Synthesis, Characterization, and Application of Nano-sized DD3R Zeolite Powder in Thin DD3R Membrane Synthesis

**M. J. Vaezi,[*] M. G. Geranbaha,
S. S. Moghimi, and A. A. Babaluo**
Nanostructure Material Research Center (NMRC),
Chemical Engineering Faculty, Sahand University
of Technology, P.O.Box 53318-17634, Tabriz, Iran

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DD3R zeolite powder was synthesized within a brief period using tetramethyl orthosilicate through a sonochemical method combined with hydrothermal treatment. The highest crystallinity with average particle size of 47 nm was achieved within five days. This nano-sized powder was used for seeding the surface of a support modified with TiO_2-Boehmite, facilitating the synthesis of a thin (less than 5 μm) and uniform DD3R zeolite layer. The resulting membrane exhibited perm-selectivities of N_2 and CO_2 over CH_4 that were 3 and 4 times greater than those reported in literature. The surface modification of the synthesized layer using a polydimethylsiloxane solution further improved the perm-selectivity of N_2/CH_4 and CO_2/CH_4 by up to 12 and 260, respectively. The straightforward synthesis of the initial layer before modification positively influenced the perm-selectivity of N_2/CH_4, achieving a three-fold increase compared to similar works in the literature.

Keywords
DD3R zeolite powder, sonochemical method, hydrothermal treatment, nano-sized powder, surface modification, perm-selectivity

Introduction

Zeolites are crystalline, microporous aluminosilicates containing molecular-sized pores and channels in their frameworks. Their unique properties, including high thermal, mechanical, and chemical stability, render them interesting for various industrial applications[1]. One notable application is their use as zeolite membranes in gas separation and natural gas purification[2]. Zeolite membranes with continuous pore sizes in the microporous range of 3–10 Å (such as CHA (3.8 × 3.8 $Å^2$), LTA (4.1 × 4.1 $Å^2$), MFI (5.3 × 5.6 $Å^2$), and FAU (7.4 × 7.4 $Å^2$), are favorable candidates for molecular sieve membranes[3,4]. However, only a few studies have discussed small-pore zeolite membranes for gas separations in detail[5]. In 2016, Kosinov *et al.*[3] reviewed all zeolite membranes applied in gas separation, highlighting that high silica membranes with eight-membered-ring pores hold great potential for highly efficient recovery or removal of small-gas molecules. Moreover, these membranes maintain their separation performance in the presence of water, other polar impurities, and harsh conditions. In this context, various methods have been developed for synthesizing zeolite membranes. Among these methods, the secondary growth method, coupled with proper support seeding, offers several advantages. The most significant advantage is the avoidance of competing phase formation[6]. When considering α-alumina as a support for zeolite layer synthesis, using seeds with micron particle size might be appropriate. However, seeding with micron-sized particles on an α-alumina support results in the synthesis of a thick and non-uniform zeolite layer. This layer affects the separation performance of the zeolite membrane by increasing defects during the calcination step and mass transfer resistance of gases through the membrane. To achieve a continuous and uniform zeolite layer with low thickness, not only should the size of seeds be small, but also surface modification of the α-alumina support as an intermediate layer is required. Through support surface modification, the surface pore size is reduced, and depending on the support's pore size, sub-micron/nano-size seeds are necessary[9].

Among zeolites, the all-silica 8-membered-ring DD3R zeolite (deca- and dodecahedra, 3 layers, rhombohedral) characterized by high hydrophobicity and stability at elevated temperatures, holds promising potential for various adsorptive separations[10]. The DD3R zeolite imparts the membrane

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[*] Corresponding author: E-mail address: m_vaezi@sut.ac.ir (m.j. vaezi), Tel.: +984133459170; Fax: +984133444355

with robust resistance against water vapor and hydrogen sulfide, the common components of natural gas[11]. Furthermore, the DD3R zeolite membrane demonstrates excellent separation performance in simultaneously separating N_2 and CO_2 from CH_4 due to its small pore size (0.36×0.44 nm)[12–17]. Wang *et al.*[18] recently reported that a DD3R membrane exhibited great prospects for on-stream CO_2 removal from a special gas system.

This zeolite type has crystallization fields close to competitive phases like DOH (dodecahedra, 1 layer, hexagonally stacked) and Sigma-2 (the synthesis conditions of different phases overlap), requiring a significant amount of time for nucleation and synthesis. Therefore, utilizing a secondary growth method is essential for achieving a high-quality DD3R zeolite membrane[19]. Gies was the first to report the hydrothermal synthesis method of DD3R zeolite powder. By 2013, other researchers had synthesized DD3R zeolite powder with micron-sized particles using various methods[19–22]. The synthesis of sub-micron DD3R zeolite powder with the conventional hydrothermal method is only described in patent literature, providing limited information. Zhou and Nair reported a different synthesis method of DD3R zeolite powder with an average particle size of 398 nm. The major drawback of this method is the high amount of seeds (5 g – 10 g per 30 g of synthesis mixture)[7]. Despite the reproducibility challenges, obtaining this amount of DD3R powder is exceptionally difficult[23]. Therefore, it is crucial to explore a new, simple, fast, and effective method for the synthesis of fine DD3R zeolite powder. A sonochemical method is an efficient synthesis method that has been applied to obtain DD3R powder with small particle size within a short time without seeding the synthesis mixture[1,24,25]. Table 1 presents the different conditions of the methods used to synthesize nano-sized DD3R powder.

Sen *et al.*[1] described a new synthesis method (sonochemical method) for achieving DD3R zeolite powder with a particle size as small as 100 nm at room temperature without conventional heating. Following a similar approach, Bose *et al.*[24] reduced the sonication time and subjected the mixture to a hydrothermal process. On the other hand, crystal growth at a low rate can result in better control of the crystallization process and particle size of products. With this in mind, tetramethyl orthosilicate (TMOS) was used instead of silica sol, reducing the crystal growth rate by a factor of 7 as reported in the literature[26]. Mubashir *et al.*[27] synthesized DD3R zeolite crystals through hydrothermal heating coupled with ultrasonic irradiation. The duration of hydrothermal heating and ultrasonic irradiation varied from 0.5–10 days and 1–3 hours, respectively. The results indicated that only the sample synthesized in 0.5 day with 1 h of ultrasonic irradiation failed to exhibit DD3R topology. The FESEM images showed micron-sizedparticles synthesized employing the reported procedure. Some studies suggest that prolonged sonication might have a destructive effect on previously formed particles and may not significantly impact the crystals size reduction[28]. However, to the best of our knowledge, the synthesis of nano-sized DD3R powder using TMOS as a silica source via a sonochemical method with short sonication time has not yet been reported.

Table 1 – *Different conditions of methods used for the synthesis of nano-sized DD3R powder*

	Sen *et al.*[1]	Bose *et al.*[25]	This work
Silica source	Ludox HS-30	Ludox HS-30	TMOS
Sonication time	3 hours	1 hour	40 min
Aging time	1–9 days	–	–
Treatment time	–	2 days	5 days

In this study, particular emphasis is placed on the synthesis of nano-sized DD3R zeolite powder without seeding, achieved through a sonochemical method coupled with conventional heating in the oven. Additionally, the optimal duration for sonication of the synthesis mixture was considered. These nano-sized DD3R particles were employed as seeds to coat the surface of an α-alumina support, modified with TiO_2-Boehmite to obtain a thin DD3R membrane layer. To the best of our knowledge, the synthesis of a DD3R membrane on a modified α-alumina support using TiO_2-Boehmite has so far not been reported. Subsequently, CO_2, H_2, N_2, and CH_4 gas permeations were measured to assess the performance of the obtained membrane in separating impurities from natural gas.

Experimental

DD3R zeolite crystal synthesis

The synthesis gel was prepared by combining two solutions. In the first solution, 4.23 g of tetramethyl orthosilicate (TMOS, $SiC_4H_{12}O_4$, Merck, > 99 %) was added using a syringe pump (20 mL h^{-1}) to 25 mL of deionized water under vigorous stirring. The second solution was prepared by adding 2.1 g of 1-adamantane amine (1-ADA, $C_{10}H_{17}N$, Sigma Aldrich, > 97 %) into 6.67 g of ethylenediamine (EDA, $C_2H_8N_2$, Merck, > 99 %). Subsequently, 25 mL of water was added at once to the second solution. After 1 h, the second solution was added to the first solution at a rate of 80 mL h^{-1} using a syringe pump under vigorous stirring. The final gel composition, expressed in molar ratio, was 50 1-ADA: 400 EDA: 100 SiO_2: 10000 H_2O. After 15 min, the prepared gel underwent sonication for 40 min at 250 W. The resulting synthesis gel was then transferred to a PTFE reaction vessel and placed in a steel autoclave for hydrothermal treatment at 170 °C with agitation at 12 rpm. The obtained powder was thoroughtly washed multiple times to reduce the pH.

Synthesis of the DD3R zeolite layer

Support surface modification and seeding

The tubular α-alumina support (outer diameter, inner diameter, and thickness were 10, 6, and 2 mm, respectively) with a porosity of 42 % – 47 % and an average pore size of 0.57 µm [29] was utilized for synthesizing the DD3R zeolite layer. The support's surface was modified with TiO_2-Boehmite using the dip-coating method[30]. Seeding of the modified support surface was accomplished by immersing it into a 0.3 wt. % seed suspension for 3 min.

Preparation of the synthesis gel for the zeolite layer

The synthesis gel was prepared by adding specific quantities of 1-adamantane amine (0.702 g, $C_{10}H_{17}N$, extracted from 1-adamantane amine hydrochloride) into 2.39 g of ethylenediamine ($C_2H_8N_2$, Merck, > 99 %). Subsequently, 20 mL of water was added at once and mixed for 1 h. The resulting solution was refluxed at 95 °C for 1 h, cooled, and 2.2 g of silica sol ($[SiO_x(OH)_{4-2x}]_n$, Merck, 27 wt. % SiO_2) was added dropwise while stirred vigorously using a magnetic stirrer. Refluxing continued for an additional 3 h at 95 °C, resulting in a clear and homogeneous solution. The final molar ratio of the gel composition for membrane layer synthesis was 47 1-ADA: 404 EDA: 100 SiO_2: 11240 H_2O. To synthesize the membrane on the outer surface of the support, the two ends of the seeded support were sealed with Teflon tape. The hydrothermal conditions were set at 160 °C and maintained for 4 days. The resulting membrane was washed multiple times to reduce the pH.

Surface modification of the DD3R zeolite membrane

To enhance the separation performance of the synthesized zeolite membrane, and to compare its effectiveness with our previous work, the final zeolite membrane underwent surface treatment through coating with a polydimethylsiloxane (PDMS) solution, according to the method detailed in our previous work[31].

Characterization

The crystalline structure of the synthesized powder and membrane was analyzed through X-ray diffraction (XRD) patterns. The XRD patterns were recorded using a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu-K Alpha anode (λ=1.54 Å), operating at 40 kV and 40 mA. The microstructure and morphology of the synthesized powder were examined using field emission scanning electron microscopy (FESEM, TESCAN, Czechia). The particle size distribution of the nano-sized powder was determined using a laser particle size analyzer (LPSA, ANALYSETTE 22 Nano-Tec-Fritsch, Germany). The morphology of the synthesized membrane, both cross-section and surface, was investigated using scanning electron microscopy (SEM, TESCAN, Czechia).

Single gas permeation measurements

To assess the separation performance of the synthesized membranes, single gas permeation measurements were conducted. The membranes were positioned within a stainless-steel module and sealed with O-rings. Utilizing a soap-film flow meter, the single gas permeations were measured. These permeation measurements were conducted under varying feed pressures at room temperature. Gas permeance, and the perm-selectivity of gases were calculated as follows[31,32]:

$$\text{Permeance (mol m}^{-2}\text{Pa}^{-1}\text{s}^{-1}) = 1.301881\cdot 10^{-5}\cdot\frac{V\left(\text{cm}^3\right)}{D_m(\text{mm})\cdot L(\text{cm})\cdot \Delta P(\text{bar})\cdot t(\text{s})} \tag{1}$$

$$\text{Perm-selectivity} = \frac{\text{Permeance of gas 1}}{\text{Permeance of gas 2}} \tag{2}$$

where V represents the volume of gas permeate through the membrane, D and L are the diameter and effective length of the membrane, respectively. ΔP is the pressure difference applied across the membrane; t is the measurement time required for a certain volume of gas to permeate.

Results and discussion

Fig. 1 shows the XRD patterns of the synthesized powders. Fig. 1a shows the XRD pattern after 5 days of aging without hydrothermal treatment. Figs. 1b and 1c show the XRD pattern of the synthesized powders treated hydrothermally without aging time. The hydrothermal treatment, performed at 170 °C with 12 rpm, was applied for 2 and 5 days. In Fig. 1a, the obtained sample with aging time of 5 days shows an indistinct structure, with some peaks appearing between the angles of 20–25°. The XRD pattern obtained after 2 days of hydrothermal treatment (Fig. 1b) reveals the characteristic peaks of DD3R, despite their low intensity. The positions of the peaks are well-matched with those reported in JCPDS (Joint Committee on Powder Diffraction Standards) file no. 71-0962, sug-

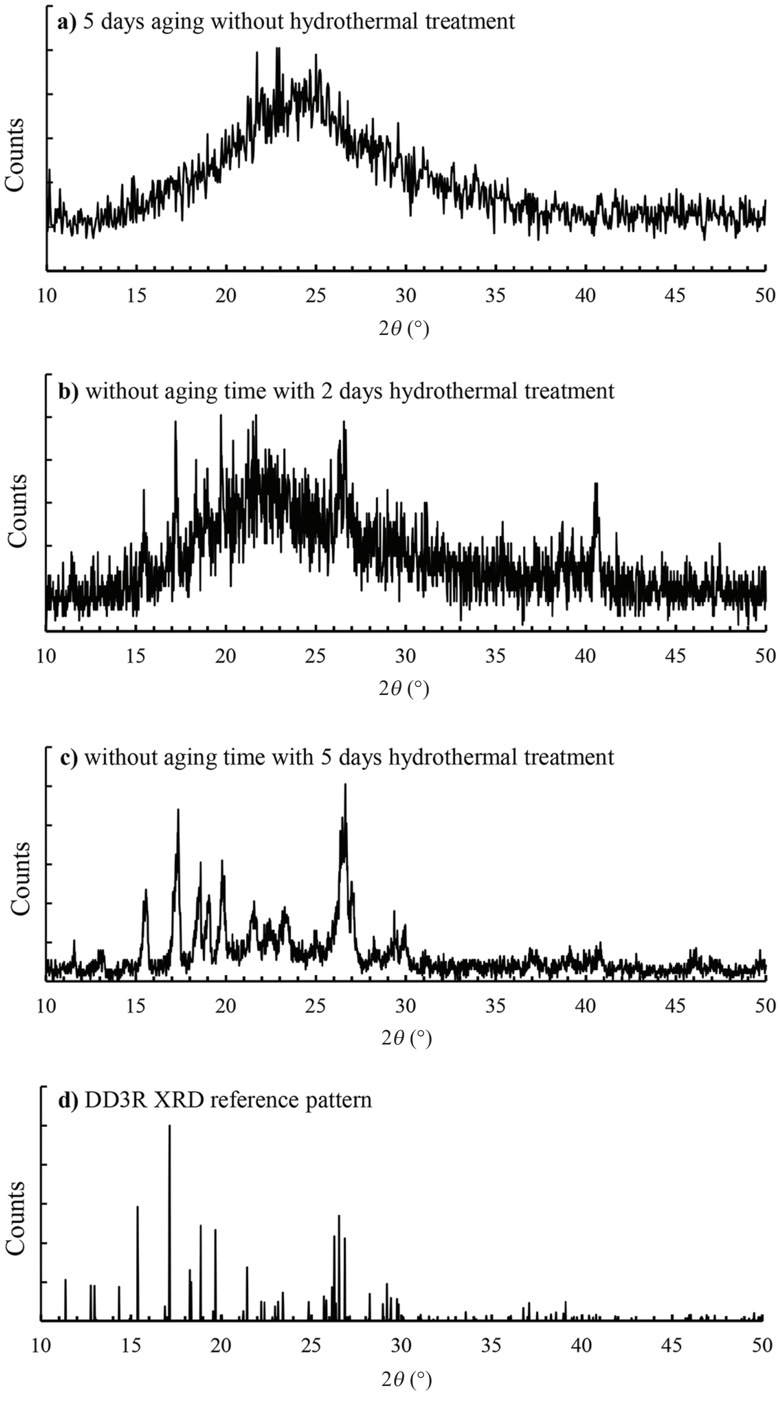

Fig. 1 – *XRD patterns of the synthesized powders: (a) at room temperature with aging for 5 days, (b) without aging time with 2 days of hydrothermal treatment (c) without aging time with 5 days of hydrothermal treatment, and (d) DD3R XRD reference pattern*

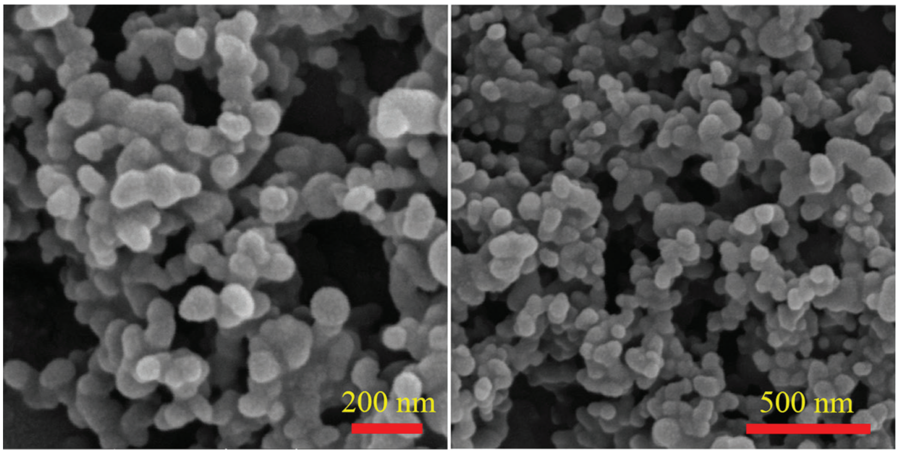

Fig. 2 – *FESEM images of the synthesized DD3R zeolite powder hydrothermally treated for 5 days*

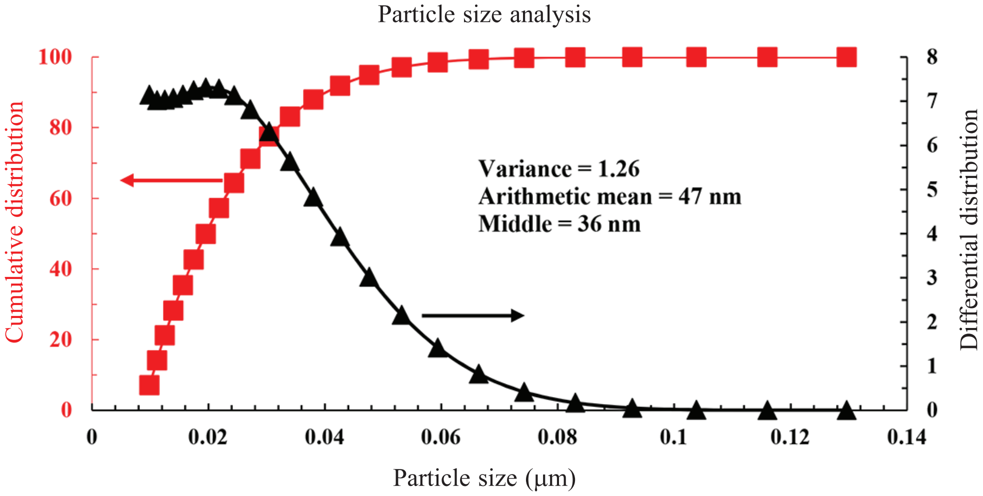

Fig. 3 – *Particle size distribution of the synthesized DD3R zeolite powder hydrothermally treated for 5 days*

gesting growth of the DD3R zeolite[25]. Extending the hydrothermal treatment time to 5 days resulted in an increase in peak intensity, and the XRD pattern confirmed the formation of the DD3R zeolite within this period (Fig. 1c). Therefore, the presented procedure allows for the production of high-crystallinity DD3R zeolite seeds without the need for seeding the synthesis solution in a short synthesis time.

Fig. 2 describes the particle size and shape of the synthesized DD3R crystalline seeds after 5 days of hydrothermal treatment. The FESEM images, captured at various resolutions, reveal that the synthesized DDR seeds are nano-sized (20 nm – 50 nm). In contrast to the diamond shape typically associated with micron-sized DD3R zeolite, the obtained seeds exhibited a sperical shape. This different morphology is attributed to the small size of the obtained seeds. The reduction in particle size resulted in decreased crystallinity and the shape of the particles is seen as spherical. This is evident in the XRD pattern of the nano-sized powders. Furthermore, the FESEM images show a uniform size distribution of the synthesized DD3R powders at the nanometric scale.

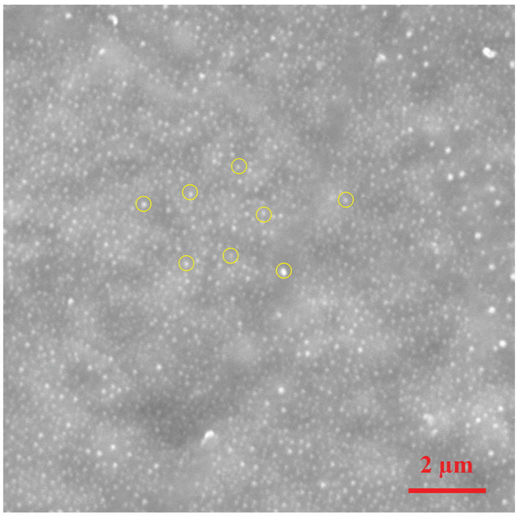

Fig. 4 – *SEM image of the support surface seeded with nano-sized DD3R powder*

Fig. 3 shows the particle size distribution of the synthesized DD3R seeds after undergoing a 5-day hydrothermal treatment. This analysis confirmed the findings from the FESEM images, affirming that the size of the DD3R seeds obtained through sonication combined with the hydrothermal method is less than 100 nm. The nano-sized DD3R powder, acting as seeds, was employed to synthesize a DD3R zeolite membrane on the modified support surface, resulting in the formation of a thin, continuous, and uniform zeolite layer with proper coverage.

Fig. 4 depicts the SEM image of the support surface seeded with nano-sized DD3R powder using the dip-coating method. Clearly, the dip-coating method proved effective in obtaining an appropriate and homogeneous coverage of the modified support surface with seeds. The presence of sufficient seed coverage on the surface led to the formation of the desired zeolite phase during the hydrothermal process.

The XRD pattern of the membrane layer synthesized using nano-sized powder as a seed is presented in Fig. 5. It is worth noting that the peaks corresponding to the TiO$_2$-Boehmite layer and α-alumina support are denoted by "↓" and "■" in the XRD pattern, respectively. The synthesis of the DD3R membrane on the modified support surface was confirmed by the XRD pattern. No additional diffraction peaks corresponding to competitive phases (DOH and Sigma-2) appeared, affirming the achievemtnt of a pure DD3R zeolite layer.

Fig. 6 shows the SEM images of surface and cross-section views of the DD3R zeolite membrane layer synthesized using nano-sized DD3R powder as a seed. The support surface was entirely covered with a continuous crystalline DD3R zeolite layer. Moreover, the crystals exhibited proper growth and connectivity (inter-grown structure), with no visible voids on the surface. The cross-section image of the synthesized layer reveals a dense and thin membrane layer with a thickness of less than 5 µm.

The pure gas permeance of N_2, H_2, CO_2, and CH_4, as well as the perm-selectivities of N_2/CH_4 and CO_2/CH_4 through the non-modified DD3R zeolite

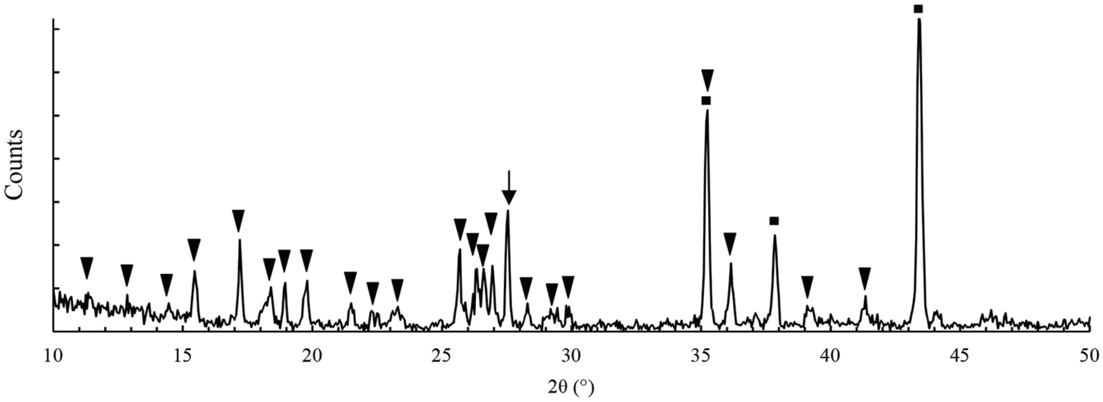

Fig. 5 – *XRD pattern of the DD3R membrane synthesized on the modified surface of the support [(■): α-alumina, (↓): TiO$_2$-Boehmite, and (▼): DD3R]*

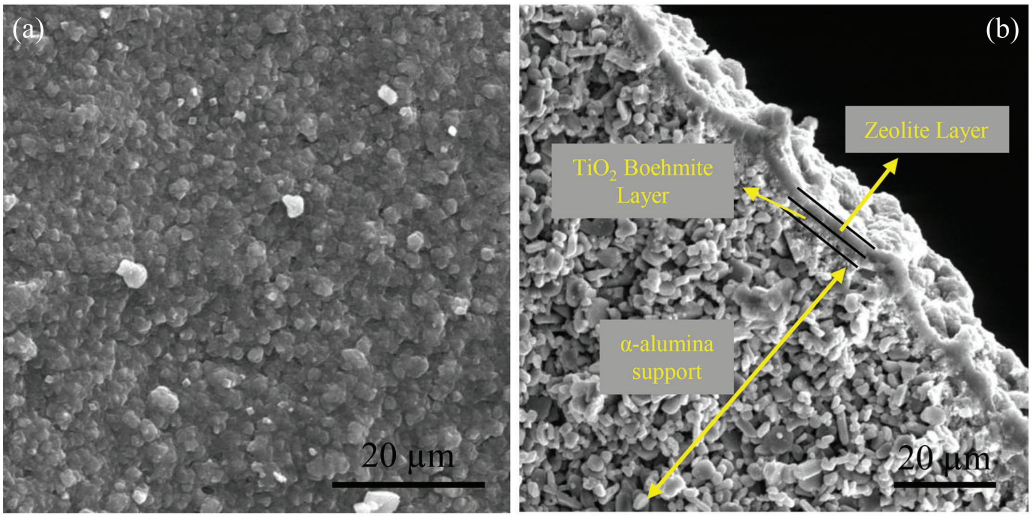

Fig. 6 – *SEM images depicting (a) surface, and (b) cross-section views of the synthesized DD3R zeolite layer*

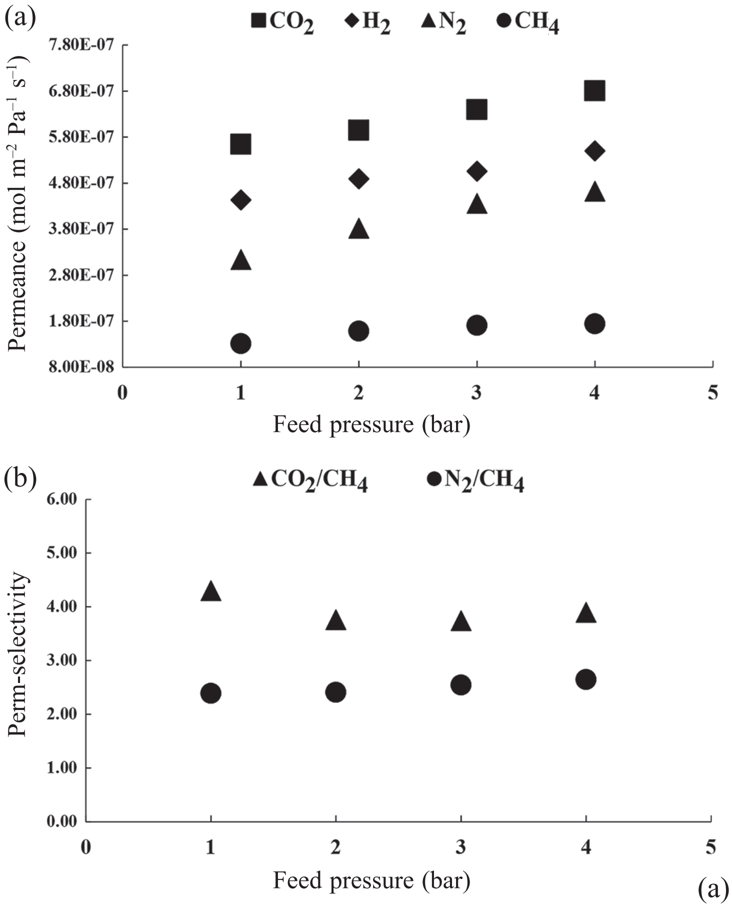

Fig. 7 – *Pure gas permeance of: (a) N_2, H_2, CO_2, and CH_4, and the perm-selectivities, and (b) N_2/CH_4 and CO_2/CH_4 for the synthesized DD3R zeolite membrane*

membrane, are shown in Fig. 7. The obtained gas permeance order was: $CO_2 > H_2 > N_2 > CH_4$. This suggests that the adsorption-diffusion mechanism governed the gas separation, but the presence of some non-zeolite pores led to low perm-selectivities (3.5±0.5 for CO_2/CH_4 and 2.5±0.5 for N_2/CH_4). In the adsorption-diffusion mechanism, molecules such as CO_2 with high adsorption, and molecules like H_2 and N_2 with high diffusion (small kinetic diameter) would exhibit high permeance compared to molecules like CH_4, which has low adsorption and a large kinetic diameter. Comparing these results with our previous work[30] revealed improved N_2/CH_4 and CO_2/CH_4 separation for the membrane synthesized in this work, attributable to the formation of a dense and thin membrane layer.

To enhance the perm-selectivities of N_2/CH_4 and CO_2/CH_4, the synthesized zeolite layer's surface was treated with a PDMS solution using the dip-coating technique. The pure gas permeance of N_2, H_2, CO_2, CH_4, and the perm-selectivities of N_2/CH_4 and CO_2/CH_4 after surface modification are shown in Fig. 8. The permeance of CH_4, N_2, H_2, and CO_2 decreased by 200, 43, 17, and 3 times, respectively, after surface modification. This permeance reduction resulted from plugging non-zeolitic pores with PDMS polymer. Coating the PDMS solution on the zeolite membrane surface allows the PDMS polymer to penetrate the non-zeolite pores due to their large pore size. PDMS polymer cannot penetrate zeolite pores, but may cover their surface. This result indicates that surface modification had the most significant effect on CH_4 permeance, i.e. on the molecule with the higher kinetic diameter (3.8 Å) compared to other investigated gas molecules. Therefore, it can be concluded that the main contribution to CH_4 permeance is related to the presence of non-zeolite pores in the zeolite layer structure before surface modification. Thus, the zeolite pores can play their roles effectively in separating N_2 and CO_2 from CH_4 after the surface modification of zeolite layer.

Table 2 presents the permeance of N_2, CO_2, CH_4, and the perm-selectivities of N_2/CH_4 and CO_2/CH_4 for the DD3R zeolite membrane synthesized under different conditions. In our previous work, the α-alumina support was used without surface modification, and support seeding was carried out with micron-sized DD3R particles. In this work, the permeance of various gases through the synthesized

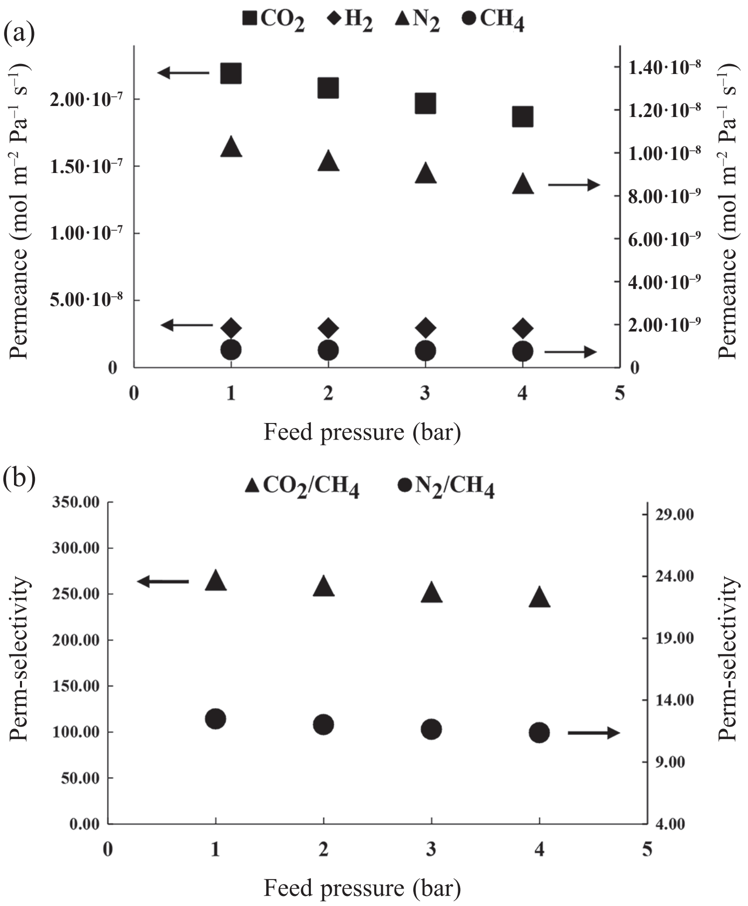

Fig. 8 – *Pure gas permeance of: (a) N_2, H_2, CO_2, and CH_4, and the perm-selectivities, and (b) N_2/CH_4 and CO_2/CH_4 for the DD3R zeolite membrane after surface modification*

Table 2 – *Gas separation performance of the synthesized membrane compared to our previous work*[32] *before and after surface modification at 2 bar as feed pressure*

	Before modification					After modification				
	Permeance ($\cdot 10^{10}$)			Perm-selectivity		Permeance ($\cdot 10^{10}$)			Perm-selectivity	
	CO_2	N_2	CH_4	CO_2/CH_4	N_2/CH_4	CO_2	N_2	CH_4	CO_2/CH_4	N_2/CH_4
Our previous work[32]	6170	6190	7710	0.8	0.8	2565	84.3	9.52	270	8.85
This work	5940	3820	1580	3.76	2.42	2080	96.5	8.02	260	12.05

membrane is lower, and the perm-selectivities of N_2 and CO_2 over CH_4 are 3 and 4 times greater than those in our previous work before surface modification. This improvement is attributed to the formation of a uniform and well inter-grown zeolite layer through the synthesis procedure described in this work. The key feature of this synthesis procedure is the use of nano-sized DD3R particles as seeds on the modified support surface, resulting in the growth of a zeolite layer with fewer intercrystalline (non-zeolite) pores. However, the low presence of non-zeolite pores predominates the adsorption-diffusion mechanism in gas permeation, particularly observed after the modification of the synthesized DD3R zeolite layer. While the permeance of CO_2 and CH_4 in this study is lower than in our previous work, the N_2 permeance is higher. PDMS can decrease the rate of adsorption by covering the surface of zeolite crystals, thereby reducing the adsorption of CO_2 on the DD3R zeolite membrane and its permeance. On the other hand, it does not affect the diffusion of N_2 molecules through the zeolite pores.

The previously described syntheses of DD3R zeolite membranes using micron-sized DD3R powder as a seed revealed a need to repeat the synthesis procedure and apply the hydrothermal conditions several times to achieve a selective zeolite layer. On the other hand, the membrane described here can be obtained by applying the synthesis procedure once, which is its main advantage over the previously described syntheses.

Permeation and selectivity data for the DD3R zeolite membrane are presented in a trade-off diagram (Fig. 9). This diagram allows for a direct com-

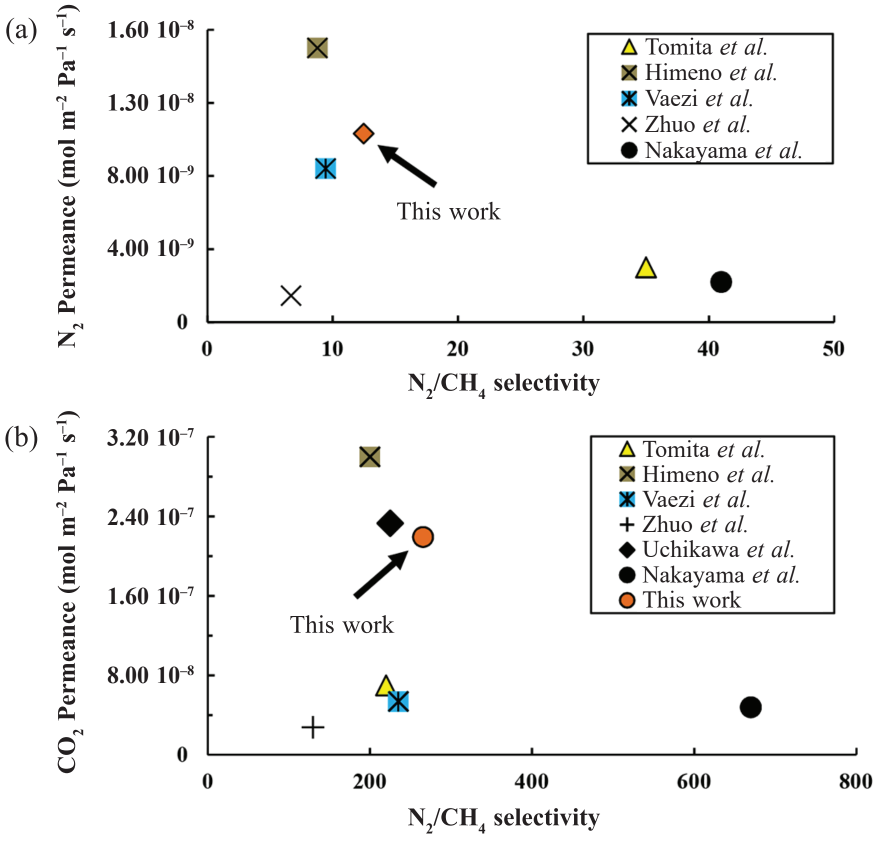

Fig. 9 – *Performance of DD3R zeolite membranes in the separation of (a) N_2/CH_4 and (b) CO_2/CH_4*[7,12,31,33–35]

parison between the synthesized DD3R membrane in this work and the literature. As evident, the performance of the present membrane is well-positioned in the diagrams. It outperforms the membrane synthesized in our previous work, indicating that the use of nano-sized powder as a seed on the surface of a support modified with TiO_2-Boehmite had dramatically improved the performance of the synthesized membrane. Comparing the obtained results with the results reported by Zhou *et al.*[7] shows that the membrane synthesized here perform well. The performance of the membrane synthesized here in comparison with the membranes synthesized by Nakayama *et al.*[33], Tomita *et al.*[12], and Himeno *et al.*[34] is also commendable. The permeance of the membrane synthesized here is higher than the permeance of the membranes synthesized by Nakayama *et al.*[33] and Tomita *et al.*[12] On the other hand, the perm-selectivity of this membrane is higher than the selectivity of the membrane synthesized by Himeno *et al.*[34]

When dealing with the separation of carbon dioxide from methane, the performance of the membrane synthesized in our previous work[31] is the same as the performance of the membrane synthesized by Tomita *et al.*[12] However, in terms of permeance or selectivity, it is at a lower level in comparison with the membranes synthesized by Himeno *et al.*[34], Yuchikawa *et al.*[35], Nakayama *et al.*[33], and with the membrane synthesized in this work. The position of the present membrane, in comparison with other membranes in the separation of carbon dioxide from methane, is the same as its position in the separation of nitrogen from methane.

Conclusions

It can be concluded that the sonochemical method combined with hydrothermal treatment is a practical approach to the synthesis of nano-sized DD3R zeolite powder within a short synthesis time. The utilization of TMOS as a silica source played a vital role in the synthesis of nano-sized DD3R powder. Seeding the surface of the TiO_2-Boehmite sublayer with nano-sized seeds led to the formation of a dense and highly crystalline zeolite membrane layer with low thickness. Additionally, the gas permeation investigations demonstrated that the described procedure for the synthesis of zeolite layer resulted in layers with very few intercrystalline pores. The limited presence of intercrystalline pores contributed to the high gas separation performance of the membrane. When the zeolite layer possesses these features, the effect of surface modification by the coating method becomes more apparent. Therefore, the perm-selectivity of molecules, such as N_2 with a low kinetic diameter and high diffusion, increased by about 50 %.

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STATEMENTS AND DECLARATIONS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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