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Benzimidazole-linked polymer membranes for efficient syngas (H₂/CO/ CO_2) separation

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Keywords: BILP-101x membrane PBDI membrane H ₂ /CO separation Syngas ratio adjustment Interfacial polymerization	Precise syngas ratio control is crucial for efficiently producing high-quality clean fuels such as naphtha, kerosene, and diesel. In light of the rising demand for energy-efficient hydrogen separation, this study investigates the $H_2/$ CO separation performance of novel benzimidazole-linked polymer (BILP-101x) and poly(p-phenylene benzo- bisimidazole) (PBDI) membranes fabricated via a simple interfacial polymerization process. The effects of temperature, pressure, and H_2 molar fraction on the membranes' separation performance were comprehensively evaluated. Both membranes displayed high H_2 permeance (BILP-101x~136 GPU; PBDI~76 GPU) and selectivity (BILP-101x~78; PBDI~50) for H_2 /CO separation at 150 °C. The superior H_2 permeance of BILP-101x was attributed to its higher fractional free volume and diffusion coefficients compared to PBDI, as confirmed by molecular simulations. Notably, both membranes demonstrated remarkable stability during long-term testing under simulated syngas conditions (50/25/25H ₂ /CO ₂ /CO, 100 °C for 120 h), outperforming most polymeric membranes reported in literature for H_2 /CO separation. The superior H_2 /CO separation performance coupled with the excellent stability (over 120 h) endows BILP-101x and PBDI membranes with an attractive application prospect for industrial syngas ratio adjustment.

1. Introduction

Hydrogen, often produced through steam reforming of natural gas, is essential for advancing sustainable energy systems. It is regarded as a vital industrial feedstock for producing valuable petrochemicals and serves as a clean fuel for powering future vehicles and electricity generation through fuel cells [1–3]. Among the applications of hydrogen, Gas-to-Liquid (GTL) technology represents a valuable process for converting natural gas into specific liquid fuels, petrochemical products, and intermediate chemicals. The GTL process comprises three key stages: 1, Syngas Production: natural gas is transformed into a mixture of H₂ and CO, commonly referred to as syngas; 2, Fischer-Tropsch (FT)

Synthesis: syngas is transformed into liquid hydrocarbons using specialized cobalt-based or iron-based catalysts within FT reactors [4]; 3, The reforming process: the obtained liquid hydrocarbons are refined and converted into specific products [5-8].

Achieving the desired H₂/CO ratio in syngas is crucial for synthesizing various high-quality products [9-11]. Membrane separation technology emerges as a compelling alternative to conventional techniques such as pressure swing adsorption (PSA) and cryogenic distillation for syngas adjustment. This technology offers advantages such as lower operating costs, continuous processing, and environmental friendliness [12–14]. However, a key challenge lies in selecting suitable membrane materials that efficiently manipulate the H₂/CO ratio.

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Despite significant research exploring novel membrane materials for H₂/CO separation, only polymeric membranes have achieved commercial viability at industrial scale. Various polymer membranes like cellulose acetate, polyimide, and polysulfone, have been reported for H₂/CO separation [15-22]. The PRISM polysulfone membrane, pioneered by Wu et al., has achieved notable success in commercial H₂/CO syngas separation [20]. Barbieri et al. were the first to utilize P84 (BTDA-TDI/MDI co-polyimide) for H2 separation, with their hollow fiber membrane reaching an impressive hydrogen selectivity of up to 60 [21]. Peer and colleagues examined how different feed conditions, including pressure, flow rate, and operating temperature, influenced the separation of hydrogen from syngas using commercially available polyimide membranes [12]. Likewise, Toshiba et al. identified cellulose acetate membranes as promising for manipulating the H₂/CO ratio in syngas [22]. Their two-stage membrane system offers the potential for both syngas composition adjustment and selective CO product recovery [22]. Despite their potential, these membranes are often limited by low permeability, poor thermochemical stability, and ease of plasticization, hindering their widespread application. Therefore, the development of novel polymeric membrane materials that are plasticization resistant and stable at high temperatures is necessary.

Polybenzimidazoles (PBIs) are a type of heterocyclic polymer characterized by their rigid molecular structure. This rigidity, combined with tight chain packing, grants them exceptional resistance to plasticization, high thermochemical stability and intrinsic high H₂ selectivity [23-29]. However, the microstructural rigidity and tight chain packing of PBI membranes also restrict their H₂ permeability, presenting a key challenge in optimizing PBI membranes for industrial applications. Benzimidazole-linked polymers (BILPs) and poly(p-phenylene benzobisimidazole) (PBDI) holding a comparable aromatic heterocyclic benzimidazole fused ring structure to PBIs, can be classified as novel PBIs. In previous works, BILPs and PBDI membranes fabricated through interfacial polymerization have been explored for H₂/CO₂ separation with promising H₂ permeability owing to their microporosity and free volume [30-36]. Despite that H₂/CO₂ separation with PBI membranes has attracted significant interest, research on CO transport through the membranes remains limited. As far as we know, there have been no previous studies that have investigated the performance and mechanisms governing H₂/CO separation in PBI membranes.

This study explores the potential of PBDI and BILP-101x membranes for H_2/CO separation. PBDI and BILP-101x membranes were fabricated through interfacial polymerization on alumina substrates. Typically, the support was immersed in an aqueous solution. The pore of the support was filled with the aqueous solution containing amine monomers. This process consists of immersing the substrate in an aqueous solution with amine monomers, followed by transferring it to an organic solution with aldehyde monomers. Finally, a dense and uniform brown BILP-101x or PBDI layer was formed on the alumina substrate. The impacts of feed temperature, pressure, and H_2 concentration on H_2/CO separation performance of the membranes were systematically investigated. Additionally, long-term stability tests were conducted to assess their potential for industrial use.

2. Experimental section

Materials. 1,2,4,5-Benzenetetramine tetrahydrochloride (BTA, 99%), terephthal aldehyde (TPA, 99%), 1,3,5-triformylbenzene (TFB), toluene (anhydrous, 99.8%), N, N-dimethylformamide (anhydrous, 99.8%), and ethanol (95%) were obtained from Sigma-Aldrich. The asymmetric α -Al₂O₃ substrates (average pore size $\sim 2.5 \ \mu$ m) have a diameter of 18 mm and a thickness of 2 mm with γ -Al₂O₃ layer on top (average pore size $\sim 5.0 \ n$ m) and were acquired from Fraunhofer-Institut für Keramische Technologien und Systeme IKTS.

Preparation of BILP-101x and PBDI membrane. The two membranes were prepared with similar approaches. For the BILP-101x membrane, the α -alumina disk was first immersed in a 1.5 wt% BTA

aqueous solution under a reduced absolute pressure of 0.2 bara for roughly 20 min. The BTA containing substrates were taken out from the aqueous solution, dried with compressed air until no visible droplets remained on the surface, and then immersed in a 0.5 wt% TFB solution in toluene for 2 h. The newly prepared membrane was stored in the fume hood overnight. Subsequently, the membrane was washed twice with toluene to eliminate any unreacted monomers, dried at room temperature for approximately 8 h, and then placed into a custom-made permeation setup for performance testing. For the PBDI membrane, the preparation procedure was the same as the BILP-101x membrane except that the TPA toluene concentration was 1.0 wt% for PBDI membrane.

Preparation of BILP-101x and PBDI free-standing films. 0.5 wt% TFB/1.0 wt% TPA toluene solution was gently poured onto the surface of the 1.5 wt% BTA aqueous solution. After a few seconds, a brown free-standing film of BILP-101x or PBDI appeared at the interface of the two solutions. A large number of films obtained were cleaned twice with toluene and dried overnight in a vacuum at 393 K for subsequent characterization.

Characterization methods. The surface and cross-section morphology of the composite membranes were examined using emission scanning electron microscopy (SEM, JSM-6010LA, JEOL). The lamellar morphology of the two free-standing films was analyzed with transmission electron microscopy (TEM, Tecnai G2 F30). The elemental composition of the BILP-101x composite membrane surface was analyzed using X-ray photoelectron spectroscopy (XPS) on K-Alpha Thermo Fisher Scientific spectrometer with monochromatic Al $K\alpha$ radiation.

Membrane performance evaluation. The membrane (effective membrane diameter of 1.3 cm) performance such as single and mixed gas permeance, and separation selectivity was measured by the Wicke-Kallenbach technique. The temperature was adjusted between 298 K and 423 K by adjusting the temperature control of the convection oven. The feed pressure is regulated by the pressure controller in the range of 1.0–5.05 bara. Gas chromatography (Interscience Compact GC) was used for the single and mixed gas tests, and the sweep gas was argon with a flow rate of 20 mL/min. A $50/25/25H_2/CO_2/CO$ mixture was employed to evaluate the stability of the membranes. For the single gas test, He, H₂, CO₂, CO, N₂, and CH₄ were utilized at a flow rate of 20 mL/min under standard atmospheric pressure. The total feed flow rate for H₂/CO mixture gas separation is 40 mL/min. For each component gas test, the whole gas separation test system was stable for at least 2 h and GC analysis was performed no less than 10 times.

The permeance P_i (1 GPU = 3.3928×10^{-10} mol m⁻² s⁻¹ Pa⁻¹) of the tested gas component *i*, the ideal selectivity S_{ij} of single gases and the separation factor a_{ij} of the mixture gases were calculated as follows:

$$P_i = \frac{J_i}{\Delta p_i} \tag{1}$$

$$S_{ij} = \frac{P_i}{P_j} \tag{2}$$

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j} \tag{3}$$

Where J_i (mol·m⁻²·s⁻¹) represents the gas permeation flux; Δp_i (Pa) is the pressure difference across the membrane of component *i*; x_i , x_j (feed side) and y_i , y_j (permeate side) stand for the molar fractions of components *i* and *j* in the mixture.

3. Results and discussion

3.1. Characterization of BILP-101x and PBDI membranes

The condensation polymerization reactions of BILP-101x and PBDI



Fig. 1. (a) Reaction equation for BILP-101x and PBDI formation; (b) Schematic diagram of BILP-101x or PBDI membrane for H₂/CO separation; (c and d) Crosssectional and surface SEM images of PBDI membrane and (e and f) BILP-101x membrane; (g) C1s XPS spectrum of BILP-101x membrane.



Fig. 2. Permeance evolution upon activation of (a) PBDI and (b) BILP-101x membranes at 100 °C.

composite membranes are depicted in Fig. 1a and b. The reactions occur at the interface between two immiscible solutions containing TPA or TFB and BTA monomers. This confined interface allows for in-situ formation of a highly crosslinked and continuous thin membrane layer on top of the alumina substrate. Scanning electron microscopy (SEM) images of the cross-sections and top surfaces (Fig. 1c-f) reveal the successful fabrication of continuous, smooth, and defect-free PBDI and BILP-101x composite membranes after reaction times of 3 h and 2 h, respectively. The membrane thicknesses are approximately 1.6 µm and 1.2 µm for PBDI and BILP-101x, respectively. High-resolution transmission electron microscopy (HR-TEM) was utilized to further examine the morphology of freestanding BILP-101x and PBDI films prepared at the free toluene-water interface under identical conditions as the composite membranes (details in the experimental section). As shown in Figs. S1a and b, these films exhibit a continuous sheet-like structure with some crumpling, indicating their flexibility.

In addition, the chemical composition of the BILP-101x composite

membrane surface was investigated using X-ray photoelectron spectroscopy (XPS, Fig. 1g and S2). The presence of C—N bonds in the benzimidazole ring structure is evident from the binding energies observed in the XPS spectra: 286.52 eV (C1s) and 398.35 eV (N1s). Trace amounts of oxygen were also detected, likely originating from residual aldehyde monomers.

3.2. Activation of BILP-101x and PBDI membranes

To assess the gas separation performance of the prepared membranes, the as-prepared BILP-101x and PBDI membranes were first activated in a H_2 gas flow at 100 °C until a steady state was reached (Fig. 2a and b). Under these conditions, the gas permeance progressively increases with extended activation time, which is ascribable to the removal of residual water, solvents, and oligomers in the membrane at elevated temperature. Furthermore, the gas separation performance of the membrane remains stable after a certain activation time and then we



Fig. 3. (a) Single gas permeance and (b) ideal selectivity of BILP-101x membrane at 1 bara and 100 °C; Purple and Orange columns represent the ideal and Knudsen selectivity of He to other components, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 4. (a) Temperature-dependent separation performance of the BILP-101x membrane for an equimolar H_2 /CO mixture (at 1 bara); (b) Influence of H_2 molar fraction on H_2 /CO separation performance (at 100 °C); (c–d) Pressure-dependent separation performance of the BILP-101x membrane for an equimolar H_2 /CO and CO₂/CO mixture (at 100 °C).

start the following test.

3.3. Single gas permeation of BILP-101x membrane

The single gas permeance (He, H₂, CO₂, N₂, CO, and CH₄) of the activated BILP-101x membrane was tested and analyzed utilizing the Wicke-Kallenbach technique with a feed pressure of 1.0 bara. The results indicate a roughly negative correlation between single gas permeance and the kinetic diameter of the gas molecules tested (Fig. 3a and b). Helium exhibits the highest permeance (68 GPU) and demonstrates exceptional ideal selectivity over CO₂ (22.2), N₂ (44.8), CO (46.8), and CH₄ (27.7), all significantly exceeding the Knudsen diffusion selectivity, suggesting a molecular sieving mechanism. However, CH₄ permeance deviates slightly from the trend predicted by kinetic diameter. This could tentatively be attributed to the preferential adsorption of CH₄ by BILP-101x compared to N₂, a phenomenon also observed in previous studies on imidazole-linked polymers [27,37,38].

3.4. Mixed gas separation performance of BILP-101x membrane

Generally, gas transport and permeation of dense polymeric

membranes follow the solution-diffusion model [39-41]. CO owns a higher condensability and thus obtains higher solubility while the larger kinetic diameter (3.76 Å) results in a lower diffusivity compared to H₂ (2.89 Å) [42,43]. Temperature is a crucial factor in gas permeation process of one specific membrane. Thus, the H₂/CO mixed-gas test was conducted at various temperatures to gain insight into the gas permeation behavior of gas molecules within the BILP-101x membrane. The permeance of both H₂ and CO rises with increasing temperature, suggesting a temperature-activated mechanism for their diffusion through the BILP-101x membrane. The Arrhenius relation was employed to calculate the apparent activation energies for H2 and CO permeation, which were determined to be 22.3 kJ mol⁻¹ and 4.7 kJ mol⁻¹, respectively (Fig. 4a and S3a). The result suggests that the permeation of the smaller H₂ molecules is more significantly affected by temperature than CO [30]. Consequently, the H₂/CO separation selectivity exhibits a rising trend as the temperature increases from 25 to 150 $^\circ$ C.

The influence of H_2 molar fractions on H_2 /CO separation performance was present in Fig. 4b. The BILP-101x membrane exhibits a slight increase in H_2 permeance as the H_2 molar fraction in the feed gradually rises due to the increasing hydrogen partial pressure. Conversely, CO permeance shows a subtle decrease under these conditions. This



Fig. 5. (a) Temperature-dependent separation performance of the PBDI membrane for an equimolar H_2/CO mixture (at 1 bara); (b) Effect of H_2 molar fraction on H_2/CO separation performance (at 100 °C); (c–d) Pressure-dependent separation performance of the PBDI membrane for an equimolar H_2/CO and CO_2/CO mixture (at 100 °C).

interplay of opposing trends leads to an improvement in overall H₂/CO separation selectivity. This behavior is likely attributed to a slight competitive adsorption effect between H₂ and CO molecules within the membrane [28]. Fig. 4c shows the pressure dependence of the separation performance of BILP-101x membrane for an equimolar H₂/CO mixture at 100 °C, with applied pressures ranging from 1.0 to 5.05 bara. CO permeance exhibits a slight increase with pressure, while H₂ permeance shows minor fluctuations. This interplay leads to a modest decrease in H₂/CO selectivity. Nevertheless, the BILP-101x membrane retains a remarkable H₂/CO selectivity of 16 at 100 °C and 5 bar absolute

feed pressure. Carbon monoxide (CO) can be generated through various established industrial processes, including the partial oxidation or gasification of carbon-containing feedstocks like coal, biomass, or hydrocarbons, as well as the steam reforming of natural gas. However, these processes often produce CO_2 as a byproduct. Thus, the potential of BILP-101x membrane in CO_2/CO separation was explored. Fig. 4d reveals a similar trend as the H₂/CO mixture test: both CO and CO_2 permeance increase as the feed pressure rises. This indicates that small defects in the membrane become more significant at high pressures. As expected, the CO_2/CO selectivity was relatively low (~1). This can be



Fig. 6. Three-dimensional view of an amorphous cell containing (a) BILP-101x and (c) PBDI network. The green surface represents the van der Waals surface, and the grey surface is the Connolly surface with a probe radius of 1.55 Å. (b) and (d) are the *MSD* - *t* curves for the transport of H_2 in BILP-101x and PBDI membranes, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 7. Stability of the (a) BILP-101x and (b) PBDI membrane for 50/25/25H₂/CO₂/CO mixture separation at 1 bara and 100 °C.

ascribed to the slightly larger size of CO in comparison to CO_2 , coupled with the stronger adsorption of CO_2 by the polymer membrane. These opposing factors resulted in a negligible difference in permeation rates [44].

3.5. Mixed gas separation performance of PBDI membrane

The effects of testing temperature, pressure, and H₂ molar fraction on the gas separation performance of PBDI membranes were also examined under similar test conditions as BILP-101x membrane. Both the PBDI and BILP-101x membranes exhibited similar trends in gas separation performance when these factors were varied. This similarity likely stems from the comparable benzimidazole-linked structure of the two membranes (Fig. 1a). Fig. 5a shows that both H₂ and CO permeance rises with increasing temperature, indicating a temperature-activated transport mechanism. The Arrhenius equation was applied to calculate the activation energies for H₂ and CO transport in the PBDI membrane, which were found to be 23.0 kJ/mol and 4.1 kJ/mol, respectively. The higher activation energy for H₂ indicates a stronger influence of temperature on its permeation compared to CO. Consequently, the H₂/CO separation selectivity exhibits a gradual increase with rising temperature (Fig. 5a and S3b). Furthermore, when the H₂ molar fraction was gradually increased, a slight increase in H2 permeance and a slight decrease in CO permeance were observed (Fig. 5b). This can be attributed to a competitive permeation effect between the two gases. Fig. 5c and d shows the impact of pressure on the gas separation performance of the PBDI membrane. Similar to the BILP-101x membrane, the permeance of CO₂ and CO in the PBDI membrane also increased with increasing pressure, while the permeance of H₂ is almost constant. It is worth noting that under the same preparation and test conditions, the gas permeance and H₂/CO separation selectivity of BILP-101x membrane are higher than PBDI membrane. The influence of pressure on the gas separation performance of the PBDI membrane is depicted in Fig. 5c and d. Similar to the BILP-101x membrane, the permeance of CO_2 and CO in the PBDI membrane increases with increasing pressure, while H_2 permeance remains relatively constant.

Interestingly, under identical preparation and testing conditions, the BILP-101x membrane displayed higher gas permeance and H_2 /CO

separation selectivity than the PBDI membrane. This difference can be ascribed to the branched-chain structure of the tetrahedral core in BILP-101x, which allows the formation of higher microporosity and free volume compared to the linear structure of PBDI. To elucidate the underlying mechanisms governing microstructure and gas permeation behavior, molecular dynamics simulations were conducted. Fig. 6a and c show the three-dimensional view of the modeled amorphous cell containing BILP-101x and PBDI network. The green and grey color represent the accessible surface at a probe radius of 1.55 Å. (see details in supporting information). The calculated fractional free volume (FFV) of the BILP-101x was 0.42 %, consistent with the reported experimental value [34]. This value is notably higher than the FFV of PBDI membranes (0.22 %). To assess molecular diffusion, mean squared displacement (MSD) were calculated and analyzed. The mean-squared displacements of gas molecules in the membranes can be calculated through the following equations:

$$MSD(t) = \frac{1}{N} \sum_{i=1}^{N} |\vec{r_i}(t) - \vec{r_i}(0)|^2 = 6D_i t + C$$

where *N* represents the number of atoms diffusing through the membrane, $r_i(t)$ refers to the position vector associated with *i*th molecule at time *t* and D_i is the diffusion coefficient of gas component *i*. Fig. 6b and d presents the *MSDs* of two gases versus time over a certain period, $D_i = a/6$ can be derived by fitting the straight line $MSD = a^*t + C$. The computed D_i of BILP-101x for H₂ was 1.867×10^{-6} cm²/s, higher than that of PBDI membrane $(1.358 \times 10^{-6} \text{ cm}^2/\text{s})$, in line with the FFV results. Overall, the branched structure of BILP-101x facilitates the formation of a higher degree of microporosity, leading to enhanced free volume and H₂ diffusion.

3.6. Stability test of BILP-101x and PBDI membranes

The composition of syngas primarily consists of H_2 , CO_2 , and CO after the water gas shift reaction [45]. The long-term operational stability of the BILP-101x and PBDI membranes was measured under a gas mixture containing 50 vol% H_2 , 25 vol% CO_2 , and 25 vol% CO at 1 bar and 100 °C for 120 h (Fig. 7a and b). The gas permeances measured in



Fig. 8. The H₂/CO separation performance of BILP-101x and PBDI membranes (at 1 bara and 150 °C) in this work compared with the polymeric membranes reported in literature (See supporting information for details).

the H₂/CO/CO₂ gas mixture were slightly lower than those observed for the H₂/CO gas mixture. This decrease in performance can be attributed to competitive adsorption and permeation effects among the different gas specie. Although CO permeance shows slight fluctuation, both H₂ and CO₂ permeance and separation selectivity remain nearly constant throughout the testing period, demonstrating excellent stability. This indicates that competitive adsorption and permeation between the different gases reached equilibrium in both BILP-101x and PBDI membranes at 100 °C. The above results highlight the substantial potential of these membranes for syngas ratio adjustment.

3.7. Comparison of membrane separation performance

Fig. 8 presents a comparative analysis of the H_2/CO separation performance of BILP-101x and PBDI membranes against previously reported membranes in the literature. Compared with other membranes, the reported PBDI and BILP-101x membranes exhibit an excellent balance of high H_2 permeance and H_2/CO selectivity. The high H_2/CO separation selectivity is due to the stricter size-exclusion property of the two polymeric membranes [27,30]. The outstanding H_2/CO separation performance makes the BILP-101x and PBDI membranes hold significant potential for applications in syngas ratio adjustment.

4. Conclusions

In summary, novel BILP-101x and PBDI membranes were successfully fabricated via interfacial polymerization and exhibited exceptional H_2 /CO separation performance. BILP-101x membrane showed a high H_2 permeance of 136 GPU and H_2 /CO selectivity of 78, while PBDI membrane exhibited a high H_2 permeance of 76 GPU) and H_2 /CO selectivity of 50 at 1 bara, 150 °C. These membranes outperformed most previously reported polymeric membranes regarding both H_2 permeance and H_2 / CO selectivity. Moreover, the membranes demonstrated remarkable stability during long-term testing under 1 bara, 100 °C using a H_2 /CO/ CO₂ gas mixture over 120 h. These promising results highlight the potential of BILP-101x and PBDI membranes for syngas purification and ratio adjustment.

CRediT authorship contribution statement

Shaofan Duan: Writing – original draft, Investigation, Data curation. **Haiyan Xu:** Writing – original draft, Methodology, Data curation. Jingjing Zhang: Investigation. Meixia Shan: Writing – review & editing, Methodology, Funding acquisition, Data curation. Shumiao Zhang: Investigation. Yatao Zhang: Writing – review & editing. Xuerui Wang: Writing – review & editing, Methodology, Investigation, Funding acquisition, Data curation. Freek Kapteijn: Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2024.123595.

Data availability

Data will be made available on request.

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