CO₂-Selective Membranes Containing Sterically Hindered Amines for CO₂/H₂ Separation

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ABSTRACT: This work exploited amine steric hindrance effect to developing next-generation CO₂-selective facilitated transport membranes for H₂ purification for fuel cells. The new membrane was synthesized by incorporating moderately hindered poly-N-isopropylallylamine as a fixed-site carrier along with mobile carriers into cross-linked polyvinylalcohol-poly(siloxane) network. The new membrane exhibited high CO₂ permeability of greater than 6500 Barrers, CO₂/H₂ selectivity of more than 300, and CO₂/N₂ selectivity of at least 650 at 110 °C and a feed pressure of 2 atm. Better membrane separation results were achieved as the sweep-side water content was increased. The membrane also showed good stability of at least 430 h at 110 °C and 2 atm. The membrane performance reduced as temperature was increased from 107 to 180 °C as a result of the reduction of water retention ability of the membrane; however, it still held a good CO₂/H₂ selectivity of about 34 at 180 °C.

1. INTRODUCTION

Hydrogen is an important chemical used in many industrial processes such as ammonia production, chemical hydrogenation, and refining hydroprocessing. Hydrogen is also the preferred fuel for fuel cells, especially for proton-exchange membrane fuel cells, due to high energy-efficient conversion and clean emission. In industry, hydrogen is mainly from syngas, which is generated by reforming of hydrocarbon fuels followed by water–gas shift (WGS) reaction. The reforming step converts hydrocarbon fuels to H₂, CO, and CO₂, while the WGS reaction converts more CO to H₂. Thus, the resulting syngas consists of a CO₂/H₂ mixture, and the removal of CO₂ from H₂ to produce high-purity H₂ becomes an important industrial process.

Major available technologies for CO₂ removal include amine scrubbing, pressure swing adsorption, cryogenic separation, and physical solvent absorption. In recent years, membrane technology is gaining more and more attention due to inherent advantages, such as reduced energy consumption, operation simplicity, compact system, absence of moving parts, and no thermodynamic limitation for solubility. The potential application of membrane technology for syngas purification relies strongly on the development of new membranes that exhibit high separation performance and long-term durability at practical operating conditions.

The separation performance of a membrane is mainly characterized by two parameters. One is the permeability \( P \), which is defined as

\[
P = \frac{N_i}{\Delta P} \quad (1)
\]

The common unit of \( P \) is Barrer, which is \( 10^{-10} \text{ cm}^3 (\text{STP})/\text{cm}^2/\text{s}/\text{cm Hg} \). \( (P)/i \) is referred as the permeance, and its common unit is the gas permeation unit (GPU), which is \( 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2/\text{s}/\text{cm Hg} \). The permeability for component \( i \) is commonly expressed by the product of diffusivity coefficient \( D_i \) and solubility coefficient \( S_i \):

\[
P = D_i S_i \quad (2)
\]

The other parameter is selectivity (or separation factor), which is defined as

\[
\alpha_y = \frac{x_y / y_y}{x_x / y_x} \quad (3)
\]

If the downstream pressure is negligible compared to the upstream pressure, the selectivity can be expressed as the ratio of permeabilities, that is, the product of diffusivity selectivity and solubility selectivity:

\[
\frac{P_y}{P_x} = \left( \frac{D_y}{D_x} \right) \left( \frac{S_x}{S_y} \right) \quad (4)
\]

For most conventional polymer membranes, CO₂/H₂ separation follows the solution-diffusion mechanism; that is, the overall CO₂/H₂ selectivity is dominated by the diffusivity selectivity. In most polymers, CO₂ is more soluble \( S_{CO₂}/S_{H₂} > 1 \) but has much lower diffusivity than H₂ \( D_{CO₂}/D_{H₂} \ll 1 \) due to a larger penetrant size. Therefore, the polymer matrices are more permeable to H₂ than to CO₂. As a result, H₂ is enriched in the permeate side (also called "sweep side") with a lower pressure and requires recompression for utilization, which significantly diminishes the energy and capital efficiencies of the...
membrane process. Special polymers can be made more permeable to CO$_2$; however, the selectivity and permeability are still in the low range, and increasing CO$_2$ permeability of such membranes is often accompanied by a decreasing CO$_2$/H$_2$ selectivity and vice versa.$^{4,5}$

CO$_2$-selective facilitated transport membranes can be used for H$_2$ purification, including for fuel cell application. Figure 1 presents a schematic of the facilitated transport mechanism, which involves reversible reactions of both fixed-site carriers and mobile carriers with CO$_2$ for CO$_2$ flux augmentation in addition to the solution-diffusion mechanism for the physical dissolution and diffusion of CO$_2$. The facilitated transport mechanism has been described in our previous publications.$^{3,6}$ Due to the specific, reversible reaction between amine carriers and CO$_2$ molecules, high CO$_2$ permeability accompanied with high selectivities versus H$_2$, N$_2$, CO, and CH$_4$ can be achieved by the facilitated transport membrane, especially at low CO$_2$ partial pressures. High permeability results in the reduced membrane area requirement and offers the possibility of cost reduction, while high CO$_2$/H$_2$ selectivity ensures high H$_2$ recovery. Since CO$_2$ is highly permeable, H$_2$-enriched product stream can be maintained at the high-pressure retentate side after the membrane process, which saves substantial energy from H$_2$ recompression for downstream utilization. The permeated CO$_2$ can be quickly swept away by steam, air, or vacuum, keeping a high driving force for the membrane separation process as well as providing convenience for CO$_2$ capture and sequestration while using steam or vacuum. Ease of CO$_2$ separation from sweep gas can be expected if steam is used as the sweep gas.

Facilitated transport membranes of different types have been studied. Early stage facilitated transport membranes were in the form of a supported liquid membrane (SLM), which consists of a liquid phase containing a carrier species immobilized in the pores of a microporous polymer support.$^{2}$ As an improvement of SLMs, ion-exchange membranes were first introduced by LeBlanc et al. in 1980.$^7$ In ion-exchange membranes, charged carrier species are anchored by electrostatic forces to countercations in polymer backbone. SLMs and ion-exchange membranes have overcome Robeson’s trade-off limitation on permeability and selectivity; however, leakage of carriers, low resistance to high transmembrane pressure, evaporation loss of solvents, and slow reaction kinetics have undermined their practical applications. In recent years, dendrimer polymers and ionic liquids have emerged as new groups of nonvolatile carriers for SLMs with much improved stability.$^8,9$ Solid polymeric membranes containing carriers have always received considerable research attention because this type of membrane is believed to have better stability (vs SLMs and ion-exchange membranes), mechanical properties, processing flexibility, and economical costs. Polymer-based facilitated transport membranes involving 2-aminoisobutyric acid-potassium salt as the mobile carrier and polyallylamine (PAA) as the fixed-site carrier demonstrated high CO$_2$ selectivity and permeability for CO$_2$ removal in a water–gas shift reactor or H$_2$ purification for fuel cells.$^{3,10,11}$

Figure 1. Schematic of gas permeation through a facilitated transport membrane.

Amine carriers are directly responsible for the final separation performance of a facilitated transport membrane. Amine carriers exhibiting higher capability, rate, and degradation resistances in CO$_2$ absorption and desorption are always desired. The amine carriers that have been reported in the literature include: ethylenediamine,$^7,12$ alkanolamines,$^{13,14}$ aminoacid salts,$^{15,16}$ polyethyleneimine,$^{17,18}$ polyallylamine,$^{10,11,18}$ poly(amidoamine) dendrimers,$^8$ polyvinylamine,$^{19}$ amino groups in polyamide prepared by interfacial polymerization,$^{20}$ and chitosan.$^{21}$ The reversible reaction between CO$_2$ and a conventional amine can be described by the zwitterion mechanism and consumes 2 mols of amines to convert 1 mol of CO$_2$ into carbamate ion.$^{22,23}$ A sterically hindered amine is defined as either a primary amine in which the amino group is attached to a tertiary carbon or a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon.$^{24}$ The attached bulky group causes “steric hindrance” effect, that is, the formed carbamate ion is unstable and undergoes hydrolysis easily to yield the bicarbonate ion as the sink for CO$_2$, resulting in a stoichiometric CO$_2$ loading up to 1 mol per mole of hindered amine, as shown by eq 5.$^{25}$

$$\text{CO}_2 + \text{R}_2\text{NH-R}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \quad (5)$$
The enhanced CO₂ loading capacity has made aqueous sterically hindered amine solutions as the improved CO₂ absorbers used in commercial amine scrubbing processes, such as FLEXSORB SE, FLEXSORB SE Plus, FLEXSORB PS, and FLEXSORB HP. Membrane-based applications of sterically hindered amines have rarely been reported. A PVA-based facilitated transport membrane containing 2-amino-2-methyl-1-propanol (AMP) was synthesized for CO₂/N₂ based facilitated transport membrane containing hindered poly-N-alkylpolyamine. Our previous work for the improved CO₂ selectivity via sterically hindered amine solutions as the improved CO₂ absorbers used in commercial amine scrubbing processes, such as FLEXSORB SE, FLEXSORB SE Plus, and FLEXSORB HP. Membrane-based applications of sterically hindered amines have rarely been reported. A PVA-based facilitated transport membrane containing 2-amino-2-methyl-1-propanol (AMP) was synthesized for CO₂/N₂ separation, which demonstrated a CO₂/N₂ selectivity of 62 and a CO₂ permeance of 0.45 × 10⁻⁵ cm³(STP)/(cm²·s·cm Hg) at 23 °C and a CO₂ partial pressure difference of 54 kPa. The CO₂ absorption performances of various absorbents including aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA), and AMP solutions were compared in a polytetrafluoroethylene (PTFE) hollow fiber membrane, and AMP exhibited the highest absorption capacity and a moderate absorption rate. All the described research focuses on aqueous solutions of sterically hindered amines. Our previous work for the first time investigated the effect of amine steric hindrance in a solid polymeric membrane and exhibited dramatically enhanced CO₂ transport by sterically hindered polyamines.

This work addresses the application of amine steric hindrance in developing high-performance CO₂-selective facilitated transport membranes containing hindered poly-N-isopropylallylamine (PAA-C₃H₇) as the fixed-site carrier for CO₂ separations vs hydrogen and nitrogen. The synthesized membranes were tested under conditions similar to intended applications for hydrogen purification for fuel cells at 100–120 °C and 2 atm. The membrane stability at 110 °C and 2 atm was investigated for at least 430 h. Also investigated were the effects of sweep-side water content on CO₂ permeability, CO₂/H₂ selectivity, and CO₂/N₂ selectivity.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(allylamine hydrochloride) (MW = 120 000–200 000) was bought from Polysciences Inc. (Warrington, PA). Polyvinylalcohol (Poval S-2217, 92% purity) was donated by Kuraray America Inc. (Houston, TX), and it was a copolymer of vinyl alcohol and 2-(acrylamido)-2-methyl propane sulfonic acid sodium salt. Potassium hydroxide (pellets, ≥85%, MW = 56.11), 2-bromopropane (99%, MW = 122.99), 2-aminobutyric acid (98%, MW = 103.12), (3-aminopropyl)triethoxysilane (99%, MW = 221.37), glutaaraldehyde (50 wt % solution in H₂O, MW = 100.12), and fumed silica (powder, 0.007 μm, MW = 60.08) were purchased from Sigma-Aldrich Corp. (St. Louis, MO). Methanol (anhydrous, ≥99.8%, FW = 32.04) was obtained from Mallinckrodt Baker Inc. (Phillipsburg, NJ). Hydrochloric acid (36.5% – 38.0%, FW = 36.46) was acquired from Fisher Scientific Inc. (Pittsburgh, PA).

Microporous polysulfone support (thickness = ~140 μm including nonwoven fabric support and average pore size = 0.05 μm) was provided by NL Chemical Technology, Inc. (Mount Prospect, IL). Two gas mixtures of certified grade were used as feed gases, which were purchased from Airgas Great Lakes (Independence, OH). The gas compositions (on dry basis) were (1) 10% CO₂, 40% H₂, and 50% N₂ and (2) 17% CO₂, 45% H₂, 1.0% CO, 50 ppm H₂S, and 37% N₂. The third feed gas, which contained a certified grade of 20% CO₂, 40% H₂, and 40% N₂ (on dry basis), was purchased from Praxair Inc. (Danbury, CT). Prepurified argon was used as the sweep gas and acquired from Praxair Inc. (Danbury, CT).

2.2. Membrane Preparation. CO₂-selective facilitated transport membranes with a thin-film-composite structure were synthesized by the solution casting technique. In a particular experiment, 3.4 g of as-received polyvinylalcohol (PVA) was dissolved in 18 g of deionized water at room temperature under minor stirring overnight. One gram of (3-aminopropyl)triethoxysilane (APTESOS) and 0.15 g of hydrochloric acid (HCl) were added to the aqueous PVA solution and the acid-catalyzed sol–gel reaction was carried out at 80 °C for 80 min under vigorous stirring to produce the PVA-poly(siloxane) hybrid matrix. After the sol–gel reaction was done, a calculated amount of glutaraldehyde (cross-linking reagent) for a 100 mol % cross-linking degree for PVA, that is, 3.5 g of glutaraldehyde, and 2.0 g of potassium hydroxide (KOH, cross-linking catalyst) in aqueous solution were added. The cross-linking reaction was carried out at 80 °C for 2.5 h under stirring. The transparent aqueous PVA-poly(siloxane) solution turned dark brown in color with a significant increase...
in viscosity due to cross-linking. The sol–gel reaction and the cross-linking reaction are described in Scheme 1.

Separately, a 2-aminoisobutyric acid-potassium salt (AIBA-K) solution was prepared by reacting 2-aminoisobutyric acid with KOH (1 equiv) at room temperature under stirring for 24 h. As-received poly(allylamine hydrochloride) was converted to free polyallylamine by the reaction of poly(allylamine hydrochloride) with KOH (1 equivalent) in methanol under stirring at room temperature for 48 h. The resulting potassium chloride formed was insoluble in methanol and thus precipitated from the solution, and it was then removed from the solution. To synthesize the moderately hindered poly-N-isopropylallylamine, 1 equiv of 2-bromopropane as well as KOH was added to the polyallylamine/methanol solution and reacted with PAA at 50 °C for 48 h. The resulting potassium bromide formed was insoluble in methanol and precipitated from the solution. The conversion from the primary amino groups of polyallylamine to the secondary amino group of poly-N-isopropylallylamine was confirmed by Fourier transform infrared (FT-IR) spectroscopy using a Nicolet 470 FTIR spectrometer (Thermo Electron Co., Waltham, MA).

To prepare a casting solution, aqueous poly-N-isopropylallylamine solution was first made by replacing methanol with deionized water under a nitrogen atmosphere. Based on the solid membrane composition, calculated amounts of AIBA-K solution, KOH solution, cross-linked PVA-poly(siloxane) solution, APTEOS, and fumed silica (SiO₂) were sequentially added to the aqueous poly-N-isopropylallylamine solution under stirring. Finally, the casting solution was centrifuged at 8000 rpm for 3 min to remove impurities and air bubbles before it was cast on a flat-sheet microporous polysulfone support using a GARDCO adjustable film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The cast membrane was kept inside a fume hood at room temperature for about 16 h to evaporate most of the water and then cured at 120 °C for 6 h in a Thermolyne 30400 muffle furnace (Thermo Scientific, Waltham, MA) for the removal of residual water and the complete cross-linking reaction of PVA with glutaraldehyde. Each of the solid membranes used in this work contained 20 wt % cross-linked PVA-poly(siloxane) (100 mol % of hydroxyl groups cross-linked), 17.2 wt % poly-N-isopropylallylamine or polyallylamine, 25.7 wt % AIBA-K, 16.6 wt % KOH, 12 wt % SiO₂, 8 wt % APTEOS, and 0.5 wt % KCl.

The total thickness of each of the composite membranes was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corp, Aurora, IL) with an accuracy of ±0.5 μm. The thickness of the active dense layer was obtained by subtracting the measured polysulfone support thickness from the measured total thickness of the composite membrane. The active layer thickness was controlled at about 25 μm.

2.3. Gas Permeation Measurements. The measurements of membrane transport properties were conducted by using a gas permeation apparatus shown in Figure 2. The membrane was loaded in a circular stainless-steel cell with an active membrane area of 45.6 cm² inside an oven (BEMCO Inc., Simi Valley, CA) with accurate temperature control. The feed and the sweep gas flows were designed to be counter-current in the cell.

The pressure was controlled by a back-pressure regulator and measured by a pressure gauge. The feed pressure was set at 2 atm, and the sweep pressure was set close to atmospheric pressure. Dry gas flow rates were accurately controlled by flow meters (Brooks Instrument, Hatfield, PA) at 60 cm³/min for the feed side and 30 cm³/min for the sweep side. Liquid water was pumped into the testing system under controlled flow rates by Varian ProStar solvent delivery modules (Model 210, Varian Inc., Palo Alto, CA), vaporized, and well mixed with feed gas and sweep gas in their respective humidifiers. The liquid water injection rates for both the feed and the sweep sides were set at 0.03 cm³/min, corresponding to water contents of 40.5 mol %
in the feed gas and 57.6 mol % in the sweep gas, unless otherwise specified.

After the membrane separation process, both the retentate and permeate streams leaving the oven were cooled to ambient temperature in their respective water knockout vessels to remove the condensed water before the streams entered an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA) for gas composition analyses. The gas chromatograph column used was of the SUPELCO Carboxen 1004 micropacked type (Sigma-Aldrich, St. Louis, MO). Each of the membrane permeation measurements was taken after the membrane had been exposed to the feed and permeate streams under a specific condition (temperature, pressure, and water rates) for at least 6 h, which allowed for steady-state permeation.

### Table 1. Gas Separation Results of Crosslinked PVA/ Poly(siloxane)-Based Facilitated Transport Membranes Containing Amines

<table>
<thead>
<tr>
<th>fixed-site carrier</th>
<th>membrane no.</th>
<th>CO₂ permeability (Barrer)</th>
<th>selectivity (CO₂/H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA-C₅H₅</td>
<td>N4-P114-2</td>
<td>6446</td>
<td>336</td>
</tr>
<tr>
<td></td>
<td>N4-P116-4</td>
<td>6414</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>N4-P123-3</td>
<td>6963</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td>N4-P129-2</td>
<td>6842</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>N5-P87-1</td>
<td>6220</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>6577</td>
<td>340</td>
</tr>
<tr>
<td>PAA</td>
<td>N4-P149-3</td>
<td>4440</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td>N5-P10-1</td>
<td>3094</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>N5-P17-1</td>
<td>4322</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td>3952</td>
<td>161</td>
</tr>
</tbody>
</table>

“Membrane thickness = 25 μm. Test conditions: temp. = 110 °C; pressure = 2/1.08 atm (feed/sweep); dry gas flow rates = 60/30 cm³/min (feed/sweep); water injection rates = 0.03/0.03 cc/min (feed/sweep).”

### Table 2. Liquid Water Injection Rates, Water Contents, and Relative Humidities for Figure 5

<table>
<thead>
<tr>
<th>temp. (°C)</th>
<th>water rate (cm³/min)</th>
<th>water content (mol %)</th>
<th>relative humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>feed</td>
<td>sweep</td>
<td>feed</td>
</tr>
<tr>
<td>0.03</td>
<td>0.03</td>
<td>40.5</td>
<td>57.6</td>
</tr>
<tr>
<td>0.03</td>
<td>0.06</td>
<td>40.5</td>
<td>73.1</td>
</tr>
<tr>
<td>0.03</td>
<td>0.12</td>
<td>40.5</td>
<td>84.5</td>
</tr>
<tr>
<td>0.03</td>
<td>0.24</td>
<td>40.5</td>
<td>91.6</td>
</tr>
<tr>
<td>0.03</td>
<td>0.48</td>
<td>40.5</td>
<td>95.6</td>
</tr>
</tbody>
</table>

“Dry gas flow rates = 60/30 cm³/min (feed/sweep).”

### Table 3. Liquid Water Injection Rates, Water Contents, and Relative Humidities for Figure 6

<table>
<thead>
<tr>
<th>temp. (°C)</th>
<th>water rate (cm³/min)</th>
<th>water content (mol %)</th>
<th>relative humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>feed</td>
<td>sweep</td>
<td>feed</td>
</tr>
<tr>
<td>0.03</td>
<td>0.03</td>
<td>40.5</td>
<td>57.6</td>
</tr>
<tr>
<td>110</td>
<td>0.03</td>
<td>0.03</td>
<td>40.5</td>
</tr>
<tr>
<td>120</td>
<td>0.03</td>
<td>0.03</td>
<td>40.5</td>
</tr>
<tr>
<td>140</td>
<td>0.06</td>
<td>0.06</td>
<td>57.6</td>
</tr>
<tr>
<td>160</td>
<td>0.12</td>
<td>0.12</td>
<td>73.1</td>
</tr>
<tr>
<td>180</td>
<td>0.15</td>
<td>0.15</td>
<td>77.3</td>
</tr>
</tbody>
</table>

“Dry gas flow rates = 60/30 cm³/min (feed/sweep).”

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Amine Steric Hindrance on Separation Performance.

The CO₂-selective facilitated transport membrane in this work was synthesized by incorporating amines as CO₂ carriers into cross-linked PVA-poly(siloxane) network. Polyallylamine or poly-N-isopropylallylamine was used as the fixed-site carrier. Polyallylamine is a long alkyl chain with one pendant aminomethyl group in each repeating unit. Due to the abundance of amino groups, this unhindered polyamine has been used as a CO₂ carrier in several facilitated transport membranes.6,18,31,32 Poly-N-isopropylallylamine is a sterically hindered polyamine derived from polyallylamine by the modification reaction.6 The conversion from polyallylamine to poly-N-isopropylallylamine was confirmed by FT-IR spectroscopy, as described in a previous publication.31 Due to the steric hindrance effect, poly-N-isopropylallylamine has demonstrated a stronger enhancing effect on CO₂ transport across a solid polymeric phase compared with polyallylamine.8 However, the application of sterically hindered amines as fixed-site carriers in membranes has not been found in the literature. This work developed new CO₂-selective facilitated transport membranes containing the hindered poly-N-isopropylallylamine and demonstrated the superior CO₂ transport capacity of this new fixed-site carrier.

In addition to the fixed-site carrier, the membrane contained two mobile carriers, AIBA-K and KOH (KOH was introduced into the membrane due to its use as a catalyst for cross-linking PVA). PVA was chosen as the polymer matrix due to its high hydrophilicity, good compatibility with carriers, good film forming ability, and low cost. PVA was polycondensed with APTEOS and was cross-linked by glutaraldehyde to form a strong network.

Table 1 compares the mixed gas permeation test results between the membranes made with polyallylamine and those with poly-N-isopropylallylamine at 110 °C and a feed pressure of 2 atm. Each of the solid membranes in Table 1 contained 20 wt % cross-linked PVA-poly(siloxane) (100 mol % of hydroxyl groups cross-linked), 17.2 wt % poly-N-isopropylallylamine or polyallylamine, 25.7 wt % AIBA-K, 16.6 wt % KOH, 12 wt % SiO₂, 8 wt % APTEOS, and 0.5 wt % KCl. As can be seen from Table 1, a CO₂ permeability of as high as 6577 Barrers accompanied with a CO₂/H₂ selectivity of greater than 320 was achieved by the membranes containing poly-N-isopropylallylamine. The enhancements in CO₂ permeability and CO₂/H₂ selectivity are 66.4% and 111.2%, respectively, compared with the membranes containing polyallylamine.

The new membrane containing poly-N-isopropylallylamine exhibited superior separation performance. Its CO₂/H₂ separation results are compared with literature data on solution-diffusion membranes33 and polymeric facilitated transport membranes15,18,21,34–36 in a permeability-selectivity data map shown in Figure 3. Clearly, the results in terms of permeability and selectivity achieved by the membrane containing poly-N-isopropylallylamine are higher than those reported in the literature, indicating that the membrane containing the sterically hindered amine constitutes a new class of CO₂-selective facilitated transport membranes.

The improved membrane performance can be explained by the steric hindrance effect. In poly-N-isopropylallylamine, the bulky isopropyl group attached to the amino group lowers the tendency to form carbamate ion when CO₂ reacts with the amine as the carbamate ion is unstable and undergoes...
doubled CO₂ loading capacity, more free amines become available for achieving an accelerated reaction rate, which is considered as another contribution to the improved membrane separation performance. The CO₂-amine forward reaction rate is governed by a second-order reaction, that is, by free CO₂ concentration and free amine concentration. Steric hindrance reduces the reaction rate constant to some extent, but results in more free amines to react with CO₂. The overall enhancement in CO₂ permeation through the hindered amines in aqueous solutions. In this work, faster absorption rate has been demonstrated by sterically hindered amine carriers (mobile and fixed-site) and the cross-linked poly-N-isopropylallylamine-containing membrane in this work.

Figure 3. Selectivity—permeability data map for CO₂/H₂ separation: (△) solution-diffusion membranes reported in the literature, (●) facilitated transport membranes in the literature, and (□) poly-N-isopropylallylamine-containing membranes in this work.

Membrane Stability. Membrane stability is a great challenge to the viability of a membrane for commercial use. A major problem from which facilitated transport membranes generally suffer is their instability. However, the poly-N-isopropylallylamine-containing membrane developed in this work showed good stability in an evaluation carried out at 110 °C and a feed pressure of 2 atm for an experimental period of 430 h (~18 days). Figure 4 depicts the stability test results including CO₂ permeability, CO₂/H₂ selectivity, and CO₂/N₂ selectivity. As seen in this figure, no significant drops in CO₂ permeability and selectivities vs H₂ and N₂ were observed during this experimental period, which suggests that the membrane stability could be maintained for longer periods than the 18-day test. The good membrane stability could be explained by the following reasons. First, PVA was cross-linked by glutaraldehyde to form a strong network. The incorporation of the inorganic silica fillers was also beneficial to the membrane mechanical strength. Moreover, poly-N-isopropylallylamine was retained in the membrane matrix via the entanglement with the cross-linked PVA-poly(siloxane) network. The hydrogen bonds formed between amino groups and hydroxyl groups further strengthened the affinity between the amine carriers (mobile and fixed-site) and the cross-linked PVA-poly(siloxane) network. Therefore, this membrane is beneficial from the stability point of view.

Although excellent durability of over 25 days has been observed in cross-linked polyvinylamine membrane, poly-(vinylbenzyltrimethylammonium fluoride)/CsF membrane, polyvinylalcohol/polyethylene glycol/polyethyleneimine blend membrane, and diethanolamine/PVA membrane, their membrane performances were not so good in comparison with that of the membrane containing poly-N-isopropylallylamine in the present work. Moreover, all the published stability data were obtained at a low temperature range from 23 to 35 °C. The membranes reported may not survive under high temperatures at or above 100 °C over a long time period.

3.3. Effect of Relative Humidity on Membrane Separation Performance. Water retention in the membrane matrix is governed by relative humidity or water content in the feed and sweep streams. We studied the enhancing effect of relative humidity or water content on the membrane separation performance at 120 °C using a feed gas consisting of 17% CO₂, 45% H₂, 37% N₂, 1% CO, and 50 ppm H₂S (dry basis), which is a typical composition for the synthesis gas derived from autothermal reforming of gasoline using air as the oxygen source. In the mixed gas permeation test, the metered amounts of liquid water were introduced into the feed and sweep streams by the accurate metering pumps employed. The liquid water was vaporized and well mixed with each of the feed and sweep gas streams separately in their humidifiers before the water vapor moisturized the solid membrane. Detailed operating conditions can be found in Table 2. The water content of the sweep stream varied from 5.76 mol % to 95.6 mol % by adjusting the output rate of the water pump, while the feed-side water content was kept constant at 40.5 mol %.

As can be seen from Figure 5, the separation performance of the membrane containing poly-N-isopropylallylamine demonstrated an ascending trend with increasing moisture surrounding the membrane at 120 °C and a feed pressure of 2 atm. CO₂ permeability increased with the sweep-side water content and achieved a very high value of 8285 Barrers at 95.6 mol %. As described by Zou and Ho, increasing water content or relative humidity of the sweep gas allowed more water to be retained in the membrane matrix. The reaction rates of carriers with CO₂ and the mobilities of amine carriers were therefore increased, resulting in a larger CO₂ permeability. Higher water content of

Figure 4. Stability test results: (●) CO₂ permeability, (■) CO₂/H₂ selectivity, and (▲) CO₂/N₂ selectivity of the membrane containing 17.2 wt % poly-N-isopropylallylamine at 110 °C and a feed pressure of 2 atm (liquid water injection rates for feed/sweep streams = 0.03/0.03 cm³/min using a feed gas composition of 20% CO₂, 40% H₂, and 40% N₂ (on dry basis)).
the sweep gas also lowered the permeated CO₂ concentration, leading to an increased driving force for the CO₂ transport.

Figure 5 also shows that high values of CO₂/H₂ selectivity (i.e., greater than about 180) and CO₂/N₂ selectivity (i.e., above 2340) were obtained with the sweep-side water content ranging from 57.6 mol % to 95.6 mol %. Moreover, both the selectivities demonstrated increasing trends with the sweep-side water content in the range investigated. The reason is that the CO₂ permeability increased with the sweep-side water content as described earlier, but the H₂ or N₂ permeability remained constant as a result of the solution-diffusion mechanism.

The effect of water content on membrane performance has practical significance in industrial applications, where steam alone can be used as the sweep gas to provide even higher relative humidity for the membrane. It is expected to give high CO₂ permeability as well as the ease of CO₂ separation from the sweep gas by condensation.

3.4. Membrane Separation Performance at High Temperatures. Few data on membrane performance at greater than 100 °C could be found in the literature. This work investigated the effects of temperature, ranging from 107 to 180 °C, on CO₂ permeability, CO₂/H₂ selectivity, and CO₂/N₂ selectivity of the synthesized membrane containing 17.2 wt % poly-N-isopropylallylamine at a feed pressure of 2 atm (the water contents of both the feed and sweep gases were gradually raised with temperature, as shown in Table 3). As illustrated in Figure 6, the CO₂ permeability was greater than 3000 Barrers at 107−140 °C, along with a CO₂/H₂ selectivity of higher than 90 as well as a CO₂/N₂ selectivity of higher than 150. However, all the three gas transport properties were observed to reduce as temperature was increased. Specifically, CO₂ permeability reduced to 1574 Barrers accompanied with lower selectivities of 34.4 (CO₂/H₂) and 33.6 (CO₂/N₂) as the temperature was increased to 180 °C.

The performance decrease was due to the reduction of water retention in the polymer matrix as the temperature increased (owing to the reduced relative humidity, as shown in Table 3). Water plays a vital role in the facilitated transport of CO₂ by amine carriers via participating in the reversible reactions (i.e., the hydrolysis of zwitterion and carbamate ion) and increasing CO₂ diffusivity by plasticizing the membrane matrix. In the mixed gas permeation tests conducted in this work, both the feed and the sweep gases were humidified by water vapor before contacting with the polymeric membrane matrix. Therefore, CO₂ permeation was facilitated by water and the reactions. As the relative humidity surrounding the membrane matrix was reduced with an increasing temperature, less water was held in the membrane matrix. The reduction of water retention impedes the mobility of mobile and fixed-site carriers and the reaction rates of CO₂ with the carriers, resulting in a consequent decrease in CO₂ permeability. Sartori et al. also found that temperature beyond 120 °C could drive the reversible reaction between CO₂ and amine in aqueous solution toward CO₂ desorption.

However, the membrane still held a good CO₂/H₂ selectivity of about 34 at 180 °C. The data were obtained using the average of three data points collected after the membrane was exposed to the specific condition for about 8 h, which allowed for steady-state gas permeation. The temperature of 180 °C is regarded as being high for polymeric membranes.

For all operating conditions investigated so far, that is, in the temperature range 107−180 °C and sweep-side water contents of 57.6−95.6 mol %, no CO in the permeate samples could be detected by gas chromatography. This indicates that a high CO₂/CO selectivity of at least 2000 is expected from the investigated membranes.

4. CONCLUSIONS

New CO₂-selective facilitated transport membranes were synthesized by incorporating poly-N-isopropylallylamine, a moderately hindered polyamine as the CO₂ fixed-site carrier, and CO₂ mobile carriers into cross-linked PVA-poly(siloxane) membrane matrix. The new membrane exhibited significantly enhanced performance and long-term stability in CO₂/H₂ and CO₂/N₂ separations under relatively high temperatures. At 110 °C and a feed pressure of 2 atm, it showed a high CO₂ permeator of greater than 6500 Barrers, CO₂/H₂ selectivity of more than 300 and CO₂/N₂ selectivity of at least 650. Better membrane separation results were achieved as sweep-side water content was increased. The membrane also showed good stability of at least 430 h at 110 °C and 2 atm. The membrane performance reduced as temperature was increased from 107 to 180 °C due to the reduction of the water retention ability of the membrane; however, it still held a good CO₂/H₂ selectivity of about 34 at 180 °C. At the fuel-cell operating temperatures of 100−120 °C, this type of membrane represents a new class of efficient, durable gas separation membranes, which opens a new
approach to practical membrane separation processes for CO₂ removal or H₂ purification for fuel cells.

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**Notes**

The authors declare no competing financial interest.

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**NOMENCLATURE**

\[ C = \text{concentration in the membrane [cm}^3 \text{(STP)/cm}^3] \]
\[ D = \text{diffusivity coefficient [cm}^2/\text{s}] \]
\[ l = \text{membrane thickness [cm]} \]
\[ N = \text{steady-state flux [cm}^3 \text{(STP)/cm}^2\cdot\text{s}] \]
\[ \Delta P = \text{partial pressure difference across the membrane [cm Hg]} \]
\[ P = \text{permeability [Barrer, 1 Barrer = 10}^{-10} \text{cm}^3 \text{(STP)}\cdot\text{cm/ (cm}^2\cdot\text{s}\cdot\text{cm Hg}) \]
\[ S = \text{solubility coefficient [cm}^3 \text{(STP)/cm}(3 \text{cm Hg}) \]
\[ x = \text{mole fraction in the retentate stream, dimensionless} \]
\[ y = \text{mole fraction in the permeate stream, dimensionless} \]

**Greek Letters**

\[ \alpha_{ij} = \text{selectivity of component i over component j, dimensionless} \]
\[ \alpha_{ij}^* = \text{ideal selectivity of component i over component j, dimensionless} \]

**Subscripts**

\[ ij = \text{species} \]

**REFERENCES**


