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ORIGINAL PAPER

Theoretical screening of zeolites for membrane separation of propylene/propane mixtures

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ABSTRACT

In this paper, the performances of potential zeolite membranes were estimated by the Maxwell-Stefan model and then they were placed in Robeson plot of propylene/propane separation. Additionally, the effects of feed pressure and the mole fraction of propylene in the feed on both the propylene permeabilities and membrane permselectivities were investigated. The results showed that zeolite membranes had better performances than carbon and polymer membranes. However, the performances of carbon membranes were better than those of zeolites 4A and ITQ-3. Also, among various zeolites studied, a DD3R zeolite membrane had the highest propylene permselectivity. According to the minimum requirement needed for membranes (i.e., a minimum selectivity of 35 and a permeability of 1 Barrer) for propylene/propane separation, it was found that the zeolite membranes of DD3R, SAPO-34, Si-CHA and ITQ-12 had this performance requirement. However, DD3R and SAPO-34 zeolite membranes were more preferred than the polymer, carbon and composite membranes due to their higher performances. **Polyolefins J (2018) 5: 23-30**

Keywords: Propylene; membrane; zeolite; Maxwell-Stefan model; gas separation.

INTRODUCTION

Propylene is usually produced by fluid catalytic cracking of hydrocarbon feedstocks. It is widely used in the production of petrochemical products such as polypropylene, acrylonitrile, propylene oxide, isopropanol, allyl chloride, acrylic acid and its esters, cosmetics, textile products and paints [1, 2]. Separation of propylene from a mixture of propylene/propane is one of the main energy-consuming processes in the petrochemical industries because it is commonly done through energy-intensive cryogenic distillation [3].

The global increasing demand for propylene makes it necessary to find energy efficient processes for propylene/propane separation. Development of separation processes based on adsorption, membrane separation [4-9] and membrane-distillation hybrid separation [10] has been suggested.

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For adsorptive separation, various adsorbents such as zeolites including 4A [11], 5A[12], DD3R [13], Si–CHA [14], ITQ-3[15], ITQ-12 [16], ITQ-32 [17], SAPO-34 [18] have been utilized. These zeolites have different pore sizes and chemical compositions which affect their adsorptive and diffusion properties for propylene and propane molecules. The differences in their pore size and chemical composition are presented in Table 1. According to this table, Si-CHA and SAPO-34 have a similar structure but a different composition of the framework. On the other hand, crystal structure and Si/Al ratio of both 4A and 5A zeolites are the same. They are different in the cation type of the structure. Zeolites 4A and 5A have Na^+ and Ca^{2+} cations, respectively, in the cavity. In my recent paper [19], the propylene/propane separation performance of the mentioned adsorbents along with MOFs was investigated by binary adsorption calculations. The results revealed that the MOFs had a higher adsorption capacity while the zeolites especially pure silica DD3R zeolite showed a very high equilibrium selectivity of more than 1000.

In membrane-based separation, it has been proposed that a minimum permeability of 1 Barrer and a selectivity of 35 are needed for a membrane to be economically feasible [3, 20]. Many types of membranes including polymers, carbon molecular sieves (CMS), mixed matrix (MMM) and facilitated transport membranes have been synthesized but, almost all the investigated polymeric membranes don't meet the desired permeability and selectivity simultaneously. On the other hand, some carbon molecular sieve and facilitated transport membranes meet the required performance standards, however, they suffer from scale-up difficulty and long-term instability, respectively [20].

Fallanza et al. [21] fabricated facilitated transport membranes containing an ionic liquid and a silver salt. The composite membrane was developed using PVDF-HFP as the polymer, $BMImBF_4$ as the ionic liquid and $AgBF_4$ as the silver salt. The membrane with 80%polymer-20% ionic liquid showed a reasonable mechanical resistance. The membrane containing Ag^+ concentration of 80% w/w showed C_3H_6 permeability of about 2000 Barrer and C_3H_6/C_3H_8 selectivity over 700 at 293K. This performance is well above the Robeson upper bound for carbon and polymeric membranes. Recently, Heseong et al. [22] investigated the performance of a mixed matrix membrane containing ZIF-67 nanoparticles. They fabricated 6FDA-DAM/ZIF-67 (80/20 wt/wt) membranes which had an ideal selectivity of 29.9 and a C_3H_6 permeability of 34.14 Barrer for single gas tests at 35°C. According to this reference, the neat polymer and ZIF-67 have C_3H_6 permeabilities of 1.47 and 150.7 Barrer with C_3H_6/C_3H_8 selectivities of 16.63 and 251, respectively. Therefore, incorporation of ZIF-67 into the polymer matrix increased both the permeability and selectivity. Long-term analysis showed a gradual reduction of C_3H_6 permeability of the MMM (~17% reduction after 75 days of operation).

Zeolite membranes have higher permeability and selectivity than other types of membranes due to their crystalline structure. Prior to synthesizing and testing other types of zeolite membranes, investigation of their expected performances is highly interesting. Additionally, identification of highly selective zeolites with favorable permeability is helpful for improvement of polymeric membranes performances and development of mixed matrix membranes.

Thus, the main objective of this paper is to estimate the inherent performances of several potential zeolites as membranes for propylene/propane separation. It

Table 1. Pore size and chemical composition of zeolites studied in propylene/propane separation.

Zeolite type	Pore size (A°)	Si/Al ratio	Structure code
4A	4	1	LTA
5A	5	1	LTA
Si-CHA	3.8×3.8	∞ (Pure silica)	CHA
DD3R	3.6×4.4	∞ (Pure silica)	DDR
ITQ-3	3.8×4.3/2.7×5.8	∞ (Pure silica)	ITE
ITQ-12	3.9×4.2/2.4×5.4	∞ (Pure silica)	ITW
ITQ-32	3.5×4.3	∞ (Pure silica)	IHW
SAPO-34	3.8×3.8	0.26*	CHA

* Si/(Al+P) value

is achieved by mathematical modeling of gas permeation trough zeolite films. To do this binary propylene/propane permeations have been obtained by Maxwell-Stefan mass transfer modeling at different gas compositions (0.1-0.9 propylene mole fractions) and feed pressures (100-900 kPa). Finally, a comparison has been made between the performances of the zeolites and other types of membranes.

THEORY AND MODELING

Adsorption and diffusion characteristics of all components in a gas mixture determine the permeation flux of a component through zeolite membranes. Thus, mixture permeations and separation selectivities are different from single component permeation data. The faster moving species are slowed down and, concurrently, the more slow-moving species are accelerated because of their interactions [23]. Thus, the relation between the adsorption and diffusion, and also the coupling between species diffusion must be taken into account in the mass transfer model describing the zeolite membrane permeations. In this regard, Maxwell–Stefan (M–S) formulation is extensively utilized for description of multicomponent permeations across zeolite membranes. The M-S model is now well-developed by Krishna and his colleagues for gas mixture diffusion through zeolite membranes. Steady state M-S modeling of a binary gas mixture permeation across zeolite membranes leads to the following molar fluxes of components1 and 2 [24]:

$$N_1=-\rho\frac{\text{Đ}_1\left[\left\{\Gamma_{11}+\theta_1\frac{\text{Đ}_2}{\text{Đ}_{12}}(\Gamma_{11}+\Gamma_{21})\right\}\nabla q_1+\left\{\Gamma_{12}+\theta_1\frac{\text{Đ}_2}{\text{Đ}_{12}}(\Gamma_{12}+\Gamma_{22})\right\}\left(\frac{q_1^{sat}}{q_2^{sat}}\right)\nabla q_2\right]}{\theta_2\frac{\text{Đ}_1}{\text{Đ}_{12}}+\theta_1\frac{\text{Đ}_2}{\text{Đ}_{12}}+1} \tag{1}$$

$$N_2=-\rho\frac{\text{Đ}_2\left[\left\{\Gamma_{22}+\theta_2\frac{\text{Đ}_1}{\text{Đ}_{12}}(\Gamma_{22}+\Gamma_{12})\right\}\nabla q_2+\left\{\Gamma_{21}+\theta_2\frac{\text{Đ}_1}{\text{Đ}_{12}}(\Gamma_{21}+\Gamma_{11})\right\}\left(\frac{q_2^{sat}}{q_1^{sat}}\right)\nabla q_1\right]}{\theta_2\frac{\text{Đ}_1}{\text{Đ}_{12}}+\theta_1\frac{\text{Đ}_2}{\text{Đ}_{12}}+1} \tag{2}$$

Where, N is the molar flux, ρ is the framework density of zeolite, θ is the fractional adsorption loading, Đ is the Maxwell-Stefan diffusivity and q is the adsorption loading on the zeolite surface. Đ_{12}, exchange coefficient, is estimated by the following equation:

$$\text{Đ}_{12}=\text{Đ}_1{}^{\theta_1/(\theta_1+\theta_2)}\text{Đ}_2{}^{\theta_{21}/(\theta_1+\theta_2)} \tag{3}$$

is the thermodynamic factor which is defined as:

$$\Gamma_{ij}=\frac{\theta_i}{p_i}\frac{\partial p_i}{\partial \theta_j} \tag{4}$$

These equations show that the molar flux of a component depends not only on its adsorption and diffusion characteristics but also on the adsorption and diffusion characteristics of the other components present in the mixture.

Calculation of molar fluxes depends on the information about binary adsorption equilibria on the zeolite surface and the diffusivities. In this paper, the binary adsorption equilibria as well as the thermodynamic factors are numerically calculated by IAST (Ideal Adsorbed Solution Theory). However, they may be calculated analytically [25]. The IAST calculation for propylene/propane mixtures with different gas compositions has been reported in our previous paper [19]. The single component adsorption isotherms reported in Ref. [19] for propylene and propane on zeolites are now used in this paper.

Diffusivities of propylene and propane in zeolites extracted from the literature are reported in Table 2.

In modeling of all potential zeolite membranes, the external mass transfer resistances including gas phase and porous support are ignored and it is assumed that micropore diffusion is the only dominant mechanism.

Table 2. Diffusivity of propylene and propane in zeolites.

Zeolite type	Temperature (K)	Diffusion coefficient (m²/s)		Ref.
		Propylene	Propane	
Si-CHA	353	2×10^{-14}	5×10^{-18}	[26]
DD3R	323	5×10^{-16}	6×10^{-20}	[26]
5A	323	1×10^{-12}	1×10^{-12}	[26]
ITQ-32	298	3.86×10^{-17}	2.7×10^{-20}	[17][1]
SAPO-34	303	8.64×10^{-15}	4.76×10^{-19}	[18][2]
4A	423	8×10^{-15}	1×10^{-14}	[27]
ITQ-12	300	2.4×10^{-14}	2.1×10^{-16}	[16]
ITQ-3	353	1.52×10^{-16}	2.96×10^{-19}	[14][3]

[1] It is assumed that the particle size equals to 1 μm

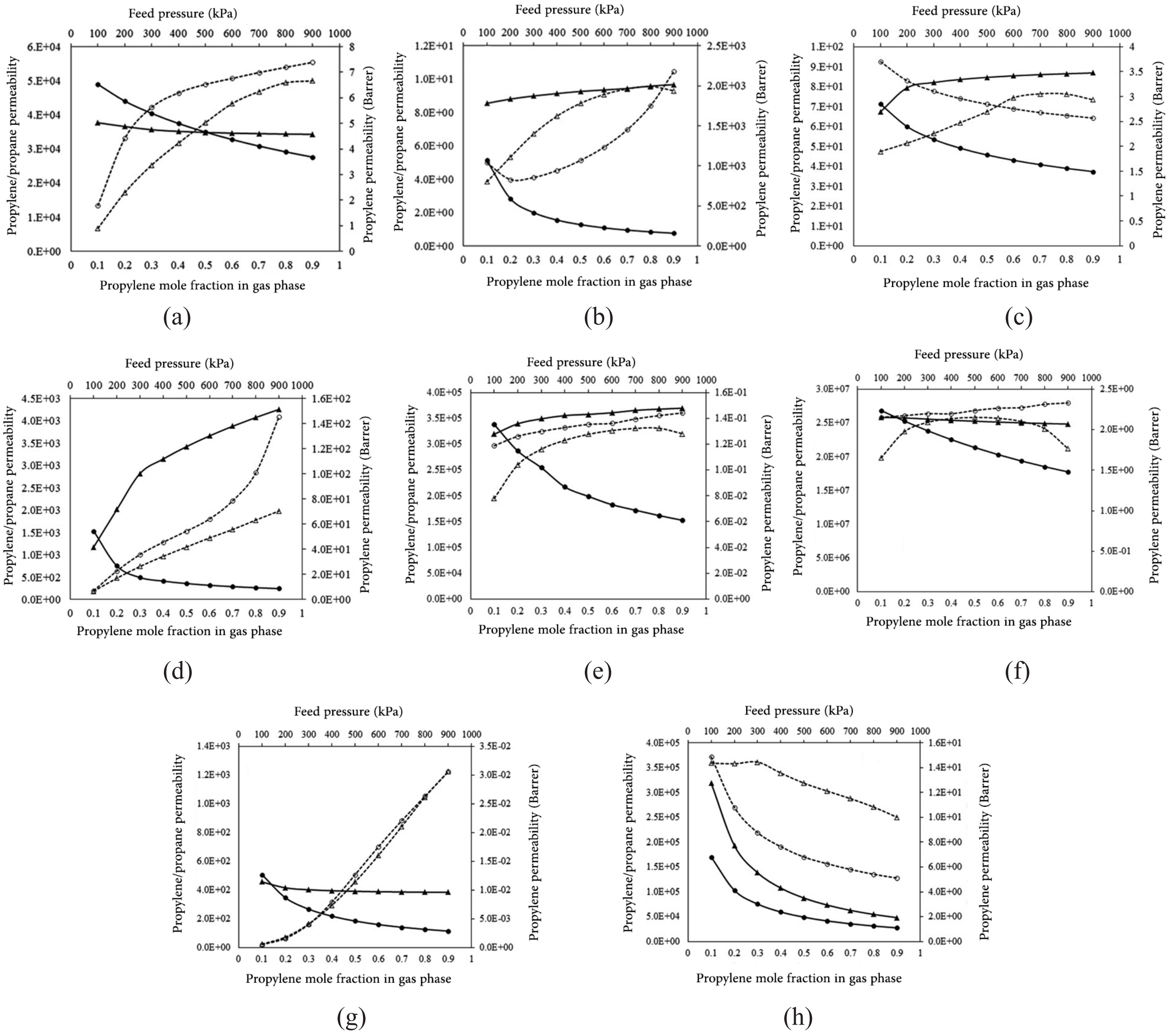
[2] It is assumed that the particle size equals to 20 μm

[3] It is assumed that the particle size equals to 0.2 μm

RESULTS AND DISCUSSION

Steady state performance is investigated for all the potential zeolite membranes. The effects of feed pressure and the fraction of propylene in the feed on both the propylene permeabilities and the membrane permselectivities are shown in Figure 1. It should be stated that the feed pressure effect is investigated for an equimolar mixture while the feed composition effect is examined at feed pressure of 100 kPa. According to the results, the propylene permeability of all the zeolite membranes decreases with increase in the feed pressure. On the other hand, the variation of propylene permeability with the feed composition shows different behaviors. It decreases for 4A and SAPO-34, increases for Si-CHA, ITQ-32, ITQ-12, ITQ-3 and DD3R and even shows a minimum for 5A at y_{C3H6}=0.2. The increase or decrease of permeability depends strongly on how the adsorption loading changes with the partial pressure, i.e. the isotherm type.

Additionally, propylene/propane permselectivity increases with propylene fraction in the feed for Si-CHA, ITQ-12 and ITQ-3. However, a maxima is observed for 5A, 4A and ITQ-32 at y_{C3H6}=0.8, for SAPO-34 at y_{C3H6}=0.3 and for DD3R at y_{C3H6}=0.5. The maximum point for SAPO-34 is in agreement with the work of Agarwal et al. [18]. They modeled a tubular



(a) (b) (c)

(d) (e) (f)

(g) (h)

Figure 1. Propylene permeability (circle) and propylene/propane selectivity (triangle) versus total feed pressure (solid lines) and feed composition (dashed lines) at the temperatures listed in Table 1. Si-CHA (a), 5A (b), 4A (c), ITQ-12 (d), ITQ-32 (e), DDR (f), ITQ-3 (g), SAPO-34 (h) membrane of SAPO-34. According to their results, a very high selectivity of 80000 was reported which confirms the selectivity values obtained in the present study.

Furthermore, propylene/propane permselectivity increases with pressure for 4A, 5A, ITQ-12 and ITQ-32. Also, it decreases for Si-CHA, ITQ-3, SAPO-34 and DD3R.

Analysis of the results and comparison between the permselectivites of the zeolite membranes seem to be interesting. For this purpose, Figures 2 and 3 are presented. Figure 2 compares the adsorption and diffusion (kinetic) selectivities of the studied zeolites. The adsorption selectivities presented in this figure are obtained from the literature [19]. According to the figures, the kinetic selectivity of SAPO-34 zeolite is higher than that of DD3R. But, the permselectivity of DD3R membrane is estimated to be higher than that of SAPO-34 membrane. This can be attributed to the higher adsorption selectivity of DD3R than that of SAPO-34. The same is observed for Si-CHA against ITQ-32, ITQ-3 against ITQ-12 and 4A against 5A. These results imply that the permselectivity is a product of kinetic and adsorption selectivities. Figure 3 confirms the existence of such a relationship between the permselectivity, adsorption and kinetic selectivities. This figure is highly useful for screening zeolites according to their selectivities. High selective zeolite can also be utilized for fabrication of mixed matrix membranes.

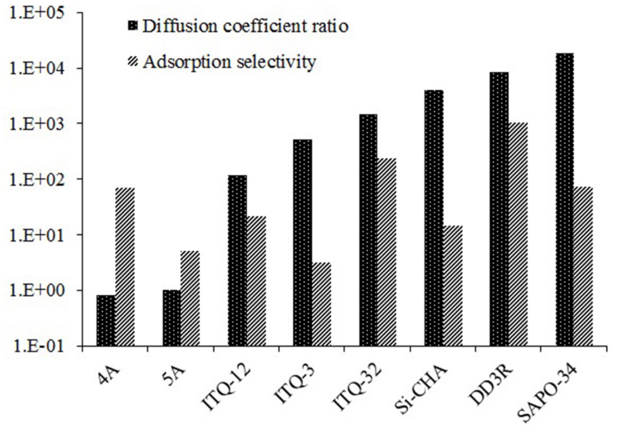


Figure 2. Propylene/propane adsorption and kinetic selectivities for various zeolites at the temperatures listed in Table 1.

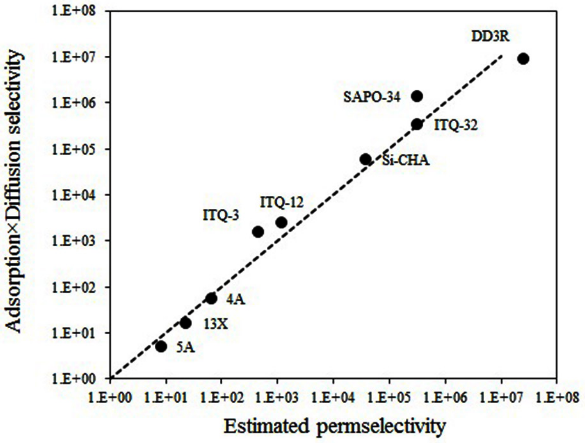


Figure 3. Estimated propylene/propane permselectivity vs. expected selectivity of zeolite membranes.

Finally, it is highly interested to compare the separation performances of the potential zeolite membranes studied in the present study with the performances of other types of membranes, e.g. carbon, polymer and composite membranes. For this purpose, Robeson plot (Figure 4) of propylene/propane separation was re-constructed from the data presented in the literature [20, 21, 28]. It is clear from Figure 4 that the separation performances of all the zeolite membranes are above the upper bound limit of the separation performances the polymer membranes. Additionally, the performances of carbon membranes are better than those of zeolites 4A and ITQ-3. It is estimated that 5A zeolite has a performance slightly better that the carbon membranes. It should be mentioned that the presence of even small amounts of defects in the zeolite film will result in a large decrease in the separation selectivity [29]. Thus, it is important to note that

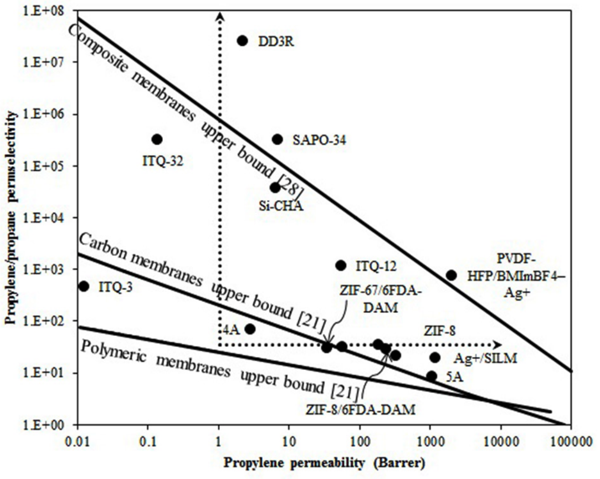


Figure 4. Propylene permeability and propylene/propane selectivity of zeolite membranes for an equimolar mixture at 100 kPa feed pressure compared with other types of membranes.

the estimated performances of zeolite membranes are belong to the defect-free films. In other words, they are the highest expected performances of the studied zeolite membranes and the experimental performances strongly depend on the quality of the zeolite films.

Important information taken from Figure 4 are that the composite membranes have better performances than the carbonic types. The performances of the mixed matrix membrane of 6FDA-DAM polymer containing ZIF-8 filler (ZIF-8/6FDA-DAM), supported ionic liquid membrane containing Ag^+ (Ag^+/SILM), and especially PVDF/BMImBF$_4$-Ag^+ are well above the upper bound of the carbon membranes. Among the zeolite membranes, the performances of ITQ-32, Si-CHA, ITQ-12 and 5A are placed below the upper bound of the composite membranes. On the other hand, the zeolite SAPO-34 and more especially DD3R have a better performance than the composite ones.

Figure 4 reveals that the membrane of zeolite DD3R has the highest propylene permselectivity. Furthermore, it is clear that the zeolites SAPO-34 and Si-CHA have a similar permeability for propylene, because they have similar structures with the same pore sizes. However, the presence of cations in the structure of SAPO-34 leads to a smaller diffusivity for propane and hence a higher selectivity for propylene. As mentioned in the introduction, a minimum selectivity of 35 and a permeability of 1 Barrer are needed for membranes as alternatives of common distillation units. Thus, according to this limit, it can be inferred that the zeolites DD3R, SAPO-34, Si-CHA and ITQ-12 are proper candidates for membrane applications. However, DD3R and SAPO-34 zeolites are more preferred candidates. Figure 4 is also helpful for researchers to find a proper zeolite as a molecular sieve in the preparation of mixed matrix membranes to enhance the selectivity of polymer membranes.

CONCLUSION

Maxwell-Stefan mass transfer model was utilized to estimate the performances of potential zeolites as membranes for separation of propylene from propane. The results confirmed the contribution of both adsorption and diffusion in the selectivity of zeolite membranes. In other words, calculated steady state permselectivities of zeolite membranes were in good agreement with the expected values (product of adsorption and kinetic selectivities). The estimated performances of zeolite membranes were placed in Robeson plot of propylene/propane separation. The results showed that DD3R zeolite membrane had the highest propylene permselectivity. According to the minimum requirements of membranes for propylene/propane separation (minimum selectivity of 35 and permeability of 1 Barrer), the zeolite membranes of DD3R, SAPO-34, Si-CHA and ITQ-12 could be considered as suitable candidates. However, only the performances of DD3R and SAPO-34 membranes were well above the composite membranes upper bound level.

REFERENCES

1. Sridhar S, Khan A (1999) Simulation studies for the separation of propylene and propane by ethylcellulose membrane. J Membrane Sci 159: 209-219
2. Fallanza M, Ortiz A, Gorri D, Ortiz I (2012) Experimental study of the separation of propane/propylene mixtures by supported ionic liquid membranes containing Ag^+–RTILs as carrier. Sep Purif Technol 97: 83-89
3. Zhang C, Dai Y, Johnson JR, Karvan O, Koros WJ (2012) High performance ZIF-8/6FDA-DAM mixed matrix membrane for propylene/propane separations. J Membrane Sci 389: 34-42
4. Faiz R, Li K (2012) Olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques. Chem Eng Sci 73: 261-284
5. Nymeijer K, Visser T, Assen R, Wessling M (2004) Super selective membranes in gas–liquid membrane contactors for olefin/paraffin separation. J Membrane Sci 232: 107-114
6. Nymeijer D, Visser T, Assen R, Wessling M (2004) Composite hollow fiber gas–liquid membrane contactors for olefin/paraffin separation. Sep Purif Technol 37: 209-220
7. Kim HS, Ryu JH, Kim H, Ahn BS, Kang YS (2000) Reversible olefin complexation by silver

ions in dry poly (vinyl methyl ketone) membrane and its application to olefin/paraffin separations. Chem Commun 1261-1262

8. Huang J-F, Luo H, Liang C, Jiang D-e, Dai S (2008) Advanced liquid membranes based on novel ionic liquids for selective separation of olefin/paraffin via olefin-facilitated transport. Ind Eng Chem Res 47: 881-888
9. Feiring AE, Lazzeri J, Majumdar S (2015) Membrane separation of olefin and paraffin mixtures. US Patent 20,150,025, 293
10. Xu L, Rungta M, Brayden MK, Martinez MV, Stears BA, Barbay GA, Koros WJ (2012) Olefins-selective asymmetric carbon molecular sieve hollow fiber membranes for hybrid membrane-distillation processes for olefin/paraffin separations. J Membrane Sci 423: 314-323
11. Grande CA, Gigola C, Rodrigues AE (2003) Propane–propylene binary adsorption on zeolite 4A. Adsorption 9: 321-329
12. Jarvelin H, Fair JR (1993) Adsorptive separation of propylene-propane mixtures. Ind Eng Chem Res 32: 2201-2207
13. Gascon J, Blom W, van Miltenburg A, Ferreira A, Berger R, Kapteijn F (2008) Accelerated synthesis of all-silica DD3R and its performance in the separation of propylene/propane mixtures. Micropor Mesopor Mat 115: 585-593
14. Olson DH, Camblor MA, Villaescusa LA, Kuehl GH (2004) Light hydrocarbon sorption properties of pure silica Si-CHA and ITQ-3 and high silica ZSM-58. Micropor Mesopor Mat 67: 27-33
15. Olson DH (2002) Light hydrocarbon separation using 8-member ring zeolites. US Patent No. 6488741 B2
16. Gutiérrez-Sevillano JJ, Dubbeldam D, Rey F, Valencia S, Palomino M, Martín-Calvo A, Calero S (2010) Analysis of the ITQ-12 zeolite performance in propane− propylene separations using a combination of experiments and molecular simulations. J Phys Chem C 114: 14907-14914
17. Palomino M, Cantín A, Corma A, Leiva S, Rey F, Valencia S (2007) Pure silica ITQ-32 zeolite allows separation of linear olefins from paraffins. Chem Commun 1233-1235
18. Agarwal K, John M, Pai S, Newalkar B, Bhargava R, Choudary N (2010) SAPO-34 assisted C3 separation: Modeling and simulation. Micropor Mesopor Mat 132: 311-318
19. Maghsoudi H (2015) Equilibrium adsorption analysis of microporous adsorbents in propene/propane binary mixture separation. Adsorption 21: 547-556
20. Pan Y, Li T, Lestari G, Lai Z (2012) Effective separation of propylene/propane binary mixtures by ZIF-8 membranes. J Membrane Sci 390: 93-98
21. Fallanza M, Ortiz A, Gorri D, Ortiz I (2013) Polymer–ionic liquid composite membranes for propane/propylene separation by facilitated transport. J Membrane Sci 444: 164-172
22. An H, Park S, Kwon HT, Jeong H-K, Lee JS (2017) A new superior competitor for exceptional propylene/propane separations: ZIF-67 containing mixed matrix membranes. J Membrane Sci 526: 367-376
23. Krishna R, Baur R (2004) Analytic solution of the Maxwell–Stefan equations for multicomponent permeation across a zeolite membrane. Chem Eng J 97: 37-45
24. Kapteijn F, Moulijn J, Krishna R (2000) The generalized Maxwell–Stefan model for diffusion in zeolites: Sorbate molecules with different saturation loadings. Chem Eng Sci 55: 2923-2930
25. Lito PF, Cardoso SP, Rodrigues AE, Silva CM (2015) Kinetic modeling of pure and multicomponent gas permeation through microporous membranes: Diffusion mechanisms and influence of isotherm type. Sep Purif Rev 44: 283-307
26. Ruthven DM, Reyes SC (2007) Adsorptive separation of light olefins from paraffins. Micropor Mesopor Mat 104: 59-66
27. Da Silva FA, Rodrigues AE (2001) Vacuum swing adsorption for propylene/propane separation with 4A zeolite. Ind Eng Chem Res 40: 5758-5774
28. Wang Y, Goh TY, Goodrich P, Atilhan M, Khraisheh M, Rooney D, Thompson J, Jacquemin J (2017) Impact of ionic liquids on silver thermoplastic composite membrane polyure-

thane for propane/propylene separation. Arab J Chem: (in press)
29. Maghsoudi H (2016) Defects of zeolite membranes: Characterization, modification and post-treatment techniques. Sep Purif Rev 45: 169-192