Journal of
Applied Sciences

ISSN 1812-5654

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Journal of Applied Sciences 14 (11): 1161-1167, 2014
ISSN 1812-5654 / DOI: 10.3923/jas.2014.1161.1167

Zeolite Imidazole Frameworks Membranes for CO_2/CH_4 Separation from Natural Gas: A Review

Li Sze Lai, Yin Fong Yeong, Kok Keong Lau and Mohd Shariff Azmi
School of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar,
Tronoh, 31750, Perak, Malaysia

Abstract: Carbon dioxide (CO_2) which exists in natural gas is one of the undesirable impurities that can reduce the caloric power of the natural gas. The implications of CO_2 on the economic loss of the natural gas processing have provoked the development of CO_2 separation technology. In the past decades, membrane technology has emerged as an environmental friendly, economic feasible and easy-operating method in CO_2 removal. ZIFs membranes presented to be relatively new materials, which possessed high stability and good performance in CO_2 separation under harsh condition. The tunability of the pore apertures and plentiful diversity of the frameworks associated with ZIFs membranes provide massive potential for the researchers to enhance the properties of ZIFs membranes in CO_2 separation. This review attempts to summarize the current performance of the ZIFs membrane in CO_2/CH_4 separation process, considering CH_4 as the main constitutions in natural gas. Extensive study on molecular structures, membrane formation and separation mechanism is emphasized on ZIF-8 membranes owing to their exceptionally high CO_2 permeability. To this end, separation performance involved in ZIF-8 membrane is discussed, which affected by the synthesis method, molar composition of the growth solution and modification of the supports.

Key words: CO_2/CH_4 separation, ZIFs membrane, ZIF-8 membrane, molecular structures, membrane formation, separation mechanism

INTRODUCTION

In the past decades, natural gas has played an important role as fuel used in industrial, agricultural and transportation sectors. It is a complex gas mixture containing different kinds of gaseous components, with methane (CH_4) as the main constitution and other impurities such as carbon dioxide (CO_2), hydrogen sulphide (H_2S) and water (H_2O) (Zhu *et al*., 2006; Scholes *et al*., 2012). Recently, composition of CO_2 presence in natural gas as high as 70% has been reported (Lin *et al*., 2006). The presence of high concentration of CO_2 in natural gas can corrode the pipelines mainly due to its acidic behaviour and reduce the caloric power of the natural gas (Zhu *et al*., 2006). Therefore, separation of CO_2 from CH_4 in natural gas processing is an essential steps in order to lessen the economic losses (Drioli and Barbieri, 2011).

Membrane technologies has drawn unprecedented attention of many researchers for CO_2 gas separation owing to its low energy consumption (Zornoza *et al*., 2013), compact and simple design (Zhu *et al*., 2006) environmental friendly (Lau *et al*., 2012), high CH_4 recovery (Basu *et al*., 2011), smaller capital cost (Chew *et al*., 2011), ease of operation and easy to scaled-up (Venna, 2010). Among the different types of the existing membranes, Zeolite Imidazolate Frameworks (ZIFs) membrane as the sub-category of metal-organic framework (MOF) membrane has emerged as a relatively new membrane material for CO_2 separation. This was mainly attributed to its remarkable properties such as exceptionally high thermal and chemical stability (Bux *et al*., 2009; Fairen-Jimenez *et al*., 2011; Xu *et al*., 2011; Hu *et al*., 2012), variety framework diversity with adjustable chemical functionality (Assfour *et al*., 2010; Fairen-Jimenez *et al*., 2011), high adsorption capacities, high specific surface areas and high pore volumes (Rosi *et al*., 2003).

The present review attempts to summarize the current performance of the ZIFs membrane in CO_2/CH_4 separation. Beginning with the brief introduction of ZIF and ZIFs membranes, reported literature on the performance among the ZIFs membranes in CO_2/CH_4 separation were summarized. In this regards, ZIF-8 membrane was chosen for extensive study due to its characteristics which are beneficial for CO_2/CH_4 separation. Subsequently, the

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Corresponding Author: Yin Fong Yeong, School of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia Tel: +605-3687564 Fax: +605-3656176

molecular structures and the mechanisms involved in membrane formation and CO_2/CH_4 separation of ZIF-8 were presented. Furthermore, the effect of the synthesis conditions on the formation of ZIF-8 membranes including (1) synthesis method, (2) molar composition of the growth solution and (3) modification of the supports, as well as the separation performance of the resultant membranes in CO_2/CH_4 were discussed. Finally, concluding remarks and future directions were suggested.

ZEOLITE IMIDAZOLATE FRAMEWORKS (ZIFS)

ZIFs presented in formula $M(Im)_2$, where M is the transition metal (Zn^{2+} or Co^{2+}) and Im is the imidazolate linker. The transition metal cations are connected by imidazolate anions through N (nitrogen) atoms into tetrahedral frameworks, subtend at an angle of 145° at M-Im-M center that resembling the zeolite topologies (Zhou *et al*., 2008; Cravillon *et al*., 2009; McCarthy *et al*., 2010; Amrouche *et al*., 2011; Diaz *et al*., 2011; Huang *et al*., 2011; Morris *et al*., 2012). The pores of ZIFs are formed by 4, 6, 8 and 12-membered rings of the ZnN_4 and CoN_4 clusters (Venna *et al*., 2010). The plentiful frameworks diversity and tunable pore apertures of the ZIFs promise their potential in gas separation.

ZEOLITE IMIDAZOLATE FRAMEWORK-8 (ZIF-8) MEMBRANES

Introduction to ZIF-8 membranes: ZIFs crystals that grow continuously on porous support will form thin layer of membrane eventually. The ZIFs membranes exhibit different performance in CO_2/CH_4 separation as shown in Table 1 (Venna and Carreon, 2009; Huang *et al*., 2010; Li *et al*., 2010; Liu *et al*., 2011; Zhang *et al*., 2013). Based on the reported results shown in Table 1, ZIF-8 membranes showed the highest CO_2 permeance (~240×10^{-7}mol/m^{2}sPa) and CO_2/CH_4 selectivity (~7) as compared to the other types of ZIFs membranes, such as ZIF-7, -69, -90 and -9-67. Apart from its high CO_2 permeance and CO_2/CH_4 selectivity, ZIF-8 membranes show hydrophobic characteristics and resist to some aromatic hydrocarbon such as benzene (Venna and Carreon, 2009) organic solvents and boiling alkaline water (Park *et al*., 2006). In addition, ZIF-8 membranes exhibit high thermal stability by sustaining the temperature up to 400°C in air and 550°C in N_2 (Madhusoodana *et al*., 2006). The outstanding properties showed by ZIF-8 membranes reveal their advantages over other type of membranes in gas separation application under harsh condition.

Molecular structures of ZIF-8: ZIF-8 ($Zn(meIm)_2$, meIm = 2-methylimidazole) possesses large cavities with the size of 11.6 Å, encompassed by six-membered ring window forming small apertures of 3.4 Å (Venna *et al*., 2010; Fairen-Jimenez *et al*., 2011; Xu *et al*., 2011). It is classified under cubic space group I-43 m with the Zn^{2+} ion connected to the N atoms of meIm groups through coordination bond, forming sodalite (SOD) zeolite topology (Hu *et al*., 2012). Figure 1 shows the three-dimensional structure of ZIF-8 in cubic unit cell at <111>

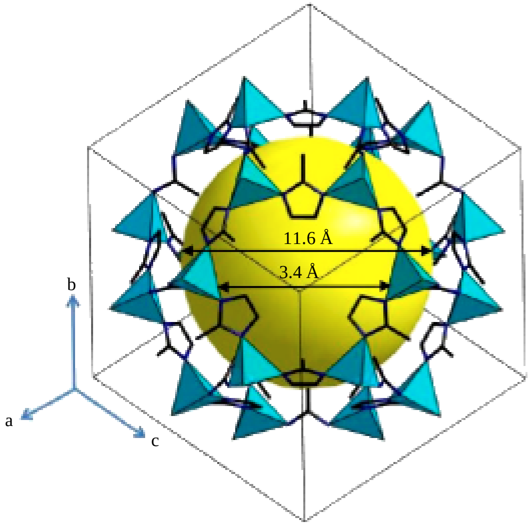

Fig. 1: Three-dimensional structure of ZIF-8 in cubic unit cell at <111> plane, showing large cavity (sphere region) with size 11.6Å and small apertures (six-membered ring window) with size 3.4Å. Adapted from (Markov, 2003; Park *et al*., 2006)

Table 1: CO_2 separation performance of different types of ZIFs membranes

Types of ZIFs membranes	Feed pressure (kPa)	Temperature (K)	CO_2 permeance ($\times10^{-7}$mol m^{-2}s Pa^{-1})	CO_2/CH_4 selectivity	References
ZIF-8	139.5	298	240	7*	Venna and Carreon (2009)
ZIF-7	100.0	493	0.035	1.13**	Li *et al.* (2010)
ZIF-69	101.3	298	1.0	4.6*	Liu *et al.* (2011)
ZIF-90	101.3	473	0.348	2.22**	Huang *et al.* (2010)
ZIF-9-67	N/A	298	15.8	0.3**	Zhang *et al.* (2013)

*$CO_2:CH_4$ = 50:50, **Ideal selectivity

plane (Markov, 2003; Park *et al*., 2006). Small apertures (~3.4Å size) are presented by the six-membered rings window and large cavity (~11.6Å) is presented by the sphere region.

Mechanism for ZIF-8 membrane formation: ZIF-8 membrane is formed through the continuous nucleation and crystallization process of ZIF-8 crystals on the porous supports. Initially, building unit of ZIF-8 emerges when Zn^{2+} cation attacks the meIm anion which is rich in electron. Nucleation process happens when each of the building unit of ZIF-8 is linked to the other building units through N atoms forming ZnN_4 clusters, which connect together and form the unit cell of ZIF-8 with the window cages. After nucleation process, ZIF-8 starts to grow through the collision and particle-monomer attachment process, indicating the occurrence of crystallization. The porous supports used for synthesizing ZIF-8 membrane to date including alumina (Venna and Carreon, 2009; Bux *et al*., 2011; Tao *et al*., 2013), titania (Bux *et al*., 2009) and YSZ ceramic fiber (Pan *et al*., 2012). Those selected porous supports possess inert characteristics and did not influence the growth of the membrane. Comprehensive schematic diagram on the ZIF-8 membrane formation is presented in Fig. 2 (Banerjee *et al*., 2008; Friscic *et al*., 2013).

Mechanism for CO_2/CH_4 gas separation in ZIF-8 membranes: In ZIF-8 membranes, CO_2 molecules permeate over the membrane through adsorption-desorption and diffusion mechanism (Chmelik *et al*., 2012) as displayed in Fig. 3. First, CO_2 molecules are selectively attracted by ZIF-8 membrane. Then, the molecules will diffuse through the matrix of the membrane owing to the gradient of chemical potential based on Maxwell-Stefan diffusion theory (Kapteijn *et al*., 2000). Finally, the CO_2 molecules are desorbed from the membrane to achieve equilibrium with the surrounding. Schematic diagram of the mass transfer of CO_2 molecules through ZIF-8 membrane in steady state is shown in Fig. 4 (Bux, 2011). Gas phase A and B existed at the feed and permeate sides of the membrane corresponding to constant pressure and respectively. The adsorption and desorption of CO_2 molecules on both sides of membrane at different pressure resulted in different concentration and chemical potentials of the molecules.

CO_2 molecules are preferentially adsorbed by ZIF-8 as compared to CH_4 molecules. This was due to the presence of the electrostatic potential (ESP) at the three methyl rings and the six imidazole rings of ZIF- 8 (Liu *et al*., 2012). Existence of ESP favours the attraction of CO_2 molecules with larger quadrupolar moment (13.4×10^{-40} Cm^2) as compared to CH_4 molecules, which are non-polar with the absence of quadrupolar moment (D'Alessandro *et al*., 2010). Besides, the diffusivity of CO_2 is larger than CH_4 under the same amount of molecules loading. This was due to the larger size of CH_4 molecules (~3.8Å) than CO_2 molecules (~3.3 Å) that contributed to higher steric hindrance during the interaction with the window cage of ZIF-8 (~3.4Å).

Effect of synthesis conditions on the formation and CO_2/CH_4 gas separation of ZIF-8 membranes: There are several factors affecting the quality of ZIF-8 membranes formed such as the synthesis method, molar composition of the synthetic solution and modification of the supports through the seeding methods. Correlation between those factors and the gas separation performance (CO_2/CH_4 selectivity) of the membranes was compared and listed in Table 2 (Bux *et al*., 2009; Venna and Carreon, 2009; Bux *et al*., 2011; Pan *et al*., 2012). ZIF-8 membrane which showed highest selectivity was reported by Venna and Carreon (2009). Secondary seeded growth method was used for the synthesis with the molar composition of the synthesis solution of Zn^{2+}: Hmim: MeOH of 1:8:700. The thickness of the resultant membrane was ~5 to 9 μm. CO_2/CH_4 selectivity of ZIF-8 membranes reported by Pan *et al.* (2012) and Bux *et al.* (2009) was relatively low,

Table 2: Comparison for ZIF-8 membranes synthesized at different parameters

Types of ZIF membranes	Molar composition	Synthesis method and duration	Membrane thickness (μm)	CO_2/CH_4 selectivity	References
ZIF-8	Zn^{2+}: Hmim: MeOH 1:8:700	In situ crystallization with solvothermal synthesized seeds and secondary seeded growth (rubbing) with α-alumina tubular supports; 5h	~5-9	~7*	Venna and Carreon (2009)
ZIF-8	Zn^{2+}: Hmim: H_2O 1:70:1238	Secondary seeded growth method (dip-coating for 10s) with hollow YSZ ceramic fiber; 6h	~2.5	~3.33**	Pan *et al.* (2012)
ZIF-8	Zn^{2+}:Hmim: MeOH:NaCOOH 1:1.5:250:1	Microwave-assisted solvothermal with asymmetric titania disc; 4h	~30	~2.77**	Bux *et al.* (2009)
ZIF-8	Zn^{2+}:Hmim: MeOH:NaCOOH 1:1.52:506.4:1.03	Microwave-assisted solvothermal secondary seeded growth (dip-coating) with porous PEI[a] modified α-alumina support; 0.5-4h	~12	N/A	Bux *et al.* (2011)

*CO_2:CH_4 = 50:50, **Ideal selectivity, [a]polyethyleneimine

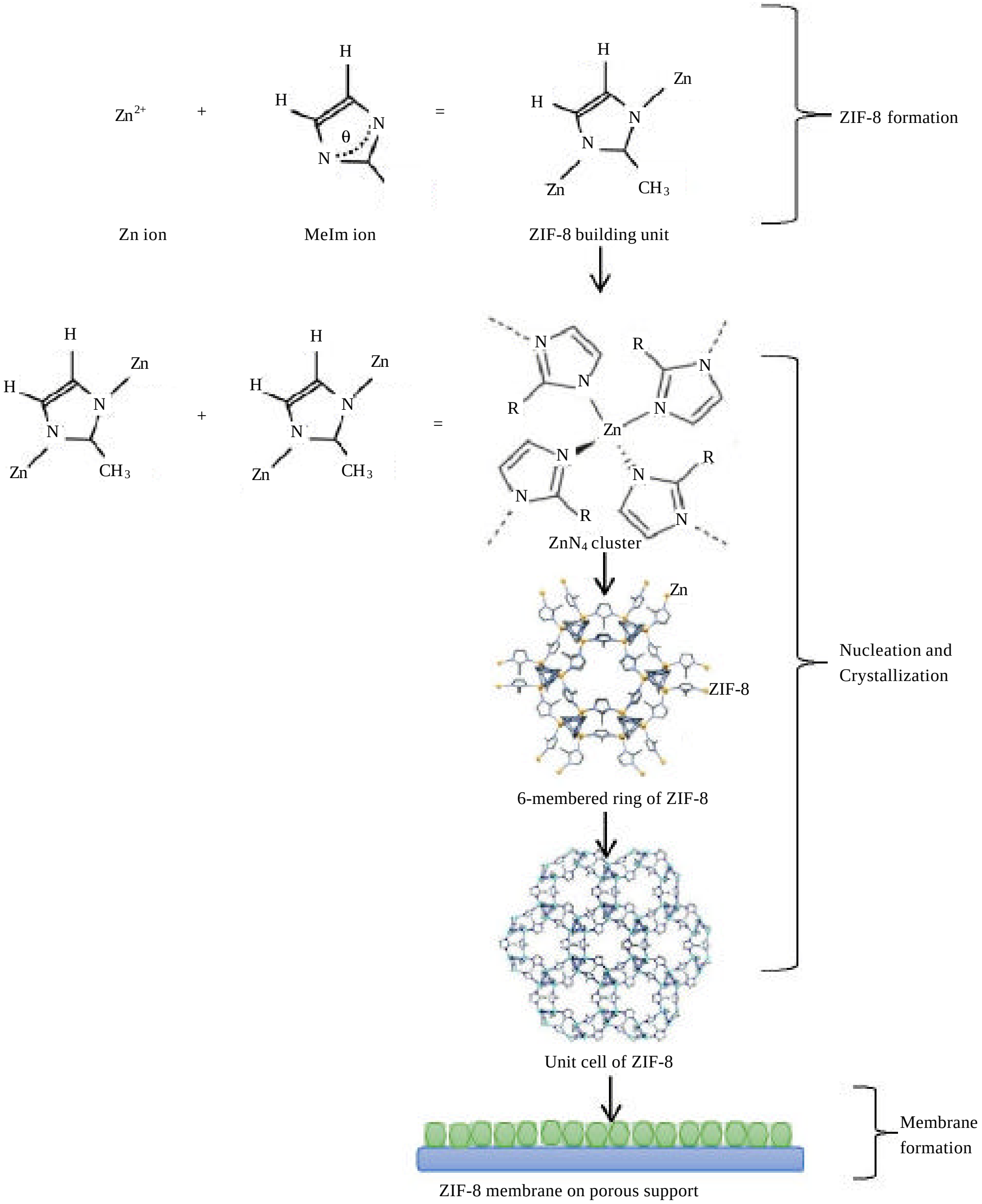

Fig. 2: Schematic diagram of ZIF-8 membrane formation involved nucleation and crystallization processes, adapted from (Banerjee *et al*., 2008; Friscic *et al*., 2013)

regardless of their thickness and different molar composition of the synthesis solution (using water (Zn^{2+}: Hmim: H_2O of 1:70:1238) or sodium formate (Zn^{2+}: Hmim: MeOH:NaCOOH of 1:1.5:250:1)). However, microwave-assisted solvothermal synthesis process reported by Bux *et al.* (2009) required less synthesis duration of 4 h as compared to the other methods such as in situ crystallization and secondary seeded growth (5-6 h). On the other hand, by using microwave-assisted solvothermal secondary seeded growth, Bux *et al.* (2011) successfully produced a thinner membrane (~12 μm) as compared to their previous work (~30 μm) using in situ crystallization (Bux *et al*., 2009). However, the CO_2/CH_4 separation performance of the resultants ZIF-8 membranes was not reported by Bux *et al.* (2011). Hence, the CO_2/CH_4 gas separation performance for ZIF-8 membrane is still in

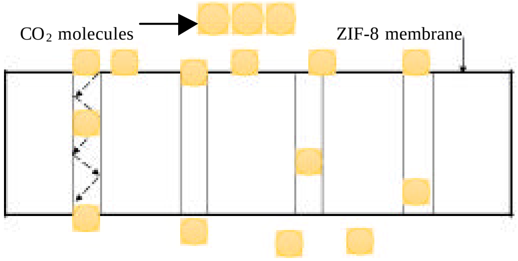

Fig. 3: CO_2 adsorption-desorption and diffusion mechanism of ZIF-8 membranes

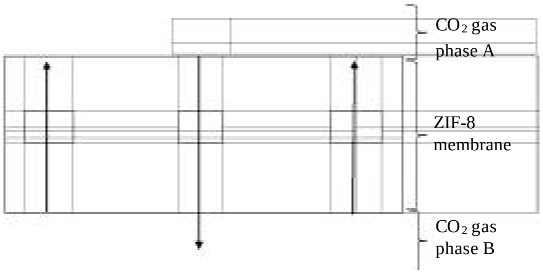

Fig. 4: Schematic diagram of mass transfer of CO_2 through ZIF-8 membranes in steady state, adapted from (Bux, 2011)

the initial stage due to inconsistency of the reported results in the literature. Formation of a thin layer of ZIF-8 membranes with low defects and excellent CO_2/CH_4 separation performance still remains as a challenging task. Therefore, development of a reproducible synthesis method for synthesizing high quality ZIF-8 membranes exhibit a great potential for further research study. A standardized ZIF-8 membranes formation method with the attractive properties and high CO_2/CH_4 separation performance need to be investigated and established.

CONCLUSION AND FUTURE PERSPECTIVE

The present review study provides comprehensive account on the CO_2/CH_4 separation from natural gas using ZIFs membranes. ZIF possess desirable properties such as high stability, large surface area and pores volumes. We have emphasized on ZIF-8 membrane due to its outstanding CO_2 permeance and relatively high CO_2/CH_4 selectivity as compared to the other ZIFs membranes. Nevertheless, improvement of the current ZIF-8 membrane formation and its separation performance is still needed. In this vein, we suggest that further research could be carried out on the development of a feasible and reproducible synthesis method for ZIF-8 membranes. This requires the interdisciplinary understanding on the mechanism of the membrane formation and CO_2/CH_4 separation process. Then, the membrane can be formed by controlling the microstructure, thickness and eliminating the defects thus increasing its CO_2/CH_4 separation performance.

ACKNOWLEDGEMENTS

The financial support provided by Universiti Teknologi PETRONAS under STIRF Grant (Cost Centre: 158200-000) and YUTP-FRG (Cost Centre: 0153AA-A62) is duly acknowledged.

REFERENCES

Amrouche, H., S. Aguado, J. Perez-Pellitero, C. Chizallet and F. Siperstein *et al.*, 2011. Experimental and computational study of functionality impact on sodalite-zeolitic imidazolate frameworks for CO_2 separation. J. Phys. Chem. C, 115: 16425-16432.

Assfour, B., S. Leoni and G. Seifert, 2010. Hydrogen adsorption sites in zeolite imidazolate frameworks ZIF-8 and ZIF-11. J. Phys. Chem. C, 114: 13381-13384.

Banerjee, R., A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O.M. Yaghi, 2008. High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture. Science, 319: 939-943.

Basu, S., A. Cano-Odena and I.F. Vankelecom, 2011. MOF-containing mixed-matrix membranes for CO_2/CH_4 and CO_2/N_2 binary gas mixture separations. Sep. Purif. Technol., 81: 31-40.

Bux, H., F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, 2009. Zeolitic imidazolate framework membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. J. Am. Chem. Soc., 131: 16000-16001.

Bux, H., 2011. Preparation and characterization of metal-organic framework membranes for gas separation. Institute of Physical Chemistry and Eletrochemistry, Leibniz University Hannover, Germany.

Bux, H., A. Feldhoff, J. Cravillon, M. Wiebcke, Y.S. Li and J. Caro, 2011. Oriented zeolitic imidazolate framework-8 membrane with sharp H2/C3H8 molecular sieve separation. Chem. Mater., 23: 2262-2269.

Chew, T.L., A.L. Ahmad and S. Bhatia, 2011. Ba-SAPO-34 membrane synthesized from microwave heating and its performance for CO_2/CH_4 gas separation. Chem. Eng. J., 171: 1053-1059.

Chmelik, C., J. van Baten and R. Krishna, 2012. Hindering effects in diffusion of CO_2/CH_4 mixtures in ZIF-8 crystals. J. Membr. Sci., 397-398: 872-891.

Cravillon, J., S. Munzer, S.J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, 2009. Rapid room-temperature synthesis and characterization of nanocrystals of a prototypical zeolitic imidazolate framework. Chem. Mater., 21: 1410-1412.

D'Alessandro, D.M., B. Smit and J.R. Long, 2010. Carbon dioxide capture: Prospects for new materials. Angewandte Chem. Int. Edn., 49: 6058-6082.

Diaz, K., M. Lopez-Gonzalez, L.F. del Castillo and E. Riande, 2011. Effect of zeolitic imidazolate frameworks on the gas transport performance of ZIF8-poly (1, 4-phenylene ether-ether-sulfone) hybrid membranes. J. Membr. Sci., 383: 206-213.

Drioli, E. and G. Barbieri, 2011. Membrane Engineering for the Treatment of Gases: Gas-Separation Problems with Membranes. Royal Society Of Chemistry, London, UK., ISBN: 9781849731713, Pages: 318.

Fairen-Jimenez, D., S.A. Moggach, M.T. Wharmby, P.A. Wright, S. Parsons and T. Duren, 2011. Opening the gate: Framework flexibility in ZIF-8 explored by experiments and simulations. J. Am. Chem. Soc., 133: 8900-8902.

Friscic, T., I. Halasz, P.J. Beldon, A.M. Belenguer, F. Adams, S.A.J. Kimber, V. Honkimaki and R.E. Dinnebier, 2013. Real-time and *in situ* monitoring of mechanochemical milling reactions. Nat. Chem., 5: 66-73.

Hu, Z., L. Zhang and J. Jiang, 2012. Development of a force field for zeolitic imidazolate framework-8 with structural flexibility. J. Chem. Phys., Vol. 136. 10.1063/1.4729314

Huang, A., W. Dou and J. Caro, 2010. Steam-stable zeolitic imidazolate framework ZIF-90 membrane with hydrogen selectivity through covalent functionalization. J. Am. Chem. Soc., 132: 15562-15564.

Huang, H., W. Zhang, D. Liu, B. Liu, G. Chen and C. Zhong, 2011. Effect of temperature on gas adsorption and separation in ZIF-8: A combined experimental and molecular simulation study. Chem. Eng. Sci., 66: 6297-6305.

Kapteijn, F., J.A. Moulijn and R. Krishna, 2000. The generalized Maxwell-Stefan model for diffusion in zeolites: Sorbate molecules with different saturation loadings. Chem. Eng. Sci., 55: 2923-2930.

Lau, C.H., D.R. Paul and T.S. Chung, 2012. Molecular design of nanohybrid gas separation membranes for optimal CO_2 separation. Polymer, 53: 454-465.

Li, Y., F. Liang, H. Bux, W. Yang and J. Caro, 2010. Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation. J. Membrane Sci., 354: 48-54.

Lin, H., E. van Wagner, R. Raharjo, B.D. Freeman and I. Roman, 2006. High-performance polymer membranes for natural-gas sweetening. Adv. Mater., 18: 39-44.

Liu, Y., G. Zeng, Y. Pan and Z. Lai, 2011. Synthesis of highly c-oriented ZIF-69 membranes by secondary growth and their gas permeation properties. J. Membr. Sci., 379: 46-51.

Liu, D., Y. Wu, Q. Xia, Z. Li and H. Xi, 2012. Experimental and molecular simulation studies of CO_2 adsorption on zeolitic imidazolate frameworks: ZIF-8 and amine-modified ZIF-8. Adsoprtion, 19: 25-37.

Madhusoodana, C.D., R.N. Das, Y. Kameshima and K. Okada, 2006. Preparation of ceramic honeycomb filter supported zeolite membrane modules by microwave-assisted in-situ crystallization. Key Eng. Mater., 317: 697-700.

Markov, I.V., 2003. Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy. 2nd Edn., World Scientific, Singapore.

McCarthy, M.C., V. Varela-Guerrero, G.V. Barnett and H.K. Jeong, 2010. Synthesis of zeolitic imidazolate framework films and membranes with controlled microstructures. Langmuir, 26: 14636-14641.

Morris, W., C.J. Stevens, R.E. Taylor, C. Dybowski, O.M. Yaghi and M.A. Garcia-Garibay, 2012. NMR and X-ray study revealing the rigidity of zeolitic imidazolate frameworks. J. Phys. Chem. C, 116: 13307-13312.

Pan, Y., B. Wang and Z. Lai, 2012. Synthesis of ceramic hollow fiber supported Zeolitic Imidazolate Framework-8 (ZIF-8) membranes with high hydrogen permeability. J. Membr. Sci., 421: 292-298.

Park, K.S., Z. Ni, A.P. Cote, J.Y. Choi and R. Huang *et al*., 2006. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc. Nat. Acad. Sci., 103: 10186-10191.

Rosi, N.L., J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe and O.M. Yaghi, 2003. Hydrogen storage in microporous metal-organic frameworks. Science, 300: 1127-1129.

Scholes, C.A., G.W. Stevens and S.E. Kentish, 2012. Membrane gas separation applications in natural gas processing. Fuel, 96: 15-28.

Tao, K., C. Kong and L. Chen, 2013. High performance ZIF-8 molecular sieve membrane on hollow ceramic fiber via crystallizing-rubbing seed deposition. Chem. Eng. J., 220: 1-5.

Venna, S.R. and M.A. Carreon, 2009. Highly permeable zeolite imidazolate framework-8 membranes for CO_2/CH_4 separation. J. Am. Chem. Soc., 132: 76-78.

Venna, S.R., 2010. Molecular engineering design of the SAPO-34 and ZIF-8 membranes for CO_2 separation from CH_4 and N_2. Ph.D. Thesis, Department of Chemical Engineering, University of Louisville, Louisville, Kentucky.

Venna, S.R., J.B. Jasinski and M.A. Carreon, 2010. Structural evolution of zeolitic imidazolate framework-8. J. Am. Chem. Soc., 132: 18030-18033.

Xu, G., J. Yao, K. Wang, L. He, P.A. Webley, C.S. Chen and H. Wang, 2011. Preparation of ZIF-8 membranes supported on ceramic hollow fibers from a concentrated synthesis gel. J. Membr. Sci., 385-386: 187-193.

Zhang, C., Y. Xiao, D. Liu, Q. Yang and C. Zhong, 2013. A hybrid zeolitic imidazolate framework membrane by mixed-linker synthesis for efficient CO_2 capture. Chem. Commun., 49: 600-602.

Zhou, W., H. Wu, T.J. Udovic, J.J. Rush and T. Yildirim, 2008. Quasi-free methyl rotation in zeolitic imidazolate framework-8. J. Phys. Chem. A, 112: 12602-12606.

Zhu, W., P. Hrabanek, L. Gora, F. Kapteijn and J.A. Moulijn, 2006. Role of adsorption in the permeation of CH_4 and CO_2 through a silicalite-1 membrane. Ind. Eng. Chem. Res., 45: 767-776.

Zornoza, B., C. Tellez, J. Coronas, J. Gascon and F. Kapteijn, 2013. Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential. Microporous Mesoporous Mater., 166: 67-78.