Research Article

Separation of CO₂ from Small Gas Molecules Using Deca-Dodecasil 3 Rhombohedral (DDR3) Membrane Synthesized via Ultrasonically Assisted Hydrothermal Growth Method

Muhammad Mubashir,1 Yeong Yin Fong,2 Sidra Saqib,3 Ahmad Mukhtar,2 Sikander Rafiq,4 Muhammad Bilal K. Niazi,5 Muhammad Babar,2 Sami Ullah,6 Abdullah G. Al-Sehemi,6 and Farrukh Jamil3

1Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Netherlands
2Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), Seri Iskandar, Perak 32610, Malaysia
3Department of Chemical Engineering, COMSATS University Islamabad (CUI), Lahore Campus, Punjab 54000, Pakistan
4Department of Chemical, Polymer and Composite Materials Engineering, University of Engineering and Technology Lahore, New Campus, Pakistan
5School of Chemical and Materials Engineering, National University of Sciences and Technology, Islamabad 44000, Pakistan
6Department of Chemistry, College of Science, King Khalid University, Abha 61413, P.O. Box 9004, Saudi Arabia

Correspondence should be addressed to Muhammad Mubashir; m.mubashir@tue.nl and Sikander Rafiq; sikanderafiq@gmail.com

Received 27 March 2020; Revised 11 June 2020; Accepted 19 June 2020; Published 20 July 2020

Academic Editor: Gyorgy Szekely

Copyright © 2020 Muhammad Mubashir et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Deca-dodecasil 3 rhombohedral (DDR3) membrane has received much attention in CO₂ separation from small gas molecules because of its molecular sieving property and stable characteristics. Therefore, the present work is focusing on the utilization of previously fabricated membrane (synthesized in 3 days as reported in our previous work) to study the effect of hydrocarbons and its durability at the previously optimized conditions. Subsequently, gas permeation study was conducted on the DDR3 membrane in CO₂ separation from small gas molecules and it was found that the permeance of H₂, CO₂, N₂, and CH₄ decreased in the order of H₂ > CO₂ > N₂ > CH₄, according to the increase in kinetic diameter of these gas molecules.

Besides, it was observed that the ideal selectivities of the gas pairs decreased in the sequence of CO₂/CH₄ > CO₂/N₂ > H₂/CO₂. On the other hand, it was found that the presence of hydrocarbon impurities in the gas mixture containing CO₂ and CH₄ has directly affected the performance of DDR3 membrane and contributed to the losses of CO₂ permeability, CH₄ permeability, and CO₂/CH₄ selectivity of 39.1%, 14.8%, and 4.2%, respectively. Consequently, from the stability test, the performance of DDR3 membrane remained stable for 96 h, even after the separation testing using CO₂ and CH₄ gas mixture containing hydrocarbon impurities.

1. Introduction

Over the last few decades, much research has been done on the CO₂ separation especially in syngas production (mainly H₂) and natural gas purification. The presence of CO₂ in the syngas reduces the yield of hydrogen and methane recovery during the Fischer-Tropsch (FT) process [1, 2]. Similarly, the presence of CO₂ decreases the heating value of natural gas and caused equipment corrosion in the existence of water [3, 4]. Meanwhile, membrane separation technology has received much attention in CO₂ separation mainly due to its advantages compared to the conventional separation technologies [5–11]. Zeolite membrane is favored in the CO₂ separation among the membrane materials over polymeric and mixed matrix membranes due to its characteristics, including well-specified pores, the molecular filtering property, and
2. Materials and Methods

2.1. Permeation Study

2.1.1. Pure Gas Permeability. The performance of the resultant DDR3 membrane was investigated using the permeation test rig as shown in Figure 1. The membrane was sealed in the permeation cell, and the flow rate of the targeted gases including $\text{H}_2$, $\text{CO}_2$, $N_2$, and $\text{CH}_4$ was fixed at 200 ml/min while the temperature (MKS instrument) and feed pressure were maintained at room temperature and 2 bar, respectively. Temperature and feed pressure were controlled with an error of $\pm 0.1 ^\circ\text{C}$ and 0.1 bar using MKS instrument temperature and feed pressure controllers, respectively.

The gas permeation was calculated using equation (1), while ideal selectivity was calculated using equation (2) as follows,

\[ P_i = \frac{J_i}{\Delta P}, \tag{1} \]

\[ \alpha_{ij} = \frac{P_i}{P_j}, \tag{2} \]

where $J_i$ is the flux (mol/m$^2$s) and $\Delta P$ is the pressure drop (Pa) while $\alpha_{ij}$ is the gas pair selectivity.
2.1.2. Effect of Hydrocarbon Impurities and Stability Test on DDR3 Membrane. The effect of hydrocarbon impurities and stability test over the resultant membrane in CO$_2$ separation from CH$_4$ was also conducted using the same permeation test rig. The experiments were conducted in three consecutive steps in which the first and third steps were used to investigate the stability of DDR3 membrane. Meanwhile, the second step of the experiment was carried out to study the effect of hydrocarbon impurities on the performance of the resultant membrane in CO$_2$ separation from CH$_4$.

During the first step of the experiment, temperature, inlet pressure, and CO$_2$ inlet composition were maintained at 30.1°C, 1 bar, and 10 vol% (90 vol% of CH$_4$), respectively, because this experimental condition was obtained as the optimum CO$_2$/CH$_4$ separation condition as reported in our previous work [10]. After 24 h, the second step of the testing was conducted by feeding the CO$_2$ and CH$_4$ gas mixture containing hydrocarbon impurities with the compositions of 35.84% CO$_2$, 44.50% CH$_4$, 6.27% C$_3$H$_8$, 3.44% C$_4$H$_{10}$, and 9.94% C$_2$H$_6$ into the system. This composition resembled the natural gas composition presence in North Sumatra Basin, Indonesia. After 48 h of testing, the feed gas was cut off and the experiment was continued using the feed gas composition applied in the first step of the testing. After each step, prior to the measurement of gas permeances, the system was allowed to stabilize for 30 min.

Gas compositions were calculated using gas chromatographs in feed, permeate, and retention streams (PerkinElmer Clarus 580). The CO$_2$ and CH$_4$ permeations were determined with equation (1) with the amount of pressure decrease obtained by equation (3) [24]. The selectivity of the composition of CO$_2$/CH$_4$ was determined subsequently from the mole fractions as defined in equation (4).

$$\Delta P_i = (P_f - P_p),$$

where $P_f$ and $P_p$ are partial pressures in feed and permeate, respectively.

$$\text{Composition selectivity} = \frac{(X_i/X_j)_p}{(X_i/X_j)_F},$$

where $X_i$ and $X_j$ are mole fractions of the $i$ and $j$ elements of the binary mixture. $P$ and $F$ subscriptions reflect both permeate and feed.

3. Results and Discussion

3.1. Characterization. The details on XRD, FESEM, FTIR, and EDX analysis on DDR3 membrane have been described in our previous work [10]. The significant XRD peaks and FESEM images obtained from the resultant membrane showed comparable crystallinity and hexagonal morphology which are analogous with those findings documented in the researches for DDR3 membrane [9, 10, 25, 26]. The surface and cross-sectional view of the membrane showed that a uniform, flat, and fully intergrown membrane layer was formed.
3.2. Gas Permeation. Figure 2 shows the performance of the membrane at ambient temperature and feed pressure of 2 bar. Referring to Figure 2, H₂, CO₂, N₂, and CH₄ permeances of $4.10 \times 10^{-7}$ mol/m²sPa, $2.46 \times 10^{-7}$ mol/m²sPa, $9.11 \times 10^{-8}$ mol/m²sPa, and $4.73 \times 10^{-8}$ mol/m²sPa are obtained, respectively. It can be observed from Figure 2 that H₂ permeance is higher than that of those values obtained for CO₂, N₂, and CH₄ gases. This could be due to the significant difference in the Knudsen diffusion value of the gases through the membrane. H₂ with a molecular diameter of 0.29 nm is smaller than that of the molecular diameter of CO₂, N₂, and CH₄, as well as the DDR3 pore channel. Meanwhile, the molecular diameter of CO₂, N₂, and CH₄ of 0.33 nm, 0.36 nm, and 0.38 nm, respectively, is closer to the DDR3 pore channel. Thus, H₂ can diffuse faster compared to CO₂, N₂, and CH₄ gases.

From Figure 2, it is found that the gas permeances are decreased in the order of H₂ > CO₂ > N₂ > CH₄. This decreasing trend is mainly attributed to the molecular sieving behaviour of DDR3 membrane and Knudsen diffusion mechanism of the gases [25–28]. The diffusion rate of these gases through the DDR3 membrane decreases when the kinetic diameter of the gases increases, and thus, decreasing order of gas permeance has been observed [17]. Moreover, H₂, CO₂, N₂, and CH₄ permeances obtained from the membrane were comparable with those results reported in the literature [17, 20, 25].

As shown in Figure 2 also, the ideal selectivities of CO₂/CH₄, CO₂/N₂, and H₂/CO₂ of 5.22, 2.27, and 1.66, respectively, are obtained. It is interesting to note that the ideal selectivities of the gas pairs decreased in the sequence of CO₂/CH₄ > CO₂/N₂ > H₂/CO₂. This result is attributed to the CH₄ permeance, which is much smaller than the permeance of H₂ and N₂ as shown in Figure 3. Overall, although the gas permeance and ideal selectivity results obtained in the present work are comparable with those results reported in the literature [25], the relatively low performance of DDR3 membrane could be due to the presence of minor defects or intercrystalline pores which have reduced the performance of the membrane. Thus, it is suggested that the membrane should be modified with a TEOS solution to minimized intercrystalline defects to enhance its performance in gas separation [24]. TEOS could penetrate into intercrystalline defects and seal it through the formation of hydrogen bonding between membrane zeolite materials and TEOS. In addition, it also slows down the CH₄ permeation by providing extra resistance due to its higher kinetic diameter [25].

3.3. Effect of Hydrocarbon Impurities on the Performance of DDR3 Membrane. Figure 4 shows the stability test and effect of hydrocarbon impurities on the performance of the membrane in CO₂ separation from CH₄ for the testing duration of 96 h. Sections I and III shown in Figure 4 display the stability results of DDR3 membrane in CO₂ separation from a binary gas mixture of CO₂ and CH₄ at a temperature of 30.1°C, inlet pressure of 1 bar, and CO₂ inlet composition of 10 vol% because this experimental condition was obtained as the optimum CO₂/CH₄ separation condition which provided higher permeation performance of DDR3 membrane as reported in our previous work [10].

Meanwhile, section II in Figure 4 exhibits the effect of hydrocarbon impurities on the performance of DDR3 membrane in CO₂ separation from CH₄ at a temperature of 30.1°C and feed pressure of 1 bar. Referring to Figure 4, at points C and E, CO₂ and CH₄ permeances of $3.13 \times 10^{-8}$ mol/m²sPa and $2.81 \times 10^{-8}$ mol/m²sPa are obtained, respectively. Meanwhile, CO₂/CH₄ selectivity of 2.59 was obtained at point G. Results at points C*, E*, and G* were obtained when the feed gas was changed from a pure binary mixture of CO₂/CH₄ to CO₂/CH₄ gas mixture containing hydrocarbon impurities. At points C*, E*, CO₂ and CH₄ permeances of $3.11 \times 10^{-8}$ mol/m²sPa and $2.83 \times 10^{-8}$ mol/m²sPa are obtained, respectively. On the other hand, CO₂/CH₄ selectivity of 2.59 was obtained at point G*.

It can be seen from Figure 4 that the performance of the membrane slightly decreases when the gas mixture containing hydrocarbon impurities is fed into the system. Besides, from Figure 4, it is found that CO₂ and CH₄ permeances decrease from point E* to F and C* to D, respectively, after

![Figure 2: Single gas permeation results of small molecular gas over DDR3 membrane at room temperature and feed pressure of 2 bar (inset: ideal selectivities for H₂/CO₂, CO₂/N₂, and CO₂/CH₄).](image-url)
testing duration of 40 h (from 32 h to 72 h). Meanwhile, CO₂ and CH₄ permeances of $1.91 \times 10^{-8}$ mol/m²sPa and $1.65 \times 10^{-8}$ mol/m²sPa were obtained at point F and point D, respectively. This result shows that CO₂ permeance is gradually dropped by about 39.1% with respect to the value of CO₂ permeance obtained at point E. Similarly, CH₄ permeance decreased by about 14.8% with respect to the initial value of CH₄ permeance obtained at point C. The decrease in CO₂ and CH₄ permeances could be due to the adsorption of hydrocarbon impurities in DDR3 pores which inhibited the diffusion of CO₂ and CH₄ molecules [3]. Adsorption of hydrocarbon impurities into the pores of DDR3 pore reduced its capacity for the diffusion of CO₂ and CH₄ molecules. Subsequently, adsorption of hydrocarbon impurities may also cause saturation for adsorption of CO₂ and CH₄ molecules which may also resulted to drop the performance of the membrane. In addition, a competitive sorption effect has been reported previously that mixed gas performance is always lower than pure gas due to a competitive sorption mechanism [4, 16]. However, CO₂/CH₄ selectivity of 2.54 was found at point H, which is slightly lower than the CO₂/CH₄ selectivity obtained at point G. It is found that
the loss of CO$_2$/CH$_4$ selectivity at point H was only about 4.2% compared to the CO$_2$/CH$_4$ selectivity which was initially obtained at point G$^*$. Furthermore, it can be seen from Figure 4 (section I) that, when the hydrocarbon impurities are not presented in the feed gas, the performance of DDR3 membrane remains stable. After 24 h, nearly constant CO$_2$ and CH$_4$ permeances of $7.23 \times 10^{-8}$ mol/m$^2$sPa and $4.51 \times 10^{-8}$ mol/m$^2$sPa were obtained, respectively, while CO$_2$/CH$_4$ selectivity of 3.66 was achieved (line A). These results are similar to those values obtained for CO$_2$ permeance, CH$_4$ permeance, and CO$_2$/CH$_4$ selectivity when the feed gas was changed to the binary gas mixture of CO$_2$ and CH$_4$ at the testing duration from 80 h to 96 h. In section III, CO$_2$ and CH$_4$ permeances of $7.08 \times 10^{-8}$ mol/m$^2$sPa and $4.41 \times 10^{-8}$ mol/m$^2$sPa were obtained (line B), while CO$_2$/CH$_4$ selectivity of 3.69 was achieved.

Therefore, it can be concluded that the presence of hydrocarbon impurities in CO$_2$ and CH$_4$ gas mixture has affected the performance of DDR3 membrane and caused a slight reduction of CO$_2$ and CH$_4$ gas over a testing duration of 40 h (from 32 h to 72 h). Consequently, CO$_2$/CH$_4$ selectivity of DDR3 membrane remained stable at testing condition of temperature of 30.1°C and feed pressure of 1 bar and CO$_2$ feed composition of 10 vol%.

3.4. Stability of DDR3 Membrane. Figure 4 also shows the stability of DDR3 membrane in CO$_2$ separation from CH$_4$. It can be seen from Figure 4 that CO$_2$ permeability, CH$_4$...
permeability, and CO$_2$/CH$_4$ selectivity (7.06 × 10$^{-8}$ mol/m$^2$·sPa, 4.38 × 10$^{-8}$ mol/m$^2$·sPa, and 3.66, respectively) obtained over DDR3 membrane after 24 h are comparable with those values achieved after 96 h (CO$_2$ permeance = 7.08 × 10$^{-8}$ mol/m$^2$·sPa, CH$_4$ permeance = 4.41 × 10$^{-8}$ mol/m$^2$·sPa, and CO$_2$/CH$_4$ selectivity = 3.69). Overall, after 96 h of testing duration, CO$_2$ permeability, CH$_4$ permeability, and CO$_2$/CH$_4$ selectivity were dropped by about 0.28%, 0.68%, and 0.81% compared to the original values obtained at line A shown in Figure 4. From these results, it has been found that membrane performance was dropped in small quantity and thus, it was decided that the membrane was stable in the presence of hydrocarbons.

In conclusion, the permeation performance of DDR3 membrane in the separation of CO$_2$/CH$_4$ remained steady up to 96 h with small losses of CO$_2$ permeability, CH$_4$ permeability, and CO$_2$/CH$_4$ selectivity. Thus, the separation performance of DDR3 membrane is durable and stable in the presence of hydrocarbon impurities.

The findings seen in the literature under the same temperature and pressure condition assess the efficiency of DDR3 membrane in CO$_2$/CH$_4$, H$_2$/CO$_2$, and CO$_2$/N$_2$ separations. With respect to Figure 5(a), the ideal CO$_2$/CH$_4$ selectivity obtained in this analysis is comparable to the published findings by Yajima and Nakayama [21]. However, this value is below the published results by Himeno et al. [18] and van den Bergh et al. [25]. Relatively low CO$_2$/CH$_4$ ideal selectivity of the DDR3 membrane obtained during the present research may be triggered by the existence of slight membrane defects which may influence CO$_2$ or CH$_4$ transport pathways via the membrane.

On the other hand, the performance of DDR3 membrane in CO$_2$/N$_2$ and H$_2$/CO$_2$ separation is shown in Figures 5(b) and 5(c). From Figure 5(b), it is found that the CO$_2$/N$_2$ selectivity obtained in the present work is lower than those results reported by Nakayama et al. [19]. Referring to Figure 5(c), the ideal selectivity of H$_2$/CO$_2$ obtained in the present study is slightly higher than those results reported by Tomita et al. [20] and Zheng et al. [26]. However, these values were lower than those results reported by Bose et al. [17]. Low ideal selectivity values of CO$_2$/N$_2$ and H$_2$/CO$_2$ obtained in the present work could be because of the similar reason as described previously for the performance of the membrane in CO$_2$/CH$_4$ separation. The presence of defects on the membrane affected the transport mechanisms of N$_2$, H$_2$, and CO$_2$ through the membrane and lowered the selectivity values of CO$_2$/N$_2$ and H$_2$/CO$_2$.

4. Conclusions

In the present work, the performance of DDR3 membrane for the CO$_2$ separation from gas molecules exhibiting comparatively smaller kinetic diameters, i.e., N$_2$ and CH$_4$, has been successfully conducted. The permeances of the gases obtained over the membrane decreased in the order of H$_2$ > CO$_2$ > N$_2$ > CH$_4$. Subsequently, it was also found that the DDR3 membrane demonstrated an ideal selectivity of 5.22 for CO$_2$/CH$_4$ which was higher than the ideal selectivity of H$_2$/CO$_2$ and CO$_2$/N$_2$ gas pairs. Besides, ideal selectivities obtained from DDR3 membrane decreased in the sequence of CO$_2$/CH$_4$ > CO$_2$/N$_2$ > H$_2$/CO$_2$. Furthermore, it was observed that the presence of hydrocarbon impurities in the CO$_2$ and CH$_4$ gas mixture directly affects the performance of DDR3 membrane and contributed to the losses of CO$_2$ permeability, CH$_4$ permeability, and CO$_2$/CH$_4$ selectivity of 39.1%, 14.8%, and 4.2%, respectively. Consequently, from the stability test, it can be suggested that the permeation performance of DDR3 membrane remained stable for 96 h, even after the separation testing of a gas mixture containing hydrocarbon impurities, with losses of CO$_2$ permeability, CH$_4$ permeability, and CO$_2$/CH$_4$ selectivity of 2.35%, 4.43%, and 0.55%, respectively. From the comparison study, it was concluded that the permeation performance of DDR3 membrane in CO$_2$ separation from H$_2$, CH$_4$, and N$_2$ still needs to be improved mainly due to the presence of defects in the membrane.

Data Availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References


