption constant, \( c_{\text{gas}} \) is the concentration of “free gas” and \( c_{\text{ads sites}} \) is the number of sites available in the adsorption monolayer. Similarly, the rate of desorption,

\[
 r_{\text{des}} = k_{\text{des}} c_a
\]

Equation 2-33

Where, \( k_{\text{des}} \) is the desorption constant and \( c_a \) is the concentration of molecules adsorbed on the surface. At equilibrium \( r_{\text{ads}} = r_{\text{des}} \), therefore,

\[
\theta = \frac{k_{\text{ads}} c_{\text{gas}}}{k_{\text{des}} + k_{\text{ads}} c_{\text{gas}}}
\]

Equation 2-34

Taking \( K = \frac{k_{\text{ads}}}{k_{\text{des}}} \), and from the Langmuir assumptions using ideal gas law to relate concentration to pressure, we obtain the expression for the Langmuir isotherm,

\[
\theta = \frac{KP}{1+KP}
\]

Equation 2-35

In the limit of low pressures, the Lagmuir isotherm becomes Henry’s law,

\[
\lim_{P \to 0} \frac{KP}{1+KP} = KP
\]

Equation 2-36

Under Langmuir assumptions and if a monolayer of gas on an homogeneous surface applies, Langmuir isotherm is a very useful simplified model, however as pressure increases it may under predict adsorption due to the excess of molecules present in the bulk phase or to the increasing adsorption in multiple layers due interactions between molecules. Values of Langmuir constants
and adsorption capacities have been presented for several MOFs studied for CO$_2$ capture including MOF-5 and MOF-177$^{2,10}$, and to other widely studied adsorbents like zeolites and activated carbons.$^{17,18}$

Freundlich proposed an empirical model that relates the quantity of gas adsorbed to the pressure of the system$^{10}$, from Henry’s law, at low pressure the extent of adsorption is proportional to pressure,

$$\theta \propto P$$  \hspace{1cm} \text{Equation 2-37}

And, at high pressures the extent of adsorption will be independent of pressure, (this assumption is one of the limitations of the model),

$$\theta \propto P^0$$  \hspace{1cm} \text{Equation 2-38}

Therefore at intermediate values of pressure, the extent of adsorption must be proportional to the pressure raise to an exponent between 0 (high pressures) and 1 (low pressures), that proportionality is given by $k$, the Freundlich adsorption constant,

$$\theta = KP^{1/n}$$  \hspace{1cm} \text{Equation 2-39}

In this expression $k$ is an indication of adsorption capacity, and $1/n$ is an indication of the strength of adsorption, that is, a more heterogeneous adsorption bidding environment will be suggested by values of $1/n$ far away from the Henry’s law value. Freundlich isotherm will over predict the behavior of adsorption at high pressures as it considers a constant increase of adsorption with pressure as pressure increases.

A model that tries to overcome the shortcoming of Langmuir and Freundlich model is the Langmuir-Freundlich isotherm also known as SIPS model$^{16,17}$. This model improves the Langmuir adsorption model by considering heterogeneous adsorption sites by including an $1/n$ term from Freundlich empirical model, this model performs better predicting behavior for monolayers of
ideal gases at high pressures, however the Langmuir parameter will lose physical significance by the inclusion of the empirical quantity $n$.

$$\theta = \frac{KP^{1/n}}{1 + KP^{1/n}}$$

Equation 2-40

Depending upon the characteristics of the material and the adsorbed gas one of the above models is chosen to have a correlation between concentration of the gas and pressure of the system, this fitted value of pressure can then be substituted in Clausius-Clapeyron equation or Van't Hoff equation to obtain values for thermodynamic variables, in the case of the Clausius-Clapeyron the following expression will be used,

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1T_2}$$

Equation 2-41

where $P_i = $ pressure for isotherm $I$, $T_i = $ temperature for isotherm $I$ and $R = 8.315 J/K mol^{-1}$, if the isotherm is above the critical temperature the following expression for the Van’t Hoff equation will then be used,

$$-\frac{\Delta G_{ads}}{RT} = \ln \kappa_{ads} = \frac{-\Delta H_{ads}}{RT} + \frac{\Delta S}{R}$$

Equation 2-42

In this case a plot of $k_{ads}$ vs $1/T$ should be made to obtain values of $\Delta H_{ads}$ as the slope of the curve that are valid within a range of temperatures. (with $\Delta S$ as intercept) A particular case of Van’t Hoff equation is given by Arrhenius equation, where kinetic equilibrium constants are known, in this particular case, the $\Delta H$ term will be the activation energy for adsorption and the pre-exponential factor will be given by the intercept of the plot, the Arrhenius equation has the following form:

$$K_{eq} = Ae^{\frac{-E_A}{RT}}$$

Equation 2-43

where $K_{eq}$ is the adsorption equilibrium constant, $A$ the Arrhenius pre-exponential factor related to the entropy of the system and $E_A$ the activation energy for adsorption.
2.3.4. Adsorption Selectivity.

In the absence of mixed-gas adsorption isotherms, adsorption selectivity can be estimated by different methods from single-gas adsorption experiments to find a selectivity factor.

A first approximation is to calculate the adsorption selectivity as the ratio of Henry’s Law constant obtained by fitting experimental data at low pressures to the ideal gas model. This value would give an idea of the initial selectivity as surface coverage (and pressure) goes to zero, it is preferably to calculate this value at pressures/temperatures that are relevant to the process in study; pre-combustion capture or post-combustion capture. If Henry’s constants are found, selectivity can be found as given by equation 2-44

\[
S = \frac{H_1}{H_2}
\]

Equation 2-44

where \( S \) is the selectivity of \( I \) over \( 2 \) and \( H_1 \) and \( H_2 \) are the Henry’s law constant for both gases on the material at the pressures and temperatures in study.

A second approach to estimate selectivity is to consider the selectivity factor\(^1\), which relates the molar ratio of the gases being adsorbed at the partial pressures that are relevant to a given process; the selectivity factor is calculated as,

\[
S = \frac{q_1/q_2}{p_1/p_2}
\]

Equation 2-45

where \( q_i \) is the mass of adsorbed gas \( i \) at the relevant partial pressure, and \( p_i \) is the partial pressure of component \( i \).

A final approach to estimate adsorption selectivity is using the Ideal Adsorbed Solution Theory (IAST). Under the assumptions about adsorption defined in the previous section (Ideal gas applies, adsorbent is chemically inert and its area does not change, Gibbs definition of adsorption applies and Surface for adsorption is homogeneous), it is proposed that the activity coefficients for a mixed adsorbed mixture can be defined in the same way a fluid mixture is defined thermodynamically.
The derivation of this theory is beyond the scope of this dissertation, however it may be found elsewhere\textsuperscript{20}. If adsorption isotherms for both components at relevant pressures for adsorption are fitted to the isotherm models previously presented, the mole fraction of each species in mixture can be calculated by\textsuperscript{1},

\[ \int_0^P \frac{y_i}{x_i} \frac{F_i(P)}{P} dP = \int_0^P \frac{y_j}{x_j} \frac{F_j(P)}{P} dP \]

Equation 2-46

where $F_i$ is the fit for component $i$, $F_j$ is the fit for component $j$, $P$ is the total pressure and $x_i$ and $y_i$ are the adsorbed and bulk phase mole fractions of component $i$. This method has been shown to be accurate in predicting selectivity of gases on MOF\textsuperscript{1}, values of CO$_2$:N$_2$ and CO$_2$:CH$_4$ selectivity have been previously presented on other MOF materials\textsuperscript{11}, and H$_2$ selectivity on MOFs has been reported for pre-combustion CO$_2$ capture\textsuperscript{21}.

2.4. Kinetics of Sorption.

The modelling of adsorption is fundamental to understand the phenomena behind these processes and for the design of possible industrial applications, there are two main components that describe adsorption/desorption processes on a solid surface, thermodynamics equilibrium and kinetics. Thermodynamics of adsorption give us an insight to the equilibrium of the adsorption process, they only provide information about the final state of the system once equilibrium has been reached; however adsorption/desorption processes are time dependent and to fully understand their nature is imperative to study the rate of change in their chemical properties with time, the dynamics of sorption. Kinetics provide information about the rate of adsorption, the adsorption efficiency of adsorbents, the transport characteristics of an adsorbent, residence times of adsorbents on surfaces and an insight of the mechanisms of adsorption and rate controlling steps. Numerous models have been suggested to study kinetics of adsorption which can be classified as
Adsorption Diffusion models and Adsorption Reaction models, the main difference between both approaches is in the way they describe the kinetics of adsorption.22

Adsorption diffusion models describe kinetics as processes constructed by different steps, describing each step individually, in the general case of physical adsorption 6 steps are involved in the adsorption/desorption process. Three steps for adsorption and three desorption steps; (1) Diffusion of the gas particles from the bulk phase to the surface of the solid (film diffusion), (2) Diffusion of the gas molecules from the pore mouth through the pores/along the pore walls to the adsorption sites (intraparticle diffusion), (3) Adsorption of gas molecules at the active sites of the solid (adsorption equilibrium, usually studied by thermodynamics), (4) Desorption of the particles from the solid after they have overcome the internal energy threshold to leave the surface (desorption equilibrium, usually studied by thermodynamics), (5) Diffusion of the gases from the interior of the surface through the pores/along the pore walls to the external surface, (6) Diffusion from the external surface to the bulk fluid. In general, from the kinetics study of physical adsorption point of view steps (3) and (4) are rapid and negligible equilibrium processes (often studied by adsorption thermodynamics), physical adsorption is then dominated by film diffusion or intraparticle diffusion.

Generally in a pure gas adsorption process with no resistance to film diffusion, kinetics will be controlled by intraparticle diffusion, which is diffusion from the external surface through the pores to the active sites of adsorption. Among the kinetics models to describe adsorption as an adsorption diffusion process are the Liquid Film diffusion model (Film diffusion mass transfer rate equation), the Intraparticle diffusion model (Homogeneous solid diffusion model, Webber-Morris model and Dumwald-Wagner model) and the Double exponential model, it is beyond the scope of this chapter.
a detailed description of each of these models, literature reviews have been presented in this regard\textsuperscript{22,23}.

In the case of adsorption reaction models, they consider the whole process of adsorption without considering each individual step, mass transfer resistances are lumped as a single film making resistance to adsorption/desorption. It is important to emphasize the fact that adsorption-reaction can refer to the formation of a weak bond at the active site of adsorption and not necessarily the formation of a chemical bond. It is then intuitive the relationship between adsorption-diffusion models and adsorption-reactions models, if one step only of the adsorption-diffusion model is considered as rate controlling, values of coefficients obtained from adsorption-reaction models must be related to this adsorption step. Among the most important adsorption diffusion models are the pseudo-first order rate equation, pseudo-second order rate equation, First-order rate equation, second order rate equation and the Elovich’s equation. Numerous studies have been made to relate adsorption-diffusion models to adsorption-reaction models and make it possible to deduce information about adsorbent-adsorbate interaction from kinetic models\textsuperscript{22,23}.

This work concentrates in adsorption of single gases and therefore no external barriers to transport of gases to the external surface of the adsorbent are expected; moreover, the adsorption of the gas at equilibrium sites is considered instantaneous once the gas has travelled through the porous channels of the adsorbent (which is dominated by thermodynamics and not kinetics), therefore it can be safely assumed that all the resistance to transport is given by intraparticle diffusion. Adsorption-reaction methods and one adsorption-diffusion method will be studied in detail in the following section to describe kinetics of adsorption of gases of MOFs.
2.4.1. Driving force for transport.

The first step to study the transport of molecules from the bulk of the gases to the interior of the pores of an adsorbent (active adsorption sites) is to understand the driving forces that are causing the transport process. The most detailed way to describe driving forces for transport comes from thermodynamics, using the chemical potential as the driving force for transport\(^\text{24}\), the chemical potential driving force model (CPFD) postulates that,

\[
J(r, t) = -B \cdot C(r, t) \left[ \frac{\partial(\mu(r,t)/RT)}{\partial r} \right]_t
\]

Equation 2-47

where \(J(r,t)\) is the flux of gas at radius \(r\) and time \(t\), \(C(r,t)\) is the instantaneous concentration of adsorbate, \(T(r,t)\) is the local temperature, \(B\) is the mobility of the adsorbate, \(\mu\) the instantaneous chemical potential and \(R\) is the ideal gas constant. The chemical potential can be defined from classical excess thermodynamics as,

\[
\mu(r, t) = \mu^0(T) + RT\ln(P(r, t))
\]

Equation 2-48

where \(\mu^0\) is the standard state gas phase chemical potential of the pure gas and \(P(r,t)\) is the pure gas partial pressure in equilibrium with the adsorbate phase. In the particular case of isothermal adsorption, equation 2-47 reduces to,

\[
J(r, t) = -D \left[ \frac{\partial C}{\partial r} \right]_t \text{, at constant } T
\]

Equation 2-49

where,

\[
D = B \left[ \frac{d\ln P}{d\ln C} \right]_T
\]

Equation 2-50

The Isothermal Fickian diffusion model, \(D\) is the diffusivity of the gas related to \(B\) by the Darken correction\(^\text{24}\), the derivative term in equation 2-50 is the inverse slope of the equilibrium adsorption isotherm.
A simplified approximation to express the driving force is to consider a linear driving force for transport, dealing with average adsorbate concentrations inside the adsorbent particle rather than a differential term. The Linear Driving Force model proposed originally by Glueckauf and Coates suggest that the rate of uptake into adsorbent is proportional to the deviation from equilibrium, that is, the difference between the equilibrium amount adsorbed of gas that would be in equilibrium with the gas phase at a given temperature, and the amount of absorbate taken by the adsorbent at a given time which can be found from gravimetric measurements. This model uses a mass balance and assumes that mass transfer resistances are lumped in a film inside the adsorbent particle, therefore it gives a global mass transfer coefficient that considers all the resistances to mass transfer, intra and extra particle resistances. The following mass balance can be applied considering the adsorbent particle as our system,

\[
\text{Rate of accumulation of adsorbate in the adsorbent} = \text{rate of transfer of adsorbate across the mass transfer resistances} \quad \text{Equation 2-51}
\]

The rate of accumulation will be given by,

\[
\text{rate of accumulation} = \frac{\partial q}{\partial t} \quad \text{Equation 2-52}
\]

where \( q \) is the average adsorbate concentration on the adsorbent, since this is a linear model the driving force is the concentration change, given by,

\[
driving \ force \ for \ mass \ transport = (q^* - q) \quad \text{Equation 2-53}
\]

where \( q^* \) is the adsorbate concentration that would be in equilibrium with the gas phase partial pressure of the adsorbent (assumed as the equilibrium concentration) and \( q \) is the amount of gas taken by the adsorbent at a given time. A lumped mass transfer coefficient relates the accumulation term to the driving force for transport, \( k_t \), finally the LDF equation is given as,

\[
\frac{\partial q}{\partial t} = k_t (q^* - q) \quad \text{Equation 2-54}
\]
This model has been widely used in the study of kinetics of zeolites, carbon fibers and monoliths\textsuperscript{2,18,26,27}. Depending on the geometry of the adsorbent the values of mass transfer coefficients \( k_f \) can be related to effective diffusion coefficients, solutions for a number of different adsorbent geometries have been provided previously\textsuperscript{26}. The use of this model provides an analytical, simple and physically consistent approach to understand the kinetics of adsorption and estimate mass transfer coefficients.

Desorption kinetics can be studied following a similar procedure as described for adsorption kinetics, the Linear driving force model will have the exact same solution but with inverted limits of integration in equation 2-54. In the particular case where one molecule is adsorbed and then desorbed without any changes in the process (i.e. chemical reaction or chemisorption), a first order process can be assumed as in equation 2-55,

\[
M(ads) \rightarrow M(des) 
\]

Equation 2-55

When first order kinetics are assumed and the linear driving force model is applied to predict rate constants, the transport coefficient in intimately related to the surface residence time, which is the average time that a molecule will be adsorbed on a surface before it desorbs back to the bulk gas at the given pressure and temperature of the experiment, the average residence time \( \tau \) will be given by equation 2-56,

\[
\tau = \frac{1}{k_{des}} 
\]

Equation 2-56

where \( k_{des} \) is the transport constant estimated using the Linear Driving Force model. Activation energies for the kinetics of adsorption/desorption can be estimated using Arrhenius equation as in section 2.3.3.
2.4.2. Micropore diffusion model.

A second approach to calculate diffusion coefficients for intraparticle diffusion\cite{28} is the use of a numerical correlation, under an isobaric system the following boundary conditions can be defined in a crystal structure,

\[
q = q_\infty \text{ within the surface for } t > 0
\]

\[
q = q_0 \text{ inside the crystal at } t = 0
\]

The mass transfer flow in an amorphous and homogeneous sphere or radius \( R \), with constant diffusion coefficient (independent of concentration) can be expressed as,

\[
\frac{\partial q}{\partial t} = \frac{D_A}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
\]

where \( q \) is the concentration of gas in the adsorbent varying with radial position and \( D_A \) is the transport coefficient, independent of \( q \). A solution for this equation has been obtained elsewhere for the case of an infinite bath and the given boundary conditions\cite{28},

\[
\frac{q}{q_\infty} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} \exp \left( -\frac{D_A n^2 \pi^2 t}{R^2} \right)
\]

The average value of concentration in a spherical particle is given by, \( \bar{q} \) as,

\[
\bar{q} = \frac{3}{R^2} \int_0^R q(r) r^2 dr
\]

Substituting equation 2-59,

\[
\frac{\bar{q}}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_A n^2 \pi^2 t}{R^2} \right)
\]

For short times, given as \( \bar{q}/q_\infty < 0.3 \), equation 2-60 can be written as,

\[
\frac{\bar{q}}{q_\infty} = 6 \left( \frac{-D_A t}{R^2 \pi} \right)^{1/2}
\]

Equation 2-61 can be linearized to obtain values of \( D_A \) from the slope of the curve. This solution gives values assuming constant surface concentration, which is a reasonable assumption at low coverage. Some studies\cite{10} suggest the use of an approximation of equation 2-60 for long
times, however this approximation implies the assumption of constant surface concentration, this assumption is likely to be violated at long time and therefore equation 2-61 represents the best approximation for this model.

2.5. MOF membrane separations.

Gas separations using membranes are processes in which one chemical specie is separated from a mixture in the presence of a barrier due to the preferential affinity for the membrane. This preferential affinity in mainly caused by favorable chemical interactions between molecules and the solid; or differences in diffusion properties of the components of the mixture. Membranes have been addressed for years as one of the main research focuses when trying to solve environmental related issues that arise from anthropogenic emissions. Recently, one of the main focuses of MOFs research is the adsorption, separation and conversion of CO2 from industrial processes to mitigate the effects of the production of greenhouse gases; researchers are actively looking for solutions at stationary point sources as in the case of power plant emissions and natural gas separation processes. MOFs present a solid alternative when trying to find materials with ideal properties for this capture and separation processes. There are two main approaches to take advantage of the MOF structures and chemical properties when separating gases: Kinetic-based separations and Thermodynamic separations. In kinetic based separations the diffusivities of gases to the surface and inside the pores of the material are the parameters to model, three main mechanisms describe the diffusion of gases inside pores of crystalline materials, viscous flow, Knudsen diffusion and surface flow, depending on the relative size to the gas molecules, the interactions among gases and between gases and pores, and the driving force that makes diffusion possible. In the case of thermodynamic separations, the affinity and interactions of the material with each of the components in the gas stream is the key parameter. Numerous studies have studied both
kinetic-based and thermodynamic-based processes using MOF materials as CO2 adsorbents and gas separation membranes, the fabrication of continuous MOF films has found application in different areas as supported catalysis, molecular sensors and gas separation membranes\textsuperscript{1,29,33-36}.

The synthesis of MOF as continuous films for gas separation membranes has been relatively successful and the methods used for membrane synthesis are dependent on the MOF used, the materials used for support and the potential application for the membrane\textsuperscript{29}. A complete study of the properties and applicability of crystalline membranes to a particular separation process must include a detailed description of their transport mechanisms, their physical and chemical properties, and the relative velocity and affinity of the species being separated. A description of the theory behind these characteristics follows in this section.

2.5.1. Transport mechanisms of MOF membranes.

Mass transport through a porous membrane is characterized by molecular interactions and collisions between gas molecules and the porous media\textsuperscript{32}, these are mainly affected by the pore structure, its functionality and the properties of the flowing gas\textsuperscript{37}. Three main mechanisms describe the transport of gases into porous membranes: Viscous flow, surface flow and Knudsen diffusion\textsuperscript{31,32,37}. Each flow regime is a function of the size of the crystalline pores of the material, the kinetic diameter of the molecules flowing, the driving force for transport and the molecular/superficial interactions that govern the transport\textsuperscript{32,37}. The Knudsen number ($K_n$) can be used to estimate the preferential mechanism of diffusion through the pores of a crystalline material (equation 5-2)\textsuperscript{31,32},

$$K_n = \frac{\lambda}{d_p}$$

Equation 2-62

This number relates the mean free path $\lambda$, defined as the distance that a gas molecule has to travel to collide with another gas molecule, to the pore diameter of the material ($d_p$). $K_n$ values greater than 10 suggest that Knudsen diffusion and viscous flow will be the main diffusion
mechanisms in absence of other interactions among molecules and with the pore walls. Viscous flow occurs mainly due to pressure differences inside pinholes and cracks on the membrane surface, this is the bulk flux of the gas also known as convective flow, this mechanism can be discarded is the membrane obeys the Knudsen diffusion behavior or if the transport of a non-adsorbable gas is independent of pressure. Knudsen diffusion occurs as the number of collisions between the gas molecules and the pore walls is greater than the effective number of collision between molecules. Values of \( K_n \) between 1 and 10 suggests the presence of different transport mechanisms inside the pores. Surface flux occurs when gas molecules are adsorbed by the walls of the system, molecules will stay on the surface until they acquire an energy exceeding the energy barrier to return to the gaseous phase, at this moment the molecules will escape the surface in a random direction. Transport through a porous membrane will be characterized by a combination of all these mechanisms; nonetheless, the dominant mechanism will determine the degree of separation that can be achieve with the material in study when kinetic effects dominate over thermodynamic effects.

The total molar flow of a gas \( (a) \) inside the pore of a crystalline membrane can be defined from a one-dimensional mass balance about the differential element in the control volume shown in figure 2.2 with cross sectional area \( A_c \), length \( L \) and diffusion of \( a \) through the solid represented by \( D_{ab} \). This control volume assumes no generation or consumption of \( a \) and no accumulation in the system, the balance equation will be given by equation 2-63,

\[
\text{In} - \text{Out} + \text{Gen} = \text{Acc}
\]

\[
\dot{M}_a(z) - \dot{M}_a(z + \Delta z) + 0 = 0
\]

Equation 2-63

where \( \dot{M}_a \) is the molar flow of solute \( a \) through the differential element \( \Delta z \).
Figure 2-2. Transport of gas \( a \) through solid \( b \) in a differential element.

Therefore in differential form we have\(^{40}\),

\[
\frac{dM_a}{dz} = \frac{d}{dz} (A_c N_a) = 0
\]

Equation 2-64

This states that the molar flux of \( a \) inside the pore must be constant, and using the boundary conditions at the bottom and top of the pore defined in Figure 2.2 (\( X_a = X_{a0} \) at \( z = 0 \) and \( X_a = X_{aL} \) at \( z = L \), \( X_a \) is the change in composition of \( a \) due to transport). This is combined with Fick’s Law to obtain equation 2-65\(^{40}\),

\[
N_a - x_a (N_a + N_b) = -D_{ab} \frac{dx_a}{dz}
\]

Equation 2-65

Where \( N_a \) is the total molar flux of \( a \). In the absence of convective flow, in the dilute solution approximation of Fick’s Law (\( X_a \to 0 \)), equation 2-65 can be approximated as,

\[
N_a = -D_{ab} \frac{dx_a}{dz}
\]

Equation 2-66

Equation 2-66 can be integrated directly to give a linear profile, since pressure is easily measured in a gas permeability experiment, the ideal gas law will be used to relate the composition of gas \( a \) to its change in pressure to give equation 2-67,

\[
N_a = -D_{ab} \frac{\Delta P}{L}
\]

Equation 2-67
In the case of Knudsen diffusion, $D_{ab}$ is defined by equation 2-68:

$$D_K = \frac{d_p}{3} \cdot \sqrt{\frac{8RT}{\pi M_w}}$$  \hspace{1cm} \text{Equation 2-68}$$

where $D_K$ is the Knudsen diffusion coefficient, $d_p$ is the pore diameter, $T$ the temperature in the system, and $M_w$ the molecular weight of the gas being transported. A direct relation between molar flux and molecular weight is expected in the Knudsen regime. Combining equations 2-67 and 2-68 the molar flux in Knudsen transport is given by equation 2-69:

$$N_{Kn} = -\frac{d_p}{3} \cdot \sqrt{\frac{8}{\pi TRM}} \cdot \frac{\Delta P}{L}$$  \hspace{1cm} \text{Equation 2-69}$$

2.5.2. Membrane performance and quality.

The performance of a porous membrane is defined by two factors: its permeability and selectivity\(^1\). The permeability of a membrane is defined as the ability of a gas to flow through the pores of the material, while the selectivity is a measurement of the separation efficiency given by the ratio of single-gas permeabilities. A membrane is composed of a feed side where the gas comes into contact with the pores of the material, and a permeate side where the gas exits the membrane after flowing through its pores. The permeability of a membrane is essentially a gas flux, normally measured in a constant volume as the change of pressure with time in the permeate side of the membrane. Permeability can be therefore calculated following a similar analysis as in the previous section, it can be estimated using equation 2-70,

$$P_i = \frac{N_i \cdot L}{\Delta P_i \cdot A}$$  \hspace{1cm} \text{Equation 2-70}$$

where $N_i$ is the permeate molar flow of component $i$, $\Delta P_i$ is the pressure difference between the feed and permeate side of the membrane, $A$ is the permeation area of the membrane and $L$ its thickness. If permeability is measured as the change in pressure with time in the permeate side as
the volume is kept constant, the permeability can be directly calculated from experiments from equation 2-71,

\[ P_i = \frac{\left(\frac{dP}{dT}\right)_P V}{RT} \frac{L \cdot M_w}{A \cdot \Delta P} \]  

Equation 2-71

where \( V \) is the permeate volume, \( R \) is the ideal gas constant, \( T \) is the system temperature, \( dP/dT \) is the steady-state pressure increase due to permeation, \( L \) is the membrane thickness, \( M_w \) is the molar volume of the gas, \( A \) is the permeation area of the membrane and \( \Delta P \) is the pressure difference between the feed and permeate side. When membranes have asymmetric structures as in the case of MOFs, the permeance (thickness independent) is used instead of the permeability, permeance is calculated from equation 2-72\(^1\),

\[ \text{Permeance}_i = \frac{N_i}{\Delta P \cdot A} \]  

Equation 2-72

The selectivity is estimated as the ratio of the permeances of the components in the mixture,

\[ S_{i/j} = \frac{P_i}{P_j} \]  

Equation 2-73

Where \( S_{i/j} \) is the permselectivity of gas \( i \) with respect to gas \( j \), \( P_i \) is the permeance of gas \( i \), \( P_j \) is the permeance of gas \( j \). In the Knudsen regime, selectivity will be the ratio of equation 2-69 for each gas in the mixture, given by equation 2-74,

\[ S_{Kn} = \sqrt{\frac{M_j}{M_i}} \]  

Equation 2-74

where \( S_{Kn} \) is the Knudsen selectivity of gas \( i \) with respect to gas \( j \), \( M_i \) is the molecular weight of gas \( i \) and \( M_j \) is the molecular weight of gas \( j \). Selectivity is independent of pressure or temperature in the Knudsen regime.
Effects of temperature and pressure on single gas permeability.

A plot of the average feed pressure against its permeability will produce a straight line given by equation 2-75\textsuperscript{38, 39},

\[
P_i \frac{L}{\alpha + \beta \cdot F}
\]

Equation 2-75

where \( P_i / L \) is the gas permeance, \( \alpha \) is the permeability coefficient attributed to Knudsen flow and \( \beta \) is the permeability coefficient attributed to convective flow and \( F \) is the average feed pressure. In the case of non-adsorbable gas and in absence of convective flow through pinholes, equation 2-75 will produce a straight line with a zero slope and Knudsen diffusion will be the main transport mechanism\textsuperscript{15, 16}.

The effect of temperature on selectivity in the presence of Knudsen and convective flow will be described by equation 2-78 and the behavior of the curve will depend upon the main transport mechanisms. The molar flow rate of an ideal gas \( a \) through a pore due to convection is given by equation 2-76,

\[
\dot{N}_a = \frac{VRT}{P}
\]

Equation 2-76

Where \( \dot{N}_a \) is the molar flow rate of component \( a \), \( V \) is the volumetric flow rate of gas \( a \), \( R \) is the ideal gas constant, \( T \) is the temperature in the system and \( P \) is its pressure. As previously stated, the molar flow rate predicted by Knudsen transport will be described by equation 2-68. Therefore, the total molar flux through the membrane is given by equation 2-77, obtained adding equations 2-68 and 2-76,

\[
N_T = -\frac{dP}{3} \cdot \frac{8}{\pi TRM} \cdot \frac{\Delta P}{L} + \frac{VRT}{P}
\]

Equation 2-77

Where \( N_T \) is the total molar flux. The permselectivity of gas \( a \) with respect to gas \( b \) through the membrane can then be calculated using equation 2-78, as the ratio of single gas fluxes,
\[
S_{a/b} = \frac{dp}{\sqrt{\frac{u}{\pi M_a}} \frac{\Delta p}{L} \sqrt{RT}} \frac{V_a}{\sqrt{RT}} 
\]

Equation 2-78

In the particular case of Knudsen diffusion, and in the absence of convective flow, the permselectivity will be independent of temperature as predicted by equation 2-74. A plot of permselectivity vs temperature using equation 2-78 will produce a straight line with zero slope in the absence of convective flow, confirming the absence of imperfections and pinholes in the membrane and will be an indication of Knudsen diffusion as the main transport mechanism.

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Chapter 3. Gas Sorption properties of polymorphic microporous MOFs with open Zn(II) coordination sites.

3.1. Introduction.

Metal Organic Frameworks (MOFs) are crystalline porous materials consisting of polymeric inorganic networks with high surface areas, defined pore sizes and adjustable chemical functionality. Their chemical functionality, surface area and pore size can be tuned by choosing metal centers and organic ligands that are more appropriate to each application\textsuperscript{5,11}. MOFs find application in areas such as gas storage and separation, heterogeneous catalysis, sensors and drug delivery systems among other due to their properties\textsuperscript{9,10}. It is highly desirable to develop materials for CO\textsubscript{2} capture due to increasing levels of greenhouse gas in the atmosphere\textsuperscript{6,8}, MOFs properties make them promising materials for gas separations and posterior treatments to reduce the effect of power plant emissions gases to the atmosphere. Synthetic modifications to MOFs have been shown to increase the selectivity of the material for CO\textsubscript{2} due to the higher polarizability of the carbon dioxide molecules and this separation can also be favor by modifications to the pore structure and size to enable kinetic separation.

In this chapter sorption properties and thermodynamic parameters of two new microporous MOFs that have coordinately unsaturated Zn(II) sites without the need of activation are studied, and they are compared to known MOF-69C. Adsorption curves, surface areas and pore characteristics are obtained, as well as isosteric and zero coverage heats of adsorption and entropies of adsorption, selectivity for the most promising material for CO\textsubscript{2} capture is also reported.

3.2.1. Materials.

The following materials were purchased from the indicated commercial suppliers: zinc(II) nitrate hexahydrate (Sigma Aldrich); 2,5-pyridinedicarboxylic acid (pdc; Aldrich); 1,4-benzenedicarboxylic acid (bdc; Acros, 99%); N,N-dimethylformamide (DMF; spectrophotometric grade, Spectrum); N,N-diethylformamide (DEF; Acros); carbon dioxide (gas, Airgas, 99%), nitrogen (gas, Airgas, 99%).

3.2.2. Synthesis of MOFs.

Polymorphic microporous MOFs with open Zn(II) coordination sites are synthetized as solid crystals following the procedure described below.

3.2.2.1. Synthesis of Zn$_4$(pdc)$_4$(DMF)$_2$$\cdot$3DMF (1).

In a 20 mL vial, Zn(NO$_3$)$_2$$\cdot$6(H$_2$O) (250 mg, 0.840 mmol) was dissolved in 10 mL DMF followed by the addition of 2,5-pyridinedicarboxylic acid (144 mg, 0.862 mmol). The vial was capped and sonicated until turbid and heated to 100 °C for two days. The vial containing cubic crystals was removed from the oven and allowed to cool. The crystals were collected via vacuum filtration and rinsed with DMF.

3.2.2.2. Synthesis of Zn$_2$(pdc)$_2$(DEF) (2).

In a 20 mL vial, Zn(NO$_3$)$_2$$\cdot$6(H$_2$O) (177 mg, 0.596 mmol) was dissolved in DEF (4.883 mL). To the vial, 2,5-pyridinedicarboxylic acid (33 mg, 0.197 mmol) was added along with deionized water (0.177 mL). The vial was capped and sonicated until clear and heated to 75 °C for three days. The vial containing cubic crystals was removed from the oven and allowed to cool. The crystals were collected via vacuum filtration and rinsed with DEF.
3.2.2.3. Synthesis of Zn₃(OH)₂(bdc)₂•2DEF.

In a 20 mL vial, a solid mixture of Zn(NO₃)₂•6(H₂O) (177 mg, 0.596 mmol) and 1,4-benzenedicarboxylic acid (33 mg, 0.199 mmol) was dissolved in DEF (4.883 mL) by sonication. To the reaction solution, deionized water (0.177 mL) was added. The vial was capped and sonicated until clear and heated to 100 °C for 24 h. The vial containing cubic crystals was removed from the oven and allowed to cool. The crystals were collected via vacuum filtration and rinsed with DEF.

3.2.3. Characterization.

Polymorphic microporous MOFs with open Zn(II) coordination sites were characterized by gas sorption isotherms to obtain information about their total pore volume, pore size distribution, surface area and values of thermodynamic parameters for the adsorption of different gases. Adsorption studies were performed using N₂ and CO₂ at low pressures to estimate values of zero coverage adsorption thermodynamics, and at temperatures below the critical point of the gases to obtain information about pore volume, pore size distribution and surface area, condensation of the gas phase upon adsorption can be safely assumed under these conditions.

Sorption measurements were collected on a Quantachrome Autosorb-1, MOFs samples were synthetized according to the procedure described in the previous section, all samples were placed in a 6 mm bulb sample cell and were subsequently degassed under vacuum at 90°C for 5 hours, the degas procedure continued for 19 hours at ambient temperature, this was done to prevent degrading of the MOFs samples by temperature. Adsorption isotherms for CO₂ were collected at 273 K and 296 K, while N₂ adsorption isotherms were collected at 77K and 296 K, all sorption studies were performed on the three different MOF samples. The range of pressures used was from vacuum to atmospheric pressure as suggested by the procedure described in the adsorption
instrumentation software (Autosorb). The surface area of the materials was obtained by fitting adsorption data for CO$_2$ at 273K and N$_2$ at 77K in the 0.05 – 0.3 P/P$_0$ pressure range to the BET and Langmuir equations, in this range such data behaves as a straight line and it can be safely assumed that the energy of adsorption equals the energy necessary for condensation on the surface. Total pore volumes were calculated by a single point method at P/P$_0 = 0.99$ and the pore size distribution was determined using the Autosorb software which bases its calculations on the non-local density functional theory, CO$_2$ at 273 K was used to determine the pore size distribution of the material. Relevant thermodynamic parameters for the adsorption at zero coverage of CO$_2$ on the three MOF materials were obtained by solution of the Clausius-Clapeyron equation from the adsorption isotherms at 273K and 296K, using the Langmuir-Freundlich and Virial equation to model the adsorption. Gas selectivity was also estimated.

3.3. Results and Discussion.

3.3.1. Low-Pressure and Low-Temperature Gas Sorption Measurements, Surface Area Calculations and Zero Coverage Heats of Adsorption.

Surface and pore characteristics were obtained from adsorption isotherms of CO$_2$ at 273 K and N$_2$ isotherms at 77 K on the three different MOFs in study. CO$_2$ gas sorption isotherms on (1), (2) and MOF-69C at 273 K are shown in figure 3-1, (1) behaves as a microporous material showing a reversible type-I isotherm, it also displays the greatest affinity for CO$_2$, (2) and MOF-69C display a lower affinity for CO$_2$ and they do not reach surface saturation throughout the adsorption process, this suggests that the pore sizes of these materials are too small to reach equilibrium at these pressures. BET and Langmuir surface areas were calculated from the adsorption isotherms, and values are presented in table 3-1 together with their pore characteristics, the BET and Langmuir surface areas for (1) were calculated to be 195.87 and 390.1 m$^2$/g and its total pore
volume using the single point method is 0.116 cm$^3$/g, no pore characteristics were determined for (2) and MOF-69C as their surfaces did not reach saturation. N$_2$ adsorption isotherms at 77 K show a similar behavior to CO$_2$ isotherms, (1) has the greatest affinity for N$_2$ and exhibits a type-1 isotherm, followed by MOF-69C and (2) displays the lowest affinity among the MOFs in study, values for surface areas of N$_2$ on the materials are presented in table 3-1, with (1) showing the highest surface area due to its pore characteristics.

Figure 3-1. CO$_2$ isotherms at 273 K (black) and 296 K (red) of (A) (1) (squares), (2) (triangles), and MOF-69C (diamonds) with the Langmuir-Freundlich fit shown with solid line.
Table 3-1. Surface area and thermodynamic parameters for (1), (2) and MOF-69C.

<table>
<thead>
<tr>
<th>MOF</th>
<th>BET</th>
<th>Langmuir</th>
<th>$Q_a^b$</th>
<th>$Q_{st}^b$</th>
<th>$K_F$</th>
<th>BET</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m²/g)</td>
<td>(m²/g)</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
<td>(Pa)</td>
<td>(m²/g)</td>
<td>(m²/g)</td>
</tr>
<tr>
<td>(1)</td>
<td>196</td>
<td>390</td>
<td>-29.1 ± 0.4</td>
<td>-27.7</td>
<td>45.9 ± 0.6</td>
<td>319</td>
<td>464</td>
</tr>
<tr>
<td>(2)</td>
<td>7</td>
<td>----</td>
<td>-3 ± 1</td>
<td>-2.7</td>
<td>1.7 ± 0.2</td>
<td>5</td>
<td>59</td>
</tr>
<tr>
<td>MOF-69C</td>
<td>11</td>
<td>114</td>
<td>-24.1 ± 0.3</td>
<td>-17.6</td>
<td>5.72 (±0.01) × 10⁻²</td>
<td>8</td>
<td>27</td>
</tr>
</tbody>
</table>

*a Value could not be determined.

*b Determined from the Clausius-Clapeyron equation at the onset of adsorption

c Determined from the zero limit of the virial equation

Figure 3-2. N₂ sorption isotherms at 77 K for (1) (black squares), (2) (red triangles), and MOF-69C (grey circles).
Isotherm data for CO$_2$ was also obtained at 296 K to study the behavior of the different materials with a temperature increase and to obtain thermodynamic parameters for CO$_2$ adsorption. The amount of gas adsorbed decreases with temperature as adsorption is inherently an exothermic process. All CO$_2$ isothermal data was fitted to the Langmuir-Freundlich equation (SIPS equation) to determine the amount of gas adsorbed as a function of pressure,$^{1-3}$

$$\frac{Q}{Q_m} = \frac{K_F P^{(1/t)}}{1 + K_F P^{(1/t)}}$$  \hspace{1cm} \text{Equation 3-1}

where $Q$ is the moles of gas adsorbed, $Q_m$ is the moles adsorbed at saturation, $P$ is pressure, $K_F$ is an affinity constant, and $t$ is an index of heterogeneity ($0 < 1/t < 1$). Parameters for Langmuir-Freundlich fit are shown in table 3-2. In the limit when the surface is homogeneous (equal energetic interactions between surface and molecules at all sites) the Langmuir-Freundlich equation simplifies to the Langmuir equation (for $t=1$), in all cases values of $t$ were very close to 1 with a maximum value of 1.07 suggesting an homogeneous binding environment on the surface of all the MOFs un study.

**Table 3-2.** Summary of the parameters from Langmuir-Freundlich fit of CO$_2$ isotherm data at the designated temperature.

<table>
<thead>
<tr>
<th>MOF</th>
<th>B</th>
<th>T</th>
<th>$Q_m$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.0459</td>
<td>1.0713</td>
<td>75.9879</td>
<td>0.99984</td>
</tr>
<tr>
<td>(2)</td>
<td>0.00167</td>
<td>1</td>
<td>18.5648</td>
<td>0.99896</td>
</tr>
<tr>
<td>MOF-69C</td>
<td>5.716 × 10$^{-5}$</td>
<td>1</td>
<td>880.3156</td>
<td>0.99957</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MOF</th>
<th>B</th>
<th>T</th>
<th>$Q_m$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.0179</td>
<td>1.0325</td>
<td>76.0654</td>
<td>0.99996</td>
</tr>
</tbody>
</table>
Isosteric heats of adsorption can be determined from the Clausius-Clapeyron equation which relates the changes in volume with pressures at different fixed temperatures,

\[ \ln(P_i) = \frac{Q_{st}}{RT_i} + \frac{\Delta S}{R} \]  

Equation 3-2

where \( P_i \) is the pressure for isotherm \( i \), \( T_i \) is the temperature for isotherm \( i \), \( R \) is the universal gas constant, and \( \Delta S \) is entropy. The Langmuir-Freundlich equation was rearranged to solve for pressure and substituted into the Clausius-Clapeyron equation, which was used to determine the \( Q_{st} \) and \( \Delta S \) for the MOFs, values for \( Q_{st} \) and \( \Delta S \) as a function of pressure are shown in figure 3-3.

![Diagram](image)

**Figure 3-3.** \( Q_{st} \) and \( \Delta S \) for (1) (black squares), (2) (grey diamonds) and MOF-69C (red circles) as a function of pressure.
The adsorption enthalpy for (1) decreases as CO$_2$ pressure increases as a consequence of a reduction in the number of adsorption sites available (most favorable sites will be taken) and of the model used to estimate energy which goes to infinity as pressure approaches zero; these values remain at a high negative value throughout the adsorption due to favorable interaction between CO$_2$ and (1) and to the exothermic nature of adsorption. Values of adsorption enthalpy at the onset of adsorption were estimated for all the materials, the value of $Q_{st}$ for (1) approaches -29.1 kJ/mol at low surface coverage while the adsorption enthalpy of (2) and MOF-69C at the onset of adsorption were found to be -3 kJ/mol and -24.1 kJ/mol. Values of changes of entropy upon adsorption are negative and consequent with the loss of translational entropy (degrees of freedom) that molecules undergo when they are adsorbed on the surface.

The zero-coverage heat of adsorption ($Q_{st0}$), which describes the strength of the binding sites within the material at the lowest pressures, was estimated by fitting the isothermal adsorption data to a virial-type equation,$^3,5$

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

Equation 3-3

where $P$ is the pressure, $N$ is the amount of CO$_2$ adsorbed, $T$ is the temperature, $m$ and $n$ are the number of virial coefficients required for fitting, and $a$ and $b$ are virial coefficients. Contrary to the Langmuir equation, which goes to infinity at the zero pressure limit, the limit of the virial equation results in a numerical value used to estimate $Q_{st0}$. In the equation, the parameters $a_0$ and $b_0$ are related to the $Q_{st}$ and the Henry’s Law constant ($K_H$), respectively. The enthalpies of adsorption can be estimated as a function of surface coverage,$^3$

$$Q_{st} = -R \left( \frac{d \ln P}{d \frac{1}{T}} \right)_N = -R \sum_{i=0}^{m} a_i N^i$$

Equation 3-4

and the value of $Q_{st0}$ determined by the limit of equation 3-4, as follows,$^5$

51
\[ Q_{st}^0 = -R \lim_{N \to 0} \left( \sum_{i=0}^{m} a_i N^i \right) = -Ra_0 \]  

Equation 3-5

Values of \( b_0 \) are also related to the physically meaningful quantity \( K_0 \), which is related to the Henry’s law adsorption constant, \( K_H \), by Equations 3-6 and 3-7.\(^3\)

\[ K_H = K_0 \exp \left( \frac{q_0}{RT} \right) \]  

Equation 3-6

\[ K_0 = \exp(-b_0) \]  

Equation 3-7

Values of \( Q_{st}^0 \) for \( \text{CO}_2 \) adsorption on (1), (2), and MOF-69C are presented in table 3-1, fits for the virial type equation are shown in figures 3-4 – 3-6. Since the virial equation is an empirical model with a polynomial type of expression, the number of coefficients can be adjusted to obtain a best fit of the data, nonetheless, a higher number of coefficients will introduce an undesired curvature between data points and physically meaningless coefficients. There is a point after which increasing the number of coefficients in the fit will hurt the validity of the data fit and the physical significance of coefficients, without adding any practical improvement in the description of the data. Adsorption data was accurately described by a maximum of 4 virial coefficients which suggest that there are no higher order interaction among molecules and between molecules and the material surface. Another factor to consider when fitting data to the virial type equation is the presence of multiple local minima when fitting the data, for the adsorption data in study \( Q_{st}^0 \) was dependent on the initial guess for the fitting parameters. The initial guesses entered for the virial fits were based on that calculated via analysis by the Clausius-Clapeyron equation for \( Q_{st} \) at the onset of adsorption and the initial slopes of the isothermal data for \( K_H \), which directly related to the virial parameter \( b_0 \) equations 3-6 and 3-7.
**Figure 3-4.** Virial equation fit (solid red line) to the CO$_2$ isotherm for (1) at 273 K (black squares).

**Figure 3-5.** Virial equation fit (solid red line) to the CO$_2$ isotherm for (2) at 273 K (black squares).
The calculated $Q_{st}^0$ values (from the onset of the Clausius-Clapeyron data and the virial equation) are consistent with a mechanism of CO$_2$ binding to (1) that involves the cationic Zn(II) metal sites present in the 3D structure. The calculated value of $Q_{st}^0$ (~28 kJ/mol) agrees well with that observed for CPO-27-Zn (MOF-74-Zn, -30.5 kJ/mol) in which adsorption to coordinately unsaturated Zn(II) metal sites has been reported.$^3$

3.3.2. MOF Selectivity.

MOF selectivity was studied on (1) by recording CO$_2$ and N$_2$ isotherms at 296 K and it was estimated using two different methods. Selectivity can be calculated from the ratio of Henry’s Law constants for the adsorption of both gases on (1) as the pressure goes to zero and the isotherm behaves as a straight line,$^6$ low pressure adsorption data and their fit used to calculate Henry’s constants for both gases are shown in figure 3-7.
Figure 3-7. The fitting of the initial slope of (1) adsorption isotherms at 296 K with CO$_2$ (black squares) and N$_2$ (red triangles).

It is noticeable from the slopes in figure 3-7 that (1) preferentially adsorbs CO$_2$ over N$_2$, this is consistent with the thermodynamic analysis that showed a preferential adsorption of CO$_2$, the selectivity was 42 from the ratio of the initial slopes of adsorption. This selectivity for CO$_2$ can be attributed to the fact that CO$_2$ has a larger polarizability and a smaller kinetics diameter, an oxygen atom of CO$_2$ can bind to a Lewis acidic metal node and a smaller kinetic diameter favors an easier diffusion thorough the pores of the MOF.$^{5,7}$

Selectivity can also be calculated using the Selectivity factor ($S$), $^5$

$$S = \frac{q_1}{p_1/p_2}$$ \hspace{1cm} Equation 3-8

where $q_i$ is the mass of adsorbed gas $i$ at the relevant partial pressure, and $p_i$ is the partial pressure of component $i$. The selectivity factor relates the molar ratio of adsorbed gases at the partial pressures of the gases within a mixture. For post-combustion CO$_2$ capture processes, the partial pressures of CO$_2$ and N$_2$ are 0.15 and 0.75, respectively.$^5$ It should be noted that the amount of gas adsorbed is determined from the single component sorption isotherm and does not take the
competition of the gas molecules for adsorption sites into consideration, this can be improved by using a model that considers interactions between molecules, i.e. the Ideal adsorbed solution theory (IAST), which will be applied in next chapter to estimate selectivity of gases. $S$ for (1) was found to be 14.

3.4. Conclusions.

A thermodynamic study of gas sorption properties of two previously unreported MOF was performed, both MOFs contain coordinately unsaturated Zn(II) sites without the need of activation that are ideal binding sites for the CO$_2$ molecules. Calculated zero coverage heat of adsorption and isosteric heat of adsorption suggest adsorption of carbon dioxide at these exposed metal binding sites and are in agreement with other reported MOFs exhibiting this mechanism and entropies of adsorption are consistent with a physical adsorption mechanism where molecules lose translational entropy upon adsorption. The microporous (1) displayed high selectivity for CO$_2$ over N$_2$ but further studies must be made to conclude about the applicability of this materials for CO$_2$ capture, and to have a complete understanding of the mechanisms involved in the adsorption of gases of interest.

3.5. Copyrights.

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References.


Chapter 4. Gas Sorption and Kinetics of CO₂ Sorption and Transport in a Polymorphic Microporous MOF with Open Zn (II) Coordination Sites

4.1. Introduction.

The increasing levels of anthropogenic greenhouse gas emissions and their harmful effects on the environment have made carbon capture and sequestration research a priority among the scientific community. Research has focused on materials that can effectively mitigate the environmental impacts while reducing energetic penalties that are incurred as part of these separation processes. Carbon dioxide capture and separation from flue gas is a critical step in addressing ways to reduce the effects of global warming. Adsorption separation processes through porous materials are among the most promising methods for CO₂ removal from flue gas. Materials that offer a high adsorption rate, a low desorption energy and a kinetic pathway that favors CO₂ capture in the presence of other gases are desirable for effective CO₂ separation. Metal organic frameworks (MOFs) are crystalline porous materials composed of a network of transition metal ions and bridging organic ligands. They consist of polymeric inorganic networks with high surface areas, defined pore sizes and adjustable chemical functionality. Their chemical functionality, surface areas and pore sizes can be tuned by choosing metal centers and organic ligands that are appropriate to each desired material application. MOF materials have shown potential for the separation of gas mixture, particularly in power plant emissions where CO₂ capture and separation can be applied as a post-combustion process and the interactions between the adsorbent and CO₂ play a crucial role in improving CO₂ capture performance.

An understanding of the mechanisms that govern the sorption and diffusion of gases through adsorbents is key in the development of new sustainable methods for CO₂ separation, and a
material performance evaluation under conditions that mimic post-combustion CO\textsubscript{2} capture is desirable to study ideal conditions and chemical interactions that could potentially enhance gas adsorption processes\textsuperscript{13}. Research on CO\textsubscript{2} adsorbents focuses on porous materials and the study of their functionality, pore characteristics, and interactions with different gases to determine their sorption thermodynamics and kinetics\textsuperscript{3,8,9,17}. Several MOFs have shown promise for such applications\textsuperscript{3,9,12,13,20} and this prior work indicates that surface functionalization and the presence of exposed metal sites play a crucial role in the design and development of MOF materials for CO\textsubscript{2} post-combustion capture\textsuperscript{20}.

Our research groups recently reported a promising new MOF for CO\textsubscript{2} adsorption\textsuperscript{20}. The Zn\textsubscript{4}(pydc)\textsubscript{4}(DMF)\textsubscript{2}\textbullet3DMF MOF (1) contains coordinately unsaturated Zn(II) metal nodes without the need of activation and displays a high selectivity for CO\textsubscript{2} over N\textsubscript{2} due to the presence of ideal binding sites for CO\textsubscript{2} molecules\textsuperscript{20}. Herein, we report on a thermodynamic and kinetic study of (1) to gain further insight into CO\textsubscript{2} capture and separation on Zn(II) based MOFs and to determine the applicability of (1) to post-combustion and pre-combustion CO\textsubscript{2} capture from flue gas. This study reports a simple method of calculation for thermodynamic and kinetic parameters that can be extended to other materials with a similar sorption behavior. We report the adsorption and desorption thermodynamics of different gases under conditions that mimic CO\textsubscript{2} post-combustion and pre-combustion capture, and calculate gas selectivity from the ideal adsorbed solution theory (IAST.) We also report the kinetics of adsorption and desorption to determine rate limiting steps for the CO\textsubscript{2} transport to adsorption sites and activation energies for the sorption of gases. Average values of residence times and desorption activation energies for gases on (1) were also determined. This study provides valuable insight into the transport mechanisms and potential applications of this material to different sorption applications.
4.2. Experimental

4.2.1. Materials.

Zinc(II) nitrate hexahydrate and 2,5-pyridinedicarboxylic acid (pdc) were purchased from Sigma Aldrich; N,N-dimethylformamide (DMF, spectrophotometric grade) was purchased from Spectrum Chemical; carbon dioxide (gas, 99%), nitrogen (gas, 99%), Hydrogen (gas, 99%), and methane (gas, 99%) were purchased from Airgas. All chemicals were used without further purification.

4.2.2. Synthesis of MOF Zn₄(pdc)₄(DMF)₂•3DMF (1).

A polymorphic microporous MOF with open Zn(II) coordination sites was prepared using a previously reported method. In a 20 ml vial, Zn(NO₃)₂•6(H₂O) (250 mg, 0.840 mmol) was dissolved in 10 mL DMF followed by the addition of 2,5-pyridinedicarboxylic acid (144 mg, 0.862 mmol). The vial was capped and sonicated until turbid, heated and then held at 100 °C for two days. The vial containing cubic crystals was removed from the oven and allowed to cool. The crystals were collected via vacuum filtration and rinsed with DMF and were mechanically crushed to ensure a uniform crystal size.

4.2.3. Gas Sorption Isotherms.

Sorption data was collected using an Intelligent Gravimetric Analyzer (IGA 002, Hiden Analytical Inc., UK). Approximately 100 mg of as synthesized sample were placed in a metal basket (previously cleaned by sonication in acetone.) The sample basket was placed inside a gas chamber surrounded by a water bath to control the temperature. All samples, tubing, and gas chamber were degassed by applying high vacuum (P<10⁻⁴ mbar) and heating to 90 °C over a 5 h period to remove any previously adsorbed gases. The equipment was further degassed at ambient temperature for 19 h to ensure total vacuum. Isothermal adsorption data was recorded at 308 K,
323 K, and 338 K using CO₂, N₂ and CH₄ gases at pressures ranging from vacuum to 5 bar in step changes to study post-combustion capture of CO₂. In the case of the study of pre-combustion conditions on (1), adsorption isotherms of CO₂ and H₂ at 313 K were obtained at pressures ranging from 1 bar to 20 bar in step changes. In both cases, desorption data was studied over the same range of pressures to understand the role of desorption on the separations and verify the presence or absence of hysteresis loops in the data. Thermodynamic parameters for the range of temperatures and pressures studied were obtained by application of the Van’t Hoff equation and by fitting the data to the Langmuir isotherm model. Adsorption selectivity was calculated by application of the Ideal Adsorbed Solution Theory (IAST) to the Langmuir isotherm⁵,¹¹,¹³.

4.2.4. Sorption Kinetics.

Adsorption dynamics data were collected using an Intelligent Gravimetric Analyzer (IGA 002, Hiden Analytical Inc., UK) following the same vacuum and decontamination procedure described for obtaining sorption isotherms. Kinetic data was recorded at 308 K, 323 K, and 338 K, under three different pressures for CO₂ (0.15 bar, 0.5 bar, 1 bar). Adsorption dynamics were measured as the change in sample weight as a function of time as the sample reached equilibrium for each pressure in an isotherm point at a given temperature, all the measurements were recorded for a minimum of 30 minutes and a maximum of six hours to ensure adsorption equilibrium was reached; equilibrium was achieved for all the set points in the study. All kinetic data was fitted to the linear driving force model and two intraparticle diffusion models to study material energetics and rate limiting steps¹⁵,¹⁷,¹⁸. Kinetics of desorption were also studied to understand desorption behavior of different gases on (1). Desorption dynamics were recorded as the change in sample weight as a function of time at 308 K, 323 K, and 338 K at three different pressures for CO₂ (0.15 bar, 0.5 bar, 1 bar) and at the typical outlet pressure of flue gases for N₂ and CH₄ (1 bar). Desorption
data was fitted to the Linear driving force model to calculate residence times of the molecules and activation energies of desorption.

4.3. Results and Discussion.

4.3.1. Zn₄(pdc)₄(DMF)₂•3DMF as a material for post-combustion CO₂ capture.

Sorption isotherms using CO₂, N₂ and CH₄ were obtained at 308 K, 323 K and 338 K for pressures up to 5 bar (Figure 4.1.) in conditions that mimic realistic CO₂ post-combustion capture as it has been suggested elsewhere. CO₂ exhibits the highest adsorption capacity among the gases studied at all temperatures, followed by CH₄ and N₂. This is the expected behavior for MOF materials with functionalized surfaces and open-metal sites. CO₂ is expected to exhibit the highest adsorption as it has a larger polarizability and smaller kinetic diameter than CH₄ and N₂. As a result, faster kinetics and higher binding energies are anticipated for CO₂ as there will be lower resistance to adsorption. Consequently, the relatively high CH₄ adsorption as compared with CO₂ can be attributed to the presence of unsaturated metal sites on the surface of the MOF and selective favorable sites for methane adsorption. Adsorption and desorption data shows no hysteresis, indicating that there is no irreversible binding. This characteristic will be explored further in the analysis of the kinetics of desorption. The type I isotherm behavior of CO₂ and CH₄ adsorption suggests a strong interaction with the MOF adsorption sites, while the linear behavior of the N₂ adsorption is due to the weak interaction between the MOF surface and the non-polar, symmetric nitrogen molecules.
Figure 4-1. Adsorption/desorption isotherms at 308 K (A), 323 K (B), and 338 K (C) for CO$_2$ (black squares), CH$_4$ (red diamonds) and N$_2$ (grey circles) in (1). Langmuir fits for CO$_2$ and CH$_4$ and a linear fit for N$_2$ are also shown (dotted lines).
Isotherms on (1) show that adsorption decreases as temperature increases in all cases, as is expected for an exothermic adsorption process where molecules are being physisorbed on the surface of the material. Adsorption data was fitted to the Langmuir equation5,

$$\theta = \frac{k_{ads}P}{1 + k_{ads}P}$$

Equation 4-1

where $\theta$ is the fractional coverage of the adsorption sites, $k_{ads}$ is the Langmuir adsorption constant and $P$ is the pressure of the gas in the bulk phase. Model fits to the data are shown in Figure 4-1. The Langmuir equation presents 3 advantages in the particular case of the data in study: 1) It fits data with a low error and a high $R^2$ correlation; 2) it has a simple mathematical expression, fitting a low number of parameters, which increases the physical significance of the parameters obtained; and 3) values of $k_{ads}$ for this equation can be used to calculate values of the average change of enthalpy of adsorption that are valid in the range of temperatures/pressures used in the study that fit the Langmuir assumptions.$^5$

Langmuir parameters calculated based on adsorption isotherms are presented in Table 4-1. Langmuir adsorption constants and values of adsorption capacity decrease with temperature for the three gases investigated. This suggests physisorption of the gases on the surface. Among the gases studied, CO$_2$ shows the greatest affinity for the surface, as represented by higher values of $k_{ads}$ and $Q_{eq}$ (equilibrium adsorption capacity) Methane exhibits lower values of $k_{ads}$ than CO$_2$ but similar values of $Q_{eq}$. This is due to the fact that the relatively low pressures studied for CH$_4$ adsorption are far from the point of maximum adsorption capacity (Adsorption plateau). As a result, the $Q_{eq}$ value is being overpredicted and is compensated by a low $k_{ads}$ with a steep slope that overpredicts molecule-surface energetic interactions. Nitrogen adsorption is best approximated with a linear model with a zero intercept. This is attributed to the fact that N$_2$ exhibits very low adsorption and does not reach the characteristic type I adsorption saturation knee. Values of the
Langmuir constants and adsorption capacities are comparable to those reported for other MOFs studied for CO$_2$ capture, including MOF-5 ($K_{ads}(195 \text{ K}) = 2 \cdot 10^{-6} \text{ bar}^{-1}$; $Q_{eq}(298 \text{ K}, 1 \text{ atm}) = 2.1 \text{ mol/kg}$); and MOF-177 ($K_{ads}(237 \text{ K}) = 1.4 \cdot 10^{-5} \text{ bar}^{-1}$)$^{4,6}$, and to other widely studied adsorbents such as zeolites (Zeolite 13X: $K_{ads}(298 \text{ K}) = 1 \cdot 10^{-5} \text{ bar}^{-1}$; $Q_{eq}(298 \text{ K}, 1 \text{ atm}) = 3.3 \text{ mol/kg}$) and activated carbon ($Q_{eq}(298 \text{ K}, 1 \text{ atm}) = 2.0 \text{ mol/kg}$)$^{7,8}$ Adsorption capacities in (1) at 1 bar are higher than those reported for other promising Zn-based MOFs$^{21}$ and Zeolitic imidazolate frameworks (ZIFs)$^{22,23}$.

Table 4-1. Langmuir adsorption constants and thermodynamic parameters for the adsorption of different gases on (1).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_{ads} \cdot 10^{-6}$ (bar$^{-1}$)</th>
<th>$Q_{eq}$ (mol/Kg)</th>
<th>$\Delta H_{ads}$ (KJ/mol)</th>
<th>$\Delta S$ (J/mol•K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>1.04±0.027</td>
<td>3.24±0.029</td>
<td>-23.73</td>
<td>-172.47</td>
</tr>
<tr>
<td>323</td>
<td>0.67±0.014</td>
<td>3.10±0.027</td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>0.46±0.009</td>
<td>2.96±0.027</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>0.42±0.021</td>
<td>3.14±0.068</td>
<td>-25.81</td>
<td>-187.07</td>
</tr>
<tr>
<td>323</td>
<td>0.24±0.0012</td>
<td>3.07±0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>0.17±0.0031</td>
<td>2.79±0.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>0.14±0.0027</td>
<td>2.57</td>
<td>-15.04</td>
<td>-160.75</td>
</tr>
<tr>
<td>323</td>
<td>0.11±0.002</td>
<td>2.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>0.08±0.0019</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Determined from Langmuir fit of N$_2$ adsorption data.

Thermodynamic parameters for gas adsorption in (1) were calculated by plotting the Langmuir constants, $k_{ads}$, against the inverse of temperature ($1/T$) to produce a Van’t Hoff plot.$^5$ This allowed the determination of standard enthalpies and entropies of adsorption from the Van’t Hoff equation.$^5$
\[ \ln K_{ads} = \frac{-\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \]  

Equation 4-2

where \( k_{ads} \) is the Langmuir adsorption constant, \( \Delta H_{ads} \) is the enthalpy of adsorption, \( \Delta S_{ads} \) is the entropy of adsorption, \( T \) is the temperature of the system, and \( R \) is the ideal gas constant. Van’t Hoff plots of the different gases are depicted in Figure 4-2, along with the linear fits of the data. Calculated values of the enthalpies and entropies of adsorption given in Table 4-1. The positive observed in the Van’t Hoff plot confirms the exothermic character of adsorption, and correlates well with the fact that adsorption decreases as temperature increases.

![Van’t Hoff Plot](image)

**Figure 4-2.** Van’t Hoff Plots of the adsorption constants of CO\(_2\) (black squares), CH\(_4\) (red diamonds) and N\(_2\) (grey circles) in (1) with linear fits (dotted lines).

Enthalpy of adsorption values estimated from the Van’t Hoff plot represent the average binding energy of gas molecules on the surface of a material covered with equally energetic adsorption sites. The use of the Langmuir isotherm to represent adsorption data means that no adsorbent-adsorbent interactions have been considered,\(^5\) and enthalpies of adsorption calculated in this manner have the advantage that the only approximations being made are those that arise from the
use of the Langmuir equation. All calculated enthalpy values are within the range expected for physisorption \(^8\) (< 50KJ/mol). The binding energy of CO\(_2\) is in agreement with values presented for other MOFs that need an activation step prior to opening their active metal sites\(^4,9,13\) (and therefore these MOFs need more energy to be processed) while binding energies for CH\(_4\) correlate well with other highly selective MOFs\(^{12}\). N\(_2\) exhibits the lowest value of adsorption enthalpy due to the linear behavior of the adsorption curve that suggests low energy interactions of the nitrogen molecules with the MOF surface. Adsorption of CO\(_2\), CH\(_4\) and N\(_2\) on (1) is a spontaneous exothermic physical adsorption process. Values of change in entropy upon adsorption estimated from the intercept of the Van’t Hoff plots results in negative \(\Delta S\) values. This behavior was expected due to the loss in translational entropy of the molecules upon adsorption and to low adsorbate-surface vibrational energies typical of physisorbed molecules. Negative changes in entropy have been observed for similar systems.\(^{10}\)

CO\(_2\) selectivity on (1) with respect to N\(_2\) and CH\(_4\) was calculated using isotherm data at similar temperatures. Under equilibrium conditions all adsorbed species will have the same free energy; thus, it follows that a better approximation of the adsorption selectivity will be given by the Ideal Adsorbed Solution Theory (IAST)\(^{11,13,23}\) (Equation 4-3). This method has been shown to be accurate in predicting the selectivity of gas adsorption in MOFs.\(^{13,14,23}\) For our system in particular, IAST assumptions are valid as the surface of the sorbent is approximately homogeneous and the gases mix and behave as ideal gases, the quality and fit of the pure component data is very good and well described by Langmuir model and therefore IAST equations can be applied to this set of material and gases. A system of 5 equations and 5 unknowns was solved to estimate the mole fractions, fugacity and spreading pressure of the adsorbed phase.

\[
\int_0^{P_{y_i/x_i}} \frac{F_i(P)}{p} \, dp = \int_0^{P_{y_j/x_j}} \frac{F_j(P)}{p} \, dp \quad \text{Equation 4-3}
\]

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where $F_i$ is the fit for component $i$, $F_j$ is the fit for component $j$, $P$ is the total pressure, and $x_i$ and $y_i$ are the adsorbed and bulk phase mole fractions, respectively, of component $i$. Selectivity was then calculated using equation 4.4,

$$S_{ij} = \frac{x_i y_j}{x_j y_i}$$

Equation 4-4

where $x_i$ and $y_i$ are the absorbed and bulk phase mole fractions, respectively, of component $i$.

Values of adsorbed phase compositions and selectivity for different gases are shown in Table 4-2. The values of selectivity decrease with increasing temperature, which correlates with the fact that CO$_2$ adsorption decreases with increasing temperature while N$_2$ adsorption is not strongly temperature dependent. Values of CO$_2$:N$_2$ and CO$_2$:CH$_4$ selectivity are comparable to values previously reported for other MOFs, such as MMOF-20a ($\alpha$ CO$_2$/CH$_4$ = 6.8)$^{12}$, ZIFs (ZIF-8$^{23}$, $\alpha$ CO$_2$/N$_2$ = 7.6; $\alpha$ CO$_2$/CH$_4$ = 2.75) and activated carbon (BPL activated carbon$^{23}$ $\alpha$ CO$_2$/CH$_4$ = 3.8). CO$_2$:N$_2$ selectivity can be improved significantly by decreasing the temperature, suggesting that gas separation can be enhanced by decreasing the temperature in the system. CO$_2$:CH$_4$ selectivity has no clear temperature dependence, behavior which has been previously reported in similar systems$^{23}$. No conclusions can be made about the effect of pressure, as the IAST Langmuir solution is independent of the pressure used to predict molar fractions of the adsorbed phases, and only fugacity values are affected by changes in pressure.

Table 4-2. IAST selectivity and molar fraction of adsorbed phase ($X_{CO2}$) for CO$_2$/N$_2$ in 0.15:0.75 bulk phase proportion and CO$_2$/CH$_4$ in 0.5:0.5 bulk phase proportion on (1).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO$_2$:N$_2$ adsorption 0.15:0.75</th>
<th>CO$_2$:CH$_4$ adsorption 0.5:0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Selectivity$^a$ $X_{CO2}$</td>
<td>Selectivity $X_{CO2}$</td>
</tr>
<tr>
<td>308</td>
<td>14.86 0.75</td>
<td>2.50 0.71</td>
</tr>
<tr>
<td>323</td>
<td>10.00 0.67</td>
<td>2.83 0.74</td>
</tr>
<tr>
<td>338</td>
<td>5.31 0.51</td>
<td>2.67 0.72</td>
</tr>
</tbody>
</table>

$^a$ Determined from Langmuir fit adsorption constant of N$_2$.  

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4.3.2. Pre-combustion CO$_2$ capture on (1).

Pre-combustion CO$_2$ capture refers to CO$_2$ separation from H$_2$ in a gas mixture at high pressures and slightly elevated temperatures (5-40 bar and 40°C)\textsuperscript{13}. The goal is to obtain pure H$_2$, which then can be combusted to generate electricity. Therefore, an adsorbent with high surface area, high working capacity and high CO$_2$:H$_2$ selectivity is desired.\textsuperscript{13} (1) showed a good surface functionality with open metal sites and high surface area, showing potential as an adequate material for pre-combustion CO$_2$ capture. The metrics for evaluating the performance of adsorbents include selectivity and CO$_2$ working capacity, both characteristics of (1) will be studied in this section.

![Figure 4-3. High pressure CO$_2$ isotherms at 308 K (black squares), 313 K (red diamonds) and 338 K (grey circles) on (1), SIPS fit shown with dotted line.](image)

High pressure adsorption isotherms of CO$_2$ adsorption/desorption on (1) up to 20 bar are shown in Figure 4-3, it can be observed that most of the CO$_2$ adsorption occurs at pressures lower than 5 bar, as can be expected for adsorbents with open metal sites, resulting in a relatively low CO$_2$ working capacity. The working capacity is calculated as the difference between the capacity at the
high adsorption pressure and at the lower purge pressure. For pre-combustion applications, it is desirable to minimize the energy by desorbing the CO\textsubscript{2} at a purge pressure of 1 atm. From the isotherms, it can be concluded that a decrease in pressure from pressures higher than 8 to 10 bar will not affect adsorption significantly. It has been previously shown that (1) offers a homogeneous binding environment that can be well described using the Langmuir isotherm model. However, as pressure increases, the binding environment becomes non-homogeneous and a correction factor describing non-ideal energetic interactions must be used. The SIPS model (Langmuir-Freundlich equation) modifies the Langmuir equation by including a factor $t$ that describes the heterogeneity of the binding environment.\textsuperscript{8} Fits to the SIPS equation are shown on Figure A-1 in Appendix A and $t$ values are presented in Table 4-3. The data is properly fit by this model and values of $t$ decrease as adsorption decreases with temperature.

Figure 4-4 shows single-component CO\textsubscript{2} and H\textsubscript{2} isotherms at 313K on (1). H\textsubscript{2} adsorption behaves linearly in the range of studied pressures, suggesting low interactions with the MOF. This fact also results in uncertainty when trying to predict maximum adsorption values, which is demonstrated by the fact that both SIPS model and Langmuir model failed to give an appropriate fit to H\textsubscript{2} adsorption data. H\textsubscript{2} adsorption is relatively large when compared to CO\textsubscript{2} adsorption and a low selectivity is expected, adsorption values are comparable to other MOF reported in literature.\textsuperscript{14} The calculated working capacity of CO\textsubscript{2} was 1.85 mol/Kg, which is below values of working capacities that have been reporting for promising materials for pre-combustion capture\textsuperscript{14}. The values of CO\textsubscript{2} working capacity at different temperatures are shown in table 4-3.
Figure 4-4. High pressure CO$_2$ (blacks squares) and H$_2$ (red diamonds) isotherms at 313 K.

Mixed gas adsorption was estimated using the ideal Adsorbed solution theory (IAST). The validity of this assumption to estimate adsorption of gas mixtures from single-isotherm data has been proven by numerous studies as referenced in the previous section. Selectivity was calculated for CO$_2$/H$_2$ mixtures on a 20:80 molar proportion (relevant proportion for CO$_2$ capture). The parameters for IAST were approximated using the Langmuir isotherm, since no fit to SIPS equation could be found for H$_2$ data. Selectivity was then calculated according to equation 4-4. CO$_2$/H$_2$ selectivity on (1) has a value of 1.31 from IAST, which is lower than other promising pre-combustion MOF that have been studied in the literature.$^{14}$ Another important parameter to study is the desorption of CO$_2$ by purge to understand the regeneration of the material. The binding energy of CO$_2$ in temperatures/pressures relevant to the desorption process have been estimated in previous sections. CO$_2$ shows a binding energy of 24 kJ/mol, which is similar to values presented by other MOFs and zeolites. (1) shows a relatively low working capacity and selectivity and an average value of binding energy. These characteristics do not make (1) a potential pre-combustion material.
Table 4-3. CO₂ SIPS surface heterogeneity constant, working capacity and H₂ selectivity on (1).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>t SIPS constant</th>
<th>CO₂ Working capacity (mol/Kg)</th>
<th>IAST Selectivity&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>1.26</td>
<td>1.85</td>
<td>1.67 (at 313 K)</td>
</tr>
<tr>
<td>323</td>
<td>1.20</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>1.16</td>
<td>1.62</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated at 313 K for CO₂:H₂ in a 0.2:0.8 proportion in the bulk gas phase from Langmuir constants.

4.3.3. Kinetics of CO₂ adsorption/desorption on (1).

Kinetic data for the adsorption and desorption of CO₂ on (1) was measured at three different temperatures (308 K, 323 K and 338 K) and pressures (0.15 bar, 0.5 bar and 1 bar) relevant to post-combustion carbon dioxide capture. The sample was maintained at each given pressure for a minimum time of 30 minutes to ensure that equilibrium was reached at each isotherm point. Kinetic data was fitted to a linear driving force model (equation 4-5)<sup>15</sup>:

\[
\frac{\partial q}{\partial t} = k_t (q^* - q)
\]

Equation 4-5

where \( q \) is the adsorbed phase concentration average over the entire crystal, \( q^* \) is the equilibrium concentration and \( k_t \) is the lumped mass transfer coefficient. This model assumes that differences in concentration between the bulk phase and the adsorbed phase are the driving force for adsorption. All resistances to mass transport are lumped together as one single barrier to diffusion.<sup>8</sup> This model has several advantages over other kinetic models: it has a simple mathematical expression that has been widely used to study kinetics for multiple systems/materials; first order kinetics can be assumed and therefore equilibrium constants can be directly obtained from the model, as well as kinetic properties and diffusion rate limiting steps.
CO$_2$ uptake data at 0.15 bar, 0.5 bar and 1 bar and temperatures of 308 K, 323 K and 338 K are presented in Figures 4-5 to 4-7. Fitted linear adsorption model parameters and kinetic constants predicted by the model are given in Table 4-4.

**Figure 4-5.** Kinetics of adsorption of CO$_2$ at 0.15 bar on (1). Kinetics at 308 K (black squares), 323 K (red diamonds) and 338 K (grey circles) with Linear Driving Force fit shown as a solid line.
**Figure 4-6.** Kinetics of adsorption of CO$_2$ at 0.5 bar on (1). Kinetics at 308 K (black squares), 323 K (red diamonds) and 338 K (grey circles) with Linear Driving Force fit shown as a solid line.

**Figure 4-7.** Kinetics of adsorption of CO$_2$ at 1 bar on (1) Kinetics at 308 K (black squares), 323 K (red diamonds) with Linear Driving Force fit shown as a solid line.
Table 4-4. Linear Driving Force mass transfer coefficients $k_t$ of CO$_2$ on (1) at different temperatures and pressures. Values of adsorption activation energy predicted from Arrhenius plot of mass transfer coefficients.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>$k_t$ (sec$^{-1}$) 308 K</th>
<th>$k_t$ (sec$^{-1}$) 323 K</th>
<th>$k_t$ (sec$^{-1}$) 338 K</th>
<th>$E_A$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.0266</td>
<td>0.0449</td>
<td>0.0617</td>
<td>24.32</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0134</td>
<td>0.0168</td>
<td>0.0233</td>
<td>15.91</td>
</tr>
<tr>
<td>1</td>
<td>0.0116</td>
<td>0.0130</td>
<td>- -$^a$</td>
<td>6.12$^b$</td>
</tr>
</tbody>
</table>

$^a$ Data not presented due to high uncertainty when fitting data to model at this temperature.

$^b$ Calculated by solving Arrhenius equation between 2 temperature points (308 K and 323 K).

The CO$_2$ adsorption kinetics were fast with most of the adsorption occurring in the initial four to six minutes in all cases. A good correlation, with $R^2$ values of 0.96 and above, is obtained when kinetic adsorption data is fitted to the linear driving force model. The success with which the model fits the data is attributed to the relatively low coverage of adsorbent on the surface and the fact that adsorption isotherms are well described by the Langmuir model, indicating that it is not necessary to account for higher order interactions. This behavior suggests that adsorption occurs as a monolayer inside the pore surfaces of the MOF and confirms that secondary interactions between molecules are not significant at the pressures used in the study. Sorption data at 150 mbar exhibits the poorest fit, as this data describes adsorption onto an empty surface where preferable adsorption sites with high binding energies may be present. Adsorption dynamics at 65°C and 1 bar are not shown in the plots as they presented a lot of dispersion in the values of weight and their change with pressure. This can be attributed to the MOF being closer to its degradation temperature, also, adsorption is considerably smaller at this temperature/pressure; this will make any fluctuation (in pressure or temperature) in the equipment more noticeable. Data at 65°C and 1 bar is included separately in appendix A, figure A-2.

Values of CO$_2$ concentration at equilibrium decreased with temperature at all pressures, confirming the exothermic nature of the adsorption process. Values of the linear driving force
model kinetic constants \( (k_t, \text{Table 4-4}) \) increase with temperature suggesting that the kinetic process is temperature driven; moreover, kinetic constants decrease with increasing pressure as a consequence of a reduction in the number of adsorption sites available. This is consistent with the assumption that there are no adsorbent-adsorbent interactions and that the energy of adsorption is equal for all sites. Values of \( k_t \) at 0.15 bar are considerably higher than those at 0.5 or 1 bar due to the increased availability of sorption sites and enthalpies of adsorption being closer to their zero-coverage value. The decrease in the kinetic constant with pressure is less steep as the pressure rises, since the energetics are further away from the enthalpies at the onset of adsorption and the number of sites available is closer to saturation. As pressure increases fewer sites will be available for adsorption, decreasing the free kinetic energy in the system. Higher mass transfer coefficients at post-combustion pressures are desirable for a material designed to capture CO\(_2\); furthermore, adsorption dynamics must be faster for the gas that is being adsorbed compared to the other components of flue gases (mainly N\(_2\)) and the energy required for transport must be favorable. (1) shows the highest adsorption for CO\(_2\) with a high value of \( K_t \) at the usual post-combustion capture partial pressure of 0.15 bar.

First order kinetics accurately approximate adsorption dynamics on (1), so the Arrhenius equation can be used to estimate the activation energies of adsorption from plots of the natural log of the mass transfer constants and the inverse of the temperature:

\[
k_t = A \exp \left( -\frac{E_A}{RT} \right)
\]

where \( A \) is the Arrhenius pre-exponential factor, \( T \) is the system temperature and \( E_A \) is the adsorption activation energy. Arrhenius plots of sorption data at 3 different temperatures are shown in Figure 4-8. The values of activation energies for adsorption are given in Table 4-4, and are in agreement with values reported for other MOFs (MOF-5 \( E_A(298 \text{ K, 0.5 bar}) = 11.6 \text{ kJ/mol} \)) and
zeolites (Zeolite 13x $E_A(298 \text{ K}, 0.5 \text{ bar}) = 5.167 \text{ kJ/mol}$). The $E_A$ for CO$_2$ adsorption on (1) decreases as pressure increases as an increase in adsorption pressure results in a higher density of the bulk gas in the vicinity of the surface, leading to increased interactions lower energy needed for adsorption.

![Figure 4-8](image)

**Figure 4-8.** Arrhenius plots of adsorption rate constants (black squares – 150 mbar; red diamonds – 500 mbar) for CO$_2$ on (1). Linear fits are shown with dashed lines.

The mechanism for the transport of CO$_2$ to the adsorption sites and its rate limiting step can be determined by fitting kinetic data to different mathematical models, and finding the model that best represents the dynamic sorption data. In the absence of other resistances to mass transport, as in the case of the material in study, the diffusion to and through the material is assumed to be determined by the mass transfer of the gas inside the pores. If diffusion inside the micropores is considered the rate limiting step, diffusion coefficients can be obtained from the linear driving model kinetic constants by assuming spherical particles with the same size:

$$k_t = 15 \frac{D_v}{r_p}$$

Equation 4-7
where $D_s$ is the diffusivity of the gas inside the pores and $r_p^2$ is the radius of the spherical particle. Diffusivities predicted by this model are given in Table 4-5. As expected, diffusivity increases with temperature due to increasing thermal motion. Additionally, it decreases with pressure since less adsorption sites will be available and the most favorable binding sites will be occupied by other particles; furthermore, gas particles already adsorbed inside the pores may heighten the resistance to diffusion. Diffusivity values predicted by this model are comparable to diffusivities reported for other widely studied CO$_2$ adsorbents such as functionalized silica$^{17}$, zeolites (Zeolite 13x $D/r_p^2 (308 K) = 31.7 \cdot 10^{-4}$ s$^{-1}$) $^{4,7}$ and other MOFs (MOF-5 $D/r_p^2 (313 K) = 16.4 \cdot 10^{-4}$ s$^{-1}$) $^{4,6}$.

**Table 4-5.** Diffusion coefficients predicted using the Linear Driving Force and Intraparticle Diffusion model.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$D_s/r_p^2 \cdot 10^{-4}$ (1/sec)</th>
<th>$D_s/r_p^2 \cdot 10^{-4}$ (1/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linear Driving Force</td>
<td>Intraparticle Diffusion</td>
</tr>
<tr>
<td>308</td>
<td>17.76</td>
<td>12.38</td>
</tr>
<tr>
<td>323</td>
<td>29.96</td>
<td>22.89</td>
</tr>
<tr>
<td>338</td>
<td>41.16</td>
<td>28.76</td>
</tr>
</tbody>
</table>

$^a$ Data not presented due to high uncertainty when fitting data to model at this temperature.

Kinetic data was also fitted to the Intraparticle Diffusion Model (IDM)$^{18}$ as a way to confirm that diffusion inside the pores is the rate limiting step for adsorption, diffusivity values for this model are also shown in Table 4-5. The IDM considers a homogenous solid, with equal particle size and uniform surface concentration (equal energy in all sites). This model is a solution of the 1-dimensional equation for Fickian diffusion in the radial direction and can be solved and simplified by assuming an average concentration in each spherical particle.$^{18}$

$$\frac{q}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_A n^2 \pi^2 t}{R^2} \right)$$

Equation 4-8
where $q$ is the concentration of gas in the adsorbent varying with radial position, $D_A$ is the transport coefficient and $q_\infty$ is the average value of concentration in a spherical particle. For short times and low coverages are considered ($q_\infty/q_\infty < 0.3$) equation 4-8 is simplified to:

$$\frac{q}{q_\infty} = 6 \left( \frac{-D_A t}{R^2 \pi} \right)^{1/2}$$

Equation 4-9

It has been previously reported the use of an approximation of equation 4-8 for longer times\(^4\), however this approximation requires the assumption of a constant surface concentration. This assumption is likely to be violated at long times and thus equation 4-9 represents the best approximation for this model.\(^4\) Equation 4-9 can be linearized such that values of $D_A$ from a plot of $q_\infty/q_\infty$ against $t^{1/2}$. This will result in a straight line for diffusion inside the pores and the adsorption rate will decrease with greater particle size. Adsorption dynamics data showed a good correlation to the intraparticle diffusion model with $R^2$ values of 0.98 and above confirming that diffusion inside the pores is the rate limiting step for the diffusion of CO$_2$ on (1), plots of this model at 500 mbar are shown in Figure 4-9. The observed non-zero intercepts suggest a slight deviation from the model that is attributed to the fact that $q_\infty$ is being approximated as $q_e$ at each pressure. The intercept becomes closer to zero as pressure increases. Approximating $q_\infty = q_e$ is more valid when pressure rises and surface coverage goes to one in the Langmuir isotherm model. Diffusivities predicted by this model (Table 4-5) are slightly smaller but on the same order of magnitude as those calculated using the LDF approximation, and exhibit the same dependence on temperature and pressure. The lower values predicted by this model are a consequence of the fact that the LDF model assumes a lumped mass transfer coefficient that includes all resistances to transport, and due to differences in geometry of the actual particle in study (the MOF particles are prismatic in shape.).
Figure 4-9. Fits to the intraparticle diffusion model for CO₂ at 0.5 bar on (1): black squares – 308 K; red diamonds – 323 K; and grey circles – 338 K. Linear fits are shown with solid lines.

Desorption kinetics of CO₂ in (1) were studied using a similar procedure to that for adsorption kinetics. The linear driving force model applies because no hysteresis loops were observed in the sorption isotherms and low values of adsorption binding energy were found. This suggests that no chemical reaction or migration of the gases into the bulk of the solid occur (i.e. non-porous solid sections of the crystal). First order kinetics can be assumed and adsorption residence times can be approximated from the LDF constants. Figures 4-10, 4-11, and 4-12 show desorption kinetics curves for CO₂ at 150 mbar, 500 mbar and 1 bar at 3 different temperatures and their fits to the LDF model. When applying the LDF model to desorption data, equation 4-5 still applies but the integration limits for the concentration are inverted¹⁹. A similar behavior is observed for data at 65°C and 1 bar as the one described for kinetics of CO₂ adsorption, no data at this pressure/temperature is presented in this section; however this data is shown in Appendix A, figure A-3.
Predicted transport constants based on desorption kinetics are shown in Table 4-6. Values of desorption kinetics constants rise as temperature increases because more thermal energy is available to overcome the threshold for desorption. This is in accordance with the behavior of adsorption of CO$_2$ on (1). In this case, no decomposition is expected and a single molecular desorption can be assumed: one molecule is adsorbed and then desorbed without any changes in the process (i.e. chemical reaction or chemisorption). As a result, this is a first order kinetic process and is described by the following equation:

$$M(ads) \rightarrow M(des) \quad \text{Equation 4-10}$$

![Figure 4-10](image)

**Figure 4-10.** Kinetics of desorption of CO$_2$ at 0.15 bar on (1): black squares – 308 K; red diamonds – 323 K; and grey circles – 338 K. Linear Driving Force fits shown with solid lines.
Figure 4-11. Kinetics of desorption of CO$_2$ at 0.5 bar on (1): black squares – 308 K; red diamonds – 323 K; and grey circles – 338 K. Linear Driving Force fits shown with solid lines.

Figure 4-12. Kinetics of desorption of CO$_2$ at 1 bar on (1): black squares – 308 K; and red diamonds – 323 K. Linear Driving Force fits shown with solid lines.
When first order kinetics are assumed and the linear driving force model is applied to predict rate constants, the transport coefficient is intimately related to the surface residence time. This is the average time that a molecule will be adsorbed on a surface before it desorbs back to the bulk gas at the given pressure and temperature. The average residence time, $\tau$, is given by:

$$\tau = \frac{1}{k_{des}}$$  \hspace{1cm} \text{Equation 4-11}

where $k_{des}$ is the transport constant estimated using the Linear Driving Force model. Table 4-6 lists values of residence times for CO$_2$ molecules on (1) at common pre-combustion capture pressures and temperatures. Residence times decline with increasing temperature, as molecules will have a greater internal energy and more mobility. However, residence time values increase with pressure, as molecules have to overcome a higher resistance to leave the surface as the pressure increases.

**Table 4-6. CO$_2$ desorption transport coefficients and residence time on (1) estimated from first order desorption rate constants.**

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_{des}$ (sec$^{-1}$)</th>
<th>$K_{des}$ (sec$^{-1}$)</th>
<th>$K_{des}$ (sec$^{-1}$)</th>
<th>$\tau$ (sec)</th>
<th>$\tau$ (sec)</th>
<th>$\tau$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15 bar</td>
<td>0.5 bar</td>
<td>1 bar</td>
<td>0.15 bar</td>
<td>0.5 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td>308</td>
<td>0.021</td>
<td>0.012</td>
<td>0.011</td>
<td>48.24</td>
<td>85.44</td>
<td>86.97</td>
</tr>
<tr>
<td>323</td>
<td>0.026</td>
<td>0.015</td>
<td>0.015</td>
<td>38.14</td>
<td>65.78</td>
<td>68.13</td>
</tr>
<tr>
<td>338</td>
<td>0.042</td>
<td>0.027</td>
<td>0.025</td>
<td>23.59</td>
<td>37.14</td>
<td>40.45</td>
</tr>
</tbody>
</table>

Similar to the case of adsorption, the Arrhenius equation can be used to estimate activation energies of desorption at a given pressure. Desorption at 1 bar will be studied as this pressure is more representative for industrial processes in which carbon dioxide is captured and then desorbed. In order to compare energies and residence times, parameters for CH$_4$ and N$_2$ desorption kinetics were also obtained at 1 bar. Desorption curves for different gases at 323 K and 1 bar are shown in Figure 4-13 with the Linear Driving Force model fits. The Arrhenius plot of CH$_4$ at 1 bar is included in Appendix A, figure A-4, and calculated values for residence time and desorption
activation energies are given in Table 4-7. The activation energy of desorption for CO$_2$ is slightly lower than that of CH$_4$ and less than 1/3 of the value for N$_2$. The residence time for CO$_2$ is more than twice that for CH$_4$ and N$_2$, suggesting that CH$_4$ and N$_2$ will be preferably desorbed compared to CO$_2$. The absolute rate of CO$_2$ desorption is considerably faster, as shown in Figure 4-13, which is further explained by the calculated values of the activation energies for desorption. The data suggest that N$_2$ will be desorbed first, followed by CH$_4$, leaving CO$_2$ on the surface longer. This is a promising scenario for CO$_2$ post-combustion capture$^{13,20}$.

![Figure 4-13. Kinetics of desorption at 323 K and 1 bar on (1). Desorption curves of CO$_2$ (black squares), CH$_4$ (red diamonds) and N$_2$ (grey circles) with Linear Driving Force fit shown with solid line.](image)

**Table 4-7. Residence time and desorption activation energy of different gases on (1).**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau$ (sec)</td>
<td>$E_A$ (KJ/mol)</td>
<td>$\tau$ (sec)</td>
</tr>
<tr>
<td>308</td>
<td>86.97</td>
<td>-</td>
<td>38.07</td>
</tr>
<tr>
<td>323</td>
<td>68.13</td>
<td>14.28$^b$</td>
<td>30.13</td>
</tr>
<tr>
<td>338</td>
<td>-a</td>
<td>17.64</td>
<td>-a</td>
</tr>
</tbody>
</table>

$^a$ Data not presented due to high uncertainty when fitting data to model at this temperature.

$^b$ Calculated by solving Arrhenius equation between 2 temperature points (308 K and 323 K).
4.4. Conclusions.

Adsorption and desorption studies of CO₂, CH₄, and N₂ in a microporous MOF with open Zn(II) coordination sites at temperatures and pressures relevant to post-combustion CO₂ capture were performed. CO₂ exhibited the highest adsorption on (1) among the gases studied, with all the gases showing a type-1 adsorption with no adsorption/desorption hysteresis. CO₂ also exhibited the highest enthalpy of adsorption and a high IAST selectivity over N₂ and CH₄, which suggests that (1) is a promising material for post-combustion CO₂ capture, selectivity values over N₂ suggest that separation can be enhanced by a decrease in temperature. The adsorption dynamics of CO₂ are well described by the linear driving force model and diffusion inside the pores was found to be the rate-limiting mechanism for CO₂ transport to adsorption sites. Values of diffusion coefficients were estimated from the linear driving force model and the intraparticle diffusion model. These values increase as temperature increases due to an increase in available energy, but decrease with increases in pressure due to partial pore saturation. Activation energies were calculated from an Arrhenius plot and the activation energy required for the molecules to diffuse through the material decreases with pressure. Desorption kinetics for CO₂, N₂ and CH₄ are well-described by the LDF model assuming a first order desorption process. Residence times were estimated from kinetic data showing that CO₂ has greater residence times at all temperatures and the lowest value of desorption activation energy among the three gases as predicted from the Arrhenius equation. A low desorption activation energy on (1) combined with high residence times favors the selective adsorption and capture of CO₂ in industrially relevant processes.

References.


Chapter 5. Fabrication, Characterization and Permeation Study of a Metal Organic Framework Membrane with Open Zn(II) Coordination Sites on a Porous Support.

5.1. Introduction.

Metal organic frameworks (MOFs) are crystalline porous materials consisting of polymeric inorganic networks with high surface areas, defined pore sizes and adjustable chemical functionality\(^1,2,8\). MOFs structural and chemical properties make them ideal in the development of continuous films and membranes for the adsorption and separation of gases, as their chemistry can be tailored to serve a particular application\(^1,9\). Recently, one of the main focuses of MOFs research is the adsorption, separation and conversion of CO\(_2\) from industrial processes to mitigate the effects of the production of greenhouse gases; researchers are actively looking for solutions at stationary point sources as in the case of power plant emissions and natural gas sweetening processes\(^9,10,11\). MOFs present a solid alternative when trying to find materials with ideal properties for these capture and separation processes. There are two main approaches to take advantage of the MOF structures and chemical properties when separating gases: Kinetic-based separations and Thermodynamic separations\(^1,9\). In kinetic based separations the diffusivities of gases to the surface and inside the pores of the material are the parameters to model. Three main mechanisms describe the diffusion of gases inside pores of crystalline materials, viscous flow, Knudsen diffusion and surface flow\(^5,17\), depending on the relative size to the gas molecules, the interactions among gases and between gases and pores, and the driving force that makes diffusion possible. In the case of thermodynamic separations, the affinity and interactions of the material with each of the components in the gas stream is the key parameter\(^1,9\). Numerous studies have studied both kinetic-based and thermodynamic-based processes using MOF materials as CO\(_2\) adsorbents and as gas
separation membranes. The fabrication of continuous MOF films has found application in different areas as supported catalysis, molecular sensors and gas separation membranes. 

The synthesis of MOF as continuous films for gas separation membranes has been relatively successful and the methods used for membrane synthesis are dependent on the MOF used, the materials used for support and the potential application for the membrane\textsuperscript{10}. Different synthesis techniques have been used in the formation of MOF and ZIF membranes, among the methods commonly used for the synthesis of membranes are the layer-by-layer method\textsuperscript{9,10}, secondary growth method and direct solvothermal synthesis\textsuperscript{2,6,8,9}. Most of the research on MOF membranes is dedicated to find materials that would separate gases above the Knudsen separation factor \textsuperscript{8,9,10}, with the focus of these studies being on the formation of continuous, defect-free films that can be tested for permeation. However, only a few studies have focused in detail on the transport mechanisms that occur inside the pores of the membrane and on the presence of intercrystalline boundary defects. The presence of macrodefects, mainly pinholes, cracks and crystal boundary defects is one of the consequences of using a supported method for the fabrication of crystalline membranes\textsuperscript{10}, the use of a thin polymer layer has been successfully used with carbon nanotubes to test the gas permeation without making major modifications to the MOF membrane synthesis process\textsuperscript{5}.

Our research groups previously reported on the gas adsorption properties of a Zn(II)-based MOF with coordinately unsaturated Zn(II) metal nodes without the need of activation\textsuperscript{1}, this MOF displays a favorable adsorption for CO\textsubscript{2} as well as fast and preferential sorption dynamics. Herein we present a method for the formation of a MOF/polymer membrane with high gas fluxes and Knudsen diffusion inside the pores of the material. The focus of this study is on the separation performance of gases that are of interest in flue gas and natural gas separation streams. We present
a study of the diffusion mechanism that govern the transport of gases through the MOF and a new method to study the presence of intercrystalline defects.

5.2. Methods.

5.2.1. Materials.

The following materials were purchased from the indicated commercial suppliers: Zinc(II) nitrate hexahydrate (Sigma Aldrich, 98%); 2,5-pyridinedicarboxylic acid (pdc, Sigma Aldrich); N,N-dimethyformamide (DMF, Spectrum Chemical, spectrophotometric grade); polyethylenimine (PEI; Sigma Aldrich, 50%); cetyltrimethylammonium bromide (CTAB, Sigma Aldrich); Tetraethyl orthosilicate (TEOS, Sigma Aldrich), anhydrous ethanol (Decon Labs Inc., 100%); Polysulfone (PSF, UDEL P-3500, Solvay); alumina ceramic membrane supports (Kerafol GmbH, 25 mm diameter, 0.5 μm pore size on front side, 2 μm on opposite side); carbon dioxide (gas, 99%), nitrogen (gas, 99%), hydrogen (gas, 99%) and methane gas tanks (gas, 99%) were purchased from Airgas.

5.2.2. Synthesis of Zn₄(pdc)₄(DMF)₂•3DMF (1).

MOF crystals were synthesized following the procedure previously reported by our research groups¹. In a 20 mL vial, Zn(NO₃)₂•6(H₂O) (375 mg) was dissolved in 15 mL DMF followed by the addition of 2,5-pyridinedicarboxylic acid (216 mg). The vial was capped and sonicated until turbid and heated to 100 °C for two days. The vial containing cubic crystals was removed from the oven and allowed to cool. The crystals were collected via vacuum filtration and rinsed with DMF. They were allowed to dry for one day at room temperature and then they were mechanically crushed to ensure a more uniform crystal size.
5.2.3. Membrane fabrication and characterization.

5.2.3.1. Porous membrane fabrication.

Supported (1) membranes were fabricated using a modified seeded growth procedure, this technique has been previously applied elsewhere for the formation of Cu-based MOFs membranes and zeolite membranes on alumina supports.\textsuperscript{2,3} Films were formed in a 5 steps procedure, it is especially important to control temperature and pH conditions during steps related to the superficial modification of alumina supports. For the successful formation of continuous films of Zn-based MOF membranes, the surface of the support must be previously smoothed and functionalized to achieve sufficient binding between the surface of the material and the MOF crystals. A description of the steps for membrane formation follows.

**Step 1. Support surface modification.** Porous alumina ceramic supports were used as substrates for the growth of MOF films; initially a smooth mesoporous silica layer was formed by a sol-gel technique including a two-step hydrolysis procedure described elsewhere\textsuperscript{3}. This silica layer provides a smooth surface for membrane formation, preventing crystallization inside the pores\textsuperscript{3}, it was synthesized by a typical sol-gel polymerization of tetraethyl orthosilicate (TEOS) in ethanol and water. Cetyltrimethylammonium bromide (CTBA) was added to this homogeneous solution as a catalyst to form a rigid gel consisting of silica and solvent filled pores after undergoing a sol-gel transition. This gel is subsequently aged and added to the porous supports, followed by calcination to activate the surface and unblock the pores.

First, 63 mL anhydrous ethanol, 60 mL tetraethyl orthosilicate and 4.87 g DI water were mixed and the pH of the mixture was adjusted to 4 by adding 0.07 M HCl dropwise; this mixture was hydrolyzed by refluxing at 60°C for 1.5 h and stored at 3°C for later use. Subsequently, 40 ml of the initial solution were mixed with 4 g of cetyltrimethylammonium bromide (CTAB surfactant)
and the pH of the resulting clear solution was adjusted to 2 by adding 0.07 M HCl under stirring conditions, this pH was regulated adding 0.1 M NaOH. The obtained solution was then aged for 60 hours at 50°C to prevent penetration inside the pores of the support, this aging step reduces the crystallization rate of the silica solution, and it also forms a viscous solution that can be consequently dissolved in ethanol to control the final silica layer thickness. 1 ml of this aged solution was dissolved in 256 ml of ethanol and the final dilute solution was applied to porous alumina supports by slip-coating, an as received support was half immersed into the solution with the smaller pore size side facing downward, supports were soaked for 1 min and immediately slipped away and stopped in a vertical position for 1 min to dry the excess. Modified supports containing silica films were calcined at 480°C for 4 h with a ramp rate of 1 °C/min in a Blue M oven for activation and to prevent blockage of the pores.

**Step 2. Porous silica membrane modification.** Ceramic alumina membrane supports containing a silica layer were further modified by using polyethyleneimine (PEI) with aims to enhance the attachment of MOF crystal seeds via H-bonding. PEI has been previously applied to the formation of zeolite and MOF membranes as its functionality facilitates the formation of seed crystal layers. Alumina membrane supports were dip coated in a PEI-water solution (1:30 w/w) followed by drying under vacuum for 15 min at 80°C, this process was repeated three times to ensure total surface coverage of the support with PEI. The modified supports were left to dry at room temperature for 24 hours.

**Step 3. Manual Assembly of Microcrystal monolayers on substrates.** Crushed crystals of (1) were deposited onto the modified support surface by rubbing the MOF crystals on the surface with a finger in a circular movement repeatedly for 20 s, H-bonding is formed due to the kinetic energy added in the rubbing step and plays a fundamental role in this part of the procedure.
Step 4. Secondary growth. Seeded supports were placed vertically in a homemade Teflon reactor containing the MOF synthesis solution described above, the reactor was heated to 100 °C for two days in a blue M oven. The reactor containing cubic crystals on the surface of the seeded support was removed from the oven while hot, the resulting MOF membrane was washed with DMF and dried under vacuum for 15 min, and subsequently the MOF membrane was left to dry at ambient temperature for a minimum of 24 hours.

Step 5. Polysulfone (PSF) thin layer formation. Synthesized MOF membranes fabricated in the previous step could potentially have cracks and imperfections on their surface. Their tested gas permeability was extremely fast, comparable to that of the alumina support without any modifications, suggesting the presence of pinholes and structural defects on the surface of the MOF membrane. Structural defects on the membrane surface can be corrected by applying a thin layer of a polymer with low permeation to gases. PSF is a tough, rigid, high-strength thermoplastic polymer with low gas permeance, it has an outstanding hydrolytic resistance and serves both as a material to impart mechanical strength and to seal the structure of the membrane. PSF has been widely studied as a material with favorable mechanical and chemical properties for gas permeation. A dilute polymer solution of PSF in DMF (7.5% w/w) was used to ensure that the polymer will penetrate well among the synthesized MOF crystals forming the surface of the membrane. The dilute polymer solution was spin coated on the sample to form a sealing polymer layer, the PSF solution was initially poured dropwise onto the surface, waiting for 30 seconds for it to penetrate well among the crystals, this was followed by spin coating for 20 seconds at 1500 rpm (Laurell Technologies, W-400B). The formed layer was dried at room temperature for 24 hours filling and correcting any imperfections or pinholes present on the MOF membrane surface. The obtained modified membrane was ready to be tested for gas permeation.
5.2.3.2. Imaging.

Scanning electron microscopy (SEM) was performed using an a LEO (Zeiss) 1550 field-emission scanning electron microscope at 5.0 kV for high-resolution images of the films, resolutions from 200 nm to 200 μm were employed on Au/Pd sputter coating on membrane supports.

5.2.3.3. X-ray diffraction.

X-ray diffractometry was used to confirm the structure of the as-synthesized membranes, membrane disks were directly placed in the instrument for their analysis. Experiments were carried out on a Bruker AXS D2-Phaser, measurements were carried out over a 2θ range of 3 - 50° in continuous scanning mode with 0.01° steps at a rate of 1°/min.

5.2.3.4. Single gas permeation.

A constant volume varying pressure permeation setup is used for single gas permeation measurements. A schematic of the permeation apparatus is shown in figure 5.1.

![Permeation apparatus for single gas transport experiments.](image)

Figure 5-1. Permeation apparatus for single gas transport experiments.

A homemade removable convection oven is included around the permeation cell to control the temperature of the described system when needed (Figure 5-2), a thermocouple/temperature controller is used to monitor the temperature inside the oven; including the membrane cell, feed pipe and permeate pipe. The system is connected to a PC where the permeation setup is controlled.
using a LabView platform, several conditions of this system can be modified including feed pressure, system temperature, permeation time, degassing time and permeate volume. Feed pressure is controlled via an on/off valve and a gas regulator connected to the gas tank providing the gas pressure. The LabView platform is divided into three sequences: degas, permeation and shutdown. The degas and shutdown sequences are fundamental as vacuum inside the system is achieved during these steps to ensure an accurate measurement of the permeability of gases; most of the issues that can be found when using the system are related to the pipes and permeation cell effectively going to vacuum. Troubleshooting includes testing the different pipes and valves to look for any gas leaks, they can also be caused by the gas permeation membrane cell. The time required to complete each sequence and the maximum permeate pressure can be modified by the user, the number of cycles to complete in each run can also be selected. Data is recorded for feed and permeated pressures, testing time and averaged temperature.

The permeation membrane cell is a fundamental part of the system since the sample is contained inside, figures 5-3 and 5-4 show images of the membrane cell used for gas permeation; this cell was designed to work exclusively with 2 mm thickness and 25 mm diameter substrates; however thinner samples have been modified by filling the empty space with ultrafiltration filter paper in order to adjust their size and be successfully used in this permeation cell.

Figure 5-2. Homemade oven with temperature controller containing gas permeation cell.
The membrane cell is sealed and kept at vacuum by applying pressure with six stainless steel screws, gas leaks in the system are minimized with two Viton O-rings. The membrane is supported by a porous metal disk on the feed side, this also gives some mobility to the sample to avoid cracks due to uneven pressure against the solid stainless steel forming the permeation cell. Since alumina supports of 2 mm in thickness are being used, it is important to apply pressure uniformly throughout the surface of the membrane, the membrane cell must have a diameter that is big enough to allow for the deposition of the sample without risking the possibility of leaks in the system due to the sample being too small for the system.
To minimize errors in calculations of single gas permeance, the permeate side volume was accurately determined using a known volume cylinder and two pressure transducers with errors of less than 2%. Using impermeable aluminum tape, both sides of the permeation cell were separated, the system was taken to vacuum and then filled with nitrogen at a given high value of pressure, subsequently the system was taken to a lower value of pressure, closing the valve that was connected to the known volume cylinder (valve-1). Vacuum was applied to the rest of the system and then valve-1 was opened, the system was taken to equilibrium pressure and with the three values of pressure recorded and a mole balance the volume of the permeate side was determined as 17.51 cc. The system was also checked for leaks by degassing the setup to vacuum and recording changes in pressure with time when the system is in idle mode, if no significant changes are observed (less than 0.03 cmHg increase in pressure inside the system in 2 hours) the system can be used to test permeability accurately.

In a typical permeation experiment, the system was initially maintained under vacuum for 2 hours in a degas procedure, after degassing a constant pressure feed of gas is applied to the feed side of the membrane until a pressure of 10 cmHg is reached on the permeate side of the constant volume permeation apparatus. Gas permeation experiments were performed using CO₂, CH₄, N₂ and H₂ maintaining a constant feed pressure, with variable temperatures in the 23°C to 45°C range. The gases and conditions used in the experimental procedure are relevant to important separation applications as in the case of flue gas and natural gas separation.

5.3 Results and Discussion.

5.3.1 Membrane formation and characterization.

A MOF continuous film is successfully formed following the procedure described in the previous section, characterization studies are made to the different steps of the membrane
formation procedure to ensure a quality membrane. Figure 5-5 describes the expected chemistry in steps 1 to 4 of the membrane formation procedure; PEI attaches to a functionalized silica layer, allowing for the formation of H-bonds between the PEI chains and the MOF crystals.

![Diagram of MOF structure](image)

**Figure 5-5.** PEI-mediated hydrogen bonding between the surface hydroxyl groups of MOF and silica modified support.

The structure of the synthesized membrane was studied by X-ray diffraction and compared to the patterns produced by a sample of powder of the MOF and the powder pattern simulated in Mercury. (Figure 5-6) These results confirm the formation of a thin layer of (1) on the alumina supports after the secondary growth method.
Figure 5-6. XRD patterns of as synthesized MOF membranes and MOF powders.

Each step of the modified MOF membrane film formation before and after the PSF layer addition were further studied by SEM imaging. Figure 5-7A-D shows images of the different steps of the membrane formation. 5-7C suggests the presence of pinholes and possible structural defects on the MOF membrane that are later corrected in 5-7D, which is achieved by adding a PSF layer. It can be observed that the PSF layer is only correcting the imperfections on the membrane but not blocking the pores of the material, crystals are still exposed above the polymer matrix. This thin layer is only about 500 nm in thickness but PSF is expected to be 7 orders of magnitude slower in gas permeance than the MOF.
Figure 5-7. SEM images of different stages of MOF membrane growth (A) Bare alumina support, (B) seed layer, (C) MOF membrane after secondary growth, (D) MOF membrane covered by a thin PSF layer.

Modified MOF films with a covering PSF layer as presented in figure 5-7D can be used to study the permeance of different gases as well as for the understanding of transport mechanisms and temperature effects. Similar membranes with asymmetric structures have been previously reported in the literature with many reports focusing on the growth of MOF films on α-alumina supports, the solvothermal synthesis method has been successfully applied for the formation of MMOF membranes, MOF-5 membranes, NH2-MIL-53(Al) MOF membranes, ZIF-8, ZIF-90, HKUST-1 and ZIF-90 among others obtaining different asymmetric structures and variable thicknesses. Polysulfone has been previously used as a sealing material to correct imperfections
and impart mechanical strength; however, this is the first report using PSF after a solvothermal membrane synthesis to the best of our knowledge.

5.3.2. Single gas permeation experiments.

Single gas permeation experiments of CO$_2$, CH$_4$, N$_2$, and H$_2$ were performed at different temperatures relevant to CO$_2$ separation from flue gas and natural gas sweetening using the permeation setup described in the previous section. Figure 5-8 shows a masked MOF membrane using aluminum tape to control the permeation area, this tape also reduces leaks through the sides of the support, as the tape has practically no permeation to gases.

**Figure 5-8.** Top-view of masked alumina support with effective permeation diameter of 0.9 cm.

Permeation data is recorded as the change in permeate pressure with time, and the permeance, $P_i$, defined as the ability of a gas to flow through the porous membrane, is calculated according to equation 5-18,14,23,

$$ P_i = \frac{N_i}{\Delta p_i \cdot A} $$

Equation 5-1

Where $N_i$ is the permeate flow rate of component $i$, $\Delta p_i$ is the pressure difference between the feed and permeate side and $A$ is the permeation area of the membrane. Gas permeance of CO$_2$, CH$_4$, N$_2$, He and H$_2$ through a (1) membrane was measured at 23°C, 35°C and 45°C following this procedure. These pressures and temperatures are relevant to multiple applications as in the case of
flue gas separation and natural gas extraction\textsuperscript{9,10,11}. Each permeation measurement was repeated at least 3 times to ensure repeatability in the data.

The transport of gases through a porous membrane can be described by three main mechanisms: viscous flow, Knudsen Diffusion and surface flow\textsuperscript{17}. Each flow regime is a function of the size of the crystalline pores of the material, the kinetic diameter of the molecules flowing, the driving force for transport and the molecular/superficial interactions that govern the transport. The Knudsen number ($K_n$) can be used to estimate the preferential mechanism of diffusion through the pores of a crystalline material (equation 5-2)\textsuperscript{5,17},

$$K_n = \frac{\lambda}{d_p}$$  

Equation 5-2

This number relates the mean free path ($\lambda$, distance that a gas molecule has to travel to collide with another gas molecule) to the pore diameter of the material ($d_p$) ($d_p = 7.17$ Å for (1)). $K_n$ values greater than 10 suggest that Knudsen diffusion and viscous flow will be the main diffusion mechanisms in absence of other interactions among molecules and with the pore walls. Viscous flow, which is the bulk flow of the gas, occurs mainly due to pressure differences inside pinholes and cracks on the membrane surface, this mechanism can be discarded if the membrane obeys the Knudsen diffusion behavior or if the transport of a non-adsorbable gas is independent of pressure\textsuperscript{5,15,16}. Knudsen diffusion occurs as the number of collisions between the gas molecules and the pore walls is greater than the effective number of collision between molecules. Values of $K_n$ bellow 10 suggests the presence of a greater number of interactions among gas molecules and among active surfaces and gas molecules\textsuperscript{5,17}. Table 5-1 shows values of mean free path and Knudsen number for the diffusion of different gases through (1).
Table 5-1. Mean free path and Knudsen number at 296 K and 1 atm of different gases on (1).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Kinetic diameter (Å)</th>
<th>Mean free path (nm)</th>
<th>Knudsen number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.30</td>
<td>83.65</td>
<td>116.67</td>
</tr>
<tr>
<td>N₂</td>
<td>3.64</td>
<td>68.75</td>
<td>95.89</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.76</td>
<td>64.44</td>
<td>89.87</td>
</tr>
<tr>
<td>H₂</td>
<td>2.80</td>
<td>116.19</td>
<td>162.05</td>
</tr>
</tbody>
</table>

Reported values of Knudsen number in Table 5.1 are greater than 10 suggesting that diffusion will be mainly due to Knudsen type transport and viscous flow, if structural defects are present on the surface of the membrane. This will be further studied by measuring the permeance of gases through the membrane as a function of temperature.

Figure 5-9. Gas molecular weight vs. permeation on a (1) MOF membrane at 296 K.
The relation between permeation and the molecular weight of the gases permeating at 23°C is presented in figure 5-9, it can be observed that the flux of gases is related to the molecular weight of the gas and not to the kinetic diameter, this is in agreement with the Knudsen diffusion of gases through the membrane. The diffusion coefficient of gases through a membrane in Knudsen flow, \( D_K \), can be calculated using equation 5-3, this equation relates the flux of gases to the pore size diameter, \( d_p \), the temperature in the system, \( T \), and the molecular weight of the gas being transported, \( M_w \), a relation between permeance and molecular weight is expected. This behavior also suggests that the diffusion rate has a major effect on the permeation of gases through this membrane and therefore adsorption and other molecular interactions are not as significant.

\[
D_K = \frac{d_p}{3} \cdot \sqrt[3]{\frac{8RT}{\pi M_w}}
\]

Equation 5-3

It follows that in Knudsen regime the permeance of gases through the membrane is inversely proportional to the square root of the molecular weight of the permeant gases, figure 5-10 shows a linear relationship between the permeance of the individual gases and the inverse square root of the molecular weight, values fit accurately to the Knudsen diffusion equation. Values of permeance are among the higher values reported for MOFs \(^9,10\), ZIF-8 presents a higher permeance to CO\(_2\) under similar experimental conditions \(^18\), this can be attributed to the properties of the pores of the material, their functionality, and the effect of the alumina supports where the MOF membrane was grown. The alumina supports used for film growth are composed of a thin alumina layer with pore sizes of 0.5\(\mu\)m while the rest of the support has a pore size of 2 \(\mu\)m, this creates an additional pressure differential that increases the flux of gases through the membrane.
Figure 5-10. Single gas permeance as a function of the inverse square root of the molecular weight of the permeant gas on a (1) MOF membrane at 296 K.

The selectivity from single gas adsorption data is calculated using equation 5-4 (permselectivity); a fast transport of gases is important when designing systems that offer effective solutions to the separation of CO₂; however, equally important is the selectivity of the membrane to one of the gases⁹,¹⁰,¹¹. Ideally, the focus of research is on membranes with high transport and values of selectivity above that predicted by the Knudsen model⁸,¹⁰,¹¹, the selectivity predicted by the Knudsen diffusion model relates the selectivity of gases, \( S_{i/j} \), to the inverse square root of the molecular weight of the species being separated (equation 5-5)⁵,¹⁹. The selectivity from single gas adsorption data was calculated using equation 5-4 (permselectivity); these values were then compared to the ideal Knudsen selectivity and are presented in table 5-2.
\[ S_{i/j} = \frac{P_i}{P_j} \]  \hspace{1cm} \text{Equation 5-4}

\[ S_{i/j} = \frac{M_j}{\sqrt{M_i}} \]  \hspace{1cm} \text{Equation 5-5}

Where \( S_{i/j} \) is the permselectivity of gas \( i \) with respect to gas \( j \), \( P_i \) is the permeance of gas \( i \), \( P_j \) is the permeance of gas \( j \), \( M_i \) is the molecular weight of gas \( i \) and \( M_j \) is the molecular weight of gas \( j \). Values of permselectivity and Knudsen constant in table 5-2 show similar values further confirming Knudsen diffusion. The difference in the values of the permselectivity of \( \text{H}_2 \) is most likely due to differences in diffusion properties and the effects of adsorption\(^8\), also the smaller kinetic diameter of \( \text{H}_2 \) will play a role when accounting for other diffusion mechanisms besides Knudsen transport. Figure 5-11 shows the adsorption of \( \text{CO}_2 \) and \( \text{H}_2 \) at 308 K. This plot helps explain how the adsorption of \( \text{H}_2 \) relative to \( \text{CO}_2 \) plays a role in explaining the permeance and permselectivity of both gases, as the adsorption of \( \text{H}_2 \) is lower but steeper at low pressures (<1 atm), it is likely that other diffusion mechanisms will be significant in the case of \( \text{H}_2 \) and adsorption will be important slowing down the permeance of hydrogen.

Figure 5-11. High pressure isotherms at 308 K, \( \text{CO}_2 \) (blacks squares) and \( \text{H}_2 \) (red diamonds).
Table 5-2. Single gas permselectivity and ideal Knudsen constant of different gases with respect to the permeance of CO₂.

<table>
<thead>
<tr>
<th>Gas (i/j)</th>
<th>Permselectivity</th>
<th>Knudsen Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂/CO₂</td>
<td>1.15 ± 0.0025</td>
<td>1.25</td>
</tr>
<tr>
<td>CH₄/CO₂</td>
<td>1.59 ± 0.0026</td>
<td>1.66</td>
</tr>
<tr>
<td>H₂/CO₂</td>
<td>2.93 ± 0.0036</td>
<td>4.67</td>
</tr>
</tbody>
</table>

The effect of temperature on the permeation of gases through a (1) membrane was also studied at 3 different temperatures (296 K, 308 K and 318 K) to determine if different interactions are present in the system as temperature increases; and to discard the presence of pinholes and structural defect in the membrane (by confirming Knudsen diffusion). Figure 5-12 shows a plot of the change in gas permeance with temperature for CO₂, N₂, CH₄ and H₂; as predicted by the simplified one-dimensional Knudsen solution to the Fick’s equation (equation 5-6). Flux of gases through the pores of the MOF membrane decreases slightly with temperature for all the gases in study as it is inversely related to the square root of the temperature of the system,

\[
N_{Kn} = \frac{d_p}{3} \cdot \frac{8}{\pi T R M} \cdot \frac{\Delta P}{L}
\]

Equation 5-6

Where \( J_{Kn} \) is the gas flux, \( \Delta P \) is the pressure difference between the permeate side and the feed side of the membrane, \( L \) is the membrane thickness, \( d_p \) is the pore size diameter, \( T \) the temperature in the system, and \( M_w \) the molecular weight of the gas being transported.
Figure 5.12. Single gas permeance of different gases as a function of temperature.

The permselectivity of the membrane as a function of temperature is presented in Figure 5.13; as expected, selectivity is constant with temperature due to the almost linear decrease that the permeance of all gases presents with temperature, and the fact that selectivity is independent of temperature under Knudsen regime as described by equation 5.5. All reported values of permselectivity are still below the Knudsen separation factor.
Figure 5-13. Permselectivity with respect to CO$_2$ of different gases as a function of temperature.

The fact that the selectivity of gases is independent of temperature is a confirmation of membrane quality, this plot verifies the absence of convective flow through pinholes and structural defects in the membrane. The molar flow rate of an ideal gas $i$ through membrane defects due to convective flow is given by equation 5-7,

$$\dot{N}_i = \frac{VRT}{P}$$  \hspace{1cm} \text{Equation 5-7}

Where $\dot{N}_i$ is the molar flow rate of component $i$, $V$ is the volumetric flow rate of gas $i$, $R$ is the ideal gas constant, $T$ is the temperature in the system and $P$ is its pressure. As previously stated, the molar flow rate predicted by Knudsen transport will be described by equation 5-6. Therefore, the total molar flow through the membrane due to Knudsen diffusion and convective flow, is given by equation 5-8, obtained adding equations 5-6 and 5-7,
\[
N_{Ti} = -\frac{d_p}{3} \cdot \sqrt{\frac{8 \Delta P}{\pi TR M_i}} \cdot \frac{\Delta P}{L} + \frac{\mathcal{V}_i}{p} \tag{Equation 5-8}
\]

Where \(N_T\) is the total molar flow of gas \(i\). The permselectivity of gas \(i\) with respect to gas \(j\) through the membrane can then be calculated using equation 5-9, as the ratio of single gas molar flows,

\[
S_{i/j} = \frac{\frac{d_p}{3} \cdot \sqrt{\frac{8 \Delta P}{\pi M_i}} \cdot \mathcal{V}_i}{\frac{d_p}{3} \cdot \sqrt{\frac{8 \Delta P}{\pi M_j}} \cdot \mathcal{V}_j} \tag{Equation 5-9}
\]

In the particular case of Knudsen diffusion, and in the absence of convective flow, the permselectivity will be independent of temperature as predicted by equation 5-5. The plot of permselectivity vs temperature shown in figure 5-13 produces a straight line with zero slope, confirming the absence of defects and pinholes in the membrane structure, and verifying Knudsen diffusion as the main transport mechanism.

A similar behavior in the Knudsen diffusion regime has been previously presented for different MOFs and ZIFs, permeance is inversely proportional to temperature, while temperature has little to no effect on the permselectivity.

**5.3.3. Study of transport mechanism.**

The study of the transport mechanisms of gases inside a membrane is key when trying to improve the selectivity/permeability of a crystalline membrane, and to enhance the interactions among the gas molecules and different surfaces of the crystalline pores to achieve a better separation. It is important to develop a method that allows to distinguish the transport mechanism inside the pores of the membrane; and, in the case of a crystalline membrane, to understand if transport is happening inside the pores of the MOF crystal or between adjacent MOF crystals. The previous section suggested that transport will be dominated by Knudsen diffusion, this was
expected due to the size of the pores of the MOF relative to the mean free path of the gases in study\textsuperscript{5}.

The method presented in this section has never been presented to study the transport mechanisms of a porous material to the best of our knowledge. The goal of this method is to minimize the thickness of the membrane and the number of crystals that are being tested for permeation. A thin MOF layer of approximately 2 μm has been created by following the initial 3 steps of the procedure described in section 5.2.3.1. Porous alumina supports were modified by adding a silica layer, followed by dip-coating a PEI layer. MOF crystals were consequently added via manual assembly. The formed thin layer is composed by only a few crystals, however there will be a significant number of pinholes, structural defects and crystal interfaces as the surface of the support will not be totally covered by the MOF. This was solved by dip-coating the modified supports containing MOF crystals with a thin PSF layer; as demonstrated previously. This layer covers the imperfections but the MOF crystals are still exposed, allowing for permeation to happen through the crystals only and reducing the number of crystal-crystal interfaces on the surface. An SEM image of the obtained PSF-covered-MOF-crystals on alumina supports is presented in figure 5-14, it can be observed that the layer is only formed by a few MOF crystals and only contains a couple of crystals in thickness as desired. The few interfaces between crystals are mostly covered by the thin PSF layer.
Values of permselectivity measured on this membrane are still valid as they represent the ratio of the permeation of a single gas with respect to the other, the gas is travelling through the same MOFs crystals and the same surface area. If permselectivity values are constant and follow Knudsen regime (inversely related to the square root of the molecular weight of the gases), this confirms that the gas is traveling inside the pores of the MOF crystals in the MOF membrane and not between adjacent crystals. The permeation of gases has been restricted to travel through the pores of the crystals by covering all intercrystalline boundaries with a low permeance polymer, and decreasing the number of crystal-crystal boundaries by creating a thin seed layer. Table 5-3 shows the values of permselectivity of the thin layer compared to the values of the MOF membrane and the Knudsen constant, all values are similar confirming that permeation is happening inside the pores of the crystals forming the membrane and not inside the spaces among adjacent crystals. These result also confirms a Knudsen transport mechanism inside the pores of the MOF membrane. The difference in the values with respect to Hydrogen can be attributed to the smaller kinetic
diameter of H$_2$, its adsorption properties and the relative velocity of the flow of hydrogen with respect to the other gases$^8$.

**Table 5-3.** Thin seed layer single gas permselectivity compared to the MOF membrane permselectivity and Knudsen constant of different gases with respect to CO$_2$ at 296 K.

<table>
<thead>
<tr>
<th>Gas (i/j)</th>
<th>Permselectivity</th>
<th>Thin seed layer permselectivity</th>
<th>Knudsen Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$/ CO$_2$</td>
<td>1.15</td>
<td>1.26</td>
<td>1.25</td>
</tr>
<tr>
<td>CH$_4$/ CO$_2$</td>
<td>1.59</td>
<td>1.71</td>
<td>1.66</td>
</tr>
<tr>
<td>H$_2$/ CO$_2$</td>
<td>2.93</td>
<td>3.88</td>
<td>4.67</td>
</tr>
</tbody>
</table>

**5.4. Conclusions.**

We studied the transport of CO$_2$, CH$_4$, N$_2$ and H$_2$ through a Zn(II)-based MOF/Polymer membrane. The membrane was successfully synthesized by a solvothermal secondary growth method with structural defects being covered by a thin PSF layer. The membrane showed no pinholes or defects after inspecting via SEM imaging and testing the gas selectivity as a function of temperature. This modification of the secondary growth method would facilitate the measurement of the permeation of materials that do not normally form uniform-defect free layers. The permeance of single gases shows a linear relation to the inverse square root of the molecular weight of the permeant gases, flux of gases is happening on a Knudsen regime with the permeation of gases decreasing with temperature, and their permselectivity being well predicted by the Knudsen separation factor and showing no change with temperature. A method to determine if permeation is happening inside the pores of the MOF was developed, this was achieved by forming a thin MOF seed layer spin-coated with a PSF layer, in order to cover structural defects and reduce intercrystalline spaces. This method confirmed Knudsen diffusion happening inside the pores of the MOF membrane.
References.


(6) Zhao, Z.; Ma, X.; Li, Z.; Lin, Y. S. J. Membrane Sci. 2011, 382, 82-90.


Chapter 6. Summary, Conclusions and Future Work.


We have studied the sorption, transport and gas separation properties of Zn-based metal organic frameworks (MOFs), and their use and application in the capture of CO₂. Initially a characterization of three Zn-based MOFs, Zn₄(pdc)₄(DMF)₂•3DMF (1), Zn₂(pdc)₂(DEF) (2) and Zn₃(OH)₂(bdc)₂•2DEF (MOF-69C), was performed to determine the material with the best CO₂ capture properties. This was done by studying their physical properties (surface area, pore diameter, chemical structure and thermal properties) and adsorption isotherms and thermodynamics. (1) showed the best capture properties, this material was further investigated under realistic conditions to the post-combustion and pre-combustion capture of CO₂. This second part of the study was performed to understand the thermodynamics of sorption under this conditions (adsorption enthalpy and entropy), the selectivity of the MOF to CO₂, the dynamics of adsorption and desorption of different gas molecules, and to determine the diffusion mechanisms in the material. The thermodynamics and kinetics of the sorption of gases in (1) was found to be favorable for CO₂ capture and separation, with diffusion happening inside the pores of the MOF. Finally, a method for the formation of a Zn-based MOF membrane was developed using a solvothermal method adding a thin polysulfone layer to covert the surface. The membrane was studied via XRD and SEM to confirm its structure and examine its surface. The permeance of different gases under conditions realistic to power plant emissions and natural gas processing was studied, selectivities were calculated and the transport mechanisms of gases through the membrane were determined. The membrane presented high gas fluxes but low permeabilities. Results of the sorption, kinetic and membrane separation studies are used to conclude about the best scenarios
for CO\textsubscript{2} capture on (1). Hereinafter, I am presenting a summary of the main conclusions from each part of the study.

(a) Initially, a thermodynamic study of gas sorption properties of two previously unreported MOF was performed, both MOFs contain coordinately unsaturated Zn(II) sites without the need of activation that are ideal binding sites for the CO\textsubscript{2} molecules. Calculated zero coverage heat of adsorption and isosteric heat of adsorption suggest adsorption of carbon dioxide at these exposed metal binding sites, values are in agreement with other reported MOFs exhibiting this mechanism. Entropies of adsorption are consistent with a physical adsorption mechanism where molecules lose translational entropy upon adsorption. The microporous (1) displayed high selectivity for CO\textsubscript{2} over N\textsubscript{2} but further studies must be made to conclude about the applicability of this materials for CO\textsubscript{2} capture, and to have a complete understanding of the mechanisms involved in the adsorption of gases of interest. (1) was further investigated to evaluate its potential applications in CO\textsubscript{2} capture and separation.

(b) Adsorption and desorption studies of CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} on (1) at temperatures and pressures relevant to post-combustion and pre-combustion CO\textsubscript{2} capture were performed. CO\textsubscript{2} exhibited the highest adsorption on (1) among the gases studied, with all the gases showing a type-1 adsorption with no adsorption/desorption hysteresis (no energetic penalties for regeneration). CO\textsubscript{2} also exhibited the highest enthalpy of adsorption and a high IAST selectivity over N\textsubscript{2} and CH\textsubscript{4}, which suggests that (1) is a promising material for post-combustion CO\textsubscript{2} capture. Selectivity values over N\textsubscript{2} suggest that separation can be enhanced by a decrease in temperature. The adsorption dynamics of CO\textsubscript{2} are well described by the linear driving force model and diffusion inside the pores was found to be the rate-limiting mechanism for CO\textsubscript{2} transport to adsorption sites. Values of diffusion coefficients were estimated from the linear driving force model (LDF) and the intraparticle
diffusion model. These values increase as temperature increases due to an increase in available energy, but decrease with increases in pressure due to partial pore saturation. Activation energies were calculated from an Arrhenius plot and the activation energy required for the molecules to diffuse through the material decreases with pressure. Desorption kinetics for CO₂, N₂ and CH₄ are well-described by the LDF model assuming a first order desorption process. Residence times were estimated from kinetic data showing that CO₂ has greater residence times at all temperatures and the lowest value of desorption activation energy among the three gases as predicted from the Arrhenius equation. A low desorption activation energy on (1) combined with high residence times favors the selective adsorption and capture of CO₂ in industrially relevant processes. Further industrial applications of (1) as a CO₂ adsorbent are to be studied as part of a future work. (1) did not show favorable results when tested for CO₂ capture in a pre-combustion scenario.

(e) The transport of CO₂, CH₄, N₂ and H₂ was studied through a (1) membrane. The membrane was synthesized via a solvothermal method, structural defects were covered dip-coating the membrane surface with a thin polysulfone layer. The membrane showed no pinholes or defects after inspecting via SEM imaging and testing the gas selectivity as a function of temperature, the structure was confirmed via XRD. The membrane formation method is a modification of the secondary growth method, it facilitates the measurement of the permeability of materials that do not normally form uniform-defect free layers. The permeance of single gases showed a linear relation to the inverse square root of the molecular weight of the permeant gases, flux of gases is happening on a Knudsen regime with the permeation of gases decreasing with temperature. Permselectivity is well predicted by the Knudsen separation factor showing no change with temperature. A newly developed method was used to determine if permeation is happening inside the pores of the MOF, this was achieved by forming a thin MOF seed layer spin-coated with a PSF
layer, in order to cover structural defects and reduce intercrystalline spaces. This method confirmed Knudsen diffusion happening inside the pores of the MOF membrane.

(d) Adsorption separation methods in (1) present better properties than those studied in a continuous film membrane separation. The focus of the future work on this field should be in the use of application of (1) as a CO₂ adsorbent, some suggestions for future work follow in the next section.

In summary, we have investigated on the applicability of Zn-based MOFs in the different CO₂ capture scenarios; as an adsorbent and as a gas separation membrane. We have developed a complete understanding of the physical properties of the material, its adsorption properties and thermodynamics, the kinetics of the adsorption of gases, the diffusion mechanisms in adsorption, the desorption properties, the best conditions for the regeneration of the material, the gas separation properties as a membrane material and the transport mechanisms inside the membrane. From this study we can conclude that (1) has better properties for future applications in post-combustion CO₂ capture as an adsorbent, it has a high surface area, high CO₂ adsorption, fast dynamics of adsorption and desorption and high selectivity towards CO₂.

6.2. Directions for future research.

From my study on the sorption, transport and gas separation properties of Zn-Based metal organic frameworks (MOFs) and their application in CO₂ capture, I would like to briefly describe some of the directions for future research in this area and some of the ways to address CO₂ capture and separation in porous materials and MOFs.

a) Study of mixed-gas adsorption and membrane permeability. A deeper understanding of the adsorption and transport properties can be achieved by studying the mixed-gas adsorption and separation of the materials that commonly form flue gas. Another important
factor is studying the impact of water and other minor components present in flue gas, this would help to have a parameter to quantify the stability of the MOF and conclude about the effects of this minor components on the regeneration of the material\textsuperscript{1,2}.

b) Fabrication of MOF-Pellets and study of MOF degradation upon exposure to water. MOF materials are usually not stable to reactive species such as water, however it has been suggested that some MOFs (MOF-5) are more stable to water than expected, they have a threshold under which only minor degradations to their structure occur in presence of reactive species\textsuperscript{3}. The stability of MOFs can be further enhanced by the formation of pellets, this has been previously achieved for similar MOFs by using a die and a press, additives as expanded natural graphite or alumina can be added to the process to improve the properties of the pellets.

c) Development of a Packed Bed Adsorption process. From the study of the adsorption selectivity of (1) it was demonstrated that a greater selectivity can be achieved at lower temperatures. This suggest that a decrease in temperature could be used to enhance the separation and an increase in temperature to regenerate the material, this can be combined with the benefits of pressure swing adsorption to enhance the separation and gas selectivity. Pellets of (1) can be potentially used to perform mixed gas adsorption experiments to study if (1) can be used as a packed-bed adsorption material. A packed bed adsorption type of system can be implemented by using an adsorption vessel filled with pellets of (1), and using inert ceramic balls to control the flux of the gases. The flux would be preferably directed downwards to avoid bed fluidization.

d) Study of different conditions to have a better control of the membrane structure and orientation. Even when permeability did not show the best separation, films of the MOF
could be potentially used for adsorption. The selectivity of the membrane can be enhanced by controlling the orientation of the crystals forming the structure, this can be achieved by controlling the orientation of seed crystals or by modifying the conditions of the solvothermal gel solution. This would increase the control over the reproducibility of the synthesis of membranes which has been one of the main issues in MOF membrane formation. The transport under different conditions can be studied if the seed layer orientation is controlled and then applying the method for the transport study described in section 5.3.3.

e) Fabrication of MOFs membranes using less expensive and more flexible support materials. Silica supports have shown potential in MOF membrane formation, this would make processes industrially feasible by reducing costs.

f) Study adsorption in a film-like configuration. Even when the selectivity of a (1) membrane is below that predicted by Knudsen diffusion, this material showed good adsorption properties. By using this material as an adsorbent in a film-like configuration the separation would be further enhanced by the differences in diffusion properties of different gases.

g) Study the formation of films on conductive substrates. This would be done to analyze the application of (1) as a catalyst for electron transfer in CO₂ reduction, this should be done for further applications after CO₂ capture besides the classical sequestration approach.

References.


Appendix A. Supporting figures.

**Figure A-1.** High pressure CO$_2$ isotherms at 308 K (black squares), 313 K (red diamonds) and 338 K (grey circles) and their fit to SIPS equation.

**Figure A-2.** Kinetics of adsorption of CO$_2$ at 1 bar and 338 K on (1) with Linear Driving Force fit shown in dashed line.
Figure A-3. Kinetics of desorption of CO$_2$ at 1 bar and 338 K on (1) with Linear Driving Force fit shown in dashed line.

Figure A-4. Arrhenius plot of kinetics constants for desorption kinetics of CH$_4$ on (1) at 1 bar with Linear fit shown with dashed line.
Appendix B. Control experiments and previously reported data.

Single gas permeation experiments on every step of the MOF/Polymer membrane formation procedure were performed following the procedure and apparatus described in chapter 5. Permeability calculations could not be performed in most of the steps of membrane formation as the permeant gas would completely fill the permeation volume in less than 2 seconds, indicating that permeation was extremely fast and happening in convective flow through macropores. The following permeation experiments were performed and exhibited this fast gas permeance behavior:

- Bare alumina porous supports.
- Silica layer.
- PEI layer.
- Seed MOF crystals covering alumina supports.
- MOF membrane on porous alumina supports.

In the case of the single gas permeation of a seed MOF crystal layer coated with a thin polysulfone layer, this membrane had a slower permeability compared to the MOF membrane covered with a PSF thin layer, this is due to the fact that most of the effective permeation area is covered with PSF. PSF is a tough, rigid, high-strength thermoplastic polymer with low gas permeance. The gas permeability of pure polysulfone (UDEL P-3500, Solvay) used in our experiments has been previously reported by our research group\(^1\), similarly, other values of permeability for PSF (Ultrason 6010, Merck and UDEL P-1700) have been previously reported in the literature\(^2,3\). Pure polysulfone has a permeance slower to that predicted by the MOF/polymer membrane by 6 orders of magnitude and its permeance exhibits an opposite behavior compared to the MOF/polymer membrane (PSF permeance is not a function of molecular weight and does not behave according to Knudsen transport). Values for the permeability of the pure polysulfone
membrane, the seed MOF crystals sealed with PSF and the MOF/polymer membrane are shown in table B-1. Data for the permeability of the MOF/polymer membrane is presented as a range of values as the membrane surface is asymmetric with a membrane thickness in the 50–150 μm range.

Table B-1. Gas permeability of CO₂, N₂, CH₄ and H₂ in the different stages of membrane formation and control data for the permeability of pure polysulfone.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeability CO₂ (Barrer)</th>
<th>Permeability N₂ (Barrer)</th>
<th>Permeability CH₄ (Barrer)</th>
<th>Permeability H₂ (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone¹</td>
<td>3.9</td>
<td>0.17</td>
<td>0.17</td>
<td>N/A</td>
</tr>
<tr>
<td>Polysulfone²</td>
<td>6.5</td>
<td>1.5</td>
<td>1.4</td>
<td>13.2</td>
</tr>
<tr>
<td>Polysulfone³</td>
<td>4.5</td>
<td>0.18</td>
<td>0.17</td>
<td>N/A</td>
</tr>
<tr>
<td>PSF coated seed layer</td>
<td>1724.08</td>
<td>2166.40</td>
<td>2955.80</td>
<td>6678.44</td>
</tr>
<tr>
<td>MOF/Polymer</td>
<td>1.46E+06 -</td>
<td>1.68E+06 -</td>
<td>2.32E+06 -</td>
<td>4.28E+06 -</td>
</tr>
<tr>
<td>Membrane (50 – 150 μm)</td>
<td>4.39E+06</td>
<td>5.04E+06</td>
<td>6.96E+06</td>
<td>1.28E+07</td>
</tr>
</tbody>
</table>

References.

