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Colloidal Zeolite Supported Ionic Liquid Membranes for CO$_2$/N$_2$ Separation

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By

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Abstract

Ionic liquids (ILs) are a relatively new class of solvents which has shown promises for CO₂ separation because of their green chemistry nature, high thermal stability, extremely low vapor pressure, and reusability. A number of ILs have been found to exhibit high CO₂/N₂ absorption selectivity. In recent years, supported ionic liquid membranes have been developed for various gas separations by solution-diffusion mechanism. IL membranes have shown good potential to separate CO₂ from combustion flue gas (mainly containing CO₂ and N₂) with high efficiency. The supported IL membranes (SILMs) are commonly made by loading ILs in porous polymeric or inorganic supports by impregnation or infiltration, where the porous materials serve as inert substrates to retain the viscous ILs by capillary force. SILMs have advantages of being thermally stable, environmentally friendly, low-cost due to minimized consumption of the expensive IL (compared to the large quantity required in absorption/curbing processes), highly CO₂-selective, self-prevention of defect formation by its fluid nature, and adaptability for retrofitting existing process. SILMs on different substrates have been reported in the literature with good CO₂/N₂ selectivity but low or moderate CO₂ permeance. The relatively low CO₂ flux in SILMs was caused by low permeability and large membrane thickness, which must be significantly improved in order to make the SILMs practically useful.

In this thesis, colloidal silicalite (i.e. pure silica MFI-type zeolite) film supported IL membranes have been developed aiming to improve the IL membrane CO₂ separation performance by enhancing the CO₂ permeance while maintaining high CO₂ selectivity. In the silicalite film supported IL membrane, the entire membrane area is active for CO₂ permeation rather than just the open area (porosity) between dense particles in the conventional porous supports because the silicalite particles are highly permeable to CO₂ as well. Also, because silicalite preferentially adsorbs CO₂ over the non-adsorbing N₂, using colloidal silicalite support may also benefit the overall CO₂/N₂ selectivity in the SILM. The porous substrate used in this research has a macroporous alumina base (pore size of 0.1 μm and 2 mm in thickness) with a thin (<5 μm thick) skin of colloidal zeolite on the top. The silicalite
particles are largely spherical with an average diameter of 70 nm that give nominal pore diameter of the inter-particle space of around 20 nm. The IL is loaded in the zeolite inter-particles voids but not inside the zeolitic pores because the IL molecules are much larger than the effective diameter (0.56 nm) of the zeolitic pores. When the inter-particle pores of the colloidal zeolite film is much smaller than the pore size of the alumina base support, the ionic liquid will be first soaked into the colloidal zeolite layer due to stronger capillary force. The colloidal zeolite film is theoretically capable of forming IL membrane with the same small thickness of the zeolite skin only. Thus, by significantly reducing the IL membrane thickness and utilizing the permeability in the zeolitic pores, the CO₂ permeance of the new zeolite supported IL is anticipated to increase significantly because of decreased mass transfer resistance.

Silicalite nano-particles (dia. ~ 70 nm) were synthesized from a precursor solution with molar ratio of 0.33(SiO₂): 0.1(TPAOH): 0.035(NaOH): 5.56(H₂O). The colloidal silicalite layer on the porous alumina disk was fabricated by dip-coating from a colloidal suspension of the silicalite nanoparticles. The suspension contained Hydroxyl propyl cellulose (HPC) which served as binder for drying control and crack prevention. The colloidal silicalite layer, after controlled drying and firing, was 2~3 μm thick. The [bmim][BF₄] ionic liquid which was chosen as the IL membrane material in this study based its high CO₂ adsorption selectivity and solubility reported in the literature. The IL membrane was loaded into the zeolite-coated substrates by a simple brushing-soaking process.

A pinhole-free IL membrane was obtained on the colloidal silicalite coated support at an IL-load of 20 mg-IL/cm² while no pinhole-free IL membrane could be formed on the bare alumina support with the same IL-load because the large pore size and broad pore size distribution of the alumina make it impossible to close up the largest pores by capillary suction before the disc is fully soaked with IL. This zeolite supported IL membrane was investigated by single gas permeation measurement for molecules relevant to CO₂ capture and for separation of CO₂/N₂ mixtures. The effects of common impurities in the feed stream, such as O₂, H₂O, and SO₂, and the operation conditions, including
temperature and the permeate side conditions, on the CO$_2$ separation factor and permeance were experimentally studied. At room temperature 25°C and atmospheric pressure, the CO$_2$ and N$_2$ single gas permeance of the IL membrane were $6.3 \times 10^{-9}$ mol/m$^2$·s·Pa and $3.5 \times 10^{-10}$ mol/m$^2$·s·Pa, respectively, that gave a CO$_2$/N$_2$ ideal selectivity (or permselectivity) of 18. The effects of temperature, pressure, CO$_2$ composition, water vapor, SO$_2$, and downstream pressure were studied. Increasing the operating temperature increased CO$_2$ permeance but decreased the CO$_2$/N$_2$ selectivity. When temperature increased from 25 to 118 °C, the CO$_2$ permeance increased from $6.3 \times 10^{-9}$ to $11.7 \times 10^{-9}$ mol/m$^2$·s·Pa whereas the CO$_2$/N$_2$ permselectivity decreased from 18 to 4.8. These indicate that the enhancement of CO$_2$ diffusivity overpowered the decrease of solubility as temperature increased in the tested range; and the N$_2$ permeability (given by the product of solubility and diffusivity) is more sensitive to temperature than the CO$_2$ permeability.

The temperature dependences of CO$_2$ permeance and selectivity in the mixture separation were found to be similar to those observed from the single gas permeation because there were no strong interactions between the dissolved CO$_2$ and N$_2$. Increasing the CO$_2$ concentration (i.e. CO$_2$ partial pressure) in feed gas increased the CO$_2$ flux because of greater resultant driving force. However, the CO$_2$ permeance and CO$_2$/N$_2$ separation selectivity were found initially decreasing with CO$_2$ feed concentration and eventually become independent of pressure, suggesting that the saturation of dissolved gas and increase of CO$_2$ partial pressure in permeate stream will be the limiting factors for permeance at high feed pressure. Pressure tolerance tests demonstrated that the IL membrane remained stable without rupturing under 5 bars (the highest test in this work) of differential pressure across the membrane even at elevated temperatures of >100 °C. The presence of water vapor in the feed stream was found to enhance both the CO$_2$ permeance and CO$_2$/N$_2$ selectivity at low CO$_2$ partial pressure due to increased CO$_2$ solubility and diffusivity after water is incorporated into the IL; however, water vapor had no apparent influence on the separation under high CO$_2$ feed pressure. The existence of SO$_2$ impurity (500 ppmv in feed) caused slight decrease in CO$_2$ and N$_2$ permeance
without significantly affecting the CO₂/N₂ separation selectivity. The minimal influence of the SO₂ and somewhat positive effect of water vapor on the CO₂ separation are desirable in practical applications because the coal-firing flue gases commonly contain ppm-level SO₂ and near-saturation water vapor. It was also demonstrated that both CO₂ permeance and CO₂/N₂ selectivity were higher when the permeate side was vacuumed (to create the driving force) as compared to the condition of helium sweeping. This is because that vacuum condition avoids the resistance caused by counter-diffusion of the sweeping gas in the substrate porosity and IL film.

This thesis research demonstrated that the colloidal silicalite layer was effective in forming defect-free IL membrane with reduced IL loading. However, because the porous alumina (disc) support used in this work had a relatively small average pore size with broad size distribution, there is large amount of pores throughout the alumina disc with sizes close to the inter-particle pore size in the silicalite layer. Thus, a large portion of the IL was taken into the small pores of the alumina substrate when filling up the inter-particle spaces in the zeolite top layer. The IL loaded in the alumina substrate increases the resistance for gas transport that leads to lower CO₂ permeance. For future work, it is suggested that base substrates with pore size much larger than the zeolite inter-particle pores should be used to minimize the penetration of IL into the base support.
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Chapter 1 Introduction

1.1 CO₂ Capture

The increasing concerns over global warming effects have drawn public attention to emission of greenhouse gases, especially carbon dioxide (CO₂). CO₂ generated by human activities is primarily resulted from combustion of fossil fuels (coal, petroleum and natural gas) and chemical productions¹. Coal-firing power plants are responsible for roughly a third of the human-made CO₂ emission in the United States and this situation is anticipated to continue in the foreseeable future. Also, coal-firing electricity production is predicted to grow in the next couple of decades in fast developing countries such as China and India. CO₂ capture and sequestration (CCS) for coal-firing processes is therefore critical to the mitigation of CO₂ emission. Among the currently proposed three methods of CO₂ capture, namely the pre-combustion CO₂ capture, post-combustion CO₂ separation, and oxy-combustion, only the post-combustion approach is realistically applicable for retrofitting the large number of existing coal-firing power plants. Success of the post-combustion strategy depends on the availability of cost-effective technologies for CO₂ capture, which involves CO₂ separation from N₂ and a number of coexisting gas impurities.²,³ There are three major separations methods for CO₂ capture from combustion flue gases — liquid absorption, solid adsorption, and membrane permeation. Gas-liquid absorption, which uses physical solvents or chemical solvents, has many advantages, such as well-established process design and operation, high gas solubility and selectivity. Some liquid solvents, such as glycols and aqueous amines, have been extensively studied and used in industry for large scale CO₂ capture.⁴⁻⁹ Adsorption by solid adsorbents has similar advantages as gas-liquid absorption in terms of technology readiness. Most solid sorbents are made of porous solids or high-surface-area particulates, such as activated carbon, zeolites, and other porous silica-based materials. The primary mode of CO₂ uptake is physisorption, resulting from interactions between the gas and the material surface.¹⁰⁻¹² The solvent scrubbing and pressure swing adsorption (PSA) processes are intermittent and energy-intensive operations that make them economically inefficient for the purpose
of massive scale CO$_2$ separation for sequestration.

Membrane based separation is a promising alternative technology for energy-efficient, reliable and environmentally benign carbon capture. Most industrial membranes for CO$_2$ separation (e.g. in CO$_2$ removal from nature gas) are polymer membranes$^{13}$ They separate gases by solution-diffusion mechanism. Some inorganic membranes, such as zeolite membranes and microporous silica membranes also showed potential for industrial applications because of their high permeance and good selectivity. However, membrane separation of CO$_2$ from combustion flue gases is currently expensive in terms of cost of energy primarily due to the lack of low-cost membranes that can provide both high CO$_2$ selectivity and permeance.

1.2 Ionic Liquids

In searching for more energy-efficient and environmentally friendly CO$_2$-capture methods, ionic liquids (ILs) have recently attracted broad interests as absorbents and liquid membrane materials for CO$_2$ separations.$^{14}$ Ionic liquids (ILs) are a family of liquid state salts of which the molecules typically consist of an organic cation and an inorganic or organic anion. ILs are considered green solvents because of their nontoxic nature with extremely low vapor pressures even at elevated temperatures (e.g., around 100 °C) and thermal stability up to a few hundred degrees Celsius. Many ILs can dissolve CO$_2$ with high selectivity over other gases involved in coal-firing flue gases except for SO$_2$ which may have higher solubility than CO$_2$.$^{15}$ The dissolved CO$_2$ molecule locates between the cation and anion of the IL and the weak CO$_2$-IL interaction, primarily van de Waals force, allows for CO$_2$ desorption without significant heat consumption.$^{16}$

CO$_2$ capture ability can be enhanced by modifying ILs with specific functional groups. Due to the unique characteristics of ILs, alkaline group such as -NH$_2$ can be attached to the structure of cations or anions of ILs. Experimental studies showed that the molar uptake of CO$_2$ per mole of amino-functionalized task-specific ionic liquids (TSIL) reached 0.5, which is the theoretical maximum for CO$_2$ sequestration as an ammonium carbamate salt. The molar uptake of CO$_2$ by the
amine-appended TSIL is comparable to those of standard sequestering amines such as monoethanolamine (MEA), β,β’-hydroxyaminoethyl ether (DGA), and diisopropanolamine (DIPA). The process of CO₂ absorption is reversible. CO₂ can be released from the IL by heating to 80-100 °C under vacuum pressures. The recovered IL has been repeatedly used for CO₂ sorption without appreciable loss of efficiency. The high selectivity and solubility for CO₂, excellent thermal stability, and ease of regeneration (CO₂ desorption) are very desirable for physical ILs to be used in CO₂ capture by solvent scrubbing processes. However, industrial applications of the IL scrubbing processes have been discouraged by the prohibitive cost of large volume ILs and low mass transfer rates caused by their high viscosity.

1.3 Supported Ionic Liquid Membranes

CO₂-selective ILs have been made into supported membranes, which could offer a number of advantages including minimal amount of IL needed, continuous operation mode, stability in porous support because of its high viscosity and negligible volatility, and more importantly, better energy efficiency and readiness for retrofitting existing plants. Supported IL membranes are typically formed by loading ILs in porous substrates of polymeric or ceramic materials using liquid impregnation or infiltration techniques. There have been several reports on the use of porous hollow fibers as IL supports to achieve large membrane packing densities (area per volume, m²/m³) that are critical to large scale applications.

The number of publications on IL solvent and membrane development for CO₂ separations has been fast growing for the past decade. So far, the research efforts have been largely focused on measuring IL thermodynamic and transport properties, studying CO₂ selectivity and permeance for pure gases and simple binary mixtures, and finding new or modifying existing ILs for enhanced separation performances. Figure 1.1 presents the Robeson up boundary of CO₂ separation by supported IL membranes up to 2013. The chemical composition and molecular structure of IL has significant effects on CO₂ permeability and CO₂/N₂ separation factor. The [bmim][PF₆] and
[bmim][Tf₂N] showed CO₂ permeability up to 4×10⁻¹² mol/m·s·Pa with CO₂/N₂ separation factors of less than 15. [bmim][BF₄] demonstrated high CO₂/N₂ separation factor of up to 86 while the CO₂ permeability was only ~9×10⁻¹⁴ mol/m·s·Pa. Also, some task-specific ionic liquids (TSIL) were studied for CO₂ capture. TSIL can enhance CO₂ capture ability by adding functional groups, such as amino groups. Kasahara et al. fabricated CO₂-selective membranes containing amino acid ionic liquids (AAIL-FTMs). A tetrabutylphosphonium proline-based FTMs showed a good CO₂ permeability of 4.7×10⁻¹² mol/m·s·Pa, and a CO₂/N₂ separation factor of 100 at 373 K under dry condition.

Anion effects on IL membrane properties have also been studied by several groups. Scovazzo et al. studied [emim]⁺ based RTIL-membranes made from the following water-stable anions: [Tf₂N]⁻, [CF₃SO₃]⁻, [Cl]⁻ and [dca]⁻. They reported CO₂ permeability of 1.17×10⁻¹³ mol/m·s·Pa (for [Cl]⁻) and 3.35×10⁻¹³ mol/m·s·Pa (for [Tf₂N]⁻) with CO₂/N₂ permselectivity of 15 (for [Cl]⁻) and 61 (for [dca]⁻).

Albo et al. studied four paramagnetic ionic liquid membranes, including [P₆,₆,₆,₁₄][CoCl₄], [P₆,₆,₆,₁₄][FeCl₄], [P₆,₆,₆,₁₄][MnCl₄] and [P₆,₆,₆,₁₄][GdCl₆] in combination with PVDF supports. The CO₂ permeability ranged from 5.1×10⁻¹⁴ (for [CoCl₄]²⁻) to 9.0×10⁻¹⁴ (for [FeCl₄]⁻) mol/m·s·Pa and their CO₂/N₂ separation factor ranged from 23 (for [CoCl₄]²⁻) to 41 (for [MnCl₄]²⁻). The Polymer substrate used in literature had typical thicknesses ranging from 40 to 300 μm, which led to CO₂ permeance in the order of 10⁻⁸ mol/m²·s·Pa or lower. Efforts have been made to increase membrane packing density using porous hollow fiber supports. The PVDF hollow fiber-supported [emim][Tf₂N] IL membrane was reported with a CO₂ permeability of over 8.7×10⁻¹³ mol/m·s·Pa. Various ionic liquid membranes on α-alumina hollow fiber supports displayed CO₂ permeance of 5~50×10⁻¹⁰ mol/m²·s·Pa combined with CO₂/CH₄ permselectivity of 5~30. Close et al. reported improved IL membrane thermal stability and mechanical strength in alumina supports. They fabricated membranes of seven ionic liquids containing different alkyl imidazolium cations and bis(trifluoromethylsulfonyl)imide, acetate and trifluoroacetate anions. The CO₂ permeability values of
these membranes was greater than $3.4 \times 10^{-13}$ mol/m·s·Pa with CO$_2$/N$_2$ permselectivity between 12 and 21.

**Figure 1.1** The Robeson boundary (2013) of supported IL membrane for CO$_2$/N$_2$ separation: experimental data on CO$_2$/N$_2$ selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) vs. CO$_2$ permeability ($P_{b,\text{CO}_2}$).

In summary, supported IL membranes have shown potential for possible CO$_2$ separation from fossil fuel combustion flue gases. Literature reports however are still very limited on IL membrane performance evaluation as functions of operation conditions, e.g. temperature, partial pressure, and impurity etc., and the CO$_2$ selectivity and permeance of the current IL membranes are still requiring significant improvements for practical considerations.

*Generally, the CO$_2$ flux for a given IL membrane material can be effectively enhanced by (1) minimizing the thickness of the IL membrane, (2) improving supported membrane structure for larger active area, (3) increasing the separation temperature for increased diffusivity, and (4) increasing the feed side CO$_2$ partial pressure for larger transport driving force. Increasing feed pressure requires*
large energy consumption for compression of gas containing mainly N₂ and is therefore undesirable from the economic standpoint. Instead, research has indicated that using vacuum pressure on the permeate side is a more energy-efficient way to provide driving force for CO₂ separation because, in this case, the volume work is needed only for the produced CO₂ stream.

1.4 Research Objectives

The goal of this research is to investigate a new type of colloidal-zeolite thin film supported ionic liquid membranes for enhanced CO₂ gas separation. The research will focus on the proof-of-concept of the proposed IL membranes using colloidal silicalite (i.e. pure silica MFI-type zeolite) coated alumina as substrates and [bmim][BF₄] as the ionic liquid membrane material. The [bmim][BF₄] IL is selected because of its well-characterized thermodynamic and transport properties. The thesis research includes membrane preparation and measurements of CO₂ selectivity and permeance for various gas mixtures as a function of operating temperature and CO₂ partial pressure. The specific objectives of this research are to:

(1) synthesize nanometer sized (<100 nm in diameter) silicalite spheres and fabricate colloidal silicalite top layers (a few µm thick) on disc-shaped macroporous α-alumina substrates;
(2) fabricate IL membranes on the silicalite-coated alumina substrates;
(3) examine the supported IL thin membrane for CO₂ separation from CO₂/N₂ mixtures in a temperature range from room temperature to 120 °C and as a function of CO₂ feed partial pressure.
(4) study the effects of common impurities (such as water vapor and SO₂) on CO₂ separation performance of the IL membrane.
1.5 Thesis Structure

This thesis includes four chapters. In Chapter 1, the background of this thesis research is briefly introduced followed by a statement of the proposed research objectives. Chapter 2 focuses on the synthesis and characterization of the nanometer sized silicalite particles and the fabrication of colloidal silicalite films on alumina substrates and the supported IL membranes (SILMs). In Chapter 3, the SILMs are tested for CO$_2$/N$_2$ separation and the influences of temperature, CO$_2$ partial pressure, and the presence of water vapor and SO$_2$ are experimentally investigated. Chapter 4 provides a brief summary of the results and main finding of this thesis research.
Chapter 2 Fabrication and Characterization of Colloidal Zeolite Membrane-Supported Ionic Liquid Membranes

2.1 Introduction

Zeolites are crystalline aluminosilicate materials possessing a three-dimensional framework structure formed by TO₄ tetrahedrons (T = Si, Al) units. Zeolites have uniform and ordered pores of molecular dimensions with pore openings defined by rings of interconnected tetrahedrons. Zeolite pore sizes can vary from 0.3 nm to over 1 nm depending on the crystalline structure. The pore volumes of zeolites are typically in a range of 0.10-0.35 cm³/g with enormous internal surface areas of 400-1000 m²/g. Zeolites can thus achieve molecular sieving effect by admitting molecules of kinetic sizes smaller than their effective pore size while excluding molecules that are too large to enter the zeolitic pore opening. The conventional industrial applications of zeolites include molecular adsorbents, shape-selective catalysts, ion exchangers and molecular sieve membranes. New applications of zeolites include zeolite-based sensors, catalysts for photochemical organic transformations, and conversion of solar energy.

Zeolites have been extensively studied as adsorbents and membranes for CO₂ separation. Among many zeolites investigated in the literature, the MFI-, FAU-, DDR- and SAPO-34-type zeolites showed the greatest potential for CO₂ separation. The pure silica-MFI zeolite, also called silicalite, has an effective pore size of 0.56 nm and is known to be CO₂ permselective over non-adsorbing or weakly adsorbing gases like H₂, N₂, and O₂ etc. The silicalite is also well-known of its extremely high thermochemical stability in corrosive environments. Thus silicalite was selected as the substrate material for supporting the IL membranes in this work. Also, to provide necessary mechanical strength of the supported IL membrane, the zeolite colloidal film was coated on a strong macroporous alumina thick support.
MFI-type zeolite is one of the most intensively studied zeolite materials. Spherical particles of silicalite have been synthesized with diameters around tens of nanometers. In this chapter, nanometer-sized silicalite spheres were synthesized by the conventional in-situ crystallization process. The silicalite nanoparticles were coated on the macroporous alumina disc to form a colloidal film by dip-coating method. The [bmim][BF₄] IL was then loaded into the zeolite-coated disc support.

2.2 Membrane Preparation

2.2.1 Synthesis of Zeolite Nanoparticles

Materials and chemicals: The chemicals used in this work included fumed silica powders (99.8%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 1M solution, Aldrich), sodium hydroxide (99.998%, pellet, Aldrich), aluminum sulfate (Al₂(SO₄)₃ · 18H₂O, >98%, Aldrich), Hydroxyl propyl cellulose (HPC, Mw=100,000, Aldrich), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄], >98%, TCI). The carbon dioxide (bone dry), nitrogen (UHP), helium (UHP), oxygen (extra dry), air (breathing quality) and 500 ppm and 20% CO₂ in balanced air (certified mixture) gases were obtained from Wright Brothers, Inc.

Synthesis procedure: The procedures for synthesis of nanometer-sized silicalite spheres (diameter controllable in a range of 60-120 nm) have been previously established in our group using either conventional heating or microwave heating method. In this work, the silicalite nanoparticles were prepared by conventional heating method. The zeolite synthesis precursor solution had a molar ratio of 0.33(SiO₂): 0.1(TPAOH): 0.035(NaOH): 5.56(H₂O). This precursor was obtained by dissolving appropriate amounts of fumed silica and NaOH pellets in 1M TPAOH solution at 80 °C under rigorous stirring. The TPAOH was used as the structure directing agent (SDA) in crystallization which was later removed from the zeolitic pores by firing in air at high temperature (>400 °C). The precursor was aged at room temperature for 4 h before hydrothermal treatment. The hydrothermal crystallization reaction was conducted in a Teflon-lined autoclave at 60 °C for 15 days to obtain a
particle size of 60-80 nm. After the hydrothermal crystallization process, the resultant silicalite nanoparticle slurry was washed in DI water with the assistance of centrifuge.

Aluminum-containing MFI-type zeolite (i.e. ZSM-5) particles were also synthesized by the same procedure as described above using various Si/Al atomic ratios in the synthesis precursor. The precursor solution for ZSM-5 zeolite particle synthesis had a molar composition of 0.33(SiO$_2$): 0.1(TPAOH): 0.035(NaOH): 5.56(H$_2$O): xNaAlO$_2$. The value of “x” was varied for different Si/Al ratios. Appropriate amounts of sodium aluminate (NaAlO$_2$) and NaOH pellets were first dissolved in 1M TPAOH solution. Fumed silica was then added to the solution and dissolved at 80 °C under stirring. The precursor was aged at room temperature for 4 h before hydrothermal reaction. The hydrothermal synthesis temperature and duration for precursors of different Si/Al ratios are listed in Table 2.1. After hydrothermal synthesis, the resultant ZSM-5 zeolite nanoparticle slurry was washed in DI water with the assistance of centrifuge until the suspension pH reached ~7.0.

2.2.2 Coating Colloidal Silicalite Film on α-Alumina Substrate

The membrane substrates used in this study were home-made porous α-alumina discs (2 mm thick and 27 mm in diameter). The disc was made of α-alumina powders (average diameter of 0.48 μm, SG-16, Alcoa) by dry pressing and sintering process. The porosity and mean pore size of the substrates were about 30% and 70-100 nm, respectively. One side of the alumina disc (for coating the zeolite film) was sequentially polished by #320 and #800 SiC sand papers. After being cleaned with DI water and dried, the sides and edges of the polished discs were sealed with glass coatings. The active membrane area was 2.54 cm$^2$ after sealing the edge of the disc.

The suspension for coating colloidal silicalite thin films consisted of silicalite nanoparticles, HPC and DI water and peptized by HNO$_3$ solution. The HPC was used as binder and drying control agent. In preparation of the HPC solution, 0.25g HPC powder was added into 50 ml DI water in a 250 ml glass flask and stirred at room temperature for 45 minutes followed by 2-h stirring at 50 °C. Certain amounts of silicalite suspension, 0.5% HPC solution and DI water were mixed to form a 10g
suspension. The redispersed silicalite suspension was then peptized by 1M HNO₃ solution. The final stable colloidal silicalite suspension had a pH of 3–4. After stirring for 4 h at room temperature, the suspension was ready for dip-coating.

The silicalite content and HPC concentration of the colloidal suspension were optimized to achieve uniform and defect-free zeolite colloidal thin films, which will be discussed later in this chapter. Repetition of the dip-coating process was used in most cases to repair cracks or pinholes that could possibly form during the coating, drying, and firing processes. The zeolite films were obtained by a 5-second contacting time for the dip-coating step. The wet films were dried at 40 °C for two days and then fired at 450 °C for 8 h to remove the template molecules from the intracrystalline zeolitic pores of the silicalite and consolidate the colloidal film.

**2.2.3 Fabrication of IL Membrane on the Supported Colloidal Silicalite Film**

The colloidal silicalite film-coated alumina disc was used to support the [bmim][BF₄] IL membrane. Meanwhile, the α-alumina substrate without a zeolite coating was also used for loading IL for comparison. The IL was loaded by a simple brush-coating method. The disc substrate was held horizontally on a stand with the zeolite coated surface facing downward. The IL was brushed on the surface of the colloidal zeolite film surface. The brush coating was repeated once after the first brush-coating to ensure that IL covered the entire substrate surface. The IL-loaded disc was allowed to set for 1 min and then any excessive IL remaining on the surface was removed by gently wiping with a powderless tissue. The amount of the IL loaded was determined by weighing the disc before and after IL loading. The thickness of the IL layer was estimated based on the substrate porosity and the amount of IL loaded. However, it must be noted that the thus estimated IL membrane thickness is likely to be inaccurate because the substrate had a broad pore size distribution which could lead to IL-uptake in small pores throughout the disc thickness but not limited within a clear-cut depth.
2.2.4 Test of the IL membrane Integrity

To evaluate the integrity of the IL membrane loaded in the substrates, single gas permeation tests were performed at 25 °C and atmospheric pressure for N₂ and CO₂, respectively. During the experiments, N₂ or CO₂ gas was fed to the IL side of the membrane at a flow rate of 20 cm³(STP)/min and the other side was swept by He at a flow rate of 10 cm³(STP)/min. The membrane flux of gas \( i \) (\( J_{ai} \), mol/m²·s) was calculated by

\[
J_i = \frac{Q_i}{t \cdot A_m}
\]  

(2-1)

Where \( Q_i \) (mol) is the amount of gas \( i \) permeating though a membrane area \( (A_m) \) in a time period of \( t \). The gas permeance of the membrane \( (P_{m,i}, \text{mol/m}^2\cdot\text{s}\cdot\text{Pa}) \) is defined by

\[
P_{m,i} = \frac{Q_i}{\Delta p_i} = \frac{Q_i}{(p_{i,f} - p_{i,perm}) \cdot t \cdot A_m}
\]  

(2-2)

Where \( \Delta p_i \) (Pa) is the transmembrane partial pressure of gas \( i \); and \( p_{i,f} \) and \( p_{i,perm} \) are partial pressures (Pa) of gas \( i \) in the feed and permeate sides, respectively. The N₂/CO₂ ideal selectivity (i.e. permselectivity, \( \alpha_{CO2/N2}^{o} \)) is given by the ratio of CO₂ and N₂ pure gas permeance:

\[
\alpha_{CO2/N2}^{o} = \frac{P_{m,CO2}}{P_{m,N2}}
\]  

(2-3)

Where \( P_{m,CO2} \) and \( P_{m,N2} \) are permeance values measured using single gas feed.

2.3 Results and Discussion

2.3.1 Zeolite Nanoparticles

As shown in Figure 2.1, the XRD patterns of the synthesized particles matched exactly with the standard XRD pattern of MFI zeolite powders.
Figure 2.1 XRD patterns of calcined silicalite nano-particles and colloidal silicalite membrane coated on the alumina support together with the standard XRD pattern of silicalite powders.

Table 2.1 presents the particles synthesized under various conditions to investigate the effects of synthesis temperature, aluminum content, and synthesis duration on the size and morphology of the resultant particles. The SEM pictures and XRD results are shown in Figure 2.2 and Figure 2.3, respectively. When the precursor had a Si/Al=15 and hydrothermal reaction temperature was varied from 120 °C to 160 °C, the XRD patterns show that the resultant solids were amorphous and no zeolite crystal was formed after synthesis duration of 24 h. When the Si/Al was increased to 25, the XRD patterns indicate that zeolite was formed at 150 °C after 24 h reaction but the solid particles exhibited irregular shapes which are likely due to the existence of significant amounts of amorphous materials. When the precursor had a Si/Al=50, nearly spherical ZSM-5 zeolite crystals were
successfully synthesized with particle size of ~150 nm and ~350 nm after reaction for 24 h at 120 °C and 150 °C, respectively. From these experiments, it was found that Si/Al ratio is the most influential parameter affecting zeolite formation and crystal growth in the conditions of this study. Zeolite forms only when Si/Al ratio is high enough within the relatively short durations. The crystal size can be varied effectively by controlling the hydrothermal reaction temperature. Extended synthesis duration does not necessary result in bigger zeolite particle probably because of lack of reactant for further zeolite growth after the vast amount of nucleation and initial crystal growth. Because the smallest ZSM-5 zeolite particle size achieved in this work was around 150 nm, which is still too large to form inter-particle pore small enough for preferential loading of IL over the ~70nm pore alumina support, IL membrane was not loaded on the ZSM-5 zeolite film coated alumina disc. Further investigation is needed to synthesize sufficiently small ZSM-5 particle.
Table 2.1 ZSM-5 synthesis conditions and results

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Si/Al ratio in precursor</th>
<th>Synthesis temperature, °C</th>
<th>Synthesis duration, h</th>
<th>ZSM-5 crystal</th>
<th>Si/Al ratio in zeolite</th>
<th>Particle size, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z01</td>
<td>15</td>
<td>120</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z02</td>
<td>15</td>
<td>140</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z03</td>
<td>15</td>
<td>150</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z04</td>
<td>15</td>
<td>160</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z05</td>
<td>25</td>
<td>120</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z06</td>
<td>25</td>
<td>140</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z07</td>
<td>25</td>
<td>150</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z08</td>
<td>25</td>
<td>160</td>
<td>24 h</td>
<td>No</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Z09</td>
<td>50</td>
<td>120</td>
<td>24 h</td>
<td>Yes</td>
<td>~40</td>
<td>~150</td>
</tr>
<tr>
<td>Z10</td>
<td>50</td>
<td>150</td>
<td>24 h</td>
<td>Yes</td>
<td>~20</td>
<td>~350</td>
</tr>
<tr>
<td>Z11</td>
<td>50</td>
<td>100</td>
<td>36 h</td>
<td>Yes</td>
<td>~27</td>
<td>~150</td>
</tr>
<tr>
<td>Z12</td>
<td>50</td>
<td>100</td>
<td>72 h</td>
<td>Yes</td>
<td>~22</td>
<td>~150</td>
</tr>
</tbody>
</table>
Figure 2.2 SEM images of the synthesized ZSM-5 zeolite nanoparticles by conventional heating under various synthesis conditions: (Z01) Si/Al=15, 120°C for 24 h, (Z05) Si/Al=25, 120°C for 24 h (Z06) Si/Al=25, 140°C for 24 h, (Z07) Si/Al=25, 150°C for 24 h, (Z09) Si/Al=50, 120°C for 24 h, (Z10) Si/Al=50, 150°C for 24 h, (Z11) Si/Al=50, 100°C for 36 h, and (Z12) Si/Al=50, 100°C for 72 h.
Figure 2.3 XRD patterns of as synthesized ZSM-5 zeolite particles by different synthesis conditions together with the spectrum of standard MFI zeolite.
2.3.2 Supported Colloidal Zeolite Thin Film

**Effect of HPC Concentration:** Concentration of the binder HPC, which was also used as suspension viscosity modifier and drying control agent for prevention of crack formation, has critical influence on the coating results. Figure 2.4 shows the SEM images of the substrates with colloidal silicalite layers obtained by dip-coating using suspensions containing 0.5wt% silicalite solid but varied HPC contents of 0.1wt%, 0.2wt% and 0.3wt%, respectively. As shown in Figure 2.4, the silicalite film (S02) dip-coated from the suspension with 0.2wt% HPC was densely packed with uniform thickness (~2-3 μm) and no obvious cracks. Small cracks penetrating through the zeolite film thickness were clearly seen in the films obtained from the suspensions containing 0.1wt% and 0.3wt% HPC. Thus, the HPC content of 0.2wt% was used for future suspension preparation in this work.
Figure 2.4 SEM images of colloidal silicalite layers on alumina substrates obtained from suspensions containing: (S01) 0.5% silicalite and 0.1% HPC (left–surface and right–cross section); (S02) 0.5% silicalite and 0.2% HPC (left–surface and right–cross section); and (S03) 0.5% silicalite and 0.3% HPC (left–surface and right–cross section).
**Effect of Silicalite Content:** The silicalite top layer thickness can be controlled by varying the solid content of the suspension. The solid content of the suspension were varied in order to identify proper conditions for coating membranes with smooth surface and minimized defects. Figure 2.5 shows the surface SEM images of the supported silicalite layers obtained by dip-coating using suspension containing 0.2wt% HPC and varied silicalite content of 0.3wt%, 0.4wt%, 0.5wt% and 0.8wt%, respectively.
Figure 2.5 SEM images of the silicalite layers on substrates obtained dip-coating from suspensions containing: (S04) 0.3\% silicalite and 0.2\% HPC (left–surface and right–cross section); (S05) 0.4\% silicalite and 0.2\% HPC (left–surface and right–cross section); (S02) 0.5\% silicalite and 0.2\% HPC (left–surface and right–cross section); and (S06) 0.8\% silicalite and 0.2\% HPC (left–surface and right–cross section).
For the suspension with 0.3% silicalite solid, the top layer thickness was ~1 µm by single coating; the thickness increased to 4 µm when a 0.8%-silicalite suspension was used. However, when solid content is too high, for example 0.8%, the colloidal film often contained cracks after drying and firing. It was found that uniform crack-free colloidal silicalite layer could be obtained with excellent reproducibility using the suspension containing 0.4% of silicalite particles and 0.2% of HPC. The colloidal silicalite film obtained by single coating had a thickness of 2~3 µm. In rare cases, some small cracks or non-uniform coverage were found on the film surface as shown by an example in S05 of Figure 2.6. Therefore, in this work, dip-coating process was repeated once for all films using a suspension containing 0.2% of silicalite particles and 0.2% of HPC to ensure full coverage and repair any possible cracks. The surface quality can be significantly improved by the second coating as shown in S07 of Figure 2.6. Table 2.2 summarizes the results of film coating from different suspensions.
Figure 2.6 SEM images of the colloidal silicalite layer on substrates showing defects in (S05) single time dip-coated film using suspension containing 0.4% silicalite and 0.2% HPC and improvement by a second time dip-coating (S07) using a suspension containing 0.2% silicalite and 0.2% HPC.
Table 2.2 Results of film formation by dip-coating using different suspension compositions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Silicalite weight content</th>
<th>HPC weight percentage</th>
<th>Coated times</th>
<th>Thickness, µm</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01</td>
<td>0.5%</td>
<td>0.1%</td>
<td>1</td>
<td>~2</td>
<td>Cracks</td>
</tr>
<tr>
<td>S02</td>
<td>0.5%</td>
<td>0.2%</td>
<td>1</td>
<td>~2.5</td>
<td>Cracks</td>
</tr>
<tr>
<td>S03</td>
<td>0.5%</td>
<td>0.3%</td>
<td>1</td>
<td>~2</td>
<td>Cracks</td>
</tr>
<tr>
<td>S04</td>
<td>0.3%</td>
<td>0.2%</td>
<td>1</td>
<td>~1</td>
<td>Particle penetration into substrate and cracks</td>
</tr>
<tr>
<td>S05</td>
<td>0.4%</td>
<td>0.2%</td>
<td>1</td>
<td>~2.5</td>
<td>Mostly crack-free</td>
</tr>
<tr>
<td>S06</td>
<td>0.8%</td>
<td>0.2%</td>
<td>1</td>
<td>~4</td>
<td>Poor adhesion, cracks</td>
</tr>
<tr>
<td>S07</td>
<td>0.4% (1st time)</td>
<td>0.2% (1st time)</td>
<td>2</td>
<td>~3</td>
<td>Crack-free</td>
</tr>
<tr>
<td></td>
<td>0.2% (2nd time)</td>
<td>0.2% (2nd time)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3.3 Colloidal Zeolite Supported IL Membrane

The IL membrane was fabricated by brush-loading on the colloidal silicalite-coated substrate and bare alumina substrate for comparison. A summary of the results of integrity tests for the IL membranes supported on colloidal silicalite film and the bare alumina support is presented in Table 2.3. The membranes were also tested by separation of CO₂/N₂ binary mixtures and the results are shown in Figure 2.7.
Table 2.3 Gas permeation results for the IL membranes supported on the colloidal silicalite-coated alumina disc and the bare alumina substrate (at 25 °C)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>IL load, mg/cm²</th>
<th>IL thickness*, mm</th>
<th>$P_{m,N₂}$, $10^{-10}$ mol/m².s.Pa</th>
<th>$P_{m,CO₂}$, $10^{-10}$ mol/m².s.Pa</th>
<th>$α_{CO₂/N₂}^p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare alumina (No IL)</td>
<td>0</td>
<td>NA</td>
<td>7290</td>
<td>5870</td>
<td>0.8</td>
</tr>
<tr>
<td>Silicalite-coated</td>
<td>0</td>
<td>NA</td>
<td>6750</td>
<td>5350</td>
<td>0.8</td>
</tr>
<tr>
<td>alumina (No IL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicalite-coated</td>
<td>20</td>
<td>0.499</td>
<td>3.52</td>
<td>62.7</td>
<td>17.8</td>
</tr>
<tr>
<td>alumina</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare alumina</td>
<td>19</td>
<td>0.461</td>
<td>876</td>
<td>877</td>
<td>1.0</td>
</tr>
<tr>
<td>Bare alumina</td>
<td>37</td>
<td>0.910</td>
<td>385</td>
<td>431</td>
<td>1.1</td>
</tr>
<tr>
<td>Bare alumina (Fully soaked)</td>
<td>83</td>
<td>2.06</td>
<td>0.987</td>
<td>0.596</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* The thickness was calculated based on the cross-section area of the pores in substrate that is likely not the true depth of IL prenatration into the substrate. ** Theoretical value of IL-load under full load in porosity was 70~80 mg/cm².

For the colloidal silicalite-coated substrate, a continuous and pinhole-free IL membrane was obtained with an IL-load of 20 mg/cm². The successful formation of defect free IL film is indicated by the drastic decrease in N₂ permeance ($P_{m,N₂}$) and increase in $α_{CO₂/N₂}^p$ as compared to the values before loading IL. The $P_{m,N₂}$ and $α_{CO₂/N₂}^p$ changed from $3\times10^{-7}$ mol/m²·s·Pa and 0.9, respectively,
before IL loading to $3.52 \times 10^{-10}$ mol/m$^2 \cdot$ s·Pa and 17.8, respectively, after IL loading. Without IL loading, the CO$_2$/N$_2$ permselectivity was only slightly greater than the Knudsen diffusion selectivity ($\alpha_{CO2/N2,Knudsen}^e = \sqrt{M_{N_2}/M_{CO2}} = 0.8$) because of the gas flow was mainly by gaseous diffusion through the nanometer scale inter-particle pores with very small contributions from the CO$_2$ selective permeation through the zeolitic pores$^{41}$.

It was observed that no continuous and defect free IL membrane could be obtained in the bare alumina substrate before the disc was fully soaked. In the bare substrate, increasing the IL load from 19 to 37 mg/cm$^2$ reduced the $P_{m,N2}$ by about 60% from $8.76 \times 10^{-8}$ mol/m$^2 \cdot$ s·Pa to $3.85 \times 10^{-8}$ mol/m$^2 \cdot$ s·Pa but $\alpha_{CO2/N2}^e$ remained nearly unchanged at 1.0~1.1, which was only slightly greater than the $\alpha_{CO2/N2,Knudsen}^o$. The near Knudsen-factor $\alpha_{CO2/N2}^e$ values suggest that gas permeation was mainly through the unclosed large pores in the alumina support. When that alumina disc was fully soaked with IL after immersing the disc in IL, the $P_{m,N2}$ values decreased to near zero ($<10^{-10}$ mol/m$^2 \cdot$ s·Pa) because of the very large thickness of the IL film. In this case, the very minimal non-selective gas leaking through sealing defects appeared to be significant in relative contribution to the total flux that resulted in an $\alpha_{CO2/N2}^o$ of 0.6.
(a)

(b)

(c)
Figure 2.7 Results of CO₂/N₂ mixture permeations with and without IL loading. (a) N₂ and CO₂ flux, (b) N₂ permeance, (c) CO₂ permeance, (d) CO₂/N₂ selectivity.

The inability of the IL to form a defect-free membrane in the bare alumina substrate can be attributed to the fact that the alumina disc has larger pores (average diameter ~70nm) and broad pore size distribution (PSD). With the broad PSD, IL fills into the smaller pore spaces as depicted in Figure 2.8 (a). When the colloidal silicalite top layer exists, the smaller and more uniform PSD of the zeolite layer has a stronger capillary force to retain the IL and help the formation of a defect-free IL film. However, the substrate used in this study had a pore size that was not significantly larger than that of the inter-particle pore and hence a substantial amount of IL penetrates into the alumina disc where the pore sizes are similar to or even smaller than the average pore size of the top layer.
Figure 2.8 Schematic illustration of IL loading in (a) Non-uniform large pore thick substrate and (b) Colloid silicalite coated substrate.

2.4 Conclusion

Silicalite nano-particles were synthesized from a precursor solution with a molar composition of 0.33(SiO$_2$): 0.1(TPAOH): 0.035(NaOH): 5.56(H$_2$O). The silicalite particles were nearly spherical with an average size of ~70 nm. The colloidal silicalite layer on porous alumina disk was fabricated by dip-coating from a colloidal suspension of the silicalite nanoparticles using HPC as binder for drying control and crack prevention. The optimal suspension had a zeolite solid content of 0.4wt.% silicalite with 0.2wt.% of HPC. Dip-coating was conducted for the second time using a suspension containing 0.2wt.% silicalite and 0.2wt.% HPC to minimize possible cracks and defects existed after the first coating. The colloidal silicalite layer had a uniform thickness of 2-3 μm. [bmim][BF$_4$] ionic liquid was loaded into the colloidal silicalite-coated substrates by a simple brushing-soaking process. With an IL-loading of 20 mg/cm$^2$, continuous and pinhole free IL membrane was successfully formed on the colloidal silicalite film coated alumina substrate while no defect-free IL membrane could be obtained on the bare alumina disc support before its porosity was fully soaked. The CO$_2$ permeance and CO$_2$/N$_2$ separation selectivity of the silicalite supported [bmim][BF$_4$] membrane were comparable to the best values reported in the literature.
Chapter 3 Investigation of CO₂ Separation by the Supported Ionic Liquid Membrane

3.1 Introduction

The general principles of membrane gas separation apply to the supported IL membranes. For gas “a”, the permeability \( P_{ba,a} \) (mol/m·s·Pa) of a membrane is determined by the gas solubility \( C_{s,a} \) (mol/m³·Pa) and its transport diffusivity \( D_a \) (m²/s) in the membrane material:

\[
P_{ba,a} = C_{s,a} \times D_a
\]  

(3-1)

For a specific IL, the thermodynamic property \( C_{s,a} \) is a function of temperature and pressure and the \( D_a \) is theoretically dependent of temperature and molecular concentration. Henry’s law can be applied to the correlation of \( C_{s,a} \) with temperature when pressure of gas \( a (p_a) \) is low:

\[
C_{s,a} = H_a \times p_a; \quad H_a = H'_a \exp(-E_{s,a} / RT)
\]  

(3-2)

Where \( H_a \) is Henry’s constant (mol/m³·Pa) and \( E_{s,a} \) is heat of dissolution (or sorption) (J/mol). When IL is used as solvent for absorption, the CO₂/N₂ sorption selectivity \( \alpha_{sp,CO₂/N₂} \) is then obtained as following

\[
\alpha_{sp,CO₂/N₂} = \frac{C_{s,CO₂}}{C_{s,N₂}}
\]  

(3-3)

The transport diffusivity \( D_a \) is given by

\[
D_a = D'_a \exp(-E_{d,a} / RT)
\]  

(3-4)

Where \( E_{d,a} \) is the diffusion activation energy (J/mol) and \( D'_a \) is the pre-exponential coefficient. Because \( E_{s,a} < 0 \) (dissolution generates heat) and \( E_{d,a} > 0 \) (mass transport consumes energy), \( C_{s,a} \) decreases while \( D_a \) increases with increasing temperature; and thus the gas permeability often exhibits a maximum as a function of temperature, which is very similar to the temperature-dependence of permeability in adsorption-diffusion controlled solid state membranes. The permeance \( P_{m,a} \) (mol/m²·s·Pa), flux \( J \) (mol/m²·s), and flow rate (for a module, \( F \) mol/s) are given by:
\[ P_{m,a} = (P_{a} \cdot \varepsilon)/(\delta \cdot \tau) \]

(3-5)

\[ J_a = P_{m,a} (\Delta p_a) = P_{m,a} (p_{a,f} - p_{a,perm}) \]

(3-6)

\[ F_a = J_a \times S_m \times V_m \]

(3-7)

Where \( \delta \) is membrane thickness (m); \( \varepsilon \) is the porosity of the substrate hosting the IL membrane; \( \tau \) (\( \approx 1.5 \text{–} 2.0 \)) is the tortuosity; \( S_m \) is membrane packing density (m\(^2\)/m\(^3\)); \( V_m \) is the volume of the membrane module (m\(^3\)). The selectivity of CO\(_2\) over N\(_2\) (separation factor), \( \alpha_{CO2/N2} \), is defined as

\[ \alpha_{(CO2/N2)} = \frac{(y_{CO2} \times y_{N2})_{perm}}{(y_{CO2} \times y_{N2})_{f}} \]

(3-8)

Where \( y_{CO2} \) and \( y_{N2} \) are mole fractions of CO\(_2\) and N\(_2\), respectively; and subscripts “f” and “perm” denote feed side and permeate side, respectively. The membrane’s performance of CO\(_2\) separation is determined by its \( \alpha_{CO2/N2} \) and \( P_{m,CO2} \). In many cases, ideal selectivity, or so called permeaselectivity (\( \alpha_{CO2/N2}^{\circ} \)), is also used to characterization membrane separation properties. The permeaselectivity is defined as the ratio of permeance obtained from pure gas permeation, as expressed by equation (3-9). The permeaselectivity (\( \alpha_{CO2/N2}^{\circ} \)) is often different from the separation factor (\( \alpha_{CO2/N2} \)) when there is significant interaction between the two permeating gas molecules in the membrane.

\[ \alpha_{CO2/N2}^{\circ} = \frac{P_{m,CO2}}{P_{m,N2}} = \frac{C_{s,CO2} \times D_{CO2}}{C_{s,N2} \times D_{N2}} \]

(3-9)

The IL membrane separation performance can be significantly affected by operation conditions, such as temperature, feed pressure, feed composition, and impurities in feed stream. The temperature and pressure effects on CO\(_2\) solubility and diffusivity in [bmim][BF\(_4\)] have been studied in the literature.\(^{43}\) However, the N\(_2\) and air solubility and diffusivity in [bmim][BF\(_4\)] are so far not reported. In general, increasing pressure increases the amounts of gas sorption at a given temperature. Thus, increase the CO\(_2\) partial pressure in the feed is expected to enhance the CO\(_2\) flux until saturation is
reached at the feed side membrane/gas interface when the permeate side is effectively maintained at constantly low pressure. The gas diffusivity in the IL increases as temperature rises. Because CO$_2$ dissolution is exothermic and gas diffusion is activated (endothermic), the CO$_2$ permeability, which is the product of CO$_2$ solubility and transport diffusivity, may exhibit a maximum as a function of temperature and thus an optimum operating temperature exists depending on the IL properties.

The impurities in the feed stream can affect the sorption and transport of CO$_2$ and N$_2$ in ILs. Water vapor and SO$_2$ commonly exist in fossil fuel combustion flue gases. Zhao et al. studied the effect of water in [bmim][BF$_4$] on membrane CO$_2$/N$_2$ separation performance. The addition of small amount of water (<5mol%) into the [bmim][BF$_4$] was found to enhance both the CO$_2$ permeance and CO$_2$/N$_2$ selectivity. The increase of CO$_2$ permeance in the water-containing [bmim][BF$_4$] membrane was attributed to the consequential reduction of viscosity that increased CO$_2$ diffusivity. Okabe et al. studied the effect of SO$_2$ on CO$_2$/N$_2$ separation for a gel-supported IL-facilitated transport membrane. They found that CO$_2$ permeance decreased in the presence of SO$_2$. Overall, studies on the effects of operation conditions on CO$_2$ separation in IL membrane are quite limited, especially on factors that are relevant to practical applications.

In this study, the IL membrane supported on the colloidal silicalite coated alumina disc was investigated for pure gas permeation and CO$_2$ separation from mixtures that are related to CO$_2$ capture from coal-combustion flue gases. The separation performance, in terms of CO$_2$ permeance and selectivity, was experimentally investigated as functions of temperature, CO$_2$ partial pressure and the presence of various impurities.

3.2 Experimental Procedures

3.2.1 Gas permeation Test Setup

The supported IL membrane was tested for single gas permeation and CO$_2$ separation for a variety of mixtures using the apparatus schematically shown in Figure 3.1, which was a modification
of a previously reported membrane reactor system\textsuperscript{45}. The supported IL was mounted in a stainless steel cell by O-ring seals also schematically shown in Figure 3.1. The feed stream was regulated by mass flow controllers and flowed over the IL membrane surface. The outlet of the feed side (retentate) was analyzed by an online gas chromatographer (GC) and a mass spectroscope (MS). The permeate side of the membrane was either swept by a helium flow or vacuumed to create trans-membrane partial pressure difference as driving force, i.e., $\Delta P_i = \Delta P_{i,f} - \Delta P_{i,p}$, where $P_{i,f}$ and $P_{i,p}$ are the partial pressures of $i$ in the feed and permeate sides, respectively. When sweeping gas was used, the composition and flux of the permeate stream was measured by the online GC-MS system. The entire membrane permeator was hosted in an oven for temperature control and preheating coils were used to ensure that the feed and sweeping gases reached setting temperature before contacting the membrane.

![Figure 3.1 Schematic diagram of the membrane gas permeation measurement system (V4 and V5 are 3-way valves; V1, V2, V3 are stop valves).](image-url)
During the gas permeation and separation experiments, the membrane was purged with pure helium gas on both feed side and permeate side at 120 °C for overnight to removed dissolved gas residuals from prior experiment before a new permeation test. An 8 hour stabilization period was used when switching temperature, pressure, and feed gas composition. The permeation stabilization was confirmed by monitoring the permeate gas composition and flux. When two consecutive measurements performed at one hour apart gave a relative deviation of <2%, the system was considered reached steady state or stabilized.

The IL was examined by FTIR measurements before and after absorbing individual gases involved in the experiments to identify the interactions between the dissolved gas and the IL molecules and the type of absorption, i.e. chemisorption or physical sorption. Before each FT-IR test, the IL was first degased at 120 °C by stripping with helium at flow rate of 5 cm³ (STP)/min for overnight. The sample gas was then bubbled through 1 ml of degassed IL in a test tube for overnight at room temperature with a gas flow rate of 10 mL/min to ensure equilibration. The test tube was then sealed with a rubber stopper to prevent degassing or contamination by absorbing air components. The IL was taken immediately to conduct FTIR measurements. After FTIR test, the gas-absorbed IL was degased and then re-tested with FTIR to observe the reversibility of gas absorption.

3.3 Results and Discussion

3.3.1 FTIR Study of Gas Sorption in IL

Figure 3.2 presents the IR spectra of the IL sample after being treated in different conditions for gas absorption and desorption. As expected, dissolution of N₂ into the [bmim][BF₄] is a physical process that has caused no change in the IR spectrum of the IL. IR spectrum showed CO₂ peaks at wavenumber of 2342 cm⁻¹ after exposure to CO₂ with no other new peaks besides those of the IL, meaning that CO₂ absorption is also of physical type. Water peaks are found at wavenumber of 1634 and 3626 cm⁻¹ after exposing to saturate water vapor (3%) in helium at 25 °C and atmospheric pressure. Although SO₂ is reported to have high solubility in [bmim][BF₄] ⁴⁶, no SO₂ peaks were
found after the IL sample was equilibrated with the air containing 500 ppm SO₂ (specialty gas prepared and certified by Wright Brothers, Inc.). This is perhaps a result of the very low SO₂ concentration. In all cases, no new IR absorption peaks other than the characteristic peaks of the [bmim][BF₄] IL and individual gases appeared after different gas treatments, suggesting that absorptions of gases involved in this work are physical with weak gas-IL interaction. The characteristic peaks of CO₂ and water completely disappeared after the degassing process that indicates good reversibility of the absorption for all gas components.

Figure 3.2 FTIR spectra of IL after different gas treatments.
3.3.2 Effect of Temperature

The effect of temperature on gas permeation in the IL membrane was studied in a range from 25 to 120 °C under atmospheric pressure. During the experiments, the feed stream was at a flow rate of 20 cm$^3$ (STP)/min and the permeate side was swept by Helium at a flow rate of 10 cm$^3$ (STP)/min. Single gas permeation was performed for N$_2$, O$_2$, and CO$_2$ at 25, 40, 60, 80, 100 and 120 °C, respectively. Before gas permeation test at each temperature, the membrane was degassed by purging with helium at 120 °C for overnight. The tests were performed in the order of N$_2$, O$_2$, and CO$_2$ at each temperature. The permeation experiments were first conducted from low to high temperature and then the re-measured when temperature was changed from high to low. The results of gas permeation measured during both temperature increasing and decreasing processes are presented in Figure 3.3.

As shown in Figure 3.3, the permeance of CO$_2$, N$_2$, and O$_2$ increased with increasing temperature while the CO$_2$/N$_2$ and CO$_2$/O$_2$ permselectivities decreased with temperature. It was observed that gas permeation results, both permeance and selectivity, were consistent between values measured during temperature increasing and decreasing processes. This again demonstrates that the IL membrane was stable in the tested temperature range and the temperature-caused changes in permeance and selectivity are reversible.

Generally, the temperature dependence of gas permeance ($P_m$) can be expressed by the Arrhenius equation when the permeation is governed by the solution-diffusion mechanism:

$$P_m = P_m^o \exp\left(-E_{p,a}/RT\right)$$  \hspace{1cm} (3-10)$$

Where $P_m^o$ is the pre-exponential constant and $E_{p,a}$ is the apparent permeation activation energy (J/mol). Figure 3.3 (c) shows the Arrhenius plot of gas permeance from this work and CO$_2$ permeability from literature. The apparent activation energies for permeation of the gases ($E_{p,a}$) are listed in Table 3.1. The activation energies of O$_2$ and N$_2$ permeation are much greater than that of CO$_2$. Thus, as temperature increased, the permeance increased more rapidly for N$_2$ and O$_2$ than for CO$_2$ that led to decreases in permselectivity of CO$_2$ over N$_2$ and O$_2$. 
Figure 3.3 Temperature dependences of single gas permeance (solid lines: measured from low temperature to high temperature; dashed line: measured from high temperature to low temperature) and permselectivity. (a) Permeance (left) and flux (right) for N\textsubscript{2}, O\textsubscript{2} and CO\textsubscript{2}, (b) CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/O\textsubscript{2} permselectivity, (c) Arrhenius plot of gas permeance from this work and CO\textsubscript{2} permeability from literature\textsuperscript{43}.

Table 3.1 Apparent activation energy for permeation of CO\textsubscript{2}, N\textsubscript{2} and O\textsubscript{2} in the colloidal silicalite supported [bmim][BF\textsubscript{4}] IL membrane

<table>
<thead>
<tr>
<th>Permeation activation energy, kJ/mol</th>
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<tbody>
<tr>
<td>CO\textsubscript{2}</td>
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<tr>
<td>This work</td>
</tr>
<tr>
<td>Literature</td>
</tr>
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</table>
3.3.3 Effect of CO₂ Concentration in Feed

The N₂ and CO₂ binary mixture was fed at a flow rate of 20 cm³ (STP)/min and the permeate side of the membrane was swept by Helium at a flow rate of 10 cm³ (STP)/min. The gas separation was performed for various CO₂ mole fractions of 0.05, 0.1, 0.15, 0.25, 0.5 and 0.75 in the feed at room temperature and 50 °C, respectively. The experiments were conducted from low CO₂ concentration to high CO₂ concentration feed streams to avoid the any possible residual CO₂ (as N₂ is more weakly absorbing) in the IL from the prior experiment. Figure 3.4 presents the gas flux and permeance as a function of yCO₂ (CO₂ mole fraction in feed).

The CO₂ flux (JCO₂) increased and the N₂ flux (JN₂) decreased with yCO₂ because increasing yCO₂ increases ΔpCO₂ and decreases ΔpN₂. However, the CO₂ permeance (Pm,CO₂) and CO₂/N₂ separation factor were found to decrease with increasing yCO₂ partial pressure in low CO₂ concentration range (0-20%) and essentially remained constant at yCO₂ above ~20%. Such dependencies of CO₂ permeance and separation selectivity are likely caused by the nonlinear relationship between CO₂ solubility and its partial pressure as well as the increased CO₂ concentration in the permeate stream that offset the driving force (ΔpCO₂). The trend of Pm,CO₂ change with the CO₂ feed partial pressure in feed is qualitatively in good agreement with the literature findings on the relationship between CO₂ permeability and partial pressure. It was also observed that increasing the operation temperature from 26 to 53 °C increased the CO₂ flux as a result of enhanced diffusivity but decreased the CO₂ selectivity because of the reduction in solubility as well as the fact that the permeance of N₂ is more sensitive to temperature than CO₂.
Figure 3.4 The gas flux, permeance and CO₂ separation factor as functions of CO₂ mole fraction in the feed stream: (a) CO₂ and N₂ flux, (b) N₂ permeance, (c) CO₂ permeance, (d) CO₂/N₂ separation factor.
3.3.4 Effect of Water Vapor in Feed

Significant amount of water vapor exists in fossil fuel combustion flue gases. The absorption of water into the IL membrane can change the chemical and physical properties of the ionic liquid. It has been reported that the incorporation of water into the IL changes the solubility and diffusivity of other gases and hence affects permeation. In this study, water vapor was introduced to the feed stream by bubbling the CO$_2$/N$_2$ binary gas mixture through a water saturator (see Figure 3.1). The partial pressure of water vapor in the feed was controlled by adjusting the temperature of the water vapor saturator. The binary mixture feed stream was at a flow rate of 8 cm$^3$ (STP)/min and the permeate side of the membrane was swept by Helium at flow rate of 5 cm$^3$ (STP)/min. Gas separation was performed at 50 °C for different CO$_2$ mole fractions in the feed, including $y_{CO2}$ (dry gas basis) of 0.1, 0.3, 0.5 and 0.7, respectively. The experiments were conducted from low CO$_2$ concentration to high CO$_2$ concentration. According to the Antoine Equation, the temperature of the water saturator was set at 0 °C, 35 °C and 44 °C to obtain water partial pressure (in feed) of 0.6, 5.6 and 9.0 kPa, respectively. The gas permeation was operated at 50 °C, which is above the temperature of water saturator, to avoid water condensation in the permeation cell.

The results of CO$_2$/N$_2$ separation with various water contents in the feed are shown in Figure 3.5. The addition of water in the feed stream led to improved CO$_2$ permeance and CO$_2$/N$_2$ selectivity for low CO$_2$ concentration feed streams. These results are consistent with findings in the literature where the increase of CO$_2$ permeance in the water-containing IL membranes was attributed to the consequential reduction of viscosity that increased CO$_2$ solubility and diffusivity. For high CO$_2$ concentration feed gases, the effect of water content on CO$_2$ separation was much less pronounced possibly because of the high concentration of dissolved CO$_2$ that formed [HCO$_3^-$] which is more difficult to be released. Overall the existence of water appeared to be beneficial or at least not harmful to the CO$_2$ separation.
Figure 3.5 Results of permeation of CO$_2$/N$_2$ mixtures with different water vapor pressure in the feed as a function of CO$_2$ molar fraction (at 50 °C and atmospheric pressure): (a) N$_2$ permeance (left) and flux (right), (b) CO$_2$ permeance (left) and flux (right), (c) CO$_2$/N$_2$ separation factor.

3.3.5 Effect of SO$_2$ in Feed

SO$_2$ is a common impurity in coal and natural gas combustion flue gases. It is also preferentially absorbed by most amine type ionic liquids$^{14}$. In this study, the feed stream, which contained 500 ppm and 20% CO$_2$ in balance air, was fed to the membrane separator at a flow rate of 20 cm$^3$ (STP)/min. The permeate side of the membrane was swept by Helium at flow rate of 10 cm$^3$ (STP)/min. Gas separation was performed at different temperatures of 25, 40, 60, 80 and 100 °C, respectively. The experiments were conducted in the order of low temperature to high temperature. At each temperature, the feed pressure was increased from 1 to 6 atm, while permeate pressure was kept at 1 atm.

The separation results for the SO$_2$-containing CO$_2$/air mixtures are shown in Figure 3.6. The separation results at atmospheric pressure were compared with those of the SO$_2$-free mixture (20%
CO\textsubscript{2} and 80\% air) as a function of temperature in Figure 3.6 (a). The presence of 500 ppm SO\textsubscript{2} in the feed stream slightly lowered the CO\textsubscript{2} and N\textsubscript{2} permeance but had no appreciable change to the CO\textsubscript{2}/N\textsubscript{2} separation selectivity. Okabe et al. also found similar results on the effect of SO\textsubscript{2} on CO\textsubscript{2} separation in IL.\textsuperscript{44} They attributed the decrease of CO\textsubscript{2} permeance to obstructed CO\textsubscript{2} transportation by the dissolved SO\textsubscript{2}. They also proposed that the dissolved SO\textsubscript{2} may increase the resistance for CO\textsubscript{2} dissolution that reduces the concentration of carrier IL at the gas-liquid interface. In Figures 3.6 (b) and (c), the effect of SO\textsubscript{2} partial pressure (by increasing the total pressure of feed) was found to have rather moderate impact on the CO\textsubscript{2} and N\textsubscript{2} permeances; thus, to some extent, the SO\textsubscript{2} accumulation in the IL seemed to be tolerable for the \texttt{[bmim][BF\textsubscript{4}]} IL membrane.
Figure 3.6 Permeation results for the 20% CO$_2$ (in balanced air) with 500 ppm SO$_2$ at different temperature and pressure. (a) In comparison with permeance for feed without SO$_2$, (b) Air permeance (left) and air flux (right), (c) CO$_2$ permeance (left) and CO$_2$ flux (right), (d) CO$_2$/air separation factor.

Figure 3.6 also shows that the CO$_2$ permeance decreased slightly with increasing the feed pressure. This is partially caused by the nonlinear dependence of CO$_2$ dissolution on the CO$_2$ pressure. Also, when CO$_2$ concentration in IL is high, CO$_2$ diffusivity tends to decrease. Shiflett et al. found that solubility and diffusivity of CO$_2$ in [bmim][BF$_4$] decreased slightly with increasing CO$_2$ gas pressure$^{43}$. They found that, at 25 °C, $P_b$ of CO$_2$ in the IL decreased from 7.16×10$^{-14}$ to 6.78×10$^{-14}$ mol/m$^2$·s·Pa when CO$_2$ pressure increase from 0.1 to 0.7 MPa.
3.3.6 Stability of the Supported IL Membrane

The colloidal silicalite membrane-supported [bmim][BF_4] IL membrane was operated for nearly one year to obtain the results reported in this thesis without reloading IL. The membrane experienced a differential pressure of 5 bars at 103 °C for several days without any sign of IL membrane rupturing. As shown in Figure 3.6, when $\Delta p (= p_{\text{feed}} - p_{\text{permeate}})$ increased from 0 to 5 bars, air and CO$_2$ permeance did not experience any sudden increase. This means that the membrane could at least operate under a transmembrane pressure of 5 bars.

3.3.7 Permeation under Vacuum Pressure in Permeate Side

In practical applications, the use of sweep gas is not a viable option because the sweeping gas would have to be removed by further separation processes. Furthermore, pressurizing the feed gas for creation of driving force, as combustion flue gas comes out at atmospheric pressure, would require tremendous volumetric work to compress the non-permeating component air rather than CO$_2$. In contrast, a downstream vacuum pressure would theoretically only require volumetric work for the permeating gas (CO$_2$), and is thus more energy efficient.

In the experiments, the feed stream was at a flow rate of 6 cm$^3$ (STP)/min and contained 50% CO$_2$ and 50% N$_2$. The feed side and permeate side of the membrane were maintained at absolute pressures of 1.013 bars (i.e. 1 atm) and ~500 Pa, respectively. The gas permeation was performed at different temperatures of 25, 40, 60, 80 and 100 °C, respectively. The tests were conducted from low to high temperature. The flow rates of the feed stream were simultaneously monitored at the entrance and exit by bubble flow meters. The entering and exiting flows of the feed side were also analyzed by GC. The gas permeation results, i.e. flux and separation factor, were then calculated using mass balance equations. The results of the separation experiments are presented in Figure 3.7 together with those obtained by using helium sweep gas for comparison.
It was found that the permeance of both CO$_2$ and N$_2$ were higher when the downstream was at vacuum pressure as compared to downstream swept by helium flow. The increase of gas permeance was more significant for CO$_2$ than for N$_2$ that led to an enhanced separation factor (in Figure 3.7 (c)). The enhancement of gas permeance under vacuum pressure may be attributed to the elimination of counter diffusion of the sweeping helium in both the substrate porosity and IL membrane.
Figure 3.7 Results of gas separation as a function of temperature for the equimolar CO$_2$/N$_2$ mixture with driving force provided by downstream vacuum pressure. (a) N$_2$ permeance (left) and flux (right), (b) CO$_2$ permeance (left) and flux (right), (c) CO$_2$/N$_2$ separation factor.

3.4 Conclusion

The colloidal silicalite membrane supported [bmim][BF$_4$] IL membrane was investigated for CO$_2$ separation from binary mixtures with and without common impurities found in coal-combustion flue gases. In general, the CO$_2$ and N$_2$ (and air) permeance increased while the CO$_2$ selectivity decreased with increasing operating temperature because the apparent diffusion activation energies of N$_2$ and O$_2$ are greater than that of the CO$_2$. Increasing the CO$_2$ concentration or partial pressure in the feed stream increased the CO$_2$ flux but decreased the CO$_2$ permeance and CO$_2$/N$_2$ separation selectivity likely because of the nonlinear pressure-dependence of CO$_2$ solubility. The existence of water vapor in the feed stream was found to slightly improve the CO$_2$ permeance and selectivity when CO$_2$ concentration was low in the feed; the effect of water vapor on CO$_2$ separation was insignificant for feed stream with CO$_2$ concentration above 20%. The addition of 500 ppm SO$_2$ to the CO$_2$/air mixture reduced both the CO$_2$ and N$_2$ permeance by roughly 10% but had virtually no effect on the CO$_2$
separation factor. It is very encouraging that, when membrane downstream was vacuumed to drive the permeation, both CO₂ permeance and CO₂/N₂ separation factor increased by more than 50% as compared to those obtained using when the downstream was swept by an inert gas (helium). This is because of the elimination of sweep gas counter-diffusion when membrane downstream was vacuumed. The colloidal silicalite membrane supported [bmim][BF₄] IL membrane was operated for nearly one year without any damages or performance degradation observed. The supported IL membrane also remained defect-free when operated under a differential pressure of 5 bars at 103°C. These demonstrate that the colloidal silicalite membrane supported IL membrane was of high thermal stability and good tolerance against transmembrane pressure.
Chapter 4 Summary

The goal of this thesis research is to fabricate a colloidal silicalite film supported ionic liquid membrane and investigate its performance for CO\textsubscript{2} separation in conditions relevant to CO\textsubscript{2} capture from fossil fuel combustion flue gases.

Silicalite nano-particles have been synthesized from a precursor solution with molar ratio of 0.33(SiO\textsubscript{2}): 0.1(TPAOH): 0.035(NaOH): 5.56(H\textsubscript{2}O). The silicalite particles were nearly spherical with an average diameter of ~70 nm. The colloidal silicalite layer on porous alumina disk was fabricated by dip-coating from colloidal suspensions of silicalite nanoparticles using HPC as binder and drying control agent. The silicalite and HPC contents in the suspension for film coating were optimized. The silicalite colloidal film was obtained by two times of dip-coating. The optimized suspension for the initial coating had a zeolite solid content of 0.4wt.% silicalite with 0.2wt.% of HPC. Dip-coating was conducted for the second time using a suspension containing 0.2wt.% silicalite and 0.2wt.% HPC to minimize possible cracks and defects. The colloidal silicalite layer, after controlled drying and firing had a uniform thickness of 2-3 µm. [bmim][BF\textsubscript{4}] ionic liquid, which was chosen as the membrane material in this study, was loaded into the colloidal silicalite-coated substrates by a simple brushing-soaking process. With an IL-loading of 20 mg/cm\textsuperscript{2}, continuous and pinhole free IL membrane was successfully formed on the colloidal silicalite film coated alumina substrate while no defect-free IL membrane could be obtained on the bare alumina disc support before its porosity was fully soaked. The CO\textsubscript{2} permeance and CO\textsubscript{2}/N\textsubscript{2} separation selectivity of the silicalite supported [bmim][BF\textsubscript{4}] membrane were comparable to the best values in the literature.

The colloidal silicalite film supported [bmim][BF\textsubscript{4}] IL membrane was investigated for CO\textsubscript{2} separation from binary mixtures with and without impurities common found in coal-combustion flue gases. In general, CO\textsubscript{2} and N\textsubscript{2} (and air) permeance increased while the CO\textsubscript{2} selectivity decreased with increasing operating temperature because the apparent diffusion activation energies of N\textsubscript{2} and O\textsubscript{2} are
greater than that of the CO\textsubscript{2}. Increasing the CO\textsubscript{2} concentration or partial pressure in the feed stream increased the CO\textsubscript{2} flux but decreased the CO\textsubscript{2} permeance and CO\textsubscript{2} selectivity because of the nonlinear pressure-dependence of CO\textsubscript{2} solubility. The existence of water vapor in the feed stream was found to slightly improve the CO\textsubscript{2} permeance and selectivity when CO\textsubscript{2} concentration was low in the feed; the effect of water vapor on CO\textsubscript{2} separation was insignificant for feed streams with CO\textsubscript{2} concentrations above 20%. The addition of 500 ppm SO\textsubscript{2} to the CO\textsubscript{2}/air mixture reduced both the CO\textsubscript{2} and N\textsubscript{2} permeance by \textasciitilde10\% but had virtually no effect on the CO\textsubscript{2} separation factor. It is very encouraging that, when the membrane downstream was vacuumed to drive the permeation, both CO\textsubscript{2} permeance and CO\textsubscript{2}/N\textsubscript{2} separation factor increased by more than 50\% as compared to those obtained using sweep gas (helium) on the permeate side. This is because of the elimination of sweep gas counter-diffusion when membrane downstream was vacuumed. The colloidal silicalite membrane supported [bmim][BF\textsubscript{4}] IL membrane was operated for nearly a year without any damages observed. The supported IL membrane also remained defect-free when operated under a differential pressure of 5 bars at 103°C. These demonstrate that the colloidal silicalite membrane supported IL membrane was of high thermal stability and good tolerance against transmembrane pressure.

Future works are suggested to use base substrates with higher porosity (for enlarged effective IL membrane surface area) and pore size significantly larger than the inter-particle pores in the colloidal zeolite layer. It is anticipated that, when the base substrate pores are significantly larger than the inter-particle pores of the colloidal top layer, the IL may be loaded only in the colloidal zeolite film without penetrating into the base support. In this case, the IL membrane thickness can be reduced to a few micrometers, and because the zeolite particles are also permselective to CO\textsubscript{2}, colloidal silicalite membrane supported IL membrane can potentially achieve significantly increased CO\textsubscript{2} permeance and flux with good CO\textsubscript{2} selectivity.
Appendix: Basic Properties of 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4])

(1) Basic Information

Chemical formula: C_8H_{15}BF_4N_2
Molecular weight: 226.023

The schematic of [bmim][BF_4] molecular structure

(2) Physical Properties

Table a.1 Densities ρ/(g·cm\(^3\)), surface tension σ/(mN·m\(^{-1}\)), dynamic viscosities η/(mPa·s) and kinematic viscosity ν/(Cst) of [bmim][BF_4] at temperatures from 278.15 K to 368.15 K

<table>
<thead>
<tr>
<th>T/K</th>
<th>density ρ/(g·cm(^3))</th>
<th>surface tension σ/(mN·m(^{-1}))</th>
<th>dynamic viscosity η/(mPa·s)</th>
<th>kinematic viscosity ν/(Cst)</th>
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(3) Thermal Stability

The \([\text{bmim}][\text{BF}_4]\) begins to decompose at 350°C.

![TGA and DTGA for \([\text{bmim}][\text{BF}_4]\)](image)

**Figure a.1** TGA and DTGA for \([\text{bmim}][\text{BF}_4]\)\(^{50}\)

**Table a.2** Equilibrium vapor pressure of \([\text{bmim}][\text{BF}_4]\) under various temperatures\(^{51}\)

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(4) Solubility and Diffusivity of [bmim]BF₄

Table a.3 Solubility (C), Diffusivity (D), and permeability of CO₂ (Pₚ) in [bmim][BF₄] at different temperature and pressure⁴³

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<th>T/K</th>
<th>p/MPa</th>
<th>C (×10^2 mol/m³)</th>
<th>D (×10^-11 m²/s)</th>
<th>Pₚ (×10^-14 mol/m.s.Pa)</th>
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References


