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# Gas Transport Behavior of Novel Modified MCM-48/ Polysulfone Mixed matrix membrane Coated by PDMS

Jomekian A<sup>1</sup>, Pakizeh M<sup>1</sup>, Mansoori SAA<sup>1</sup>, Poorafshari M<sup>1</sup>, Hemmati M<sup>2</sup> and Ataee Dil P<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, P.O. Box 91775-1111, Iran <sup>2</sup>Research Institute of Petroleum Industry, Division of Polymer Science and Technology <sup>3</sup>South Pars Gas Complex

#### Abstract

Mesoporous MCM-48 silica was synthesized by templating method and the structure of particles was characterized by XRD, TEM, FTIR, TGA and N<sub>2</sub> adsorption techniques. The surface modification of particles in order to introducing into PSF matrix was performed by DMDCS sylilation agent. PDMS surface coating of membranes was performed to repair possible surface defects and enhance selectivities of membranes. For all gases tested (N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>andO<sub>2</sub>), the permeability increased in proportion to the weight percent of MCM-48 present in the film and calculating CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> selectivities of PDMS coated membranes showed enhancement in ideal and actual selectivities both.

**Keywords:** Mesoporous MCM-48; Polysulfone; DMDCS; PDMS; Mixed matrix membrane.

# Introduction

Polymeric membranes have been very useful in addressing industrially important gas separations, thereby providing economical alternatives to conventional separation processes. However, there is always a trade-off between permeability and selectivity of these membranes.

For gas separation applications as shown in upper bound curves developed by Robeson [1]. This intrinsic property of polymers limited their use in gas separation processes. Therefore, there is a need for innovation in polymeric membrane technology so that the new types of membranes can successfully be used in these applications [2-5].An important recent discovery in the membrane science is the polymer nanocomposite membrane [6-9]. Here in this structurally engineered nanocomposite membranes, the nanoparticles act asto create preferential permeation pathways for selective permeation while posing a barrier for undesired permeation in order toimprove separation performance [3]. In recent years, significant improvements in the performance of polymer nanocomposite membranes for gas separation have been made. Clearly the success of the polymer nanocomposite membranes depends largely on the quality of the interface between the nanofiller and the polymer [10-13]. Ordered mesoporous silicas (OMS) are a class of materials possessing unique properties at the nanoscale and can be used as nanofiller in polymer matrix. Since their initial discovery by the Mobil labs in the early 1990s these materials have been heavily investigated. These porous solids have desirable properties including highly uniform pore sizes in the 2-10 nm range that possess long-range order, despite that the matrix material is morphous silica [4,5]. Recently, mesoporous molecular sieves have been used in nanocomposite membranes to enhance permeability or selectivity [14,15]. As a remarkable work, an application of polysulfone (PSF) nanpcomposite membrane with mesoporous MCM- 41 for gas separation has been reported [16]. Kim et al. enhanced gas permeability of PSF by incorporating mesoporous MCM-48 [17]. They showed that the permeability of PSF nanocomposite membraneincreased by introducing mesoporous materials whereas the selectivity did not changed significantly and that was because of suitable compatibility between nanoparticles and polymer matrix. However, in these cases the selectivity performance of membranes did not improved and this important alternative of membrane property remained unchanged. The introduction of nanoscale inorganic particles in polymer matrix should give more polymer/particle interfacial area and provide the chance to introducehigher loading of the molecular sieves into thepolymer matrix. In addition, nanoscale molecular sievesare more suitable for commercialization of nanocomposite membranes whereas they have very thin selective layers than micron-sized zeolites ormolecular sieves. Finally, the possibility of additional functionalization and surface coating of membrane that can further enhance sorption effects in these particles and raise gas selectivity, have been investigated [19-21]. As a new work, the functionalization of particles was performed by DMDCS. Organosilicon compounds have many applications in organic chemistry, most notably as derivatizing and protecting reagents, intermediates in organic synthesis and reducing agents. Silicon is considerably less electronegative than either carbon or hydrogen with consequent implications for the polarity of bonds between silicon and other elements. TheDMDCS is one of these materials that introduces a dimethylsilylene group into the substrate molecule, chemically binds thin, water-repellentsilica. The surfaces coated by that, are neutral, hydrophobic, and non-oily, are not affected by solvents and are not readily hydrolyzed. Recently, many studies have been carried out on transport properties of pure and binary gas mixtures of O2, N2, H2, CO, CO2 and CH<sub>4</sub> using PDMS membrane[22-24]. Hence, as a new approach, we decided to use this polymer to coat the surface of nanocomposite MCM-48/PSF membrane in order to fill the possible surface voids and improve membrane selectivity for gas separation. The main purpose of this studyis fabrication and characterization of organic-inorganic nanocomposite membrane coated by PDMS based on MCM-48

\*Corresponding author: Jomekian A, Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, P.O. Box 91775-1111, Iran, Fax: +985118816840; E-mail: <u>abolfazl.jomekian@gmail.com</u>

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nanoparticles introduced to a polymer matrix that possess the superior gas separation properties compared to neat polymeric membranes.In the first step, MCM-48 nanoparticles was produced then its structure was investigated with several adequate characterization methods such as X-ray diffraction (XRD) analysis, pore size analysis and transmission electron microscopy (TEM) Then, the structure properties of fabricated polysulfone-MCM-48 nanocomposite membranes were characterized by SEM. Finallysurface coating quality of membranes wasinvestigated by SEM and gas permeationtests.

### Experimental

#### Synthesis and functionalization of MCM-48 nanoparticles

The nanoparticles of MCM-48 was synthesized through the selfassembly of inorganic silica precursor and organic template under hydrothermal conditions. The source of silicon was tetra ethyl ortho silicate (TEOS, Merck). The structure-directing agent was cetyl trimethyl ammonium bromide (CTAB, Merck). A typical synthesis gel was prepared by adding 5.78 g of TEOS to an aqueous solution containing 5.9 g of CTAB and 0.57 g of NaOH and 30 ml of deionized water. After stirring for about 2 h at room temperature, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 373 K in a Teflon lined autoclave for 96 h. The molar composition of the initial gel mixture was 1.0:0.58:0.50:60 TEOS/CTAB/NaOH/H2O. The solid product was obtained by filtration, washed with deionized water, dried in vacuum oven at 353 K and calcined in air at 833 K for 10 hwith 1 K/min of heating rate to remove the CTAB. This method results the unmodified version of MCM-48 nanoparticles [25]. As shown in Figure 1, surface modification of MCM-48 particles was performed this way: Before removing CTAB, sylilation of MCM-48 with dimethylsilane was achived by immersionof MCM-48 nanoparticles into liquid dimethyldichlorosilane (DMDCS,Merck) for 72 h. Afterwards CTAB was removed by means of soxhlet extraction apparatus using 300 ml of methanol and 30 ml of aqueous HCL (10% vol). The extraction process was continued for about 24 h then the mixture was filtered and washed with 200 ml of ethanol and in the end the modified mesoporous MCM-48 samples were filtered and washed in Soxhlet apparatus with hexane, and then dried at 333 K in oven [26].

#### Synthesis of membranes

Before using PSF (Ultrason 6010, Merck) in synthesis process, it must be degassed at 423 K for 2 h under vacuum to remove all of its water content. To prepare a 20 wt% of MCM-48/PSF nanocomposite membrane, about 0.4 g of the pure PSF was dissolved in 3 ml of N,N-Dimethylacetamide (DMAc,Merck) and mixed for 12 h then approximately 0.1 gr of MCM-48 powder was dissolved in 1 ml of N,N-Dimethylacetamide with about 5 drops of PSF solution and sonicated in ultrasonic bath for about 20 min. After that, This MCM-48 solution was added to the polymer solution and the mixture was allowed to mix





for 4 h at room temperature then the mixture was sonicated for 10 min, after which it was allowed to mix for 10 min and this procedure repeated several times to ensure perfect dispersion. The prepared casting solution was cast on a glass substrate using casting blade. The glass substrate was covered with a glass cover to slow down the evaporation rate of the solvent, allowing for the formation of a film with a uniform thickness without curling. After about 1 min the glass substrate were placed into a coagulation bath of methanol. Solidification of film immediately occurred and the membrane formed and separated from glass substrate. The membrane remained in methanol bath for about 24 h to complete the phase separation process then dried in air at 323 K.Coating solutions were prepared 30 wt% of (PDMS, Merck) in n-hexane. The flat type PDMS/polymer/MCM-48 nanocomposite membranes were prepared in a multi-step dip-coating procedure: pre-treatment with pure n-hexane for 4 h, dip-coating of the nanocomposite supports with coating solutions for 5 s and then drying at room temperature for 30 min, dip-coating of the pretreated supports in coating solutions for 30 s, and then drying at room temperature for overnight and finally post-cross linking at 100°C for 24 h. Finally a 4 cm diameter circular sample was cut from the film and used for permeation tests. Gas permeation experiments are one of the most important methods for finding the efficiency of synthesized membranes. In order to perform these experiments, a constant volume apparatus that used for single gas permeation measurements of membranes was assembled. Permeability was measured directly, and the time-lag method wasapplied to the recorded data to determine the diffusivity coefficient.

#### Characterization

Powder X-ray diffraction (XRD) data were recorded using a Philips Analytical X-pert diffractometer with Cu Ka radiation (l=1.54056A°) with a step size of 0.02 °/s.N<sub>2</sub> adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 analyzer using standard continuous procedures, and samples were first degassed at 573 K for 5 h. Surface areas were determined by BET method [27], and the pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) formula [28]. SEM (LEO 1450VP) was used to study the morphology of the membranes. The transmission electron micrographs (TEM) were obtained on a Zei (LEO912AB) transmission electron microscope. The permeability tests were carried out in a constant volume apparatus. The gases used for permeation measurements were, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub>. Each gas possessed a purity of 99.99% and was used as received. The feed pressure and temperature kept constant at 4 bar and 298 K respectively for all experiments. Each gas was passed through a membrane five times



**Figure 3:** The N<sub>2</sub> adsorption–desorption isotherms of unmodified MCM-48particles at 77 K.



Figure 4: The  $\rm N_{2}$  adsorption–desorption isotherms of DMDCS modified MCM-48particles at 77 K.





and the average results and the standard deviations were recorded. Permeabilities are reported in units of Barrer.(1 Barrer =  $1 \times 10^{-10}$  cm<sup>3</sup> (STP) cm/(cm<sup>2</sup> s cm Hg)).

# **Results and Discussion**

# Characterization results of MCM-48 nanoparticles

The XRD pattern of three types of MCM-48 is shown in Figure 2. The observation of several peaks at low reflection angles ( $2\theta$ = 2.5–7.0), which are relevant to (211), (240) and (420) can be indexed in a cubical lattice and correspond well to the cubical arranged pore structure of MCM-48, is the proof of a long-range order and consequently of the good quality of the sample. As the material is not crystalline at the atomic level, no reflections at higher angles are observed. The peaks in the patterns of samples with removed surfactant are sharper than the peaks from surfactant contained sample. The reason is because of good reflection from crystalline walls exist in surfactant removed samples and does not exist in samples with surfactant. The nitrogen adsorption-desorption isotherm of calcined and extracted MCM-48 at 77 K, exhibits both a reversible type IV isotherm and a sharp pore filling step at p/p<sub>0</sub> 0.2-0.3 which are characteristic of uniform pores (Figure 3 and Figur 4). The difference between these isotherms is the volume of N2 adsorbed in the pores. This volume is higher for DMDCS modified sample. The reason is related to effect of modification that makes the particles not being agglomerated and also makes the porosity of particles increases. The agglomeration of unmodified particles is the consequence of hydrophilicity that turn into hyriphobicity in the process of silvlation. The both samples shows high specific surface area, approximately 930 m<sup>2</sup>/g, and a narrow distribution of pore diameters centered at 2.1 nm(Figure 5 and Figure 6). The reason of no change in the pore diameters of particles in both samples is that the silylation has no effect on the pores and wall of particles and the only effect of that is decreasing of attraction between particles that affects the amount of available free volume for adsorption of gas molecules. The TEM images of the extractedMCM-48 particles in Figure 7show the existence of highly ordered cubical structures with uniform mesopores indicating the properties of MCM-48 particles. The template or surfactant content of the cubical mesoporous MCM-48 can be identified using FT-IR (Figure 8). The FT-IR spectrum of the as synthesized mesoporous MCM-48 (Figure 8A) clearly shows the presence of the template molecules while that of the calcined product (Figure 8B) shows no peaks related to the surfactant. The spectrum of the mesoporous sample after modification and extraction of the surfactant (Figure 8C) also displays no peaks related to the CTAB, showing that the extraction procedure was very effective for removing the template. The TGA result



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Figure 8: FT-IR spectra of (A) as-synthesized MCM-48, (B) calcined MCM-48 and (C) DMDCS modified MCM-48.





Figure 10: SEM images of (a) unmodified and (b) modified MCM-48/PSF composite membrane.



Figure 11: SEM photographs of a) surface and b) cross section of 20% wt DMDCS-MCM-48/PSF nanocomposite membrane coated with 30%wt PDMS solution.

from as synthesized samples shows two distinct levels of losing weight. The first level is relevant to evaporation of adsorbed water and the second and also main level is relevant to decomposition of surfactant (Figure 9). These XRD patterns, pore size analysis, FTIR analysis, TGA and TEM results are in agreement with previously published results on nano-sized mesoporous silica materials [29,30].

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The formation of undesirable gaps or aggregation of inorganic particles in the polymer may happen because of incompatibility between the polymer and the inorganic material, deducting the selectivity and mechanical properties of the membrane. In order to investigate the quality of dispersion of MCM-48 nanoparticles into the polymer matrix we utilized SEM images of surface of two kinds of nanocomposite membranes, filled with unmodified MCM-48 and contained sylilated MCM-48.Surface SEM images of 20 wt% unmodified and DMDCSmodified MCM-48/PSF nanocomposite membranes are shown in Figure 10. Figure 10(a) shows that in unmodified version of membrane the unfavorable voids between polymer matrix and inorganic particles and agglomeration of particles is obvious. However, the dispersion quality of DMDCS modified MCM-48 nanoparticles in polymer matrix appears to be high and there are no distinct voids between two phases (Figure. 10(b)). The reason of these two different kinds of behaviors is related to silanol groups. Since they have hydrophilic property and the surface of unmodified MCM-48 nanocomposite membrane is covered by them, the MCM-48 particles easily adhere to each other via hydrogen bonding and form irregular agglomeration in the polymer matrix [29]. However, in modified version, the surface of membrane is sylilated with dimethylsilyl groups hence the hydrophilic surface of membrane turns to hydrophobic surface. This treatment prevents the particles from being agglomerated and enhances the interaction between particles and polymer producing a composite with well-dispersed mesoporous particles in the polymer matrix.

# Permeability of DMDCS-MCM48/PSF nanocomposit membrane

The gas permeability tests were performed in constant volume varying pressure apparatus. The permeability results and ideal selectivity for the DMDCS-MCM-48/PSF nanocomposite membranes and pure PSF before coating are shown in Tables 1 and Table 2, respectively. For all tested gases ( $CO_2$ ,  $O_2$ ,  $N_2$ , and  $CH_4$ ), the enhancement of permeability values is proportional to the amount of MCM-48 loading in the PSF matrix. The addition of 10 wt% and 20 wt% MCM-48 to PSF resulted in respective at least 68% and 98% increases in the permeability of all gases tested which is higher than those achieved without modification by previous researchers [17]. Fortunately, there

Membrane	MCM-48wt%	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	0 <sub>2</sub>
Dense PSF	0	3.2	0.12	0.11	0.45
PSF	0	4.5	0.18	0.17	0.98
MCM41/PSF	10	7.6 (69%)	0.33 (83%)	0.34 (100%)	1.65 (68%)
MCM41/PSF	20	8.9 (98%)	0.38 (111%)	0.40 (135%)	1.9 (94%)
MCM41/PSF	40	16.1 (257%)	0.98 (444%)	1.1 (547%)	3.92 (300%)

 
 Table 1: Gas permeabilities (Barrer) of various gases in the pure polysulfone and DMDCS-MCM-48/PSFnanocomposite membranes.

Membrane	MCM-48wt%	O <sub>2</sub> / N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Dense PSF	0	6.9	31
PSF	0	5.4	23
MCM41/PSF	10	5	22
MCM41/PSF	20	5	22
MCM41/PSF	40	4	14.5

 Table 2: Ideal selectivity for polysulfone and DMDCS-MCM-48/PSFnanocomposite membranes.

Membrane	MCM-48wt%	$D_{02}/D_{N2}$	D <sub>CO2</sub> /D <sub>CH4</sub>	S <sub>02</sub> /S <sub>N2</sub>	S <sub>CO2</sub> /S <sub>CH4</sub>
PSF	0	2.9	3.96	2.03	4.89
MCM41/PSF	10	3.92	2.74	1.3	6.52
MCM41/PSF	20	3.7	2.73	1.29	6.98
MCM41/PSF	40	4.3	2.77	1.24	7.23

 Table 3: Measured uncoated MCM-48/PSF diffusivity and solubility selectivities of gases.

MCM-48/PSF	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	0 <sub>2</sub>
10wt%	6.1 (35%)	0.26 (44%)	0.25 (47%)	1.42 (45%)
20 wt%	7.7 (71%)	0.28 (56%)	0.28 (65%)	1.73 (76%)
40wt%	13.2 (193%)	0.44 (144%)	0.41 (141%)	3.12 (218%)

 Table 4: Gas permeabilities (Barrer) of various gases in the DMDCS-MCM-48/

 PSFnanocomposite membranes coated by 30% wt PDMS solution.

MCM-48/PSF	O <sub>2</sub> / N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
10wt%	5.52	24
20 wt%	6.2	27.2
40wt%	7 1	32.7

Table 5: Ideal selectivity forDMDCS-MCM-48/PSF nanocomposite membranes coated by 30% wt PDMS solution.

Pure gas	S×10 <sup>2</sup> (cm <sup>3</sup> (STP)/cm <sup>3</sup> (mHg)		
N <sub>2</sub>	0.12		
0,	0.24		
ĊH₄	0.27		
0.0	1 75		

**Table 6:** The PDMS solubility of four pure gases  $N_2$ ,  $O_2$ ,  $CH_4$  and  $CO_2$ .

Nanocomposite membrane	composite brane Modifier agent		Ideal selectivity O <sub>2</sub> /N <sub>2</sub>	References
20% wt MCM- 48/PSF	No modifier	23.58	5.38	[17]
20% wt MCM- 41/PSF	No modifier	18.9	5.47	[16]
20% wt modified MCM- 48/PSF	Trimethylchlorosilane (TMCS)	23	5	[18]
20% wt modified MCM- 48/PSF coated by PDMS	Dimethyldichlorosilane (DMDCS)	27.2	6.2	Present work

Table 7: Ideal selectivity comparison of coated 20% MCM-48/PSF MMM of this work with 20% MCM-48/PSF and 20% MCM-41/PSF MMMs of previous researches.

was no significant or slight decrease in the selectivities. The increase in permeability could be a consequence of the presence of mesopores within the MCM-48 framework rather than voids at the polymer/ MCM-48 interface. When a penetrant gas molecule crosses over from the polymer phase into an MCM-48 pore, it should encounter less resistance to flow as it is translated through the 21 Å wide channels which is occupied by some measure of polymer. To test the quality of DMDCS modification and see whether the observed increases in permeability were due to the presence of nonselective voids at the MCM-48/PSF interface, the effect of varying the upstream pressure was investigated. For pure PSF,  $\mathrm{O}_{\scriptscriptstyle 2}$  and  $\mathrm{N}_{\scriptscriptstyle 2}$  permeabilities are virtually independent of driving pressure while CO<sub>2</sub> permeability decreases slightly with increasing upstream pressure. If such nonselective passages exist in the composite membranes, the change in pressure with respect to time on the downstream side of the membrane will be directly proportional to the driving pressure on the upstream side. In the case of a 10% MCM-48/PSF composite membrane, the O<sub>2</sub> permeability remained almost constant from 1.1 Barrers (1 atm) to 1.12 Barrers (3 atm), N<sub>2</sub> permeability increased slightly from 0.30 Barrers (1 bar) to 0.32 Barrers (3 bar), and CO<sub>2</sub> permeability decreased slightly from that the increased permeability observed as a function of MCM-48 loading is not due to the presence of nonselective pores. Diffusivity and solubility selectivities for each MCM-48/PSF composite membrane were calculated from the measured time-lags and permeabilities, and are presented in Table 3. For  $O_2/N_2$ , the diffusivity selectivity increases with the addition of MCM-48 in the membrane while the solubility selectivity decreases. Although the diffusivity of both gases increases with increasing MCM-48 loading, the diffusivity of O<sub>2</sub>, with its smaller kinetic diameter, increases more rapidly than that of N<sub>2</sub>, which is the likely reason that diffusivity selectivity increases. The solubility of N<sub>2</sub> remains virtually unchanged upon introduction of MCM-48, while the solubility of O2 decreases slightly with increasing MCM-48 loading, causing the observed decrease in solubility selectivity. The net result is that the ideal O2/N2 selectivity is hardly changed as a result of adding MCM-48 to the PSF membrane. For CO<sub>2</sub>/CH<sub>4</sub>, the diffusivity selectivity decreases with addition of MCM-48 in the membrane, while the solubility selectivity increases (the inverse of the trend observed for  $O_2/N_2$  (Table 3). The increase in  $CO_2/CH_4$  solubility selectivity is a consequence of the calculated decreased CH<sub>4</sub> solubility in the MCM-48 impregnated films. In this case, the decrease in diffusivity selectivity is offset by the increase in solubility selectivity resulting in an ideal CO<sub>2</sub>/ CH<sub>4</sub> selectivity which is virtually unaffected by the addition of MCM-48. The 30% wt PDMS surface coating quality of 20% wt MCM-48/PSF is shown in Figure 11(a). Figure 11(a) shows the cross sectional SEM image of coated membrane. As can be seen the surface of membrane is completely coated by layer of PDMS that repairs the possible membrane surface defects and Figure 11 (b) SEM image from surface of membrane confirms that too. The permeabilities of gases even after surface coating of MCM-48/PSF membranes are still higher than neat PSF membrane (Table 4). The ideal selectivities in mixed matrix membrane prepared by 30 wt% PDMS solutions is desirable and in the case of CO<sub>2</sub>/CH<sub>4</sub> it is remarkable (Table 5). The reason is related to PDMS properties. PDMS has weak molecular sieves ability due to its weak intermolecular forces, resulting in broad distribution of inter segmental gap sizes responsible for gas diffusion. The diffusion coefficients of penetrants often change less than solubility coefficients so that more soluble penetrants are more permeable. Consequently the relative permeability of the penetrants through PDMS is mainly determined by its relative solubility. the solubility of four gases, N2, O2, CH4 and CO2 in PDMS, as listed in Table 6. For the least soluble penetrants  $O_2$ ,  $CH_4$  and  $N_2$ , the solubilities are independent of pressure. In contrast, the solubility of the more soluble penetrant CO<sub>2</sub> increases with pressure, so CO<sub>2</sub> is more permeable than  $CH_a$ , O, and  $\tilde{N_a}$  in PDMS. Despite the slight reduction in permeabilities of modified membranes after coating caused by reducing diffusivity of membranes. This process make O<sub>2</sub>/N<sub>2</sub> and specially CO<sub>2</sub>/CH<sub>4</sub> ideal selectivities enhances even more than those before coating by PDMS solution compare to neat polymeric membrane. The comparison between this work and previous researches is available in Table 7 [16, 17, 18]. Table 7. compares ideal selectivities of CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> for PDMS coated 20% wt MCM-48/PSF membrane that fabricated in this study with 20% wt MCM-41/PSF and 20% wt MCM-48/PSF that synthesized by other previous researchers. As can be seen in Table 7. The synthesized membrane in this work has superior selectivity for both CO2/CH4 and O2/N2 compared to the other researches. The reason is probably related to good quality coating of surface of MMMs by PDMS that has remarkable separation properties and is suitable for membrane coating applications.

4.46 Barrers (1 bar) to 4.31 Barrers (3 bar). These results demonstrate

# Conclusion

Mesoporous MCM-48 offers the favorable effect of dramatically increasing the permeability of the composite over that of PSF. The

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trimethylsylil groups, which after modification, decorate the internal surface of MCM-48, prevent the unnecessary functionality for hydrogen bonding which results in better dispersion quality, while the 21 Å pore size is large enough to readily enable penetration of the polymer. Together, these attributes make MCM-48 an attractive additive for universally enhancing the gas permeability of PSF without sacrificing selectivity. This enhancement in permeability are likely attributable to a reduced resistance to gas flow inside the large channels of MCM-48. The performance of PDMS coated membranes were investigated, SEM photographs showed that the PDMS layer on the composite membranes prepared was uniform and PDMS solution did not penetrate into pores of supports. The coated membranes by 30 wt% PDMS solution, showed remarkable enhancement in selectivities of all gases tested with slight decreasing in permeabilities of them. The reasons are related to high quality coating of surface of membranes and also thickness of coated film because of high concentration of coating solution. In summary, introducing MCM-48 nanoparticles into the matrix of polymer and surface coating of these membranes result in both higher permeability and selectivity for gas separation compared to neat polymeric membranes.

#### References

- Robeson LM (1991) Correlation of separation factor versus permeance for polymeric membranes. J Membr Sci 62: 165.
- Merkel TC, Freeman BD, Spontak RJ, He Z, Pinnau I, Meakin P, Hill AJ(2002) Ultrapermeable, reverse-selective nanocomposite membranes. Science 296: 519.
- Boom JP, Punt IGM, Zwijnenberg H, De Boer R, Bargeman D, Smolders CA, Strathmann H(1998) Transport through zeolite filled polymeric membranes. J Membr. Sci. 138:237.
- Kresge CT, Leonowics M.E, RothWJ, Vartulli JC, Beck JS (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature 359: 710.
- Beck JS, Vartuli JC, Roth WJ, Leonowics ME, Kresge CT, et al. (1992) A newfamily of mesoporous molecular sieves prepared with liquid crystal templates, J Am Chem Soc 114: 10834-10843.
- Moermans B, Beuckelaer WD, Vankelecomm IFJ, Ravishankar R, Martens JA, et al. (2000) Incorporation of nano-sized zeolites in membranes. Chem Commun 2467-2468.
- Wang YC, Fan SC, Lee KR, Li CL, Huang SH, et al. (2004) Polyamide/ SDSclay hybrid nanocomposite membrane application towater–ethanol mixture pervaporation separation. J Membr Sci 239: 219.
- Yeh JM,Yu MY, Liou SJ (2003) Dehydration of water–alcohol mixtures by vaporpermeation through PVA/clay nanocomposite membrane. J Appl Polym Sci 89: 3632-3638.
- 9. Gao Z, Yue Y, Li W (1996) Application of zeolite-filled pervaporation membrane. Zeolites 16: 70-74.
- Zimmerman CM, Singh A, Koros WJ (1997) Tailoring mixed matrix compositemembranes for gas separations. J Membr Sci 137: 145.

- 11. Mahajan R, Koros WJ (2000) Factors controlling successful formation of mixedmatrix gas separation materials. Ind Eng Chem Res 39: 2692-2696.
- Gur TM (1994) Permselectivity of zeolite filled polysulfone gas separation membranes. J Membr Sci 93: 283-289.
- 13. Okumus E, Gurkan T, Yilmaz L (1994) Development of a mixed-matrix membrane for pervaporation. Sep Sci Technol 29: 2451-2473.
- Vu DQ, Koros WJ, Miller SJ (2003) Mixed matrix membranes using carbon molecular sieves. I. Preparation and experimental results. J Membr Sci 211: 311-334.
- Wang HT, Holmberg BA, Yan YS (2002) Homogeneous polymer-zeolite nanocompositemembranes by incorporating dispersible template-removed zeolite nanocrystals. J Mater Chem 12: 3640-3643.
- ReidB D, Ruiz-Trevino FA, Musselman IH, Kenneth J, Balkus J, et al. (2001) Gas Permeance Properties of Polysulfone Membranes Containing the Mesoporous Molecular Sieve MCM-41. Chem Mater 13: 2366.
- Kim S, Marand E, Ida J, Guliants VV (2006) Polysulfone and Mesoporous Molecular Sieve MCM-48 Mixed Matrix Membranes for Gas Separation. Chem Mater 18: 1149-1155.
- Kim S, Marand E (2008) High permeability nano-composite membranes based on mesoporous MCM-41 nanoparticles in a polysulfone matrix. Micro Meso Mater 114: 129-136.
- 19. Shimizu S, Matsuyama H,Teramoto M (2005) Gas separation properties of polyimide membrane containing mesoporous material, Seoul, South Korea, August 177: 21.
- Ladewig BP, Martin DJ, Knott RB, Diniz da Costa JC, Lu GQ (2007) Nafion-MPMDMS nanocomposite membranes with low methanol permeability. Electrochemical Communication 9: 781-786.
- Stern SA, Shah VM, Hardy BJ (1987) Structure–permeance relationships in silicone polymers. J Polym Sci B: Polym Phys 25: 1263.
- Shah VM, Hardy BJ, Stern SA (1986) Solubility of carbon dioxide, methane, and propane in silicone polymers: effect of polymer side chains. J Polym Sci B: Polym Phys 24: 2033-2047.
- Fleming GK, Koros WJ (1986) Dilation of polymers by sorption of carbon dioxide at elevated pressures. 1. Silicone rubber and unconditioned polycarbonate. Macromolecules 19: 2285-2291.
- Merkel TC, Bondar VI, Nagai K, Freeman BD, Pinnau I (2000) Gas sorption, diffusion and permeation in poly(dimethylsiloxane). J Polym Sci B: Polym Phys 38: 415-434.
- Merkel TC, Gupta RP, Turk BS, Freeman BD (2001) Mixed-gas permeation of syngas components in poly (dimethylsiloxane) and poly(1-trimethylsilyl-1propyne) at elevated temperatures. J Membr Sci 191: 85-94.
- Chen H, Wang Y (2002) Preparation of MCM-41 with high thermal stability and complementary textural porosity. Cerm Int 28: 541-547.
- Kim S, Ida J, Guliants VV, Lin YS (2005) Tailoring Surface Properties of MCM-48 Silica by Bonding 3-Aminopropyltriethoxysilane for Selective Adsorption of Carbon Dioxide. J Phys Chem B 109: 6287-6293.
- Brunauer S, Emmett PH, Teller E (1938) Adsorption of Gases in Multimolecular Layers. J Am Chem Soc 60: 309.
- 29. Constantinescu F, Blum J (1995) Adsorption characterisation of the dealumination effect on H-mordenites. Journal of porous mater 2: 35-41.