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Communication

Continuous polycrystalline ZIF-8 membrane supported on CO_2 selective mixed matrix supports for CO_2/CH_4 Separation

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Thin and compact ZIF-8 membranes were successfully synthesized on PES-ZIF-8 mixed matrix supports *via* secondary growth. The concept of incorporating both selective ZIF-8 layer and PES-ZIF-8 mixed matrix support in a membrane has demonstrated an enhancement in the overall CO_2/CH_4 selectivity.

Development of energy efficient and environmental friendly separation processes has become the current research trend dealing with global issues such as natural gas purification and CO_2 capture. With lower energy costs and fewer negative environmental impacts, membrane separation technology stand out to be an alternative as compared to conventional industrial processes [1]. Extensive research efforts have been performed during the last three decades [2] to enhance both permeability and selectivity of polymeric membranes, due to a trade-off between permeability and selectivity suffered by conventional polymeric membrane, as encapsulated in Robeson upper bound relationship in 1991 [3], and revisited in 2008 [4].

To overcome the trade-off limitations of polymeric membrane, the idea of mixed matrix membranes (MMMs) with selective fillers deposited into polymeric membranes is expected to complement the permeability and selectivity of the overall membrane by combining the advantages of both phases. Though MMMs [5-7] have been reported to exhibit attractive separation properties, unresolved issues of poor adhesion between the filler phase and polymer continuous phase resulting in deteriorating selectivity have impeded them to be successfully utilized in industrial application. ZIF-8, with sodalite topology connected from zinc(II) cations and 2-methylimidazole anions possessing pore cavity of 1.16 nm and pore aperture of 0.34 nm, has attracted attention as fillers for mixed matrix membranes [8-10] due to their good compatibility with polymers combined with their molecular sieving effect.

For supported metal organic frameworks (MOFs) membrane, the compatibility between the selective layer and support is vital in determining the integrity of the overall membrane and the permeation stability. Several published studies related to ZIF-8 membranes were directed towards the growth of continuous and thin ZIF-8 layers on porous supports where the used supports are predominantly an inorganic material such as Al_2O_3 [11-14] or TiO_2 [15]. Nonetheless, continuous and defect free membranes cannot be formed on the ceramics without support modification or seeding steps [16-18] due to weak interactions of MOFs on the inorganic supports. The fabrication of MOFs composite membranes would be more facile and straightforward using porous polymer as support layers particularly due to the rapid preparation method of polymer support, easily scale up as compared to inorganic supports, and better adhesion of MOFs with polymers due to favourable interactions between polymer support and organic ligands of MOFs.

Consequently, several researchers have diverted towards synthesizing ZIFs membranes on polymeric supports. For instance, Brown et al. [19] reported the synthesis of ZIF-90 membranes on Torlon hollow fiber supports, achieving CO_2/N_2 and CO_2/CH_4 selectivities of 3.5 and 1.5, respectively, well above their corresponding Knudsen selectivities (0.8 and 0.6). On the other hand, Ge et al. [20] fabricated thin and continuous ZIF-8 layer on porous polyethersulfone (PES) substrate, showing good affinity of both ZIF-8 and PES materials. Their PES supported ZIF-8 membrane successfully achieved H_2/Ar, H_2/O_2, H_2/N_2 and H_2/CH_4 ideal separation factors of 9.7, 10.8, 9.9, and 10.7, respectively. Barankova et al. [21] synthesized ZIF-8 membranes on mixed matrix support coated with polyetherimide and zinc oxide nanoparticles, where these zinc oxide particles served as a secondary metal source for the growth of ZIF-8 membrane. Their membrane exhibited H_2/C_3H_8 ideal selectivity of 22.4, exceeded 4 times of the corresponding Knudsen selectivity. Recently, Cacho-Bailo et al. [22] prepared ZIF-8 membrane on a porous polysulfone (PSF) support, where the ZIF-8 comprises over 75 wt% of the

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overall membrane, indicating an almost self supported MOF membrane. Their permeation tests of gas mixtures separations displayed H_2/CH_4 and H_2/N_2 selectivities of 10.5 and 12.4, respectively.

To the best of our knowledge, the performance of ZIF-8 membrane supported on mixed matrix supports (PES/ZIF-8) for CO_2/CH_4 gas separation has not been reported yet. ZIF-8 was selected due to its high hydrothermal stability as one of the most stable and promising MOFs for gas separation applications. Here in, we demonstrate the synthesis of dense ZIF-8 membrane supported on tailor-made polyethersulfone (PES)/ZIF-8 mixed matrix supports for CO_2/CH_4 separation. We prepared continuous ZIF-8 layers on neat PES, 5 wt% and 10 wt% ZIF-8 loadings in PES supports, as shown in Fig. 1, where PES was chosen as the polymer matrix due to its feasibility in gas separations [23, 24]. Better performance can be expected by fabricating a dense ZIF-8 on the mixed matrix support as compared to the polymer support *via* short time secondary seeded growth. The ZIF-8 crystals embedded in the PES polymer as mixed matrix supports are speculated to have a positive effect in the overall CO_2/CH_4 selectivity predominantly due to its CO_2 adsorption effect [25]. One side of the membrane is covered with continuous selective ZIF-8 layer, while on the other side of the membrane, PES-ZIF-8 mixed matrix will act as the membrane support as well as engaged in the overall CO_2/CH_4 separation performance.

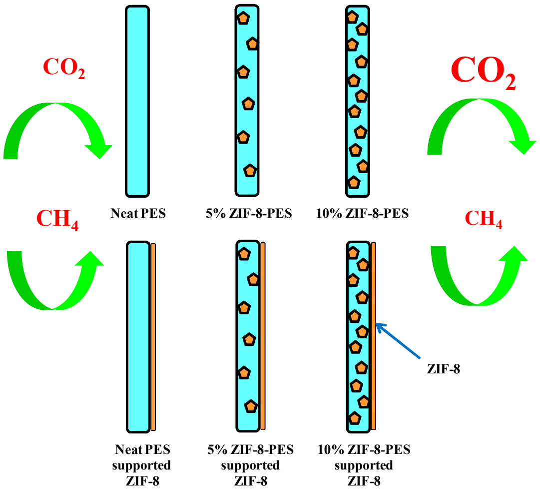

Fig 1. Schematic illustration of ZIF-8 membranes fabricated on neat PES, 5% ZIF-8-PES, and 10% ZIF-8-PES mixed matrix supports for CO_2/CH_4 separations.

As a vital role in CO_2/CH_4 separation, the top layer ZIF-8 membrane should be continuous and dense to avoid gas leakage leading to insignificant selectivity. Several researchers [25-27] have reported that the presence of sodium formate in the precursor solution enhances the intergrowth of ZIF-8 crystals, mainly due to the higher deprotonation of 2-methylimidazole leading to growth of ZIF-8 crystals in all directions. In this work, ZIF-8 membranes were prepared by secondary seeded growth on the mixed matrix support using synthesis precursor with molar ratio of $1ZnCl_2$:5.8Hmim(2-methylimidazole):4HCOONa(Sodium Formate):180Methanol. In addition, seeding step is essential in determining the quality of the final ZIF-8 membrane formed as the seeds on the support acted as a base layer for the formation of gap-free ZIF-8 during secondary growth. We adopted the seeding technique recommended by Liu et al. [28] by performing rub seeding followed by dip coating in 1% ZIF-8 solution (Refer to ESI†). These ZIF-8 seeds will be fixed on the surface of the porous supports after seeding to provide nucleation sites for the growth of ZIF-8 crystals into dense membrane during solvothermal process, ensuring the adhesivity between ZIF-8 layer and the supports.

Fig. 2 shows the SEM cross sectional micrographs of the ZIF-8 membranes after secondary seeded growth. Continuous ZIF-8 membranes were fabricated on sponge like PES and PES-ZIF-8 mixed matrix supports. No visible interface between the ZIF-8 layer and supports (Fig. 2a-c) can be seen in SEM revealing that both ZIF-8 and the mixed matrix supports are well compatible and adhered together, indicating the successful fabrication of asymmetric membranes. The cross sections also clearly show the continuous and homogeneous morphology of ZIF-8 across their thickness of ~6.5 - 8 µm after 6 hours of growth. Our composite membranes with mixed matrix supports not only has a greater degree of flexibility as compared to conventional inorganic supports, but with ZIF-8 crystals fixed within the PES polymeric also play an important role in enriching the CO_2 adsorption [25] participating in CO_2/CH_4 separation. On the other hand, top view of the secondary growth ZIF-8 layer are shown in Fig. 3. In the lower magnified view as shown in Fig. 3a, it can be observed that the layer is very dense and compact with no visible cracks present. Further magnified of the pictures shown in Fig. 3b presented a well inter-grown and continuous ZIF-8 membranes. Besides, the shape and intergrowth of crystals are comparable to those of ZIF-8 membranes synthesized on inorganic supports.

Fig. 4 shows the x-ray diffraction (XRD) patterns of the ZIF-8 membrane supported on neat PES, 5 wt% and 10 wt% PES-ZIF-8 mixed matrix supports. The high crystallinity of the synthesized ZIF-8 membranes were verified by powder X-ray diffraction (XRD) analysis, which are comparable to the literatures [29, 30]. The peaks appeared at 2θ = 7.3, 10.3, 12.6, 14.5, 16.3, and 18.0° attributed to ZIF-8 peaks, implying that high quality ZIF-8 crystals in the absence of amorphous phase were prepared. The ZIF-8 crystals exhibited pore volumes and BET surface areas of 0.603 cm^3/g and 1107 m^2/g, respectively, comparable to the literatures [8, 14, 31]. These crystals were used as seeds for the synthesis of membranes *via* secondary growth as well as the fillers in the PES mixed matrix support. Both CO_2 and CH_4 adsorptions on the ZIF-8 crystals were investigated to evaluate the strength of adhesion between the gas molecules, reported in our previous work [25]. The volume of CO_2 (2.4 mmol CO_2/g ZIF-8) adsorbed across ZIF-8 crystals was larger than that of CH_4 (1.1 mmol CH_4/g ZIF-8), mainly caused by the narrow bottle neck structure of the ZIF-8 pore aperture, where ZIF-8 crystalline structure is constituted of large cavities (1.16 nm) connected through small apertures (0.34 nm) [32]. In addition, it could also be attributed to the polar nature of the carbon oxygen bond in CO_2 which is able to interact strongly with 2-methylimidazole molecules or ZIF-8 crystal sites. [11].

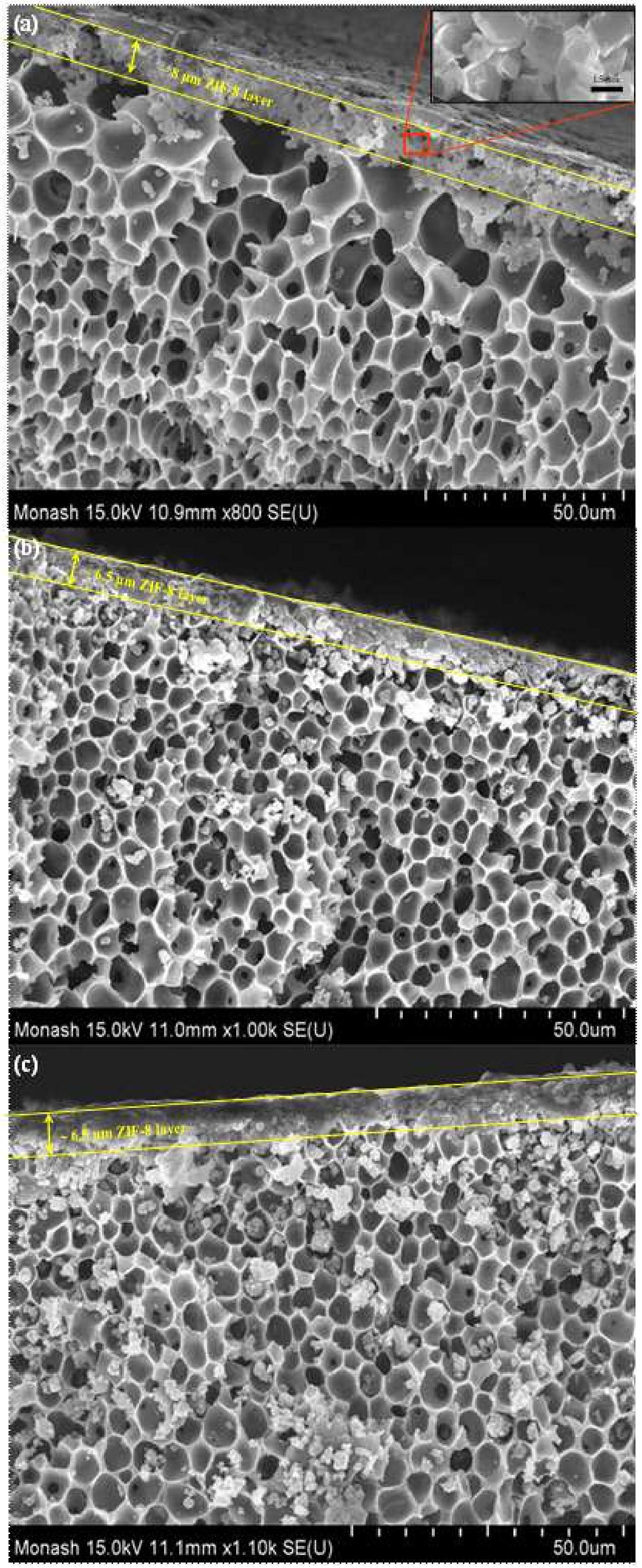

Fig 2. FESEM cross sectional micrographs of the continuous ZIF-8 membranes supported on (a) Neat PES, (b) 5 wt% ZIF-8-PES, (c) 10 wt% ZIF-8-PES, mixed matrix support.

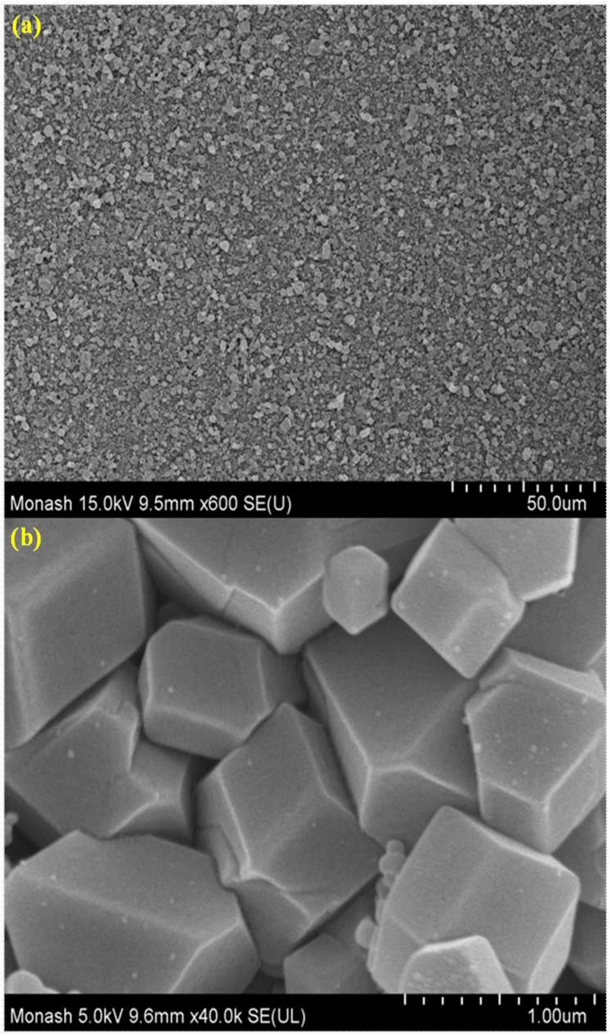

Fig 3. FESEM on surface morphologies of the mixed matrix supported ZIF-8 membranes with (a) low magnified and (b) high magnified micrographs.

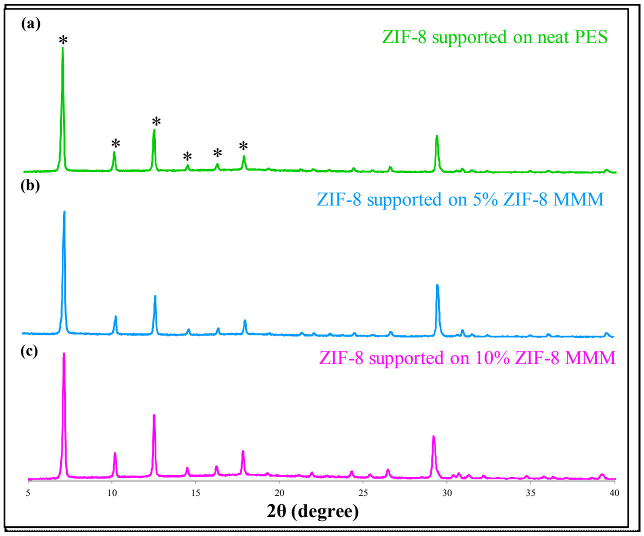

Fig 4. X-ray diffraction patterns of ZIF-8 membranes supported on (a) neat PES, (b) 5 wt% ZIF-8-PES MMM, (c) 10 wt% ZIF-8-PES MMM. (The symbol * represents ZIF-8 peaks)

For the mixed matrix supports, we obtained both improved permeance and selectivity by introducing ZIF-8 crystals into PES continuous phase demonstrated *via* single gas permeations, shown in Table 1. An increase in both CO_2 and CH_4 permeance were observed on both 5 wt% ZIF-8-PES and 10 wt% ZIF-8-PES, respectively, as compared to the neat PES membrane. The increase in permeance could be reasoned by the interaction between both polymer chains and ZIF-8 crystals, where the ZIF-8 crystals will interrupt the chain packing of polymer matrix leading to an increase free volumes among the polymer chains resulting in higher gas permeance. Though these mixed matrix membranes have shown improvement in terms of their permeance, nonetheless, their CO_2/CH_4 selectivity remained intact without exhibiting a trade-off. The uninterrupted CO_2/CH_4 selectivity as a result of further increment in ZIF-8 loadings is most likely due to the higher presence of selective particles in the matrix supports, which allows for more selective adsorption of CO_2 on the ZIF-8 than CH_4 gas, leading to increase in CO_2/CH_4 selectivity. Looking at Table 1, the 5 wt% and 10 wt% ZIF-8-PES mixed matrix supports show 6% and 15.3% increase in CO_2 permeance as compared to the neat PES, respectively; while the 5 wt% and 10 wt% ZIF-8-PES mixed matrix membranes show a 2.7% and 7.4% increase in CH_4 permeance as compared to that of neat PES, respectively. Therefore, it can be deduced that the unaffected selectivity was contributed by the larger CO_2 permeance as a result of CO_2 adsorption on ZIF-8 crystals. To the contrary, though attempts have been performed to increase the ZIF-8 loadings in PES polymer to 20 wt%, unfortunately, their poor mechanical properties with unselective voids were not sufficient to endure gas permeance measurements which hampered the efforts of gas separations. Moreover, secondary growth of the ZIF-8 layer on 20 wt% ZIF-8-PES was affirmed to be non feasible, leading to cracking of the membranes into pieces during solvothermal growth associated with its brittleness.

Table 1. CO_2 and CH_4 gas separation performances of mixed matrix supports and mixed matrix supported ZIF-8 membranes

Membranes	**CO_2 Permeance (10^{-9} mol/m^2.s.Pa)**	**CH_4 Permeance (10^{-10} mol/m^2.s.Pa)**	**Ideal Selectivity**
Neat PES	8.36	9.29	9.0
5 wt% ZIF-8-PES	8.86	9.54	9.3
10 wt% ZIF-8-PES	9.64	9.98	9.7
*Neat PES	7.06	4.80	14.7
*5 wt% ZIF-8-PES	7.47	4.91	15.2
*10 wt% ZIF-8-PES	8.05	5.13	15.7
Membranes	**CO_2 Permeance (10^{-9} mol/m^2.s.Pa)**	**CH_4 Permeance (10^{-10} mol/m^2.s.Pa)**	**Binary Selectivity**
*Neat PES	6.55	4.75	13.8
*5 wt% ZIF-8-PES	6.80	4.85	14.0
*10 wt% ZIF-8-PES	7.34	5.03	14.6

*The symbol * refer to secondary growth of ZIF-8 layers supported on mixed matrix supports.*

For secondary growth of ZIF-8 layer on the mixed matrix supports, their CO_2/CH_4 selectivities are indeed enhanced to a greater extent (~63%), where both CO_2 and CH_4 have shown an average of ~16% and ~49% reduction in their permeances, respectively, as compared to only mixed matrix supports. It is astonishing that the additional ZIF-8 layer does not impose significant resistance to its gas permeations, possibly due to the inherent pore flexibility of MOF. Reported ZIF-8 membranes have generally shown moderate CO_2/CH_4 selectivity in the range of 3-7 [14, 33-35], possibly due to their flexible framework structure [36]. However, the remarkable improvement in CO_2/CH_4 selectivities from ~9 to ~15 after fabrication of the ZIF-8 layer on mixed matrix supports could be ascribed to its imperative effect in combined molecular sieving and CO_2 adsorptions of the ZIF-8 layer, as well as playing a vital role in defect abatement by diminishing the existing defect flow through the skin layer of the mixed matrix membranes. Nevertheless, they improved the overall selectivity owing to its molecular sieving effect, corroborating the advantages of ZIF-8 layer on mixed matrix membranes. A rough estimate of improvement on the CO_2/CH_4 selectivity with the top layer ZIF-8 membranes is ~5-6, whereby the overall good CO_2/CH_4 selectivity of the membrane were also contributed by CO_2 selective support rather than solely the ZIF-8 layers.

On the other hand, although the improvement in CO_2/CH_4 selectivities of the mixed matrix supports were not as compelling as compared to its gas permeability which increases substantially with increasing ZIF-8 loadings, the conceptual theory of fabricating an additional selective ZIF-8 layer on the mixed matrix membranes which could stimulate the overall CO_2/CH_4 selectivities would serve as an innovative approach in future research. Distinctly, presuming the additional selective layer to be fabricated on existing high performance mixed matrix membranes [7, 37, 38], definitely it will have a positive impact on the gas permeation properties of the overall membrane.

The secondary growth ZIF-8 membranes on mixed matrix supports were further evaluated by single gas permeation up to 2 bar pressure difference, shown in Fig. 5. It was self-evident that the neat PES, 5 wt%, and 10 wt% supported ZIF-8 show a modest decrease in CO_2 permeance with increasing pressure difference. With ZIFs reported to be the promising CO_2 storage material exhibiting high CO_2 adsorption [39, 40], the decrease in CO_2 permeance with increasing pressure difference could be reasoned by the rapid filling up of CO_2 on the ZIF-8 crystals adsorption sites, which further lead to a decrease in the jumping frequency of CO_2 molecules to their neighbouring sites of ZIF-8 structure [41]. Therefore, in our study, a slight decrease of CO_2 permeance was observed in driving the decrease in CO_2 permeance of the neat PES-ZIF-8 supported ZIF-8 membrane. However, it has been generally reported that an increase in pressure difference on polymeric membrane usually entail membrane compaction and a reduction of free volume within the polymer, leading to reduced gas mobility and a decrease in permeance. As a control experiment, the CO_2 permeance on neat PES was also measured up to a pressure difference of 2 bar. However, it shows a slight permeance increase, which exclude the possibility of permeance reduction due to the nature of polymeric support, with up to 2 bar pressure difference condition.

Owing to their superior separation performances, mixed gas permeations of CO_2/CH_4 (50/50 mol%) were performed on mixed matrix supported ZIF-8 membranes at room temperature and 1 bar pressure difference. In comparison to single gas permeation data, both CO_2 and CH_4 presented a decrease in permeance and selectivity for all supported ZIF-8 membranes. Particularly CO_2, shows an average of 8.4% decrease in permeance while CH_4 shows an average of 1.3% decrease in permeance as compared to their single permeation data, respectively. Perhaps it was due to the competitive adsorption and permeation between the two penetrants, where the slow permeating CH_4 largely hinders the CO_2 permeation rate. Notwithstanding the interactions between both gases, their CO_2/CH_4 selectivities were still kept at ~14, marking the evidence of its feasible application in mixed gas separations.

The separation performances of these membranes have also been included in the Robeson plot, as shown in Fig. 6. An average thicknesses of 100 µm and 7 µm were used to calculate the permeability in Barrers for mixed matrix supports and top layer ZIF-8 membranes, respectively. These data points are close to the present upper bound for polymeric membranes, and slightly lower than those of thermally rearranged polymeric membranes.

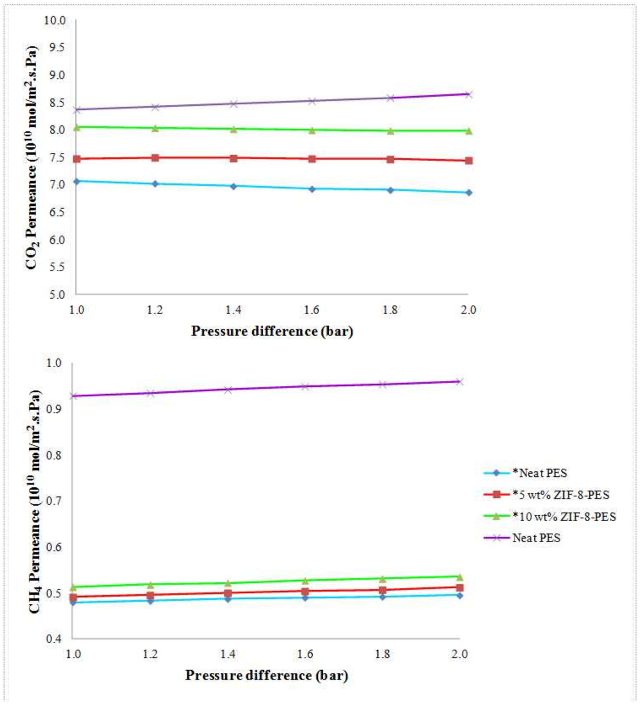

Fig 5. CO_2 and CH_4 single gas permeations with effect of pressure gradient up to 2 bar on the mixed matrix supported ZIF-8 membranes.

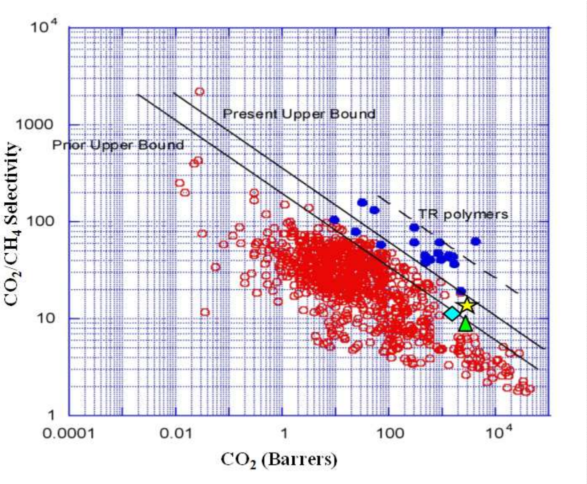

Fig 6. Robeson plot for CO_2/CH_4 mixtures [4]. ☆ and ◇ symbols represent the performance of the MMM supported ZIF-8 membranes on single gas and binary gas permeation, respectively; while △ symbol represents the performance of MMM supports.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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