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Gas transport behavior of DMDCS modified MCM-48/polysulfone mixed matrix membrane coated by PDMS

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Abstract–Mesoporous MCM-48 silica was synthesized by templating method and the structure of particles was characterized by XRD, TEM and N_2 adsorption techniques. The surface modification of particles in order for introducing into PSF matrix was performed by dimethyldichlorosilane (DMDCS) silylation agent. SEM images of as-synthesized and modified MCM-48/PSF MMMs indicate that in the modified MCM-48 silica particles adhered well to the PSF matrix and that the synthesized MMMs were defect free. The incorporation of MCM-48 particles in to the PSF matrix and also surface coating of these MMMs by polydimethylsiloxane (PDMS) were performed. The quality of surface coating was investigated by SEM images and permeability tests. For all gases tested (N_2, CO_2, CH_4 and O_2), the permeabilities increased in proportion to the weight percent of MCM-48 present in the film and the calculated CO_2/CH_4 and O_2/N_2 selectivities of PDMS coated membranes showed enhancement in ideal and actual selectivities both.

Key words: 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 membrane, the nanoparticles act as to create preferential permeation pathways for selective permeation while posing a barrier for undesired permeation in order to improve 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 membrane increased by introducing mesoporous materials, whereas the selectivity did not change significantly, and that was because of suitable compatibility between nanoparticles and polymer matrix. However, in these cases the selectivity performance of membranes did not improve 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 introduce higher loading of the molecular sieves into the polymer matrix. In addition, nanoscale molecular sieves are more suitable for commercialization of nanocomposite membranes, whereas they have very thin selective layers than micron-sized zeolites or molecular 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, has been investigated [19-21]. As a new work, the functionalization of particles was performed by DMDCS as an organosilicon compound. These materials 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. The DMDCS is one of these materials that introduces dimethylsilylene group into the substrate molecule, chemically binds thin, water-repellent silica. 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 O_2, N_2, H_2, CO, CO_2 and CH_4 using PDMS membrane [22-24]. Hence, as a new

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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 study is fabrication and characterization of organic-inorganic nanocomposite membrane coated by PDMS based on MCM-48 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 property of fabricated polysulfone-MCM-48 nanocomposite membranes was characterized by SEM. Finally, surface coating quality of membranes was investigated by SEM and gas permeation tests.

EXPERIMENTAL

1. Synthesis and Functionalization of MCM-48 Nanoparticles

The nanoparticles of MCM-48 were synthesized through the self-assembly of inorganic silica precursor and organic template under hydrothermal conditions. The source of silicon was tetraethylorthosilicate (TEOS, Merck). The structure-directing agent was cetyltrimethylammonium 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 0.67 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/H_2O. 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 h with 1 K/min of heating rate to remove the CTAB. This method results in the unmodified version of MCM-48 nanoparticles [25]. As shown in Fig. 1, surface modification of MCM-48 particles was performed this way: Before removing CTAB, silylation of MCM-48 with dimethylsilane was performed by immersion of 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 n-hexane, then dried at 333 K in oven [26].

2. Synthesis of Membranes

Before PSF (Ultrason 6010, Merck) is used in the synthesis process, it must be degassed at 460 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 resulting mixture was allowed to mix for 4 h at room temperature; then this mixture was sonicated for 10 min, after which it was allowed to mix for 10 min and this procedure repeated several times to ensure proper dispersion. The prepared casting solution was cast on a glass substrate using a 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. 30 wt% PDMS coating solution was prepared by dissolving the appropriate amount of PDMS 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. To carry out these experiments, a constant volume apparatus for single gas permeation measurements was assembled. Permeability was measured directly, and the time-lag method was applied to the recorded data to determine the diffusivity coefficient.

3. Characterization

Powder X-ray diffraction (XRD) data were recorded using a Philips Analytical X-pert diffractometer with Cu Kα radiation (λ=1.54056A°)

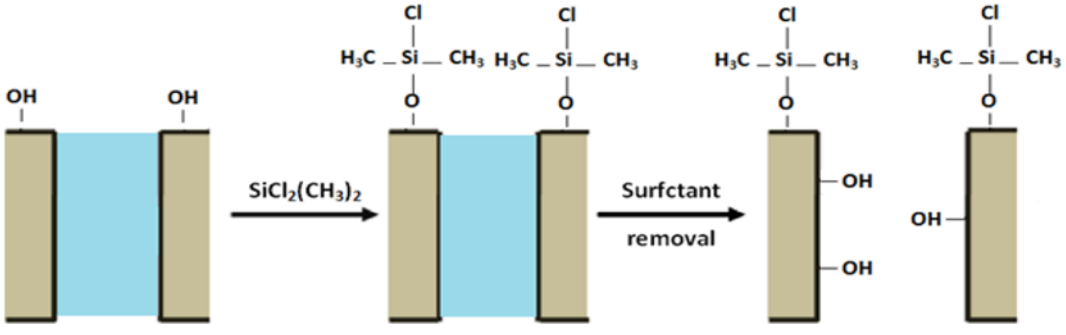

Fig. 1. Schematic of sylilation of MCM-48 nanoparticles.

with a step size of 0.02°/s. N_2 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_2, N_2, O_2 and CH_4. Each gas possessed a purity of 99.99% and was used as received. The feed pressure and temperature were kept constant at 4 bar and 298 K, respectively, for all experiments. Each gas was passed through a membrane five times and the average results and the standard deviations were recorded. Permeabilities were reported in units of Barrer. (1 Barrer=1×10^{-10} cm^3 (STP) cm/(cm^2 s cm Hg)).

RESULTS AND DISCUSSION

1. Characterization Results of MCM-48 Nanoparticles

The XRD pattern of the mesoporous MCM-48 is shown in Fig. 2. The observation of several peaks at low reflection angles (2θ=2.5-7.0), which are relevant to (211), (220), (321), (400), (420), (332), (422) and (510) 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 nitrogen adsorption-desorption isotherm of extracted MCM-48 at 77 K, exhibits both a reversible type IV isotherm and a sharp

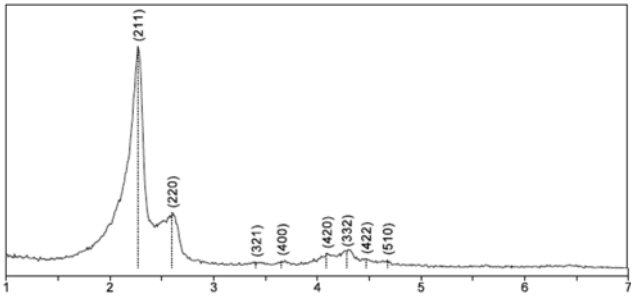

Fig. 2. XRD pattern of MCM-48 particles.

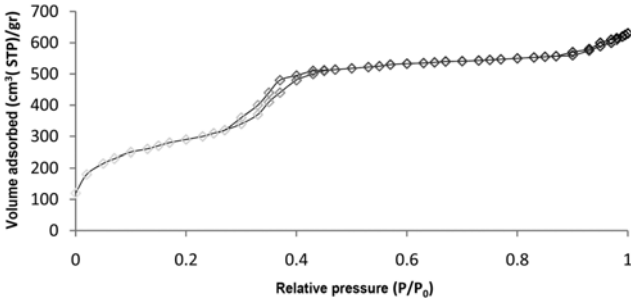

Fig. 3. The N_2 adsorption-desorption isotherms of MCM-48 particles at 77 K.

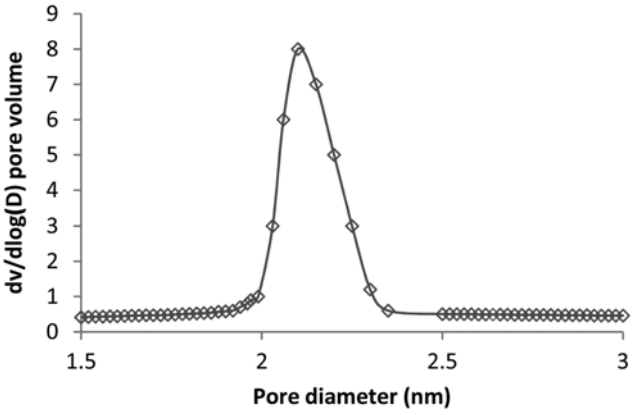

Fig. 4. The pore size distribution of MCM-48 particles.

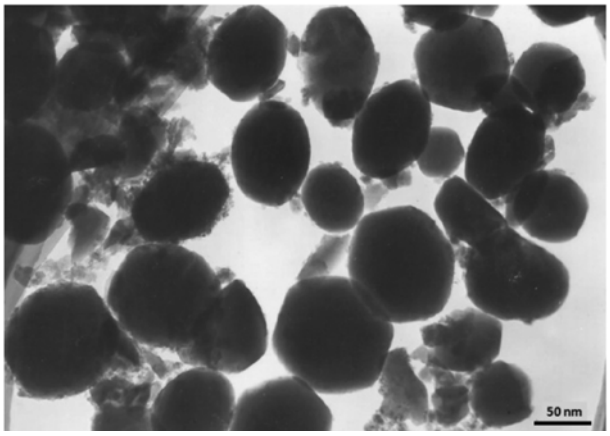

Fig. 5. The TEM image of MCM-48 particles.

pore filling step at p/p_0 0.2-0.3 which are characteristic of uniform pores (Fig. 3). The sample shows high specific surface area, approximately 930 m^2/g, and a narrow distribution of pore diameters centered at 2.1 nm (Fig. 4).

The TEM images of the extracted MCM-48 particles in Fig. 5 show the existence of highly ordered hexagonal structures with particle size in the range of 80±30 nm. These XRD patterns, pore size analysis and TEM results are in agreement with previously published results on nano-sized mesoporous silica materials [29,30].

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 that reduces the selectivity and mechanical properties of the membrane. 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 filled with silylated MCM-48. Surface SEM images of 20 wt% unmodified and DMDCS-modified MCM-48/PSF nanocomposite membranes are shown in Fig. 6. Fig. 6(a) shows that in the unmodified version of the membrane the unfavorable voids between polymer matrix and inorganic particles and agglomeration of particles are 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 (Fig. 6(b)). The reason

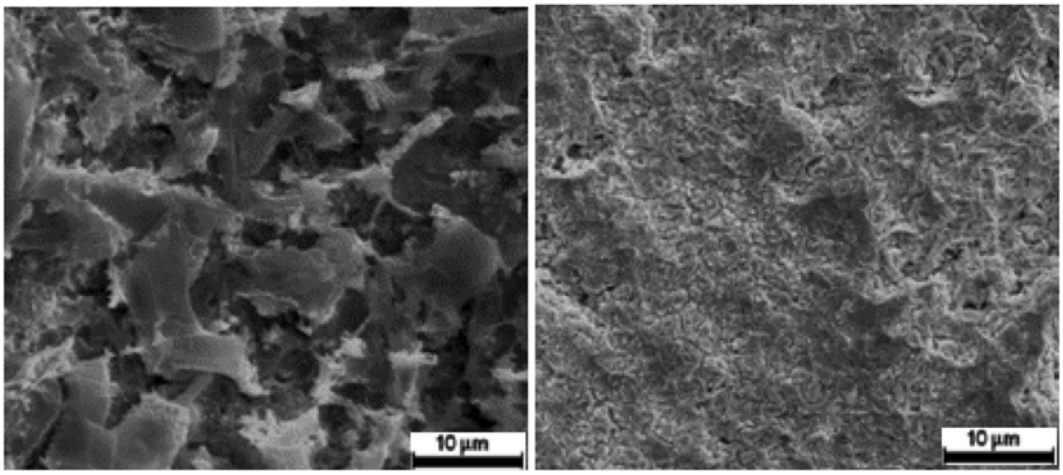

Fig. 6. SEM images of (a) unmodified and (b) modified MCM-48/PSF composite membrane.

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

Membrane	MCM-48 wt%	CO_2	N_2	CH_4	O_2
PSF	0	4.5	0.18	0.17	0.98
MCM48/PSF	10	7.6 (69%)	0.33 (83%)	0.34 (100%)	1.65 (68%)
MCM48/PSF	20	8.9 (98%)	0.38 (111%)	0.40 (135%)	1.9 (94%)
MCM48/PSF	40	16.1 (257%)	0.98 (444%)	1.1 (547%)	3.92 (300%)

( ) Percent change from pure polymer

for these two different kinds of behaviors is related to silanol groups. Since they are hydrophilic 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 [31]. However, in the modified version, the surface of particles in the membrane is silylated with dimethylsilyl groups, hence the hydrophilic surface of particles turns to hydrophobic surface. This treatment prevents the particles from being agglomerated and enhances the interaction between polymer and them, producing a composite with well-dispersed mesoporous particles in the polymer matrix.

2. Permeability of DMDCS-MCM41/PSF Nanocomposite Membrane

The gas permeability tests were performed in constant volume varying pressure apparatus. The permeability results and ideal selectivities for the DMDCS modified MCM-48 nanocomposite membranes and also neat PSF membrane before coating, are shown in Tables 1 and 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 at least 68% and 98% enhancement in the permeability of all tested gases, respectively, which is higher than those achieved without modification by previous researchers [17]. Fortunately, there was slight or even no significant 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 are 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, O_2 and N_2 permeabilities are virtually independent of driving pressure, while CO_2 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_2 permeability remained almost constant from 1.1 Barrers (1 atm) to 1.22 Barrers (3 atm), N_2 permeability increased slightly from 0.30 Barrers (1 bar) to 0.32 Barrers (3.4 bar), and CO_2 permeability decreased slightly from 4.46 Barrers (1 bar) to 4.31 Barrers (3 bar). These results demonstrate that the increased permeability

Table 2. Ideal selectivity for polysulfone and DMDCS modified MCM-48 nanocomposite membranes

Membrane	MCM-48 wt%	O_2/N_2	CO_2/CH_4
PSF	0	5.4	23
MCM48/PSF	10	5	22
MCM48/PSF	20	5	22
MCM48/PSF	40	4	14.5

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

Membrane	MCM-48 wt%	D_{O_2}/D_{N_2}	D_{CO_2}/D_{CH_4}	S_{O_2}/S_{N_2}	S_{CO_2}/S_{CH_4}
PSF	0	2.9	3.96	2.03	4.89
MCM48/PSF	10	3.92	2.74	1.3	6.52
MCM48/PSF	20	3.7	2.73	1.29	6.98
MCM48/PSF	40	4.3	2.77	1.24	7.23

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 are presented in Table 3. For O_2/N_2, the diffusivity selectivity increases with 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_2, with its smaller kinetic diameter, increases more rapidly than that of N_2, which is the likely reason that diffusivity selectivity increases. The solubility of N_2 remains virtually unchanged upon introduction of MCM-48, while the solubility of O_2 decreases slightly with increasing MCM-48 loading, causing the observed decrease in solubility selectivity. The net result is that the ideal O_2/N_2 selectivity is hardly changed as a result of adding MCM-48 to the PSF membrane. For CO_2/CH_4, 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_4 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_2/CH_4 selectivity which is virtually unaffected by the addition of MCM-48. The surface coating quality of 20 wt% MCM-48/PSF nanocomposite membrane with 30 wt% PDMS solution is shown in Fig. 7(a). Fig. 7(a) shows the cross sectional SEM image of coated membrane. As can be seen in this figure, the surface of membrane is completely coated by layer of PDMS that repairs the possible membrane surface defects. Fig. 7(b) is a SEM image from surface of membrane. This figure confirms the good quality of surface coating of membrane too. The permeabilities of gases for the MCM-48/PSF nanocomposite membranes even after surface coating of them are still higher than permeabilities for neat PSF membrane (Table 4). The ideal selectivities in nanocomposite membranes prepared by 30 wt% PDMS solutions are desirable and in the case of CO_2/CH_4 are remarkable (Table 5). The reason is related to PDMS

Table 4. Gas permeabilities (Barrer) of various gases in the DMDCS modified MCM-48 nanocomposite membranes coated by 30% wt PDMS solution

MCM-48/ PSF	CO_2	N_2	CH_4	O_2
10 wt%	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%)
40 wt%	13.2 (193%)	0.44 (144%)	0.41 (141%)	3.12 (218%)

( ) Percent change from pure polymer

Table 5. Ideal selectivity for DMDCS modified MCM-48 nanocomposite membranes coated by 30% wt PDMS solution

MCM-48/PSF	O_2/N_2	CO_2/CH_4
10 wt%	5.52	24
20 wt%	6.2	27.2
40 wt%	7.1	32.7

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

Pure gas	$S \times 10^2$ (cm^3(STP)/cm^3(mHg))
N_2	0.12
O_2	0.24
CH_4	0.27
CO_2	1.75

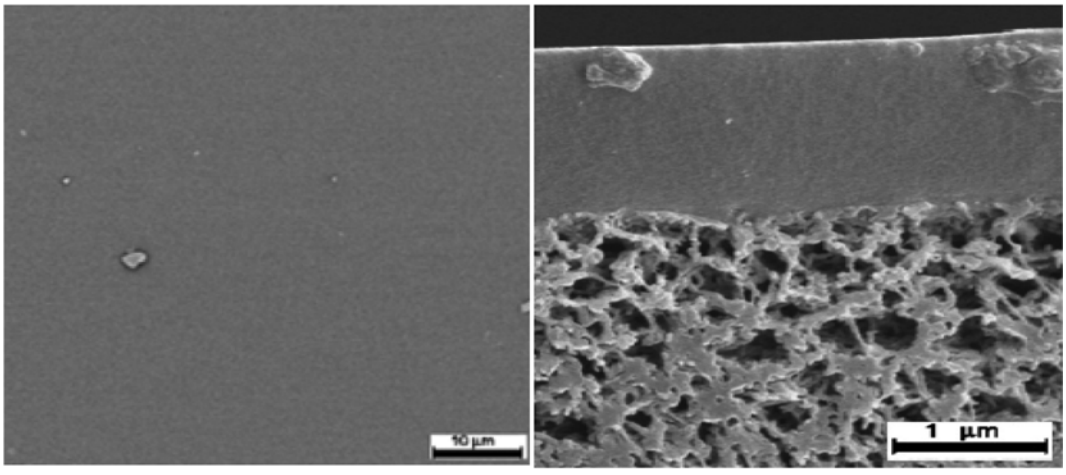

Fig. 7. SEM photographs of (a) surface and (b) cross section of 20% wt MCM-48/PSF composite membranes coated with 30% wt PDMS solution.

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

Nanocomposite membrane	Modifier agent	Ideal selectivity CO_2/CH_4	Ideal selectivity O_2/N_2	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

properties. PDMS has weak molecular sieves ability due to its weak intermolecular forces, resulting in broad distribution of intersegmental 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 solubilities of four gases, N_2, O_2, CH_4 and CO_2 in PDMS, are 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_2 increases with pressure, so CO_2 is more permeable than CH_4, O_2 and N_2 in PDMS. Despite the slight reduction in permeabilities of modified membranes after coating caused by reducing diffusivity of membranes, this process makes O_2/N_2 and specially CO_2/CH_4 ideal selectivities enhance 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 [16-18]. Table 7 compares ideal selectivities of CO_2/CH_4 and O_2/N_2 for PDMS coated 20 wt% MCM-48/PSF membrane that were fabricated in this study with 20 wt% MCM-41/PSF and 20 wt% MCM-48/PSF membranes synthesized by other previous researchers. As can be seen in Table 7, the synthesized membranes in this work have superior selectivity for both CO_2/CH_4 and O_2/N_2 compared to the other researches. The reason is probably related to good quality coating of surface of nanocomposite membranes by PDMS that has remarkable separation properties and is suitable for membrane coating applications.

CONCLUSION

Mesoporous MCM-48 offers the favorable effect of dramatically increasing the permeability of the nanocomposite membranes over that of PSF. The trimethylsilyl 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 is likely attributable to a reduced resistance to gas flow inside the large channels of MCM-48. The performance of PDMS coated membranes was 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 their permeabilities. 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 PSF to produce nanocomposite membranes and surface coating of these produced membranes resulted in both higher permeability and selectivity for gas separation compared to neat PSF membrane.

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