Zeolite-like performance for xylene isomer purification using polymer-derived carbon membranes

Yao Ma^a, Nicholas C. Bruno^b, Fengyi Zhang^a, M. G. Finn^{b,1}, and Ryan P. Lively^{a,1}

^aSchool of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332; and ^bSchool of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332

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Polymers of intrinsic microporosity (PIMs) have been used as precursors for the fabrication of porous carbon molecular sieve (CMS) membranes. PIM-1, a prototypical PIM material, uses a fused-ring structure to increase chain rigidity between spirobisindane repeat units. These two factors inhibit effective chain packing, thus resulting in high free volume within the membrane. However, a decrease of pore size and porosity was observed after pyrolytic conversion of PIM-1 to CMS membranes, attributed to the destruction of the spirocenter, which results in the “flattening” of the polymer backbone and graphite-like stacking of carbonaceous strands. Here, a spirobifluorene-based polymer of intrinsic microporosity (PIM-SBF) was synthesized and used to fabricate CMS membranes that showed significant increases in *p*-xylene permeability (approximately four times), with little loss in *p*-xylene/*o*-xylene selectivity (13.4 versus 14.7) for equimolar xylene vapor separations when compared to PIM-1-derived CMS membranes. This work suggests that it is feasible to fabricate such highly microporous CMS membranes with performances that exceed current state-of-the-art zeolites at high xylene loadings.

membranes | carbon | xylene | pyrolysis | polymers

Xylenes are widely used chemical feedstocks for solvents and the production of synthetic polymers. *para*-Xylene (*p*-xylene), produced on a global scale of 29 million tons per year (1), is an important raw material for materials such as polyester and polyethylene terephthalate. *ortho*-Xylene (*o*-xylene) can be converted into phthalic anhydride, an important plasticizer precursor (2), and *meta*-xylene (*m*-xylene) can be converted into isophthalic acid (3), a precursor for polyethylene terephthalate. Xylenes are mostly produced via catalytic reforming, which converts naphtha distillates into octane-rich liquids (4) known as reformates that are important resources of aromatic compounds. While benzene, ethylbenzene, and toluene can be easily separated, the xylene isomers are difficult to resolve by conventional distillation due to their similar atmospheric boiling points: 144 °C for *o*-xylene, 139 °C for *m*-xylene, and 138 °C for *p*-xylene. The number of theoretical plates required for xylene separation to commercial specifications exceeds 360, which is not feasible (5).

State-of-the-art separation techniques for xylene isomers are instead fractional crystallization and adsorption. The former separates xylene isomers based on their different freezing points: −25 °C for *o*-xylene, −48 °C for *m*-xylene, and 13 °C for *p*-xylene. While fractional crystallization accounts for ~25% of *p*-xylene separations, it has two main drawbacks (6, 7): the *p*-xylene recovery rate of crystallization is around 60 to 70% due to the eutectic point and economic considerations in crystallizer operation, and the required cooling makes the process energy-intensive. Therefore, in most commercial projects, crystallization is applied only to streams in which *p*-xylene concentration exceeds 80% (5). Adsorption separation of xylene isomers, which features greater efficiency and lower energy penalty than crystallization, is performed at industrial scale on simulated moving beds (SMBs), a technology developed by Universal Oil Products (UOP) in the 1960s. A typical SMB unit employs faujasite (FAU)-type zeolites as the adsorbent operating at around 180 °C, giving *p*-xylene recovery of 97 to 99% and purity of 99.7 to 99.9%. It is important to note that an added

distillation separation between *p*-xylene and *p*-diethylbenzene (the desorbate in the SMB process) is often required. To further improve on these energy-intensive and expensive methods, membranes using such materials as polymers, silica gel, zeolite, and metal–organic frameworks (MOFs) have been explored for xylene separation.

Polycrystalline zeolite MFI-type membranes have been widely studied, typically using pervaporation or vapor permeation separation modalities (8, 9). From a fundamental perspective, these zeolites are unlikely to be surpassed for xylene isomer separations, given the precision by which their pore structures can be tuned for the task. For instance, Lai and coworkers optimized the microstructure of Zeolite Socony Mobil-5 (ZSM-5) zeolite membranes for xylene pervaporation (9), providing oriented ZSM-5 membranes with *p*-xylene/*o*-xylene separation factors as high as 400 and *p*-xylene permeance as high as 3×10^{-7} mol/m²·s·Pa. However, such materials often do not maintain idealized structures in practice: the MFI framework can undergo structural distortions upon the adsorption of xylene molecules, especially near ambient temperatures and at high xylene loadings. This distortion can induce a phase change of the MFI crystals from an orthorhombic phase (ORTHO) to a second orthorhombic phase (PARA) that renders the structures unable to distinguish between the xylene isomers and reduces the separation efficiency of the membrane (10, 11). This issue, coupled with low xylene permeances at high fractional occupancies of the guest molecule, suggests that MFI-type zeolite

Significance

Xylenes are essential feedstocks for manufacturing packaging materials, versatile chemicals, industrial solvents, etc. The purification of xylene isomers is one of the most important yet energy-intensive organic mixture separations in the chemical industry. We achieved the separation of xylene isomers using carbon molecular sieve (CMS) membranes derived from a spirobifluorene-based polymer of intrinsic microporosity (PIM-SBF), which could potentially reduce the energy consumption, carbon emissions, and equipment footprint. CMS membranes are solvent- and temperature-resistant materials that can withstand high transmembrane pressures when fabricated into the form of hollow fibers. The new CMS membrane produced here shows competitive performance with state-of-the-art zeolites under high xylene loadings, and its development has provided fundamental insight and guidance into the manipulation of CMS pore structure.

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¹To whom correspondence may be addressed. Email: mgfinn@gatech.edu or ryan.lively@chbe.gatech.edu.

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membranes will struggle to provide satisfactory xylene isomer separation under the fully loaded conditions that may be required for an industrial process. In addition, these membranes require expensive supports and are difficult to produce on a large scale (12). While these longstanding issues are solvable in principle, they have inhibited the practical application of MFI membranes for xylene separations despite their exceptional performance in the laboratory.

Nanoporous carbon molecular sieve (CMS) materials are produced by the pyrolysis of a well-defined polymeric precursor under controlled temperature and atmosphere (13–16). CMS membranes are solvent- and temperature-resistant and have the ability to withstand high transmembrane pressures when fabricated into the form of hollow fibers (17–19). Hollow fibers can be fabricated as “asymmetric membranes,” which have a thin separating layer that transitions to a more porous substructure that provides mechanical support. Typically, this membrane asymmetry is created during a single-step phase inversion process. An asymmetric structure is critical for enabling high product permeances while providing mechanical integrity to the membrane and bypasses issues with fabricating defect-free layers on membrane supports. We have recently shown that asymmetric CMS hollow fiber membranes derived from cross-linked polyvinylidene fluoride have the ability to separate xylene isomers in a modality known as “organic solvent reverse osmosis” (OSRO) (20). While CMS membranes have advantages in scalability and resistance to realistic operating conditions, the existing materials exhibit lower *p*-xylene/*o*-xylene selectivity and lower performance than zeolites. We have therefore turned our attention to the production of CMS membrane with improved properties by varying both the polymer precursor (21) and the pyrolysis conditions by which it is processed.

Under a high-temperature inert atmosphere, the polymer chains are pyrolytically activated and rearranged into stable, highly carbonized structures. While precise details about the molecular details of this process are unknown, the resulting structures likely have short range order in the form of well-defined microporous spaces, the generation of which is driven by entropy (22). This local ordering can be engineered, thus enabling the differentiation of certain molecular pairs. A polymer with high free volume or interconnected micropores [e.g., polyimide (18, 21, 23, 24), PIM-1 (16, 19, 25), functionalized polyimides of intrinsic microporosity (PIM-PI) (26–32), etc.] tends to form highly porous CMS materials. As demonstrated in previous work (16, 19, 25), PIM-1 (Fig. 1A) is a successful precursor for the fabrication of highly porous CMS membranes that are useful for organic solvent separations. Its rigid, contorted random-coil structure, comprised of spirocentered diaromatic monomers linked by fused-ring connectors, results in high free volume within the membrane via the inhibition of effective chain packing (33–38). However, it was found that the size of the ultramicropores inside the PIM-1-derived CMS is quite similar to N₂ (3.64 Å), which severely limits the transport rate of *p*-xylene (16). Previous work demonstrated that PIM-1-derived CMS pyrolyzed under a reducing environment (4% H₂/Ar) yields ultramicropores ranging from 5 to 7 Å, which intersect with the size of xylene molecules (5.8 to 6.8 Å) (25). Nevertheless, compared with the polymer precursors, a decrease of pore size and porosity was still observed for PIM-1-derived CMS after the H₂-included pyrolysis (16, 25).

We suggest that such undesired pore collapse may be attributed to the destruction of the spirocarbon center, which would result in the “flattening” of the carbonaceous strands derived from the pyrolysis reaction. Consistent with previous suggestions that more rigid polymer chains provide better performance for polymeric membranes (i.e., enhanced permeability and permselectivity between gas molecules) (39, 40), we believe that greater rigidity and perhaps thermal stability in the spirocenter building block may prevent chain flattening and subsequent pore collapse during pyrolysis and thus lead to the formation of CMS membranes with a

better separation performance. We describe here a successful application of this principle.

Having rotatable C–C bonds in the indane unit, the spiro-center of the PIM-1 spirobisindane monomer has a certain degree of conformational flexibility (41). McKeown and coworkers demonstrated improved gas separation performance with a spirobifluorene variant, presumably because of the replacement of the flexible indane with a rigid aromatic moiety (42). Here, we show that this spirobifluorene-based polymer of intrinsic microporosity (PIM-SBF, Fig. 1B) is an attractive polymer precursor for CMS membrane fabrication. Two properties of the polymer are thought to contribute to this outcome. First, we believe that the highly aromatic nature of the spirobifluorene structure favors the formation of contorted carbonized chains that do not efficiently pack together, compared to the sp³ centers of PIM-1, which may tend to fragment or allow for chain mobility. Second, PIM-SBF is more thermally stable, showing the start of significant degradation by thermal gravimetric analysis (SI Appendix, Fig. S1) at 580 °C, compared to 490 °C for PIM-1, perhaps helping to prevent pore collapse during pyrolysis. The first derivative of the thermogravimetric analysis (DTGA) curves (SI Appendix, Fig. S1) highlight a minor degradation of PIM-SBF, which starts as low as 400 °C, indicating that PIM-SBF may adopt a “prepyrolysis” rearrangement phase at low pyrolysis temperature (e.g., 500 °C), but is clearly pyrolyzing in a higher temperature. PIM-SBF-derived CMS membranes have higher performance than other CMS membranes for xylene isomer separations and are competitive with the properties of zeolites, especially at high xylene loadings.

Background and Theory

The intrinsic transport properties of sorption-diffusion type membranes are described by two main parameters: “permeability,” a measurement of intrinsic productivity, and “selectivity,” a measurement of separation efficiency. For single-component permeation, permeability ($\mathbb{P}_A$), is equivalent to the ratio of the thickness-normalized flux and the transmembrane fugacity:

$$\mathbb{P}_A = \frac{N_A \ell}{\Delta f_A}, \quad [1]$$

where N_A is the penetrant flux through the membrane of a thickness of ℓ under a transmembrane fugacity difference of Δf_A . In the sorption-diffusion transport mechanism, guest molecules sorb into the upstream side of the membrane and diffuse through it due to the presence of a chemical potential gradient and desorb at the downstream side. The permeability can be expressed as the product of D_A , the transport diffusion coefficient, and $\mathbb{S}_A$, the solubility or sorption coefficient:

$$\mathbb{P}_A = D_A \times \mathbb{S}_A. \quad [2]$$

The sorption coefficient, $\mathbb{S}_A$, is a thermodynamic factor governed primarily by the condensability of a gas penetrant and the membrane-penetrant interactions. The diffusion coefficient, D_A , is a kinetic property, related to the ability of a guest molecule to “jump” within the membrane; in small pore, microporous membranes, the diffusivity is well-described by transition state theory (43).

The ideal permselectivity for guest molecule A versus B, α_{AB} , reflects the separation efficiency of the membrane and is defined as the ratio of the permeability of the fast component to the slow component when a downstream vacuum is applied. The dominating factors in the selectivity can be defined using the sorption-diffusion model, which shows the permselectivity as the product of the diffusive selectivity D_A/D_B and sorptive selectivity $\mathbb{S}_A/\mathbb{S}_B$:

Fig. 1. Reaction scheme and material characterization. (A) Reaction scheme for the synthesis of PIM-1. (B) Reaction scheme for the synthesis of PIM-SBF. Digital photograph of (C) PIM-SBF polymeric film and (D) PIM-SBF-derived CMS dense membrane. (E) SEM cross-sectional image of a PIM-SBF-derived CMS dense membrane. (F) Pore size distributions measured by nitrogen physisorption at 77 K.

$$\alpha_{AB} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \times \left(\frac{S_A}{S_B} \right). \quad [3]$$

Results and Discussion

Characterization of Polymer Precursors and CMS Membranes. The pore structure of PIM-SBF polymer precursors and the corresponding PIM-SBF-derived CMS membranes (Fig. 1 C–E) were characterized by nitrogen physisorption experiments performed at 77 K. As shown in *SI Appendix, Fig. S2*, the final pyrolysis temperatures (i.e., 500, 800, and 1,100 °C) was investigated under a fixed hydrogen volume fraction in the pyrolysis gas of 4 vol % H₂, while two hydrogen volume fractions (i.e., 0 and 4 vol % H₂) were studied under a final pyrolysis temperature of 500 °C. As illustrated in *SI Appendix, Fig. S2 A and C*, PIM-SBF precursors displayed a sharp uptake in the low pressure range, followed by a more linear rise that has been attributed to sorption-induced polymer dilation (44–46). The apparent absence of dilation in the PIM-SBF-derived CMS samples (*SI Appendix, Fig. S2 B and D*) indicates that the CMS samples possess more rigid structures compared with the polymer precursor, as expected. As shown in *SI Appendix, Table S1*, the PIM-SBF-derived CMS

membranes possess high surface areas (366 to 855 m²/g) and large pore volumes (0.153 to 0.380 cm³/g). It is worth noting that some of the PIM-SBF-derived CMS membranes (i.e., CMS_PIM-SBF_500 °C_4% H₂) were observed to have an increase of the surface area and pore volume relative to the precursor. These results agree with our hypothesis that a more rigid polymer precursor may prevent the polymer chains from flattening and the pores from collapsing to some degree during pyrolysis. Importantly, the Brunauer–Emmett–Teller (BET) surface area and pore volume are larger for PIM-SBF-derived CMS relative to the values for PIM-1-derived CMS fabricated under the same pyrolysis conditions. These higher pore volumes are advantageous as they contribute to the high permeability (i.e., flux or throughput) of the CMS membranes.

The pore size distribution of the polymer precursors and the CMS membranes was derived from the nitrogen isotherms at 77 K using the two-dimensional nonlocal density functional theory (2D-NLDFT) method. The pore size distribution curves are illustrated using two different y axis scales to make both the ultramicropores and micropores visible. As shown in Fig. 1F, PIM-SBF has ultramicropores ranging from 5 to 8 Å. After the pyrolysis (under the pure argon or 4% H₂/Ar environment), the

“mid-sized” ultramicropores (i.e., 5 to 7 Å) were maintained inside the CMS membranes, which will result in effective molecular separation between appropriately sized organic solvents molecules (e.g., xylene isomers). It is worth noting that reasonable nitrogen physisorption isotherms at 77 K for CMS_PIM-1_500 °C_0% H₂ cannot be obtained, which indicates that the size of ultramicropores within this CMS is quite similar to N₂ (3.64 Å), thus resulting in extremely slow N₂ diffusion (16). In contrast, the CMS_PIM-SBF_500 °C_0% H₂ revealed ultramicropores ranging from 5 to 7 Å, suggesting that it is feasible to fabricate CMS membranes with “mid-sized” micropores without reducing environments. The avoidance of hydrogen species in the pyrolysis environment will make the pyrolysis process safer and reduce the complexity of the overall fabrication process.

The full width at half maximum (FWHM), the average pore size, and the micropore and ultramicropore volumes for PIM-SBF-derived CMS are summarized in Table 1. The distributions of ultramicropores were narrower, and the average ultramicropore size was smaller as the hydrogen content decreased from 4 vol% to 0 vol%. By comparing the pore size distributions for PIM-SBF-derived CMS samples pyrolyzed under 500, 800, and 1,100 °C, it can be summarized that the average size of the ultramicropores decreased with the increase of the pyrolysis temperature, indicating the tightening of CMS matrix under a higher pyrolysis temperature. The micropore volumes inside the PIM-SBF-derived CMS membranes increased with the decrease of the pyrolysis temperature or the increase of the hydrogen content. As shown in Table 1, the pyrolysis of PIM-SBF under relatively low temperatures (≤800 °C) will lead to the fabrication of CMS membranes with large ultramicropore volumes (0.230 to 0.280 cm³/g). However, very high pyrolysis temperatures (e.g., 1,100 °C) will induce a decrease of both the micropore and ultramicropore volumes. It is worth noting that CMS_PIM-SBF_500 °C_4% H₂ has a narrow distribution of ultramicropores (an FWHM of 1.30 Å versus 2.69 Å) but a slightly larger average ultramicropore size (7.1 Å versus 5.6 Å) relative to CMS_PIM-1_500 °C_4% H₂. These two effects compete against each other (i.e., larger pore size will result in a decrease in selectivity, but a tighter pore size distribution will increase selectivity), and so it is difficult to estimate a priori how the membrane performance will change based on the change in the precursor. As will be shown later, the selectivity is largely maintained while the permeability increases dramatically.

The CMS membranes were further characterized by X-ray photoelectron spectroscopy (XPS) to investigate the carbon bonding nature within the membranes. The C1s spectrum (SI Appendix, Fig. S3) for different CMS samples can be deconvoluted into three Gaussian peaks. Good fits were obtained as indicated by a square root of reduced χ^2 smaller than 3 and a coefficient of determination R² higher than 0.99 for all the CMS samples. The two most substantial peaks with a relative binding energy distance of around 1 eV correspond to two different hybridization states. The higher binding energy signal is associated with *sp*³ hybridized carbon, while the signal with an energy shift of about 1 eV is attributed to *sp*² hybridized carbon (47–49). Besides, the peak observed around 289 eV demonstrates the presence of the C-O carbon

state (50). The *sp*³ hybridized carbon is a three-dimensional structure that disrupts carbonaceous plate packing and can contribute to high guest molecule flux. The *sp*² hybrid carbon (a two-dimensional graphite layered structure) enables plate packing, resulting in a more compact microstructure with smaller ultramicropore gaps in the plate (25). Our previous study has demonstrated that a higher *sp*³/*sp*² hybridized carbon ratio in PIM-1-derived CMS resulted in a more permeable but less selective structure (25). In this study, the *sp*² and *sp*³ hybridized carbon content in each PIM-SBF-derived CMS sample can also be estimated by the ratio of the peak area of its XPS spectrum. As illustrated in Table 1, similar to the results for PIM-1-CMS, the *sp*³/*sp*² carbon ratio in the PIM-SBF-CMS also increased as the pyrolysis temperature decreases or the hydrogen concentration increases. It is worth noting that the *sp*³/*sp*² carbon ratio for PIM-SBF-derived CMS is higher relative to the values for PIM-1-derived CMS fabricated under the same pyrolysis conditions. The higher *sp*³/*sp*² carbon ratio in PIM-SBF-CMS is useful for imparting higher guest molecule flux of the CMS membranes. The supplementary N₂s XPS, Fourier-transform infrared spectroscopy (FTIR), and Raman spectra for PIM-SBF and 500 °C pyrolyzed CMS_PIM-SBF samples and the respective analysis can be found in SI Appendix, Figs. S4–S6.

Sorption and Diffusion Property of Xylene Isomers in CMS Membranes.

The sorption isotherms of *p*-xylene and *o*-xylene for CMS_PIM-SBF_500 °C_4% H₂ and CMS_PIM-1_500 °C_4% H₂ were collected at 55 °C. As shown in Fig. 2A and B, all isotherms display a sharp increase in adsorption levels in the low saturation region and then plateau at higher saturation values. As expected, for the same type of CMS membranes, the sorption uptake for *p*-xylene at each pressure condition is quite similar to that of the *o*-xylene (uptake differences are within 5 wt%) because of their similar chemical and physical properties, which indicates the absence of a sorption-selective separation mechanism within CMS membranes. It is worth noting that sorption uptakes of the CMS_PIM-SBF_500 °C_4% H₂ membranes for *p*-xylene and *o*-xylene are both a little bit higher (i.e., ~1.2× higher) than that of the CMS_PIM-1_500 °C_4% H₂ at all relative pressures, indicating a more porous structure in the spirobifluorene case. This observation agrees well with the nitrogen physisorption measurements (Table 1), which illustrated a higher micropore volume value for CMS_PIM-SBF_500 °C_4% H₂ (0.043 cm³/g versus 0.034 cm³/g) relative to CMS_PIM-1_500 °C_4% H₂.

Even though *p*-xylene and *o*-xylene possess similar sorption properties within the PIM-SBF CMS, the “mid-sized” ultramicropores (i.e., 5 to 7 Å) inside the rigid CMS membranes enable diffusion-based molecular separations of the xylene isomers. The single-component kinetic uptake curves (SI Appendix, Fig. S7) were determined by the vapor sorption analysis method and were utilized to estimate the transport diffusivities, *D* of xylene isomers in different CMS samples. The transport diffusion coefficients for xylene isomers in CMS_PIM-1_500 °C_4% H₂ and CMS_PIM-SBF_500 °C_4% H₂ and the transport diffusion selectivity between *p*-xylene and *o*-xylene for these two kinds of CMS materials were

Table 1. The full width at half maximum, average pore size, micropore, and ultramicropore volumes for PIM-SBF-derived CMS formed under different conditions compared with CMS_PIM-1_500 °C_4% H₂

Sample	Full width at half maximum (Å)	Average ultramicropore size (Å)	Micropore volume (cm ³ /g)	Ultramicropore volume (cm ³ /g)	<i>sp</i> ³ / <i>sp</i> ² C ratio
CMS_PIM-SBF_500 °C_4% H ₂	1.30	7.1	0.043	0.230	0.888
CMS_PIM-1_500 °C_4% H ₂	2.69	5.6	0.034	0.113	0.652
CMS_PIM-SBF_500 °C_0% H ₂	0.93	6.0	0.023	0.280	0.767
CMS_PIM-SBF_800 °C_4% H ₂	0.69	6.1	0.016	0.276	0.742
CMS_PIM-SBF_1100 °C_4% H ₂	0.77	5.8	0.007	0.133	0.290

Fig. 2. Sorption and diffusion properties of CMS. Single-component sorption isotherms of *p*-xylene and *o*-xylene in (A) CMS_PIM-1_500 °C_4% H₂ and (B) CMS_PIM-SBF_500 °C_4% H₂ measured at 55 °C. (C) The transport diffusion coefficients for xylene isomers in CMS_PIM-1_500 °C_4% H₂ and CMS_PIM-SBF_500 °C_4% H₂.

illustrated in Fig. 2C. The transport diffusion coefficients for both *p*-xylene and *o*-xylene in the PIM-SBF-derived CMS increase obviously relative to the PIM-1-derived CMS samples in the same pyrolysis environment (4.0×10^{-9} versus 1.0×10^{-9} cm²/s for *p*-xylene, 2.3×10^{-10} versus 4.0×10^{-11} cm²/s for *o*-xylene). Consistent with our observations from the nitrogen physisorption measurements, CMS_PIM-SBF_500 °C_4% H₂ has a much higher pore volume (0.161 cm³/g versus 0.380 cm³/g as shown in *SI Appendix, Table S1*) relative to that of CMS_PIM-1_500 °C_4% H₂, which will result in the more rapid diffusion of guest molecules through PIM-SBF-derived CMS. Importantly, CMS_PIM-SBF_500 °C_4% H₂ exhibits a smaller diffusion selectivity (17.4 versus 25.0) relative to that of CMS_PIM-1_500 °C_4% H₂, which is mainly contributed by the larger average ultramicropore size (7.1 Å versus 5.6 Å).

Permeation and Separation of Xylene Isomers. The separation performance of CMS membranes was tested using a Wicke–Kallenbach permeation setup, where the total pressure difference across the membrane is maintained at zero. The feed, an equimolar *p*-xylene/*o*-xylene mixture vapor carried by nitrogen, flushes the upstream while a nitrogen sweep carries the permeate to a gas chromatograph to determine the xylene flux across the membrane. The influence of polymer precursor on the permeation performance of CMS membranes for the xylene isomers is illustrated in Fig. 3A. As shown, the CMS membranes derived from PIM-SBF gain around four times higher *p*-xylene permeability than the membranes derived from PIM-1. This is consistent with our characterization results that the pore volume for PIM-SBF-derived CMS is larger relative to the values for PIM-1-derived CMS fabricated under the same pyrolysis conditions (0.380 cm³/g for CMS_PIM-SBF_500 °C_4% H₂ versus 0.161 cm³/g for CMS_PIM-1_500 °C_4% H₂ as shown in *SI Appendix, Table S1*). The larger pore volume inside the spirobifluorene-based CMS membranes will create more diffusion pathways for guest molecules to pass through and lead to an increased diffusivity, which ultimately benefits permeability. Unlike the permeability, the *p*-xylene/*o*-xylene permselectivity exhibits a much smaller change. This is likely owing to the fact that permselectivity is mainly dominated by the ultramicropores inside the CMS membranes. The size of the ultramicropores inside both the CMS_PIM-SBF_500 °C_4% H₂ and CMS_PIM-1_500 °C_4% H₂ is around 5 to 7 Å (note that the xylene isomers to be separated, *p*-xylene and *o*-xylene, have kinetic diameters of 5.8 Å and 6.8 Å, respectively). The small full widths at half maximum (1.30 Å for CMS_PIM-SBF_500 °C_4% H₂ versus 2.69 Å for CMS_PIM-1_500 °C_4% H₂) enable the high *p*-xylene/*o*-xylene permselectivity.

The single component sorption and diffusion data were utilized as inputs into the Maxwell–Stefan (M-S) model to predict the mixture permeabilities with and without molecular frictional coupling effects (51). Here, the frictional coupling effects between xylene isomers were estimated using a Vignes-type correlation (52, 53). Fig. 3A also shows the comparison of experimental results of an equimolar *p*-xylene/*o*-xylene vapor mixture separated by dense CMS_PIM-SBF_500 °C_4% H₂ membranes measured at 55 °C by Wicke–Kallenbach tests and predictions by the M-S model (detailed modeling parameters can be found in *SI Appendix, Table S2*). The experimental *p*-xylene permeability is slightly higher (1.05 times) than the M-S model predicted value using frictional coupling effects and is observed to be 60.6% lower than the result predicted by the M-S model without coupling effects. In this work, the maximum loading of the xylene isomers in the CMS materials was estimated by utilizing the total pore volume of the membrane (measured by nitrogen physisorption tests at 77 K) and the molar volume of the xylene isomers. However, this assumption may overestimate the amount of xylene isomer sorption for Wicke–Kallenbach tests. It is the micropore volume that mainly contributes to the sorption of xylene molecules while the ultramicropore volume contributes little. Such an overestimation would lead to an overestimation of the model predicted permeability. The experimental *p*-xylene/*o*-xylene selectivity falls between the selectivity predicted by the M-S model with and without the coupling effects. The result suggests that selectivity losses in the membrane were not as severe as predicted by the M-S mixture case with frictional coupling effects considered. This indicated that the Vignes-type correlation, which was used to estimate the frictional coupling effects here, is not accurately capturing the extent of the frictional coupling. Alternatively, there could be a gradient of frictional coupling effects, which are not considered here (i.e., a constant “cross coupling” diffusivity, $\bar{D}_{12}$, was used in these estimates). Such a gradient would indicate that the xylene isomers are highly coupled on the high activity side of the membrane yet relatively uncoupled on the low activity side, which plausibly explains the difference between the two models and the experiment.

The effect of the final pyrolysis temperatures and the hydrogen concentration in the pyrolysis environment on the separation performance of PIM-SBF-derived CMS membranes is also shown in Fig. 3A. It is shown that a higher *p*-xylene permeability and a similar permselectivity was observed when the hydrogen concentration in the pyrolysis environment was increased from 0 to 4 vol%. This result agrees with the nitrogen physisorption measurements that hydrogen will help to create CMS membranes with a higher BET surface area and a larger pore volume. In addition, as expected, a lower *p*-xylene permeability and a

Fig. 3. Permeation and separation of xylene isomers. (A) Experimental (equimolar xylene vapor mixture Wicke–Kallenbach tests at 55 °C) separation performance of CMS_PIM-SBF_500 °C_4% H₂ (blue square marker), CMS_PIM-SBF_500 °C_0% H₂ (orange diamond marker), CMS_PIM-SBF_800 °C_4% H₂ (green left triangle marker), CMS_PIM-SBF_1100 °C_4% H₂ (pink right triangle marker), and CMS_PIM-1_500 °C_4% H₂ (red up triangle marker). Maxwell–Stefan model predicted performance for CMS_PIM-SBF_500 °C_4% H₂ with (solid blue circle marker) and without (hollow blue circle marker) considering frictional coupling effects. (B) The *p*-xylene/*o*-xylene separation performance of PIM-SBF-derived CMS as a function of *sp*³/*sp*² hybridized carbon ratio based on equimolar xylene vapor mixture Wicke–Kallenbach tests at 55 °C. Lines are drawn to guide the eye. (C) The *p*-xylene/*o*-xylene separation performance of PIM-1-derived CMS as a function of *sp*³/*sp*² hybridized carbon ratio based on equimolar xylene vapor mixture Wicke–Kallenbach tests at 55 °C (25). Lines are drawn to guide the eye. (D) Estimation of *p*-xylene vapor permeance through MFI zeolite (silicalite-1) membranes and CMS_PIM-SBF_500 °C_4% H₂ as a function of *p*-xylene feed pressure (operating temperature = 55 °C). CMS_PIM-SBF_500 °C_4% H₂ with a permeate *p*-xylene pressure = 0.1 Pa (red line) or 100 Pa (pink line). MFI zeolite (silicalite-1) membranes with a permeate *p*-xylene pressure = 0.1 Pa (black line) or 100 Pa (blue line).

higher permselectivity were observed when the final pyrolysis temperature was increased from 500 to 1,100 °C.

As discussed previously, the *sp*³/*sp*² hybridized carbon ratio for PIM-SBF-derived CMS is higher relative to the values for PIM-1-derived CMS fabricated under the same pyrolysis conditions. We believe that the higher *sp*³/*sp*² hybridized carbon ratio in PIM-SBF-CMS is useful for imparting high guest molecule flux of the CMS membranes. Fig. 3B illustrates the separation performance for PIM-SBF-CMS membranes as a function of *sp*³/*sp*² hybridized carbon ratio. As shown in Fig. 3B, as the *sp*³/*sp*² hybridized carbon ratio increases from 0.29 to 0.89, the permeability of *p*-xylene through the PIM-SBF-CMS membranes improves significantly from 4.3×10^{-14} to 2.4×10^{-13} mol-m/(m²-s-Pa) (>5×, 458% increase) while the permselectivity decreases only slightly from 17.9 to 13.4 (25% decrease). This observation suggests that the improved separation performance of the CMS membranes can be achieved through tuning the *sp*³/*sp*² hybridized carbon ratio of CMS membranes. Fig. 3C shows the separation performance for PIM-1-CMS membranes as a function of *sp*³/*sp*² hybridized carbon ratio (25). The response of the *p*-xylene permeability to the *sp*³/*sp*² hybridized carbon ratio (Fig. 3B and C) indicates the difference between the CMS structures derived from PIM-1 and PIM-SBF. For PIM-SBF derived CMS, the permeability-promoting effect of *sp*³-rich carbon strands increases as the concentration of *sp*³-rich carbon strands increases. However, for PIM-1-derived CMS, the permeability-promoting effect of *sp*³-rich carbon strands decreases as the concentration of *sp*³-rich carbon strands increases. Further research is required to understand the source of this differing response. We hypothesize that further disruptions of carbonaceous plate formation via increases in *sp*³ hybridized carbon inclusion will continue

to increase the porosity of the polymer but ultimately disrupt the formation of well-defined ultramicropores.

Compared with the state-of-the-art zeolite membranes, CMS_PIM-SBF_500 °C_4% H₂ is expected to exhibit better performance in the practical separation of concentrated xylene mixture. Fig. 3D compared the theoretical *p*-xylene vapor permeance through a perfect MFI zeolite (silicalite-1) membrane (20) and the CMS_PIM-SBF_500 °C_4% H₂ membrane as a function of *p*-xylene feed pressure (the detailed performance estimation process can be found in *SI Appendix*). An increase in *p*-xylene feed pressure with a constant xylene diffusivity will result in a decreasing sorption coefficient of *p*-xylene (determined by the nature of Langmuir isotherm), ultimately decreasing *p*-xylene permeance through CMS_PIM-SBF_500 °C_4% H₂ membranes. As shown in Fig. 3D, when the *p*-xylene permeate pressure is 0.1 Pa, *p*-xylene permeance through CMS_PIM-SBF_500 °C_4% H₂ gradually decreases from 2.1×10^{-2} to 4.4×10^{-6} mol/m²-s-Pa (by four orders of magnitude) as the *p*-xylene feed pressure increases from 0.11 Pa to 5475.7 Pa (saturation pressure of *p*-xylene under 55 °C). Unlike CMS_PIM-SBF_500 °C_4% H₂, it has been shown that the silicalite-1 nanopores exhibit a strong confinement effect to *p*-xylene molecules, which results in a decrease in *p*-xylene diffusivity as the loading of *p*-xylene increased (54). In this case, the *p*-xylene permeance through silicalite-1 membranes dramatically decreases as feed pressure increases. Specifically, when the *p*-xylene permeate pressure is 0.1 Pa, *p*-xylene permeance through silicalite-1 membrane dramatically decreases from 4.7×10^{-2} to 8.4×10^{-7} mol/m²-s-Pa (by five orders of magnitude) as the *p*-xylene feed pressure increases from 0.11 Pa to 5475.7 Pa. Even though silicalite-1 membrane exhibits higher *p*-xylene permeance than CMS_PIM-SBF_500 °C_4% H₂ under a low loading condition, the dramatic diffusivity decrease results in a

substantially lower *p*-xylene permeance through silicalite-1 membranes under high loadings. When the *p*-xylene permeate pressure is increased to 100 Pa, the silicalite-1 membrane exhibits roughly three orders of magnitude lower *p*-xylene permeance than CMS PIM-SBF 500 °C 4% H₂ under the same feed pressure. While both CMS- and MFI-type membranes exhibit significant losses in permeance as xylene loading increases, CMS materials are more successful in maintaining permeance levels relative to MFI. The experimental xylene vapor separation performance of the PIM-SBF-CMS, PIM-1-CMS, and state-of-the-art MFI-type zeolite membranes are also compared, as shown in *SI Appendix, Fig. S8*. The PIM-SBF-derived CMS membrane exhibits roughly five times improvement in *p*-xylene permeability with a negligible sacrifice of *p*-*o*-xylene selectivity compared with PIM-1-CMS. Considering both *p*-xylene permeability and *p*-*o*-xylene selectivity, PIM-SBF-derived CMS exhibits comparable performance with silicalite-1 membranes under similar operating conditions.

Conclusion

CMS membranes fabricated from PIM-SBF under standard and hydrogen-added pyrolysis conditions showed significantly better performance in xylene isomer separations than membranes fabricated from PIM-1. While hydrogen concentration in the pyrolysis atmosphere and the final pyrolysis temperature were found to have significant effects on the pore structures of the resulting CMS membranes, the spirobifluorene-based CMS materials were found to possess high surface areas and pore volumes without requiring reducing atmospheres, which will ultimately streamline the fabrication process. The optimized PIM-SBF-derived CMS membrane demonstrated a diffusion selectivity of ~17.4 between *p*-xylene of *o*-xylene, a value of significant practical utility, and enhanced parameters in Wicke–Kallenbach permeation experiments. The high permeability of the PIM-SBF-derived CMS membranes is thought to be due to their larger pore structure (characterized using nitrogen physisorption), BET surface area, and pore volume. Sorption isotherms of *p*-xylene of *o*-xylene were also measured, showing no sorption-selective separation between xylene isomers within PIM-SBF-derived CMS membranes. Moreover, the theoretical *p*-xylene vapor permeance through the CMS membrane derived from PIM-SBF at 500 °C and 4% H₂ as a function of *p*-xylene feed pressure was found to be more robust toward higher xylene loadings than for MFI zeolite membranes, suggesting that the CMS materials may be useful in high-throughput separations.

Materials and Methods

Details regarding reagents, synthesis of monomers, material characterization methods, organic sorption test, and Wicke–Kallenbach permeation measurement are provided in *SI Appendix*.

Synthesis of PIM-1. PIM-1 was synthesized using the low-temperature polycondensation method, as shown in Fig. 1A (35). The two purified monomers, tetrafluoroterephthalonitrile (TFTPN) and 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (TTSBI), were added to anhydrous dimethylformamide (DMF) at an equimolar ratio in a round-bottom flask. Anhydrous highly crushed K₂CO₃ (2.5 mol eq. times with respect to TFTPN) was added to the solution after the monomers were completely dissolved. Then, the polymerization reaction was continuously stirred under a nitrogen atmosphere at 65 °C for 72 h. After the reaction, upon cooling, deionized water was used to quench the reaction and precipitate the PIM-1 polymer. The crude product was then collected by filtration and washed with additional deionized water to remove salts and residual solvent. Repeated reprecipitation from chloroform further purified the polymer. Finally, the fluorescent yellow PIM-1 polymer was dried at 70 °C under vacuum for 12 h. The molecular weight as determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) was *M_n* = 46,500 with a polydispersity index (PDI) = 1.5 when compared against polystyrene standards.

Synthesis of PIM-SBF. PIM-SBF was synthesized using the standard PIM-forming aromatic nucleophilic substitution polymerization reaction, as shown in Fig. 1B (35, 42). A flame-dried 250 mL round-bottomed flask equipped with a magnetic stir bar and rubber septum was charged with 2,2',3,3'-tetrahydroxy-9,9'-spirobifluorene (4.18 g, 11 mmol, 1 equiv.) and tetrafluoroterephthalonitrile (2.2 g, 11 mmol, 1 equiv.). Dry DMF (55 mL) was added by syringe, and the reaction mixture was stirred under nitrogen at room temperature until the complete dissolution of both monomers. Potassium carbonate (12.1 g, 88 mmol, 8 equiv.) was added in one portion, and the reaction mixture was stirred at 65 °C for 92 h. After completion, the reaction mixture was poured into water, filtered, and washed with water, methanol, and acetone. The crude material was redissolved in chloroform, precipitated into 2:1 methanol:acetone, filtered, and dried in a vacuum oven at 100 °C to provide the title compound as a vibrant yellow powder. The weight average molecular weight as determined by GPC in THF against polystyrene standards was *M_w* = 54,000 with a PDI = 1.5. A substantial, higher molecular weight portion was also present (as shown in *SI Appendix, Fig. S9*). The observed *M_w* of this material by GPC was 721,701 kDa, which we regard as unrealistic. Instead, we presume that this material is hyperbranched, caused by the reaction of tetrafluoroterephthalonitrile with trace water or potassium carbonate (55). The molecular structures of all the chemicals involved during the synthesis of PIM-SBF are shown in *SI Appendix, Table S3*, and their synthesized detail are provided in *SI Appendix*.

Dense Polymeric Film Preparation. The dried PIM-SBF or PIM-1 was dissolved in chloroform to form a 10 wt% polymer solution and placed on a roller at room temperature for 6 h to form a homogeneous polymer solution. The resulting solution was then used to prepare polymeric films by a solution casting method at room temperature. A glove bag (Glas-Col) equipped with the polymer solution vial, a glass plate, a doctor blade, and a beaker containing excess chloroform was placed in a fume hood prior to film casting. The glove bag was saturated with chloroform for 5 h after being sealed and purged with nitrogen for three times. Afterward, the polymer solution was transferred from the vial to the glass plate and cast into a uniform film. Subsequently, the film solidified as the chloroform slowly evaporated in the glove bag for 3 d, followed by another 24 h vacuum drying at 70 °C.

Fabrication of CMS Membranes Derived from Polymer Precursor. CMS membranes were fabricated from the pyrolysis of polymeric precursor (PIM-SBF or PIM-1) in a furnace located inside a fume hood, as shown in *SI Appendix, Fig. S10*. Polymer precursors were first placed on a stainless steel mesh plate, placed into a quartz tube, and loaded into a three-zone tube furnace (OTF-1200X-III-S-UL, MTI Corporation). Sealing of the quartz tube was insured by a pair of SS 304 vacuum flanges with double high-temperature silicone o-rings. A hydrogen (4 vol%)/argon mixed gas cylinder was used to provide hydrogen included pyrolysis environment. Before pyrolysis, the entire system was purged with the desired gas mixture for at least 12 h until the oxygen concentration in the tube furnace was below 0.5 ppm as measured by an inline oxygen analyzer (R1100-ZF Rapidox 1100ZF, CEA Instruments, Inc.) (25). A surface-mounted hydrogen detector is triggered if the hydrogen concentration exceeds 8,000 ppm inside the fume hood for the sake of safety. The heating protocols used are illustrated in *SI Appendix, Table S4*.

Wicke–Kallenbach Permeation Tests. The separation performance of CMS Membranes was tested using a Wicke–Kallenbach permeation setup, where the total pressure difference across the membrane is maintained at zero. The feed, an equimolar *p*-xylene/*o*-xylene mixture vapor carried by nitrogen, flushes the upstream while a nitrogen sweep carries the permeate to a gas chromatograph to determine the xylene flux across the membrane. The free-standing dense CMS membranes were fixed between rings of aluminum tape (0.003 inches thick, McMaster-Carr) with an outer diameter of 1 inch and the inner diameter of 3/8 inch and sealed by a chemically resistant epoxy (MarineWeld 8272, JB Weld).

Data Availability. All data are available in the main text and *SI Appendix*.

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