A NARROW PORE ZEOLITE: ZSM-25 FOR NATURAL GAS PURIFICATION

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Due to both increased greenhouse gas emissions and increased natural gas demand, the development of separating CO₂ and N₂ from methane-rich streams (e.g. natural gas, biogas and landfill gas) has arisen worldwide research interest. Greenhouse gas emissions can be mitigated by post-combustion technology and switching the energy structure to CH₄-based energy sources. Natural gas is the most significant source of CH₄, which typically contains around 80%-95% CH₄, less than 10% CO₂ and N₂, and small amounts of hydrocarbons. Hence, removing the CO₂ and N₂ is critical for purifying natural gas, with the respect of both increasing the energy density and preventing the corrosion of the pipeline caused by acid CO₂ for transporting CH₄.

Adsorption-based capture of CO₂ and N₂ from natural gas has attracted tremendous interest owing to its economic advantages. Porous materials play very important roles in the adsorption process where the material is exposed to the gas mixture at high pressure and then desorbs at low pressure or vacuum. The significant index of evaluating a porous material is the selectivity, capacity, adsorption kinetics and regenerability. Narrow-pore zeolite (8MR zeolite) has significant potential in natural gas purification via pressure-swing adsorption (PSA), which is attributed to its pore size fitting between CO₂ and CH₄, and close to N₂. Hence, the selectivity is relatively much higher than other zeolites (e.g. FAU, ZSM-5). However, the slow adsorption kinetics are limiting its application in the natural gas industry, and no zeolites have been found with preferential adsorbing N₂ from CH₄ at equilibrium, unable to effectively separate N₂ from natural gas.

This thesis describes the development of small-pore ZSM-25 based zeolites, and their applications in membrane separations. The study provides a rational strategy of designing ZSM-25 zeolite for effective CO₂/CH₄ and N₂/CH₄ separation in the natural gas purification industry:

In this thesis, an extensive literature on 8MR zeolite for natural gas purification and their modification approaches has been sourced and analyzed in Chapter 1.
Chapter 2: a Li⁺/ZSM-25 zeolite (LZZ) was developed via partial ion exchange of the Na⁺ with Li⁺. This exchange enabled higher CO₂ capacity and adsorption kinetics due to higher pore volume and stronger affinity of CO₂ with Li⁺, and the ultra-high CO₂/CH₄ selectivity remained. The CO₂ isotherms showed deviation from typical Type I isotherm and “breathing” behavior. This observation was explained by synchrotron in situ X-ray powder diffraction, demonstrating a gradual structural expansion induced by CO₂. This expansion resulted in the increased CH₄ admission in binary gas adsorption. This work enables the possibility of applying small-pore zeolites in natural gas purification which are kinetically-limited.

Chapter 3: The Li⁺/ZSM-25 zeolite (LZZ) was incorporated into a commercial polymer Matrimid® 5218 yielding a mixed-matrix membrane (MMM). Li⁺/ZSM-25 was chosen as filler because of its fitting pore diameter between CO₂ and CH₄, which merely adsorbed CH₄ while allowing considerable CO₂ transport. The CO₂/CH₄ separation performance of the optimal MMMs at 5 wt% filler loading, showed higher CO₂/CH₄ selectivity than that of the pristine Matrimid in both single- and mixed-gas separation. The dominant molecular sieving effect contributed to the increasing selectivity with increased pressure, showing unusual plasticization-resistance behavior. The optimized membrane (M–5) achieved ideal CO₂/CH₄ selectivity of 169, which surpassed the latest CO₂/CH₄ upper bound.

Chapter 4: A new “trapdoor” material K-ZSM-25 was designed for N₂/CH₄ separation by incorporating K⁺ as a “door-keeping” cation. The extent of the temperature-dependent oscillations of the K⁺ cation regulated the accessibility of the cage, controlling the adsorption capacity of the material. There were distinguishable gate-opening temperatures (Ts) between N₂ and CH₄ molecules. Within this temperature range, N₂ molecules had full access to the pathway into the cage, while CH₄ molecules were hindered due to the blockage of K⁺. Both the experimental results and simulations demonstrated that K-ZSM-25 can achieve effective N₂/CH₄ separation at around ambient temperature with outstanding selectivity of over 30 in single gas adsorption and 5.7 in dynamic breakthrough simulation. The large N₂ capacity, outstanding N₂/CH₄ selectivity, fast kinetics of K-ZSM-25, and it is readily regenerated at
around room temperature, all of which makes this adsorbent ideally suited to PSA-based industrial separations.
Declaration

This is to certify that:

i. This dissertation comprises only my original work towards to the Ph.D.

ii. Due acknowledgement has been made in the text to all other materials used

iii. The dissertation is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Jianhua Zhao

18-Dec-2019
Preface


• All the results in this publication are my work.

ii. The Chapter 3 is a paper “Enhancing plasticization-resistance of mixed-matrix membranes with exceptionally high CO$_2$/CH$_4$ selectivity through incorporating ZSM-25 zeolite”. *Journal of Membrane Science.*, 583, 23-30

• All the results in this publication are my work.

iii. The Chapter 4 is a paper “Removal of nitrogen impurity from methane via a new “trapdoor” K-ZSM-25 zeolite” submitted.

• All the results in this publication are my work.
List of Publications


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This PhD is one of the most difficult and challenging tasks I have accomplished in my life to date. During my PhD, I met many nice and important people that contributed to finish this thesis. I would like to express the deepest appreciation to thank those great people who helped and guided me throughout my PhD life.

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To Kai, Mum and Dad:

This thesis is dedicated to you.
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Chapter 1

Introduction, Literature Review and Research Objectives

1.1 General Introduction

Greenhouse gas (GHG) is primarily CO₂, which results in an average of 33 °C temperature increase on the earth’s surface. CO₂ emission has a rapid increase since the Industrial Revolution (1750s) due to human activities. The major anthropogenic CO₂ emissions is caused by the combustion of fossil fuels. To effectively reduce the GHG emission, apart from the carbon capture and storage (CCS) from the post-combustion of fossil fuels, potential energy alternatives need to be developed with high quality, economic viability and environmental sustainability. Worldwide attention has been focused on the renewable CH₄ carrier: natural gas and biogas to alleviate the global warming and meet the rapid industrial growth. However, these CH₄-rich gas streams contain significant quantities of impurities, such as CO₂, hydrocarbons and N₂. The amount of the unwanted components varies depending on the sources of raw natural gas (Table. 1.1). The acid gas CO₂ and H₂S are deleterious for fuel quality and erode the pipeline during transportation and additional ecological hazards. Therefore, the raw natural gas and biogas need to be processed to removal the undesired components before they can be transported.

Table 1.1 The compositions of a raw natural gas and pipeline composition specifications

<table>
<thead>
<tr>
<th>Component</th>
<th>Component Content (mol %)</th>
<th>Pipeline Requirement (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>29.98-90.12</td>
<td>&gt; 75</td>
</tr>
<tr>
<td>Ethane (C₂H₆)</td>
<td>0.55-14.22</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Propane (C₃H₈)</td>
<td>0.23-12.54</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Butanes (C₄H₁₀)</td>
<td>0.14-8.12</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Pentanes (C₅H₁₂)</td>
<td>0.037-3.0</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>0.06-42.66</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>0.21-26.10</td>
<td>&lt; 3</td>
</tr>
</tbody>
</table>
Hydrogen Sulfide (H₂S) 0.0-3.3 < 0.0004
Water Vapor (H₂O) 0.0-1.3 < 0.012

The natural gas purification and biogas upgrading are basically dominated by four treatments: 1. Chemical Absorption 2. Adsorption (PSA, TSA) 3. Membrane-based separation 4. Cryogenic approach. Adsorption and membrane-based separation are two potential solutions to reduce the costs of CO₂ capture from the fuel gas streams. For pressure swing adsorption (PSA), the solid adsorbents can selectively adsorb CO₂ by either equilibrium type or kinetics type. Generally, the PSA for CCS require the porous adsorbents with high CO₂ capacity, selectivity of CO₂/CH₄ or CO₂/N₂, working capacity and adequate adsorption kinetics. Microporous materials including activated carbons (ACs), metal–organic frameworks (MOFs), and zeolites are the primary candidates for CCS. Recently, Zeolitic imidazolate framework (ZIF) and covalent organic frameworks (COFs) have been observed as a candidate for CCS due to the high CO₂ capacity. However, compared to these state-of-art porous materials, zeolites exhibit high stability, tuneable pore structure and ease of mass production, which can potentially reduce the capital costs of PSA. The key area of the PSA is the zeolite itself including its CO₂ capacity, CO₂/CH₄ selectivity, adsorption kinetics etc. One class of zeolite is especially promising for the upgrading of fuel gas e.g. small-pore zeolite. Its performance can be regulated by adjusting window sizes and type of extra-framework cation (EFC). The key investigation on zeolites mainly involves:

1. Zeolite-based adsorption mechanism
2. Zeolite material (CO₂ capacity, CO₂/CH₄ selectivity, adsorption kinetics etc.)
3. Zeolite application

Apart from the PSA, membrane-based separation also provides potential in fuel gas upgrading in terms of economic and technical aspects. The advantages of membrane-based separation are recognised as high energy efficiency, high integrity with other separation methods and ease of scale-up. To seek a membrane for natural gas upgrading, high permeability and selectivity over gas pairs are the most important consideration followed by the thermal stability, mechanical strength and ease of fabrication. The development of mixed matrix membranes (MMMs) has
attracted world-wide interest in separation of CO₂/CH₄, CO₂/N₂ and olefin/paraffin. Zeolites can be embedded into the polymer matrix as fillers yielding the MMMs. The combination of polymer and non-polymeric material enables the MMMs to show the merits of each element. Owing to the heterogeneous components, the challenges are the compatibility between the zeolite and the polymer matrix, and the membrane shows reducing selectivity at high pressure due to the plasticization. Hence, it becomes one of our research focuses.

1.2 Adsorption principles

Adsorption is a process in which a substance is separated from one phase and concentrates or accumulates at the surface of another. The adsorption takes place at an adsorbent’s surface or interface.

This process takes place at the surface or interface of the adsorbent and greatly relies on the binding forces between the surface and the adsorbates’ molecules or ions. Adsorption can be categorized into four types: exchange adsorption, physical adsorption, chemical adsorption and specific adsorption. The principles of each type of adsorption are described as follows: Exchange adsorption is based on the electrostatic attachment of ions to the sites where the charge is opposite at the surface of the adsorbent, and the ions at the surface of the adsorbent is replaced by other ionic adsorbates with higher electrostatic affinity. Physical adsorption is based on Van der Waals forces by means of which the gas molecules can be attached to the surface of solid adsorbents. Chemical adsorption results from the reaction between an adsorbate and adsorbent by exchanging the orbital electrons. New chemical compounds therefore are formed. Specific adsorption takes place when the adsorbates are attached to the functional group on the surface of an adsorbent based on specific interactions. Here, we only focus on physical adsorption.

1.2.1 Adsorbent Properties

The properties of an adsorbent markedly affect the adsorption capacity and the adsorption rate. These properties are categorized into physical properties and chemical properties. Physical properties include surface area, pore size, distribution of pores and particle form. The former three are determinant to the adsorption capacity, and the last one affects the use of a specific adsorbent in the application of the adsorption process. Activated carbon (ACs) and zeolites are
the most common adsorbents and can adsorb a wide range of adsorbates. They both have large internal surfaces connecting the massive pores and channels resulting in high surface area. However, the actual surface area is usually different from the total surface area due to the fact that the accessibility of the pores is related to the molecular size of the adsorbates and its form.

Chemical properties are also important for adsorption performance. The presence of functional groups and the degree of ionization on the surface can cause chemical interactions with particular adsorbates. For example, the adsorption performance of activated carbon can be adjusted by changing its properties of surface chemistry. The basal plane areas on the surface of ACs can increase by reduction treatment to greatly improve the physical adsorption of nonpolar substance.

1.2.2 Adsorption equilibria

Adsorption equilibria is defined as the distribution of a substance which is adsorbed from one phase to a surface of another in a specific system when this system reached equilibrium. No more transition from one phase to another phase of the adsorbate takes place. The distribution of adsorbate between two phases is usually depicted by a plot of the quantity of adsorbate adsorbed per unit weight of an adsorbent, \( q_e \), and its pressure or residual concentration of adsorbate in the solution, \( C_e \), at constant temperature. This plot is termed the “adsorption isotherm”.

An isotherm can give us much information such as the adsorption capacity, the sensitivity to adsorbate’s pressure change and the affinity of a substance for the adsorbent. Therefore, the isotherms are very important for evaluating the potential application of an adsorbent and determining the feasibility of adsorption process. Furthermore, the modelling and designing of the adsorption process is also based on the isotherms. Additionally, the isotherms provide the information for interpretation of kinetic parameters including heats of adsorption and adsorption rate. There are a wide variety of equilibrium models being developed to describe the adsorption isotherms up to date. Each model is preferred differently in respect to adsorption process modelling and computational accuracy. More independent parameters in a model contribute to its accuracy, while causing mathematical difficulty and computational intensity for process
simulation. The applicability of an isotherm model in process simulation is generally related to its mathematical simplicity. For example, a linear isotherm model only has two independent variables and may be unable to fit many adsorption isotherms accurately, but it is often used in the adsorption process studies due to its mathematical simplicity.

1. **Linear Model**

The Linear model is the simplest isotherm model describing the adsorption system where the amount of substance adsorbed on the surface is proportional to the pressure of the adsorbate or the residual concentration in solution phase. The linear isotherm model is given in Equation 1.1

\[ q_e = K_p C_e \]  

Where \( K_p \) is the Henry adsorption constant and is temperature dependent. The linear isotherm model is only applicable in describing the initial part of the isotherms where the surface coverage is low, and the surface is homogeneous.

2. **Langmuir Model**

The Langmuir isotherm model is developed for describing the gas-to-solid adsorption. This model is valid under several assumptions: (1) the surface is homogeneous, (2) monolayer adsorption (surface of adsorbent is only covered by one molecule in thickness). (3) The adsorption only happens on localized sites which are equivalent and identical. (4) no further interaction and mobility between adsorbed molecules. The model can be derived from kinetic equilibrium of condensation (adsorption) and evaporation (desorption) of adsorptive gas. The fraction of occupied sites by gaseous molecules is \( \theta \) is introduced to represent on the surface of a solid adsorbent. The fraction of uncovered sites on the surface is therefore \( (1 - \theta) \). Hence, the rate of condensation of free gaseous molecules towards surface is a proportional to fraction of available sites on surface and absolute pressure of gas \( P \). The rate of evaporation of adsorbed gas is depending on the fraction of occupied site on adsorbent surface. At equilibrium, rate of evaporation is equal to rate of condensation, given in the following Equation 1.2:

\[ K_a P (1 - \theta) = K_d \theta \]  

Equation 1.1

Equation 1.2
Where $K_a$ and $K_d$ represent the equilibrium constant for adsorption and desorption, respectively. The **Equation 1.2** is given in term of $\theta$:

$$\theta = \frac{K_aP}{K_d+K_aP} = \frac{KP}{1+KP}$$

(1.3)

Where $K = \frac{K_a}{K_d}$, is the adsorption coefficient. **Equation 1.3** is known as the Langmuir isotherm model.

3. Freundlich Model

An empirical expression was developed by Freundlich (1926) to describe the relationship between the amount of gas adsorbed per unit weight of an adsorbent and pressure.

$$q_e = K_F C_e^{1/n}$$

(1.4)

Where $K_F$ and $1/n$ are constant of which the values are determined by adsorbent and gas at given temperature. The values of $K_F$ can be regarded as an indicator of adsorption capacity, and the value of $1/n$ is related to the intensity of adsorption. Adsorption with higher $1/n$ is more favourable. Log is put on both sides of the **Equation 1.4**, the equation turned into a straight-line **Equation 1.5** with $\frac{1}{n}$ as the slop and $\ln K_F$ as the y-axis intercept.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(1.5)

4. BET Model

The BET model can fit a broader range of adsorption than the Langmuir isotherm model by considering multilayer adsorption. Adsorbed gas can randomly distribute on adsorptive sites on the surface covered by multiple layers of adsorbate molecules. The BET model was proposed under the assumption that (1) Langmuir theory is applicable on each layer. (2) adsorbed gas cannot migrate between layers can only interact with adjacent layers. (3) heats of adsorption for the second layer and higher ones are equal to the heat of liquefaction of the adsorbate. (4) the heat of adsorption for the first layer is greater than the other layers. Hence the BET model is formulated in **Equation 1.6**:
\[
\frac{1}{v \left( \frac{p}{p_0} \right)^{-1}} = \frac{c^{-1}}{v_m c} \left( \frac{p}{p_0} \right) + \frac{1}{v_m c}
\]  

(1.6)

Where \( p \) and \( p_0 \) are the pressure of equilibrium and saturation of gas at adsorption temperature, respectively. \( v \) is the quantity of gas adsorbed, \( v_m \) is the monolayer of gas adsorbed quantity, \( c \) is a constant related to the energy of adsorption, given in Equation 1.7.

\[
c = \exp \left( \frac{E_1 - E_2}{RT} \right)
\]

(1.7)

where \( E_1 \) is the heat of adsorption of first layer, \( E_2 \) is the heat of adsorption of second layer and higher and equals to the heat of condensation. Equation 1.6 can be also plotted as a straight line with \( \frac{1}{v \left( \frac{p}{p_0} \right)^{-1}} \) as y variable and \( \frac{p}{p_0} \) as x variable. Therefore, the quantity of gas adsorbed \( v_m \) and BET constant \( c \) can be calculated according to the slop and y-intercept. This linearized BET plot is only maintained when \( 0.05 < \frac{p}{p_0} < 0.35 \). BET model is most commonly used to calculate the surface area of an adsorbent.

1.2.3 Adsorption isotherm Type

The shape of isotherms varies from adsorbates and adsorbents at different temperatures. The isotherms are mainly classified into five types, as shown in Figure 1.1. Figure 1.2 depicts the distribution of adsorbates on the surface of each type of isotherm.

![Figure 1.1 Five types of adsorption isotherms based on Brunauer, adapted from 2.](image)

Figure 1.1 Five types of adsorption isotherms based on Brunauer, adapted from 2.
Type I isotherm can be well fitted and explained by the Langmuir Model. It describes the phenomena when adsorption is taking place on the surface of a microporous adsorbent where only a monolayer of the gaseous molecules occupies. The adsorbent eventually saturates when its accessible micropores being fully filled. Type II isotherm is observed for adsorbents with more than one adsorptive site. The second adsorption site can be a new site on the surface or the second monolayer. The adsorption starts with a rapid increase of adsorbed amount and followed by a “flat” region when the first monolayer formation completes. Then the multilayer starts to form corresponding to the sharp increase. Type III isotherm depicts the phenomenon that there is strong attractive interaction between adsorbates leading to condensation. No “flat” region is observed indicating no monolayer being formed. Type IV isotherm is very similar to Type II isotherm. It also occurs when there is multilayer adsorption on surface. The multilayer starts to form before the monolayer saturates. However, there is a finite multilayer formation corresponding to its “flat” region in the end. Type V isotherm is a variation of Type III isotherm. There is no adsorption initially and only attractive interaction between adsorbates leading to condensation. The surface eventually saturates and cannot hold more adsorbates.

Figure 1.2 Distribution of adsorbates on surface of each type of isotherm.
1.3 Microporous adsorbent materials

The main requirement for applying an adsorbent is considering its adsorption properties (capacity, selectivity), physical characteristics and regeneration capability. The selectivity is dependent on the difference in either adsorption equilibrium or diffusivities of each component. There are various number of porous materials for effective separation with respect to viable applications.

1.3.1 Activated Carbon

Activated carbons are the most commonly used adsorbent and made by carbonaceous materials via a variety of processing including thermal decomposition and activation. The pores are formed during the activation process by removing the tarry carbonization products, and the pore size distribution and porosity may vary depending on the activation. Activated carbons are normally classified into powdered activated carbon, granular activated carbon, extruded activated carbon etc on the basis of the particle sizes and preparation methods. The activated carbons are considered as decent materials for CO₂ capture and storage due to considerable porosity and BET surface area varying from 400 to 3000 m²/g. A great variety of modified ACs have been investigated to enhance the adsorption properties toward CO₂. The two main approaches for ACs modification to improve the CO₂ capacity are incorporating basic species by ammonia impregnation and importing N-functionalized group by adopting N-containing chemicals as carbon precursors. The former strategy does not significantly improve the CO₂ capacity due to the blockage of pores. For example, the total basic groups on the surface can increase as a consequence of removing the acidic oxygen-containing groups at elevated temperature during ammonia impregnation. As a result, the CO₂ capacity can reach 3.22 mmol/g at 1 bar and 298 K, which only increases 10.2% compared to the original AC. Recently, N-doped porous carbons were developed via KOH activation of polypyrrole and were able to adsorb large amount of CO₂ (3.9 mmol/g) at 298K and 1 atm. The CO₂ capacity can be further improved by tuning the pore size under 1 nm according to recent investigations in respect to pore sizes of ACs. Specifically, fine micropores smaller than 0.8 nm contributes to ultra-high CO₂ capacity at 1
atm. Hence, remarkably high CO₂ capacity (4.6 mmol/g at 296 K and 1 bar) was observed on phenolic resin-based ACs where the pore sizes are controlled below 0.8 nm via KOH activation of polymeric spheres. Despite the decent CO₂ capacity, the ACs have a broad band of affinity for various gas and therefore not suitable for the effective separation for gas pairs such as CO₂/CH₄ and CO₂/N₂.

1.3.2 Carbon Molecular Sieves
Carbon Molecular sieves (CMS) originate from activated carbons after particular process of activation. CMS has narrow pore size distribution and a relatively high micropore volume. Initially, the CMS derived from decomposition of polyvinylidene dichloride, but various starting materials have been investigated to prepare CMS recently. The commercial CMS are mostly prepared by carbonaceous materials, such as hard coal or anthracite under oxidation and thermal treatment. Subsequent treatment may apply to tune the pore size, such as controlled cracking of hydrocarbons. Therefore, the pore size of CMS can vary from 0.4 nm to 0.9 nm. Hence these features provide higher selectivity and lower adsorption capacity compared to ACs. The major difference between ACs and CMS is that ACs separates the gas based on the difference in adsorption equilibrium, while the CMS discriminate the gas through the difference in the adsorption rate. Thus, this separation feature makes CMS suitable in pressure swing adsorption (PSA) in which gas dynamics is dominant, such as the separation of N₂ and CH₄. Many approaches have been proposed recently to tailor the CMS to further improve the selectivity regarding the application in the natural gas purification and coal-bed methane upgrading. For example, Facilitated CO₂ adsorption capacity was observed when CMS was loaded with K₂CO₃ followed by calcination at 773–873 K, because K₂O was generated. Therefore, the selectivity of CO₂/CH₄ increase 94% compared to the original CMS. Another treatment is plasma modification to improve the selectivity of CH₄/N₂. The separation coefficient of CH₄/N₂ of CMS treated by plasma in N₂ environment can reach 3.32.

1.3.3 Metal-organic Frameworks
Metal-organic frameworks (MOFs) are porous materials constructed by the coordinate bonds between organic ligands and metal atoms or metal contained clusters. In general, MOFs have
uniform pore structure, high specific surface area (up to 6200 m² g⁻¹) and pore volume, making them promising adsorbents for gas separation. The most significant characteristic of MOFs is the good tunability of their structures and pore surface properties, in comparison to other absorbents such as activated carbons, carbon molecular sieves and zeolites. The pore size and pore geometry of MOFs can be adjusted by careful selecting the building blocks, which can enhance some specific separation performance. In addition, the pore surface affinity toward specific molecules can be enhanced by introducing functional groups onto the ligands, or by adjusting charge densities of the pore walls. For example, by tailoring the side functional groups of the UiO-66, the CO₂ uptake can be enhanced by ca. 80%, accompanied by the increase of CO₂/CH₄ and CO₂/N₂ ideal selectivity of 80% and 66%, respectively. Similar results are also found in the amino- or triazo-functionalized MIL-101. A recent simulation-experiment research suggested that, the side functional group in the copper- 5-((triisopropylsilyl)ethynyl) isophthalic acid MOF can lead to the “trapdoor” adsorption behavior in this MOF. UTSA-16 prepared from the complexation of cobalt, potassium cation and citric acid exhibit a CO₂/CH₄ and CO₂/N₂ selectivity of 315 and 30, respectively. This is ascribed to the small pore aperture size (0.33 × 0.54 nm) coupled with the existence of potassium cations which are more interactive to CO₂ molecules. MIL-91(Ti), consists of TiO₆ octahedra and protonated bisphosphonate, has a channel-type pore aperture with the dimensions of 0.35 × 0.40 nm. The exposed phosphate moieties in MIL-91(Ti) can contribute a strong interaction between MOF pore wall and the CO₂ molecules. This effect results in a high CO₂/N₂ adsorptive selectivity of 80-100 at 1 bar in CO₂/N₂ mixture. fcu-MOF-1 (e.g. [Tb₆(µ3-OH)₈-(O₂C⁻)₆(N₄C⁻)₆]) that constructed from the conjunction of hexanuclear clusters show a high CO₂ isosteric heat of 58.1 kJ mol⁻¹ at low loading. Such high CO₂ affinity is oriented from the interaction between the CO₂ molecule and the high charge density at the pore surface. Consequently, this MOF shows a high CO₂/N₂ adsorption selectivity of 370 in 1% CO₂/99% N₂ mixture. The small pore aperture is the key to this behavior. Despite promising adsorption properties and good tunability, the MOFs have high synthesis costs and low stability in humidified environment. Those drawbacks hamper the industrialization application of the MOFs.
1.3.4 Zeolites

Zeolites are aluminosilicate minerals with high porosity. The zeolites are also called “molecular sieves”, as the guest molecules can be discriminated by their sizes. The frameworks are built up by an elementary structure which are assembled by (SiO₄)⁴⁺ and (AlO₄)⁵⁺ tetrahedra (TO₄). These tetrahedra combine with adjacent tetrahedra by sharing oxygen atoms and form a special geometric shape. This special arrangement is called secondary building units (SBUs). The SBUs have various forms including double eight ring (D8R), single eight ring (S8R) and some more complex units. These units are linked together to produce channels and cages where guest molecules can pass through. A zeolite’s unit cell consists of various types of SBUs. There are 23 types of SBUs being identified so far, as shown in Figure. 1.3. Figure. 1.4 illustrates the way of producing zeolite framework by linking the SBUs together. This different arrangement of SBUs results in various type of zeolite crystalline structure. Each SBU contains many rings which varies in T-atoms from as few as 3 to as many as 14. Hence, the size of the ring is determined by the number of T-atoms, and the ring is named after the number of the T-atom, as shown in Figure. 1.5. For instance, a ring containing eight T-atoms and the corresponding eight O atom is called 8 membered ring (8MR). Zeolites are normally categorized into 4 types based on the ring size. A zeolite with ring size limited by 8MR is defined as small-pore zeolite, such as CHA, RHO, LTA and ZSM-25. In the same way, materials with openings up to 10MR and 12MR are called as medium and large-pore zeolites, respectively. Other zeolites with ring size greater than 12MR are defined as extra-large pore zeolites. Some typical zeolites and corresponding structures are listed in Table 1.2. The zeolites with different pore sizes and structures can be utilised in different applications. Some small pore zeolites are potential candidates for the separation of light hydrocarbon, CO₂/CH₄ and CO₂/N₂ due to the similar pore aperture size to the gas pairs. All silica CHA (Si-CHA) presents a high kinetic selectivity of propene/propane (46000 at 303K and 600 Torr). This effective kinetic separation is because the pore size of Si-CHA (0.38 nm) is very narrow, hence propane diffusion is impeded. Additionally, the small-pore zeolites are also able to remove incombustible impurities (N₂ and CO₂) from natural gas. RHO zeolite shows excellent selectivity of CO₂/CH₄, because the size of 8MR of RHO is between the kinetic diameter of CO₂ and CH₄, which prohibits the admission of CH₄. Similarly, ZK-5 (framework type KFI) presents a
very high selectivity of CO₂ over N₂ (a_{CO₂/N₂}=121) at ambient temperature by using [18]-crown-6 as OSDA during synthesis.  

The pore size of medium pore zeolite varies from 0.45 nm to 0.60 nm. ZSM-5 (framework type MFI) is a typical medium pore zeolite with right and sinusoidal channels of 0.54 × 0.56 nm and 0.51 × 0.55 nm in size, respectively. ZSM-5 normally has high Si/Al ratio. When H⁺ is present as the cation, with the increase of Al³⁺, the H-ZSM-5 turns to be more acidic due to more H⁺ cations which are required to make the material charge-neutral. Hence, ZSM-5 is normally used for acid-catalysed reactions in petrochemical processes such as xylene isomerization and alkylation of hydrocarbons. The pore openings of large-pore zeolite range from 0.60 nm to 0.80 nm. Large-pore zeolite such as 13X (framework type FAU) is a decent candidate for CO₂ capture and CH₄ enrichment in natural gas via pressure swing adsorption process (PSA) due to large pore volume and surface area. The selectivity of CO₂/CH₄ can be from 26 at 4 bar and 303K to 2 at 6 bar and 323K.50

One special property of zeolite is that the extra-framework cations (EFC) can be exchanged with other cations and perform different adsorptive functions. Each aluminium atom in the framework brings one negative charge because of the difference in the oxidation states of Al (III) and Si (IV) in the framework. Therefore, the negative charges are balanced by extra-framework cations such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. These cations are rather loosely held in the preferred sites in the frameworks and can be exchanged for others. The cation types play an important role in determining the adsorption properties of the zeolite, therefore, ion-exchange treatment has become a major method for zeolite modification. 53,54
Figure 1.3 Types of Secondary Building Units (SBUs) and corresponding symbols. Number in parentheses refers to the frequency of occurrence. Adapted from 25
Figure 1. 4 The arrangement of Secondary Building Units (SBUs) to produce different zeolite frameworks. Adapted from 25

Figure 1. 5 Composition and diameter of the rings with different T-atoms. Adapted from 25
Si/Al ratio is another important aspect determining the adsorption property of zeolites. Si/Al ratio can be tuned from at least 1.0 to infinity (all Silica). The zeolites with a very low Si/Al ratio show high affinity for water and polar molecules. However, the zeolites with high Si/Al ratio can be hydrophobic with an affinity for n-paraffins. Therefore, various approaches have been developed for changing the Si/Al ratio of zeolites for specific application purposes.

In the early days, zeolites were used as adsorbents and molecular sieves in sorption and separation application due to the fit between the molecules and the pore openings. Therefore, their adsorptive performance enabled the application in solving environmental issues such as removing acid gases (SO₂, CO₂ and NO, etc.) to mitigate the greenhouse gas effects and upgrade natural gas and biogas. The zeolites were subsequently investigated as ion exchangers. They are able to remove the heavy metal ions in the waste water and soften the laundry water.
by exchanging Mg$^{2+}$ and Ca$^{2+}$ as laundry detergent builders. Later on, zeolite Y (FAU) was found to be capable of fluid catalytic cracking of oil, and ZSM-5 was found commercial catalytic application in olefin isomerization. Lately, more and more zeolites have been investigated for catalytic uses in petrochemistry.

The usefulness and the applications of zeolites in natural gas purification is addressed in section 1.4.

1.4 8MR Zeolites for natural gas purification

1.4.1 General introduction to 8MR zeolite

Currently, 248 framework types have been identified and approved according to the International Zeolite Association (IZA). Among those, the zeolites where the openings are limited by 8-membered ring (8MR) are recognised by small-pore zeolite or 8MR zeolite. The size of 8MR varies in the range of 0.30 nm to 0.45 nm. Up to date, considering only aluminosilicates (zeolites), there are forty-four 8MR zeolites documented. However, only a small group of 8MR zeolites have been investigated and industrially applied, as they can be easily synthesized and have high hydrothermal stability. Given the fit between the 8MR zeolites and the molecules, 8MR can potentially excel in separation of small molecules and dealing with ions. Later, more potential uses of 8MR zeolites have been developed especially in the field of catalytic applications, such as converting methanol to olefins and reduction of NOx. In this section of the thesis, we will only address the application in gas separation and review the modification approaches to improve the capacity and selectivity reported for those microporous 8MR zeolites. The most significant 8MR zeolite are listed in Table 1.3.

<table>
<thead>
<tr>
<th>IZA Code</th>
<th>Material name</th>
<th>Pore</th>
<th>Cage</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEI</td>
<td>SSE-39, AIPO-18, SIZ-8</td>
<td>8 × 8 × 8</td>
<td>✓</td>
</tr>
<tr>
<td>AFX</td>
<td>SAPO-56, SSZ-16</td>
<td>8 × 8 × 8</td>
<td>✓</td>
</tr>
<tr>
<td>ANA</td>
<td>Analcime, AIO-24</td>
<td>8 × 8 × 8</td>
<td>×</td>
</tr>
<tr>
<td>CHA</td>
<td>SSZ-13, SAPO-34</td>
<td>8 × 8 × 8</td>
<td>✓</td>
</tr>
<tr>
<td>DDR</td>
<td>ZSM-58</td>
<td>8 × 8</td>
<td>✓</td>
</tr>
<tr>
<td>ERI</td>
<td>UZM-12, AIPO-17</td>
<td>8 × 8 × 8</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 1.3 The list of most significant 8MR zeolite
1.4.2 Introduction to 8MR zeolite for natural gas purification

With the increasing demand for natural gas as raw materials and civil gas, natural gas purification technology has become a matter of interest. Natural gas is extracted from reservoirs in combinations with impurities including carbon dioxide, nitrogen and water. These impurities can reduce the calorific value of natural gas and cause corrosion to the pipeline. Hence, the development of new separation techniques with less energy consumption to replace the high-energy-demanding separation process have received significant attention worldwide. Pressure swing adsorption process is widely applied in natural gas purification, because the high-purity methane can be collected with low energy consumption and emission level. Zeolite plays a very important role in separating impurities from methane in PSA. Among the various zeolites which have been studied as potential adsorbents in natural gas purification, 8MR has advantages in terms of high selectivity compared to medium pore zeolites and large pore zeolites. Although the CO$_2$ uptake amount on large pore zeolites is attractive, they lose the selectivity at high pressure particularly. The remarkable selectivity of 8MR zeolite is attributed to the sizes of the 8MR which are close to the kinetic diameter of the gas molecules. The kinetic diameter of CO$_2$ (0.33 nm) is smaller than that of CH$_4$ (0.38 nm) and N$_2$ (0.36 nm). Hence, the gas molecules can be
distinguished by molecular sieving effect on 8MR zeolite. In this section, we will only address the adsorption and separation performance of CO₂ and CH₄ on 8MR zeolites.

The adsorption properties of zeolites and their separation performance were firstly investigated by Barrer and his co-workers.⁶²–⁶⁷ In the early stage, their research were focused on sorption properties of the natural zeolite materials, such as natural chabazite, Gmelinite and Mordenite.⁶² These zeolites are capable of separating mixtures by selective adsorption. The diffusion of various adsorbates in zeolites was subsequently studied, which paves the way to the development of kinetic separation.⁶⁸,⁶⁹ Chabazite (CHA) is a typical 8MR zeolite with a basic building unit comprising of a double-six-membered ring and a large ellipsoidal cavity accessed by a 8MR (0.38 nm × 0.38 nm), which suggested its potential for separation of CO₂ from natural gas or flue gas.⁷⁰,⁷¹ The extra-framework cations are exchangeable by various alkaline ions and located in different sites in the framework.⁷² The structure of CHA and the typical cation locations are shown in Figure 1.6.

![Figure 1.6 The structure of CHA and the typical cation locations. Adapted from 72](image)

The natural chabazite was firstly investigated by Barrer and his co-workers and it exhibited the molecular sieving effect by which the hydrocarbons can be separated based on their shapes.⁷³,⁷⁴
The isotherms of CO₂ and SO₂ can be well fitted by the Freundlich equation. Inui and his associates also studied the CO₂ separation performance on natural CHA by pressure swing adsorption method, showing CHA can adsorb 3.17 mmol/g of CO₂ at 2.5 bar with only 14.3% irreversible adsorption ratio. Owing to the narrow openings of CHA, it was able to remove bulk CO₂ from natural gas with high selectivity especially at low temperatures based on the adsorption study of gas mixtures. CHA could reduce the CO₂ mole fraction to about 0.0002 at equilibrium from the mixture (95% CH₄ and 5% CO₂) at 244K. CHA can be also synthesised and various ion-exchanged versions of chabazite have been extensively studied. Apart from the hydrocarbon separation, more potential separations were investigated subsequently, such as air separation, natural gas purification, oxygen/argon purification and flue gas/exhaust gas cleanup. In terms of natural gas purification, CHA can adsorb a high amount of CO₂ due to its high pore volume, which results in effective separation of CO₂ and CH₄. The CO₂ uptake of Na-CHA was 4.3 times higher than that of CH₄ at 100 kPa and 298K (Figure 1.7).

![Figure 1.7 Adsorption (solid) and desorption (hollow) isotherms of CO₂ (▲), CH₄ (■), and N₂ (●) on Na-CHA at 298K. Adapted from 80](image-url)
LTA (Linde Type A) zeolite also has a three-dimensional framework with a large cage accessed by eight membered rings (8MR) where a number of cations are populated to balance the charge. The pore opening sizes are largely dependent on the type of extra-framework cations. Monovalent ions prefer to sit in the 8MR and partially block the opening. LTA with Na\(^+\) as EFC has an opening of around 0.38 nm in diameter, so it is accordingly called 4A zeolite.\(^{81}\) Similarly, the pore openings can be tuned by from 0.3 nm to 0.5 nm by introducing K\(^+\) and Ca\(^{2+}\), respectively. Hence, K-LTA is called 3A, and Ca-LTA is called 5A based on the diameter of pore aperture. The structure of LTA is illustrated in Figure 1.8.\(^{82}\)

*Figure 1.8 The structure of LTA and its potential cation site, adapted from \(^{82}\)*

Since being reported by Breck,\(^{82}\) the adsorptive property of LTA has been widely studied, and it showed potential in extensive applications such as separation, drying and purification use.\(^{83,84}\) The isotherms on 4A and 5A of various adsorbates have been investigated by Breck and his coworkers. 4A could adsorb 4.27 mmol/g of CO\(_2\) at 700mmHg and room temperature due to its super cage and quadrupole of CO\(_2\). 5A exhibited higher CO\(_2\) capacity than 4A because of the increase of the effective pore sizes.\(^{85}\) CO\(_2\) capacity on 4A was observed to be higher than that of activated carbon when the pressure was lower than 30 psi and 298K, but at higher pressures, activated carbons exhibits much higher CO\(_2\) uptakes.\(^{86}\) Harper et al pointed out that the polar...
surface of LTA and large electrical fields near the EFC also contributed to the impressive CO₂ capacity.\textsuperscript{83} However, CH₄ was less adsorbed because the percolation was hindered by the Na⁺ occupying the 8MR.\textsuperscript{54} The preference of taking CO₂ indicated that this LTA was a suitable adsorbent for removing CO₂ from natural gas or biogas. The adsorption of CH₄ was very slow and controlled by diffusion at low temperatures, while the CO₂ adsorption was controlled by the isotherm shapes, which boosted the practical selectivity.\textsuperscript{87} The initial steep range in the CO₂ isotherms (Figure. 1.9 (b)) indicated that more process would apply to reach a low vacuum required for regeneration. Hence 4A zeolite is not ideally applicable in PSA processes.

![Figure 1.9 CH₄ (a) and CO₂ (b) adsorption isotherms on 4A zeolite at different temperatures. Solid lines refer to the fitting curves using Virial model, adapted from 87](image-url)
The CO₂ diffusion in zeolite 4A crystal and commercial pellets have been extensively studied. It was pointed out that intracrystalline diffusion was dominant in CO₂ diffusion in 4A zeolite. For commercial 4A pellets, the diffusion rate of CO₂ was controlled by micropore diffusion.⁸⁸ In a PSA cycle, 4A zeolite ran higher CO₂ capacity in the first cycle than that of the following cycles (Figure. 1.10), which indicated the adsorption was slightly irreversible.⁸⁶,⁸⁹ The adsorption behaviour can be further tuned by changing the EFCs and Si/Al to fit the potential application. These approaches and corresponding performance will be addressed in detail in section 1.4.3.

![Figure 1.10 Adsorption isotherms in each cycle of CO₂ on 4A zeolite at 25 °C, adapted from ⁸⁹](image)

RHO type zeolites also have three-dimensional frameworks limited by 8MR. The framework has a body-centred structure which is composed of ita cages connected by double-8-membered ring. The Si: Al ratios are around 5:1. This zeolite with high Si/Al ratio has low affinity of CO₂, and hence promotes the desorption.⁷⁷ RHO was found to be potentially used for CO₂ and CH₄ separation, because it had a large pore volume of 0.26 cm³/g and pore aperture (0.36 nm) just falling in between kinetic diameter of CO₂ (0.33 nm) and CH₄ (0.38 nm). RHO zeolite exhibited high CO₂ capacity of 4mmol/g at 293K and 100 kPa and the selectivity of CO₂/CH₄ could reach 100 at 100 kPa and 10 at 500 kPa, as shown in Figure. 1.11 (b).³⁷ The selectivity was much higher than that of most zeolites such as 13X, CHA, LTA and DD3R,⁹⁰–⁹³ which was attributed to its appropriate pore size. RHO was observed to exhibit a flexible structure rather than rigid frameworks, as exemplified by the distorted 8MR with temperature increase. ⁹⁴ The distortion of 8MR also
happened when RHO was ion exchanged by other cations. Ca²⁺ was preferable locating in the centre of double eight-membered ring (d8r), hence this coordination to four framework oxygen atoms distorted the 8MR to highly anisotropic ellipses.⁹⁵ Unsimilar to Ca-RHO, instead of forcing the d8r to distort, Cd²⁺ migrated to a favourable single 6-membered ring (S6R) when the temperature is higher than 300℃, because the distortion of d8r could not be able to satisfy the coordination requirements at elevated temperatures.⁹⁶ The framework of RHO zeolite also exhibited “breathing” phenomenon while adsorbing and desorbing CO₂, as evidenced by the deviation of Type I isotherm.²⁸ Lozinska et al studied the structure transition in depth by preparing the RHO fully exchanged by various univalent ions. The distortion during adsorbing CO₂ resulted from cation swing and was dependent on the location of cations and their migration. The cations shifted to other sites or temporarily deviate to allow the admission of CO₂ molecules. Cs-RHO underwent a structural transformation from a symmetric structure I-43m to Im-3m above 1 bar due to the migration of Cs⁺ from D8R to S8R.²⁸,⁹⁷ The some univalent cation exchanged-RHO zeolites were also observed to show a “cation gating” phenomenon on CO₂ adsorption. The cations acted as a reversible molecular valve which could be able to interact with CO₂ and move away from the original site, while the motion was not possible for hydrocarbons of which the interaction with cations are much weaker than that of CO₂. Hence, their diffusion was prohibited.⁴⁶,⁹⁸ This “trapdoor” mechanism provided a highly selective CO₂ adsorption over CH₄, and flexible structure expanded caused by the motion of cations during adsorption further enhanced the CO₂ capacity and contributed to a high selectivity of CO₂/CH₄. The capacity, selectivity and kinetics were strongly controlled by the composition of EFCs via ion exchange treatment.⁴⁶
Many other 8MR zeolites have also been studied for CO₂ adsorption and separation. Silica zeolite DDR (Si₁₂₀O₂₄₀) has 8-membered windows which are 0.36 × 0.44 nm in size. DDR showed higher selectivity for CO₂/CH₄ than other high-Silica zeolites such as silicalite-1 and beta due to the presence of 8MRs and higher concentrations EFCs to balance charge.⁹⁹ The most significant property of DDR zeolite is the difference in diffusion of CO₂ and CH₄ molecules. The diffusion of CH₄ was mainly controlled by the energy barrier when the CH₄ molecules pass through the 8MR between cages. The diffusivity increased as the CH₄ was continuously adsorbed due to the interaction between the adsorbates and resulting in the reduction on energy barrier. However, the diffusion of CO₂ was hindered by the CO₂ molecules which had been already adsorbed, hence the diffusivity showed a decrease when the CO₂ loading increased. It was attributed to the preference of CO₂ molecules sitting in the 8MR window and blocking the other molecules.¹⁰⁰ Hence, diffusion selectivity was dependent on the gas loading.¹⁰¹ The diffusion of CO₂ was little affected in the presence of CH₄, while the diffusion of CH₄ was largely hindered by the existing CO₂, which was not a common situation in mixed gas. This unique property made this material promising as a membrane for CO₂/CH₄ separation.¹⁰²

Clinoptilolite is one of the most common natural zeolites of which the structure possesses tetrahedral framework with open channels of 8-10MR.¹⁰³⁻¹⁰⁵ Clinoptilolite also showed attractive CO₂ adsorption properties (2.7 mmol/g at 10 bar and 277K), as shown in Figure. 1.12.¹⁰⁵ Higher CO₂ capacity was observed after increasing the Si/Al ratio by dealumination process.¹⁰³ The study of the adsorption kinetics of CO₂, N₂ and CH₄ showed that CO₂ was adsorbed much faster than
those of the latter two, which was attributed to stronger quadrupolar CO$_2$ molecule interaction with the electric field generated by the cations in the framework than N$_2$ and CH$_4$ molecules.$^{106}$ This big difference in the diffusivity made it attractive materials for kinetics separation in natural gas purification.$^{107,108}$

Figure 1.12 Isotherms on natural clinoptilolite of CO$_2$ and CH$_4$ at different temperatures up to 10 bar, adapted from$^{105}$
1.4.3 Modification of 8MR zeolite

1.4.3.1 Ion-exchange treatment

Ion exchange treatment of zeolites is the most common modification approaches applied in zeolite products used for adsorption and catalysis applications. There is a great amount of literature studying the performance of ion-exchanged zeolites involving the selectivity, capacity, kinetics and structural characteristics. The ion exchange treatment is of particular interest because the pore size of these materials can be tuned, and the interaction between cations and sorbates also varied. The type of cation can be able to change the pore volume and has a great influence on the electric field inside the pores where the adsorbates pass through. Hence the adsorptive properties of the zeolites are accordingly changed.

Breck et al firstly exchanged LTA with various alkaline cations including Li+, K+, Rb+, Cs+, Ag+, NH4+, Mg2+, Ca2+ etc. in the early years. The isotherms for exchanging Na+ with Ca2+, Sr2+ and Ba2+ were also determined. It was found that selectivity coefficient continuously reduced with the increasing ion loading. Ca-LTA (5A) derived from 4A via ion exchange treatment by which the pore size was adjusted to 0.5 nm. It has been widely used for separating branched paraffin and normal paraffin. However, it did not show attractive CO2/CH4 selectivity (1.77 at 303K and 1000 kPa) due to inappropriate window size. Further reduction of the window size was achieved by K+ exchange obtaining K-LTA (3A) whose application was limited by the too narrow pore aperture (0.3 nm). Hence 3A zeolite was mostly exploited in water removal from ethanol. Practically as the same diameter as water molecules and too small for ethanol molecules to penetrate through.

In order to enhance the separation performance of LTA on CO2/CH4, Hedin and his group developed a LTA which was partially exchanged with K+ cations, by which the window size was tuned between 0.3 nm and 0.4 nm depending on the content of K+ cations (Figure. 1.13). The K+ was preferentially located in the centre of 8MR and provided the hindrance of CH4 and N2 penetration. Therefore, the selectivity of CO2 over N2 achieved 172 at 298.15 K and 0.85 bar on NaK-LTA with the optimal K+ amount of 17 at.%. However, further increasing the K+ content caused the reduction of CO2 capacity due to small effective pore size.
A variant of zeolite A (|Na_{12-x}K_x|-LTA) (1.8 ≤ x ≤ 3.2) with different K⁺ content was developed and studied in the respect of CO₂/CH₄ separation. With the increase K⁺ content, the uptake of CH₄ significantly reduced, and CO₂ capacity slightly decreased. Very high selectivity was obtained due to the hindrance of CH₄ diffusion. They compared the results with other small pore zeolites (SAPO-56, SAPO-CHA, and AlPO-17) and found CO₂ capacity on 4A and |Na_{8.8}K_{3.2}|-LTA was largest. However, the working capacity of CO₂ on both LTAs was very low due to the steepness of the isotherms. The access to the pores of LTA was further tuned by introducing Cs⁺ to optimise the separation of CO₂ over CH₄. With the increase of Cs⁺ content, CH₄ was barely adsorbed. For the optimal ion-exchange LTA (|Na_{10.2}K_{Cs0.8}|-LTA), the selectivity of CO₂/CH₄ increased to more than 1500 at 293K and 50 kPa without compromising the CO₂ capacity (3.2 mmol/g). The significant enhancement of selectivity was attributed to occupation of 8MR. The LTA framework contained three types of the pore apertures including 8MR, 6MR and 4MR. Only the 8MR was of great significance and controls the percolation of the gas molecules, because the rest two were too small for gas to diffuse through. Due to the small ionic radius of Na⁺, it was preferentially located off the centre of 8MR and had a better contact with O atoms in the frameworks. Therefore, the percolation of CO₂ and CH₄ molecules were not hindered in the presence of Na⁺. However, Cs⁺ and K⁺, being large cations, prefer to sit at the centre of 8MR, and hinder the percolation of the gas molecules as a result. As CH₄ has larger ionic diameter, its diffusion is obstructed by K⁺ and Cs⁺ more greatly than CO₂. However, Mace et al. argued that the
enhancement of selectivity was not only attributed to the blocking by the large cations, but also the interaction with adsorbates. They studied the mobility of ions by both GCMC and MD simulations on NaK-LTA and concluded the effective molecular sieving was attributed to the difference in mobility between ions and exclusive interaction with CO$_2$ molecules, as observed by the increasing diffusion of Na$^+$ and K$^+$ in the presence of CO$_2$.\textsuperscript{128} Larin \textit{et al.} proposed another explanation for highly selective CO$_2$/CH$_4$ behaviour. They pointed out the high CO$_2$ capacity was attributed to the carbonate formation of K$^+$ cations which sat in the centre of 8MR in the presence of CO$_2$. This chemisorption of CO$_2$ on the NaKA would result in the relocation of K$^+$ and hence make the 8MR accessible for CO$_2$ molecules to pass through. However, there was no chemisorption of CH$_4$ and N$_2$ taking place on NaK-LTA. Hence, the diffusion of both gases was obstructed by the K$^+$.  

The ion exchange treatment is also very popular on CHA, as it has the advantage of suitable pore size for distinguishing CO$_2$ and CH$_4$.\textsuperscript{129} Webley’s group has been studying the alkali-exchanged chabazite and its adsorption properties in their early research.\textsuperscript{78,130,131} They prepared the various CHA ion-exchanged by both monovalent ion (Li$^+$, Na$^+$, K$^+$) and divalent (Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$). CO$_2$ was observed to be more significantly adsorbed than N$_2$ and CH$_4$ on the all the ion-exchanged CHA samples. Li-CHA had the highest CO$_2$ capacity (4.5 mmol/g at 273K and 100 kPa). The CO$_2$ capacity an equilibrium came in the sequence of Li-CHA > Na-CHA > Ca-CHA > K-CHA > Mg-CHA > Ba-CHA. They explained this sequence by giving two reasons. Firstly, the intensity of the electrostatic field became stronger in the sequence of K < Na < Li. Hence there was stronger interaction with CO$_2$ molecular quadrupole moment resulting in the increase of CO$_2$ adsorption energy. The other reason was free volume increased when the CHA was exchanged by ions with smaller diameter.
They also calculated the heat of adsorption for CO₂ depending on loading. The heat of adsorption of both Na-CHA and Li-CHA increased slightly with the increase of CO₂ loading indicating the strong interaction between adsorbates. However, for K-CHA, Ba-CHA and Mg-CHA, the enthalpy of CO₂ adsorption had a drop at high coverage. This was attributed to the weaker cation-quadrupole interaction at high loading and the interaction between adsorbates. K-CHA showed reasonably high preference adsorbing CO₂ and considerable porosity. K-CHA was observed to barely adsorb N₂ and Ar at 77 and 87 K, respectively, indicating a pore blockage behaviour. They attributed this behaviour to the decreasing mobility of K⁺ in 8MR at low temperatures and cause the pore blockage. Shang et al subsequently investigated the behaviour of “temperature” controlled nanovalve on K-CHA and developed its potential use as gas storage container. However, Ca-CHA and Na-CHA showed considerable N₂ uptakes at 77K, indicating no blockage for N₂ diffusion. Na⁺ has the most preference of sitting in S1 followed by SII and SIII’. The same as the case of Ca⁺ cations (Figure. 1.15). Hence, they did not render the hinderance of gas molecules. An unique isobar of CH₄ and N₂ was observed on K-CHA showing a “bell” shape at all pressures (Figure. 1.16). K-CHA showed highest N₂ and CH₄ uptake.
at certain temperatures. They proposed an encapsulation approach for N₂ and CH₄ storage by tuning the accessibility of 8MR depending on temperature.¹³¹

**Figure 1.15** Schematic representation of extra-framework cations positions in chabazite structure, adapted from¹³⁴
In the case of RHO, the change in adsorption properties after ion exchange treatment were similar to that of CHA. RHO exchanged with different univalent cation forms varied in CO₂ capacity and CO₂-over-CH₄ selectivity. The CO₂ capacity was in the sequence of Na⁺ > K⁺ > Cs⁺ due to the decreasing free ore volume and they all barely adsorb CH₄. By calculating the ideal selectivity based on the single component gas isotherm, Na-RHO exhibited an attractive selectivity (25 at 9 bar) across the entire pressure range and CO₂ capacity (up to 6 mmol g⁻¹ of CO₂ at 298 K and 9 bar), as shown in Figure 1.17. Na-RHO also showed relative advantage in terms of adsorption rate because of the small size of Na⁺. surface polarity of zeolite RHO. They attributed this high CO₂ capacity and selectivity to the cation motions caused by the interaction with CO₂. The extra-framework cations moved to other sites in the presence of CO₂ and allowed CO₂ to percolate the window. However, this motion did not occur in the presence of CH₄ due to the much weaker interactions. This momentary motion will be addressed in detail in the next section “trapdoor” effect. Table 1.4 is a summary of CO₂ capacity and CO₂-over-CH₄ selectivity at 50 kPa at different temperatures on ion-exchanged 8MR zeolites.
Table 1. List of CO\textsubscript{2} capacity and CO\textsubscript{2}-over-CH\textsubscript{4} selectivity at 50 kPa at different temperatures on ion-exchanged BMR zeolites

<table>
<thead>
<tr>
<th>Zeolite Composition</th>
<th>Temperature (K)</th>
<th>n\textsubscript{CO2} (mmol/g)</th>
<th>n\textsubscript{CH4} (mmol/g)</th>
<th>Selectivity \textsuperscript{a}</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{12}-LTA</td>
<td>293</td>
<td>4.10</td>
<td>0.45</td>
<td>9</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{11}K-LTA</td>
<td>293</td>
<td>3.90</td>
<td>0.40</td>
<td>10</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{10}K\textsubscript{2}-LTA</td>
<td>293</td>
<td>3.50</td>
<td>0.015</td>
<td>230</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{11}Cs-LTA</td>
<td>293</td>
<td>2.80</td>
<td>0.096</td>
<td>29</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{10}Cs\textsubscript{2}-LTA</td>
<td>293</td>
<td>0.78</td>
<td>0.019</td>
<td>41</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{10.6}K\textsubscript{0.6}Cs\textsubscript{0.8}-LTA</td>
<td>293</td>
<td>3.20</td>
<td>0.002</td>
<td>&gt;1500</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{10.6}K\textsubscript{0.8}Cs\textsubscript{0.6}-LTA</td>
<td>293</td>
<td>3.00</td>
<td>0.19</td>
<td>16</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Na\textsubscript{10.9}K\textsubscript{0.6}Cs\textsubscript{0.5}-LTA</td>
<td>293</td>
<td>3.40</td>
<td>0.31</td>
<td>11</td>
<td>\textsuperscript{54}</td>
</tr>
<tr>
<td>Ca-LTA</td>
<td>303</td>
<td>2.80</td>
<td>0.30</td>
<td>9.3</td>
<td>\textsuperscript{137}</td>
</tr>
<tr>
<td>Ca-LTA</td>
<td>303</td>
<td>3.50</td>
<td>1.40</td>
<td>2.5</td>
<td>\textsuperscript{122}</td>
</tr>
<tr>
<td>K-KFI</td>
<td>298</td>
<td>2.80</td>
<td>0.76</td>
<td>3.5</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Na-KFI</td>
<td>298</td>
<td>4.00</td>
<td>0.77</td>
<td>5.0</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Li-KFI</td>
<td>298</td>
<td>3.80</td>
<td>0.76</td>
<td>5.4</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Ca-KFI</td>
<td>298</td>
<td>2.20</td>
<td>0.76</td>
<td>2.8</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Na-LEV</td>
<td>298</td>
<td>2.14</td>
<td>0.18</td>
<td>11.9</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>K-CHA</td>
<td>298</td>
<td>2.00</td>
<td>0.78</td>
<td>2.6</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>K-CHA</td>
<td>273</td>
<td>4.00</td>
<td>1.20</td>
<td>3.3</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>K-CHA</td>
<td>303</td>
<td>1.01</td>
<td>0.01</td>
<td>101</td>
<td>\textsuperscript{139}</td>
</tr>
<tr>
<td>RbK-CHA</td>
<td>273</td>
<td>2.90</td>
<td>0.22</td>
<td>13.2</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>Na-CHA</td>
<td>298</td>
<td>4.46</td>
<td>1.03</td>
<td>4.3</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>CsK-CHA</td>
<td>298</td>
<td>1.72</td>
<td>0.04</td>
<td>43.0</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>KNa-CHA</td>
<td>303</td>
<td>1.55</td>
<td>0.03</td>
<td>51.7</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>KLiNa-CHA</td>
<td>273</td>
<td>0.95</td>
<td>0.04</td>
<td>23.6</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>BaNaK-CHA</td>
<td>273</td>
<td>0.73</td>
<td>0.22</td>
<td>3.32</td>
<td>\textsuperscript{138}</td>
</tr>
<tr>
<td>Li-CHA</td>
<td>298</td>
<td>4.55</td>
<td>0.93</td>
<td>4.89</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Ca-CHA</td>
<td>298</td>
<td>3.57</td>
<td>0.85</td>
<td>4.20</td>
<td>\textsuperscript{80}</td>
</tr>
<tr>
<td>Na-RHO</td>
<td>298</td>
<td>4.50</td>
<td>0.06</td>
<td>70</td>
<td>\textsuperscript{46}</td>
</tr>
<tr>
<td>K-RHO</td>
<td>298</td>
<td>3.8</td>
<td>0.06</td>
<td>63</td>
<td>\textsuperscript{46}</td>
</tr>
<tr>
<td>Cs-RHO</td>
<td>298</td>
<td>0.6</td>
<td>0.04</td>
<td>15</td>
<td>\textsuperscript{46}</td>
</tr>
</tbody>
</table>
1.4.3.2  Effect of Si/Al ratio

Although the 8MR zeolites mentioned above have decent CO₂ capacity, they are normally synthesized with low Si/Al. However, the desorption of CO₂ on zeolites with low Si/Al is a limiting factor, hence deep vacuum may apply to remove the CO₂ and reuse the zeolites in a PSA process, which is energy-intensive. To minimize the energy consumption in desorption process, the desorption process taking place at atmospheric pressure is desirable on this regard. It is known that the electrostatic field in the cavities greatly influences the adsorption capacity, which is generally affected by either the extra-framework cations balancing the charges or the Al content in the framework. ¹⁴⁰,¹⁴¹ Palomino et al. ⁵⁷ firstly investigated the CO₂ regenerablity and CO₂/CH₄ separation performance by changing the Si/Al ratio. They found out that CO₂ adsorption capacity decreased with the decrease of Al content in the LTA frameworks (Figure. 1.18). However, the isotherm became more linear, which increased the working capacity. ¹⁴²–¹⁴⁴ The LTA with high silica content was mostly regenerated in very short time. Therefore, the optimization of the CO₂ regenerability was achieved by increasing Si/Al ratio because of adjusting the affinity to polar molecules. The CO₂-over-CH₄ selectivity exponentially decreased with pressure. But the LTA with higher Al content became less sensitive to the pressure. The pure silica LTA kept the selectivity of 3.5 across the entire pressure range. Hence, the regenerability was enhanced by optimising the Al content in LTA, which minimised the energy consumption in desorption process. ¹⁴⁵
In consideration of the presence of water in natural gas, most of the 8MR zeolites are highly hydrophilic, indicating they are more selective for water than CO$_2$.\textsuperscript{146} Hence the dehydration process is required before the adsorption. Apart from this, the affinity for CO$_2$ on zeolite with low Si/Al hinders the desorption of CO$_2$, which required deep vacuum in regeneration process. Hence, hydrophobic materials are preferable in this regard. Pure silica CHA zeolite was firstly developed by Díaz-Cabañas \textit{et al.}\textsuperscript{147} and more hydrophobic than SSZ-13 or SAPO-34.\textsuperscript{55,148–150} The Si-CHA exhibited a lower CO$_2$ uptakes compared to 13X indicating the low affinity to polar molecules of the former one.\textsuperscript{151} The working CO$_2$ capacity of Si-CHA was higher than that of zeolite 13X, and the selectivity of CO$_2$-over N$_2$ was still high even in the presence of water according to the breakthrough study.

1.4.4 “Trapdoor” effect

The “Trapdoor” effect was firstly proposed by Webley’s group, as observed by the normal N$_2$ adsorption uptakes at ambient temperature (273K) on K-CHA1 and very little capacity at lower temperatures (77K). They attributed this phenomenon to the steric hindrance caused by the cations coupling with its reducing mobility at low temperatures, which resulted in the
inaccessibility of the 8MRs.\textsuperscript{131} With facilitating the temperatures, the cation mobility increased and the structure dilated. The structural dilation was also observed on LTA and the vibration of LTA lattice resulted in the large fluctuation of window aperture.\textsuperscript{152,153} However, the blockage of the pores at low temperatures was not observed on CHA exchanged with small monovalent cations and divalent such as Li\textsuperscript{+}, Na\textsuperscript{+} and Ca\textsuperscript{2+}. They attributed this “non-blockage” to the cation size and its sites. In the case of CHA, Na\textsuperscript{+} was preferentially located in of the centre of the 8MR and did not hinder the diffusion of N\textsubscript{2} molecules, while K\textsuperscript{+} was large enough to sit in the centre of 8MR where the molecules passed through and not able to mobile away from centre at low temperatures. For Ca\textsuperscript{2+}, less numbers of cations were required to balance the charge, hence gas molecules were able to diffuse through the vacancies in the 8MRs.\textsuperscript{91} To undercover this phenomenon in depth, Webley’s group also investigated the underlying mechanism through experimental and computational approaches. They found out the adsorption capacity of N\textsubscript{2}, CH\textsubscript{4} and CO\textsubscript{2} were not monotonously decreased with the temperature increase and showed a temperature-dependent behaviour. The isobar exhibited a “bell” shape and had a threshold temperature “T\textsubscript{c}”. K-CHA with Si/Al = 2.2 (denoted r2KCHA) showed ignorable CH4 and N2 capacity below 279 and 266 K, respectively, indicating a pore blockage taking place when the temperature was below T\textsubscript{c}. However, the pores were fully accessible when taking in CO\textsubscript{2} molecules, as shown in \textbf{Figure. 1.19 (a)}. The same behaviour was also observed on Cs-CHA with Si/Al = 2.5 (r2CsCHA), as shown in \textbf{Figure. 1.19 (b)}. It was pointed out that the thermal dilation of the pore aperture was not applicable in this case, as confirmed by the Synchrotron powder X-ray diffraction measurements. In fact, the Cs\textsuperscript{+} and K\textsuperscript{+} originally occupied SIII\textsuperscript{′} site (very centre of the 8MRs) and migrated away from the 8MRs at elevated temperatures. This migration leaded to the accessibility of a fraction of 8MR, hence the gas molecules were able to diffuse through the doorways into the supercavities. The successful passage of the gas molecules was achieved when the extra-framework cations deviated temporarily off the 8MR centre. This deviation took place by either of the two conditions: increasing the thermal dynamics of the cations or swinging the potential well by the interaction between extra-framework cations and the guest molecules.\textsuperscript{91} The CO\textsubscript{2} molecules were able to interact with the cations and facilitate the temporary deviation of the cations at any temperatures. However, the interaction between cations and gases such as
CH₄ and N₂ was very weak at the temperature below T_c, hence the migration of the cation did not occur. Therefore, the CH₄ and N₂ were barely adsorbed at low temperatures. The extra-framework cations acted as “door-keeper” and only allowed for certain gas molecules to pass through at low temperatures. Hence, the effective separation of CO₂/CH₄ and CO₂/N₂ were achieved by this special feature of the 8MR zeolites (Figure. 1.20).

Figure 1.19 Isobars of CO₂, N₂, and CH₄ on (a) r2K-CHA and (b) r2Cs-CHA at 100 kPa showing the “pore-blockage” below threshold temperatures (T_c) for N₂ and CH₄ and the full accessibility of pores for CO₂ across the entire temperature range. (c) Isobars of CO₂ and N₂ showing the “pore-blockage” existing on both gases. Adapted from ⁹¹

Figure 1.20 Schematic illustration of the “trapdoor” effect Adapted from ⁹¹
This “trapdoor” feature was not applicable for all the CHA zeolites, Jin et al. further investigated the rule for determining the “trapdoor” chabazite. The original location of the cations and the Si/Al was determinant. Only when the Si/Al was smaller than 3, there were at least nine cations per unit cell, and these cations must reside at the centre of 8MRs (site SIII′) as the door-keeping cations (Figure. 1.21).

An adsorption model was proposed to describe the isobars of “trapdoor” for four gases including H₂, Ar, CH₄ and N₂. This model introduced an item “fraction of pore-keeping oscillators” that changed depending on temperatures.

Lozinska et al. also found out the “trapdoor” effect on some of the univalent cation forms RHO zeolites. They studied the cation migration routine of RHO in the form of Na⁺, K⁺ and Cs⁺ with Si/Al= 3.9 in detail when adsorbing CO₂. K⁺ and Cs⁺ cations migrated significantly in the presence of CO₂, however the motion of Na⁺ was much weaker. Na⁺ only showed a small deviation or

**Figure 1.21** The demonstration of the initial location of door-keeping cations in 8MR, which indicates nominal accessible pore aperture is reduced to 0.6 Å in the presence of K⁺. Adapted from 154.
oscillation with the single eight ring (S8R). For Cs+, it moved from D8R to S8R and stayed with the window. K* shifted from window site to cage sites as a response of CO2 (Figure 1.22). Hence, the 8MR became accessible for CO2 molecules. However, the interaction energy of CH4 with the door-keeping cations was too weak to trigger the relocation of these cations. 46 RHO zeolites undertook a more complex process than CHA, because the former was flexible and showed a “breathing” behaviour when CO2 was adsorbed and desorbed.

Recently, another 8MR zeolite Merlinoite zeolite (IZA code MER) showed similar adsorption behaviour as the zeolites in RHO family.155 The MER zeolites underwent an obvious structural expansion when CO2 pressure elevated. This phenomenon took place in all cation-form MER

Figure 1.22 The cation motion of RHO in the form of (top) Na-RHO, and (middle) K-RHO, and (bottom) Cs-RHO. (left) dehydrated zeolite RHO and (right) RHO in the presence of CO2. Na+(yellow); K+, (green); Cs+, (purple). CO2 molecules: C, (black); O, (red). Adapted from 46
zeolite, but the “triggered” pressure varied depending on the cation types. The “trigger” pressure of Na-MER was highest compared with K⁺- and Cs⁺-form MER, as it had the largest number of cations located in the d8r and resulted in highest energy barrier to undergo a structure transformation. The structural phase transition of Cs-MER was associated with the migration of Cs⁺ from centre of the d8r to the S8R, which was similar to Cs-RHO. MER zeolites exhibited a cation-controlled adsorption behaviour which associated with breathing and CO₂-induced pore opening. By Careful considerations and use of these effects, the effective CO₂/CH₄ separation may be achieved.¹⁵⁵

1.4.5  ZSM-25

ZSM-25 is a 8MR zeolite and firstly reported, synthesized using TEA⁺ ions as template in a US patent in 1981.¹⁵⁶ However, the structure of ZSM-25 was only revealed by Suk Bong Hong and his group in a recent study and showed a body-centred cubic with two scaffolds interpenetrated. Each cubic is comprised of seven types of cages where 8MR and is the largest pore aperture (ca. 3.6 Å) and the only access of the gas molecules. The structure scheme is shown in Figure. 1.23.

Figure 1.23 the interpenetration of two cubic scaffolds of ZSM-25. (b) the framework structure of ZSM-25 with four types of cages embedded in the cubic scaffolds and three types of cages building the edge of the scaffold. (c) the seven different cages of ZSM-25. Adapted from ³⁰

ZSM-25 showed potential small-molecule separation such as selective CO₂ adsorption from natural gas or fuel gas. NaTEA-ZSM-25 was found to demonstrate high capacity for CO₂ (3.5mmol/g at 1.0 bar and 298K) and low capacity of N₂ and CH₄ (Figure. 1.24). The CO₂/CH₄ selectivity was greater than that of K-CHA, which was attributed to the cation-gating, where the cations were able to interact with CO₂ molecules and move away from the passage consequently,
whilst remain blocking the 8MR in the presence of weak interaction molecules such as CH\textsubscript{4} and N\textsubscript{2}.\textsuperscript{30}

The separation performance of ZSM-25 was studied with and without the TEA\textsuperscript{+} template by calcination at 500 °C over a wide pressure range (0–25 bar) and in the presence of water.\textsuperscript{157} Na-TEA-ZSM-25 and Na-ZSM-25 showed remarkable CO\textsubscript{2} uptake and considerably lower CH\textsubscript{4} uptake at high pressure compared to Na-CHA and Na-A (Figure 1.25). NaTEA-ZSM-25 exhibited a striking CO\textsubscript{2}/CH\textsubscript{4} selectivity >40 at 25 bar, which suggested this zeolite were potentially useful as a high-pressure CO\textsubscript{2} adsorbent. This effect was ascribed to the “trapdoor effect” where the cations blocked the 8MR and hindered the admission of CH\textsubscript{4}. Na-ZSM-25 demonstrated less steep CO\textsubscript{2} isotherm at low pressure than that of Na-TEA-ZSM-25, which resulted in higher CO\textsubscript{2} working capacity in a PSA cycle. The dynamic separation performance of Na-TEA-ZSM-25 by breakthrough experiments also showed superior CO\textsubscript{2}/CH\textsubscript{4} separation and excellent durability even in the presence of water vapor (Figure 1. 26). It shows the highest CO\textsubscript{2}/CH\textsubscript{4} selectivity 298K and 25 bar compared to other zeolite materials tested thus far and remarkably high CO\textsubscript{2} capacity. Therefore, ZSM-25 based zeolite appears to be promising candidates for CO\textsubscript{2} separation at both ambient pressure and high pressure.

![Figure 1.24 Adsorption isotherms of CO\textsubscript{2} (navy), CH\textsubscript{4} (green) and N\textsubscript{2} (pink) on NaTEA-ZSM-25 at 298K, adapted from\textsuperscript{30}](image-url)
1.5 The current challenges in natural gas purification

The major impurity in the natural gas is CO$_2$, hence a variety of zeolite types have been investigated for CO$_2$/CH$_4$ separation via pressure swing adsorption (PSA). 8MR zeolites showed appreciable CO$_2$/CH$_4$ selectivity, but they are kinetically-limited and show a decreasing selectivity with the pressure increase. The enhancement of kinetics of 8MR and remaining the high selectivity at high pressure are the future direction and main challenge.
The removal of nitrogen is even more challenging, as N₂ and CH₄ are physically-alike and have similar kinetic diameter. Currently, only cryogenic distillation has been commercially applied for N₂ removal in large scale. However, the huge operating costs and intensive energy-consumption are unfavorable in the respect of economy and energy. PSA can be potentially used for nitrogen-methane separation owing to its low operating and capital costs. Most of the reported zeolites take the advantage of difference of kinetics of the N₂ and CH₄, however the selectivity of N₂ over CH₄ is not appreciable. The adsorbents used for equilibrium-based separation of N₂ and CH₄ are CH₄-selective. Hence the CH₄ is adsorbed firstly and released via regeneration process, which losses the original pressure advantage. The main challenge is seeking for a N₂-selective adsorbent and realizing the effective separation at near ambient temperature.

1.6 Objectives

The aim of this thesis commenced with modifying an 8MR zeolite (e.g.ZSM-25) to enhance the kinetics of CO₂ adsorption without reducing the CO₂-over-CH₄ selectivity over the pressure range (up to 10 bar). By partially replacing the Na⁺ with Li⁺, this material is able to adsorb CO₂ ten times faster than the untreated zeolite (ZSM-25) without compromising the selectivity. The second aim of this thesis was to fabricate a mixed-matrix membrane (MMM) by incorporating this ZSM-25 as fillers. The CO₂ permeability increases, but the CH₄ permeability reduced due to the hinderance of ZSM-25 zeolite. Hence, it showed significantly enhanced CO₂ permeability and unique increase of selectivity with pressure increase because of the predominant molecular sieving effect. The third aim of this thesis was to resolve the N₂/CH₄ separation challenge by developing an 8MR zeolite which is N₂-selective and achieve the separation at around ambient temperature. A novel “trapdoor” zeolite was developed by introducing “door-keeping” cations. These “door-keeping” cations exclusively allow N₂ molecules to diffuse into the cages, and CH₄ molecules are hindered. This material shows an outstanding N₂/CH₄ selectivity at near ambient temperature.

1.7 Thesis outline

In Chapter 2, a Li⁺/ZSM-25 zeolite (LZZ) was developed via ion exchange treatment with high CO₂ adsorption capacity and kinetics, which are favorable for PSA-based CO₂/CH₄ separation. The adsorption behavior of the Na-ZSM-25 derived LZZ was tuned by modifying the synthesis
procedure. Measurements of adsorption isotherms and the rate of adsorption (ROA) measurements show that the LZZ exhibits higher CO₂ adsorption capacity as well as faster adsorption kinetics (9.84 times) without compromising the CO₂/CH₄ adsorptive selectivity. The feasibility of the LZZ in dynamic CO₂/CH₄ separation is also confirmed by breakthrough experiments. A curious gradual structural expansion induced by CO₂ is also observed, and it allows more uptake of CH₄ and hence lowers its selectivity, as demonstrated by synchrotron in situ X-ray powder diffraction and breakthrough experiments. This chapter was published as a paper on *The Journal of Physical Chemistry C* 122 (33), 18933-18941.

In **Chapter 3**, LNZ-25 nanoparticles were incorporated into a commercially available Matrimid matrix to yield mixed matrix membranes (MMMs). The incorporation of ZSM-25 can effectively enhance the selectivity of CO₂ over CH₄ with simultaneous improvement of CO₂ permeability. Moreover, the optimized MMM demonstrates an >400% increase of CO₂/CH₄ selectivity as the feed pressure increases from 2 bar to 5 bar. In contrast, the CO₂/CH₄ selectivity of the pristine Matrimid in this pressure range is similar. This performance is especially encouraging for natural gas purification where the membrane selectivity at high pressure is more important. This is because several side effects such as plasticization and concentration polarization can dramatically reduce the selectivity compared to that measured at lower feed pressure (< 3 bar). This result reveals the feasibility of using the LNZ25 as an effective filler for enhancing the CO₂/CH₄ separation performance in MMMs. This chapter was published as a paper on *Journal of Membrane Science* 583, 23-30.

In **Chapter 4**, a new “trapdoor” zeolite was designed for efficient N₂ over CH₄ separation based on ZSM-25 by incorporating the door-keeping cation. Specifically, potassium was introduced into ZSM-25 as extra-framework cations by ion-exchange treatment. In this zeolite, the pores are inaccessible for CH₄ while free for N₂ below certain temperatures, because K⁺ can thermally deviate from the gas pathway and triggered the admission of N₂, while CH₄ is rejected on the basis of higher threshold temperature of the latter one. K-ZSM-25 can achieve the effective N₂/CH₄ separation at around ambient temperature with ultra-high selectivity of over 200 in single gas adsorption. This feature of K-ZSM-25, as a new “trapdoor” material, provides a potential strategy for the separation of N₂ and CH₄ or other gas pairs physically alike but with
distinguishable threshold temperatures. To the best of our knowledge, this zeolite has the best N\textsubscript{2}/CH\textsubscript{4} separation performance compared to any zeolite and MOF reported in the open literature. **Chapter 5** is the conclusion of the PhD work and the key findings and gives some recommendations for future research.

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Chapter 2

Li⁺/ZSM-25 Zeolite as a CO₂ Capture Adsorbent with High Selectivity and Improved Adsorption Kinetics, Showing CO₂-Induced Framework Expansion

Chapter Perspectives

A variety of 8MR zeolite types have been investigated for CO₂/CH₄ separation, showing an appreciable CO₂/CH₄ adsorptive selectivity at low pressures and reduced selectivity at high pressures. Na-ZSM-25 is an 8MR zeolite and shows a remarkable CO₂/CH₄ selectivity due to its pore size fitting between the kinetic diameter of CO₂ and CH₄. Hence, Na-ZSM-25 seems to be a promising platform for developing the next generation of adsorbents in natural gas purification and carbon capture and storage (CCS). However, current ZSM-25-based zeolites suffer from slow adsorption kinetics, which limits its potential application in PSA processes. In this chapter, we developed a Li⁺/ZSM-25 zeolite (LZZ) by partially replacing the Na⁺ with Li⁺. Measurements of adsorption isotherms and the rate of adsorption (ROA) measurements show that the LZZ exhibits higher CO₂ adsorption capacity as well as faster adsorption kinetics (9.84 times) without compromising the CO₂/CH₄ adsorptive selectivity. The feasibility of the LZZ in dynamic CO₂/CH₄ separation is also confirmed by breakthrough experiments. During these measurements, we observed a curious gradual structural expansion induced by CO₂ that allows more uptake of CH₄ and hence lowers its selectivity, as demonstrated by synchrotron in situ X-ray powder diffraction and breakthrough experiments. This high CO₂ adsorption capacity and kinetics are favorable for PSA-based CO₂/CH₄ separation.

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Li⁺/ZSM-25 Zeolite as a CO₂ Capture Adsorbent with High Selectivity and Improved Adsorption Kinetics, Showing CO₂-Induced Framework Expansion

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ABSTRACT: The structure of ZSM-25, a RHO family zeolite, was resolved recently. Recent reports focused on Na-ZSM-25 as a promising CO₂ adsorbent with high CO₂ working capacity and exceptional CO₂/CH₄ ideal selectivity for pressure swing adsorption. However, these reports discuss single-gas adsorption performance of Na-ZSM-25 and are unable to provide the CO₂/CH₄ separation behavior in practical scenarios where the adsorption is performed using mixed gases. Furthermore, Na-ZSM-25 suffers from slow adsorption kinetics that limits its industrial applications. In this study, Li⁺/ZSM-25 zeolites (LZZs) are developed to enhance the CO₂ adsorption kinetics without compromising selectivity. The adsorption performance was examined using both single-(isotherm) and binary-(breakthrough) gas measurements. The results indicate that the CO₂ adsorption rate of LZZ is 9.84 times that of Na-ZSM-25 with a simultaneous increase of the CO₂ adsorption capacity by 6.1% at 303 K and 9.5 bar. The very high CO₂/CH₄ adsorptive selectivity is successfully inherited from Na-ZSM-25 zeolite in both single- and binary-gas adsorption. Furthermore, in situ XRD reveals CO₂-induced framework expansion, which explains the origin of the high working capacity and type-II-like isotherms of the ZSM-25-based zeolites. This study implies promising application of LZZ in natural gas purification and biogas upgrading.

INTRODUCTION

CH₄ is one of the three major pillars of the world’s fossil fuels, since it is efficient and clean, and it is widely used in power generation as a feedstock for chemicals and as an industrial and civilian gas.¹ CH₄ is the major component in landfill gas, natural gas, and biogas, so its utilization is of great economic significance. However, these methane-rich gas streams may contain up to 15−50 vol % carbon dioxide, which reduces the calorific value and also causes corrosion/blockage of pipelines and equipment, especially in the presence of water. Therefore, technology for separating CO₂ from CH₄ is attracting worldwide interest. Among the existing gas separation methods,³−⁸ physical adsorption is a promising approach because of its low operating and capital costs.⁹ Ideally, the adsorbent, the key in the adsorption process, should possess high adsorption capacity and selectivity for CO₂ over other components as well as fast adsorption kinetics and easy regenerability.

Various porous materials, such as activated carbons (ACs),¹⁰,¹¹ metal−organic frameworks (MOFs),¹²,¹³ and zeolites have been investigated as adsorbents for CO₂/CH₄ separation.¹⁴ ACs have long been used for CO₂/CH₄ separation because of their high CO₂ adsorption capacity.¹⁵−¹⁷ However, ACs usually have low selectivity especially at high pressures, which limits their application.¹⁸ Carbon molecular sieves (CMS), derived from ACs, have very high kinetic CO₂-over-CH₄ selectivity because of the slow CH₄ diffusion and are suitable for adsorption-driven biogas upgrading.¹⁹,²⁰ Recently, MOFs as CO₂ adsorbents have gained considerable interest.²¹ Despite their high adsorption capacity and good adsorptive selectivity, the applications of MOFs in industry are limited by their high costs as well as low stability. Compared with ACs and MOFs, zeolites are more favorable for CO₂/CH₄ separation because of their high adsorption capacity, solid acidity, tunable pore structure, high stability, and ease of mass production.²²−³⁰

Supporting Information

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A variety of zeolite types have been investigated for CO2/CH4 separation,2,24−26,28,30 showing a CO2/CH4 adsorptive selectivity of 1.9−20 at high pressure. NaTEA-ZSM-25 (TEA: tetraethylammonium bromide, which is a structure directing template), a zeolite recently resolved by Guo et al.,31 has a small pore aperture size of ca. 3.6 Å and a body-centered cubic structure that is similar to RHO and PAU.31 NaTEA-ZSM-25 is attracting attention in CO2/CH4 separation, because at 298 K and 1 bar, it exhibits a high CO2 adsorption capacity of 3.5 mmol/g and an exceptionally high CO2/CH4 selectivity.32 The exclusive admission of CO2 and rejection of CH4 are hypothesized to be the result of molecule sieving effects. The working capacity of an adsorbent is an important consideration for application to pressure swing adsorption (PSA) and is defined as the difference of the CO2 loading over the working pressure region (i.e., adsorption pressure and desorption pressure). Referring to this criterion, in spite of its high absolute adsorption capacity, NaTEA-ZSM-25 has a low working capacity in PSA application (0.5 mmol/g from 10 to 1 bar) because of its typical type-I isotherm for CO2 adsorption. Thus, very low desorption pressure is needed to regenerate the adsorbent, which is very energy intensive. Recently, Na-ZSM-25 has been prepared by removing TEA from the original NaTEA-ZSM-25 zeolite.32 Na-ZSM-25 possesses a much higher CO2 adsorption working capacity (1.5 mmol/g from 10 to 1 bar) than that of NaTEA-ZSM-25 as well as most of the other zeolites. This is because the CO2 adsorption isotherm of the Na-ZSM-25 significantly deviates from type I, i.e., the CO2 uptake of the Na-ZSM-25 continuously increases with pressure increase. Apart from the superior working capacity, Na-ZSM-25 also shows a remarkable CO2/CH4 selectivity. Hence, Na-ZSM-25 seems to be a promising platform for developing the next generation of adsorbents in natural gas purification and carbon capture and storage (CCS). However, current ZSM-25-based zeolites suffer from slow adsorption kinetics. According to the previous report, the uptake of CO2 on NaTEA-ZSM-25 reached equilibrium in 2−5 min at 298 K and 1 bar.31 Our study (discussed later in this paper) also confirms the slow adsorption kinetics of Na-ZSM-25. The low rate of adsorption/desorption of current ZSM-25-based zeolites are the principal factor that hampers their application to PSA.31 The ion-exchange treatment of zeolites can affect their adsorptive properties by adjusting the composition of the zeolite.33 Replacement of sodium of zeolite A by calcium was initially revealed to enlarge the pore openings.34 The extra-framework cations can regulate the gas molecular diffusion rate by narrowing (larger cations) or enlarging (smaller cations) the pore size. Therefore, for some specific compositions, larger molecules (N2 or CH4) are blocked, while smaller molecules (CO2) can still be admitted into the pores. In this regard, the CO2/CH4 selectivity and kinetics of the zeolites can be improved by this method.35−37

In the current work, we developed a Li+/ZSM-25 zeolite (LZZ) with high CO2 adsorption capacity and kinetics, which are favorable for PSA-based CO2/CH4 separation. The adsorption behavior of the Na-ZSM-25 derived LZZ was tuned by modifying the synthesis procedure. Measurements of adsorption isotherms and the rate of adsorption (ROA) measurements show that the LZZ exhibits higher CO2 adsorption capacity as well as faster adsorption kinetics (9.84 times) without compromising the CO2/CH4 adsorptive selectivity. The feasibility of the LZZ in dynamic CO2/CH4 separation is also confirmed by breakthrough experiments. During these measurements, we observed a curious gradual structural expansion induced by CO2 that allows more uptake of CH4 and hence lowers its selectivity, as demonstrated by synchrotron in situ X-ray powder diffraction and breakthrough experiments.

2. EXPERIMENTAL SECTION

2.1. ZSM-25 Preparation and Li+ Exchange. 1.92 g of aluminum hydroxide (Al(OH)3, 24.6 mmol, Sigma-Aldrich; reagent grade) was added to 3.04 g of 50 wt % sodium hydroxide solution (NaOH, 38.0 mmol, Sigma-Aldrich) in 60.73 g of distilled water at room temperature resulting in a translucent solution. Then, 10.80 g of Ludox AS-40 colloidal silica and 11.15 g of TEA bromide (53 mmol, 98%, Sigma-Aldrich) were added into the above translucent solution. The gel was stirred at room temperature for 24 h. Afterward, the gel was transferred to a Teflon-lined autoclave and heated under rotation for 7 days in an oven at 408 K. Then, the autoclave was cooled very slowly in air to room temperature. The as-made Na-ZSM-25 was filtered and dried overnight at 333 K followed by calcination at 773 K in air for 6 h to remove the template. The pristine Na-ZSM-25 was then collected.

Li+/ZSM-25 zeolite samples were prepared via ion exchange of the Na+ in Na-ZSM-25 with Li+ in a solution.38 In a typical procedure, 1 g of Na-ZSM-25 zeolite was ultrasonically dispersed in 2 mL of 1 mol/L LiCl solution for a half minute and placed at room temperature for 1 h to yield the Li+/ZSM-25 zeolite. Then, the zeolite was washed with deionized water five times and dried in the air at 333 K for 10 h. This ion-exchange procedure was repeated several times to obtain Li(0.063)-ZSM-25, Li(0.10)-ZSM-25, and Li(0.13)-ZSM-25, where the numbers in brackets refer to the Li+/Na+ ratio acquired from ICP-MS. After the ion exchange, Na+ was partially replaced by Li+, and more Na+ cations were exchanged with the increase of exchange times. However, Na+ cannot be fully exchanged because of structural collapse after four ion exchanges.

2.2. Characterization and Measurements. 2.2.1. Characterization. The compositions of samples and Si/Al ratios were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Powder X-ray diffraction (Bruker D2 Phaser) using Cu Kα (λ = 1.540598 Å) was used for identification of the as-made ZSM-25 and Li+/ZSM-25 zeolites (LZZs). The morphology of the synthesized zeolites was examined using a JEOL 7001F scanning electron microscope (SEM).

2.2.2. Adsorption Isotherms and Kinetics. The CO2 and CH4 adsorption isotherms of all samples were recorded on a Micromeritics ASAP2050 system. Sample temperature was controlled by a circulating oil bath with heating and chilling functions. The samples were degassed at 573 K for 10 h at a 1 K/min heating rate to down to 1.2 Pa before measurements. Adsorption isotherms for CO2 and CH4 on activated zeolites were measured. The adsorption was carried out using two different equilibrium interval times, viz., 120 and 25 s, to explore the intrusion of adsorption kinetics on equilibrium measurements. In addition to these isotherm measurements, kinetics measurements were conducted by adsorbing CO2 at 303 K and at stepped pressure increments, from 0.1 to 1 bar on the Micromeritics ASAP2010. For each pressure increment, the ROA software on ASAP2010 reports the volume adsorbed with time ranging from 1 s to 1000 s.
25, TEA removal of the TEA unit cell formulas are listed in Table 1. As expected, the Li+/Na+ ratio increases with the increase in the degree of ion exchange, while the Si/Al ratio remains almost constant. We can confidently conclude from these measurements (XRD, SEM, and ICP-MS) that ion exchange was successful and that the crystal structure of the original zeolite was preserved.

3. RESULTS AND DISCUSSION

3.1. Characterization. The crystallinity of as-made NaTEA-ZSM-25, Na-ZSM-25, and LZZs was confirmed by powder X-ray diffraction (XRD). The XRD pattern (Figure 1a) of the as-made NaTEA-ZSM-25 sample is in agreement with reported patterns (Figure 1a).39 The XRD pattern of Na-ZSM-25 is different to that of the as-made sample because of the removal of the TEA-Br template. In the as-made NaTEA-ZSM-25, TEA-Br fills up the pau and t-plg cages;31 after the removal of TEA-Br, these cages shrink, resulting in the right-shift of the corresponding diffraction peaks. The cage shrinkage is ascribed to the flexibility of the zeolite framework that is commonly observed in the RHO zeolite family.30,40 The XRD patterns of the LZZs with three different Li+/Na+ ratios are presented in Figure 1b; we can see that the XRD patterns of LZZs are almost identical to that of Na-ZSM-25. The SEM images of Na-ZSM-25 (Figure S1a,b) and Li(0.13)-ZSM-25 (Figure S1c,d) show almost identical spherical-looking morphology with a diameter ca. 0.8 μm. ICP-MS analysis was conducted to determine the composition of Na-ZSM-25 and LZZs, and their unit cell formulas are listed in Table 1. As expected, the Li+/Na+ ratio increases with the increase in the degree of ion exchange, while the Si/Al ratio remains almost constant. We can confidently conclude from these measurements (XRD, SEM, and ICP-MS) that ion exchange was successful and that the crystal structure of the original zeolite was preserved.

Table 1. ICP Elemental Analysis of ZSM-25-Based Zeolites

<table>
<thead>
<tr>
<th>sample</th>
<th>Li+ exchange ratio</th>
<th>Si/Al atom</th>
<th>unit cell formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-ZSM-25</td>
<td>0</td>
<td>3.06</td>
<td>Na_{270}[H_{4}Al_{135}Si_{1085}O_{2880}]</td>
</tr>
<tr>
<td>Li(0.063)-ZSM-25</td>
<td>0.063</td>
<td>3.06</td>
<td>Li_{3}Na_{225}[H_{116}Al_{354}Si_{1084}O_{2880}]</td>
</tr>
<tr>
<td>Li(0.10)-ZSM-25</td>
<td>0.10</td>
<td>3.05</td>
<td>Li_{3}Na_{199}[H_{134}Al_{346}Si_{1094}O_{2880}]</td>
</tr>
<tr>
<td>Li(0.13)-ZSM-25</td>
<td>0.13</td>
<td>3.15</td>
<td>Li_{2}Na_{176}[H_{143}Al_{354}Si_{1086}O_{2880}]</td>
</tr>
</tbody>
</table>

To gain insight into the high working capacity of Na-ZSM-25 and the type-II-like isotherm of CO2 upon CO2 adsorption at 303 K, an in situ synchrotron powder XRD experiment was performed. As shown in Figure 2, an apparent shift to a lower angle of all diffraction peaks can be observed as the CO2 pressure increases, indicating the gradual structural expansion of ZSM-25 while adsorbing CO2. This structural expansion can be interpreted as the effect that the building unit contains two interpenetrated cubic scaffolds, and these interconnected parts expand as the CO2 loading increases, resulting in larger lattices.32 Hence, the flexible structure enables Na-ZSM-25 to adsorb more CO2 molecules continuously, and the working capacity is accordingly higher than that of nonflexible zeolites such as CHA,31 LTA,33 and FAU.42

3.2. Adsorption Isotherms. The adsorption/desorption isotherms of Na-ZSM-25 and LZZs are shown in Figures 3, S2, and S3. All of the isotherms deviate from type I and exhibit strong desorption hysteresis. The strong desorption hysteresis can be attributed to the slow intracrystalline diffusion as a result of the entrapment of CO2 inside the cages during desorption—as a result, this means the desorption branch does
The CO₂ uptake of Li(0.13)-ZSM-25 compared to Na-ZSM-25 is shown in Figure S3. The CO₂ uptakes for all of the samples at an EIT of 25 s for Na-ZSM-25 as well as the LZZs were also recorded and are included in the Supporting Information as kinetics measurements reported later. Methane uptakes of Na-ZSM-25 and Li (0.13)-ZSM-25 are below the detection limit even at a long EIT of 120 s at 303 or 353 K with our equipment (Figure S4). The molecular sieving effect is one possible cause of the low CH₄ uptake, because the pore aperture sizes of the ZSM-25-based zeolites are smaller than the kinetic diameter of CH₄.

In addition to the high CO₂/CH₄ selectivity, another distinguishing property of ZSM-25 is that the adsorption isotherms deviate from typical type I. Unlike the ordinary zeolites such as CHA⁴⁶ and LTA,³⁵ the isotherms of Na-ZSM-25 have a type-II-like shape (Figure 3) with distinct inflection regions. For example, at 303 K, the CO₂ uptake of Li-CHA reached a high value of 5.5 mmol/g at 40 kPa, and a further increase of gas pressure barely increased the CO₂ uptake in this case.⁴⁷ In contrast, CO₂ adsorption increases continuously with pressure in all the cases of ZSM-25-based zeolites. This abnormal inflection of isotherms as described above can be explained by the flexible structure. Such “breathing behavior” has been observed in other flexible zeolites such as the Rho zeolite⁴⁸ and is attributed to a CO₂-induced framework structural distortion.

The adsorption properties including the working capacity (as defined earlier) of the selected ZSM-25 derived zeolite samples as well as other types of zeolites in the literature are shown in Table 2. Typically, natural gas is available at a high pressure of 100 bar with up to 10% of CO₂, and the partial pressure of CO₂ is therefore around 10 bar. Hence, it is relevant to evaluate the performance of the adsorbent in PSA at a CO₂ partial pressure of around 10 bar. Our gas adsorption apparatus measures up to 10 bar, and we restricted operation to just less than this upper limit (9.5 bar). As seen, under similar conditions, compared with other types of zeolites,
ZSM-25 derived zeolites are higher in both a working capacity of 2.4–2.5 mmol/g and CO2/CH4 selectivity.

3.3. Isosteric Heat of Adsorption. The isosteric heat of adsorption is defined as the heat released during the adsorption process at a certain coverage, which can be used to reflect the adsorption affinities of the guest molecules to the adsorbent. Specifically, the isosteric heat of adsorption is calculated from equilibrium capacity as a function of temperature using the Clapeyron equation (eq 1)

$$\frac{\Delta Q_{st}}{RT^2} = \left[ \frac{\partial \ln P}{\partial T} \right]_q$$

where $P$ is the pressure (kPa) for certain loading $q$, $T$ is the system temperature (K), $R$ is the gas constant (JK$^{-1}$ mol$^{-1}$), $q$ is the adsorption amount (mol/kg), and $Q_{st}$ is the isosteric heat of adsorption. At a certain coverage and assuming no dependence of isosteric heat on temperature, eq 1 can be integrated and becomes a linear equation of $\ln P$ versus $\frac{1}{T}$ as shown in eq 2

$$\ln P = \frac{\Delta Q_{st}}{RT} + C$$

where $C$ is an integration constant. We determined the heats of adsorption numerically, since the isotherms cannot be well fitted with the Langmuir equation or Toth equations because of the non-type-I appearance. In this study, the isotherms at 323, 328, and 333 K are first mathematically spline fitted and then used to calculate $\Delta Q_{st}$. $\Delta Q_{st}$ is obtained from the slopes of a regression equations of $\ln P$ versus $\frac{1}{T}$ at a given gas uptake.

The dependence of the isosteric heat of CO2 on surface excess and cation coverage (as calculated by $n$(CO2)/$n$(M$^+$)) are shown in Figure 4a,b, respectively. For both Li(0.13)-ZSM-25 and Na-ZSM-25, $Q_{st}$ decreases as the CO2 uptake increases because of the reduction of high energy adsorption sites, from 33 kJ/mol at a CO2 loading of 0.4 mmol/g to 17 kJ/mol at a CO2 loading of 0.9 mmol/g for the Li(0.13)-ZSM-25 sample and 40 to 28 kJ/mol for the same loading range on Na-ZSM-25, respectively. The slightly lower isosteric heat of CO2 on Li(0.13)-ZSM-25 compared to Na-ZSM-25 can be ascribed to the slightly lower cation density of the former sample as a result of a higher Si/Al ratio in this sample. Although Li$^+$ has stronger electrostatic field and higher "polarization force", the number of Li$^+$ cations is limited in Li(0.13)-ZSM-25. CO2–Li complexes will form preferentially at lower coverages (lower than 0.298 mmol/g). Thus, Li$^+$ will not affect the heat of adsorption for a coverage higher than 0.298 mmol/g, and the Si/Al ratio is the dominating factor in determining the heat of adsorption. This more than compensates for the presence of Li instead of Na at the higher energy sites as defined in Table 1.

3.4. Adsorption Kinetics. Rate of adsorption measurements were made for Na-ZSM-25, Li(0.063)-ZSM-25, Li(0.10)-ZSM-25, and Li(0.13)-ZSM-25 at selected pressures (7.23 and 12.07 kPa). Data smoothing was first done by spline methods as shown in Figure 5. At both pressures, the time for the zeolites to reach equilibrium decreases with the increase in Li$^+$ exchange ratio. For example, at 7.23 kPa, the equilibrium times for Na-ZSM-25, Li(0.063)-ZSM-25, Li(0.10)-ZSM-25, and Li(0.13)-ZSM-25 are >1000, 827, 728, and 553 s, respectively. The fractional uptake $f(t) = (m_t - m_0)/(m_{\infty} - m_0)$, also called the fractional approach to equilibrium, exhibits a slow increase with time for Na-ZSM-25. The zeolite with the higher Li$^+$/Na$^+$ ratio has a much faster increase of the fractional uptake. These results suggest that the adsorption rate...
of ZSM-25 zeolites can be improved by incorporating Li⁺, and the kinetics can be regulated by the Li⁺ exchange ratio. To quantitatively estimate the kinetics of the ZSM-25 derived zeolites, a single microporous zeolite particle is considered. The solution for the uptake curve can be described by eq 3

$$\frac{m_t - m_0}{m_\infty - m_0} = 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{n^2 \pi^2 D t}{r_c^2}\right)$$

where \(m_\infty\) is the equilibrium uptake of a zeolite at a certain pressure \(P\) and temperature \(T\), \(m_t\) is the average non-equilibrium adsorbed amount on a zeolite at any time \(t\), \(m_0\) is the initial equilibrium adsorbed amount on the adsorbent for each gas dose. The initial time during the adsorption is used to evaluate the kinetics. In the case of \(f(t) = (m_t - m_0)/(m_\infty - m_0) < 0.3\), the uptake curve is given in the form of eq 4

$$\frac{m_t - m_0}{m_\infty - m_0} \approx \frac{6}{\sqrt{\pi}} \left(\frac{D t}{r_c^2}\right)^{1/2}$$

According to eq 4, the adsorption rate \(D_t/r_c^2\) can be acquired by the slope of a linear regression equation of data points of \(\frac{m_t - m_0}{m_\infty - m_0}\) versus \(t\).

The dependences of \(\frac{m_t - m_0}{m_\infty - m_0}\) on \(t\) are plotted in Figure 6. At both pressures, the values of the slopes for all of the samples follow the order of Na-ZSM-25 < Li(0.063)-ZSM-25 < Li(0.10)-ZSM-25 < Li(0.13)-ZSM-25, the same as the adsorption rate parameter \(D_t/r_c^2\). According to eq 4, \((D_t/r_c^2)\) was calculated and listed in Table 3. As seen, the adsorption rate of CO₂ gradually increases as the Li⁺ exchange ratio increases at both 7.23 and 12.07 kPa, indicating that the incorporation of Li⁺ increases the rate of CO₂ adsorption for the ZSM-25 zeolite. The higher adsorption rate of LZZs can be attributed to a (1) higher free volume fraction, (2) higher CO₂ affinity with the same valence, the electrostatic interaction between CO₂ and a smaller cation is stronger. LZZs exhibit a higher affinity for CO₂ molecules, which also enhances the CO₂ diffusion. Furthermore, higher CO₂ adsorption loading of LZZs contributes to a higher adsorbed CO₂ intracrystalline diffusion increases. As a result of the above-mentioned effects, the adsorption rate of CO₂ on the Li(0.13)-ZSM-25 zeolite is 9.86 and 6.74 times faster than that of pristine Na-ZSM-25 at 7.23 and 12.07 kPa, respectively. Compared to 13X at similar pressure and temperature, the adsorption rate of 13X at 308 K and 11.95 kPa is 8.5 \times 10^{-3}

Table 3. Adsorption Kinetics of CO₂ on Na-ZSM-25, Li(0.063)-ZSM-25, Li(0.10)-ZSM-25, and Li(0.13)-ZSM-25 at Different Pressures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Na-ZSM-25</th>
<th>Li(0.063)-ZSM-25</th>
<th>Li(0.10)-ZSM-25</th>
<th>Li(0.13)-ZSM-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td>7.23 kPa</td>
<td>0.43 × 10^{-4} ± 8 × 10^{-5}</td>
<td>1.65 × 10^{-4} ± 6 × 10^{-7}</td>
<td>2.01 × 10^{-4} ± 6 × 10^{-7}</td>
<td>4.24 × 10^{-4} ± 1 × 10^{-7}</td>
</tr>
<tr>
<td>303 K</td>
<td>12.07 kPa</td>
<td>1.20 × 10^{-4} ± 2 × 10^{-7}</td>
<td>2.99 × 10^{-4} ± 6 × 10^{-7}</td>
<td>3.70 × 10^{-4} ± 1 × 10^{-7}</td>
<td>8.09 × 10^{-4} ± 7 × 10^{-7}</td>
</tr>
</tbody>
</table>

Figure 6. Linear regression plots for adsorption kinetic determination at (a) 7.23 kPa and (b) 12.07 kPa for indicated samples.

Figure 7. Breakthrough profiles of Li(0.13)-ZSM-25 recorded in 50% CO₂/50% CH₄ v/v mixed gas (a,b) at total pressures of 2 bar (a) and 7 bar (b) and pure CH₄ at 3.5 bar (c). Total gas flow rate: 100 sccm; temperature: 303 K.
Table 4. Adsorbed Amounts and Selectivity Derived from Breakthrough Curves of 50% CO₂/50% CH₄ v/v Mixed Gas at 303 K and Different Pressures on Li(0.13)-ZSM-25 and Comparison with 13X in reference 54

<table>
<thead>
<tr>
<th>total pressure (bar)</th>
<th>total CO₂ uptake (mmol/g)</th>
<th>initial CH₄ uptake (mmol/g)</th>
<th>overall CH₄ uptake (mmol/g)</th>
<th>CO₂/CH₄ selectivity</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.94</td>
<td>0.19</td>
<td>0.029</td>
<td>66.9</td>
<td>this work</td>
</tr>
<tr>
<td>7</td>
<td>3.16</td>
<td>0.61</td>
<td>0.25</td>
<td>12.6</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>4.3</td>
<td>N/A</td>
<td>0.38</td>
<td>11.3</td>
<td>54</td>
</tr>
</tbody>
</table>

“This CO₂ uptake is slightly lower than that measured in the isotherm probably as a result of the difference in instrument and the incomplete activation of a small portion of the adsorbent. The uptake before the breakthrough of CO₂ was the measurement was conducted at 313 K.

It is worth noting that before the roll-up, the uptake of CH₄ was 0.61 mmol/g at a partial pressure of 3.5 bar in the case of binary gas (Figure 7b). In this particular case, however, only 0.25 mmol/g of CH₄ was adsorbed for pure CH₄ measurements at the same partial pressure (3.5 bar, Figure 7c). The difference between these two cases is ascribed to the CO₂-induced distortion of Li(0.13)-ZSM-25, that is, the expanded lattice results in more adsorption of CH₄.

Despite the distortion, Li(0.13)-ZSM-25 still shows higher CO₂/CH₄ adsorptive selectivity, because the initially adsorbed CH₄ is eluted later. The CO₂ uptakes obtained from breakthrough experiments (Table 4) are 1.94 and 3.13 mmol/g at pressures of 2 and 7 bar, respectively. The corresponding overall CH₄ uptakes are 0.029 and 0.25 mmol/g; accordingly, the CO₂/CH₄ adsorptive selectivity of Li(0.13)-ZSM-25 is 66.9 and 12.6, respectively. Under a partial pressure (1 bar) of CO₂/CH₄ (50%/50% v/v), the breakthrough experiment of 13X, a popular CO₂/CH₄ separation zeolite, shows a CO₂ uptake of 4.3 mmol/g with a CO₂/CH₄ selectivity of 11.3. The CO₂/CH₄ selectivity (11.3) of 13X is significantly lower than that of our Li(0.13)-ZSM-25 (66.9). Thus far, we concluded from the breakthrough experiment that the pressure-induced structural distortion does lead to the decay of the CO₂/CH₄ separation performance of Li(0.13)-ZSM-25 in dynamic adsorption, which is a key criterion in industrial application.

4. CONCLUSIONS

In this study, Li⁺/ZSM-25 zeolites with different Li⁺ exchange ratios were prepared by incorporating Li⁺ into Na-ZSM-25. Unlike most zeolites, the Li⁺/ZSM-25 zeolites exhibit a type-II-like CO₂ adsorption isotherm, which is attributed to CO₂-induced framework expansion.

The incorporation of Li⁺ increases the CO₂ uptakes and adsorption rate. When compared with Na-ZSM-25, the CO₂ adsorption capacity increases by 6.1% at 303 K and 9.5 bar and shows 9.8 times the adsorption rate of Na-ZSM-25 at low pressures. Meanwhile, the very high CO₂/CH₄ ideal selectivity is successfully inherited from Na-ZSM-25. In binary-gas adsorption, for the first time, we demonstrate that the Li⁺/ZSM-25 zeolites present high CO₂ uptake and CO₂/CH₄ adsorptive selectivity because of the competitive adsorption between CO₂ and CH₄. More importantly, we also employed in situ XRD studies to confirm that the high working capacity and the slight CH₄ admission in binary-gas adsorption of the ZSM-25-based zeolites originated from the CO₂-induced framework expansion and flexibility.

In summary, Li⁺/ZSM-25 zeolites exhibit high CO₂ working capacity, impressive CO₂/CH₄ selectivity, and high adsorption kinetics. It is a promising adsorbent candidate for natural gas purification and biogas upgrading.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b04152.

SEM images of Li⁺/ZSM-25 zeolite particles, additional CO₂ adsorption isotherms for samples, additional CO₂ adsorption isotherms at different interval times, and CH₄ adsorption isotherms (PDF)

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Li⁺/ZSM-25 Zeolite as a CO2 Capture Adsorbent with High Selectivity and Adsorption Kinetics Showing CO2-induced Framework Expansion
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Fig.S1 SEM images of Na-ZSM-25 (a, b) and Li (0.13)-ZSM-25 (c, d) crystals.
Fig.S2 CO$_2$ adsorption isotherms at 303K for (a) Li(0.063)-ZSM-25, and (b) Li(0.10)-ZSM-25. Closed symbol: adsorption; open symbol: desorption.

Fig.S3 Isotherms for CO$_2$ at 303K, 333K and 353K and equilibrium interval time of 25 second. (a) Na-ZSM-25 (b) Li(0.063)-ZSM-25, (c) Li(0.10)-ZSM-25 and (d) Li(0.13)-ZSM-25. Closed symbol: adsorption; open symbol: desorption.
Fig. S4 CH₄ adsorption isotherms at 303K of (a) Na-ZSM-25, (b) Li(0.13)-ZSM-25 and (c) blank tube. Closed symbol: adsorption; open symbol: desorption.
Chapter 3

Enhancing plasticization-resistance of mixed-matrix membranes with exceptionally high CO₂/CH₄ selectivity through incorporating ZSM-25 zeolite

Chapter Perspectives

Zeolites are attractive for being embedded into polymers yielding mixed-matrix membranes (MMMs). The combination potentially offers the inherent advantages of both the polymer matrix and the filler materials. In most of the MMMs for CO₂/N₂ or CO₂/CH₄ separation, the blending of porous filler improves the permeability at the expense of reducing the selectivity. This is because the ordinary porous fillers are almost non-selective CO₂/N₂ or CO₂/CH₄ gas pairs. Hence, partially Li⁺ exchanged Na-ZSM-25 zeolites (LNZ25) were incorporated into the commercial polymer Matrimid® 5218 to yield a mixed-matrix membrane (MMM). ZSM-25 has exclusive admission of CO₂ and complete exclusion of CH₄ and is therefore an ideal candidate for MMMs. The separation performance of the fabricated MMMs with 0–15 wt% filler loadings are determined by both single and binary gas permeability. Single gas permeation tests on the MMM with 5 wt% filler loading show exceptionally high CO₂/CH₄ selectivity (169 at 5 bar) and demonstrate an >400% increase of CO₂/CH₄ selectivity as the feed pressure increases from 2 bar to 5 bar. Binary gas measurements indicate the CO₂/CH₄ selectivity of the MMM is constant with an increase of pressure. This result reveals the feasibility of using the LNZ25 as an effective filler for enhancing the CO₂/CH₄ separation performance in MMM. This performance is especially encouraging for natural gas purification where the membrane selectivity at high pressure is more important.
Enhancing plasticization-resistance of mixed-matrix membranes with exceptionally high CO$_2$/CH$_4$ selectivity through incorporating ZSM-25 zeolite

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**A R T I C L E   I N F O**

**Keywords:**
- ZSM-25
- CO$_2$ capture
- Natural gas purification
- Plasticization-resistance membrane
- Enhance selectivity

**A B S T R A C T**

Partially Li$^+$ exchanged Na-ZSM-25 zeolites (LNZ25) were incorporated into the commercial polymer Matrimid® 5218 to yield a mixed-matrix membrane (MMM) via solvent-casting. ZSM-25 has exclusive admission of CO$_2$ and complete exclusion of CH$_4$ and is therefore an ideal candidate for MMMs. The fillers were evenly dispersed in the polymer matrix with good adhesion. The separation performance of the fabricated MMMs with 0–15 wt% filler loadings are determined by both single and binary gas permeability using a constant pressure variable volume apparatus. Single gas permeation tests on the MMM with 5 wt% filler loading show exceptionally high CO$_2$/CH$_4$ selectivity (169 at 5 bar) and a plasticization-resistance-like behaviour, i.e. the selectivity increases as the feed pressure increases. Binary gas measurements indicate the CO$_2$/CH$_4$ selectivity of the MMM is constant with an increase of pressure while the selectivity of the pristine Matrimid decreases with increased pressure. The exclusive admission of CO$_2$ and the rejection of CH$_4$ of the LNZ25 contributes to enhanced permeability and plasticization-resistance-like performance of the MMM.

**1. Introduction**

Polymer-based CO$_2$ mitigation technology is a candidate solution to post-combustion carbon capture (CO$_2$/N$_2$) and natural gas upgrade (CO$_2$/CH$_4$). This is due to their low expense, good processability, high mechanical strength and good selectivity [1–6]. Permeability and selectivity are the two key parameters to evaluate the performance of membrane materials [7,8]. The permeability and selectivity depend on the intrinsic properties of the membrane material. There is a trade-off between them which results in a well-known “upper bound” limitation on a selectivity vs. permeability diagram, i.e. the materials with high permeability are usually low in selectivity, and vice versa [9].

The permeability of polymer materials can be improved by incorporating inorganic/organic fillers into the polymer matrix to produce mixed-matrix membranes (MMMs) [10–12]. Inorganic porous particles (zeolites and activated carbon etc.) and metal-organic frameworks (MOF) have been intensively studied as the filler materials in dense MMM systems [13]. This configuration potentially offers the inherent advantages of both the polymer matrix and the filler materials, i.e. achieving high permeability from filler materials, maintaining selectivity, and improving processability and mechanical strength from the polymer matrix [12]. Among those fillers, zeolites are attractive owing to their high thermal- and chemical stability. Specifically, various Matrimid® based MMMs have been fabricated by embedding different types of microporous and mesoporous zeolites. MMM with 15 wt% NaY as a filler has a two-fold CO$_2$ permeability and 20% higher CO$_2$/CH$_4$ selectivity compared with pristine Matrimid [14]. The incorporation of ZSM-5 into the Matrimid/PEG composite also enhanced the CO$_2$ permeability and CO$_2$/CH$_4$ selectivity of the optimized MMM by 50% and 72%, respectively. However, these zeolites do not show size exclusion for either CO$_2$ or CH$_4$. The pore aperture size of these fillers (7.4 Å for NaY and 5.5 Å for ZSM-5) are larger than the kinetic diameters of CO$_2$ (3.3 Å) and CH$_4$ (3.8 Å) and therefore both gases can permeate the filler material. The enhancement of the CO$_2$/CH$_4$ selectivity in these cases can probably be ascribed to the rigidification of the polymer matrix [13]. Other than those special cases, in most of the MMMs for CO$_2$/N$_2$ or CO$_2$/CH$_4$ separation, the blending of porous filler improves the permeability at the expense of reducing the selectivity [15–19]. This is because the ordinary porous fillers are almost non-selective to CO$_2$/N$_2$ or CO$_2$/CH$_4$ gas pairs. To test the concept of using molecular sieving zeolites as fillers, the small-pore zeolite SAPO-34...
(pore size 3.8 Å)/Matrimid MMM was also investigated [20]. However, the resultant MMMs did not exhibit the molecular sieving effect from the zeolite due to the defects and voids at the filler/matrix interface. Although the incorporation of zeolite can potentially improve CO₂ permeability and/or CO₂/CH₄ selectivity, the performance of the Matrimid™ 5218 based MMMs are still located far below the Robeson upper bond.

ZSM-25 is a recently resolved zeolite belonging to the RHO family with a small pore aperture size of ca. 3.6 Å, which lies between the kinetic diameters of CO₂ and CH₄ [21–23]. This results in one of the most significant properties of the ZSM-25, i.e. the exclusive admission of CO₂ in CO₂/CH₄ mixed gas [21–24]. On this basis, the incorporation of ZSM-25 particles into the polymeric matrix should enhance the CO₂/CH₄ selectivity. On the other hand, according to our previous study the partial lithium exchange Na-ZSM-25 (LNZ-25) have faster CO₂ adsorption kinetics with similar CO₂/CH₄ adsorptive selectivity to that of pristine Na-ZSM-25. Moreover, the highly selective admission of CO₂ over CH₄ of the LNZ-25 has also been confirmed by the dynamic adsorption (breakthrough) experiment using CO₂/CH₄ mixed gas [24]. Both of those are key criteria for MMM fillers.

Inspired by this concept, we incorporated LNZ-25 based zeolite nanoparticles into a commercially available Matrimid matrix to yield mixed matrix membranes (MMMs). The study of the CO₂/CH₄ and CO₂/ N₂ separation performance of the resultant MMMs indicates that the incorporation of ZSM-25 can effectively enhance the selectivity of CO₂ over CH₄ with simultaneous improvement of CO₂ permeability. Moreover, the optimized MMM demonstrates an > 400% increase of CO₂/CH₄ selectivity as the feed pressure increases from 2 bar to 5 bar. In contrast, the CO₂/CH₄ selectivity of the pristine Matrimid in this pressure range is similar. This performance is especially encouraging for natural gas purification where the membrane selectivity at high-pressure is more important. This is because several side effects such as plasticization and concentration polarization can dramatically reduce the selectivity compared to that measured at lower feed pressure (< 3 bar) [15,25–27]. This result reveals the feasibility of using the LNZ25 as an effective filler for enhancing the CO₂/CH₄ separation performance in MMMs.

2. Experimental

**Materials:** Aluminium hydroxide (Al(OH)₃, reagent grade); tetraethylammonium bromide (TEA bromide, 98%); Lithium chloride (LiCl); Ludox AS-40 colloidal silica were purchased from Sigma-Aldrich and used as received. Matrimid™ 5218 was purchased from Huntsman Advanced Materials America. Chloroform was purchased from Chem-Supply Australia and used as received.

**Preparation of Li/Na-ZSM-25 (LNZ25):** Li/Na-ZSM-25 was prepared according to our previous report [24]. Specifically, 1.92 g (24.6 mmol) of Al(OH)₃ was dissolved in 3.04 g of 50 wt% sodium hydroxide solution in 60.73 g of distilled water at room temperature, resulting in a translucent solution. Then 10.80 g of Ludox AS-40 colloidal silica and 11.15 g (53 mmol) of TEA bromide were added into the translucent solution. The gel was stirred at room temperature for 24 h. Afterward, the gel was transferred to a Teflon-lined autoclave and heated under rotation for 7 days in an oven at 408 K. The autoclave was slowly cooled down in the air to room temperature. The as-made TEA/Na-ZSM-25 was filtered and dried overnight at 333 K followed by calcination at 773 K in air for 6 h to remove the template, followed by collection of the pristine Na-ZSM-25. Li/Na-ZSM-25 zeolite samples were prepared via ion-exchange of the Na⁺ of Na-ZSM-25 in a Li⁺ solution. In a typical procedure, 1 g Na-ZSM-25 zeolite was ultrasonically dispersed in 2 mL of 1 mol/L LiCl solution for half a minute and placed at room temperature for 1 h. Then the zeolite was washed with deionized water five times and dried in air at 333 K for 10 h. This ion-exchange procedure was repeated three times to obtain LNZ25.

**Fabrication of mixed-matrix membrane (MMM):** The dense membranes were cast by a widely reported solution casting process [18,28–30]. Briefly, the commercialized polymer matrix (Matrimid™ 5218) was dissolved in chloroform with a concentration of 30 mg mL⁻¹. Then the desired amount of LNZ25 was mixed with 5 mL of Matrimid solution by sonication and stirring at room temperature for 3 h before being used for casting. The mixture was poured into a glass petri dish, covered by another glass petri dish to prevent contamination, and the evaporation rate controlled. The petri dish was put on a tripod platform and a level was used to make it flat. The solution was left in the fume hood for 24 h at room temperature to yield a free-standing membrane. The membrane was carefully peeled off and dried in a vacuum at 35 °C for 48 h. The dried membrane thickness varied from 50 to 60 μm. Depending on the filler loading of 0, 5, 8, 10 and 15 wt%, the resultant MMMs are denoted as M – 0, M – 5, M – 8, M – 10 and M – 15, respectively.

**Characterisation:** The gas adsorption isotherms were recorded on an ASAP 2050 Xstended Pressure Sorption Analyzer, Micromeritics at 308 K (35 °C). Scanning electron microscope (SEM) images were acquired using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. Powder X-ray diffraction (PXRD) patterns of the sample were recorded on a Bruker D8 Advance instrument with Cu Kα radiation (40 kV, 40 mA) and a nickel filter, and the samples were exposed at a scanning rate of 2θ = 0.020°·s⁻¹ in the range of 3–40°. The compositions of filler Li/Na-ZSM-25 and its Si/Al ratio were analysed by inductively coupled plasma-mass spectroscopy (ICP-MS).

**Measurements of gas separation performance of MMMs:** The single gas separation performance was measured using a constant pressure variable volume (CPVV) apparatus. The gas permeation coefficient was determined from the slope of the time–pressure curve at steady state. The mixed gas separation performance was measured using a CPVV apparatus with helium as the sweep gas on the permeate side. The gas flow rates were determined by a digital flowmeter (ADM2000, Agilent Technologies) and a gas chromatography (CP-3800, Varian). The permeate gas was measured at the gas separation performance.

3. Results and discussion

The SEM image of LNZ25 is displayed in Fig. 1a in which we can see the LNZ25 particles show a spherical morphology with a diameter range of 400–600 nm. The crystallinity of the LNZ25 was confirmed by the PXRD spectra as shown in Fig. 1b. The PXRD diffraction peaks are almost identical to that of the Na-ZSM-25, indicating the high crystallinity of the LNZ25 was preserved after ion-exchange [21,23]. The Si/Al ratio is 3.15 and its unit cell formula is Li₂Na₂Na₂H₄Al₄Si₄O₁₁(000θ), as confirmed by ICP results. The CO₂ and N₂ isotherms of the LNZ25 were recorded at 308 K and presented in Fig. 1c. At the pressure of 950 kPa, the CO₂ uptake of the LNZ25 reaches 4.1 mmol g⁻¹ while the gas uptake for N₂ is 0.53 mmol g⁻¹. More significantly, the CH₄ adsorption under the same condition is undetectable, suggesting the extremely high CO₂/CH₄ adsorptive selectivity is due to a molecular sieving effect or a molecular trapdoor effect [24]. The CO₂ adsorption under the same condition is detectable, suggesting the extremely high CO₂/CH₄ adsorptive selectivity is due to a molecular sieving effect or a molecular trapdoor effect [24]. All the isotherms exhibit high desorption hysteresis, which results from the slow intra-crystalline diffusion due to the entrapment of CO₂ inside the cages during desorption. In addition, the CO₂-induced framework expansion was also confirmed by the in-situ XRD in our previous reports [24].

The LNZ25 was then incorporated into the Matrimid to investigate its potential as the MMM filler. The commercially available polymer matrix Matrimid is adopted because it is one of the most favourable polymer materials in carbon capture technology [29,31–38]. The typical SEM images of the cross-sectional view of the membranes are presented in Fig. 2. The LNZ25 particles are evenly distributed in the Matrimid matrix with good attachment to the polymer matrix at a filler loading of 5 wt% (Fig. 2b and c), but further increase of the filler
loading results in an apparent aggregation and precipitation of the LNZ25 particles (Fig. 2d–f). The precipitation also causes the relatively significant variety of the gas separation performance (see Table 1). The tensile strengths of the MMMs are shown in Table 1, which shows a decreasing trend as the mass fraction of LNZ25 increases, as expected.

Single-gas permeation measurements were firstly carried out using a constant pressure variable volume (CPVV) apparatus with a CO$_2$, N$_2$ or CH$_4$ feed pressure of 3 bar at 308 K, and typical results are shown in Table 1 and Fig. 3. As expected, the CO$_2$ permeability increases as the LNZ25 loading increases, i.e. from 10.2 Barrer for pristine Matrimid (M–0) to 14.4 Barrer for M–5 and 19.6 Barrer for M–8. However, the CO$_2$ permeabilities of M–10 and M–15 are close to M–8, which is ascribed to the aggregation of the filler particles [13]. The CO$_2$/CH$_4$ ideal selectivity of the membranes gradually decreases as the LNZ25 loading increases, which is from 45 for pristine Matrimid to 18 for M–10. A notably low CO$_2$/CH$_4$ ideal selectivity of 4.9 is observed for

Table 1

<table>
<thead>
<tr>
<th>Membrane items</th>
<th>Tension (MPa)$^a$</th>
<th>LNZ25 content (wt.%)</th>
<th>P$_{CO_2}$ (Barrer)</th>
<th>α$_{CO_2/CH_4}$</th>
<th>α$_{CO_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–0</td>
<td>110 ± 7</td>
<td>0</td>
<td>10.2 ± 0.1</td>
<td>45 ± 1</td>
<td>23 ± 1</td>
</tr>
<tr>
<td>M–5</td>
<td>78.2 ± 5.4</td>
<td>5</td>
<td>13.1 ± 1.4</td>
<td>38 ± 3</td>
<td>27 ± 2</td>
</tr>
<tr>
<td>M–8</td>
<td>66.2 ± 2.0</td>
<td>8</td>
<td>16.3 ± 2.8</td>
<td>22 ± 2</td>
<td>17</td>
</tr>
<tr>
<td>M–10</td>
<td>79.0 ± 3.4</td>
<td>10</td>
<td>17.2 ± 2.5</td>
<td>24 ± 6</td>
<td>15</td>
</tr>
<tr>
<td>M–15</td>
<td>56.6 ± 0.7</td>
<td>15</td>
<td>20.5 ± 2</td>
<td>4.9 ± 0.8</td>
<td>5.9 ± 1.0</td>
</tr>
</tbody>
</table>

$^a$ In general, the incorporation of porous particles can either reduce [36] or increase [39] the tensile strength of the MMM. The tensile strength results of the membranes in this work is ascribed to the balance of these two effects.
The trend can be observed referring to the CO2/N2 selectivity of M-0. The performance is close to the one tested at 5 bar (refer to Fig. 4a), as the feed pressure increases, the CO2/CH4 ideal selectivity of M-0 first increases from 27 (2 bar) to 45 (3 bar) and 48 (4 bar) then decreases to 38 (5 bar), and a similar trend can be observed referring to the CO2/N2 selectivity of M-0. The changing of the selectivity for M-0 is attributed to the combination effect of plasticization and physical aging [15]. By contrast, as presented in Fig. 4b, the CO2/CH4 ideal selectivity of M-5 dramatically increases from 33 to 169 as the feed pressure increases from 2 to 5 bar, while the CO2/N2 ideal selectivity of M-5 is close to that of M-0 at different feed pressures. A selectivity of 169 is the highest CO2/CH4 ideal selectivity among the recorded polymer-based (including composite) membranes measured in single gas apparatus (refer to Table 2) [40]. Additionally, if a fresh M-5 is firstly tested at 5 bar and then at 3 bar, the performance is close to the one tested firstly at 3 bar and then at 5 bar (refer to Fig. S1). Similar results can also be observed in M-8. Plotted in Fig. S2a, as the feeding pressure increases from 3 bar to 5 bar, the CO2/CH4 selectivity increases from 24 to 42 for M-8. The enhancement of selectivity for M-8 is not as significant as that of M-5. However, as the LNZ25 content increases to 10 w.t.%, the influence of the feeding pressure is negligible, which can be concluded from M-10.

According to our studies on ZSM-25 adsorption (Fig. 1c and d), owing to the molecular-sieving effect, the ZSM-25 has high CO2 uptake, a fair amount of N2 uptake, and negligible CH4 uptake. Ideally, when the feeding pressure is negligible, which can be concluded from M-10.

incorporated into the polymeric matrix, the LNZ25 allows CO2 and N2 to diffuse through the filler while the CH4 has to by-pass the LNZ25 particles. Therefore, the higher CO2/CH4 ideal selectivity of M-5 than that of M-0 is expected in this ideal case. However, defects and voids induced by the incorporation of LNZ25 is unavoidable in zeolite based MMMs and would result in the invalidation of the above-mentioned molecular-sieving effect [13]. This is the reason why the CO2/CH4 ideal selectivity of M-5 is lower than that of M-0 at the lower feed pressure of 3 bar.

As the feed pressure increases, the permeability of M-5 is lower than that of M-0 at 5 bar. As the pressure increase because the N2 similar to CO2, can be admitted into the LNZ25. This also excludes an alternative explanation for the enhancement of CO2/CH4 ideal selectivity, i.e. the rigidification of polymer matrix [13,41]. The CO2 permeability of M-5 at 4 and 5 bar is lower than that of M-0. This result is also explained by the relationship between zeolite, voids/defects, and polymer matrix. Specifically, the CO2 permeability of M-5 is higher than that of M-0 because the voids and defects in M-5 are too much. On the other hand, no significant change (and no significant difference to that of M-0) of the CO2/N2 ideal selectivity is observed as the feed pressure increase because the N2 similar to CO2, can be admitted into the LNZ25. The CO2 permeability of M-5 is slightly lower than that of M-0 in the case of 4 bar and 5 bar.

The single-gas separation performance of the M-0 and M-5 are plotted as a function of temperature in Fig. 5a and b, respectively. As expected, the CO2/CH4 and CO2/N2 ideal selectivities decrease as the temperature increases due to the enhanced mobility of the polymer chain [43]. Noticeably, at 301 K, the CO2/CH4 ideal selectivity of the M-5 is slightly lower than that of M-0 in the case of 4 bar and 5 bar.

The single-gas separation performance of the M-0 and M-5 were further investigated using 35% CO2/65% CH4 (v./v.) mixed gas with
previous studies, the adsorption of CO2 can cause the expansion of single-gas. This result is assigned to two effects. Firstly, according to our previous studies, the adsorption of CO2 can cause the expansion of the LNZ25 aperture. The plasticization effect has been widely observed in Matrimid based membranes which usually causes the decrease of CO2/CH4 selectivity as the CO2 partial pressure and/or the CO2 exposure time increases [24]. In addition, zeolites usually exhibit low CO2/CH4 selectivity in mixed gas with low CO2 mole fraction (e.g. 0.35) due to the correlation effects in diffusion [59–61]. In this regard, the CO2/CH4 selectivity enhancement from LNZ25 in the mixed gas measurement is not as significant as that in the single-gas measurement.

As shown in Fig. 7, the CO2/CH4 single gas property of the M−5 measured at 5 bar surpasses the “upper bound” defined by Robeson at 2008 in the selectivity versus permeability diagram [9]. The selectivity of M−5 at this condition is higher than most of the Matrimid® 5218 based MMMs in the literature (Table 2, grey points in Fig. 7). In addition, the plots representing mixed gas separation performance of M−5 are closer to the upper bound line than those of M−0, implying that the incorporation of the LNZ25 can effectively enhance the CO2/CH4 separation performance of the Matrimid in a practical sense. The stability of M−5 was also studied through performing the continuous separation of CO2/CH4 mixed gas for 7 days. As displayed in Fig. 8, both the permeability and selectivity of M−5 was virtually unchanged in this period, indicating very high stability of our M−5 membrane.

### Table 2

<table>
<thead>
<tr>
<th>Filler</th>
<th>CO2 Permeability (Barrer)</th>
<th>CO2/CH4 selectivity</th>
<th>Temperature (°C)</th>
<th>Pressure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-11</td>
<td>31</td>
<td>43</td>
<td>35</td>
<td>4 bar</td>
<td>[44]</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>67</td>
<td>30</td>
<td>30</td>
<td>Unknown</td>
<td>[45]</td>
</tr>
<tr>
<td>ZIF-12</td>
<td>15</td>
<td>58</td>
<td>35</td>
<td>4 bar</td>
<td>[46]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>15</td>
<td>56</td>
<td>35</td>
<td>1.47 bar</td>
<td>[47]</td>
</tr>
<tr>
<td>Ionic liquid [Emim][Tf2N]</td>
<td>21</td>
<td>43</td>
<td>35</td>
<td>4 bar</td>
<td>[48]</td>
</tr>
<tr>
<td>Carbon nanoparticles</td>
<td>10</td>
<td>37</td>
<td>35</td>
<td>203 kPa</td>
<td>[29]</td>
</tr>
<tr>
<td>zeolite Y</td>
<td>19</td>
<td>112</td>
<td>35</td>
<td>2 bar</td>
<td>[39]</td>
</tr>
<tr>
<td>MIL-101</td>
<td>8.0</td>
<td>44</td>
<td>35</td>
<td>10 bar</td>
<td>[49]</td>
</tr>
<tr>
<td>MOF-5</td>
<td>9.0</td>
<td>36</td>
<td>35</td>
<td>2.66</td>
<td>[50]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>29</td>
<td>25</td>
<td>35</td>
<td>4 bar</td>
<td>[51]</td>
</tr>
<tr>
<td>Sod-ZMOF</td>
<td>12</td>
<td>33</td>
<td>35</td>
<td>4 bar</td>
<td>[52]</td>
</tr>
<tr>
<td>Cu3BTC2</td>
<td>18</td>
<td>62</td>
<td>35</td>
<td>5 bar</td>
<td>[53]</td>
</tr>
<tr>
<td>polyimide</td>
<td>21</td>
<td>43</td>
<td>35</td>
<td>3 bar</td>
<td>[54]</td>
</tr>
<tr>
<td>amine-grafted zeolite</td>
<td>8.9</td>
<td>33</td>
<td>35</td>
<td>150 psi</td>
<td>[43]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>5.9</td>
<td>118</td>
<td>35</td>
<td>2000 Torr</td>
<td>[55]</td>
</tr>
<tr>
<td>MIL-53</td>
<td>51</td>
<td>47</td>
<td>35</td>
<td>2 bar</td>
<td>[56]</td>
</tr>
<tr>
<td>Li/Na-ZSM-25</td>
<td>12</td>
<td>169</td>
<td>35</td>
<td>5 bar</td>
<td>This work</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, a novel mixed-matrix membrane (MMM) consisting of Matrimid as the matrix and Li/Na-ZSM-25 as the filler is fabricated. Li/Na-ZSM-25 is chosen because it shows almost zero admission of CH4, while allowing considerable CO2 transport. The CO2/CH4 separation performance of the MMMs at 5 wt% filler loading, shows higher CO2/CH4 selectivity than that of the pristine Matrimid in both single- and mixed-gas separation. M−5 shows unusual plasticization-resistance behaviour with its CO2/CH4 selectivity increases as the feed pressure increases. The optimized membrane (M−5) achieved ideal CO2/CH4 selectivity of 169, which surpassed the latest CO2/CH4 upper bound. Moreover, the origin of the performance enhancement was analysed and discussed. The plasticization-resistance, coupled with the physical-ageing-free property suggest a potential application of the ZSM-25 based zeolites as the filler of the mixed-matrix membranes for CO2/CH4.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2019.03.073.

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Figure S1. The investigation of gas pressure effect on membrane performance. #A and #B are two fresh M-5 membrane.

Figure S2. The pressure effect on gas separation performance of M-8 (a) and M-10 (b). The selectivity of M-8 increases as the pressure increases, while the selectivity of M-10 slightly decreased at higher pressure of 5 bar.
Chapter 4

Removal of nitrogen impurity from methane via a new “trapdoor” K-ZSM-25 zeolite

Chapter Perspectives

The separation of N₂ from CH₄ remains a great challenge due to their similar physical and chemical properties. Only cryogenic technology, which is energy-intensive, has been commercially used for differentiating between N₂ and CH₄. All the solid adsorbents reported to date are CH₄-selective except for a recently discovered MOF.¹ Hence, an efficient N₂/CH₄ separation requires the material to show a preferential adsorption of the minor component N₂. Many small-pore zeolites show a temperature-regulated adsorption (trapdoor) phenomenon where door-keeping cations thermally oscillate and trigger gas admission at different temperatures. The gas molecules are therefore differentiated by each admission-triggered temperature. Inspired by this concept, here we design and report a new “trapdoor” zeolite K-ZSM-25 with Si/Al = 3.0, able to selectively capture N₂ over CH₄ by controlling the temperature. K-ZSM-25 shows high N₂/CH₄ selectivity of ~34 at 253K, as confirmed by single-component isotherms obtained from integrating the experimentally simulated breakthrough curves. The outstanding N₂/CH₄ selectivity is achieved by the N₂-triggered thermal deviation of K⁺ away from the diffusion pathway and the thermally-limited cation motion in the presence of CH₄. This new design potentially opens new approaches to address the challenging N₂/CH₄ separation in industry.
4.1 Introduction

In an effort to mitigate greenhouse gas emissions, the demand for CH₄-based energy sources is increasing steadily worldwide, because CH₄ has a smaller carbon footprint and higher heating value than other fossil fuels. The most significant source of methane is natural gas. In order to be used as a clean fuel and raw material in the chemical industry, the CH₄ content in methane-rich gases must be higher than 80%. However, raw natural gas contains carbon dioxide in the range of 5%-10% and N₂ in the range of 0.21%-5.0%. To minimise the hazards on pipeline and increase the energy density, the key point is to purify the natural gas by removing the incombustible gases (e.g. N₂ and CO₂). The physically-alike properties and similar kinetic diameter of N₂ and CH₄ pose a challenge for N₂/CH₄ separation. Currently, only cryogenic distillation has been commercially utilized for N₂ removal at large scale, which is economically undesirable. Therefore, developing an efficient adsorbent where N₂ is captured has been critically desirable for nitrogen-methane separation owing to the low operating and capital costs of pressure swing adsorption (PSA). A few porous materials have been reported for effective CH₄/N₂ separation, such as ZnZSM-5-pIM, ZnY-pIM, SAPO-34, MIL-101, MOF₃[N(Cu(Me-4py-trz-ia))] and a class of typical ZIFs (e.g. ZIF-8, ZIF-68, ZIF-69). At equilibrium, they all exhibited preferential adsorption of CH₄ rather than N₂ due to the higher polarizability and condensability of the former. With these sorbents, the major component (i.e. CH₄) has to be firstly adsorbed and collected as the extract product at low pressure via regeneration in a PSA cycle, and additional processes are required to pressurize CH₄ back to pipeline pressure, which significantly increases the process cost. Hence, ideally N₂ should be the preferentially adsorbed component. The kinetic separation of N₂ from CH₄ was reported based on the faster diffusion rates of N₂ in some traditional porous materials such as clinoptilolite zeolite, ETS-4 and CMS. For example, Sr-ETS-4 can achieve a kinetic N₂/CH₄ selectivity of 6.6 at 10 bar and 295K. However, they are unable to show appreciable separation towards N₂/CH₄ for industrial application due to insufficient N₂ capacity and methane recovery. Therefore, an efficient N₂/CH₄ separation critically requires a material that is N₂-selective at equilibrium, with high N₂ capacity and selectivity at around room temperature. Only the recent discovery of a MOF with accessible Cr (III) sites shows the preference of N₂ over CH₄ with the selectivity of 1.6 at 283K, which is still far from optimal.
Recently, we discovered an adsorptive separation mechanism, i.e. the “trapdoor” mechanism, in some small-pore zeolites.\textsuperscript{15–17} In this “trapdoor” mechanism, the zeolites have a significant feature of temperature-dependent adsorption where the extent of thermal oscillation of the extra-framework cation (EFC) increases with facilitating temperature, which accelerates the gas diffusion and reaches the maximum adsorption capacity at certain temperature (gate-opening temperature). The gate-opening temperature ($T_s$) varies in different gases, which promotes a strategy to separate the gas pair by controlling the temperature. All the pre-existing trapdoor zeolites, including CHA and RHO based ones, cannot differentiate between $N_2$ and $CH_4$ effectively because of the close threshold temperatures of $N_2$ and $CH_4$.\textsuperscript{17}

Very recently we discovered that the small-pore ZSM-25 zeolite has a low Si/Al ratio and shows potential of $N_2$/$CH_4$ separation.\textsuperscript{18} This discovery allowed us to design a new “trapdoor” zeolite with low Si/Al=3 for efficient $N_2$ over $CH_4$ separation based on ZSM-25 by incorporating the “door-keeping” cation. Specifically, potassium was introduced into ZSM-25 as EFC by ion-exchange treatment. In this zeolite, $N_2$ and $CH_4$ molecules are differentiated between two distinguishable gate-opening temperatures. Within this temperature range, $N_2$ molecules are free to diffuse through the pathway, while $CH_4$ molecules are hindered due to the blockage of $K^+$. K-ZSM-25 can achieve effective $N_2$/$CH_4$ separation at around ambient temperature with outstanding selectivity of over 30 in single gas adsorption and 5.7 in dynamic breakthrough simulation. This feature of K-ZSM-25, as a new “trapdoor” material, provides a rational strategy for the separation of gas pairs physically alike but with distinguishable gate-opening temperatures.

4.2 Experimental Section

4.2.1 Material Synthesis and Characterization

K-ZSM-25 was obtained after a series of ion-exchange treatments. Specifically, 1 g of Calcined-ZSM-25 was added into 2 mL of 1 mol/L KCl solution and the solution was shaken until the zeolite powder was well dissolved. The solution was placed for 2h at room temperature. Then the solution was filtered and the zeolites washed with deionized water 4 times followed by drying at 353K overnight. After repeating this procedure for 6 times, the $Na^+$ was fully replaced by $K^+$ yielding K-ZSM-25.
Scanning electron microscope (SEM) images were measured using a FEI Quanta 200 ESEM FEG. Powder X-ray diffraction (PXRD) spectrums of the samples were carried out on a Bruker D8 Advance instrument with Cu Kα radiation, operating at 40 kV and 40 mA with a scanning rate of 2θ=0.020°·s⁻¹. The composition of K-ZSM-25 and its Si/Al ratio were determined by inductively coupled plasma-mass spectroscopy (ICP-MS).

### 4.2.2 Gas Adsorption Method

The N₂ and CH₄ adsorption isotherms on K-ZSM-25 were all measured on a BELSORP-max gas adsorption analyzer. The constant temperature was maintained by BELCryo with a controlling range from 50 K to 473K. Before loading the sample into the Belsorp-max, the sample was degassed at 573 K for 10 h at a 1 K/min heating rate to down to 1.1 Pa before measurements to prevent influence by adsorbed water and gas in the air. After each measurement, the sample was reheated to 453K under vacuum to desorb the adsorbate completely. The adsorption rates of CH₄ and N₂ on K-ZSM-25 were measured on Micromeritics ASAP 2020 using a volumetric adsorption measurement system. In Rate of Adsorption (ROA) mode of the ASAP 2020, the pressure change was automatically recorded per dose of certain amount of gas and then converted to adsorbed gas amount per unit mass of the adsorbent. In each dose, the adsorption data was collected every 0.4s until 400s, then progressed towards equilibrium (a pressure change of less than 0.01% within 30 s).

### 4.2.3 Synchrotron Powder Diffraction

Pre-treatment: The samples (particle size ca. 1 μm) were loaded into 0.7 mm quartz capillary (ca. 20 mm long) after activation at 500 K under vacuum. Once the capillary was loaded on the analyser, a quick in situ activation was carried out (i.e. heating at 1K/min to 473 K and holding for 1 hour) to ensure the quality of the samples.

After the activation, the sample was scanned under vacuum, N₂ and CH₄, respectively, while decreasing the temperature from 473 K to 110 K at a ramp rate of 6 K/min. The data was collected at every 30 K. At each selected temperature, the temperature was held constant and stabilized for 10 min before collecting the diffraction data.
4.3 Results and discussion

**Figure.1** (a) PXRD pattern for K-ZSM-25 and calcined ZSM-25 with a Si/Al ratio of 3. (b) SEM image of K-ZSM-25 particles. (c) K-ZSM-25 adsorption isotherm of nitrogen at 77K, showing inaccessible pores at low temperatures.

The unit cell of the as-made ZSM-25 is a body-centred cubic with Ita cages in the corners connected by 3 pairs of pau and d8r as chains along the edge of the scaffold. Each scaffold is filled up with 4 types of cages (t-plg, t-oto, t-gsm and t-phi) connected by d8r. Each cage is formed by various faces with ring shape where eight-member ring (8MR) is the largest in size compared with other rings. Therefore, ZSM-25-based zeolite is a typical small-pore zeolite where 8MRs are the only doorway for gas diffusing to the internal cages. Hence the accessibility of 8MR is determinative for the admission of guest molecules. K-ZSM-25 was derived from as-made ZSM-25 after calcination and followed by the ion-exchange process. K-ZSM-25 shows the same crystal structure and morphology as the pristine Na-ZSM-25 (as-made ZSM-25 after calcination) (Figure. 1a and 2b). The unit cell composition of as-prepared K-ZSM-25 was determined to be K$_{327.9}$Na$_{2.1}$[H$_{30.7}$Al$_{360.7}$Si$_{1079.3}$O$_{2880}$] by inductively coupled plasma-mass spectroscopy (ICP-MS).

The accessibility of the pore aperture can be switched off at low temperatures, as exemplified by the ultra-low quantity of N$_2$ and CH$_4$ adsorbed at 77 K and 253.15 K, respectively (Figure. 1b and 3b), indicating that admission of each gas is blocked by the K$^+$, which is possibly located in the center of 8MR. However, the accessibility of the pores can be increased by increasing the temperature, which facilitates thermal motion of K$^+$ away from the 8MR, as indicated by the increased gas uptakes at ambient temperatures (Figure. 3a and 3b). The triggered admission
is ascribed to the vibrational motion of the mobile “door-keeping” cations rather than the adsorbate-induced expansion, as confirmed by the experimental evidence obtained by synchrotron PXRD spectrums of which no shifting was observed with pressure increase of both N\textsubscript{2} and CH\textsubscript{4}, and remained the same as under vacuum, suggesting no interaction between gas molecules and cations (Figure. 4a, 4b and 4c).

Figure.2 (a) N\textsubscript{2} and CH\textsubscript{4} adsorption isobars at 1 bar (green shadow refers to the temperatures near ambient temperature which is industry-favorable (b) N\textsubscript{2}/CH\textsubscript{4} selectivity on K-ZSM-25 at 1 bar from 243K to 303K. (c) N\textsubscript{2} isobar on K-ZSM-25 at three pressures, (d) CH\textsubscript{4} isobar on K-ZSM-25 at three pressures (solid symbols referring to the experimental data with curves depicting the theoretical-fitting results using LTM model.) The full isotherms across the entire temperature range can be accessed in the supplementary information. The framework scheme in Fig 2b is reproduced with permission.\textsuperscript{19} Copyright 2015, Nature.
For both CH₄ and N₂, the adsorption capacity first increases and then decreases with temperature increase, as indicated by the isobars in Figure. 2c and Figure. 2d. For example, for N₂ at 100kPa, the uptake is only 0.09 mmol/g at 133 K and gradually increases to a maximum 1.09 mmol/g at 173 K, followed by a decrease to 0.14 mmol/g at 303 K (Figure. 2c). The same trend can also be observed at other pressures. For CH₄, only surface adsorption took place on K-ZSM-25 below 273K, and a gradual increase of the CH₄ uptake was observed with increasing temperature. The highest value of 0.12 mmol/g was reached at 353K and 100 kPa, and the capacity then reduced to 0.04 mmol/g at 423K and 100 kPa. These “bell-shaped” isobars were also observed at other pressures (Figure. 2d). The threshold temperature with the highest adsorbed gas amount is called gate-opening temperature Ts. This unique trend of the isobars is attributed to two counteracting factors: EFC motion and the physisorption capacity. Below the Ts, the gas diffusion is dominated by EFC motion. The guest molecules are impeded by the weak-oscillating EFCs which occupy most of the available space in the narrow aperture resulting in low gas uptakes. But the thermal oscillation of K⁺ becomes stronger with increased temperature, resulting in a lower energy barrier for guest molecules to pass through, which contributes to increasing gas admission. Above the Ts, the gas molecules are fully accessible to pores, and the physisorption capacity is predominant like normal cases, leading to a decrease in the gas uptake as the temperature increases.

**Figure.3** (a) N₂ isotherms on K-ZSM-25 at temperature range from 101.15K to 303.15 K. (b) CH₄ isotherms on K-ZSM-25 at temperature range from 203.15K to 403.15 K.
The big difference in $T_s$ inspired a new approach to separate the mixture of $N_2$ and $CH_4$ (two molecules with similar kinetic diameter and polarity). Specifically, the $T_s$ of $CH_4$ (353K) is much higher than that of $N_2$ (173K) due to the larger kinetic diameter of the former (Figure. 2a). This significant difference in $T_s$ enables this material to achieve effective separation at industrial-applicable temperatures with ultra-high ideal selectivity, because the $N_2$ is readily adsorbed, while $CH_4$ is blocked by the $K^+$ between the two gate-opening temperatures (i.e. 173K-353K). K-ZSM-25, for the first case, shows remarkably stronger $N_2$ equilibrium over $CH_4$ and achieves outstanding $N_2/CH_4$ selectivity across the industrial-applicable temperature range, as shown in the green shadow in Figure. 2a. At 253K and 100 kPa, the $N_2$ uptake was 0.41 mmol/g, while only surface adsorption of $CH_4$ was observed, leading to a $N_2/CH_4$ selectivity of 34.2 (Figure. 2b). Even at 273K, K-ZSM-25 can still reach an outstanding $N_2/CH_4$ selectivity of 17, which is the highest value compared with other porous materials recorded in the literature (Table. 1) to our best knowledge. These results highlight the excellent temperature-regulated separation performance of K-ZSM-25 in which the accessibility of 8MR for each gas can be controlled by temperature, allowing nitrogen and methane to be effectively differentiated.
Vacuum
$N_2$ at 1 bar
Figure 4 Synchrotron PXRD of K-ZSM-25 (a) under vacuum (b) under N2 at 1 bar (c) under CH4 at 1 bar.

Notably, when the temperature is greater than \( T_s \) (right side of isobar) for a given gas, the gas molecules are fully accessible to the pores and show fast kinetics. In this case, the adsorption isotherms are in good agreement with the desorption isotherms (Figure 5). On the other hand, below \( T_s \) (left side of isobar), the pores are only partially open to guest molecules. In this case, some adsorbed guest molecules are trapped intracrystalline and impeded by EFCs during the desorption process, resulting in a hysteresis loop on the isotherms. This hysteresis loop hampers the absorbent regeneration in industrial PSA cycles. Considering the adsorbed gas needs to be easily removed to regenerate the zeolites, the adsorption temperature is necessarily above \( T_s \) for the gas to be adsorbed (N2 in our case). K-ZSM-25 is capable of separating N2 and CH4 at around
ambient temperature (Figure 2a, green shadow) at which N₂ is quickly adsorbed and readily desorbed. Therefore, K-ZSM-25 is an ideal absorbent, not only enabling appreciable N₂/CH₄ separation at equilibrium around room temperature and ambient pressure, but also ease of regeneration in a PSA cycle, which is very important in the natural gas industry.

![Adsorption and desorption isotherms of N2 on K-ZSM-25 at 243.15 K and 273.15K, showing no hysteresis loop](image)

*Figure 5* Adsorption and desorption isotherms of N₂ on K-ZSM-25 at 243.15 K and 273.15K, showing no hysteresis loop

*Table 1* Summarized N₂/CH₄ separation performance of some popular porous materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Pressure</th>
<th>Temperature</th>
<th>N₂/CH₄ selectivity</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX-1</td>
<td>100 kPa</td>
<td>298 K</td>
<td>0.53</td>
<td>20</td>
</tr>
<tr>
<td>HAX-1</td>
<td>100 kPa</td>
<td>298 K</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>Basolite® A100</td>
<td>100 kPa</td>
<td>298 K</td>
<td>0.27</td>
<td>7</td>
</tr>
<tr>
<td>Na⁺-clinoptilolite</td>
<td>100 kPa</td>
<td>298 K</td>
<td>0.93</td>
<td>11</td>
</tr>
<tr>
<td>Li⁺-clinoptilolite</td>
<td>100 kPa</td>
<td>298 K</td>
<td>1.18</td>
<td>11</td>
</tr>
<tr>
<td>Anderson AX-21</td>
<td>100 kPa</td>
<td>298 K</td>
<td>0.33</td>
<td>21</td>
</tr>
</tbody>
</table>
To describe the observed temperature-regulated adsorption behavior from a quantitative perspective and to predict the separation performance at given temperature, an LJM model was introduced to clarify the temperature dependence of the adsorbed amount of each gas at a given feed pressure.

\[ n = \left[ \phi(T) \times (1 - \varepsilon) + \varepsilon \right] \times \bar{Q}(P, T) \]  (1)

Where \( \phi(T) \) is the fraction of gate-keeping oscillators open at a given temperature:

\[ \phi(T) = \frac{1}{2} \left( 1 + \text{erf} \left( \frac{T^2 - T_0^2}{\sqrt{2} \beta T} \right) \right) \]  (2)

\( Q(P, T) \) is the isotherm model depending on pressure \( P \) and temperature \( T \). This \( Q(P, T) \) is obtained from the isotherms which follow the normal physisorption trend (e.g. uptakes decrease with temperature increase). Here we fit the \( \text{N}_2 \) isotherms to a Langmuir model and \( \text{CH}_4 \) isotherms to a Linear isotherm model. Thus, the LJM model for \( \text{N}_2 \) and \( \text{CH}_4 \) is given by Eq. 3 and Eq. 4, respectively:

\[ n = \left[ \phi(T) \times (1 - \varepsilon) + \varepsilon \right] \times \left( \frac{m_1 b_1 P \exp(\frac{\varepsilon_1}{RT})}{1 + b_1 P \exp(\frac{\varepsilon_1}{RT})} + \frac{m_2 b_2 P \exp(\frac{\varepsilon_2}{RT})}{1 + b_2 P \exp(\frac{\varepsilon_2}{RT})} \right) \]  (3)

\[ n = \left[ \phi(T) \times (1 - \varepsilon) + \varepsilon \right] \times K \times \exp \left( \frac{A}{RT} P \right) \]  (4)

The parameters \( K \) and \( A \) are related to the total number of sites and the activation energy of these sites, respectively, while the remaining parameters refer to the accessibility of these sites: \( \varepsilon \) is the fraction of permanently accessible sites, and \( T_0 \) and \( \beta \) describe the temperature range.
over which the sites become accessible. For CH₄, to predict $K$ and $A$, it was assumed that all sites are accessible at the 3 highest measured temperatures (373K, 393K and 423K), therefore $\phi = 1$ and they obey the linear isotherm:

$$n = K \times \exp \frac{A}{RT} p$$  \hspace{1cm} (5)

Once $K$ and $A$ were fitted (Figure. 6a), the remaining parameters, $\varepsilon$, $T_0$ and $\beta$, were fitted to all data points. The predictions at 1 atm as a function of temperatures were given in Figure. 2(d). The same procedure applied to predicting the N₂ isobars (Figure. 6b). Both CH₄ and N₂ isobars are well fitted by the LJM model which can quantify the effect of temperature-regulated adsorption, elucidating the way in which K-ZSM-25 can effectively differentiate between N₂ and CH₄ via differences in pore-accessibility at different temperatures. Additionally, the well-fitted LJM model also helps to predict the adsorption equilibrium at given temperature and the selectivity for given gas pairs.

\[ \text{Figure. 6} \ (a) \text{ The CH}_4 \text{ isotherms at three highest temperatures with fully accessible sites and their fitting curves using linear isotherm model. (b) The N}_2 \text{ isotherms at three temperatures with fully accessible sites and their fitting curves using dual-site Langmuir model. (Symbol: experimental data, lines: fitted isotherms)} \]

Adsorption kinetics on K-ZSM-25 of N₂ and CH₄ were experimentally investigated, and diffusion time constants ($D/r^2$) were determined using a non-isothermal sorption model.\textsuperscript{23,24} The results showed that the K-ZSM-25 had competitive adsorption kinetics of both CH₄ and N₂, and the CH₄
was adsorbed slightly faster than N\textsubscript{2} (Table. 2). The adsorption kinetics of CH\textsubscript{4} was unable to be determined at 258K due to the negligible uptake at low temperatures.

Table 2 Diffusion time constants (D/r\textsuperscript{2}) of N\textsubscript{2} and CH\textsubscript{4} on K-ZSM-25 determined using non-isothermal sorption model at 258K, 273K and 283K.

<table>
<thead>
<tr>
<th></th>
<th>258K</th>
<th>273K</th>
<th>283K</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>4.41×10\textsuperscript{-03} s\textsuperscript{-1}</td>
<td>5.58×10\textsuperscript{-03} s\textsuperscript{-1}</td>
<td>6.32×10\textsuperscript{-03} s\textsuperscript{-1}</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>-</td>
<td>1.07×10\textsuperscript{-02} s\textsuperscript{-1}</td>
<td>8.58×10\textsuperscript{-03} s\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

The promising features of K-ZEM-25 motivated us to carry out dynamic breakthrough experiments on N\textsubscript{2}/CH\textsubscript{4} mixtures (two molar mixture compositions N\textsubscript{2}/CH\textsubscript{4}: 50/50, total pressure 2 bar). The dynamic separation at 258K flowing at 50 mL/min was experimentally simulated using a dynamic model built in Aspen Adsorption, and the scheme of the flow sheet is shown in Figure 7. The process configuration was built based on a lab-scale breakthrough experiment setup. The simulation was carried out by the isothermal dynamic fixed bed adsorption model. The simulation of the process was conducted using coupled equations including mass conservation, momentum and energy conservation between the adsorbate and adsorbent. The mass transfer coefficients were experimentally determined by the diffusion time constants (D/r\textsuperscript{2}) via kinetics investigation. The column properties and isotherm parameters that were used in our breakthrough simulation were listed in Supporting Information, Table 3 and Table 4.
Aspen adsorption flow sheet of breakthrough experiment

\[ Q = \frac{I P_1 P \exp\left(\frac{I P_2}{T}\right)}{1 + I P_3 P \exp\left(\frac{I P_4}{T}\right)} + \frac{I P_5 P \exp\left(\frac{I P_6}{T}\right)}{1 + I P_7 P \exp\left(\frac{I P_8}{T}\right)} \] (6)

*Figure* Error! No text of specified style in document..7 Aspen adsorption flow sheet of breakthrough experiment

**Table 3** Properties of K-ZSM-25 and parameters of bed and column

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hb</td>
<td>0.135</td>
<td>m</td>
<td>Height of adsorbent layer</td>
</tr>
<tr>
<td>Db</td>
<td>0.022</td>
<td>m</td>
<td>Internal diameter of adsorbent layer</td>
</tr>
<tr>
<td>Ei</td>
<td>0.43</td>
<td>m$^3$ void/m$^3$ bed</td>
<td>Inter-particle voidage</td>
</tr>
<tr>
<td>Ep</td>
<td>0.549</td>
<td>m$^3$ void/m$^3$ bead</td>
<td>Intra-particle voidage</td>
</tr>
<tr>
<td>RHOs</td>
<td>549.5</td>
<td>kg/m$^3$</td>
<td>Bulk density</td>
</tr>
<tr>
<td>Rp</td>
<td>1.5e-004</td>
<td>m</td>
<td>Adsorbent particle radius</td>
</tr>
<tr>
<td>SFac</td>
<td>1</td>
<td>n/a</td>
<td>Adsorbent shape factor</td>
</tr>
</tbody>
</table>

The gas equilibrium uptake was described by dual-site Langmuir model, which was in good agreement with the experimental data. Equation 6 describes the dual-site Langmuir model used in Aspen adsorption, and values of each parameter are given in Table 4.
Where, Q is the gas equilibrium uptakes (kmol/kg of adsorbent), P is the adsorbate pressure (bar), T is the temperature (K). IP1-IP8 are fitting parameters.

**Table 4 Mass transfer coefficient and isotherm fitting parameters of dual-Site Langmuir model**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTC(&quot;CH₄&quot;)</td>
<td>1.00E-05</td>
<td>1/s</td>
<td>Constant mass transfer coefficients</td>
</tr>
<tr>
<td>MTC(&quot;HE&quot;)</td>
<td>0</td>
<td>1/s</td>
<td>Constant mass transfer coefficients</td>
</tr>
<tr>
<td>MTC(&quot;N₂&quot;)</td>
<td>0.0662</td>
<td>1/s</td>
<td>Constant mass transfer coefficients</td>
</tr>
<tr>
<td>IP(*)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IP1</td>
<td>3.36E-09</td>
<td>6.64E-05</td>
<td>kmol·kg⁻¹·bar⁻¹</td>
</tr>
<tr>
<td>IP2</td>
<td>2499.83</td>
<td>1.20949</td>
<td>K</td>
</tr>
<tr>
<td>IP3</td>
<td>0.00376</td>
<td>26.2794</td>
<td>bar⁻¹</td>
</tr>
<tr>
<td>IP4</td>
<td>0.51904</td>
<td>1.04639</td>
<td>K</td>
</tr>
<tr>
<td>IP5</td>
<td>1.54E-08</td>
<td>1.70E-05</td>
<td>kmol·kg⁻¹·bar⁻¹</td>
</tr>
<tr>
<td>IP6</td>
<td>2795.32</td>
<td>0.93722</td>
<td>K</td>
</tr>
<tr>
<td>IP7</td>
<td>2.33E-05</td>
<td>0.00592</td>
<td>bar⁻¹</td>
</tr>
<tr>
<td>IP8</td>
<td>2848.39</td>
<td>0.62133</td>
<td>K</td>
</tr>
</tbody>
</table>

At 258K, CH₄ first exited from the packed bed after 70 s, whereas the nitrogen is retained (Fig. 8). After 480 s, the outlet gas gradually reached the original inlet feed concentrations, suggesting the outlet produces the pure methane before 480 s. The resulting dynamic N₂/CH₄ selectivity reached 5.7 at 258 K. These results, coupled with the experimental single-component isotherms, highlight the N₂-selective adsorption on this material. The adsorption performance is able to be adjusted by temperature through controlling the extent of thermal motion of the “door keeping” cations.
4.4 Conclusion

In summary, we report a new “trapdoor” material K-ZSM-25 in which K⁺ acts as a “door-keeping” cation. The extent of the temperature-dependent oscillations of the K⁺ cation regulates the accessibility of the cage, controlling the adsorption capacity of the material. Both the experimental results and simulations demonstrate that the strategy of incorporating “door-keeping” cations into small-pore zeolite ZSM-25 provides a unique opportunity to achieve efficient N₂-selective adsorption from CH₄. Notably, this material shows large N₂ capacity, outstanding N₂/CH₄ selectivity, fast kinetics and is readily regenerated at around room temperature, all of which makes this adsorbent ideally suited to PSA-based industrial separations. The design of this “trapdoor” material opens new avenues for N₂/CH₄ separations in a broad field to develop cleaner, more efficient technologies for today’s industrialized world. In addition, the adjustable pore accessibility provides a potential application for gas storage and molecular encapsulation.

Reference


17. Li, G. K. et al. Temperature-regulated guest admission and release in microporous


Chapter 5

Conclusions and General Discussions

5.1 Conclusions

This thesis describes the development of small-pore ZSM-25 based zeolites, and their applications in adsorption and membrane separations. This thesis is organised by a thorough literature review on small-pore zeolites in natural gas purification in Chapter 1, improvement of adsorption kinetics and CO₂ capacity of ZSM-25 by fine tuning the pore sizes in Chapter 2, application of the modified ZSM-25 zeolites in commercial polymer and systematic investigation of Polymer/ZSM-25 composite membranes for gas separation in Chapter 3, and design of a “trapdoor” ZSM-25 based zeolite for highly efficient N₂-selective adsorption from CH₄ with high N₂ capacity and kinetics in Chapter 4. The major contribution of this thesis is providing a rational strategy of designing ZSM-25 zeolite for effective CO₂/CH₄ and N₂/CH₄ separation in the natural gas purification industry and their promising application in membrane separation.

Chapter 2: A Li⁺/ZSM-25 zeolite (LZZ) was developed via partial ion exchange of the Na⁺ with Li⁺. This exchange enabled higher CO₂ capacity and adsorption kinetics due to higher pore volume and stronger affinity of CO₂ with Li⁺, and the ultra-high CO₂/CH₄ selectivity remained. The CO₂ isotherms showed deviation from typical Type I isotherm and “breathing” behavior. This observation was explained by synchrotron in situ X-ray powder diffraction, demonstrating a gradual structural expansion induced by CO₂. This expansion resulted in the increased CH₄ admission in binary gas adsorption. This work enables the possibility of applying small-pore zeolites in natural gas purification which are kinetically-limited.

Chapter 3: The Li⁺/ZSM-25 zeolite (LZZ) was incorporated into a commercial polymer Matrimid® 5218 yielding a mixed-matrix membrane (MMM). Li⁺/ZSM-25 was chosen as filler because of its fitting pore diameter between CO₂ and CH₄, which merely adsorbed CH₄ while allowing considerable CO₂ transport. The CO₂/CH₄ separation performance of the optimal MMMs at 5 wt% filler loading, showed higher CO₂/CH₄ selectivity than that of the pristine Matrimid in both single- and mixed-gas separation. The dominant molecular sieving effect contributed to the increasing
selectivity with increased pressure, showing unusual plasticization-resistance behavior. The optimized membrane (M−5) achieved ideal CO₂/CH₄ selectivity of 169, which surpassed the latest CO₂/CH₄ upper bound.

**Chapter 4:** A new “trapdoor” material K-ZSM-25 was designed for N₂/CH₄ separation by incorporating K⁺ as a “door-keeping” cation. The extent of the temperature-dependent oscillations of the K⁺ cation regulated the accessibility of the cage, controlling the adsorption capacity of the material. There were distinguishable gate-opening temperatures (Ts) between N₂ and CH₄ molecules. Within this temperature range, N₂ molecules had full access to the pathway into the cage, while CH₄ molecules were hindered due to the blockage of K⁺. Both the experimental results and simulations demonstrated that K-ZSM-25 can achieve effective N₂/CH₄ separation at around ambient temperature with outstanding selectivity of over 30 in single gas adsorption and 5.7 in dynamic breakthrough simulation. The large N₂ capacity, outstanding N₂/CH₄ selectivity, fast kinetics of K-ZSM-25, and it is readily regenerated at around room temperature, all of which makes this adsorbent ideally suited to PSA-based industrial separations.

### 5.2 Future Perspective

Although the ZSM-25 based zeolites naturally have potential in separating CO₂ from CH₄ and N₂ from CH₄, the study on the structural details and molecular interaction was far from enough. We only observed the CO₂-induced expansion on ZSM-25 in **Chapter 1**, showing breathing behaviour, however, the structural changes in detail (framework expansion and cation movements) have not been understood. Therefore, the fundamental mechanism needs to be understood to help develop ZSM-25 for separation technologies in the right square. Synchrotron powder X-ray diffraction can help to solve the exact structure at a given pressure and temperature via Rietveld Refinement.

In **Chapter 4**, the unique preferential N₂ adsorption was observed on K-ZSM-25 where K⁺ acted as a “door-keeping” cation and thermally oscillate depending on temperature. This oscillation enabled the admission of different gases at different temperatures. However, we still have no idea about the K⁺ location and how it migrates in the presence of N₂ and CH₄. We noticed there were no shifting of XRD spectrums under N₂ and CH₄ environment, however, the reason why the
gate-opening temperature of $N_2$ is much lower than $CH_4$, what is the energy barrier for each gas to pass through 8MR, and which 8MR is determinant for gas admission are still unknown. We can uncover this by integrating Synchrotron powder X-ray diffraction with DFT simulation.

Besides, the binary gas adsorption experiments are a very important evaluating the performance of adsorbents. These experiments are very important in the future research work because an actual breakthrough experiment conducting in a lab-scale equipment is able to reflect the real behaviour of K-ZSM-25 material and possible competitive adsorption.

Coupled with the mechanism study of the temperature-dependent adsorption behaviour of this new material, the future study on this material can be an important work and have satisfying outcomes because we firstly find out the unique adsorption behaviour in a new material with excellent separation performance (highly $N_2$-selective at around room temperature). The design and deep investigation regarding structure chemistry of this “trapdoor” material will open new avenues for $N_2/CH_4$ separations in a broad field to develop cleaner, more efficient technologies for today's industrialized world.
Appendices

6.1 Na-ZSM-25

6.1.1 Characterization

The nanocrystal structure of ZSM-25 and Na-ZSM-25 were confirmed by the powder X-ray diffraction (XRD). The removal of template TEA did not cause the structural collapse and remain its crystallinity, as shown in Fig. 6.1. The morphology of Na-ZSM-25 is nearly identical to the as-made ZSM-25, as confirmed by the SEM images (Fig. 6.2). The diameter of single crystal is ca. 0.8 μm. TGA results (Fig. 6.3) shows that calcination procedure is successful, peak at 773 K disappear. Water desorption peak at 423 K has lowered to 373 K, likely due to stronger H2O interactions with TEA+ and Br- which are gone after calcination.

![XRD patterns of ZSM-25 zeolites (red), template-free Na-ZSM-25 (blue)](image1)

*Figure 6.1 XRD patterns of ZSM-25 zeolites (red), template-free Na-ZSM-25 (blue)*

![SEM image of as-made ZSM-25 (left) and Na-ZSM-25 (right) nanocrystals; 800 nm particle size](image2)

*Figure 6.2 SEM image of as-made ZSM-25 (left) and Na-ZSM-25 (right) nanocrystals; 800 nm particle size*
6.1.2 Gas Adsorption and Separation Performance

The adsorption isotherms of CO_2 at 323.15K, 373.15K and 423.15K are shown in Fig. 6.4. The Na-ZSM-25 has a high CO_2 capacity of 0.75 mol/kg at 323.15K and 100 kPa. With the increase of the pressure, it follows the normal trend (i.e. decreasing the CO_2 uptakes). However, the uptakes for CH_4 at these three temperatures are under detecting limitation, which indicated the exceptional high CO_2/CH_4 selectivity. This rejection of CH_4 can be attributed to the molecular sieving effect, because the kinetics diameter of CH_4 is larger than the Eight-Membered Ring (8MR). In addition to the superior separation performance of CO_2/CH_4, Na-ZSM-25 can also be able to adsorb water. The adsorption isotherms at 313.15K to 343.15K are shown in Fig. 6.5. Na-ZSM-25 can adsorb 10.15 mol/kg of water vapor at 2.53 kPa. The adsorbed amount decreases as the temperature increases, as shown in Fig. 6.5(a). Water isotherms, alignment above relative humidity 0.04% suggests that accessible surface area is the same in all cases, however, at low relative humidity, the misalignment implies a different adsorption mechanism/process (Fig. 6.5b).
6.1.3 CO₂ adsorption kinetics

The rate of adsorption on Na-ZSM-25 under different temperatures and pressures are investigated. The f(t) = (P – P₀)/(P∞ – P₀), also called the fractional approach to equilibrium. The dependence fractional uptake on times are shown in Fig. 6.6. At the same temperature, the time
to reach equilibrium decreases with the increase of pressure, which is ascribed to the stronger driving force. For example, at 323K, the time reaching equilibrium at 3.4 kPa and 19.1 kPa are 7079 s and 1102 s, respectively (Fig. 6.6a). This faster adsorption rate at high pressures can be also indicated from the faster increase of the fractional uptake at the initial several seconds. At the same pressure, the adsorption rates increase with the increase of temperatures, which is attributed to the higher molecular dynamics at high temperatures. For instance, at 3.40 kPa, the times to reach equilibrium at 323K, 373K, 423K and 473K are 7079s, 2081s, 598s and 501s, respectively (Fig. 6.6a, b, c and d).

To estimate the kinetics of the Na-ZSM-25 quantitatively, the uptake curves were fitted with pseudo-second order (PSO) kinetics. PSO can fit for nearly every uptake curve, as shown in Fig.6.7. An example of the PSO fitting is shown below. This is interesting because the PSO implies a chemisorption type system.

\[
\frac{t}{v_t} = \frac{1}{k_2 \cdot v_e^2} + \frac{1}{v_e} \cdot t
\]

(1)

Where, \(k_2\) is the rate of adsorption, \(v_e\) is the CO\(_2\) adsorbed at the equilibrium. \(v_t\) is the CO\(_2\) adsorbed at the any time. \(t\) is the time. Thus, the dependence of \(t/v_t\) on \(t\) gives a linear relationship with a slope of \(1/v_e\) and an intercept of \(1/ k_2 \cdot v_e^2\). The slope gives the predicted equilibrium loading, and the intercept is used to obtain \(k_2\). For \(k_2\). The difference between the predicted and experimental is very small and can be used as an indicator for the goodness of fit.

The plots of \(k_2\) as a function of initial pressure (\(P_0\)) at different temperatures are presented in Fig. 8. The dashed lines are exponential regressions in the form \(y = a^*\left[\exp\left(b^*x\right)-1\right]\) to force a (0,0) intercept. Some experimental points deviate from the fitted lines, which is probably caused by the instrument error.
Figure 6.6 The dependence of fractional uptake on time at 323K (a), 373K (b), 423K (c) and 473K (d)

\[
323.15 \text{ K}, P_0 = 3.40 \text{ kPa}
\]

\[
t / \nu = 0.2157 t + 8.1383
\]
All the plots are combined, so $k_2$ can be clearly observed over temperatures and pressures in Fig. 6.8. The rate of adsorption increases gradually with the increase of pressure. High temperatures also contribute to the fast rate of adsorption, as evidenced by the higher $k_2$ in Fig. 6.8(e).

*Figure 6. 7 Linear regression plots of PSO model for adsorption kinetics determination at 325.15K and 3.40 kPa*

*Figure 6. 8 The dependence of adsorption rate on pressures at 323K (a), 373K (b), 423K (c) and 473K (d)*
6.1.4 Conclusion

In this study, template-free Na-ZSM-25 was synthesized. The CO$_2$, CH$_4$ and water adsorption performance was studied. Na-ZSM-25, as a small pore zeolite, has high CO$_2$ capacity of 0.75 mol/kg at 323.15K and 100 kPa and exceptional high CO$_2$/CH$_4$ selectivity due to the molecular sieving effect. Additionally, the Na-ZSM-25 can be also used for water vapor removal. It can adsorb 10.15 mol/kg of water vapor at 2.53 kPa. The kinetics of Na-ZSM-25 were fully studied. PSO model was used to evaluate the adsorption rates. The rate of adsorption increases gradually with the increase of pressure and temperatures. In summary, Na-ZSM-25 can exhibit high CO$_2$ working capacity, high CO$_2$/CH$_4$ selectivity, which indicates its potential use for biogas upgrading.

6.2 Different cationic ZSM-25

![Graphs showing CO$_2$ and CH$_4$ isotherms on partially exchange Mg-ZSM-25 (left) and K-ZSM-25 (right).](image-url)

Figure 6.9 CO$_2$ and CH$_4$ isotherms on partially exchange Mg-ZSM-25 (left). CO$_2$ and CH$_4$ isotherms on K-ZSM-25 (right)

Divalent Mg-exchanged ZSM-25 also shows trapdoor behavior, as evidenced by the negative N$_2$ uptake at 77K and higher CH$_4$ uptake at 303 K (Fig. 6.8 left and Fig. 6.9).
Figure 6. 10 N2 isotherm on Mg-ZSM-25 and K-ZSM-25 at 77K

The preferential N2 adsorption on ZSM-25 is ineffective when the pressure is higher than 10 bar.

Figure 6. 11 (a) CH4 and N2 isotherms on K-ZSM-25 at high pressures (b) Zoomed at 0-15 bar with log axis.

The preferential N2 adsorption on ZSM-25 is ineffective when the pressure is higher than 10 bar.
**Figure 6.12** In situ synchrotron PXRD of Li-ZSM-25 in N2 at 1 bar from 363K to 123K

With the increase of temperature, the peaks of spectrum shift leftwards, demonstrating only thermal expansion take place and N2 has no effect on the structure.
**Figure 6.13** In situ synchrotron PXRD of Li-ZSM-25 in CH4 at 1 bar from 363K to 123K

With the increase of temperature, the peaks of spectrum shift leftwards, demonstrating only thermal expansion take place and CH4 has no effect on the structure.
With the increase of temperature, the peak firstly shifts leftwards with decreasing intensity, then move rightwards with increasing intensity, indicating the structure changes in the presence of CO$_2$.
Figure 6. 14 In situ synchrotron PXRD of Li-ZSM-25 in CO2 at 273 K from vacuum to 490 kPa

With the increase of pressure, the peaks firstly shift towards left with decreasing intensity, then the intensity start to increase from 150 Kpa.
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