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www.elsevier.com/locate/memsci

PII: S0376-7388(15)00543-8
DOI: <http://dx.doi.org/10.1016/j.memsci.2015.06.019>
Reference: MEMSCI13777

To appear in: *Journal of Membrane Science*

Received date: 27 March 2015
Revised date: 26 May 2015
Accepted date: 12 June 2015

Cite this article as: Yichang Pan, Wei Liu, Yingjie Zhao, Chongqing Wang, Zhiping Lai, Improved ZIF-8 membrane: Effect of activation procedure and determination of diffusivities of light hydrocarbons, *Journal of Membrane Science*, <http://dx.doi.org/10.1016/j.memsci.2015.06.019>

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Improved ZIF-8 membrane: effect of activation procedure and determination of diffusivities of light hydrocarbons

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Keywords: ZIF-8, Membrane, Diffusivity, Hydrocarbon, Separation

Abstract

Zeolitic imidazolate framework ZIF-8 has shown great potential for effective separation of hydrocarbon mixtures based on its intrinsic ultramicroporous feature. In order to explore the permeation and diffusion properties of hydrocarbons through ZIF-8 membrane, high-quality ZIF-8 membranes with a separation factor of ~90 for propylene/propane are successfully prepared via optimizing the activation processes. Single-component permeation data for hydrocarbons (C1~C4) through the improved ZIF-8 membrane are measured and analyzed by Maxwell-Stefan (MS) model to get the transport diffusivities of these hydrocarbons. The diffusivity values of

hydrocarbon compare well with those obtained by other experimental techniques. Binary mixture permeation also can be well predicted through single-component adsorption parameters.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal-organic frameworks (MOFs), consists of inorganic metal ions coordinated to organic imidazolate ligands, and have large surface areas and pore volumes, and high chemical and thermal stability [1-3]. In particular, intrinsic microporous property makes ZIFs as idea candidates for the fabrication of molecular sieve membranes used in gas separation [4-6]. The ZIF-8 framework ($\text{Zn}(\text{MeIM})_2$, MeIM = 2-methylimidazole), one of representative ZIFs, features sodalite (SOD) topology and possesses large spherical cavities but nanoporous apertures (ca. 0.34 nm) [7]. Recently, it was shown that ZIF-8 membranes are highly attractive for separating hydrocarbon mixtures, such as H_2/CH_4 [8-11], CO_2/CH_4 [12], C_2/C_3 [13], ethylene/ethane [14], propylene/propane [15-19], H_2 /propane [20-23]. Caro's group first reported the in-situ synthesis of ZIF-8 membrane on titania support, exhibiting a separation factor for H_2/CH_4 of 11.2 [8]. Jeong and co-workers also successfully in-situ prepared the ZIF-8 membrane on $\alpha\text{-Al}_2\text{O}_3$ support [9]. The obtained membrane presented a selectivity of 13 for H_2/CH_4 system. Recently, we also successfully prepared a thin ZIF-8 membrane (ca. 2 μm) on $\alpha\text{-Al}_2\text{O}_3$ supports by seeded-secondary growth method [15]. The membrane exhibited a molecular sieving behavior with separation factor of 35 for propylene/propane mixtures, primarily due to its effective pore aperture size (4.0~4.2 Å) for molecule discrimination of propylene (~4.0 Å) from propane (~4.3 Å).

In view of its promising application in propylene/propane separation [24], efforts have been made by a few research groups to prepare high-quality ZIF-8 membranes using various methods [15-19]. For example, a counter diffusion-based in situ method, developed by Jeong and co-

workers, was used to prepare the high-quality ZIF-8 membrane where the propylene/propane separation factor was as high as 70 [18]. Huang and co-workers have in-situ synthesized ZIF-8 membrane on dopamine-modified α -Al₂O₃ supports, exhibiting a medium propylene/propane separation factor (~20) [22]. Lin and co-workers have also synthesized continuous ZIF-8 membranes on α -Al₂O₃ support by seeded-secondary growth method [19]. The membrane exhibit a separation factor of 30 for propylene/propane mixtures. They also examined the diffusion and adsorption performances on ZIF-8 membranes through the classic Maxwell-Stefan model [25-27]. The transport diffusivity for propylene and propane is 1.25×10^{-8} and 3.99×10^{-10} cm²/s with activation energy for diffusion of 12.7 and 38.8 kJ/mol, respectively. Nevertheless, grain boundary will significantly affect the gas permeation through the polycrystalline microporous membrane. The obtained diffusivities are significantly deviated with the real value due to the existence of some grain boundary. Recently, the idea selectivity for propylene/propane on defect-free ZIF-8 membrane was back-calculated to ca.120 by Zhang et al. from the ZIF-8/polyimide mixed matrix membrane through the Maxwell equations [16]. Above results inspire us to further improve the quality of ZIF-8 membrane and then to explore the diffusion details of hydrocarbons through ZIF-8 membranes.

In this work, ZIF-8 membrane with improved quality was firstly prepared by optimizing the activation process of water occluded in the pores of ZIF-8 crystals, which was commonly considered as a primary way to form intercrystalline defects and cracks in the MOF membrane [28,29]. The corrected diffusivities of light hydrocarbons through high-quality ZIF-8 membranes were subsequently achieved on the basis of Maxwell-Stefan (MS) models. Furthermore, the comparison of transport diffusivities of various hydrocarbon molecules on ZIF-8 materials obtained from other techniques was also carried out.

2. Experimental

2.1 Synthesis of ZIF-8 membranes

ZIF-8 membranes were hydrothermally synthesized according to our reported seeded-secondary growth method on homemade α -alumina discs [15]. Firstly, ZIF-8 seeds were prepared by the rapid aqueous-synthesis method at room temperature. In a typical synthesis, a solution of 1.17 g (3.95 mmol) of zinc nitrate in 8 mL deionized (DI) water and another solution of 22.70 g (276.50 mmol) of 2-methylimidazole in 80 mL DI water were mixed by vigorously stirring for 5 min at room temperature ($\sim 22^\circ\text{C}$). The resulting ZIF-8 nanocrystals were separated by centrifugation, followed by washing with DI water twice and finally re-dispersing in fresh methanol as seeding solution (0.1 wt%). Seeding procedure was conducted by slip-coating process, and the detailed steps can be found elsewhere [15]. The seeded support was then exposed to the secondary synthesis solution at 30°C for 10 h to allow further growth of seeds to occur. The synthesis solution was prepared by mixing 0.11 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.27 g 2-methylimidazole and 40 mL DI water. After synthesis, the as-synthesized membranes were carefully washed with a copious of water at room temperature.

2.2 Activation of the as-synthesized ZIF-8 membranes

Above as-synthesized membranes were activated via various strategies, in order to examine the effect of activation procedures on the qualities of ZIF-8 membranes. The activation methodologies can be grouped into two categories. One was activated at different temperatures without solvent (methanol) exchange and the other was activated by methanol exchange. For the first group, the water on the surface of the membranes was first removed by tissue paper,

followed by the slow drying at room temperature (22 °C) for 24 h. Activation procedures were further conducted in oven at different temperatures (50 or 100 °C) with or without vacuum afterwards. For the second group, the as-prepared ZIF-8 membranes after washing with DI water were immersed in fresh methanol for 2 days. The methanol was replenished every 12 h. Then the membranes were taken out, and followed by removing of methanol on the surface of membrane using tissue paper. Finally the membranes were dried in oven at different temperatures (22~100 °C) with or without vacuum.

2.3 Characterization

The crystal phases of ZIF-8 crystals and membranes were determined by X-ray diffraction (XRD) with Cu K α radiation (Bruker, model D8 Advance). Diffraction patterns were collected at room temperature in the range of $5 \leq 2\theta \leq 40^\circ$ with a step width of 0.02° and a scan rate of 0.2 s per step. The particle sizes of grains and morphologies of the membranes were examined by scanning electron microscopy (SEM) (FEI, NOVA-Nano 630). The near-surface compositions of ZIF-8 membranes were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha) using monochromated Al K α (1486.6 eV) excitation at 12 kV and 10 mA. The binding energies were referenced to the internal standard C 1s (284.5 eV). Prior to measurement, cleaned surface was obtained by spraying the sample with an ion beam of Ar⁺ operating at 3 keV and with an emission current of 5 mA.

2.4 Gas permeation

All permeation experiments were carried out at 295~423 K by Wicke–Kallenbach (W-K) technique. Atmosphere pressure (~1 bar) was applied to both sides of the permeation cell. The

total feed flow rate was set to 100 mL/min. On the permeate side, argon was used as the sweep gas. The flow rate was also set to 100 mL/min. The permeate stream was fed into a gas chromatograph (Agilent 7890A) for on-line composition measurements. At each permeation condition, the system was stabilized for at least 4 h and the measurement was repeated at least three times. Before each measurement, argon flowed on the both feeding and permeating sides of the membrane for 12 h, and the module was heated to 423 K to remove adsorbed species.

In order to examine the effect of partial pressure of single gas on the permeation, argon used as the diluted gas. A mixture of argon and the hydrocarbon was applied at the feed side to vary the partial pressure of hydrocarbon (0~1 bar). For the mixed-gas permeation, binary gas mixtures of ethane/propane and propylene/propane with various volume ratios were respectively fed to the membrane side. At the steady state, the permeance (F) of component i was calculated as

$$F_i = \frac{J_i}{\Delta P_i} = \frac{N_i}{\Delta P_i \times A} \quad (1)$$

Where J_i is the permeation flux of component i (mol/m² s), N_i the permeate rate of component i (mol/s), ΔP_i the trans-membrane pressure difference of component i , and A the effective ZIF-8 membrane area (m²).

The separation factor for binary gases mixture was calculated as

$$\alpha_{i,j} = \frac{(y_i / y_j)}{(x_i / x_j)} \quad (2)$$

Where x and y are the molar fraction of the component in the feed and permeate, respectively.

2.5 Modeling

The Maxwell-Stefan (MS) equation proposed by Krishna [30] provides a good rational and theoretical basis for describing transport in microporous materials, because it is based on the assumption that the gradient of thermodynamic potential as the driving force. An explicit expression for the flux of single gas through the microporous membrane based on the simple Langmuir isotherm is given by

$$J = \frac{\rho}{L} \times \varepsilon \times q_{sat} \times D_c \times \ln\left(\frac{1 + bP^{feed}}{1 + bP^{perm.}}\right) \quad (3)$$

Where J is the permeation flux, ρ is the density of membrane material (0.95 g/cm³), ε is a constant accounting for the support's porosity (0.47), L is the membrane thickness (3 μ m), q_{sat} is the amount of adsorbed gas at saturation coverage, b is the adsorption constant, $P^{perm.}$ and P^{feed} are permeate and feed side pressures, and D_c is the thermodynamically corrected diffusivity.

Under the conditions of liner adsorption isotherm ($bP \ll 1$), Eq.(3) is reduced to the liner relation. So in the Henry pressure range the flux is given by

$$J = \frac{\rho}{L} \times \varepsilon \times q_{sat} \times D_c \times b(P^{feed} - P^{perm.}) \quad (4)$$

For the two-component mixture, it is possible to predict the binary mixture permeation fluxes via MS equation (Eq. (5)) based on the diffusivity data and adsorption parameters of single-component [31].

$$J_i = \frac{\rho D_i q_{sat,i}}{L} \times \frac{b_i(P_i^{feed} - P_i^{perm.})}{b_i(P_i^{feed} - P_i^{perm.}) + b_j(P_j^{feed} - P_j^{perm.})} \times \ln\left(\frac{1 + b_i P_i^{feed} + b_j P_j^{feed}}{1 + b_i P_i^{perm.} + b_j P_j^{perm.}}\right) \quad (5)$$

Where J_i is the permeation flux of component i , b_i and b_j are Langmuir adsorption parameters of component i and j , and $P^{perm.}$ and P^{feed} are the partial pressures in permeate and feed side, respectively. The values of D_i (thermodynamically corrected diffusivity) are the ones estimated in single-file diffusion.

3. Results and discussion

3.1 Effect of activating procedures

Fig. 1 shows the SEM pictures of the ZIF-8 membranes activated without methanol exchange. As shown in Figs. 1a and c, fractures and cracks in ZIF-8 membranes were easily formed followed by activating at 100 or 50 °C, possibly resulting from the capillary stress stemming by the evaporation of guest molecules (water) [28]. However, the morphologies of grains on the membrane followed by activation are different (Figs. 1b, d and f). The surface of grains activated at 100 °C is smoother than those activated at 50 °C with and without vacuum, and some tiny pinholes on membrane activated at 50 °C under vacuum were also found between the adjacent grains (Fig. 1f). This phenomenon may come from the corrosion action of water on ZIF-8 grains, because XRD measurements confirm that the structures of both thin layers are pure ZIF-8 phase (Fig. 2). Recently, Kwon and Jeong also reported that corrosion of ZIF-8 membranes happened under methanol activation process at high temperature [32].

XPS measurements were undertaken to further elucidate the nature of ZIF-8 membranes after high-temperature activation. As shown in Fig. 3, the Zn 2p spectra exhibit two intense peaks at ~1021 and 1044 eV, which are assigned to the 2p_{3/2} and 2p_{1/2} components, respectively [33]. The intensity of the Zn 2p doublet is significantly decreased, accompanied by a slight shift of higher binding energy, when the activation temperature is increased to 100 °C. In addition, the deconvolution of the O 1s spectrum results in two peaks at 531.6 and 532.8 eV, which are attributed to the carboxylate and hydroxide species, respectively. These differences in the XPS spectra reveal some ZIF-8 grains undergo hydrolysis and transform to zinc hydroxide at high temperature (100 °C). In addition, two peaks at 398.9 and 400.2 eV of the deconvoluted N 1s

spectrum are assigned to the specific C-N group in ZIF-8 structure and C-NH₂, respectively [34]. The appearance of higher binding energy (400.2 eV) of N 1s orbital and significant decrease of peak intensity at 398.9 eV may be resulted from the considerable damage of imidazolate ligands on the ZIF-8 grains. In contrast, no obvious changes in the XPS data were found between the ZIF-8 membranes activated at 50 °C with and without vacuum. Therefore, high activating temperature in the presence of water leads to the degradation of ZIF-8 membrane. Liu et al. recently also observed that ZIF-8 grains could undergo hydrolysis under hydrothermal conditions, regardless of its size and origin, supporting our findings that the corrosion action of water on ZIF-8 grains under high-temperature activation [35].

Fig. 1. SEM pictures of the as-synthesized ZIF-8 membranes activated without methanol exchange via different strategies: (a) and (b) at 100 °C, (c) and (d) at 50 °C, (e) and (f) at 50 °C in vacuum for 2 days. Red arrows in (f) show the tiny pinholes.

Fig.2. XRD patterns of ZIF-8 membranes activated at different conditions: (a) without methanol-exchange at 100 °C for 2 days, (b) without methanol-exchange at 50 °C for 2 days, (c) without methanol-exchange at 50 °C for 2 days under vacuum, (d) with methanol-exchange at 50 °C for 2 days under vacuum, (e) with methanol-exchange at 22 °C for 2 days under vacuum, (f) with methanol-exchange at 22 °C for 4 days. The symbol ★ represents peaks from the α -alumina support.

Fig. 3. XPS spectra of ZIF-8 membranes activated without methanol exchange via different strategies: (a) 100 °C, (b) 50 °C in vacuum and (c) 50 °C.

The morphologies of as-synthesized membranes after methanol exchange were also examined. As shown in Fig. 4a, the grains of membrane activated at 50 °C for 2 days under vacuum exhibit the smooth morphology. This result further supports the corrosion action of water. However, the compactness of the activated membrane is lower than that of membrane without solvent exchange (Figs. 1e and 4a), indicating that the evaporating rate of solvent determines the qualities of final membranes. Similarly, the inter-grown performance of membrane activated at room temperature (~ 22 °C) without vacuum was also better than that activated under vacuum (Figs. 4b and c). Above results indicated that low evaporating rate of methanol (low temperature or no vacuum) favors the formation of continuous composite membrane. In order to further lower down the evaporating rate of methanol, the membrane was activated under saturated methanol pressure [29]. Inter-grown between ZIF-8 grains of rhombic dodecahedral shape [36] can be clearly observed, and no defects (such as pinholes or cracks) were observed in the entire membrane surface (Fig. 4d).

Fig. 4. SEM pictures of the methanol-exchanged ZIF-8 membranes activated: (a) at 50 °C for 2 days under vacuum, (b) at 22 °C for 2 days under vacuum, (c) at 22 °C for 4 days under ambient pressure, (d) at 22 °C for 4 days under saturated methanol pressure.

3.2 Separation of propylene/propane by activated ZIF-8 membranes

Separation measurements of equal-molar propylene/propane binary mixtures were designed to further examine the qualities of above methanol-exchanged ZIF-8 membranes activated by various procedures. The detailed results of separation performance are listed in Table 1. We can see that the separation factors (e.g. membrane quality) of these membranes are really consistent with the SEM results (Fig. 4). In addition, the separation factor (~31) of membrane activated at 22 °C under ambient pressure (M3) was dramatically lower than that (~89) of membrane activated under saturated methanol pressure (M4), although the no obvious difference from SEM pictures between these two membranes (Fig.s 4c and d). This result also accounts for the role of tiny defects that invisible under SEM inspection for gas separation.

Table 1. Gas permeation results for equal-molar propylene/propane mixtures through methanol-exchanged ZIF-8 membranes activated by various strategies.

Membrane	Activation procedure	Permeance (10^{-10} mol/m ² s Pa)		Separation factor	
		Propylene	Propane	4 h testing	48 h testing
M1	50 °C, Vacuum	120	31.7	4	4
M2	22 °C, Vacuum	162	22.3	7	7
M3	22 °C, Ambient pressure	255	8.2	31	31
M4	22 °C, Saturated	78	0.88	89	89

 condition

Even the permeation testing time was prolonged from 4 h to 48 h, we did not find obvious change of permeance and selectivity for propylene/propane mixed gas on membranes M1~M4, suggesting the permeation time (4 h) is sufficient enough to reach steady-state (see Table 1). This result was totally different with that reported by Osama Shekhah et al. [37], where the selectivity of methane/n-butane declined from ca. 250 to 4 when the permeation time was prolonged from 2 to 30 h. We think this phenomenon can be attributed to the immobilizing sorption of permeated gas on many tiny ZIF-8 crystals embedded inside the α -alumina support, resulting from their liquid phase epitaxy approach. In such a synthetic process, the pristine alumina support was first saturated with metal ion solution. The followed washing step by solvent can only remove the excessive metal ions on the surface of alumina support, but do not remove metal ions sucked inside the pores of support. Subsequently, washed support was again immersed in the ligand solution for ZIF-8 synthesis. After several cycles, not only ZIF-8 layer was formed on the surface of α -alumina support, but also many tiny ZIF-8 crystals were formed inside the support. This hypothesis was also supported by that the gas permeance of synthesized membrane is decreased by 100 fold, even its smaller membrane thickness (0.5~1.6 μm), compared with most other reports [15, 17, 19]. In contrast, for our synthesis method (seeded secondary growth method), it is not possible to produce considerable amount of ZIF-8 crystals inside the pores of α -alumina support because nothing can be found on the surface and inside the alumina support in secondary growth solution without the help of seeds [15]. Therefore, the difference of permeation performance between ZIF-8 membranes possibly originated from the different microstructures of the membranes synthesized via different methods.

The separation factor for propylene/propane ($v: v = 50: 50$) on membrane M4 is 89, and the permeances of propylene and propane are 7.8×10^{-9} and 8.7×10^{-11} mol/m² s Pa, respectively. The separation performance of membrane M4 was remarkably improved compared with our previous work [15], also far beyond the upper limit of carbon and polymer membranes (Fig. 5). In order to examine the synthetic reproducibility, another nine membranes (M5~M13) from different batches were synthesized using same synthesis and activation conditions. As shown in Table 2, seven out of ten membranes (including M4) have selectivity higher than 60 and the other three membranes have selectivity of above 40. The standard deviations of selectivity for these ten membranes are ca.16, implying an acceptable reproducibility due to the multiple synthetic steps. Furthermore, the separation factor of membrane M4 is very close to the threshold value (~122), which is back-calculated by Koros's group from the ZIF-8/6FDA-DAM mixed matrix membrane [16]. Thus the membrane M4 can be roughly considered as the defect-free membrane, and can be used to obtain the accurate diffusivities of hydrocarbons through ZIF-8 membranes.

Fig. 5. Permeation and separation properties of ZIF-8 membranes M4 prepared in this work and those of our previous work for propylene/propane mixtures [15]. The black and red lines in this figure represent the upper bound limit for polymer and carbon membranes, respectively.

Table 2. Permeances and separation factors of propylene/propane mixtures on ZIF-8 membranes synthesized from different batches and dried under same saturated methanol pressure

Membrane	Permeance (10^{-10} mol/m ² s Pa)		Separation factor
	Propylene	Propane	
M5	110	1.47	75
M6	82	0.98	84
M7	156	3.12	50
M8	167	3.85	44
M9	92	1.34	69
M10	83	1.32	63
M11	212	5.1	42
M12	91	1.23	74
M13	89	1.05	85

3.3 Transport diffusivity of single-gas permeation

Fig. 6 shows the single-component permeation fluxes of light hydrocarbons on membrane M4 at 308 K as a function of their feed partial pressure (0~100 kPa). For C1 and C2 hydrocarbon, the permeation fluxes are linear as a function of the feed partial pressure (Fig. 6a). In addition, Langmuir equation well depicts the relationship between fluxes and partial pressures on C3 and C4 hydrocarbons, as the fluxes level off at increasing partial pressure (Figs. 6b and c). In addition, the alkenes exhibit higher fluxes than their saturated analogues. The values of MS diffusivities of the various hydrocarbons between 0 and 100 kPa were calculated using Eq.(3)

and (4), based on the adsorption parameters (q_{sat} and b) reported by Koros and co-workers [16]. The results are given in Fig. 7. The MS diffusivities of above hydrocarbons are fairly constant over the partial pressure range and the maximum deviation for methane and n-butane was less than a factor of 2. The possibility to explain the increasing diffusivity values is the neglect of the counter-diffusion of the purge gas argon in the model [38]. The diffusivities of all components are overall independent on the occupancy, indicating that MS equation can well describe the single-component permeation of light hydrocarbons through the ZIF-8 membrane.

Fig. 6. Permeation flux as a function of the feed partial pressure (0~100 kPa) through the ZIF-8 membrane M4 at 308 K.

Fig. 7. MS diffusivities obtained on the prepared ZIF-8 membrane as a function of the feed partial pressure (0~100 kPa) at 308 K.

3.4 Comparison of transport diffusivity

The average corrected diffusivities of light hydrocarbons through ZIF-8 membrane M4 as well as ZIF-8 membrane prepared by Liu et al. [19] using W-K method are listed in Table 3. In addition, diffusivities obtained from other measurement techniques, such as kinetic uptake adsorption [16], mixed-matrix membrane (ZIF-8/6FDA-DAM) [16], IR-microscopy [14,39] and pulsed-field gradient nuclear magnetic resonance (PFG-NMR) [40] were also listed in Table 3. We can see that the transport diffusivities of light hydrocarbons were in general agreement with the results obtained from various measuring techniques. However, one significant difference (on the order of 10^7) for diffusivity of i-butane between our W-K method and Koros's kinetic adsorption measurement was found. We think such a large difference was attributed to the leak of i-butane through O-Ring. We tested the leak rate for VITON O-Ring is about $\sim 2 \times 10^{-6}$ mol/m² s, e.g. $\sim 2 \times 10^{-11}$ mol/m² s Pa. Thus the effect of leaking from O-Rings can't be ignored when the gas permeance was lower than order of 10^{-11} mol/m² s Pa. Table 4 lists the calculated diffusivities of propylene, propane and n-butane. Fig. 8 shows the Arrhenius plot of the diffusivity data for diffusion of propylene, propane and n-butane in ZIF-8 membrane, respectively, and the activation energy are 24.3, 33.8 and 20.8 kJ/mol. This result shows that the activation energy for n-butane is lower than propane, even propylene, implying that significant effect of O-Ring leaking for gas permeation of n-butane, even i-butane.

Fig. 8. The Arrhenius plot of diffusivity data for hydrocarbon (propylene, propane and n-butane) through ZIF-8 membrane

Table 3. Calculated thermodynamically corrected diffusivities of light hydrocarbons in ZIF-8 membrane M1 at 308 K.

Light hydrocarbons	Transport diffusivity (m^2/s)					
	Wicke-Kallenbach		Mixed-matrix membrane [16]	Kinetic adsorption [16]	IR-microscopy [14,39]	PFG-NMR [40]
	This work	Liu et al [19].				
Methane	2.8×10^{-10}	1.5×10^{-10}	$4.0 \pm 0.4 \times 10^{-11}$	—	1.3×10^{-10}	1.5×10^{-10}
Ethylene	1.9×10^{-10}	—	$3.6 \pm 1.6 \times 10^{-11}$	—	5×10^{-11}	—
Ethane	2.4×10^{-11}	—	$8.8 \pm 2.7 \times 10^{-12}$	—	1×10^{-11}	—
Propylene	1.2×10^{-12}	1.2×10^{-12}	$1.6 \pm 0.3 \times 10^{-12}$	2.9×10^{-12}	—	—
Propane	1.1×10^{-14}	3.7×10^{-14}	$1.7 \pm 0.8 \times 10^{-14}$	2.0×10^{-14}	—	—
n-butane	6.1×10^{-15}	—	—	5.7×10^{-16}	—	—
Iso-butane	1.5×10^{-15}	—	—	2.3×10^{-22}	—	—

3.5 Binary mixed gas permeation and diffusivity

Fig. 9 shows the experimental and simulation separating performance of propylene/propane and ethane/propane binary mixtures on ZIF-8 membrane M4. The partial pressure behaviors of the permeation fluxes are predicted by Eq.(5) very well over the entire pressure range examined. This result indicates that MS description for single-component diffusion can be applied well to predict the two-component permeation and separation behavior through ZIF-8 membrane, for which only single-component diffusivity and adsorption parameters are needed.

Table 4. Parameters for propylene, propane and n-butane adsorption isotherms in ZIF-8 crystals and corresponding calculated diffusivities.

Gas type	Tem. (°C)	Flux (10^{-5} mol/m ² s)	Adsorption parameter		Dc (10^{-14} m ² /s)	Ln Dc
			a_m (mmol/g)	b (1/bar)		
Propylene	50	77.9	6.02	1.182	303	-26.5
	80	67.6	6.72	0.357	601	-25.8
	120	57.7	19.2	0.037	1510	-24.9
Propane	50	1.10	6.09	0.951	5.18	-30.6
	80	1.30	13.2	0.201	9.80	-30.0
	120	1.68	26.6	0.0367	31.9	-28.8
n-Butane	25	0.49	3.97	0.493	0.29	-33.5
	35	0.57	3.85	0.325	0.39	-33.2
	55	0.72	3.82	0.151	0.63	-32.7

In addition, we also found that the permeation fluxes of propane are nearly same in both propylene/propane and ethane/propane systems. This result indicates that the effect of competitive adsorption is not obvious in the separation of binary hydrocarbon mixtures. Thus a

well prediction of binary mixtures can be obtained from the single-component adsorption parameters rather than binary adsorption parameters. In addition, the flux of faster component (propylene or ethane) increases with its partial pressure, so higher separation factor can be obtained. The separation factor for equal-molar ethane/propane binary mixtures is ~ 600 , far surpasses the value (~ 80) obtained from our previous ZIF-8 membrane [13]. It is clear that the separation performance of membrane M4 was remarkably improved because of the existence of low concentration of defects.

Fig. 9. Comparison of measured binary permeation fluxes of (a) propylene/propane and (b) ethane/propane mixtures on ZIF-8 membrane M4 with predictions of a sorption and diffusion model based on the Maxwell-Stefan formulation. The filled symbols correspond to the hydrocarbon fluxes obtained from the experiments, while the dashed lines indicate the model predictions by Eq. (5).

4. Conclusion

In summary, we have demonstrated that the microstructures of ZIF-8 membranes significantly depend on the activation processes, thereby affecting their quality for gas separation.

Solvent exchange is used to remove residual water in as-synthesized membrane to protect the ZIF-8 crystals from corrosion. Lower temperature and slower solvent-diffusion favors the successful fabrication of high-quality ZIF-8 membrane. The separation factor for equal-molar propylene/propane can reach up to 90. Apart from the separation performance, single and two-component permeation results of hydrocarbons through high-quality ZIF-8 membrane can be well described by the MS equations. The obtained transport diffusivity of hydrocarbon from single-component permeation compares well with those obtained by other experimental techniques. Binary mixture permeation also can be well predicted through single-component adsorption parameters, because the competitive adsorption of binary mixtures of hydrocarbons on ZIF-8 can be ignored.

5. Nomenclature

F_i	Permeance of component i through the membrane ($\text{mol/m}^2 \text{ s Pa}$)
J_i	permeation flux of component i ($\text{mol/m}^2 \text{ s}$)
N_i	Permeation rate of component i (mol/s)
A	Membrane area (m^2)
ΔP_i	Partial pressure difference of component i across the membrane (Pa)
x_i	Molar fraction of component i in the feed stream
y_i	Molar fraction of component i in the permeate stream
L	Membrane thickness (μm)
q_{sat}	Amount of adsorbed gas at saturation coverage
b	Thermodynamically corrected diffusivity
P^{perm}	Partial pressures in permeate side
P^{feed}	Partial pressures in feed side
D_i	Thermodynamically corrected diffusivity

Greek letters

$\alpha_{i,j}$	Separation factor for binary gases mixture
ε	Constant accounting for the support's porosity (0.47)

ρ	Density of membrane material (g/cm^3)
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Acknowledgment

This work was supported by the National Natural Science Foundation (21406106), Jiangsu Provincial NSFC (BK20130928), and Foundation of Jiangsu Educational Committee of China (14KJB530006). The authors gratefully acknowledge Dr. Gaofeng Zeng at Shanghai Advanced Research Institute for the help of XPS measurements and anonymous reviewers for their valuable comments and suggestions.

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Accepted manuscript

Highlights

1. The quality of ZIF-8 membranes was remarkably improved by optimizing the activation process.
2. The separation factor for propylene/propane equal-molar mixtures can be improved to ~90.
3. Permeation of hydrocarbons on improved membrane can be well described by Maxwell-Stefan model.
4. The transport diffusivities of hydrocarbons (C1~C4) through improved membranes were obtained.