



SYNTHESIS OF DECA-DODECASIL 3 RHOMBOHEDRAL (DD3R) MEMBRANES VIA SECONDARY HYDROTHERMAL GROWTH METHOD AND THEIR GAS PERMEATION PERFORMANCE IN CO₂ AND CH₄

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ABSTRACT

In the present work, DD3R zeolite membranes were synthesized on α -alumina support using dip-coating and vacuum-assisted seeding secondary growth methods, respectively. DD3R seeds were synthesized using two different routes; (i) ultrasonic irradiation pretreatment coupled with hydrothermal heating for 1 day at 160 °C and (ii) hydrothermal heating for 25 days at 160 °C without ultrasonic irradiation pretreatment. Subsequently, the DD3R membranes were grown on the seeded support in 2 days at 160 °C via hydrothermal heating method. The resultant membranes were characterized using X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). The XRD and FESEM results showed that all membranes demonstrated DD3R topology. The resultant membranes were subjected to gas permeation study and CO₂/CH₄ selectivity of 5.22 was obtained for the DD3R membrane synthesized via vacuum seeding method using DD3R seeds synthesized in 1 day.

Keywords: dip coating, vacuum-assisted seeding, DD3R zeolite membrane, CO₂ separation.

INTRODUCTION

CO₂ is the major contributor to global warming, and over 30 billion tons of CO₂ is added to the atmosphere each year [1]. In the recent years, micro-porous silica membranes [2], metal organic frameworks (MOF) [3], carbon membranes [4] and zeolite membranes [5,6] have been extensively reported for carbon dioxide separation from natural gas. Among micro-porous inorganic membranes, zeolite membranes including Zeolite-T [5,7], SAPO-34 [8], MFI [6], AIPO-18 [9] and DD3R [10] are the potential membranes material for CO₂ separation from natural gas because of their characteristics such as molecular sieving property, hydrophobic surface and thermal stability.

DD3R zeolite is a member of the clathrasils group having [SiO₄]⁻⁴ tetrahedral linkage in their structure and 19-hedral cages interconnected with each other through 8-ring window pore system is aperture 0.36 x 0.44nm. DD3R zeolite is an attractive candidate for CO₂/CH₄ separation because of its aperture size which can selectively removes CO₂ from CH₄. This excellent characteristic not only attractive for CO₂/CH₄ separation but also for separation of small molecule gases like CO₂, CH₄, H₂ and other light hydrocarbons [11]. Tomita *et al.* [10] firstly reported the synthesis of DD3R zeolite membrane using 27 days via secondary growth method at 160 °C. CO₂ permeance of 3.0 x 10⁻⁷ mol/ (m² s Pa) and CO₂/CH₄ selectivity of 200 were obtained at room temperature. Meanwhile, Nakayama *et al.* [12] synthesized DD3R membrane in 27 to 30 days via secondary growth method at 160 °C. They reported that CO₂ permeance of 1 x 10⁻⁹ mol/ (m² s Pa) and CO₂/CH₄ selectivity of 10 were obtained at room temperature. Subsequently, Yajima *et al.* [13] synthesized DD3R zeolite membrane by modifying the method reported by Tomita *et al.* [10] in order to improve the membrane performance in CO₂ separation.

They successfully obtained uniform DD3R membrane between 25.5 days to 30 days with CO₂/CH₄ selectivity ranging from 3.1 to 72.

As reported in the literature, two common methods have been applied for the synthesis of DD3R zeolite membranes, including i) insitu hydrothermal growth and ii) secondary seeded growth [14]. Various researchers [10,14-16] reported the successful cases for the synthesis of DD3R membranes using secondary growth method. Dip-coating [17], rub coating [18], spray coating [19] and spinning coating [20] are the common secondary growth methods reported in the literature. Among these secondary growth methods, most of the researchers [10,16,17] focused on dip-coating method due to its simplicity. Vacuum assisted seeding method is considered as effective and fast seeding method which has been successfully applied for the synthesis of ZSM-5, NaA and sodalite membranes, respectively [21-22]. However, the synthesis of DD3R membrane using vacuum assisted seeding method is yet to be reported so far.

In the present work, four DD3R membranes were synthesized using dip-coating and vacuum-assisted seeding secondary hydrothermal growth methods. Two DD3R membranes were synthesized via dip-coating and vacuum-assisted seeding methods, respectively using DD3R seeds prepared in 1 day. Similarly, for comparison purpose, another two DD3R membranes were synthesized via dip-coating and vacuum-assisted seeding method, respectively using DD3R seeds prepared in 25 days. All the resultant membranes were characterized using XRD and FESEM. The performance of the membranes in CO₂/CH₄ separation was tested.



EXPERIMENTAL SECTION

Materials

The chemicals used in the present work are tetramethoxysilane $\geq 98\%$ (TMOS), Ethylenediamine $\geq 98\%$ (EDA) and structure directing agent 1-adamantaneamine $\geq 96\%$ (1-ADA). TMOS and EDA were purchased from Merck Millipore Ltd (Malaysia) and 1-ADA was purchased from Fisher Scientific Ltd (Malaysia).

Synthesis of DD3R zeolite seeds

DD3R zeolite seeds were prepared in one day by using hydrothermal heating coupled with ultrasonic irradiation method as described in our previous work [23]. The sample mixture was prepared by adding 40.46 g of di-ionized water drop wise to a solution of 1.42 g of 1-ADA ($\geq 96\%$) in 4.85 g of EDA ($\geq 98\%$) at room temperature under continuous stirring for 1 h. Then, the solution was heated for 1 h at 95 °C with continuous stirring at 200 rpm. After ice cooling for 20 min, 3.04 g of TMOS ($\geq 98\%$) was added into the solution under continuous stirring. The resulting solution was again stirred for 3 h at 95 °C. The final molar ratio of the solution was 1-ADA: TMOS: EDA: H₂O = 47:100:404:11,240. After that, the final solution mixture was treated under ultrasonic irradiation for 1 h. After ultrasonic irradiation, stationary hydrothermal synthesis was carried out in an oven at 160 °C for 1 day and it was coded as S1. Meanwhile, S2 was synthesized in 25 days using the similar method as described for S1 but without ultrasonic irradiation pretreatment.

Seeding of the substrate

Seed solution was prepared by dispersing 1 g of DD3R seeds, S1 and S2 into 100 ml of di-ionized water and coded as ST1 and ST2, respectively. Then, both seed solutions were sonicated for 2 h. The α -alumina disks pre-coated with mesoporous layer were seeded by using dip coating and vacuum seeding methods, respectively. Dip coating method was carried out by dipping the α -alumina disks in the seed suspension (ST1) for 15 s and repeated for 5 times. The same procedure was repeated using solution ST2. After dip coating, both seeded supports were dried at 80 °C for overnight. Subsequently, vacuum assisted seeding was applied on α -alumina disks pre-coated with mesoporous layer.

The duration for the vacuum assisted seeding was maintained for 5 min. After this, seeded support was dried in an oven at 80 °C for overnight. The same procedure was repeated using ST2 seed suspension and total four seeded supports, coded as SS1-SS4 were preceded for membranes synthesis.

Synthesis of DD3R membrane

Table-1 shows the membranes synthesized in the present work using various conditions. The solution mixture used to synthesize DD3R zeolite membranes was prepared using the method as described by den Exter *et al.*

[24]. The final molar ratio of the solution mixture was similar with those solution used to synthesis DDR3 crystals. The seeded supports (SS1-SS4) were placed horizontally in a Teflon-autoclave filled with solution. Stationary hydrothermal heating was carried out in an oven at 160 °C for 2 days. After cooling to room temperature, membranes (M1-M4) were washed using di-ionized water and placed in an oven for overnight at 100 °C. After drying, membranes were calcined in a furnace at 450 °C with the ramping rate of 0.3 °C per min for 8 h. After calcination, membranes were stored in the dessicator prior to performance testing.

Table-1. Membranes synthesized in the present work under various conditions.

Membrane	Seeds synthesis duration (days)	Seed solutions	Seeded Support	Seeding Method	Membrane Synthesis duration (days)
M1	1* (S1)	ST1	SS1	Dip Coating	2
M2	1* (S1)	ST1	SS2	Vacuum assisted	2
M3	25* (S2)	ST2	SS3	Dip Coating	2
M4	25* (S2)	ST2	SS4	Vacuum assisted	2

*with ultrasonic irradiation of 1 h

*without ultrasonic irradiation

Characterization and permeation study

Resultant membranes were characterized by using XRD (Model; Philips 1710 diffractometer with CuK α radiation) and FESEM (Model: Zeiss Supra 55 VP). The performance of the membranes (M1-M4) in CO₂ and CH₄ permeation was investigated at feed pressure of 2 bars and room temperature, using gas permeation test-rig. Permeance of CO₂, CH₄ and CO₂/CH₄ ideal selectivity were calculated by using equation (1) and equation (2) [25] as follows:

$$Pi = \frac{Ji}{\Delta Pi} \quad (1)$$

$$\alpha \frac{CO_2}{CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

Where Pi is a ratio of flux (Ji) to pressure drop (ΔP) through the membrane. The flux of the membrane was calculated using bubble flow meter attached to permeate while $\alpha \frac{CO_2}{CH_4}$ is the ratio of CO₂ permeance to CH₄ permeance.

RESULTS AND DISCUSSION

X-ray diffraction (XRD)

Figure-1 shows the XRD pattern of all samples synthesized in the present work. All as-synthesized membranes showed the peaks at 2θ values of 9°, 17°, 18°, 19°, 20°, 21°, 22°, 23°, 24°, 25°, 26°, 27°, 28°, 29°, 30°, 31°, 32°, 33°, 34°, 35°, 36°, 37°, 38°, 39°, 40°, 41°, 42°, 43°, 44°, 45°, 46°, 47°, 48°, 49°, 50°, 51°, 52°, 53°, 54°, 55°, 56°, 57°, 58°, 59°, 60°, 61°, 62°, 63°, 64°, 65°, 66°, 67°, 68°, 69°, 70°, 71°, 72°, 73°, 74°, 75°, 76°, 77°, 78°, 79°, 80°, 81°, 82°, 83°, 84°, 85°, 86°, 87°, 88°, 89°, 90°.



19°, 19.5°, 20°, 26°, 36°, 38° and 44°. These significant peaks at 2θ values are consistent with those peaks reported in the literature for DD3R structure [10]. Referring to Figure-1, the presence of the significant peaks in the XRD pattern of the membranes (M1-M4) confirmed the formation of DD3R membranes. From these results, it is confirmed that the DD3R membranes (M1 & M2) can be synthesized in 2 days using DD3R seeds (S1) produced in 1 day via ultrasonic irradiation coupled with hydrothermal heating method. These two membranes (M1 & M2) showed similar XRD pattern with the membranes (M3 & M4) synthesized by using DD3R seeds (S2) produced in 25 days. It can be seen from Figure-1 that, all membranes (M1-M4) showed similar XRD peaks which concluded that the synthesis duration of DD3R membrane can be reduced significantly using seeds synthesized in 1 day (S1) via ultrasonic irradiation coupled with hydrothermal heating method.

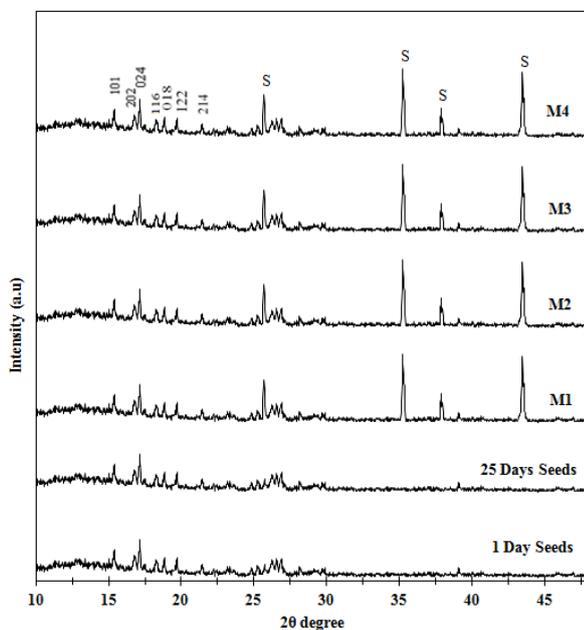


Figure-1. XRD pattern of all samples synthesized in the present work (S marks the peaks of alumina support).

Field-emission scanning electron microscope (FESEM)

Figure-2 shows the FESEM images of the DD3R membranes (M1-M4) synthesized in the present work. It can be seen from the FESEM images that DD3R morphology obtained in this study are comparable with those results reported in the literature [10,26]. Referring to Figure-2, M1 and M2 which were synthesized using DD3R seeds of S1 shows hexagonal morphology which is in coherence with the morphology of DD3R crystals reported by Zhou *et al.* [26]. Besides, M3 and M4 membranes also showed hexagonal morphology while these membranes were produced by using DD3R crystals prepared from S2. The effect of different seeding method on the distribution of DD3R crystals on the surface of the membranes can also be observed in Figure-2. More

uniform growth of crystals was obtained for M2 and M4 which the seed layer were formed via vacuum-assisted seeding method. This result shows that vacuum-assisted seeding method could produce more uniform seed layer and thus enhanced uniform growth of DD3R membrane layer on the α -alumina support as compared to dip-coating seeding method. It can be also observed from Figure-2 that all DD3R membranes (M1-M4) showed similar morphology (hexagonal) which further confirmed the synthesis duration of DD3R membrane has been successfully reduced from 27 days to 3 days by using DD3R seeds synthesized in 1 day (S1) via ultrasonic irradiation coupled with hydrothermal heating method. The FESEM results obtained for all DDR3 membranes (M1-M4) were consistent with the XRD results discussed in the earlier section.

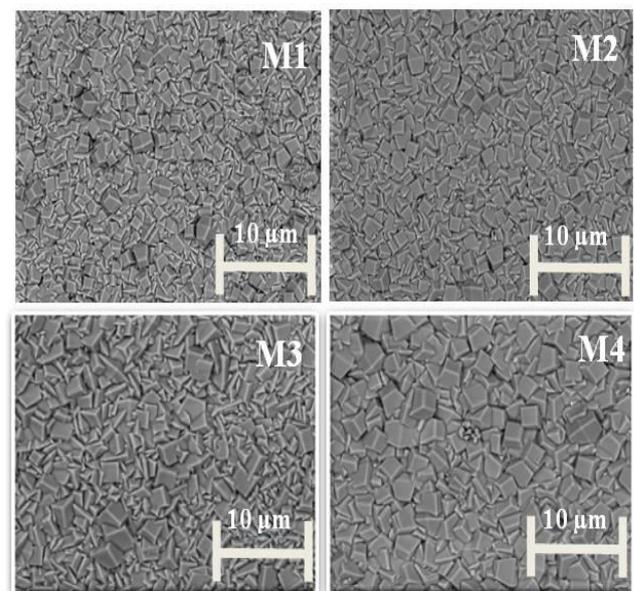


Figure-2. FESEM images of all membranes synthesized in the present work.

Gas permeation study

Table-2 shows the performance of all DD3R membranes (M1-M4) synthesized in the present work. Referring to Table-2, M1 prepared via dip-coating using S1 seed solution showed higher CO_2/CH_4 ideal selectivity of 2.45 compared to M3 which was prepared via dip-coating using S2 seed solution. Poor CO_2/CH_4 ideal selectivity of 1.60 was obtained for M3 could be due to the presence of intercrystalline defects and microcracks resulted from thermal shocks during calcination. On the other hand, M2 which was prepared via vacuum-assisted seeding method using S1 seed solution shows the highest CO_2/CH_4 ideal selectivity of 5.22 compared to M1, M3 and M4. This result further show that vacuum-assisted seeding method could enhance uniform growth of membrane layer and thus, less defective membrane is formed. Referring to Table-2 also, M1 and M2 show better separation performance compared to M3 and M4. This result could be explained by the effect of ultrasonic pre-



treatment on the morphology of the resultant DD3R seeds. Different morphology of the seeds could affect the growth of the membrane layer. DD3R seeds synthesized using ultrasonic pre-treatment coupled with hydrothermal method could enhance the growth of the membrane layer with minimum defects and thus better separation performance was obtained for M1 and M2 compared to M3 and M4.

Table-2. Performance of the DD3R membranes synthesized in the present work.

Membrane	Seeding Method	Permeance [mol/m ² .s.Pa]		Ideal Selectivity
		CO ₂ x 10 ⁻⁸	CH ₄ x 10 ⁻⁸	CO ₂ /CH ₄
M1	Dip coating	3.62	1.48	2.45
M2	Vacuum assisted	24.69	4.73	5.22
M3	Dip coating	5.22	3.26	1.60
M4	Vacuum assisted	3.11	1.81	1.72

Comparison of permeation results with the literature

Table-3 shows the CO₂ permeance and CO₂/CH₄ ideal selectivity of DD3R membranes synthesized in the present work and reported in the literature. It can be seen from Table-3 that DD3R membrane synthesized in the present work showed CO₂/CH₄ ideal selectivity of 5.22 which is comparable with the CO₂/CH₄ ideal selectivity reported by Yajima *et al.* [13]. However, CO₂/CH₄ ideal selectivity obtained in the present work is lower than those results reported in literature [10]. This phenomenon could be mainly due to the different experiment conditions, e.g. temperature and pressure as well as the presence of defects on the membrane which affect the molecular sieving property of DD3R.

Table-3. Performance of DD3R zeolite membranes in CO₂ separation.

Author	CO ₂ Permeance [mol/m ² .s.Pa]	CO ₂ /CH ₄ Selectivity	Reference
This work	2.4 x 10 ⁻⁹	5.2	This work
Yajima et al.	1.12 x 10 ⁻⁷	3.1	(Yajima and Nakayama 2008)
Tomita et al.	3.00 x 10 ⁻⁷	200	(Tomita, Nakayama et al. 2004)
Nakayama et al.	1.00 x 10 ⁻⁹	10	(Nakayama, Suzuki et al. 2004)

CONCLUSIONS

In this work, we concluded that the synthesis duration of DD3R membranes can be reduced by using DD3R seeds synthesized in 1 day. Thus, the overall synthesis duration of DD3R membrane has been

successfully reduced from 27 days to only 3 days. DD3R membranes which were synthesized by using DD3R seeds prepared in 1 day via ultrasonic irradiation coupled with hydrothermal heating method provided comparable results (XRD, FESEM and permeation study) with the membranes which are synthesized by using DD3R seeds prepared in 25 days via conventional hydrothermal heating method. DD3R membranes synthesized via vacuum-assisted secondary hydrothermal growth method showed higher CO₂/CH₄ selectivity as compared to the membranes synthesized via dip-coating secondary hydrothermal growth method. This result showed that DD3R seeds synthesized using ultrasonic pre-treatment coupled with hydrothermal method could enhance the growth of the membrane layer with minimum defects and thus, resulted in better separation performance.

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REFERENCES

- [1] B. Li, Y. Duan, D. Luebke and B. Morreale 2013. Advances in CO₂ capture technology: A patent review. *Applied Energy*. 102: 1439--1447.
- [2] Y. Gu, P. Hacıoğlu and S. T. Oyama. 2008. Hydrothermally stable silica-alumina composite membranes for hydrogen separation. *Journal of Membrane Science*. 310(1): 28--37.
- [3] Huang, N. Wang, C. Kong and J. Caro 2012. Organosilica-Functionalized Zeolitic Imidazolate Framework ZIF-90 Membrane with High Gas-Separation Performance. *Angewandte Chemie International Edition*. 51(42): 10551--10555.
- [4] Y. H. Sim, H. Wang, F. Y. Li, M. L. Chua, T.-S. Chung, M. Toriida and S. Tamai. 2013. High performance carbon molecular sieve membranes derived from hyperbranched polyimide precursors for improved gas separation applications. *Carbon*. 53: 101--111.
- [5] Y. Cui, H. Kita and K.-i. Okamoto. 2004. Preparation and gas separation performance of zeolite T membrane. *Journal of Materials Chemistry*. 14(5): 924--932.
- [6] L. Sandstrom, E. Sjöberg and J. Hedlund 2011. Very high flux MFI membrane for CO₂ separation. *Journal of Membrane Science*. 380(1): 232--240.



- [7] S. M. Mirfendereski, T. Mazaheri, M. Sadrzadeh and T. Mohammadi. 2008. CO₂ and CH₄ permeation through T-type zeolite membranes: Effect of synthesis parameters and feed pressure. *Separation and Purification Technology*. 61(3): 317--323.
- [8] S. Li, J. L. Falconer and R. D. Noble. 2008. SAPO-34 membranes for CO₂/CH₄ separations: Effect of Si/Al ratio. *Microporous Mesoporous Materials*. 110(3): 310--317.
- [9] T. Wu, B. Wang, Z. Lu, R. Zhou and X. Chen. 2014. Alumina-supported AlPO-18 membranes for CO₂/CH₄ separation. *Journal of Membrane Science*. 471(0): 338-346.
- [10] T. Tomita, K. Nakayama and H. Sakai. 2004. Gas separation characteristics of DDR type zeolite membrane. *Microporous Mesoporous Materials*. 68(1): 71-75.
- [11] T. Binder, C. Chmelik, J. Kärger, A. Martinez-Joaristi, J. Gascon, F. Kapteijn and D. Ruthven. 2013. A diffusion study of small hydrocarbons in DDR zeolites by micro-imaging. *Microporous Mesoporous Materials*. 180(0): 219-228.
- [12] K. Nakayama, K. Suzuki, M. Yoshida, K. Yajima and T. Tomita. 2004. Method for preparing DDR type zeolite film, DDR type zeolite film, and composite DDR type zeolite film, and method for preparation thereof, US Patent Application No. 10/796, 890.
- [13] K. Yajima and K. Nakayama. 2008. Process for producing ddr type zeolite membrane. US, Google Patents.
- [14] Z. Zheng, A. Hall and V. Gulians. 2008. Synthesis, characterization and modification of DDR membranes grown on α -alumina supports. *Journal of Materials Science*. 43(7): 2499-2502.
- [15] S. Himeno, T. Tomita, K. Suzuki, K. Nakayama, K. Yajima and S. Yoshida. 2007. Synthesis and Permeation Properties of a DDR-Type Zeolite Membrane for Separation of CO₂/CH₄ Gaseous Mixtures. *Industrial and Engineering Chemistry Research*. 46(21): 6989--6997.
- [16] J. van den Bergh, A. Tihaya and F. Kapteijn. 2010. High temperature permeation and separation characteristics of an all-silica DDR zeolite membrane. *Microporous Mesoporous Materials*. 132(1): 137-147.
- [17] V. Engstrom, B. Mihailova, J. Hedlund, A. Holmgren and J. Sterte. 2000. The effect of seed size on the growth of silicalite-1 films on gold surfaces. *Microporous Mesoporous Materials*. 38(1). 51--60.
- [18] K. Kusakabe, T. Kuroda, A. Murata and S. Morooka. 1997. Formation of a Y-Type Zeolite Membrane on a Porous α -Alumina Tube for Gas Separation. *Industrial and Engineering Chemistry Research*. 36(3): 649--655.
- [19] X. Zhang, J. Wang, D. Yin and C. Liu. 2000. Synthesis of ZSM-5 zeolite membrane and its influencing factors by a novel method. *Chinese Journal of Catalysis*. 21(5): 451-454.
- [20] S. Mintova and T. Bein. 2001. Microporous Films Prepared by Spin-Coating Stable Colloidal Suspensions of Zeolites. *Advanced Materials*. 13(24): 1880--1883.
- [21] J. Hedlund, M. Noack, P. Kölsch, D. Creaser, J. Caro and J. Sterte. 1999. ZSM-5 membranes synthesized without organic templates using a seeding technique. *Journal of Membrane Science*. 159(2): 263--273.
- [22] S. R. Lee, Y.-H. Son, A. Julbe and J.-H. Choy. 2006. Vacuum seeding and secondary growth route to sodalite membrane. *Thin Solid Films*. 495(1): 92-96.
- [23] M. Mubashir, Y. F. Yeong, N. S. B. M. Nazri and K. K. Lau. 2015. Accelerated synthesis of deca-dodecasil 3 rhombohedral (DDR3) zeolite crystals via hydrothermal growth coupled with ultrasonic irradiation method. *RSC Advances*. 5(29): 22658--22664.
- [24] M. J. den Exter, J. C. Jansen and H. van Bekkum. 1994. Separation of Permanent Gases on the All-Silica 8-Ring Clathrasil DD3R. *Studies in Surface Science and Catalysis*. 84, 1159-1166.
- [25] T. L. Chew, A. L. Ahmad and S. Bhatia. 2011. Ba- SAPO-34 membrane synthesized from microwave heating and its performance for CO₂/CH₄ gas separation. *Chemical Engineering Journal*. 171(3): 1053--1059.
- [26] Z. Zhengzhi and S. Nair. 2014. Zeolite membranes, US 8673057 B2, March 14, 2013.